Synthesis, Crystal Structure, and Thermal Studies of $(NH_4)_2Cd_2(SeO_4)_3.3H_2O$

M. L. MARTÍNEZ, A. RODRIGUEZ, AND L. MESTRES

Departamento de Química Inorgánica, Universidad de Barcelona, Diagonal 647, 08028 Barcelona, Spain

X. SOLANS

Departamento de Cristalografía, Mineralogía y Depósitos Minerales, Universidad de Barcelona, Martí i Franqués s/n, 08028 Barcelona, Spain

AND E. H. BOCANEGRA

Departamento de Física Aplicada II, Universidad del Pais Vasco, Aptdo 644, 48080 Bilbao, Spain

The species $(NH_4)_2Cd_2(SeO_4)_3.3H_2O$ has been synthesized and its crystal structure has been determined. Crystals were obtained by slow evaporation from an aqueous solution at 85–90°C. The compound is monoclinic, $P2_1/m$, $a = 6.836(2)$, $b = 19.372(4)$, $c = 5.690(2)$ Å, $\beta = 94.02(2)°$, $V = 751.7(6)$ Å^3, $D_x = 3.285$ g cm^{-3}, $Z = 2$; $F(000) = 692.0$, $\lambda(MoK\alpha) = 0.71069$ Å, $\mu(MoK\alpha) = 106.99$ cm^{-1}, 298 K. Refinement was terminated at $R = 0.043$ for all observed reflections. Two kinds of tetrahedrally coordinated selenium atoms occur in the structure which form double chains which in turn give the three-dimensional structure. The cadmium atoms are coordinated by five oxygen atoms from different selenate anions, and by an oxygen atom from a water molecule. This structure gives cavities, each one accommodating a water molecule and two ammonium groups. Thermogravimetry shows that the anhydrous species of langbeinite stoichiometry is not stable. © 1990 Academic Press, Inc.

Introduction

The parallelism between sulfates and selenates is a well-known fact: most selenates are isomorphous with the corresponding sulfates. This is true for double salts such as the alums, as well as in complex salts such as $K_2[Cu(H_2O)_6](SeO_4)_2$ (*1, 2*). There is only one reference on double selenates with langbeinite structure $(K_2Mg_2(SO_4)_3)$: Kohler and Franke (*3*) describe $(NH_4)_2Mn_2(SeO_4)_3$ and mixed crystals with general formula $(NH_4)_2MN_2(SeO_4, SO_4)_3$. However, examples are known of double salts with langbeinite structures with other anions: chromates (*4*) and (*5*), fluoroberyllates (*6–8*), phosphates (*9, 10*), and more recently triple vanadates (*11, 12*).

Recently, the solid–solutions $M_2^IM_2^{II}(SO_4)_x(SeO_4)_{3-x}$ ($3 > x > 2.75$ and $3 > x > 2.50$) were obtained (*13*). In an attempt to obtain selenate langbeinites, we repeated

the method described by Kohler and Franke
(3). The species obtained in all cases are in
disagreement with the results of Kohler and
Franke, they are not langbeinites. We tried
the synthesis following the method used by
McMurdie (4) to prepare the sulfate lang-
beinite. We centered our interest in the thor-
oughly studied ammonium–cadmium lang-
beinite, which presents a cubic–monoclinic
(paraelectric–ferroelectric) phase transition
(14, 15).

Experimental

An aqueous solution of $(NH_4)_2SeO_4$ and
$CdSeO_4 \cdot H_2O$ (mole ratio 1 : 2) was kept at
85–90°C until a crystal mass formed. The
colorless crystals were separated from the
mother liquor. X-ray powder diffraction pat-
terns were obtained on a Siemens D500 au-
tomatic diffractometer. Ni-filtered $CuK\alpha$ ra-
diation was used with scan speed equal to
$\frac{1}{2}\theta$ min^{-1} and θ range of 5–30°.

An equidimensional crystal (0.07 × 0.07
× 0.07 mm) was mounted on a Philips PW-
1100 four-circle diffractometer. Unit-cell
parameters were determined from auto-
matic centering of 25 reflections (4 ≤ θ ≤
12°) and least-squares refinement. Intensit-
ies were collected with graphite-monochro-
mated $MoK\alpha$ radiation using the ω-scan
technique, scan width 0.8°, scan speed 0.03°
sec^{-1}. 1645 reflections were measured in the
range 2 ≤ θ ≤ 25°; 938 of which were ob-
served with $I \geq 2.5\ \sigma(I)$. Three reflections
were measured every 2 hr as orientation and
intensity control, no significant intensity de-
cay was observed. Lorentz–polarization
and absorption corrections were made (max
and min transmission factors 0.85 and 0.73,
respectively). The structure was solved
from the Patterson synthesis, and refined
with full-matrix least-squares using the
SHELX76 computer program. The function
minimized was $\Sigma w\|F_o| - |F_c\|^2$, where $w =$
$(\sigma^2(F_o) + 0.004\ |F_o|^2)^{-1}$; f, f', and f'' were
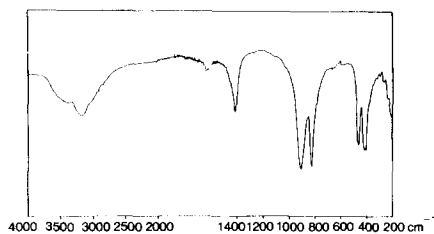taken from International Tables of X-ray

FIG. 1. IR spectra of $(NH_4)_2Cd_2(SeO_4)_3 \cdot 3H_2O$.

Crystallography (16). The final R factor was
0.043 (R_w = 0.046) for all observed reflec-
tions. Max shift/e.s.d = 0.3 in U_{23} of O(23);
max and min peaks in the final difference
synthesis were 0.3 and $-0.3\ e$ Å^{-3}, respec-
tively.

Determinations of cadmium content were
carried out by atomic absorption analysis
on a PYE Unicam S.P. 1900 spectrometer.
Hydrogen and nitrogen elemental analyses
were carried out on a Perkin–Elmer 240 mi-
croanalyzer. I.C.P. of selenium was carried
out on a Jobin Ybon analyzer. Infrared spec-
tra were recorded on a Perkin–Elmer 1330
spectrophotometer (samples prepared as
KBr pellets or Nujol mulls). Differential
scanning calorimetry of the samples were
measured with a Perkin–Elmer DSC 7 in the
temperature range from +30 to −170°C,
(rate 10.0°C/min). The thermogravimetric
analyses were performed with a Per-
kin–Elmer TGA7 in the temperature range
from +25 to 375°C (rate 10.0°C/min). All
the measurements were made on polycrys-
talline samples.

Results

The theorical values for the $(NH_4)_2Cd_2$
$(SeO_4)_3 \cdot 3H_2O$ give, in wt% are 3.76% N,
1.88% H, 30.23% Cd, and 31.85% Se. The
results of the analyses are 3.7% N, 1.9% H,
30.3% Cd, and 31.9% Se. The IR absorption
spectra (Fig. 1) clearly show the internal
vibrations of stretching (ν_3) and bending (ν_4)
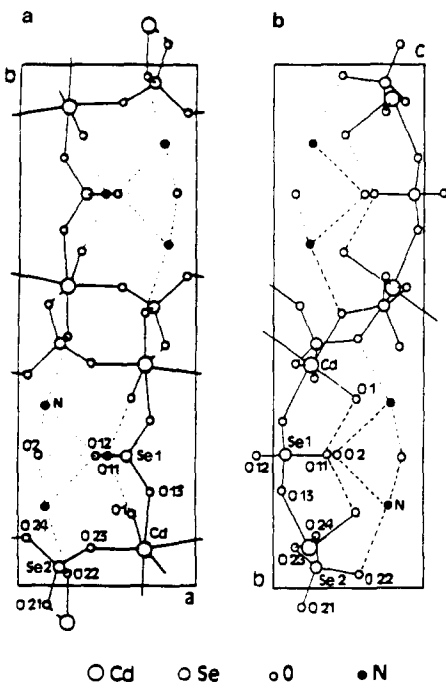of tetrahedral SeO₄ group, at 800–900 cm^{-1}

FIG. 2. (a) [001] projection of the unit cell of $(NH_4)_2$ $Cd_2(SeO_4)_3.3H_2O$. (b) [100] projection of the unit cell of $(NH_4)_2Cd_2(SeO_4)_3.3H_2O$.

FIG. 3. [001] projection of the structure of $(NH_4)_2Cd_2$-$(SeO_4)_3.3H_2O$ showing the closed groupings.

and 400–500 cm^{-1}, respectively. The ν_3 and ν_4 vibrations are split into two components each, due to the symmetry of the SeO_4 groups. The bending vibrations of NH_4^+ and H_2O appear in the region 1400 and 1600 cm^{-1}, and the stretching vibrations of the same groups appear in the region 2800–3800 cm^{-1}.

EDAX on different points of crystals or on a polycristalline mass showed no compositional variations.

Figures 2a and 2b show the projections [001] and [100] of the unit cell, respectively. There are two crystallographically different Se atoms both tetrahedrally coordinated by oxygen atoms. The Se(2) atoms form Cd–Se–Cd chains parallel to [100]. These are joined together in pairs by the Se(1) atoms forming double chains which in turn are joined among themselves by the Se(2)
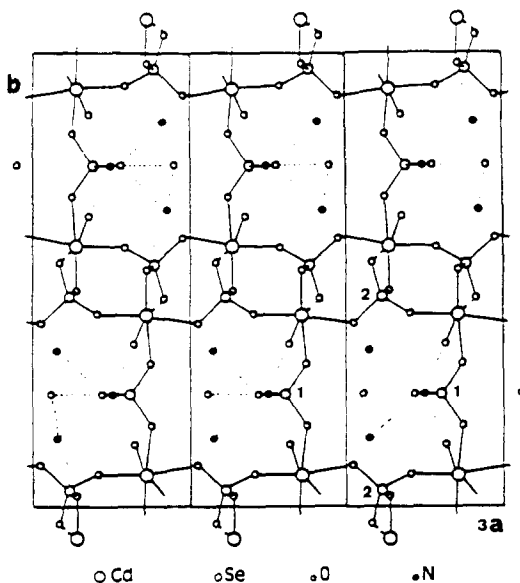
atoms, forming a three-dimensional network. The four cadmium atoms of the unit cell are crystallographically equivalent. They are coordinated by five oxygen atoms of different selenate groups and by a sixth oxygen atom from a water molecule. The projection of the structure of $(NH_4)_2Cd_2$ $(SeO_4)_3.3H_2O$ on [001] (Fig. 3) shows the closed grouping Cd–Se(2)–Cd–Se(1)–Cd–Se(2)–Cd–Se(1) containing one water mole-
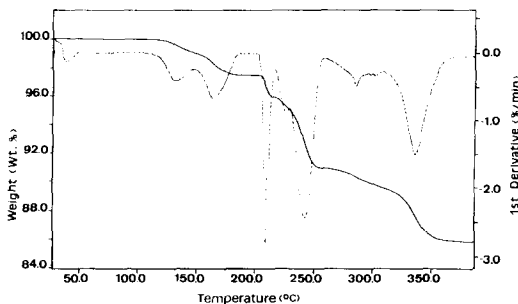

FIG. 4. T.G. and D.T.G. curves of $(NH_4)_2Cd_2$ $(SeO_4)_3.3H_2O$.

TABLE I

FINAL ATOMIC COORDINATES ($\times 10^4$) OF $(NH_4)_2Cd_2(SeO_4)_3.3H_2O$ $(B_{EQ} = 8\pi^2/3u_{ij}a_i^*a_j^*a_i a_j)$ AND ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$) FOR $(NH_4)_2Cd_2(SeO_4)_3 3H_2O$

		X/A	Y/B	Z/C	B_{eq}
	CD(1)	27502(9)	92539(3)	23077(15)	2.08(4)
	SE(1)	61730(17)	25000	93308(27)	2.05(7)
	SE(2)	77161(13)	96479(5)	26937(19)	1.92(5)
	O(11)	5110(19)	2500	6670(28)	4.29(63)
	O(12)	4439(11)	2500	11292(21)	3.19(53)
	O(13)	7520(10)	1820(3)	9582(14)	2.54(33)
	O(21)	8373(8)	10388(3)	1656(15)	2.78(34)
	O(22)	2759(11)	10233(3)	4471(15)	3.01(33)
	O(23)	5854(8)	9268(4)	1259(16)	3.64(40)
	O(24)	9506(8)	9060(3)	2607(16)	2.36(33)
	O(1)	3542(13)	8606(5)	5360(23)	6.57(65)
	O(2)	1003(18)	2500	5930(27)	4.83(73)
	N	8532(11)	8459(4)	7718(21)	3.72(54)

	u_{11}	u_{22}	u_{33}	u_{23}	u_{13}	u_{12}
CD(1)	154(4)	274(5)	384(7)	−10(3)	161(4)	0
SE(1)	256(6)	212(7)	327(12)	0	132(8)	0
SE(2)	210(5)	281(6)	254(9)	−7(3)	135(6)	4(3)
O(11)	592(59)	401(66)	653(116)	0	149(78)	0
O(12)	117(37)	889(78)	213(87)	0	69(55)	0
O(13)	398(36)	175(32)	403(57)	15(28)	101(41)	89(26)
O(21)	190(26)	211(33)	668(70)	14(30)	116(40)	6(21)
O(22)	627(42)	281(35)	261(49)	−48(28)	217(44)	−5(29)
O(23)	287(27)	867(59)	201(65)	−155(39)	−169(36)	−16(27)
O(24)	243(31)	391(38)	257(55)	34(30)	−27(38)	119(26)
O(1)	726(56)	489(53)	1280(137)	116(56)	67(80)	3(43)
O(2)	695(75)	581(77)	596(124)	0	313(90)	0
N	266(39)	340(52)	831(116)	170(45)	210(59)	−31(30)

Note. The temperature factor is in the form $\exp(-2\pi\mu_{ij}h_i h_j a_i^* a_j^*)$.

cule and two ammonium groups which are joined to the nearest oxygen atoms by hydrogen bonding.

Tables I and II give the atomic coordinates, anisotropic thermal parameters, bond lengths, and angles for $(NH_4)_2Cd_2$ $(SeO_4)_3.3H_2O$. The X-ray powder diffraction pattern was indexed from the known structure (Table III).

Figure 4 shows the T.G. and D.T.G. of $(NH_4)_2Cd_2(SeO_4)_3.3H_2O$ (sample weight 14.893 mg), temperature range 25–375°C. The weight loss of 14.13% corresponds to the loss of the three water molecules and two ammonium groups. Figure 5 shows the T.G. of the above residue after being left in the air for some time. The weight loss is 5.39%.

No phase transitions were observed in our DSC measurements between +30 and −170°C.

Discussion

We were not able to prepare the selenate langbeinites using the literature method for

TABLE II

Bond Lengths in Angstroms for $(NH_4)_2Cd_2(SeO_4)_3 \cdot 3H_2O$ and Angles in Degrees for $(NH_4)_2Cd_2(SeO_4)_3 \cdot 3H_2O$

SE(2) ---CD(1)	3.471(1)		O(22) ---SE(2)	1.684(5)	
O(13)i ---CD(1)	2.344(5)		O(23) ---SE(2)	1.637(6)	
O(2)ii --CD(1)	2.428(5)		O(24) ---SE(2)	1.675(5)	
O(22)iii -CD(1)	2.261(6)		O(12)iv--N	2.834(9)	
O(23) ---CD(1)	2.244(5)		O(2)i ---N	2.820(12)	
O(24)v ---CD(1)	2.267(5)		O(13)vi--N	3.060(9)	
O(1) ---CD(1)	2.180(11)		O(21)vii-N	3.085(9)	
O(11) ---SE(1)	1.633(16)		O(22)iii -N	2.931(9)	
O(12) ---SE(1)	1.684(8)		O(24)iii -N	3.048(9)	
O(13) ---SE(1)	1.608(5)		O(1)viii -O(11)	2.630(12)	
O(21) ---SE(2)	1.625(6)		O(2) ---O(11)	2.808(12)	
			O(2)ix ---O(24)	3.160(120	
O(21)ii -CD(1) -O(13)i	79.5(2)		O(12) -SE(1) -O(11)	109.1(5)	
O(22)iii- CD(1) -O(13)i	172.7(2)		O(13) -SE(1) -O(11)	107.3(3)	
O(22)iii- CD(1) -O(21)ii	104.7(2)		O(13) -SE(1) -O(12)	111.5(3)	
O(23) -CD(1) -O(13)	86.2(2)		O(13)x- SE(1) -O(11)	107.4(3)	
O(23) -CD(1) -O(21)	89.5(2)		O(13)x- SE(1) -O(12)	111.4(3)	
O(23) -CD(1) -O(22)iii	99.7(2)		O(13)x- SE(1) -O(13)	110.0(5)	
O(24) -CD(1) -O(13)i	80.9(2)		O(22) -SE(2) -O(21)	107.8(2)	
O(24) -CD(1) -O(21)ii	82.7(2)		O(23) -SE(2) -O(21)	116.1(2)	
O(24) -CD(1) -O(22)iii	93.7(2)		O(23) -SE(2) -O(22)	110.2(4)	
O(24) -CD(1) -O(23)	165.9(3)		O(24) -SE(2) -O(21)	111.6(3)	
O(1) -CD(1) -O(13)i	82.2(3)		O(24) -SE(2) -O(22)	108.1(3)	
O(1) -CD(1) -O(21)ii	161.5(3)		O(24) -SE(2) -O(23)	102.9(3)	
O(1) -CD(1) -O(22)iii	93.3(3)		SE(2) -O(23) -CD(1)	126.1(4)	
O(1) -CD(1) -O(23)	91.9(3)		SE(2) -O(24) -CD(1)	127.6(3)	
O(1) -CD(1) -O(24)	92.0(3)				

Note. Symmetry Codes: (i): $1 - x$; $1 - y$, $1 - z$. (ii): $1 - x$; $2 - y$; $-z$. (iii): $1 - x$; $2 - y$; $1 - z$. (iv): $1 - x$; $1 - y$; $2 - z$. (v): $x - 1$; y; z. (vi): $2 - x$; $y + 1/2$; $2 - z$. (vii): $2 - x$; $2 - y$; $1 - z$. (viii): $1 - x$; $y - 1/2$; $1 - z$. (ix): $1 - x$; $y + 1/2$; $1 - z$. (x): x; $1/2 - y$; z.

TABLE III

Powder Diffraction Lines of Monoclinic $(NH_4)_2Cd_2(SeO_4)_3 \cdot 3H_2O$

$d(Å)$	I/I_0	hkl	$d(Å)$	I/I_0	hkl	$d(Å)$	I/I_0	hkl	$d(Å)$	I/I_0 hkl	$d(Å)$	I/I_0	hkl
9.7192	62	020	3.3554	100	210	2.6884	20	102	2.1428	9 330	1.7702	7	332
6.4456	27	110	3.3001	10	141	2.5735	17	161	2.1085	18 202	1.7489	17	272
5.3732	34	011	3.2424	26	060	2.5065	7	112	2.0800	9 162	1.7264	13	133
4.8765	10	021	3.1980	38	051	2.4157	19	080	2.0597	12 310	1.7145	15	219
4.5739	87	011	3.1285	48	141	2.3175	13	171	1.9562	9 252	1.6882	15	322
4.2649	50	031	2.8522	8	151	2.2992	28	052	1.9490	8 191	1.6795	20	143
3.9806	45	140	2.8240	13	201	2.2758	12	300	1.8782	8 172	1.6679	10	401
3.4860	24	131	2.7489	59	231	2.2368	13	212	1.8021	13 322	1.6365	10	063
3.4074	26	200	2.7164	19	221	2.2082	14	152	1.7900	10 103	1.5669	15	163

FIG. 5. T.G. curve of the residue.

290°C) do not show the reflections of the langbeinite-type structure. To sum up, it does not seem possible to obtain double selenates with langbeinite structure since the cavities created by the larger selenate are occupied by water molecules forming a more stable, hydrated phase.
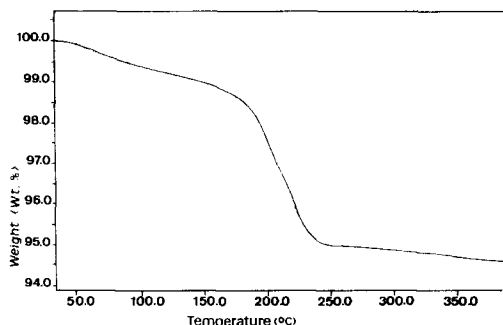
Acknowledgments

the sulfate langbeinites (4), and could only obtain hydrated compounds. The explanation of the result could be as follows: The cadmium atom in $(NH_4)_2Cd_2(SeO_4)_3 \cdot 3H_2O$ is surrounded by the larger selenate ions compared to sulfate in the langbeinite structure. This gives a more open structure which permits the accommodation of water molecules and thus the compound crystallizes as an hydrate and not as an anhydrous salt.

The first weight loss in the T.G. occurs in two steps and corresponds to the loss of one water molecule. The weight loss at higher temperature corresponds to the loss of more than two water molecules, which can be explained by the overlap of the loss of water with the loss of ammonia at the end of the T.G. After the thermal treatment the atom ratio could be adjusted to the formula $2Cd$-$SeO_4 \cdot SeO_3$ or $CdSe_2O_7 \cdot CdSeO_4$.

Figure 4 shows that the material obtained after the thermal treatment is not stable and becomes hydrated. Since the stable phase of cadmium selenate is the monohydrate (17), the weight loss in Fig. 4 can be adjusted to the formula $2CdSeO_4 \cdot SeO_3$.

The X-ray powder diffraction patterns of $(NH_4)_2Cd_2(SeO_4)_3 \cdot 3H_2O$ at different temperatures (190, 200, 220, 240, 250, 260, and

References

1. J. WHITNALL, C. H. L. KENNARD, AND F. H. MOORE, Cryst. Struct. Commun. 4, 709 (1975).
2. A. MONGE AND E. GUTIERREZ-PUEBLA, Acta Crystallogr., Sect. B 37, 427 (1981).
3. K. KOHLER AND W. FRANKE, Acta Crystallogr. 17, 1088 (1964).
4. H. F. MCMURDIE, M. C. MORRIS, J. DE GROOT, AND H. E. SWANSON, J. Res. Natl. Bur. Stand., Sect. A 75, 435 (1971).
5. P. P. CORD, P. COUTINE, AND G. PANNETIER, Bull. Soc. Chim. Fr. 7, 2461 (1971).
6. S. ALEONARD AND Y. LE FUR, Bull. Soc. Fr. Mineral. Cristallogr. 90, 168 (1967).
7. M. GENTY, Y. LE FUR, AND S. ALEONARD, Bull. Soc. Fr. Mineral Cristallogr. 91, 237 (1968).
8. Y. LE FUR AND S. ALEONARD, Mater. Res. Bull. 4, 601 (1969).
9. A. BOUJADA AND R. PERRET, J. Appl. Crystallogr. 10, 129 (1977).
10. R. PERRETT AND A. BOUJADA, C. R. Acad. Sci., Ser. C 288(21), 525 (1979).
11. M. A. NABAR AND D. S. PHANASGAONKAR, J. Appl. Crystallogr. 13, 450 (1980).
12. M. A. NABAR AND D. S. PHANASGAONKAR, Spectrochim. Acta A 37, 279 (1981).
13. M. L. MARTI'NEZ, A. RODRIGUEZ, AND L. MESTRES, J. Solid State Chem. 84, 308 (1990).
14. V. DVORAK, Phys. Status Solidi 52, 93 (1972).
15. S. KRESKE AND V. DEVARAJAN, J. Phys. C: Solid State Phys. 15, 7333 (1982).
16. "International Tables of X-Ray Crystallography," Vol. IV, pp. 99 and 149, Kynoch Press, Birmingham (1974).
17. C. G. DAUBNEY, Analyst 57, 22 (1932).