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Neustädtelite and cobaltneustädtelite, the Fe^{3+}- and Co^{2+}-analogues of medenbachite

WERNER KRAUSE,[1] HEINZ-JÜRGEN BERNHARDT,[2] CATHERINE MCCAMMON,[3] AND HERTA EFFENBERGER[4,*]

[1]Henriette-Lott-Weg 8, D-50354 Hürth, Germany
[2]Institut für Mineralogie, Ruhr-Universität Bochum, Universitätsstrasse 150, D-44780 Bochum, Germany
[3]Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany
[4]Institut für Mineralogie und Kristallographie, Universität Wien, Althanstrasse 14, A-1090 Vienna, Austria

ABSTRACT

Neustädtelite and cobaltneustädtelite, two new minerals related to medenbachite, were found on samples from the dumps of the Güldener Falk mine near Schneeberg-Neustädtel, Saxony, Germany. The general appearance of the two new minerals is very similar: small tabular crystals up to 0.2 mm in diameter, transparent to translucent, with a brown color and a light brown streak; the lustre is adamantine. Both minerals are optically biaxial negative, $2V = 65(5)°$, $n_x = 2.02(2)$, $n_y = 2.09$ (calc.), $n_z = 2.12(2)$; pleochroism is strong with X = brown to opaque, Y = yellow, Z = pale yellow. Mohs' hardness is 4.5. The cleavage parallel to {001} is good. The chemical compositions were derived by means of electron-microprobe analyses. Average contents for neustädtelite/cobaltneustädtelite are (in wt%): Bi_2O_3 52.58/51.54, PbO 0.08/0.08, CaO 0.15/0.32, Fe_2O_3 13.92/10.90, Al_2O_3 0.29/0.07, CoO 3.35/5.47, NiO 0.34/1.61, ZnO 0.09/0.39, CuO 0.07/0.00, As_2O_5 26.82/25.91, P_2O_5 0.23/0.43, H_2O (calc.) 2.56/3.01, total 100.48/99.73. Mössbauer spectra of cobaltneustädtelite and medenbachite confirmed that all of the iron is trivalent. Based on 12 O atoms, the empirical formulae for the neustädtelite and cobaltneustädtelite type materials are $(Bi_{1.94}Ca_{0.02})_{\Sigma 1.96}Fe_{1.00}(Fe_{0.50}Co_{0.38}Ni_{0.04}Al_{0.05}Zn_{0.01}Cu_{0.01})_{\Sigma 0.99}[(OH)_{2.44}O_{1.40}]_{\Sigma 3.84}[(AsO_4)_{2.01}(PO_4)_{0.03}]_{\Sigma 2.04}$ and $(Bi_{1.91}Ca_{0.05})_{\Sigma 1.96}Fe_{1.02}(Co_{0.63}Fe_{0.16}Ni_{0.19}Zn_{0.04}Al_{0.01})_{\Sigma 1.03}[(OH)_{2.88}O_{1.12}]_{\Sigma 4.00}[(AsO_4)_{1.95}(PO_4)_{0.05}]_{\Sigma 2.00}$, respectively. As derived from chemical analyses and crystal-structure investigations the ideal end-member compositions are $Bi_2Fe^{3+}Fe^{3+}O_2(OH)_2(AsO_4)_2$ (neustädtelite) and $Bi_2Fe^{3+}Co^{2+}O(OH)_3(AsO_4)_2$ (cobaltneustädtelite). Extensive solid solution is observed between these two minerals. Neustädtelite and cobaltneustädtelite crystallize in space group $P\bar{1}$; the cell parameters refined from powder data are $a = 4.556(1)/9.156(1)$, $b = 6.153(2)/6.148(1)$, $c = 8.984(2)/9.338(1)$ Å, $\alpha = 95.43(2)/83.24(1)$, $\beta = 99.22(2)/70.56(1)$, $\gamma = 92.95(3)/86.91(1)°$, $V = 246.9/492.2$ Å^3, $Z = {}^1/_2$, density (calc.) 5.81/5.81 g/cm^3. Structure investigations were performed using single-crystal X-ray data. In both minerals edge-sharing alternating $Fe^{3+}Ø_6$ and $(Fe^{3+},Co^{2+})Ø_6$/$(Co^{2+},Fe^{3+})Ø_6$ octahedra (Ø = O,OH) form chains parallel to [010] that are corner-linked by arsenate tetrahedra to layers parallel to (001). The Bi atoms are linked by O atoms to form columns parallel to [100]; these are sandwiched between layers of composition $^{[6]}M_2(OH)_2(AsO_4)_2$ (M = Fe^{3+},Co^{2+}). In neustädtelite the Bi atoms are site disordered; in cobaltneustädtelite half of the Bi atoms are ordered and half are on a split position. The partial ordering is induced by the presence of three OH groups, as compared to two in neustädtelite. A structural reinvestigation of medenbachite, $Bi_2Fe^{3+}(Cu^{2+},Fe^{3+})(O,OH)_2(OH)_2(AsO_4)_2$, proved isotypy with cobaltneustädtelite; the new cell parameters for medenbachite (refined from X-ray powder data) are: $a = 9.162(2)$, $b = 6.178(1)$, $c = 9.341(2)$ Å, $\alpha = 83.50(2)$, $\beta = 71.04(2)$, $\gamma = 85.15(2)°$, $V = 496$ Å^3, $Z = 2$.

INTRODUCTION

During studies of secondary minerals occurring in the area of Schneeberg, Saxony, Germany, a number of new minerals were discovered. Among them are brendelite, $(Bi,Pb)_2Fe^{3+,2+}O_2(OH)(PO_4)$ (Krause et al. 1998a) and the tsumcorite-group minerals cobaltlotharmeyerite, $Ca(Co,Fe)_2(AsO_4)_2(H_2O,OH)_2$, rappoldite, $PbCo_2(AsO_4)_2{\cdot}2H_2O$, schneebergite, $BiCo_2(AsO_4)_2[(H_2O)(OH)]$, nickelschneebergite, $BiNi_2(AsO_4)_2[(H_2O)(OH)]$, nickellotharmeyerite, $Ca(Ni,Fe)_2(AsO_4)_2(H_2O,OH)_2$, and cobalttsumcorite, $Pb(Co,Fe)_2(AsO_4)_2(H_2O,OH)_2$ (Krause et al. 1999, 2001, 2002; Effenberger et al. 2000). In addition, new Bi-Fe-Co-arsenates were investigated and shown to be very similar to medenbachite, $Bi_2Fe^{3+}(Cu,Fe)(O,OH)_2(OH)_2(AsO_4)_2$ (Krause et al. 1996). Subsequent microprobe analyses and structural investigations of a number of these specimens revealed varying Fe/Co ratios that were surprisingly related to two different unit cells due to order phenomena caused by a changing proton content necessary for charge balance. Thus, two new mineral species are defined: neustädtelite is the Fe^{3+}-dominant, and cobaltneustädtelite is the Co^{2+}-dominant analogue of medenbachite. Because of the small size of the available samples, the relevant data for the definition of the two miner-

* E-mail: herta.silvia.effenberger@univie.ac.at

als were taken from type and co-type specimens. Samples SCH131 and SCH162 yielded most of the essential data (crystal structure, microprobe data, Mössbauer spectrum) and were therefore assigned as type material, despite the fact that they do not represent the samples with the closest end-member compositions discussed to date.

The new minerals were named for the type locality and the chemical composition. Although there is no isotypy between neustädtelite and cobaltneustädtelite it was decided to use the same basic name, mainly because of the solid solution between the two species. Both the minerals and their names have been approved by the IMA Commission on New Minerals and Mineral Names (no. 98-016 and no. 2000-012). Type material including the crystals used for the crystal-structure investigations are deposited in the collection of the Staatliches Museum für Mineralogie und Geologie, Dresden, Germany (catalogue numbers: 18328 and 18329). In view of the new results the medenbachite type material was reinvestigated and found to be isotypic with cobaltneustädtelite. The recent investigations allow the medenbachite group to be defined with the general formula $Bi_2M1M2(O,OH)_2(OH)_2(AsO_4)_2$; M1 = Fe^{3+}; M2 = Fe^{3+}, Co^{2+}, and Cu^{2+}.

Occurrence and paragenesis

Neustädtelite and cobaltneustädtelite were found at several mine dumps in the Schneeberg area, Saxony, Germany. The type locality for both species are the dumps of the Güldener Falk mine near Schneeberg-Neustädtel; a more detailed description of this locality was given by Krause et al. (1998a) and Schlegel (2000). Further occurrences for neustädtelite/cobaltneustädtelite are mine dumps in the vicinity of Schneeberg-Neustädtel, including those at the following mines: Siebenschleken, Junge Kalbe, Friedefürst, and Peter und Paul. All are located within an area of a few square kilometers. The specimens containing neustädtelite and cobaltneustädtelite consist mainly of coarse quartz and the new minerals are crystallized in small vugs in association with preisingerite, powdery limonite/goethite, and rarely with mixite, zeunerite, and bismutite. The joint occurrence of neustädtelite/cobaltneustädtelite together with preisingerite seems to be a characteristic feature. Preisingerite forms tiny lustrous nodular aggregates as well as dull, seemingly decomposed, but still crystalline masses and aggregates. These crystalline masses are frequently overgrown by well-developed neustädtelite/cobaltneustädtelite crystals.

A further occurrence of neustädtelite was recently confirmed in dump material of the Friedrich-Wilhelm adit, Friedensgruber vein, near Lichtenberg, Bavaria, Germany, where it forms nearly black crystalline crusts and aggregates, associated with bismuth and bismutoferrite. This material is of particular interest, because it is very close to the end-member composition of neustädtelite (Table 1). Unfortunately, the Lichtenberg sample was not suitable for further investigations due to the minute grain size and the small amount of material available.

Morphological description, optical properties, and physical data

Neustädtelite and cobaltneustädtelite are very similar; they can only be distinguished by single-crystal studies and/or microprobe analyses. The physical properties of the two minerals are practically identical. Unless otherwise stated, the following data refer to both neustädtelite and cobaltneustädtelite. The new minerals usually form crystal aggregates up to 0.3 mm and very small tabular crystals, mostly <0.1 mm; one sample of cobaltneustädtelite (SCH161) exhibits crystals up to 0.2 mm in diameter and 0.1 mm thick. The crystals are transparent to translucent, and they have a brown color and a light brown streak; the lustre is adamantine and there is no fluorescence in either long- or short-wave ultraviolet radiation. The crystals are brittle and show a conchoidal fracture. The Mohs' hardness is 4.5. Morphological investigations with an optical two-circle goniometer and with the optical equipment of a four-circle X-ray diffractometer confirmed triclinic symmetry for both minerals. The crystals are tabular parallel to {001} and slightly to distinctly elongated parallel to [010] (Figs. 1 and 2). Most crystals show only a simple combination of three pinacoids; due to the different unit cells the observed forms are indexed as {001}, $\{\bar{1}01\}$, "$\{01\bar{1}\}$" in neustädtelite and {001}, {100}, "{011}" in cobaltneustädtelite; the latter also rarely shows {201}. The faces in the [010] zone could be measured with reasonable accuracy, whereas the terminating forms show more or less distinct deviations up to 15° from the calculated position of $\{01\bar{1}\}$ and {011}, respectively. Approximate forms may be $\{15\bar{3}\}$ (neustädtelite) and $\{\bar{1}43\}$ (cobaltneustädtelite), but these data are not reliable because of poor crystal quality. A parallel intergrowth of two different faces might be also considered. Good cleavage parallel to {001} is seen on individual crystals and is indicated by distinct texture effects in the X-ray powder diffraction pattern (reflection mode). No twinning was observed. The density could not be determined experimentally due to lack of material; the calculated density based on the empirical formula (Mandarino 1981) is 5.81 g/cm^3 for neustädtelite and cobaltneustädtelite. Both minerals are completely soluble in warm, dilute hydrochloric acid without effervescence.

Optical data for neustädtelite and cobaltneustädtelite were determined using an optical spindle-stage (measurements at λ = 590 nm). Within limits of error the optical data of the two minerals are identical. Neustädtelite and cobaltneustädtelite are optically biaxial negative, $2V = 65(5)°$ (from extinction curves), $n_x = 2.02(2)$, $n_y = 2.07$ (calculated from n_x, n_z, and $2V$), $n_z = 2.12(2)$. No distinct dispersion could be observed. In contrast to medenbachite the two new minerals show a strong pleochroism with X = brown to opaque, Y = yellow, and Z = pale yellow. X is very near to [010]; for crystals lying on (001) X' shows an oblique extinction of approximately 7° relative to [010]. The orientation [Fig. 2; φ/ρ relative to (010) = 0°/90°] is X (–3°/79°), Y (–107°/37°), Z (95°/55°) for neustädtelite (sample SCH131), and X (–166°/86°), Y (–74°/76°), Z (88°/15°) for cobaltneustädtelite (sample SCH162). This corresponds quite well with data obtained from medenbachite: X (–14°/74°), Y (–117°/52°), Z (95°/43°) (small cell; Krause et al. 1996); X (–160°/83°) Y (–69°/78°), Z (76°/15°) (after transformation to the larger cell).

Chemical composition: analytical and Mössbauer data

Chemical analyses were carried out by means of electron-microprobe (Table 1). The standards used were mimetite (As,

TABLE 1. Microprobe analyses of neustädtelite and cobaltneustädtelite in wt%

	Neustädtelite SCH131		Neustädtelite Lichtenberg		Ideal†	Cobaltneustädtelite SCH162		Cobaltneustädtelite SCH161		Ideal†
Constituent	mean*	range	mean*	range	calc.	mean*	range	mean*	range	calc.
Bi_2O_3	52.58	51.78–53.68	51.54	50.24–53.02	53.35	51.54	50.22–53.69	51.03	49.47–52.86	53.09
CaO	0.15	0.08–0.25	0.51	0.44–0.63	–	0.32	0.07–0.78	0.77	0.28–1.61	–
PbO	0.08	0.00–0.21	0.05	0.00–0.17	–	0.08	0.00–0.21	0.12	0.00–0.32	–
Fe_2O_3	13.92	12.36–15.84	17.47	17.18–17.85	18.28	10.90	9.75–12.52	10.34	9.44–12.09	9.10
Al_2O_3	0.29	0.17–0.39	<0.05	–	–	0.07	0.01–0.14	0.05	0.00–0.14	–
CoO	3.35	2.19–4.27	0.44	0.26–0.56	–	5.47	4.42–5.94	5.57	4.33–6.31	8.54
NiO	0.34	0.17–0.51	0.51	0.30–0.72	–	1.61	0.94–2.07	1.60	1.05–2.96	–
ZnO	0.09	0.03–0.15	0.15	0.08–0.22	–	0.39	0.22–1.34	0.38	0.22–0.64	–
CuO	0.07	0.00–0.16	0.05	0.00–0.08	–	<0.05	–	<0.05	–	–
As_2O_5	26.82	26.07–27.54	26.14	24.87–26.79	26.31	25.91	25.11–26.65	26.60	24.70–27.19	26.19
P_2O_5	0.23	0.14–0.34	0.40	0.23–0.72	–	0.43	0.10–0.94	0.22	0.11–0.36	–
H_2O	2.56	–	2.32	–	2.06	3.01	–	3.15	–	3.08
Total	100.48		99.58		100.00	99.73		99.83		100.00
					Number of ions					
Bi^{3+}	1.94	ΣM1=1.96	1.90	ΣM1=1.98	2.00	1.91	ΣM1=1.96	1.88	ΣM1=2.00	2.00
Ca^{2+}	0.02		0.08		–	0.05		0.12		–
Pb^{2+}	0.00		0.00		–	0.00		0.00		–
Fe^{3+}	1.50	ΣM2=1.99	1.88	ΣM2=2.01	2.00	1.18	ΣM2=2.05	1.11	ΣM2=1.98	1.00
Al^{3+}	0.05		0.00		–	0.01		0.01		–
Co^{2+}	0.38		0.05		–	0.63		0.64		1.00
Ni^{2+}	0.04		0.06		–	0.19		0.18		–
Zn^{2+}	0.01		0.02		–	0.04		0.04		–
Cu^{2+}	0.01		0.00		–	0.00		0.00		–
AsO_4^{3-}	2.01	ΣX=2.04	1.96	ΣX=2.01	2.00	1.95	ΣX=2.00	1.98	ΣX=2.01	2.00
PO_4^{3-}	0.03		0.05		–	0.05		0.03		–
OH^-	2.44		2.21		2.00	2.88		3.00		3.00
O^{2-}	1.40		1.75		2.00	1.12		0.96		1.00

* Mean of 13 (SCH131), 14 (Lichtenberg), 15 (SCH162), and 23 analyses (SCH161).
† Ideal composition of neustädtelite and cobaltneustädtelite.

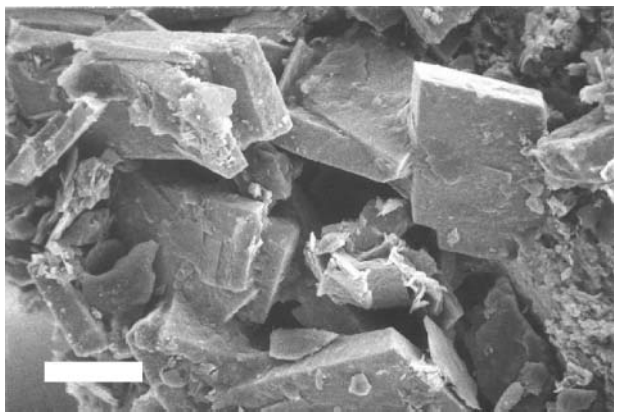

FIGURE 1. SEM micrograph of neustädtelite. Scale bar is 15 μm.

Pb), andradite (Fe, Ca), Bi_2S_3 (Bi), $AlPO_4$ (Al, P), ZnO (Zn), Co metal (Co), V metal (V), NiO (Ni), and CuS (Cu). No other elements with atomic numbers greater than 8 were detected (detection limit approximately 0.05 wt%). Analyses of additional samples (not included in Table 1) revealed similar results and gave an indication of the extent of solid solution effects. The analyses show a considerable variation in chemical composition, particularly concerning the Fe/Co ratio; Fe_2O_3 ranges from 9.44 to 17.85 wt%, CoO from 0.26 to 6.31 wt%. A solid solution between neustädtelite and cobaltneustädtelite is apparent. Small amounts of Al (≤0.74 wt% Al_2O_3), Ni (≤2.96 wt% NiO), Zn (≤1.34 wt% ZnO) and Cu (≤0.88 wt% CuO) substitute for Fe and Co. Co-rich specimens often have larger Ni-contents than the samples poor in Co. In addition, small amounts of Ca (≤1.62 wt% CaO) and/or Pb (≤0.65 wt% PbO) substitute for Bi; PO_4 (≤2.35 wt% P_2O_5) and VO_4 (≤2.68 wt% V_2O_5) substitute for AsO_4. Charge balance is achieved by the ratios $M2^{2+}/M2^{3+}$ and OH^-/O^{2-}; the ratios Bi^{3+}/Ca^{2+} and Bi^{3+}/Pb^{2+} are subordinate.

For Mössbauer spectroscopy samples of 0.8 mg cobaltneustädtelite (SCH162) and 0.9 mg medenbachite (8.0.376) were gently ground in an agate mortar with acetone to make a powder that was evenly distributed over a circular area on cellophane foil using water soluble glue (a neustädtelite sample of sufficient amount and purity was not available). Sample weights and circular area diameters were calculated to achieve the ideal sample thickness (Long et al. 1983), which was 1 mg Fe/cm^2 and 0.8 mg Fe/cm^2 for the cobaltneustädtelite and medenbachite samples, respectively. Mössbauer spectra were recorded at room temperature (293 K) in transmission mode on a constant acceleration Mössbauer spectrometer with a nominal 50 mCi ^{57}Co source in a 6 μm Rh matrix. The velocity scale was calibrated relative to 25 μm α-Fe foil using the positions certified for National Bureau of Standards, standard reference material no. 1541; line widths of 0.28 mm/s for the outer lines of α-Fe were obtained at room temperature. The spectra were fitted using the commercially available fitting program NORMOS written by R.A. Brand (distributed by Wissenschaftliche Elektronik GmbH, Germany).

Both spectra were fitted to two Lorentzian doublets (components constrained to equal widths and areas) that were sufficient to account for all spectral absorption. The doublets in the medenbachite spectrum are sufficiently resolved to conclude that there are at least two distinct environments (I and II) for Fe^{3+}, which are octahedral based on the centre shifts. These

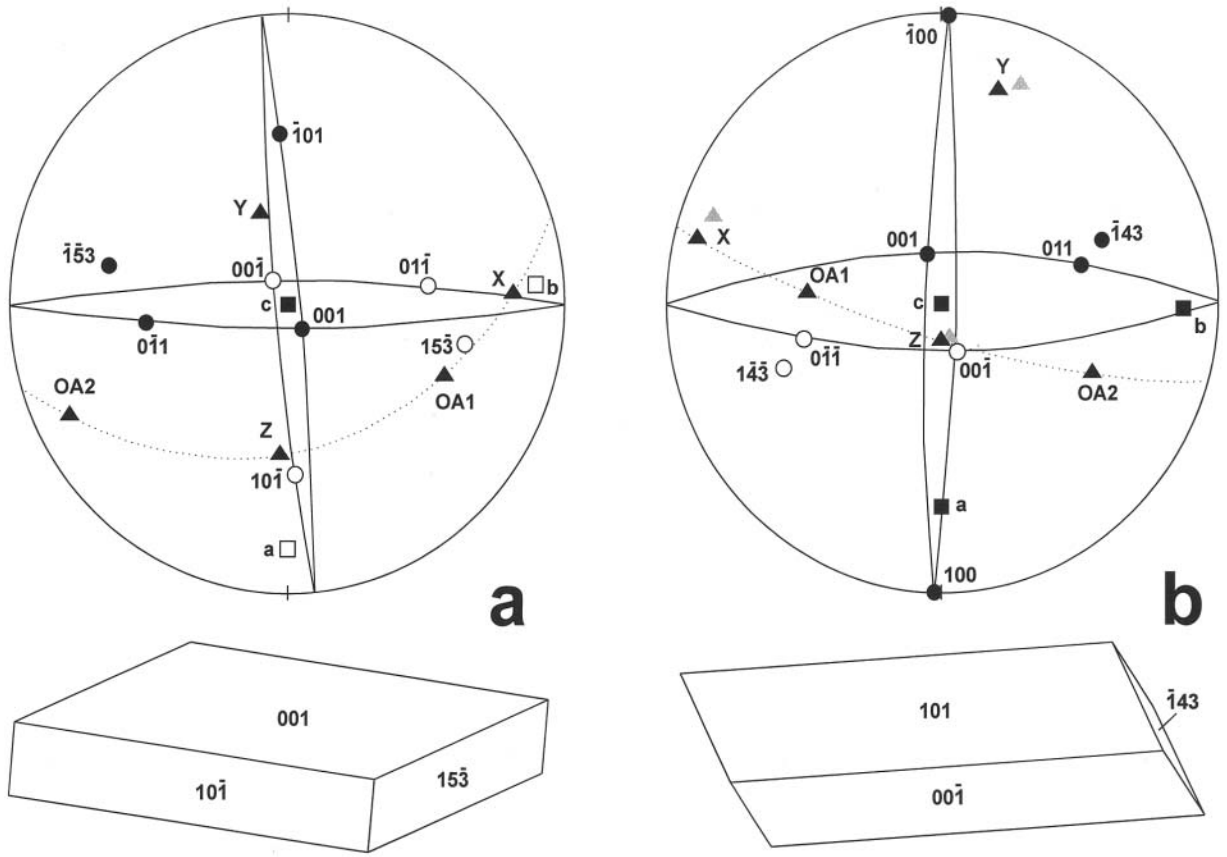

FIGURE 2. Crystal drawing, stereographic projection, morphology and optical orientation for neustädtelite (**a**) and cobaltneustädtelite (**b**). Solid symbols = upper hemisphere, open symbols = lower hemisphere; **a**, **b**, **c** = crystallographic axes; *X*, *Y*, *Z* = optic indicatrix orientation; OA1, OA2 = optic axes; dotted line = optic axial plane; solid lines = [100], [010], [001]. Gray symbols = *X*, *Y*, *Z* of medenbachite according to Krause et al. (1996).

could tentatively be assigned to M1 and M2 in the structure, where $^{I}Fe^{3+}$ corresponds to M1 and $^{II}Fe^{3+}$ corresponds to M2 based on the values of quadrupole splitting and relative site distortion. Fe^{3+} is therefore preferentially partitioned into the M1 site, although some Fe^{3+} appears to occupy the M2 site as well, which is mainly occupied by Cu. Determining accurate site occupancies is not possible, however, due to line overlap. For the cobaltneustädtelite spectrum the linewidths of both doublets were constrained to be equal since the doublets were not sufficiently resolved; the fitting to two Lorentzian doublets is consistent with the observations of medenbachite. The results are depicted in Figure 3. The spectra of both samples can be interpreted to indicate only Fe^{3+}, where the detection level for Fe^{2+} is estimated to be approximately 5% (relative to total Fe).

The new data show that medenbachite does not contain significant divalent iron; its corresponding formula is therefore $Bi_2Fe^{3+}(Cu,Fe^{3+})(O,OH)_2(OH)_2(AsO_4)_2$. In the original description (Krause et al. 1996), small amounts of Fe^{2+} were assumed based on a microchemical test with 2,2' dipyridyl (Feigl 1960). The test was found to give results that can be erronously interpreted if it is applied to Fe^{3+}-containing samples with no or at least very low Fe^{2+}. This is obviously due to a slow reduction of a ferric complex resulting in the formation of small amounts of Fe^{2+},

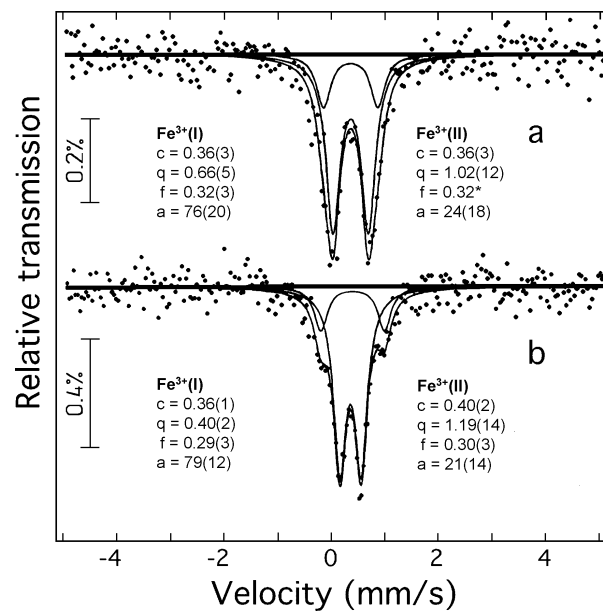

FIGURE 3. Mössbauer spectra of cobaltneustädtelite (SCH162) (**a**) and medenbachite (8.0.376) (**b**). c = center shift (relto α–Fe) (mm/s); q = quadrupole splitting (mm/s); f = full width at half maximum (mm/s); r = relative area (%).

which results in the normal red-colored Fe^{2+}-dipyridyl complex as if Fe^{2+} were present. Further details are given by Gillard (1985).

A direct determination of H_2O was impossible because of the small amount of material available. H_2O contents were calculated from the idealized empirical formulas. The presence of OH was confirmed by infrared spectroscopy. The spectra show a broad absorption between 3200 and 3500 cm^{-1} for both neustädtelite and cobaltneustädtelite. As indicated by the absence of the H_2O bending mode, there is no evidence for H_2O molecules. This is in accordance with the results determined for medenbachite (Krause et al. 1996).

The empirical formulas of the neustädtelite (SCH131) and cobaltneustädtelite (SCH162) type material based on 12 O atoms per forumula unit are: $(Bi_{1.94}Ca_{0.02})_{\Sigma 1.96}Fe_{1.00}(Fe_{0.50}Co_{0.38}Ni_{0.04}Al_{0.05}Zn_{0.01}Cu_{0.01})_{\Sigma 0.99}[(OH)_{2.44}O_{1.40}]_{\Sigma 3.84}[(AsO_4)_{2.01}(PO_4)_{0.03}]_{\Sigma 2.04}$ and $(Bi_{1.91}Ca_{0.05})_{\Sigma 1.96}Fe_{1.02}(Co_{0.63}Fe_{0.16}Ni_{0.19}Zn_{0.04}Al_{0.01})_{\Sigma 1.03}[(OH)_{2.88}O_{1.12}]_{\Sigma 4.00}[(AsO_4)_{1.95}(PO_4)_{0.05}]_{\Sigma 2.00}$, respectively. The simplified formulas derived from chemical analyses and crystal-structure investigations are $Bi_2Fe^{3+}(Fe^{3+},Co)(O,OH)_2(OH)_2(AsO_4)_2$ and $Bi_2Fe^{3+}(Co,Fe^{3+})(O,OH)_2(OH)_2(AsO_4)_2$; the ideal formulas for the end-members are $Bi_2Fe^{3+}{}_2O_2(OH)_2(AsO_4)_2$ (neustädtelite) and $Bi_2Fe^{3+}Co^{2+}O(OH)_3(AsO_4)_2$ (cobaltneustädtelite).

In Figure 4 the chemical variability of the medenbachite-group minerals is compiled in a ternary diagram with respect to the main constituents Fe^{3+}, Co^{2+}, and Cu^{2+} occupying the M2 position and assuming that the M1 position is completely occupied by Fe^{3+}. The fields for the three end-members are indicated. The currently known data show a wide variability in composition. In medenbachite Fe^{3+} substitutes for Cu^{2+} to form the solid solution between neustädtelite and cobaltneustädtelite. There is no evidence for substitution between Co and Cu, which apparently is not a crystal chemical requirement. Medenbachite occurs in a silicified barite vein at Reichenbach near Bensheim, Odenwald, Hesse, Germany. The locality is known for many secondary minerals (phosphates, arsenates, and vanadates of copper, lead, and bismuth), but cobalt and nickel are absent (Sieber et al. 1987; Krause et al. 1993). In contrast the Schneeberg area is known for Co and Ni ores and their weathering products; Fe is present but Cu is rare. Consequently the observed substitution paths Fe ↔ Cu and Fe ↔ Co seem to be related to the abundance of these elements at the type localities.

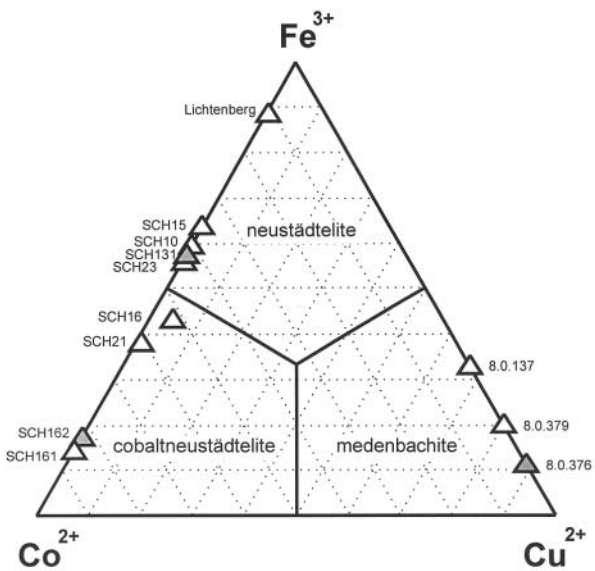

FIGURE 4. Ternary diagram Fe^{3+}-Co^{2+}-Cu^{2+} showing the occupation of the M2 position for the medenbachite-group minerals as determined from electron-microprobe analyses. Additional trivalent cations (Al) are assigned to Fe^{3+}, and divalent cations (Ni, Zn) to Co^{2+}, respectively. Gray symbols refer to the type materials.

The distinct stereochemical behaviour of Fe, Co, and Cu probably limits the possibilities of mutual substitution. $Fe^{3+}Ø_6$ (Ø = O, OH) usually forms more or less distorted octahedra. Stronger bond-length distortions were occasionally observed for $Co^{2+}Ø_6$ octahedra in inorganic compounds (Wildner 1992). The coordination polyhedron of $Cu^{2+}Ø_6$ is distinct and features an elongated tetragonal dipyramid rather than an octahedron. As a consequence, the observed substitution Fe ↔ Cu is restricted to a narrow region. In contrast, the substitution Fe ↔ Co is continuous. The expected substitution Cu ↔ Co should exceed that of Cu ↔ Fe. Future discoveries of samples from other localities might show additional variabilities in the composition.

X-RAY DIFFRACTION EXPERIMENTS

X-ray powder diffraction data for neustädtelite and cobaltneustädtelite are given in Table 2. The superstructure reflections observed by single-crystal experiments were not detected in the experimental powder diffraction pattern. In the theoretical pattern *I*(superstructure reflection)/*I*(max) is less than 0.005. The pattern of neustädtelite is nearly identical to that of cobaltneustädtelite due to the close chemical and structural relationship and the nearly equal scattering power of Fe and Co.

Single-crystal X-ray studies were performed using Weissenberg and precession-film methods as well as a four-circle diffractometer equipped with a CCD area detector. Initial attempts to determine the crystal structure of neustädtelite and cobaltneustädtelite failed because of the insufficient quality of the available material. Intense intergrowths caused broad reflection profiles, and split peaks with a separation of some degrees in ω were usually observed. In addition, the crystal size was extremely small. Eventually, tiny crystals were isolated that proved to be suitable for single-crystal investigations (samples of the type material SCH131 and SCH162). Further checks of new dump material revealed one specimen with relatively large crystals (~0.2 mm) and a Fe:(Co + Ni) ratio of ~1:1 (sample SCH161); these were also investigated.

The unit-cell volume of cobaltneustädtelite is doubled relative to neustädtelite, but the close structural relations are evident. The superstructure reflections responsible for the larger cell are weak but can clearly be seen in single-crystal experiments. The different content of protons is responsible for the two cells. In cobaltneustädtelite, M2 = Co^{2+} requires three OH groups pfu for charge balance instead of two OH groups pfu in neustädtelite (M2 = Fe^{3+}). Concerning the number of OH groups and the occupation of M2 with divalent cations, medenbachite is the analogue of cobaltneustädtelite. However, the unit cell of medenbachite given in the original description (Krause et al. 1996) does not correspond to that of cobaltneustädtelite, but it has the small cell of neustädtelite. The crystal structure

TABLE 2. X-ray powder diffraction data of neustädtelite and cobaltneustädtelite (Philips PW1710 diffractometer, Cu$K\alpha$ radiation, Si external standard)

Neustädtelite (SCH131)							Cobaltneustädtelite (SCH162)						
h	k	l	d_{calc}	I_{calc}	d_{obs}	I_{obs}	h	k	l	d_{calc}	I_{calc}	d_{obs}	I_{obs}
0	0	1	8.819	44	8.827	67	0	0	1	8.756	42	8.757	55
0	1	$\bar{0}$	6.111	13	6.119	5	0	1	0	6.104	13	6.113	4
0	1	$\bar{1}$	5.288	31	5.288	17	0	1	1	5.277	32	5.280	13
0	1	1	4.794	5	4.802	6	0	1	$\bar{1}$	4.776	4	4.781	2
0	1	1	4.794	5	4.802	6	0	1	$\bar{1}$	4.776	4	4.781	2
0	0	$\bar{2}$	4.410	6	4.416	27	0	0	2	4.378	4	4.379	12
1	0	$\bar{1}$	4.298	18	4.298	25	2	0	0	4.316	21	4.318	15
0	1	$\bar{2}$	3.767	90			2	1	1	3.754	38		
1	0	1	3.755	8	3.766	83	2	0	2	3.753	8	3.752	100
1	$\bar{1}$	0	3.740	37			0	1	2	3.751	88		
1	$\bar{1}$	$\bar{1}$	3.539	100	3.542	94	2	$\bar{1}$	0	3.551	100	3.552	55
1	1	0	3.505	62	3.505	87	2	$\bar{1}$	1	3.507	63	3.507	44
1	1	$\bar{1}$	3.492	40			2	$\bar{1}$	0	3.498	39		
0	1	2	3.411	29	3.414	34	0	$\bar{1}$	$\bar{2}$	3.392	29	3.393	26
1	1	1	3.064	5	3.055	35	2	$\bar{1}$	2	3.058	6		
0	$\bar{2}$	0	3.055	23			0	$\bar{2}$	0	3.052	22	3.052	18
1	$\bar{1}$	$\bar{2}$	2.963	11	2.961	33	2	$\bar{1}$	$\bar{1}$	3.040	4		
1	0	2	2.913	81	2.913	100	2	1	$\bar{1}$	2.965	10	2.965	13
0	2	$\bar{1}$	2.798	49	2.798	48	2	0	$\bar{3}$	2.901	80	2.901	96
0	1	$\bar{3}$	2.764	27	2.769	33	0	2	$\bar{1}$	2.792	49	2.793	29
1	0	$\bar{3}$	2.671	39	2.668	72	0	1	3	2.749	24	2.750	39
0	2	$\bar{2}$	2.644	21	2.643	18	2	0	$\bar{2}$	2.666	39	2.667	72
0	1	3	2.547	35	2.549	43	0	2	$\bar{2}$	2.638	22	2.639	18
1	$\bar{1}$	$\bar{2}$	2.521	4			0	1	$\bar{3}$	2.531	34	2.531	41
1	$\bar{2}$	$\bar{1}$	2.507	9	2.498	36	2	2	0	2.511	9	2.498	
1	$\bar{1}$	$\bar{3}$	2.498	8			2	$\bar{2}$	0	2.499	21		23
1	$\bar{2}$	1	2.497	21			2	$\bar{1}$	$\bar{2}$	2.494	11		
1	2	0	2.449	7	2.450	13	2	$\bar{2}$	1	2.447	8	2.448	9
0	2	$\bar{2}$	2.397	4	2.397	10	0	$\bar{2}$	$\bar{2}$	2.388	4	2.393	5
1	2	$\bar{2}$	2.320	23	2.320	17	2	$\bar{2}$	$\bar{1}$	2.319	24	2.319	12
2	0	$\bar{1}$	2.266	22	2.266	24	4	0	$\bar{1}$	2.277	24	2.277	16
1	$\bar{2}$	$\bar{2}$	2.253	4			2	2	$\bar{1}$	2.253	5	2.252	5
0	$\bar{2}$	$\bar{3}$	2.238	4			4	0	2	2.252	4		
1	$\bar{2}$	2	2.238	13	2.238	14	2	2	3	2.236	12	2.237	11
1	$\bar{1}$	3	2.232	7			0	2	3	2.231	4	2.229	9
0	0	4	2.205	4	2.205	10	2	1	4	2.222	7		
2	$\bar{1}$	0	2.154	4	2.149	13	0	0	4	2.189	4	2.189	16
2	0	$\bar{2}$	2.149	8			4	1	2	2.163	4	2.158	9
1	0	$\bar{4}$	2.123	7	2.123	14	4	0	0	2.158	7		
2	0	1	2.093	6	2.094	11	2	0	$\bar{3}$	2.116	6	2.117	13
0	$\bar{3}$	0	2.037	5			4	$\bar{1}$	1	2.103	4	2.097	6
2	$\bar{1}$	1	2.036	18	2.034	19	4	0	3	2.096	7		
0	3	$\bar{1}$	2.032	7			2	$\bar{1}$	$\bar{3}$	2.044	4		
0	2	3	2.016	7	1.997	10	4	1	3	2.041	19	2.041	17
1	2	2	1.999	9			0	3	0	2.035	5		
0	3	1	1.941	4			0	3	1	2.030	7		
2	1	$\bar{1}$	1.929	7	1.926	13	0	$\bar{2}$	$\bar{3}$	2.006	6	2.005	5
0	3	$\bar{2}$	1.927	10			2	$\bar{2}$	3	1.991	10	1.992	7
0	$\bar{2}$	$\bar{4}$	1.884	16	1.884	11	2	2	$\bar{2}$	1.956	4	1.955	4
1	$\bar{3}$	$\bar{1}$	1.872	6			0	$\bar{3}$	$\bar{1}$	1.937	5		
2	$\bar{1}$	$\bar{3}$	1.860	5			4	$\bar{1}$	3	1.929	8	1.927	8
1	$\bar{3}$	$\bar{1}$	1.851	13	1.850	16	0	3	2	1.925	9		
2	$\bar{1}$	2	1.848	5			0	2	4	1.875	16	1.876	17
1	$\bar{1}$	4	1.840	15			2	3	2	1.873	6		
1	3	0	1.809	8	1.805	8	4	$\bar{2}$	$\bar{1}$	1.865	4	1.863	5
2	2	1	1.802	4			4	$\bar{1}$	$\bar{1}$	1.864	5		
1	$\bar{3}$	$\bar{2}$	1.776	5			2	3	0	1.852	13	1.849	11
2	$\bar{2}$	$\bar{2}$	1.770	23	1.767	46	4	1	4	1.849	5		
0	0	5	1.764	22			2	$\bar{1}$	5	1.830	15	1.831	15
							2	$\bar{3}$	1	1.807	8	1.807	7
							4	2	3	1.807	4		
							4	$\bar{2}$	0	1.775	24	1.776	18
							2	$\bar{3}$	$\bar{1}$	1.775	7		
							4	$\bar{2}$	2	1.754	7	1.751	79
							0	0	5	1.751	20		

Notes: Calculations were performed with program LAZY PULVERIX (Yvon et al. 1977) according to the results of structure refinements; reflections with $I_{calc} \geq 4$ are listed.

of medenbachite was reinvestigated using the crystal from the earlier study (sample no. 8.0.376). Krause et al. (1996) mentioned additional weak intensities on X-ray precession photographs, but interpreted them as originating from intergrown small crystallites. In fact, there are many intensities that originate from other crystallites and do not fit with the reciprocal lattice of the main reflections. Some of the additional weak reflections are related to the strong reflections, causing a doubled unit-cell volume. This unit cell is comparable to the cobaltneustädtelite cell and new structural data confirmed isotypy

of medenbachite and cobaltneustädtelite. Apparently only medenbachite-group minerals with $M2^{3+}$, two OH groups, and two oxo-oxygen groups pfu have a "small" unit cell with $Z = 1$ (neustädtelite); in cases with $M2^{2+}$, three OH groups, and one oxo-oxygen atom pfu the unit cell is "large" and $Z = 2$ (medenbachite and cobaltneustädtelite). The intensities of the superstructure reflections originate from ordering at the split Bi site.

The cell parameters of neustädtelite and cobaltneustädtelite were refined from the powder patterns and from single-crystal X-ray data; for medenbachite the data given by Krause et al. (1996) were transformed according to the doubled cell volume. For details on data collection and structure refinements see Table 3. The X-ray intensities of neustädtelite and cobaltneustädtelite were measured with a four-circle diffractometer equipped with a CCD detector. For medenbachite the many non-lattice reflections proved to be interfere the measurement with an area detector. The probabilty of obtaining a measured background affected by non-lattice spots is greater if a ring around the reflection is used for background correction (area detector techniques) as compared to background measurements using two points or even a limited region at both sides of a scanned profile (scintillation detector measurements). Data collection with a conventional scintillation detector improved the data set. The structure refinement of neustädtelite was begun using the atomic coordinates of medenbachite given by Krause et al. (1996); their atom labels were maintained. For cobaltneustädtelite and medenbachite the starting model contained the atomic coordinates of Krause et al. (1996) after the appropriate transformation.

All Bi atoms in neustädtelite are on split positions (Bi1 and Bi2). In cobaltneustädtelite and medenbachite only 50% of the Bi atoms are on split positions (Bi1 and Bi2), whereas the others are located on a fully occupied position (Bi12). The partial order causes the doubled cell. In cobaltneustädtelite and medenbachite the atomic coordinates for all atoms except the Bi atoms exhibit a pseudotranslation vector [$^1/_2$ 0 0] within limits of error. Because of this atomic coordinates were constrained by the non-space group symmetry (xyz) and ($x + {}^1/_2yz$). The anisotropic displacement parameters in cobaltneustädtelite and medenbachite are large for the fully occupied Bi12 position. An attempt to refine these positions with split models failed; the large anisotropies were maintained but the elements in the correlation matrix increased up to 0.92. A minor splitting at this position cannot be excluded, but certainly it is much smaller than for the Bi1/Bi2 position. Hence it is rather a philosophical question whether one accepts a fully occupied position with large displacement parameters or uses a split model. We expect that the degree of splitting correlates with variations in the M^{2+}/M^{3+} ratios which induce variations in the $(OH)^-/O^{2-}$ ratios. The quality of crystals available so far does not allow us

TABLE 3. Cell parameters, single-crystal X-ray data collection, and structure refinements

	Powder X-ray data			Single-crystal X-ray data							
	Neustädtelite SCH131	Cobaltneustädtelite SCH162		Neustädtelite SCH131	Cobaltneustädtelite SCH161		Cobaltneustädtelite SCH162		Medenbachite* 8.0.376	
a (Å)	4.556(1)	9.156(1)	[4.578]	4.566(3)	9.144(3)	[4.572]	9.154(3)	[4.577]	9.162(2)	[4.581(1)]
b (Å)	6.153(2)	6.148(1)	[6.148]	6.158(4)	6.146(2)	[6.146]	6.149(2)	[6.149]	6.178(1)	[6.178(1)]
c (Å)	8.984(2)	9.338(1)	[8.928]	8.972(5)	9.337(3)	[8.934]	9.330(3)	[8.924]	9.341(2)	[8.969(2)]
α (°)	95.43(2)	83.24(1)	[95.47]	95.52(3)	83.30(2)	[95.53]	83.21(2)	[95.53]	83.50(2)	[94.29(2)]
β (°)	99.22(2)	70.56(1)	[99.48]	99.51(3)	70.67(2)	[99.54]	70.60(2)	[99.53]	71.04(2)	[99.93(2)]
γ (°)	92.95(3)	86.91(1)	[93.09]	92.85(3)	87.14(2)	[92.86]	86.96(3)	[93.04]	85.15(2)	[94.85(3)]
V (Å^3)	246.9	492.2	[246.1]	247	492	[246]	491	[246]	496	[248]
Z	1	2	[1]	1	2	[1]	2	[1]	2	[1]
Space group				$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
ρ (X-ray) (g/cm^3)				5.90	5.81		5.86		5.90	
Crystal size (μm)				40 × 30 × 20	160 × 80 × 25		70 × 25 × 20		200 × 100 × 60	
Four–circle diffractometer (Mo tube, graphite monochromator)				NONIUS Kappa†	NONIUS Kappa†		NONIUS Kappa†		STOE AED2	
Scan mode; Δφ (°/frame) or steps/reflexion and step width (°)				φ + ω; 2.0	φ + ω; 2.0		φ + ω; 2.0		θ/2θ; 70 and 0.03	
Measuring time (s/°)				570	80		310		33 to 100	
Range of data collection (°); number of frames				3 < 2θ < 50; 468	3 < 2θ < 50; 401		3 < 2θ < 50; 401		3 < 2θ < 50	
Total measured reflections ‡; $R_{int} = \Sigma \lvert F_o^2 - F_o^2\ (\text{mean}) \rvert / \Sigma F_o^2$				1722; 0.044	3445; 0.11		3454; 0.029		7127; 0.21	
Unique data set (n); observed reflections: $F_o > 4\sigma(F_o)$				873; 796	1729; 1450		1729; 1579		1749; 927	
Variable parameters (p); max Δ/σ; refinement on F^2				95; ≤ 0.001	108; ≤ 0.001		108; ≤ 0.001		108; ≤ 0.001	
$wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma(wF_o^2)^2]^{0.5}$ (all data)				0.107	0.222		0.192		0.233	
$R1 = [\Sigma(F_o - F_c) / \Sigma F_o]$ (observed data; all data)				0.047; 0.054	0.087; 0.099		0.090; 0.097		0.083; 0.165	
$w = 1/\{\sigma^2(F_o^2) + [a \cdot P]^2 + [b \cdot P]\}$, $P = [\max(0, F_o^2)] + 2 \cdot F_c^2)/3]$: a; b				0.036; 3.80	0.073; 44.1		0.031; 152		0.115; 0.0	
$GooF = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$				1.227	1.061		1.120		1.030	
Extinction parameter				0.0048(12)	0.0065(9)		0.0073(7)		0.0047(9)	
Final difference Fourier map [eÅ^{-3}]				–2.01 to +1.65	–4.53 to +2.86		–11.23 to +6.99		–4.24 to +5.62	
μ (Mo$K\alpha$) [mm^{-1}]				45	44		45		46	
Absorption correction				–	crystal shape		crystal shape		ψ–scans	
Transmission factors				–	0.024–0.164		0.250–0.694		0.042–0.098	

Notes: The average cells of cobaltneustädtelite and medenbachite corresponding to that of neustädtelite are given in brackets; the transformation matrix is (–$^1/_2$ 0 0 / 0 1 0 / $^1/_2$ 0 –1).

* Cell parameters for the average cell from Krause et al. (1996); transformed according to ($\bar{2}$ 0 0 / 0 1 0 / $\bar{1}$ 0 $\bar{1}$) during this work.

† CCD-detector, frame size: (binned mode) 621 × 576 pixels, detector-to-sample distance 28 mm, 300 μm capillary-optics collimator.

‡ Corrected for Lorentz and polarization effects; complex scattering functions for neutral atoms (Wilson 1992), program SHELXL-96 (Sheldrick 1996).

to investigate these details.

Some ordering of Fe and Co in cobaltneustädtelite at the M1 and M2 positions is evident from structure refinements and from crystal chemical considerations (M-O bond lengths and bond valences). Despite the fact that Fe and Co are adjacent to one another in the periodic table and consequently have nearly the same scattering power, a mixed occupation at the M1 and M2 positions increases the *R* values slightly and yields unusual displacement parameters. There is no doubt about separate positions for Fe and Cu in medenbachite.

The *R* values of the structure refinements for both cobaltneustädtelite samples SCH161 and SCH162 are similar. However, the refinement of the type material (SCH162) did not converge satisfactorily; the electron densities in the difference Fourier map are unusually large and the anisotropic displacement parameters of some oxygen atoms were unrealistic. The occupation of the M2 site by significant amounts of Fe^{3+} coupled with a reduced proton content likely prevents a pronounced ordering. Because the structural parameters for SCH162 (type material) are less significant as compared to SCH161 (sample with the highest Co content), only the data for the latter are given here. As expected, H atoms were not located in the final difference-Fourier summations; the highest peaks are in the vicinity of the Bi atoms. Structural parameters, interatomic bond distances and bond angles, and bond strengths are compiled in Tables 4, 5, and 6, respectively.

TABLE 4. Structural parameters

Neustädtelite, sample SCH131

Atom	*x*	*y*	*z*	Occupation factor	U_{equ}
Bi1	0.1615(6)	0.2955(8)	0.4012(6)	0.5	0.0309(8)
Bi2	0.2590(6)	0.3225(8)	0.3934(6)	0.5	0.0283(7)
M1 = Fe^{3+}	0.0	0.0	0.0	1.0	0.0191(6)
M2 = (Fe^{3+}, Co^{2+})	0.0	0.5	0.0	1.0	0.0161(6)
As	0.5462(3)	0.7913(2)	0.21425(15)	1.0	0.0195(4)
O1	0.3281(21)	0.5603(16)	0.1963(12)	1.0	0.025(2)
O2 = OH	0.1531(20)	0.7427(16)	0.8902(11)	1.0	0.024(2)
O3	0.3443(20)	0.0063(16)	0.1764(11)	1.0	0.023(2)
O4	0.2269(21)	0.2422(16)	0.9198(10)	1.0	0.024(2)
O5 = O_o	0.2699(22)	0.6196(18)	0.5353(11)	1.0	0.030(2)
O6	0.2472(23)	0.1436(19)	0.6133(12)	1.0	0.035(3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	Principal mean square displacements of *U*		
Bi1	0.0404(18)	0.0272(14)	0.0253(10)	0.0010(8)	0.0036(16)	0.0153(14)	0.049	0.025	0.018
Bi2	0.0350(17)	0.0247(12)	0.0253(10)	0.0023(7)	0.0031(15)	0.0114(13)	0.041	0.025	0.018
M1	0.0194(14)	0.0188(14)	0.0191(14)	0.0018(11)	0.0017(12)	0.0070(11)	0.025	0.019	0.013
M2	0.0171(13)	0.0147(13)	0.0177(14)	0.0045(11)	0.0038(11)	0.0054(10)	0.021	0.017	0.011
As	0.0208(7)	0.0189(8)	0.0196(8)	0.0031(6)	0.0029(6)	0.0075(6)	0.026	0.020	0.013
O1	0.025(5)	0.020(5)	0.032(6)	0.011(4)	0.003(5)	0.007(4)	0.036	0.028	0.012
O2	0.024(5)	0.022(5)	0.025(5)	0.007(4)	–0.003(4)	0.003(4)	0.033	0.024	0.015
O3	0.015(4)	0.026(5)	0.028(5)	0.007(4)	–0.001(4)	0.004(4)	0.032	0.025	0.013
O4	0.028(5)	0.026(5)	0.018(5)	0.002(4)	0.007(4)	0.013(4)	0.038	0.019	0.013
O5	0.026(5)	0.040(6)	0.020(5)	–0.008(5)	–0.004(4)	0.005(5)	0.049	0.027	0.014
O6	0.034(6)	0.040(6)	0.025(6)	–0.003(5)	–0.007(5)	0.007(5)	0.051	0.034	0.018

Cobaltneustädtelite, sample SCH161

Atom	*x*	*y*	*z*	Occupation factor	U_{equ}
Bi12	0.09029(13)	0.31050(17)	0.60632(11)	1.0	0.0362(6)
Bi1	0.6241(4)	0.2935(7)	0.5993(4)	0.5	0.0369(9)
Bi2	0.5601(4)	0.3258(6)	0.6115(4)	0.5	0.0329(9)
M1* = Fe^{3+}	0.0	0.0	0.0	1.0	0.0143(8)
M2* = Co^{2+}	0.0	0.5	0.0	1.0	0.0166(8)
As*	0.1666(2)	0.2080(3)	0.2147(2)	1.0	0.0168(6)
O1*	0.0658(12)	0.4426(21)	0.1952(13)	1.0	0.019(3)
O2* = OH	0.1318(11)	0.2563(20)	0.8879(13)	1.0	0.017(2)
O3*	0.0800(13)	–0.0081(20)	0.1801(14)	1.0	0.020(3)
O4*	0.3445(13)	0.2432(20)	0.0832(13)	1.0	0.019(3)
O5* = (OH, O)	0.1296(12)	0.6231(24)	0.4666(14)	1.0	0.024(3)
O6*	0.1824(16)	0.1427(26)	0.3897(15)	1.0	0.035(4)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	Principal mean square displacements of *U*		
Bi12	0.0624(9)	0.0265(7)	0.0215(7)	–0.0004(4)	–0.0141(5)	–0.0173(5)	0.069	0.021	0.018
Bi1	0.0473(22)	0.0355(18)	0.0273(14)	–0.0034(11)	–0.0094(17)	–0.0148(16)	0.058	0.028	0.025
Bi2	0.0426(20)	0.0310(15)	0.0269(14)	–0.0014(10)	–0.0130(16)	–0.0091(15)	0.047	0.027	0.025
M1*	0.0102(14)	0.0177(17)	0.0159(17)	–0.0031(13)	–0.0052(12)	0.0003(12)	0.018	0.015	0.010
M2*	0.0144(15)	0.0181(17)	0.0193(17)	–0.0070(13)	–0.0071(12)	0.0042(13)	0.024	0.015	0.011
As*	0.0172(9)	0.0186(10)	0.0169(9)	–0.0047(7)	–0.0080(7)	0.0013(7)	0.021	0.016	0.013
O1*	0.009(5)	0.027(7)	0.015(6)	–0.001(5)	0.001(4)	0.012(5)	0.038	0.017	0.003
O2*	0.004(5)	0.025(7)	0.019(6)	–0.005(5)	–0.001(4)	0.003(5)	0.026	0.020	0.004
O3*	0.018(5)	0.018(6)	0.027(7)	0.000(5)	–0.012(5)	0.001(5)	0.029	0.019	0.013
O4*	0.019(6)	0.022(7)	0.021(6)	–0.016(5)	–0.009(5)	0.010(5)	0.035	0.016	0.006
O5*	0.006(5)	0.040(8)	0.027(7)	–0.013(6)	–0.009(5)	–0.008(5)	0.053	0.017	0.002
O6*	0.039(8)	0.050(10)	0.027(8)	–0.006(7)	–0.028(6)	0.018(7)	0.064	0.035	0.005

Table continued on next page

DISCUSSION

The bismuth atoms

In neustädtelite, $Bi_2Fe^{3+}{}_2O_2(OH)_2(AsO_4)_2$, the Bi atoms are disordered; they are split onto two half-occupied positions, Bi1 and Bi2, that are separated by 0.486(3) Å. No indications for ordering of the Bi atoms were detected. An attempt to obtain order by reducing the symmetry to *P*1 failed. Superstructure reflections were not seen even after lengthy exposures using either photographic films or a CCD detector. Cobaltneustädtelite, $Bi_2Fe^{3+}Co^{2+}O(OH)_3(AsO_4)_2$, and medenbachite, $Bi_2Fe^{3+}Cu^{2+}O(OH)_3(AsO_4)_2$, display topologically the same building principles as found in neustädtelite, but the unit-cell volume is twice as large. Their average cells correspond to the neustädtelite cell. The most striking difference concerns the actual position of the Bi atoms and the environment of one of the oxygen atoms (O5) with respect to its coordination by Bi and H atoms. In cobaltneustädtelite and medenbachite all atoms except Bi exhibit an exact translation vector [½ 0 0]. Half of the Bi atoms show site disorder (atoms Bi1 and Bi2); their separation is larger than in neustädtelite and amounts to 0.587(3) and 0.762(4) Å, respectively. The other half of the Bi atoms are on a fully occupied atomic site (Bi12). This fully occupied Bi site corresponds approximately to the average position between Bi1 and Bi2 after application of the pseudotranslation vector [the deviations are 0.017(4) and 0.019(7) Å in the two minerals].

The coordination of the Bi atoms is irregular, with seven ligands in the coordination sphere. Two or three nearest O atom ligands are in the range 2.02–2.34 Å. Five or four additional ligands at distances up to 2.91 Å complete the coordination. The gaps between nearest- and next-nearest neighbour environments, as well as the spread of the outer coordination sphere, are unequal. Next-nearest neighbours are either Bi or O atoms, however the bond distance Bi-O ≥3.14 Å indicates only weak interactions; Bi···Bi is ≥3.20 Å. Such [2 + 5] and [3 + 4] coordinations for Bi atoms are common. In all cases the O-Bi-O angles between the nearest neighbours are ≤92°, which is characteristic of elements with stereoactive lone pairs of electrons. The nearest neighbours are either O5 = (OH,O) atoms or O6 atoms, which belong to an arsenate tetrahedron. The corner and edge connection via the O5 and O6 atoms causes an intensive linkage of the Bi atoms to chains along [100] (Fig. 5); this is a common feature for many Bi-oxo compounds.

The M sites

Of special interest are the two M positions because they are the key to the definition of the three minerals under discussion. Their coordinating ligands are two hydroxyl groups and four O atoms that belong to arsenate tetrahedra. The M-Ø distance to the hydroxyl groups is shorter than that to the O atoms of arsenate tetrahedra. Both M sites in neustädtelite and in cobaltneustädtelite, as well as the M1 site in medenbachite, are in moderately distorted octahedra; a strong length distortion responsible for the coordination [4 + 2] occurs for $M2Ø_6$ in medenbachite. The $M1Ø_6$ polyhedra are smaller than the $M2Ø_6$ polyhedra. The average <M1-Ø> bond distances are similar (2.01 to 2.03 Å), as are the <M2-Ø> distances (2.07 to 2.09 Å). Comparing the ionic radii for six-coordinated ions (Fe^{3+} 0.645 Å, Co^{2+} 0.745 Å, Cu^{2+} 0.73 Å; Shannon 1976), it is likely that the M1 positions are predominantly occupied by Fe^{3+} atoms, and the M2 positions by Co, Cu, and by the remaining Fe. For

TABLE 4.–*continued*

Medenbachite, sample 3.0.376					
Atom	*x*	*y*	*z*	Occupation factor	U_{equ}
Bi12	0.09222(19)	0.3115(3)	0.6089(2)	1.0	0.0195(6)
Bi1	0.6361(7)	0.2892(9)	0.5986(6)	0.5	0.0439(12)
Bi2	0.5520(7)	0.3308(8)	0.6168(5)	0.5	0.0403(11)
M1* = Fe^{3+}	0.0	0.0	0.0	1.0	0.0239(12)
M2* = Cu^{2+}	0.0	0.5	0.0	1.0	0.0242(10)
As*	0.1610(3)	0.1995(5)	0.2180(3)	1.0	0.0254(7)
O1*	0.0600(20)	0.436(3)	0.1982(22)	1.0	0.026(4)
O2* = OH	0.1244(21)	0.254(3)	0.9000(20)	1.0	0.026(4)
O3*	0.0765(22)	–.012(3)	0.1844(21)	1.0	0.028(4)
O4*	0.3365(25)	0.230(3)	0.0830(20)	1.0	0.034(5)
O5* = (OH, O)	0.1322(23)	0.618(3)	0.4591(23)	1.0	0.034(5)
O6*	0.1830(22)	0.142(3)	0.3904(19)	1.0	0.031(5)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	Principal mean square displacements of U		
Bi12	0.0308(9)	0.0160(8)	0.0117(8)	–.0016(5)	–.0066(6)	–.0015(5)	0.031	0.016	0.011
Bi1	0.050(3)	0.048(3)	0.032(3)	0.002(2)	–.011(2)	–.008(2)	0.054	0.047	0.031
Bi2	0.053(3)	0.039(3)	0.029(2)	–.005(2)	–.011(2)	–.003(2)	0.054	0.040	0.028
M1*	0.024(3)	0.027(3)	0.021(3)	–.002(2)	–.008(2)	0.000(2)	0.027	0.024	0.021
M2*	0.027(3)	0.022(2)	0.025(2)	–.006(2)	–.010(2)	0.004(2)	0.032	0.023	0.018
As*	0.0302(17)	0.0265(15)	0.0204(14)	–.0035(11)	–.0094(12)	0.0011(11)	0.032	0.025	0.019
O1*	0.016(10)	0.029(10)	0.033(10)	–.005(8)	–.010(8)	–.001(8)	0.034	0.028	0.015
O2*	0.026(10)	0.037(11)	0.021(9)	–.006(8)	–.013(8)	–.003(8)	0.037	0.028	0.014
O3*	0.036(11)	0.022(9)	0.035(10)	–.008(8)	–.023(9)	0.008(8)	0.047	0.021	0.016
O4*	0.047(13)	0.036(11)	0.016(10)	–.013(8)	–.008(9)	0.020(9)	0.066	0.026	0.009
O5*	0.033(12)	0.037(11)	0.040(12)	0.001(9)	–.021(10)	–.006(9)	0.047	0.035	0.021
O6*	0.031(11)	0.044(12)	0.017(10)	–.004(8)	–.005(9)	0.003(9)	0.046	0.032	0.016

Note: The anisotropic displacement parameters are defined as: $\exp[-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} \mathbf{a}_i^* \mathbf{a}_j^* h_i h_j]$, U_{equ} according to Fischer and Tillmanns (1988).
* Besides the space-group symmetry, the translation vectors (0 0 0) and (½ 0 0) have to be added to the atomic coordinates (*xyz*).

TABLE 5. Interatomic distances (Å) and bond angles (°)

	Neustädtelite	Cobaltneustädtelite	Medenbachite
Bi12–$O5^1$		2.167(13)	2.207(20)
Bi12–O6		2.266(14)	2.278(17)
Bi12–$O5^2$		2.331(10)	2.335(18)
Bi12–O5		2.465(11)	2.459(20)
Bi12–O1		2.542(11)	2.504(18)
Bi12–O3		2.688(13)	2.696(21)
Bi12–O2		2.758(11)	2.809(16)
$O5^1$–Bi12–O6		88.6(5)	85.7(7)
$O5^1$–Bi12–$O5^2$		74.7(5)	75.5(8)
O6–Bi12–$O5^2$		84.3(4)	84.5(7)
Bi1–O6	2.187(12)	2.158(14)	2.141(18)
Bi1–$O5^1$	2.212(11)	2.199(11)	2.125(20)
Bi1–$O5^2$	2.218(12)	2.242(14)	2.292(20)
Bi1–O5	2.580(10)	2.603(11)	2.685(19)
Bi1–O1	2.744(10)	2.751(11)	2.779(19)
Bi1–O2	2.749(11)	2.701(12)	2.767(17)
Bi1–O3	2.819(11)	2.782(13)	2.836(22)
O6–Bi2–$O5^1$	86.9(4)	87.3(6)	92.4(8)
O6–Bi2–$O5^2$	88.7(5)	89.5(6)	86.8(7)
$O5^1$–Bi1–$O5^2$	76.9(5)	78.4(5)	77.6(8)
Bi2–$O5^1$	2.119(12)	2.090(11)	2.021(18)
Bi2–$O5^2$	2.142(10)	2.132(14)	2.189(21)
Bi2–O6	2.357(12)	2.385(14)	2.439(18)
Bi2–O1	2.451(10)	2.381(12)	2.299(19)
Bi2–O5	2.631(10)	2.711(11)	2.783(20)
Bi2–O3	2.708(11)	2.637(13)	2.616(21)
Bi2–O2	2.885(11)	2.848(11)	2.909(17)
$O5^1$–Bi2–$O5^2$	80.3(4)	80.6(5)	82.6(8)
Bi1–Bi2	0.486(3)	0.587(3)	0.762(4)
O2···O3	2.879(11)	2.897(14)	2.92(3)
O2···O4	3.046(11)	3.068(15)	2.96(4)
M1–O2, 2×	2.002(10)	2.000(12)	1.978(19)
M1–O4, 2×	2.029(10)	2.046(10)	2.001(17)
M1–O3, 2×	2.034(10)	2.038(11)	2.052(16)
O–M1–O	81.3(4) to 98.7(4), 180	82.0(5) to 98.0(5),180	83.2(9) to 96.8(9), 180
M2–O2, 2×	2.025(9)	2.035(11)	1.954(19)
M2–O4, 2×	2.074(9)	2.079(13)	2.235(23)
M2–O1, 2×	2.105(10)	2.089(11)	2.085(18)
O–M2–O	79.6(4) to 100.4(4), 180	80.4(4) to 99.6(4), 180	77.9(7) to 102.1(7), 180
As–O1	1.674(10)	1.697(11)	1.685(17)
As–O6	1.675(10)	1.688(12)	1.682(17)
As–O3	1.680(9)	1.694(12)	1.684(19)
As–O4	1.716(9)	1.689(12)	1.700(21)
O1–As–O6	114.8(5)	114.9(7)	114.4(9)
O1–As–O3	111.2(5)	110.4(6)	110.9(8)
O1–As–O4	106.6(5)	106.0(6)	104.7(9)
O6–As–O3	106.6(5)	106.0(7)	107.4(9)
O6–As–O4	109.9(5)	109.9(6)	109.9(9)
O3–As–O4	107.7(5)	109.7(6)	109.5(10)

$Fe^{3+}O_6$ octahedra, Baur (1981) listed an average mean <Fe-O> bond distance of 2.011 Å; similarly Giester (1998) gave for Fe^{3+} selenites an average value for <Fe-O> of 2.013 Å (ranging from 1.989 to 2.044 Å). For CoO_6 polyhedra the average Co-O bond distance is 2.119 Å (Baur 1981); Wildner (1992) gave a slightly smaller overall mean value of 2.1115 Å (scattering in individual polyhedra from 2.054 to 2.182 Å). The average <M1-Ø> and <M2-Ø> bond distances are similar in neustädtelite and cobaltneustädtelite despite their different Fe:Co ratios. This is caused by the significantly higher Ni content in cobaltneustädtelite and the smaller ionic radius of Ni (0.69 Å). Mössbauer data of cobaltneustädtelite and medenbachite indicate that the Fe^{3+} atoms in general occupy only one octahedral site.

Bond valence calculations support the ordering proposed at the M sites. The sum of bond valences is close to 3.0 for the M1 sites; however, that of M2 is significantly lower, indicating preferential occupation by Co and Cu (and Ni). A mixed occupation of all M sites with M^{2+} and M^{3+} would cause an unequal distribution of the charges reaching the O atoms O1 to O4 (Table 6). In medenbachite, the coordination of the two M atoms is distinctly different. The $M1Ø_6$ polyhedron is a moderately distorted octahedron, but the $M2Ø_6$ polyhedron is a tetragonal bipyramid. The M2 position is predominantly occupied by Cu^{2+} atoms; the d^9 electron configuration causes the strong deformation of the coordination polyhedron (Jahn-Teller effect); for further discussion see Krause et al. (1996). The oxygen atoms of the $MØ_6$ octahedra belong to the second coordination sphere of the Bi atoms.

The oxygen atoms

Besides the O atoms of the arsenate group (O1, O3, O4, and O6) with bond valences around 2.0, there are two O atoms (O2 and O5) with distinctly smaller bond valences (Table 6). The O2 atoms are linked to $M1Ø_6$ and $M2Ø_6$ octahedra; in addition, O2 is in the coordination polyhedron of one Bi atom where the O2-Bi bond is ≥2.70 Å, indicating only weak interactions. Despite the actual position of the Bi atom, the cations yield too small a contribution to the bond strength reaching the O2 atom to compensate for its valence [1.05 to 1.19 valence units (v.u.)]. Consequently, O2 must be a hydroxyl group in all cases. Most probable acceptors of the hydrogen bond are the O3 and O4 atoms, which indicates a bifurcated hydrogen bond.

Up to 3 Å the O5 atoms are exclusively coordinated to three Bi atoms. The actual O5-Bi bond lengths depend on the respective position of the Bi atom due to site disorder which causes configurations with either one, two, or three Bi atoms. Considering the end-member composition, charge balance requires that all the O5 atoms in neustädtelite, $Bi_2Fe_2(OH)_2O_2(AsO_4)_2$, are O atoms. Site disorder of all Bi atoms gives rise to eight geometrically different environments for the O5 atom. Two involve unrealisticly large bond valences (>2.30 v.u.), whereas three feature a bond valence <1.7 v.u. Given that the O5 atom acts predominantly as an O atom, most reasonable bond valences are achieved if all three coordinating Bi atoms are either in the Bi1 or Bi2 position; thus the O5 atom is coordinated by two near and one distant Bi atoms.

In contrast, in cobaltneustädtelite and medenbachite $OH:O_{oxo}$ is 3:1. It is assumed that the O5 atom represents half an O atom and half a hydroxyl group. Ordering of half of the Bi atoms causes 50% of the O5 atoms to belong to hydroxyl groups and the others to be O atoms, notwithstanding the actual occupation of Bi1 or Bi2. The orientation of the O5-H dipole is not clearly defined. There are three O6 and two O1 atoms in the region O5-H···O of about 3.00 to 3.12 Å indicating weak electrostatic interactions. However, these atoms are also involved in the outer coordination sphere of the Bi atoms. As a consequence O5-H is a free hydrogen bond as often found in (partly) disordered structures. Moreover, this hydrogen bond will not contribute significantly to the bond valence sum of any acceptor O atom. On average, bond strengths at the O5 atoms are smaller than in neustädtelite. The variable occupation with

TABLE 6. Bond strengths for the oxygen atoms (valence units) calculated according to Brese and O'Keeffe (1991) for neustädtelite, cobaltneustädtelite, and medenbachite

	Coordinating cations	Neustädtelite (M1 = M2 = Fe^{3+})	Cobaltneustädtelite (M1 = Fe^{3+}; M2 = Co)	Medenbachite (M1 = Fe^{3+}; M2 = Cu)	
O1	Bi1, M2, As	1.85	1.72	1.74	arsenate group
	Bi2, M2, As	2.06	2.01	2.15	
	Bi12, M2, As	—	1.85	1.91	
O2	Bi1, M1, M2	1.17	1.11	1.19	hydroxyl group
	Bi2, M1, M2	1.12	1.05	1.14	
	Bi12, M1, M2	—	1.08	1.17	
O3	Bi1, M1, As	1.88	1.84	1.84	arsenate group
	Bi2, M1, As	1.93	1.92	1.95	
	Bi12, M1, As	—	1.89	1.90	
O4	M1, M2, As	2.06	2.05	1.94	arsenate group
O5	3 Bi atoms	1.21 to 2.51*	1.28 to 2.26†	1.15 to 2.34†	hydroxyl group or oxo–oxygen atom
O6	Bi1, As	2.05	2.07	2.13	arsenate group
	Bi2, As	1.77	1.69	1.65	
	Bi12, As	—	1.86	1.86	

* Eight theoretically different environments.
† Six theoretically different environments.

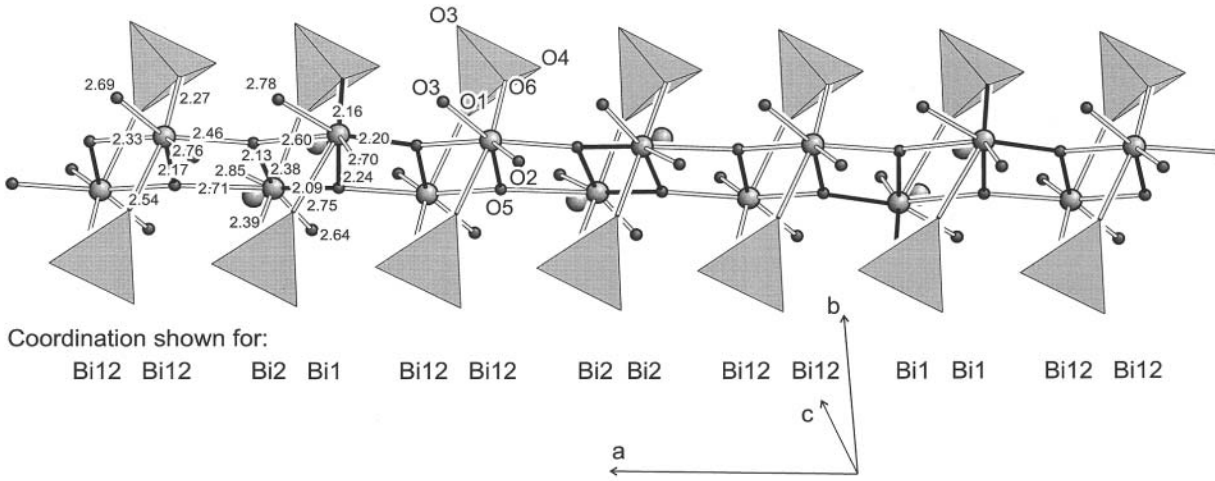

FIGURE 5. The connection of the Bi atoms in cobaltneustädtelite parallel to [100] via the O5 atoms and their additional ligands. For the split position Bi1-Bi2 only the coordination of one of the two Bi sites is indicated (for all structural drawings program ATOMS, Dowty 1999, was used).

$(O_{oxo})^{2-}$ atoms and $(OH)^-$ groups is required to balance the chemical formula according to the ratio Fe^{3+}:Co^{2+} and Fe^{3+}:Cu^{2+}.

Atoms O1, O3, O4, and O6 belong to the arsenate group; in addition, atoms O1 and O3 are coordinated by one Bi and one M atom, O4 by two M atoms, and O6 by one Bi atom. For these four O atoms bond valence values scatter around 2.0. The actual position of the Bi atoms (Bi1, Bi2, or Bi12) causes a moderate change in the bond valence sum at the O1, O3, and O6 atoms. However, these O atoms have only one Bi atom in their coordination sphere up to 3 Å. As a result, they account for changes in the contribution of the Bi atoms to the bond valence sums by slight shifts of O-As or O-M bonds. The deviation from the ideal values is distinct, as is often observed for compounds exhibiting site disorder. The large anisotropies of the displacement parameters observed for the Bi and O atoms in all refinement models of the three title compounds do not allow us to discuss bond valence sums in more detail.

STRUCTURE TYPE AND STRUCTURAL RELATIONSHIPS

The connectivity of the coordination polyhedra in the medenbachite-type structure was outlined by Krause et al. (1996): chains of edge-sharing $MØ_6$ octahedra (neustädtelite and cobaltneustädtelite) and of alternating octahedra and tetragonal bipyramids (medenbachite) run parallel to [010]. Layers in (001) are formed by vertex sharing of the chains with the arsenate tetrahedra; they are linked by Bi atoms. This causes the pronounced tabular habit of the crystals parallel to (001) and is responsible for the good cleavage. The structure may also be regarded as $^1_\infty[MØ_4]$ columns of edge-sharing $[MØ_6]$ polyhedra running parallel to [010] that are connected to

$^{1}_{\infty}$[Bi(O,OH)] chains running parallel to [100], i.e., the two chemically different chains are approximately perpendicular to each other. Arsenate tetrahedra link the chains to form a three-dimensional network. Considering the O atoms, O1 to O4 and O6 form two layers of densely packed atoms parallel to (001). Half of the octahedral sites are occupied by M atoms. The others are vacant; however an arsenate tetrahedron is alternately at the top and bottom face of the vacant tetrahedra, which results in $M^{[6]}(OH)(XO_4)$ layers (Fig. 6). Bi and O5 atoms are sandwiched between these layers. Rows of edge-sharing $M\O_6$ octahedra are common (see, e.g., Hawthorne 1990; Chopin et al. 1993; Krause et al. 1998b and references therein). Chemically related to the medenbachite-type minerals are paulkellerite, $Bi_2FeO_2(OH)_2(PO_4)$, (Grice and Groat 1988), mrázekite, $Bi_2Cu_3O_2(OH)_2(PO_4)_2{\cdot}2H_2O$, (Effenberger et al. 1994), and brendelite, $(Bi,Pb)_2Fe^{3+,2+}O_2(OH)(PO_4)$, (Krause et al. 1998a). Despite similar environments of the cations, there are only minor topological relationships.

Structural similarities are apparent with the tsumcorite-type minerals, $M1M2_2(XO_4)_2(OH,H_2O)_2$: M1 = Pb, Ca, Bi, Na; M2 = Fe^{3+}, Co, Ni, Cu, Zn, Mn^{3+}, Al, Mg; X = P, As, V, S (Krause et al. 1998b, 2002; Effenberger et al. 2000; Brugger et al. 2001 and references therein). Tsumcorite contains $M^{[6]}(OH,H_2O)(XO_4)$ layers in which $M\O_6$ octahedra share edges to form chains that are linked by XO_4. The Ø atoms form two layers of a dense-packed arrangement. Whereas in the medenbachite type structure the XO_4 tetrahedra are alternatingly at the top and bottom face of neighbouring $\square\O_6$ octahedra (Fig. 7, □ is a vacancy),

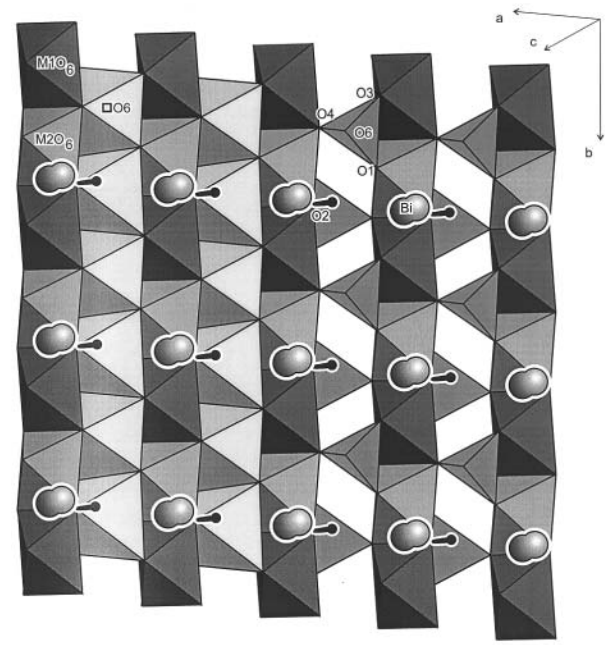

FIGURE 7. One layer formed by the octahedra and tetrahedra in neustädtelite. **(Left)** the brucite like $M1M2\square_2(OH)_2O_6$ layer formed by the $M1(O_h)_2O_4$ (dark), $M2(O_h)_2O_4$ (medium), and two $\square(O_h)O_5$ octahedra (light). **(Right)** the AsO_4 tetrahedra above and below the $\square(O_h)O_5$ octahedra are featured. The O2H groups as well as the split Bi site above the layer are indicated.

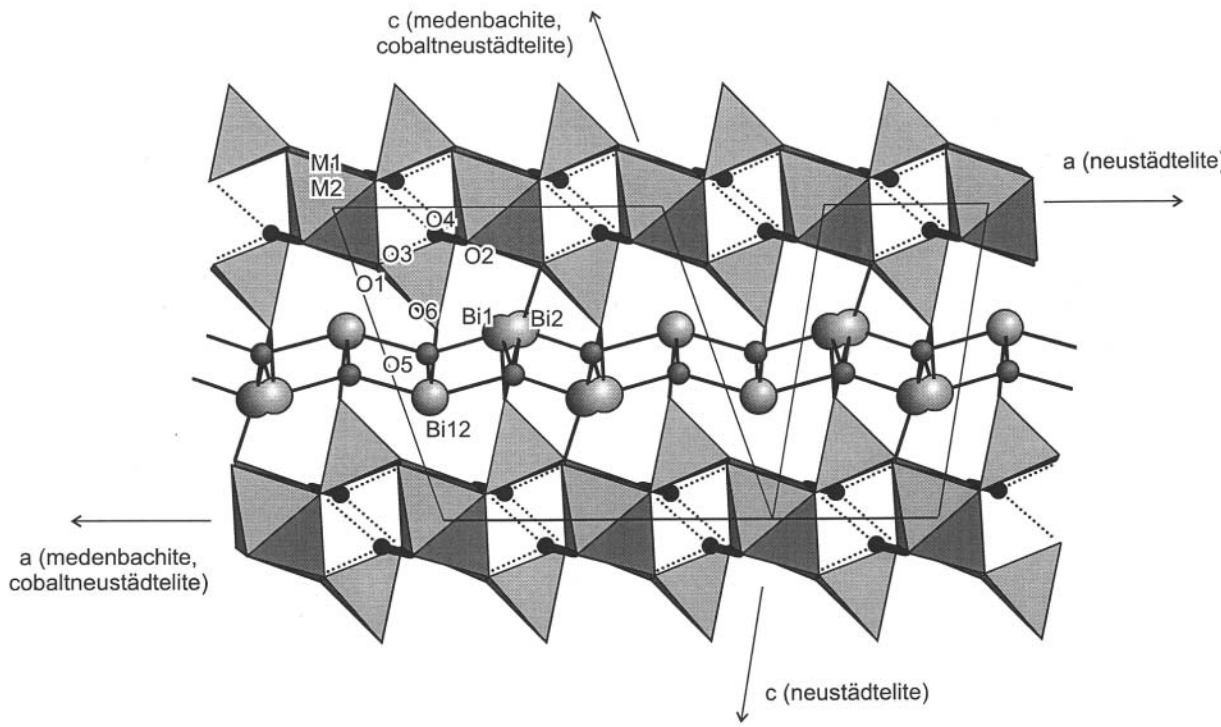

FIGURE 6. The atomic arrangement of cobaltneustädtelite and medenbachite in a projection parallel to [010]. The Bi12 atom is on a fully occupied position; in neustädtelite it exhibits a site dislocation like Bi1-Bi2. The cell corresponding to neustädtelite is indicated.

in the tsumcorite type $\square\varnothing_6$ octahedra with XO_4 tetrahedra at the bottom and top face alternate with $\square\varnothing_6$ octahedra not sharing faces with XO_4 tetrahedra. The stacking of these layers with a mutual arrangement of the vacant sites results in holes for the M1 atoms. A further analogy between the medenbachite and tsumcorite-type minerals is the charge balance for cations with different valence states which is achieved by a varying content of protons. However, in the medenbachite type the charge is balanced by the substitution $O \leftrightarrow (OH)$, whereas in the tsumcorite type it is balanced by $(OH) \leftrightarrow H_2O$.

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