1963*b*). In the other important bleaching agent used in solid detergents, $Na_2CO_3.1\frac{1}{2}H_2O_2$, these bonds are slightly stronger, as suggested by the shorter O···O distances in the range 2·54–2·65 Å (Carrondo, Griffith, Jones & Skapski, 1977).

The bleaching action of the title compound must clearly be different from that of 'sodium percarbonate', which can be regarded as a portable form of hydrogen peroxide, since in the former covalent B—O bonds have to be broken in order to release the peroxide.

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References

Allen, F. H., Rogers, D. & Troughton, P. G. H. (1971). *Acta Cryst.* B**27**, 1325–1337.
Carrondo, M. A. A. F. de C. T., Griffith, W. P., Jones, D. P. & Skapski, A. C. (1977). *J. Chem. Soc. Dalton Trans.* pp. 2323–2327.
Corazza, E., Menchetti, S. & Sabelli, C. (1975). *Acta Cryst.* B**31**, 1993–1997.
Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
Doyle, P. A. & Turner, P. S. (1968). *Acta Cryst.* A**24**, 390–397.
Hansson, A. (1961). *Acta Chem. Scand.* **15**, 934–935.
Hughes, E. W. (1941). *J. Am. Chem. Soc.* **63**, 1737–1752.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
Pedersen, B. F. (1972). *Acta Cryst.* B**28**, 1014–1016.
Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. & Hall, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Wells, A. F. (1975). *Structural Inorganic Chemistry*, 4th ed., p. 421. Oxford: Clarendon Press.
Zachariasen, W. H. (1963*a*). *Acta Cryst.* **16**, 380–384.
Zachariasen, W. H. (1963*b*). *Acta Cryst.* **16**, 385–389.

Acta Cryst. (1978). B**34**, 3554–3558

Barium Tin Chromium Oxide, A New Hollandite Phase

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The crystal structure and composition of barium tin chromium oxide were determined by single-crystal X-ray techniques. The composition was determined as $Ba_xSn_{4-2x}Cr_{2x}O_8$, with $x = 0{\cdot}70$, and checked by preparing a pure powder sample of this composition. The compound has a hollandite structure and crystallizes in the space group $I2/m$ with $a = 10{\cdot}532$ (2), $b = 3{\cdot}108$ (1), $c = 10{\cdot}012$ (2) Å, $\beta = 91{\cdot}56$ (1)°, and $Z = 2$. Transformed to space group $C2/m$ the unit-cell parameters are $a = 14{\cdot}728$, $b = 3{\cdot}108$, $c = 10{\cdot}012$ Å, $\beta = 134{\cdot}37$°, and $Z = 2$. Data were collected with a three-circle diffractometer using Mo $K\alpha$ radiation. Full-matrix least-squares refinement of 991 observed symmetry-independent reflexions gave a conventional R index of 0·037 ($R_w = 0{\cdot}049$). Sn and Cr are octahedrally coordinated, Ba has tenfold coordination. Several isomorphs have been prepared. A number of unsuccessful attempts to prepare isomorphs are also reported.

Introduction

In an investigation of some Ba–M^{4+}–M^{3+}–O systems, unknown phases with identical X-ray powder diffraction patterns were found. Because of the unknown composition we could not prepare a pure sample to index the diffraction pattern. Fortunately, needle-shaped crystals suitable for single-crystal diffraction formed in the Ba–Sn–Cr–O system.

Experimental

All starting materials were of AR quality. $BaCO_3$, SnO_2 and Cr_2O_3 were thoroughly mixed under acetone in an agate mortar in the ratio 1:3:1. The mixture was dried and heated for several days at 1450°C in air. The reaction product consisted of numerous thin needle-shaped crystals. X-ray powder diffraction showed the unknown phase to be dominant, with $BaCrO_4$ as contaminant. In order to obtain crystals suitable for X-ray diffraction, the sample was reground and heated for two weeks at 1450 °C.

Some of the newly formed crystals were selected for single-crystal X-ray diffraction experiments. The composition, which was found to be $Ba_{0.7}Sn_{2.6}Cr_{1.4}O_8$, having been established (see below), this compound was synthesized by heating a mixture of $BaCO_3$, SnO_2 and Cr_2O_3 in the ratio 1:3·71:1 for several days at a temperature of 1300 °C. The powder diffraction pattern of the reaction product could be interpreted with the cell parameters found by single-crystal diffraction. This method of composition determination is not unusual in complicated systems (Reid, Mumme & Wadsley, 1968).

Unit cell and space group

All crystals examined appeared to be twinned. A crystal with one of the twins dominating was selected by comparing Weissenberg photographs of several crystals. From zero- and first-level Weissenberg photographs (Cu $K\alpha$ radiation), a monoclinic unit cell was found with systematically absent reflexions of the type $h + k + l = 2n + 1$, indicating the space group $I2/m$. In the present investigation this space group was retained instead of space group $C2/m$, since in the former β is almost 90°. Moreover, space group $I2/m$ facilitates comparison with the tetragonal hollandite structure (Dryden & Wadsley, 1958).

The precise unit-cell parameters were determined on a single-crystal diffractometer at 20 °C using Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). The parameters of the unit cell in space group $I2/m$ are: $a = 10{\cdot}532\ (2)$, $b = 3{\cdot}108\ (1)$, $c = 10{\cdot}012\ (2)$ Å, $\beta = 91{\cdot}56\ (1)°$, resulting in the parameters $a = 14{\cdot}728$, $b = 3{\cdot}108$, $c = 10{\cdot}012$ Å, $\beta = 134{\cdot}37°$ in space group $C2/m$. The transformation matrix from $I2/m$ to $C2/m$ is:

$$\begin{pmatrix} 1 & 0 & -1 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

The twin planes are {001} or {201}, as has been determined by electron diffraction (Cadée & Prodan, to be published).

Collection and reduction of X-ray diffraction data

The needle-shaped crystal (of length 0·17 mm and maximum thickness 0·04 mm) was mounted along its b axis on a three-circle single-crystal diffractometer. Intensities were recorded by the θ–2θ scan method for all reflexions with θ between 0 and 40°, using graphite-monochromated Mo $K\alpha$ radiation. Background intensities were determined at $\theta \pm \frac{1}{2}\Delta$, with $\Delta = (0{\cdot}7 + 0{\cdot}7 \tan \theta)°$. The mean counting time was 43 s for each background and 86 s for the scan. By this method 2670 reflexions were measured.

Reflexions with intensities less than twice their standard deviations, calculated from counting statistics, were considered as not significant. All data were corrected for absorption using a computer program (de Graaff, 1973). The measured shape of the crystal was checked with the measured transmission curves of the head-reflexions 020 and 040. The transmission factors ranged from 45·8 to 56·3% for the 020 and from 43·8 to 53·6% for the 040 reflexions ($\mu = 164$ cm^{-1}). Equivalent reflexions were averaged resulting in 1156 nonequivalent reflexions, 991 of which were significant. After the reduction of the intensities to F values, a Wilson plot was calculated yielding approximate values for the scale factor and the initial overall isotropic thermal parameter B.

Structure determination and refinement

All crystallographic calculations were carried out using the Leiden University IBM 370 computer, with the aid of a set of computer programs written by Dr R. A. G. de Graaff and Mrs E. W. Rutten-Keulemans. Scattering factors for the atoms were from Cromer & Waber (1965), and used after correction for the anomalous dispersion (f'). The function minimized during the least-squares refinement was $w_f(|F_{\text{obs}}| - |F_{\text{calc}}|)^2$,

Table 1. *Positional parameters of* $Ba_xSn_{4-2x}Cr_{2x}O_8$ ($x = 0{\cdot}70$)

	Space group $I2/m$				Space group $C2/m$			
	Position	x	y	z	Position	x	y	z
Ba	4(g)	0	0·167 (1)	0	4(g)	0	0·167	0
M(1)	4(i)	0·3383 (1)	0	0·1537 (1)	4(i)	0·3383	0	0·4920
M(2)	4(i)	0·8549 (1)	0	0·3315 (1)	4(i)	0·8549	0	0·1864
O(1)	4(i)	0·2929 (5)	0	0·3546 (5)	4(i)	0·2929	0	0·6475
O(2)	4(i)	0·0432 (5)	0	0·3124 (5)	4(i)	0·0432	0	0·3556
O(3)	4(i)	0·6457 (5)	0	0·0426 (5)	4(i)	0·6457	0	0·6883
O(4)	4(i)	0·6594 (5)	0	0·3073 (5)	4(i)	0·6594	0	0·9667

where the weight factor $w_f = (\sigma_f)^{-2}$. The positions of the heavy atoms could be determined from the Patterson synthesis. The O positions were found from a Fourier synthesis. During the refinement Ba had to be shifted from (0,0,0) to $(0,\pm y,0)$, with an occupation rate lower than 0·5. The Sn and Cr atoms occupy the same position. The formula was determined by refining occupation rates according to the general formula $Ba_xSn_{4-2x}Cr_{2x}O_8$. The *R* index dropped to 6·2% and after introduction of anisotropic temperature factors to 3·7% with $x = 0{\cdot}70$. Other refinements with independent occupation rates, or $x = 0{\cdot}667$, suggesting a possible ordering by tripling the *b* axis, or a fraction of the Ba atoms at (0,0,0), did not result in lower *R* values. The final parameters are presented in Table 1.*

Discussion of the structure

The structure found (see Fig. 1) is clearly of the hollandite type (Byström & Byström, 1950). The monoclinic distortion has increased. An important difference is the positioning of the Ba atoms. Instead of the 2(*a*) position in space group *I*2/*m* at (0,0,0), Ba now occupies the 4(*g*) position $(0,\pm y,0)$, with $y = 0{\cdot}167$. The coordination of the Ba atom by O atoms is at least lowered from 12 to 10: four Ba—O distances of about 2·79 Å, two of 3·19 Å and four of about 3·32 Å. All relevant distances are presented in Table 2. The ten O atoms coordinating to the Ba atom form a nearly rectangular block, capped on two opposite faces. The very short Ba—Ba distances in Table 2 can be avoided with an occupation rate of 35%. A one-dimensional ordering of the Ba atoms in the tunnels, independent of each other (Byström & Byström, 1951), may explain the very high value of U_{22} for the Ba atoms. Ordering is not very likely as the crystals were air quenched from 1450°C. Also, powder samples heated at 1200°C and sintered at 1000°C for several days did not show diffuse X-ray reflexions due to ordering effects, as found, for example, in $K_{2x}Ti_{8-x}Mg_xO_{16}$, with $x = 0{\cdot}77$ (Beyeler, 1976).

The Sn and Cr atoms are randomly distributed over two 4(*i*) positions $(\pm x,0,\pm z)$ and are octahedrally coordinated by O atoms. The octahedra are strongly distorted (Table 3).

As regards the coordination of the O atoms, O(2) is surrounded by three metal atoms (Cr,Sn) and two Ba atoms, and O(1) and O(4) by three metal atoms and four Ba atoms, irrespective of the occupation rate of the Ba atoms. O(3) is nearly planar coordinated by the metal atoms.

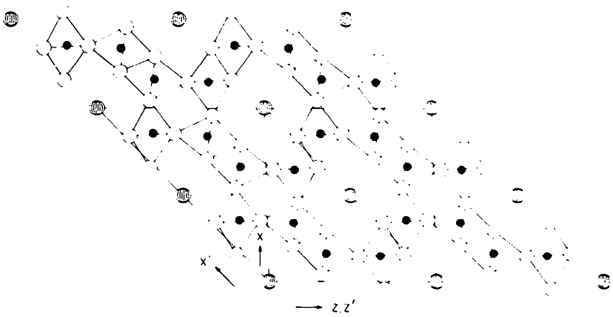

Fig. 1. Projection of the structure of $Ba_xSn_{4-2x}Cr_{2x}O_8$ ($x = 0{\cdot}70$) on the *XZ* plane. The unit cell in space group *I*2/*m* is indicated by the *X* and *Z* directions, the unit cell in *C*2/*m* by the *X'* and *Z'* directions. Ball-type circles: Ba; black circles: Sn, Cr; open circles: O. This projection was generated using the crystallographic plotting program *FIGATOM* (Langlet, 1972).

Table 2. *Relevant distances* (Å) *in* $Ba_xSn_{4-2x}Cr_{2x}O_8$ ($x = 0{\cdot}70$)

Attractive		Repulsive	
Ba–O(1)	2·789 (5) ×2	Ba–Ba	1·032 (6)
Ba–O(4)	2·792 (5) ×2	Ba–Ba	2·076 (6) ×2
Ba–O(2)	3·190 (5) ×2	O(1)–O(1)	2·741 (8) ×2
Ba–O(1)	3·315 (4) ×2	O(1)–O(2)	2·652 (7)
Ba–O(4)	3·317 (5) ×2	O(1)–O(2)	2·889 (6) ×2
M(1)–O(3)	1·977 (5)	O(1)–O(3)	2·919 (6) ×2
M(1)–O(2)	2·016 (4) ×2	O(2)–O(3)	2·939 (6) ×2
M(1)–O(1)	2·080 (4) ×2	O(2)–O(3)	2·959 (6) ×2
M(1)–O(1)	2·081 (5)	O(3)–O(4)	2·650 (7)
M(2)–O(2)	1·998 (5)	O(3)–O(4)	2·953 (6) ×2
M(2)–O(3)	2·001 (3) ×2	O(4)–O(4)	2·737 (9) ×2
M(2)–O(4)	2·066 (5)		
M(2)–O(4)	2·087 (3) ×2		

Table 3. *Relevant angles* (°) *in* $Ba_xSn_{4-2x}Cr_{2x}O_8$ ($x = 0{\cdot}70$)

O(1)–Ba–O(1)	136·3 (1)	O(1)–*M*(1)–O(1)	82·4 (2)	O(2)–*M*(2)–O(3)	94·6 (2)
O(1)–Ba–O(2)	131·3 (1)	O(1)–*M*(1)–O(1)	96·7 (2)	O(2)–*M*(2)–O(4)	89·4 (2)
O(1)–Ba–O(2)	57·3 (1)	O(1)–*M*(1)–O(2)	80·7 (2)	O(2)–*M*(2)–O(4)	167·8 (2)
O(1)–Ba–O(4)	88·7 (2)	O(1)–*M*(1)–O(2)	89·7 (2)	O(3)–*M*(2)–O(3)	101·9 (2)
O(1)–Ba–O(4)	75·3 (2)	O(1)–*M*(1)–O(2)	172·9 (2)	O(3)–*M*(2)–O(4)	80·8 (2)
O(2)–Ba–O(2)	161·4 (1)	O(1)–*M*(1)–O(3)	92·0 (2)	O(3)–*M*(2)–O(4)	93·1 (2)
O(2)–Ba–O(4)	131·7 (1)	O(1)–*M*(1)–O(3)	171·6 (2)	O(3)–*M*(2)–O(4)	174·9 (2)
O(2)–Ba–O(4)	57·0 (1)	O(2)–*M*(1)–O(2)	100·9 (2)	O(4)–*M*(2)–O(4)	82·5 (2)
O(4)–Ba–O(4)	136·3 (1)	O(2)–*M*(1)–O(3)	95·7 (2)	O(4)–*M*(2)–O(4)	96·2 (2)

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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 33781 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. Ba *and* Sr *isomorphs of the hollandite structure*

Space group $I4/m$

Compound	x	Treatment	a	c	Reference
$Ba_xSi_{4-2x}Al_{2x}O_8$	0·75	High pressure	9·415 Å	2·72 Å	Reid & Ringwood (1969)
$Ba_xTi_{4-x}Mg_xO_8$	0·50	Verneuil	10·110	2·986	Dryden & Wadsley (1958)
$Sr_xSi_{4-2x}Al_{2x}O_8$	0·75	High pressure	9·32	2·72	Reid & Ringwood (1969)
$Ba_xGe_{4-2x}Cr_{2x}O_8$	0·75	1w; 1250°C	9·804 (1)	2·904 (1)	This work
$Ba_xRu_{4-2x}Cr_{2x}O_8$	0·65	1w; 1250	9·881 (5)	3·017 (1)	This work
$Ba_xTi_{4-2x}Al_{2x}O_8$	0·60	1w; 1250	9·972 (1)	2·924 (1)	This work
$Ba_xTi_{4-2x}Ga_{2x}O_8$	0·65	1w; 1250	10·042 (1)	2·964 (1)	This work

Space group $I2/m$

Compound	x	Treatment	a	b	c	β	Comments
$Sr_xTi_{4-2x}Cr_{2x}O_8$	0·65	2w; 1250°C	10·170 (4) Å	2·951 (2) Å	9·732 (4) Å	91·53 (3)°	
	0·70	2w; 1300	10·18 (5)	2·93 (1)	9·76 (2)	91·8 (2)	
$Sr_xTi_{4-2x}Fe_{2x}O_8$	0·67	2w; 1300	10·23 (3)	2·99 (1)	9·96 (2)	90·7 (7)	
$Ba_xTi_{4-2x}Cr_{2x}O_8$	0·65	1w; 1230	10·142 (4)	2·954 (1)	9·925 (3)	90·76 (2)	
	0·67	1w; 1400	10·160 (1)	2·956 (1)	9·908 (1)	90·83 (1)	
$Ba_xTi_{4-2x}Fe_{2x}O_8$	0·65	2w; 1230	10·205 (4)	2·975 (1)	9·940 (4)	90·85 (2)	
	0·67	2w; 1200	10·19 (1)	2·96 (3)	9·94 (1)	90·84 (2)	
	0·70	2w; 1230	10·24 (3)	3·05 (1)	9·92 (2)	91·15 (9)	$BaTi_2Fe_4O_{11}$
$Ba_xSn_{4-2x}Cr_{2x}O_8$	0·70	1w; 1300	10·516 (1)	3·104 (1)	10·002 (2)	91·47 (1)	
	0·80	1w; 1300	10·522 (3)	3·102 (1)	10·000 (3)	91·56 (1)	Not pure
$Ba_xSn_{4-2x}Fe_{2x}O_8$	0·67	2w; 1300	10·537 (2)	3·126 (1)	10·129 (1)	91·22 (1)	Not pure
	0·70	1w; 1300	10·539 (1)	3·126 (1)	10·130 (1)	91·21 (1)	
$Ba_xSn_{4-2x}In_{2x}O_8$	0·70	4w; 1300	10·82 (1)	3·204 (2)	10·17 (1)	91·71 (2)	
	0·75	4w; 1300	10·844 (5)	3·206 (1)	10·172 (4)	91·72 (2)	
	0·80	2w; 1300	10·855 (1)	3·212 (1)	10·153 (1)	91·93 (1)	In_2O_3

Isomorphs

Many compounds with the hollandite structure can be found in the literature, most having tetragonal symmetry and space group $I4/m$. The majority of these compounds have a univalent atom at the (0,0,0) position (Bayer & Hoffman, 1966*a*,*b*; Kume, Matsumoto & Koizumi, 1966; Kinomura, 1973). A monoclinic hollandite was found by Endo, Kume, Kinomaru & Koizumi (1976). Also, some high-pressure phases have been found (Ringwood, Reid & Wadsley, 1967; Reid & Ringwood, 1969). The compounds with a divalent atom at (0,0,0) are listed in Table 4, together with our results. Some comments on Table 4 now follow. $Ba_xTi_{4-x}Mg_xO_8$ is the first synthetic hollandite reported (Dryden & Wadsley, 1958), with x ranging from 0·3 to 0·57. Most of our compounds have monoclinic symmetry; the unit-cell parameters are given for space group $I2/m$ to demonstrate the link with the tetragonal hollandites. Three compounds could be indexed with tetragonal symmetry, suggesting space group $I4/m$. The X-ray powder diffraction patterns were interpreted with the aid of the computer program *T*123 (Rietveld, 1969).

The X-ray diffraction patterns of the hexagonal compound $BaTi_4Al_2O_{12}$ with a = 8·860 and c = 18·458 Å (Guha & Kolar, 1972) and of tetragonal $BaTi_5Al_2O_{14}$ with a = 7·025 and c = 10·156 Å (Guha, Kolar & Volavsek, 1976) are identical with the pattern of a tetragonal hollandite with cell parameters a = 9·972 and c = 2·924 Å, except for the weakest reflexions. The formulae $BaTi_4Al_2O_{12}$ and $BaTi_5Al_2O_{14}$ both suggest hollandite phases, since they can be written as $Ba_xTi_{4-2x}Al_{2x}O_8$ with $x = 0·67$ and $x = 0·57$ respectively. The range of x in the various compounds is difficult to determine but does not seem to be very large.

We must comment on the heating conditions presented in Table 4. Samples containing Fe were not heated above 1300°C in order to prevent the formation of Fe_3O_4. The $Ba_xRu_{4-2x}Cr_{2x}O_8$ samples were preheated at 800°C in air, reground and sealed in a platinum tube to prevent loss of RuO_2 by oxidation, and heated at 1250°C. The samples containing Ge were also preheated at 800°C in air to convert GeO_2 to $BaGe_4O_9$, reground and heated at 1250°C.

In order to examine the oxidation state of Fe and Sn in $Ba_xSn_{4-2x}Fe_{2x}O_8$ with x = 0·70, Mössbauer spectra were recorded. Fe appeared to be in the trivalent state, and Sn in the tetravalent state, as was expected.

Ordering phenomena, observed in some systems by diffuse X-ray scattering, will be examined by electron diffraction (Cadée & Prodan, to be published). Table 5 presents the systems in which no hollandite phase could be detected. Finally we would like to point out that the recently reported compound TlV_5S_8 (monoclinic with a = 17·465, b = 3·301, c = 8·519 Å and β = 103·94°) (Fournès, Vlasse & Saux, 1977) possesses a hollandite-like structure. The space between the double chains of octahedra of the hollandite structure is now filled by a

Table 5. *Some unsuccessful attempts to prepare hollandite-type compounds*

Treatment: several days at 1250–1300 °C.

Compound	x	Reaction mixture
$Ba_xSn_{4-2x}Sc_{2x}O_8$	0·70	SnO_2, $BaSnO_3$, Sc_2O_3
$Ba_xZr_{4-2x}In_{2x}O_8$	0·70	ZrO_2, $BaZrO_3$, In_2O_3
$Ba_xSn_{4-2x}Mn_{2x}O_8$	0·65	SnO_2, $BaSnO_3$, Mn_3O_4
$Sr_xSn_{4-2x}Cr_{2x}O_8$	0·65	SnO_2, $SrSnO_3$, Cr_2O_3
$Sr_xSn_{4-2x}Fe_{2x}O_8$	0·65	SnO_2, $SrSnO_3$, $SrSn_2FeO_{11}$*
$Ca_xTi_{4-2x}Cr_{2x}O_8$	0·65	$CaTiO_3$, $Cr_2Ti_2O_7$(?)

* This compound is the subject of a future paper.

V atom, resulting in the formation of a new octahedron. From Fig. 1 it can be seen that filling these holes will result in infinite layers of edge-sharing octahedra in the *XY* plane. Between these layers are double chains of edge-sharing octahedra which share faces with the octahedra of the infinite layers.

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References

BAYER, G. & HOFFMAN, W. (1966*a*). *Am. Mineral.* **51**, 511–516.

BAYER, G. & HOFFMAN, W. (1966*b*). *Naturwissenschaften*, **53**, 381.

BEYELER, H. U. (1976). *Phys. Rev. Lett.* **37**, 1557–1560.

BYSTRÖM, A. & BYSTRÖM, A. M. (1950). *Acta Cryst.* **3**, 146–154.

BYSTRÖM, A. & BYSTRÖM, A. M. (1951). *Acta Cryst.* **4**, 469.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

DRYDEN, J. S. & WADSLEY, A. D. (1958). *Trans. Faraday Soc.* **54**, 1574–1580.

ENDO, T., KUME, S., KINOMARU, N. & KOIZUMI, M. (1976). *Mater. Res. Bull.* **11**, 609–614.

FOURNÈS, L., VLASSE, M. & SAUX, M. (1977). *Mater. Res. Bull.* **12**, 1–6.

GRAAFF, R. A. G. DE (1973). *Acta Cryst.* A**29**, 298–301.

GUHA, J. P. & KOLAR, D. (1972). *J. Am. Ceram. Soc.* **55**, 55.

GUHA, J. P., KOLAR, D. & VOLAVSEK, B. (1976). *J. Solid State Chem.* **16**, 49–55.

KINOMURA, N. (1973). *J. Am. Ceram. Soc.* **56**, 344–345.

KUME, S., MATSUMOTO, T. & KOIZUMI, M. (1966). *J. Geophys. Res.* **71**, 4999–5000.

LANGLET, G. A. (1972). *J. Appl. Cryst.* **5**, 66–71.

REID, A. F., MUMME, W. G. & WADSLEY, A. D. (1968). *Acta Cryst.* B**24**, 1228–1233.

REID, A. F. & RINGWOOD, A. E. (1969). *J. Solid State Chem.* **1**, 6–9.

RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.

RINGWOOD, A. E., REID, A. F. & WADSLEY, A. D. (1967). *Acta Cryst.* **23**, 1093–1095.

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Crystal Structure of $Zn_3[Co(CN)_6]_2.12H_2O$*

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The crystal structure of $Zn_3[Co(CN)_6]_2.12H_2O$ has been determined from three-dimensional single-crystal X-ray diffraction data. The residual indices R and R_w have been refined to 0·0255 and 0·0226 respectively. The space group is *Fm*3*m* (cubic) and the disordered structure contains $1\frac{1}{3}$ molecules in the unit cell [a_0 = 10·268 (3) Å]. The calculated density is 1·72 Mg m^{-3} [observed density, 1·74 (1) Mg m^{-3}]. The divalent Zn atoms are linked to the Co atoms by cyanide bridging. Dehydration and fluorescence studies were made on single crystals of $Zn_3[Co(CN)_6]_2.12H_2O$. The disordered structure is isomorphous with the twelve hydrated cobalticyanides of Mn and Cd. The important bond lengths are: Co–C = 1·901 (4), Zn–N = 2·098 (9), Zn–O(1) = 2·134 (10), and C≡N = 1·135 (13) Å.

Introduction

Structural and morphological investigations of the classic semipermeable membrane, cupric ferrocyanide, and other heavy-metal ferro-, ferri-, and cobalticyanides have been studied by infrared, Mössbauer, isobaric dehydration, electron diffraction and powder X-ray diffraction methods (Milligan, Uda, Beasley, Dillin, Bailey & McCoy, 1970). The structure of $M_3^{II}[Co(CN)_6]_2.12H_2O$ (where M^{II} = Mn or Cd) was described by a structural model proposed for Prussian blue in the early 1940's (Weiser, Milligan & Bates,

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