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

BY D. F. MULLICA, W. O. MILLIGAN, G. W. BEALL† AND W. L. REEVES

Chemistry Department, Baylor University, Waco, Texas 76703, *USA*

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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 $Fm3m$ (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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† Present address: Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA.

1942). These studies were performed with powders of the metal cyanide complexes. Around 1970, another model was proposed by Ludi and co-workers (Ludi & Gudel, 1968; Ludi, Gudel & Ruegg, 1970; Ron, Ludi & Engel, 1973), based on single-crystal analyses of transition-metal cyanide complex salts. More recently, complete crystal structural analyses of $Mn_3[Co(CN)_6]_2.12H_2O$ and $Cd_3[Co(CN)_6].12H_2O$ by neutron and X-ray diffraction methods brought forth a newer structural model for $M_3^{II}[Co(CN)_6]_2.12H_2O$ (Beall, Milligan, Korp & Bernal, 1977), in contrast to the model proposed by Ludi *et al.* (1970). The present investigation of $Zn_3[Co(CN)_6]_2.12H_2O$ was initiated in order to observe if other transition-metal cyanide complexes fit the model proposed by Beall *et al.* (1977) and because of our considerable interest in compounds analogous to Prussian blue.

Experimental

Clear octahedral crystals of $Zn_3[Co(CN)_6]_2.12H_2O$ were prepared by slow diffusion of dilute solutions of $ZnCl_2$ and $K_3Co(CN)_6$. Both $ZnCl_2$ (ACS grade) and $K_3Co(CN)_6$ (ACS grade) were obtained commercially and no further purification was deemed necessary. Potassium and chloride ion contamination tests on the single crystals were negative. The flotation method (Retgers, 1889) for determining densities was employed. The observed density for $Zn_3[Co(CN)_6]_2.12H_2O$ is 1·739 (9) Mg m^{-3} and the calculated value is 1·722 Mg m^{-3}. A Perkin–Elmer TGS-1 thermobalance was used to determine the thermal dehydration (run at 2·5 °C min^{-1}) and the results yielded 12·0 (1) water molecules per formula unit. Preliminary X-ray powder diffraction photographs using a Siemens cylindrical powder camera with a Ni filter were used to obtain the cubic lattice constant 10·268 (3) Å. Fluorescence analysis showed the presence of Zn and Co in a ratio of $1:\frac{2}{3}$.

A single crystal of $Zn_3[Co(CN)_6]_2.12H_2O$ was mounted on an Enraf–Nonius CAD-4 diffractometer. 25 centered reflections, using least-squares refinement, produced the orientation matrix for data collection. Intensities were measured by the θ–2θ scan technique at a rate of 0·4–3·3° min^{-1}, determined by a fast prescan of 3·3° min^{-1}. Data were collected in the range of $2 < 2\theta < 60°$ using Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å. Two reflections (200 and $0\overline{2}\overline{2}$) were chosen and monitored as standards every 2 h of exposure time to check crystal stability. The deviation of each monitored standard from the average standard values was less than 1·3%. Reflections used in the structural refinement obeyed the condition $I_{\rm net} > 3\sigma(I)$ with $I_{\rm net} = (I - 2\sum B)$ and $\sigma(I) = [I + 2\sum B + (0{\cdot}02I_{\rm net})^2]^{1/2}$, where $I_{\rm net}$ is the total integrated peak intensity and B is the background count. 1342 reflections were collected of which 273 were observed; after averaging redundant data, 71 reflections were unique. A residual averaging error of 0·019 was determined according to $R' = \sum |F_o - F_{\rm ave}|/\sum |F_o|$. The standard deviations of the average data were calculated from $\sigma_{\langle F\rangle} = (1/N)\sum 1{\cdot}02\sigma_{Fi}$ (Peterson & Levy, 1957), where N = number of redundant reflections and σ_{Fi} = standard deviation for each individual reflection. The data set was corrected for Lorentz and polarization effects. An absorption correction was deemed unnecessary because of the spheroidal-like shape of the crystal and the small linear absorption coefficient of $Zn_3[Co(CN)_6]_2.12H_2O$.

Crystal data

$Zn_3[Co(CN)_6]_2.12H_2O$, FW 842·404, a_0 = 10·268 (3) Å, V = 1082·6 (9) Å^3, $\rho_{\rm exp}$ = 1·74 (1), $\rho_{\rm calc}$ = 1·72 Mg m^{-3}, Z = 1·3333, μ(Mo $K\bar{\alpha}$) = 2·43 mm^{-1}.

Structural determination

The positional parameters obtained from the model proposed by Beall *et al.* (1977) for $M_3^{II}[Co(CN)_6]_2.12H_2O$ compounds were used to initiate the first cycles of the structural refinement. The metal positions for Zn and Co were confirmed from Patterson sections at z = 0·0 and 0·5; the position number sets with Wyckoff notation for Zn and Co are 4(*b*) and 4(*a*) respectively. A three-dimensional electron density map which was phased from the partial model obtained after the Patterson map revealed the C and N atoms to be in position set 24(*e*). The difference Fourier map also yielded possible atomic positions for two of the four O positions; one in the position set 8(*c*) and one in set 32(*f*). Due to an extremely high correlation between the remaining O atoms and Co and N atoms, related by competitiveness for the same positional sites, it was imperative to use the model proposed by Beall *et al.* (1977). After several cycles of isotropic refinement, an R value of 0·0427 was obtained. Several more cycles of full-matrix refinement, varying anisotropic thermal parameters and the maximum allowed parameters, yielded final residual index values of 0·0255 and 0·0226 for R and R_w respectively $[R = \sum(|F_o| - |F_c|)/\sum |F_o|$ and $R_w = \sum w^{1/2}(|F_o| - |F_c|)/\sum w^{1/2}F_o$, where $w = 1/\sigma^2]$. The applied secondary-extinction correction was g = 1·41 (8) × 10^{-6} and the scale factor was 0·198 (2). The goodness-of-fit value and the standard deviation of the residual electron density were 1·106 and 0·05 Å respectively. A correlation coefficient matrix, which is a subroutine of the full-matrix least-squares program (Larson, 1967), was applied during several of the cycles of refinement. The most striking results of the correlation matrix were that there are high correlations between N and O(1), between Co and O(2), and between O(3) and O(4). These findings are

Table 1. *Observed and calculated structure factors for* $Zn_3[Co(CN)_6]_2.12H_2O$

H	*K*	*L*	F_o	F_c	*H*	*K*	*L*	F_o	F_c	*H*	*K*	*L*	F_o	F_c
2	0	0	1919	1956	10	8	0	358	354	8	8	2	267	237
4	0	0	2500	2492	12	8	0	228	224	10	8	2	296	283
6	0	0	1736	1680	10	10	0	335	343	10	10	2	276	259
8	0	0	952	939	1	9	1	216	234	3	9	3	230	257
10	0	0	837	866	3	9	1	215	251	3	5	3	265	237
12	0	0	428	447	1	5	1	439	410	5	5	3	303	333
14	0	0	311	320	3	5	1	372	371	3	3	3	305	267
2	2	0	1584	1575	5	5	1	274	275	4	4	4	1123	1160
4	2	0	1422	1400	3	3	1	139	158	6	4	4	886	875
6	2	0	1257	1251	1	1	1	447	446	8	4	4	532	537
8	2	0	665	678	4	2	2	957	980	10	4	4	492	494
10	2	0	667	657	6	2	2	741	742	12	4	4	282	281
12	2	0	344	349	8	2	2	437	419	6	6	4	753	780
14	2	0	252	247	10	2	2	510	502	8	6	4	454	453
4	4	0	1741	1683	12	2	2	258	243	10	6	4	440	447
6	4	0	1172	1197	4	4	2	950	979	12	6	4	264	259
8	4	0	695	719	6	4	2	900	908	8	8	4	292	285
10	4	0	644	650	8	4	2	479	478	10	8	4	286	275
12	4	0	345	359	10	4	2	511	506	6	6	6	647	645
6	6	0	1037	1031	12	4	2	280	264	8	6	6	418	426
8	6	0	583	595	6	2	2	723	721	10	6	6	390	391
10	6	0	554	575	8	6	2	462	461	8	8	6	277	254
12	6	0	319	327	10	6	2	450	432	10	8	6	271	260
8	8	0	384	393	12	6	2	261	258					

consistent with those of Beall *et al.* (1977). In the least-squares refinement, the quantity minimized was $\sum w(|F_o| - |kF_c|)^2$, where *k* is the scale factor and $w = 1/\sigma^2_{\langle F_o \rangle}$ (Stout & Jensen, 1968). A final difference Fourier map revealed a maximum density peak of 0·59 e Å^{-3} which was located near the Zn atom position and a minimum electron denisty of −0·59 e Å^{-3}. None of the positive peaks were at a suitable position for a H atom; therefore, no attempt was made to locate H atom positions in the structural refinement. The largest $\Delta\xi_i/\sigma(\xi_i)$ value after the final refinement cycle was 0·02 and the average value was approximately 0·007 (ξ_i values are varied parameters). Scattering factors for all atoms in the structure were obtained from Cromer & Waber (1965). Anomalous-dispersion corrections were applied to the scattering factors of all atoms (Cromer, 1965). The final observed and calculated structure factors are in Table 1. The final atomic positions and thermal parameters are given in Table 2.

Discussion

The Enraf–Nonius CAD-4 diffractometer used in this study is equipped with a 7000 series Si(Li) Ortec solid-state detector. A routine application of the energy-dispersive detector is made in order to obtain fluorescence X-ray data on the same single crystal upon which X-ray diffraction data are to be collected.* A qualitative determination of metal constituents of a single crystal can be made in less than 30 min. Quantitative data on relative percentages of the metal elements present can be determined in approximately 2 h, at less than a 2·5% level of error. Zn and Co were quickly identified and the expected relative ratio of Zn:Co $(1:\frac{2}{3})$ was less than 2·0% in error. Fig. 1 is a representation of the disordered structure of $Zn_3[Co(CN)_6]_2.12H_2O$. This figure shows two distinct types of unit. The first section discloses an ordered arrangement of the metal atoms and cyanide ligands with a water molecule located at its center. The cyanide ligands are oriented linearly between the divalent Zn atoms and the Co atoms with the C atom toward the Co atom. The second structural unit displays disorder when two Co atoms are missing from the unit cell; then O(1) completes the coordination of the Zn and a hydrogen-bonding network is attained with O(2) and O(3). The first type of unit occurs one-third of the time, whereas the second occurs two-thirds of the time in the overall structure. For clarity the representation in Fig. 1 shows the case where only one Co atom is missing in the disordered section of the structure. The C≡N and

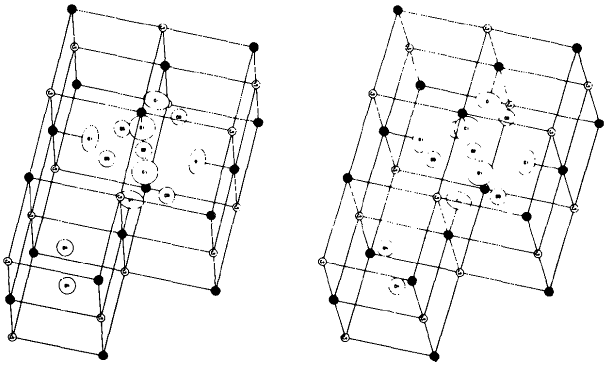

Fig. 1. Stereoscopic drawing of the ordered and disordered structural representation of $Zn_3[Co(CN)_6]_2.12H_2O$. Filled circles represent Zn atoms, open circles Co atoms. O(1) is shown bonded to Zn. O(2) is at the centre of the cell surrounded by four O(3). The lower part of the figure shows two O(4) atoms.

Table 2. *Atomic positions and thermal parameters* (Å^2 × 10^2) *for* $Zn_3[Co(CN)_6]_2.12H_2O$

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	Occupancy
Zn	0·05	0·5	0·5	3·0 (1)			1
Co	0	0	0	2·9 (2)			$\frac{2}{3}$
C	0	0	0·185 (1)	2·7 (5)	2·7 (5)	2·8 (8)	$\frac{2}{3}$
N	0	0	0·296 (1)	6·6 (7)	6·6 (7)	4·6 (1)	$\frac{2}{3}$
O(1)	0	0	0·292	16·6	16·6	3·6	$\frac{1}{3}$
O(2)	0	0	0	8·0			$\frac{1}{3}$
O(3)	0·203 (1)	0·203 (1)	0·203 (1)	6·1 (10)			$\frac{1}{8}$
O(4)	0·25	0·25	0·25	6·1 (9)			$\frac{1}{3}$

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* A complete outline and discussion of results and application methods of simultaneous diffraction and fluorescence X-ray analysis is to be published.

Table 3. *Bond lengths and contact distances* (Å) *for* $Zn_3[Co(CN)_6]_2.12H_2O$

Co—C	1·901 (14)	O(1)—O(2)	3·00 (1)
Zn—N	2·089 (9)	O(1)—O(3)	3·08 (2)
C—N	1·135 (13)	O(2)—O(3)	3·60 (3)
Zn—O(1)	2·134 (10)		

Co—C bond distances are quite reasonable when compared with values from the work of Vannerberg (1972), Ludi & Gudel (1968), Ludi, Gudel & Ruegg (1970), Ron, Ludi & Engel (1973), Ferrari, Tani & Magnano (1959), Reynhardt & Boeyens (1971), Beall *et al.* (1977), and several others whose published crystal structures are listed in *Bond Index of the Determinations of Inorganic Crystal Structures* (1972–1976). All pertinent bond lengths are listed in Table 3. This investigation of $Zn_3[Co(CN)_6]_2.12H_2O$ lends credence to the proposed model and conclusions proposed by Beall *et al.* (1977).

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Structure Cristalline de l'Hexathiodimétaphosphate d'Argent, $Ag_2P_2S_6$

PAR PATRICK TOFFOLI, PARVIZ KHODADAD ET NOËL RODIER

Laboratoire de Chimie Générale et Minérale, Faculté de Pharmacie, rue J. B. Clément,
92290 *Châtenay-Malabry, France*

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$Ag_2P_2S_6$ is monoclinic, space group $B2/m$, $a = 11.210$ (3), $b = 6.731$ (2), $c = 6.998$ (2) Å, $\gamma = 126.84$ (2)°, $Z = 2$. The structure was solved by direct methods and refined by least-squares calculations to a final R value of 0·033 from 795 independent single-crystal diffractometer data. The Ag atom is tetrahedrally coordinated. The P_2S_6 was found to be a hexathiodimetaphosphate group where the two P atoms are linked by two S bridges.

Introduction

L'étude structurale de l'hexathiodimétaphosphate d'argent a été entreprise dans le cadre de l'étude du système ternaire Ag–P–S. La méthode de préparation utilisée consiste à chauffer les éléments, pris en proportions stoechiométriques, dans une ampoule de silice transparente vidée d'air et scellée. On porte le mélange à 573 K pendant un jour, puis à 873 K pendant une semaine. Il se forme un produit de couleur orangée, d'aspect vitreux, qu'un recuit de deux jours vers 573 K permet de faire cristalliser. Le monocristal utilisé a été prélevé dans la préparation ainsi obtenue; il mesure approximativement 0,10 × 0,10 × 0,12 mm.