SHORT STRUCTURAL PAPERS

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Acta Cryst. (1980). B**36**, 2121–2123

Diammonium Nickel Bis(tetrafluoroberyllate) Hexahydrate*

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(*Received* 21 *January* 1980; *accepted* 3 *April* 1980)

Abstract. $(NH_4)_2Ni(BeF_4)_2.6H_2O$, monoclinic, $P2_1/a$, a = 9·201 (4), b = 12·482 (4), c = 6·142 (3) Å, β = 106·57 (3)°, V = 676·0 (4) Å^3, D_o = 1·84 (2), D_c = 1·832 Mg m^{-3}, Z = 2. The structure, which is isomorphous with the corresponding chromate, selenate and sulfate, has been determined by the refinement of diffractometer data to a final R value of 0·024 for 739 observed reflexions. The metal–water distances are 2·072 (2), 2·063 (2), 2·027 (2) Å.

Introduction. In the continuing study of the variations of hexaaqua ions of the first transition group of elements (Montgomery, 1979), the structure of the title compound has been determined.

$(NH_4)_2Ni(BeF_4)_2.6H_2O$ was recrystallized by slow evaporation of an aqueous solution containing 1% of aqueous HF at room temperature. A crystal 0·15 × 0·15 × 0·50 mm was used for data collection (c axis rotation). Accurate cell dimensions were determined by least-squares fitting of 13 2θ values (λ = 0·71069 Å, 2θ = 25 to 42°).

Intensity measurements were made by an automated PDP-11-controlled Picker four-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation (λ = 0·71069 Å) at 296 K. Reflexions were scanned in the $\theta/2\theta$ mode (scanning 60 steps of 0·04° in 2θ, counting for 1 s per step and for 30 s at each extremity). Three standard reflexions were recorded for every fifty observed reflexions. From an analysis of the values of the standards an instability factor for the instrument was calculated which, combined with counting statistics, gave $\sigma(I)$ for each reflexion. In all, 739 reflexions were observed (out of 878) up to 2θ = 44°, using the criterion that a reflexion was unobserved if the net count was less than $3\sigma(I)$. Intensities were corrected for Lorentz and polarization effects but not for absorption [μ(Mo $K\alpha$) = 1·45 mm^{-1}, μR for cylinder = 0·11].

Initial parameters were taken from the corresponding chromate (Montgomery, 1979) and refined by a full-matrix least-squares procedure. The programs used were those of Penfold (1969). The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Scattering factors for Ni^{2+}, Be, F, O, and N were from *International Tables for X-ray Crystallography* (1974) and those for H from Table 2

Table 1. *Final coordinates* (×10^3 *for* H; ×10^4 *for others*) *and isotropic thermal parameters, with the least-squares standard errors in parentheses*

	x	y	z	B_{eq}/B (Å^2)
Ni	0	0	0	1·6
Be	4035 (4)	1409 (3)	7431 (6)	1·6
F(3)	3993 (2)	2378 (2)	5822 (3)	3·3
F(4)	5547 (2)	839 (2)	7835 (4)	4·0
F(5)	2741 (2)	650 (2)	6202 (3)	2·5
F(6)	3789 (2)	1813 (2)	9708 (3)	2·8
O(7)	1623 (2)	1095 (2)	1694 (4)	2·3
O(8)	−1638 (2)	1059 (2)	355 (4)	2·3
O(9)	9 (2)	−671 (2)	3010 (4)	2·2
N(10)	1267 (3)	3542 (2)	3623 (5)	2·4
H(11)	69 (4)	336 (3)	246 (7)	7·3 (1)
H(12)	219 (4)	301 (3)	416 (7)	7·9 (1)
H(13)	89 (4)	352 (3)	454 (7)	5·0 (1)
H(14)	167 (4)	407 (3)	374 (7)	4·5 (1)
H(15)	194 (4)	92 (3)	302 (6)	3·5 (1)
H(16)	218 (4)	120 (3)	125 (7)	5·3 (1)
H(17)	−248 (4)	92 (3)	−46 (6)	3·9 (1)
H(18)	−139 (4)	166 (3)	28 (6)	4·5 (1)
H(19)	−76 (4)	−68 (3)	339 (7)	5·7 (1)
H(20)	28 (4)	−126 (3)	323 (6)	3·7 (1)

Table 2. *Bond lengths* (Å) *and angles* (°) *for the* BeF_4^{2-} *ion*

Be–F(3)	1·555 (3)	F(3)–Be–F(4)	108·9 (2)
Be–F(4)	1·518 (3)	F(3)–Be–F(5)	107·0 (2)
Be–F(5)	1·540 (3)	F(3)–Be–F(6)	109·5 (2)
Be–F(6)	1·563 (3)	F(4)–Be–F(5)	109·7 (2)
		F(4)–Be–F(6)	111·4 (2)
		F(5)–Be–F(6)	110·3 (2)

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* Tutton's Salts. XI.

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Table 3. *Interatomic distances* (Å) *and angles* (°) *in double salts of nickel*

	Ammonium sulfate	Ammonium chromate	Ammonium selenate	Ammonium tetrafluoro-beryllate	Guanidinium sulfate
Ni–O(7)	2·072	2·073	2·068	2·072 (2)	2·053
Ni–O(8)	2·069	2·054	2·055	2·063 (2)	2·052
Ni–O(9)	2·033	2·022	2·043	2·027 (2)	2·064
Mean	2·058	2·050	2·055	2·054	2·056
O(7)–Ni–O(8)	88·34	88·44	88·7	88·2 (1)	
O(7)–Ni–O(9)	90·13	90·80	89·5	90·0 (1)	
O(8)–Ni–O(9)	89·22	87·88	88·7	88·9 (1)	
Hydrogen bonds				(F replaces O)	Relative position of second atom*
O(7)···O(5)	2·785	2·787	2·823	2·722 (4)	x,y,z
O(7)···O(6)	2·841	2·827	2·835	2·766 (4)	$x, y, z-1$
O(8)···O(4)	2·708	2·720	2·685	2·625 (4)	$x-1, y, z-1$
O(8)···O(6)	2·759	2·741	2·763	2·730 (4)	$x-\frac{1}{2}, \frac{1}{2}-y, z-1$
O(9)···O(5)	2·765	2·744	2·710	2·708 (4)	$\frac{1}{2}-x, y-\frac{1}{2}, 1-z$
O(9)···O(3)	2·719	2·731	2·768	2·629 (4)	$-x, -y, 1-z$
N(10)···O(3)	2·951	2·935	2·945	2·880 (5)	x,y,z
N(10)···O(3)	2·978	2·940	2·959	3·022 (5)	$x-\frac{1}{2}, \frac{1}{2}-y, z$
N(10)···O(4)		3·213		2·951 (5)	$x-\frac{1}{2}, \frac{1}{2}-y, z$
N(10)···O(5)	2·867	2·816	2·848	2·777 (5)	$\frac{1}{2}-x, \frac{1}{2}+y, 1-z$
N(10)···O(6)	2·905	2·887	2·932	2·837 (5)	$x-\frac{1}{2}, \frac{1}{2}-y, z-1$

* Transformation relating each second atom of ammonium nickel tetrafluoroberyllate to the corresponding atom in the original asymmetric unit.

of Stewart, Davidson & Simpson (1965). Anomalous dispersion for the Ni^{2+} ion was also included (*International Tables*) in the last two refinement cycles as well as a weighting scheme of the form $w = 1/\sigma^2(F_o)$ where $\sigma = A + B|F_o| + C|F_o|^2 + D|F_o|^3$ (Stout & Jensen, 1968). A final cycle was run varying only the H-atom positions and individual isotropic temperature factors ($B = 5{\cdot}0$ Å^2, initially).* The final R value was 0·024 and R_w was 0·029.

Discussion. The structure follows closely that of the corresponding sulfate (Montgomery & Lingafelter, 1964), chromate (Montgomery, 1979), and selenate (Montgomery, 1980) (Tables 1, 2 and 3). The metal-ion–water distances are 2·072 (2), 2·063 (2), and 2·027 (2) Å, showing the usual orthorhombic distortion in the hexaaquanickel ion. These distances are seemingly unaffected by the anion size [Table 3, where a comparison of interatomic distances is given for various ammonium nickel salts, and for the isostructural guanidinium sulfate (Morimoto, 1970)]. A neutron diffraction study (Vicat, Tranqui, Filhol, Roudaut, Thomas & Aléonard, 1975) gives the same pattern for the hexaaquacobalt ion; the metal-ion–water distances are 2·117, 2·109 and 2·058 Å.

The tetrafluoroberyllate ion resembles the chromate ion in that the angles are regular (average 109·5°), but one bond, Be–F(4), is significantly shorter than the average for the other three (0·035 Å). A similar shortening is also observed in the chromate (Montgomery, 1979), and in the selenate (Montgomery, 1980) and is due to hydrogen bonding. F(4) has only one 'normal' hydrogen bond while the other F atoms have three or two. In general, the hydrogen bonds are shorter than in the O analogs, which may be attributed to the greater electronegativity of F. A small change from the regular pattern concerns the bonding of H(13) which is linked to F(3) and F(4) (Table 3). The 'bond' N(10)–H(13)–F(4) is shorter (2·951 Å) than N(10)–H(13)–F(3) (3·022 Å). This is the reverse of the chromate, for example, where the lengths are respectively 3·213 and 2·940 Å.

This research was supported by Defence Research Board Grant 3610-323. The use of facilities at the University of Victoria is gratefully acknowledged. Thanks are due also to Dr G. W. Bushnell for helpful discussions.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35250 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1980). B**36**, 2123–2126

New Indium Molybdenum Selenides: $InMo_6Se_8$ and $In_2Mo_{15}Se_{19}$

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(*Received* 15 *March* 1980; *accepted* 8 *April* 1980)

Abstract. $InMo_6Se_8$: rhombohedral, $R\bar{3}$, a_{hex} = 9·55 (1), c_{hex} = 11·85 (1) Å; a_{rh} = 6·78 (1) Å, α = 89·5 (3)°, Z = 1. It crystallizes with the $PbMo_6S_8$ structure type. $In_2Mo_{15}Se_{19}$: rhombohedral, $R\bar{3}c$, a_{hex} = 9·84 (1), c_{hex} = 57·47 (8) Å; a_{rh} = 19·98 (3) Å, α = 28·5 (1)°, Z = 6. It contains Mo_6Se_8 and Mo_9Se_{11} building blocks and may be considered as a stacking variant of the hexagonal $In_{\sim 3}Mo_{15}Se_{19}$ phase. The Mo—Mo distances in the Mo_6 and Mo_9 clusters are examined and the bonding is discussed. (The final R values are 0·10 and 0·08 respectively.)

Introduction. Indium is one of the few metals for which a rhombohedral molybdenum selenide of formula MMo_6Se_8 (M = metal) has not yet been found (Fischer, 1978; Yvon, 1979). There are, however, related compounds of similar composition such as hexagonal $In_xMo_{15}Se_{19}$ ($2·9 < x < 3·4$) containing Mo_6Se_8 and Mo_9Se_{11} building blocks (Grüttner, Yvon, Chevrel, Potel, Sergent & Seeber, 1979; Seeber, Decroux, Fischer, Chevrel, Sergent & Grüttner, 1979; Chevrel, Sergent, Seeber, Fischer, Grüttner & Yvon, 1979), and hexagonal $InMo_3Se_3$ containing one-dimensional $^1_\infty(Mo_3Se_3)$ fibres (Hönle, von Schnering, Lipka & Yvon, 1980). The apparent absence of a rhombohedral phase in this system was curious because a rhombohedral $InMo_6S_8$ phase in the corresponding sulphur system exists (Yvon, 1979; Yvon & Paoli, 1977).

In this article we report on the synthesis and structural analysis of the rhombohedral selenide $InMo_6Se_8$ which contains Mo_6Se_8 building blocks. It forms simultaneously with another rhombohedral phase of composition $In_2Mo_{15}Se_{19}$ containing Mo_6Se_8 and Mo_9Se_{11} building blocks similar to those found in the more In-rich hexagonal $In_{\sim 3}Mo_{15}Se_{19}$ phase. The existence of a rhombohedral $In_2Mo_{15}Se_{19}$ phase has been reported recently (Potel, Chevrel, Sergent, Decroux & Fischer, 1979) but no atomic coordinates and no details of its formation were given.

The two crystals investigated in this work were isolated from a sample of approximate composition In:Mo:Se = 1:6:8 whose preparation has been described (Grüttner *et al.*, 1979). The heat treatment was carried out at about 1450 K in an evacuated quartz tube for a few days. A Guinier photograph showed that the powder pattern was different from those of the hexagonal $In_{\sim 3}Mo_{15}Se_{19}$ and $InMo_3Se_3$ phases. The diffraction lines were relatively diffuse, indicating that the compounds were not well crystallized. This was later confirmed by the structural analysis which showed that the quality of the single crystals was rather poor. Both substances have a rhombohedral structure. For $InMo_6Se_8$ the cell parameters and space group ($R\bar{3}$) suggested isotypy with $PbMo_6S_8$ (Marezio, Dernier, Remeika, Corenzwit & Matthias, 1973). For $In_2Mo_{15}Se_{19}$ the Laue group ($\bar{3}m$) and the systematically absent reflexions ($h\bar{h}0l$ with $l = 2n + 1$) indicated the possible space groups $R\bar{3}c$ and $R3c$ (*International Tables for X-ray Crystallography*, 1969). A comparison of the hexagonal cell parameters a_{hex} and c_{hex} with those of $In_{\sim 3}Mo_{15}Se_{19}$ ($a \sim a_{hex}$, $c \sim c_{hex}/3$) suggested that the two compounds were structurally related.

Integrated intensities of 480 ($InMo_6Se_8$) and 236 ($In_2Mo_{15}Se_{19}$) reflexions with $I > 3\sigma(I)$ were recorded on an automated diffractometer to a limit of $\sin\theta/\lambda$ = 0·5 Å^{-1}. For $In_2Mo_{15}Se_{19}$ the data were collected at

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0567-7408/80/092123-04$01.00