TABLE VI

A COMPARISON OF THE DIMENSIONS OF SOME COBALT–DITHIOLENE COMPLEXES

	$Co(S_2C_6H_3(CH_3))_2(o\text{-phen})^-$ [a]	$Co(S_2C_2(CN)_2)_2(o\text{-phen})^-$ [b]	$Co(S_2C_6H_3(CH_3))_2^-$ [c]	$Co(S_2C_2(CN)_2)_2^{2-}$ [d]	$Co_2(S_2C_2(CF_3)_2)_4^0$ [e]	$Co_2(S_2C_6Cl_4)_4^{2-}$ [f]
Bond Distances, Å						
Co–S	2.253 (7), 2.215 (7)	2.247 (5), 2.213 (5)	2.166 (4)	2.161 (3)	2.161 (4)	2.185 (7)
Co–S′ (dimer bridge)	. . .	. . .	. . .	. . .	2.382 (4)	2.404 (7)
Co–N (adduct)	2.04 (2)	2.01 (1)	. . .	. . .	. . .	. . .
S–C	1.76 (2)	1.72 (2)	1.77 (2)	1.723 (7)	1.694 (4)	1.76 (2)
C–C	1.41 (3)	1.36 (2)	1.38 (2)	1.34 (1)	1.39 (2)	1.41 (3)
Bond Angles, Deg						
S–Co–S (intra)	91.0 (3)	92.3 (2)	91.3 (2)	91.4 (1)	89.8 (2)	90.1 (2)
Co–S–C	104 (1)	101 (1)	105.3 (5)	103.8 (3)	105.5 (2)	104.8 (7)

[a] This work. [b] Reference 2. [c] Reference 9. [d] Reference 11. [e] Reference 12. [f] Reference 10.

$(CH_3))_2^-$ and the dimeric system $Co_2(S_2C_2(CN)_2)_4^{2-}$. This conclusion is reinforced by the observation that the Co–S dimer linkages in the structurally known dimeric systems (Table VI) are considerably longer than the Co–S distances in the basal planes of these complexes. The important differences in the properties of the two bis-dithiolene complexes $Co(S_2C_6H_3(CH_3))_2^-$ and $Co_2(S_2C_2(CN)_2)_4^{2-}$ relate directly to the π-acceptor properties of their respective dithiolene ligands. The π acidity of the ligand system, in turn, influences the electron density in the vicinity of the Co atom in these complexes. For those systems in which sufficient electron density is withdrawn from the Co atom to favor the formation of a five-coordinate dimer structure, the aforementioned equilibrium lies strongly in favor of the Lewis base adduct whereas for those complexes in which there is little or no tendency for axial ligation and dimer formation, the equilibrium lies in favor of the original bis planar complex. The significantly reduced importance of differences in ligand π acidity in six-coordinate complexes is demonstrated by the nearly identical structures we find for the two *o*-phenanthroline adducts of the cobalt–bis(dithiolene) complexes.

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CONTRIBUTION FROM THE INSTITUT FÜR ANORGANISCHE, ANALYTISCHE UND PHYSIKALISCHE CHEMIE, UNIVERSITÄT BERN, CH-3000 BERN 9, SWITZERLAND

The Structural Chemistry of Prussian Blue Analogs. A Single-Crystal Study of Manganese(II) Hexacyanocobaltate(III), $Mn_3[Co(CN)_6]_2 \cdot xH_2O$

BY ANDREAS LUDI, HANS-ULRICH GÜDEL, AND MAX RÜEGG

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The crystal structure of hydrated manganese(II) hexacyanocobaltate(III), $Mn_3[Co(CN)_6]_2 \cdot xH_2O$ (x = 12–14), has been determined from three-dimensional X-ray data using integrated precession photographs. The cubic face-centered cell with a = 10.421 (5) Å of space group O_h^5-Fm3m contains $1^1/_3$ formula units. The measured and calculated (for x = 13) densities are 1.65 and 1.62 g/cm³. The final R factor is 10.5%. Co–C–N–Mn bridges connect octahedral CoC_6 and $MnN_4(H_2O)_2$ groups to a three-dimensional framework with 4 Mn at 4a (0, 0, 0) and $2^2/_3$ Co randomly distributed on 4b ($^1/_2$, $^1/_2$, $^1/_2$); 16 C and 16 N are at 24e (x, 0, 0) and 8 water molecules belonging to the coordination octahedron of Mn are situated close to the empty nitrogen positions. Additional water molecules are distributed around 8c ($^1/_4$, $^1/_4$, $^1/_4$). The Co–C, C–N, Mn–N, and Mn–O distances are 1.865 (2), 1.136 (3), 2.209 (2), and 2.391 (6) Å. The shortest O · · · H–O distances of 2.67–2.90 Å are in agreement with hydrogen-bond lengths obtained from infrared spectra.

Introduction

Although the polynuclear transition metal cyanides of the Prussian Blue type have been known for a long time, the complete solution of their crystal structure has not yet been achieved. Due to their extremely low solubility these compounds have been prepared only as colloidal precipitates.[1] The products resulting when aqueous solutions of a metal salt and of a hexacyanometalate are mixed contain variable amounts of water and often also of potassium. Most of the polynuclear

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[1] D. Britton in "Perspectives in Structural Chemistry," Vol. 1, J. D. Dunitz and J. A. Ibers, Ed., Wiley, New York, N. Y., 1967, p 109.

cyanides of the general composition $K_lM^A{}_m[M^B(CN)_6]_n \cdot xH_2O$ ($M^A = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Cr^{3+}, Fe^{3+}$; $M^B = Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Rh^{3+}, Ir^{3+}, Fe^{2+}, Ru^{2+}, Os^{2+}$) show a simple X-ray powder pattern corresponding to a cubic face-centered unit cell with a lattice constant of about 10 Å.[2]

Until recently all the structural investigations by powder methods were based on the model proposed some 30 years ago by Keggin and Miles.[3] Figure 1 shows this postulated structure which subsequently has been adopted by various authors.[4-8] This unit cell of space group $O_h{}^5$-Fm3m can be described as being composed of eight small cubes whose corners are occupied alternatively by metal ions M^A and M^B. The cyanide ions are situated on the edges of the small cubes. Depending on the oxidation states of M^A and M^B a certain fraction of the centers of the small cubes are assumed to be occupied by further M^A ions or potassium ions in order to obtain electroneutrality. The CN groups are so oriented as to form carbon-coordinated hexacyanometalate $M^B(CN)_6{}^{n-}$ ions. Linkage isomerization occurs only in a few cases during the precipitation.[8]

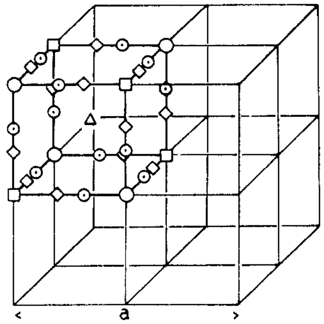

Figure 1.—The cubic unit cell of $Mn_3[Co(CN)_6]_2 \cdot xH_2O$. Comparison of the two models. Atoms are shown only in one small cube (one-eighth of the unit cell of space group $O_h{}^5$-Fm3m[13]). Symbols for the old model[3] and our modified model, respectively: ○, 4 Mn at 4a, 4 Mn at 4a; □, 4 Co at 4b, $2^2/_3$ Co at 4b; ◇, 24 C at 24e, 16 C at 24e; ⊙, 24 N at 24e, 16 N at 24e and 8 O_1 near 24e; △, 2 Mn at 8a, 8 O_2 near 8c.

For the hexacyanocobaltates(III) of divalent metals the model of Keggin and Miles[3] postulates a cell containing two formula units of $M_3[Co(CN)_6]_2$. Accordingly two M^{2+} ions would have to be distributed on the eight centers of the small cubes. In this model no well-defined positions are provided for the water molecules, although the analytical data indicate 12–14 water molecules per formula unit. It has always been assumed that this water is present as zeolitic or/and as adsorbed water.[5,6] The interpretation of the X-ray powder data obtained from the hydrated compounds has therefore been based on the completely water-free model.[6,7] Infrared spectra, however, reveal that these polynuclear cyanides contain coordinated as well as zeolitic water.[9,10] Also the comparison of calculated and measured densities demonstrates that the original structure of Keggin and Miles[3] has to be modified to account for the various experimental facts.

It is the purpose of this paper to discuss the structural properties of Prussian Blue analogs on the basis of a new model and to verify this model by a single-crystal study of manganese(II) hexacyanocobaltate(III).

Experimental Section

To grow single crystals of manganese(II) hexacyanocobaltate(III) the following procedure was applied. Two small beakers (25 ml) containing 0.2 g of $MnCl_2 \cdot 4H_2O$ (1 mmol) and 0.15 g of $H_3Co(CN)_6$[11] ($^2/_3$ mmol), respectively, were placed in a 500-ml glass jar. The beakers and the jar were carefully filled with doubly distilled water, tightly sealed, and kept in a water bath at 50°. The polynuclear compound was formed by the slow interdiffusion of the two components. Very pale yellow-green cubelike crystals with edges of 0.1–0.4 mm could be collected after about 10 days. The crystals were washed with water and air dried.

Carbon, hydrogen, and nitrogen analyses were performed by the analytical laboratory of Dr. A. Wander AG, Bern. Analytical data for manganese and cobalt were obtained by complexometric titration. The water was also determined thermogravimetrically. *Anal.* Calcd for $Mn_3[Co(CN)_6]_2 \cdot 13H_2O$: C, 17.4; H, 3.2; N, 20.3; Co, 14.2; Mn, 19.9; H_2O, 28.3. Found: C, 17.2; H, 3.2; N, 20.3; Co, 13.9; Mn, 19.9; H_2O, 27.5.

The various hexacyanocobaltates(III) of divalent metals yield analytical results corresponding to 12–14 water molecules per formula unit.[6,10] As a consequence we prefer to formulate the hydrates as $M_3[Co(CN)_6]_2 \cdot xH_2O$ rather than to give a fixed number for the water molecules. Products which are dried over potassium hydroxide have a considerably smaller amount of water.

Density measurements were performed by the flotation method (chlorobenzene–methyl iodide) as well as pycnometrically (decahydronaphthalene).

All the calculations were carried out using van der Helm's IBM 1620 programs adapted to the GE-BULL Gamma 30 by Engel.[12]

Unit Cell Data

The cell constant $a = 10.421$ (5) Å of $Mn_3[Co(CN)_6]_2 \cdot xH_2O$ has been determined from Si-calibrated high-angle Weissenberg photographs (λ(Cu $K\alpha_1$) 1.5433 Å, λ(Cu $K\alpha_2$) 1.5405 Å, λ(Cu $K\beta$) 1.3922 Å, a_0(Si) = 5.4308 Å). The other hexacyanocobaltates(III) have been investigated by powder methods (Guinier camera, λ(Fe $K\alpha$) 1.9373 Å) using potassium chloride as standard (a_0(KCl) = 6.2931 Å). Precession photographs of $Mn_3[Co(CN)_6]_2 \cdot xH_2O$ confirm the cubic face-centered unit cell. The systematic absences ($h + k, k + l, l + h \neq 2n$) are consistent with the space groups T^2-F23, $T_h{}^3$-Fm3, O^3-F432, $T_d{}^2$-F43m, and $O_h{}^5$-Fm3m.[13] The measured density $d_m = 1.65$ g/cm^3 corresponds to $1^1/_3$ formula units of $Mn_3[Co(CN)_6]_2 \cdot xH_2O$ per cell. With $x = 13$ the calculated density is $d_c = 1.62$ g/cm^3.

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Collection of Intensities

A crystal of $Mn_3[Co(CN)_6]_2 \cdot xH_2O$ of the dimensions 0.45 × 0.34 × 0.26 mm was mounted along the longest edge, the edges coinciding with the (100), (010), and (001) directions, respectively. Integrated precession photographs (Mo Kα) were recorded of the *hk*0, *hk*1, *hk*2, *hk*3, *hk*4, and *hhl* zones. For each net a set of films with 1, 2, 4, 8, 16, 32 integration cycles was produced and each set of films was processed simultaneously. The intensities were determined with a recording Joyce-Loebl microdensitometer. Unobserved reflections were assigned half the intensity of the weakest observed reflection in the corresponding ϑ range. For the 104 unique reflections (including 24 which were unobserved) Lorentz and polarization corrections were applied but no correction for absorption, the linear absorption coefficient for Mo Kα being $\mu = 22$ cm^{-1}. The corresponding transmission factor calculated for a plate of the dimensions of the crystal is 0.57 for the (*hk*0) zone and 0.49 for the (*hk*4) zone but is constant for each zone.[14] For the strongest reflections with $d >$ 1.0 Å the single-crystal intensities were supplemented with powder data using a counterdiffractometer. After applying interfilm, interzone, and single-crystal powder scaling factors the observed structure factors $|F_o|$ were brought to an approximately absolute basis using the data of the previous work on cobalt(II) hexacyanocobaltate(III).[10]

Refinement

The atomic scattering factors tabulated by Ibers[15] for C, N^-, O^-, Mn^{2+}, and Co^{3+} were used, the effects of anomalous dispersion being neglected. In the first calculation the atomic coordinates were chosen in such a way that Co–C and C–N distances were in agreement with recent investigations.[10,16] To select reasonable starting parameters for the oxygen atoms, the positions of the water molecules resulting from our previous work[10] were used.

The first structure factor calculation gave a value of R of 15.1% ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; F_o is the observed and F_c is the calculated structure factor). Isotropic least-squares refinement using block matrix notation converged to an R factor of 10.5%. The function minimized was $\Sigma w(F_o - F_c)^2$ where the weighting function w given by Hughes[17] was chosen.

When the unobserved reflections were omitted, the R factor was 9.2%. Table I lists the final values of F_o and F_c in electrons; Table II, the final atomic parameters.

In a difference Fourier map calculated with the observed structure factors given in Table I only a very diffuse peak smaller than about 20% of the electron density of the carbon atom is observed close to Co.

Discussion

The original model of Keggin and Miles[3-9] postulates two formula units of $Mn_3[Co(CN)_6]_2 \cdot xH_2O$ per cell. Our density data, however, demonstrate that the unit cell contains only $1^1/_3$ formula units (Table III). The originally proposed structure is modified in the following way. First the two bare (*i.e.*, uncoordinated) Mn^{2+} ions randomly distributed on the centers of the eight small cubes (position 8c of space group O_h^5-Fm3m, Figure 2) are omitted. Accordingly $1^1/_3$ $Co(CN)_6^{3-}$ groups have to be removed from the cell to reach electroneutrality again. That means that each lattice point of position 4a is occupied by Mn but only two-thirds of the sites 4b and 24e are filled with Co, C, and N, respectively. As a consequence water molecules can now be placed close to the former nitrogen positions (O_1) and within the eight small cubes (O_2). Our modified structural description of the cubic polynuclear cyanides leads to a cubic cell containing $1^1/_3$ formula units of the ideal composition $Mn_3[Co(CN)_6]_2 \cdot 12H_2O$.

The noninteger number of formula units appears at first somewhat unfamiliar. It must be emphasized, however, that the old model has also postulated non-

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS (IN ELECTRONS) FOR $Mn_3[Co(CN)_6]_2 \cdot xH_2O$[a]

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	1	1	17	25	7	3	3*	6	1	9	5	3	12	10	9	9	1	4	6
2	0	0	202	182	8	2	0	53	54	10	4	0	52	47	12	4	2	17	15
2	2	0	125	133	6	4	4	61	69	8	6	4	34	35	10	8	0	28	26
3	1	1	13	16	8	2	2	31	31	10	4	2	29	33	8	8	6	21	15
2	2	2	40	42	6	6	0	75	76	11	1	1*	2	7	10	8	2	18	17
4	0	0	279	258	7	5	1*	4	3	7	7	5*	2	5	13	1	1*	2	0
3	3	1	10	12	5	5	5*	9	5	8	8	0	34	28	11	7	1*	2	6
4	2	0	113	116	6	6	2	47	56	11	3	1*	2	4	11	5	5*	2	3
4	2	2	68	76	8	4	0	54	57	9	7	1*	2	2	9	9	3	6	8
5	1	1	23	23	9	1	1	15	12	9	5	5*	2	4	10	6	6	29	27
3	3	3	18	15	7	5	3*	4	1	10	4	4	36	35	12	4	4	23	20
4	4	0	154	150	8	4	2	30	38	8	8	2	21	19	13	3	1*	2	2
5	3	1	17	19	6	6	4	52	55	10	6	0	42	39	11	7	3*	2	3
6	0	0	140	137	9	3	1	15	13	8	6	6	32	30	9	7	7*	2	0
4	4	2	71	79	8	4	4	36	39	11	3	3*	2	1	12	6	0	28	24
6	2	0	97	99	9	3	3	16	13	9	7	3*	2	4	10	8	4	23	19
5	3	3	15	15	7	7	1*	6	8	10	6	2	26	30	12	6	2	17	17
6	2	2	48	49	7	5	5*	4	1	12	0	0	39	37	13	3	3*	2	2
4	4	4	81	93	10	0	0	68	63	8	8	4	23	19	8	8	8	19	10
7	1	1	14	9	8	6	0	42	48	11	5	1*	2	5	14	0	0	29	23
5	5	1	14	13	10	2	0	54	46	7	7	7*	2	4	14	2	0	19	17
6	4	0	88	97	8	6	2	26	32	12	2	0	21	26	10	10	0	23	22
6	4	2	67	67	9	5	1	8	8	12	2	2	20	17	10	10	2	17	17
7	3	1*	4	4	7	7	3*	3	3	10	6	4	32	29	12	8	2	15	11
5	5	3	14	14	10	2	2	30	31	11	5	3*	2	2	12	10	2	12	10
8	0	0	83	84	6	6	6	45	50	12	4	0	29	27	12	6	6	12	17

[a] Asterisk indicates an unobserved reflection.

TABLE II

POSITIONAL AND THERMAL PARAMETERS OF $Mn_3[Co(CN)_6]_2 \cdot xH_2O$ (p = OCCUPANCY)

	p	x	y	z	B, Å^2
Mn	1	0	0	0	3.2 (2)
Co	$^2/_3$	0.5	0	0	2.3 (2)
C	$^2/_3$	0.321 (2)	0	0	3.2 (4)
N	$^2/_3$	0.212 (2)	0	0	4.0 (4)
O_1	$^1/_{24}$	0.223 (6)	0.010 (24)	0.053 (7)	5.1 (20)
O_2	$^1/_{24}$	0.305 (7)	0.274 (17)	0.259 (14)	5.9 (20)

TABLE III

LATTICE CONSTANTS (Å) AND DENSITIES (G/CM^3) OF $M_3[Co(CN)_6]_2 \cdot xH_2O$ (d_c FOR x = 13)

M	a	d_c old model	d_m	d_c new model
Mn	10.421 (5)	2.43	1.65	1.62
Fe	10.31 (1)	2.52	1.67	1.68
Co	10.210 (5)	2.63	1.74	1.75
Ni	10.145 (5)	2.67	1.71	1.78
Zn	10.26 (1)	2.66	1.75	1.77
Cd	10.590 (5)	2.81	1.89	1.87

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(14) M. J. Buerger, "The Precession Method," Wiley, New York, N. Y., 1964.

(15) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

(16) K. N. Raymond and J. A. Ibers, *Inorg. Chem.*, **7**, 2333 (1968).

(17) E. W. Hughes, *J. Amer. Chem. Soc.*, **63**, 1737 (1941).

integer numbers, *e.g.*, Prussian Blue where $Z = 1^1/_3$ according to Keggin and Miles[3,5] but $Z = 1$ for our modified structure.[18]

The structure factor calculations leading to $R = 10.5\%$ for our model were also carried out for the original model of Keggin and Miles.[3,6] According to this description the water was completely neglected and two formula units were placed in the cell, both assumptions being in rather pronounced disagreement with density and analytical findings. Shriver[9] discussed the structure of Prussian Blue analogs in terms of the original model but assumed that the interstitial metal ions at 8c are coordinated octahedrally by six water molecules. Since our Co–C and C–N distances are in good agreement with a recent structure determination,[16] we used these values to compare the R factors for the different models for the structure of Prussian Blue analogs. For this comparison the water molecules in our model were constrained to special sites, 24e for O_1 and 8c for O_2. The calculations gave the following results: Keggin and Miles,[3] $R = 30\%$; Shriver[9] $R = 26.2\%$; our model, 16.1%. By least-squares refinement and removing the constraints of the oxygen atoms the R factors could be reduced to 21.6, 22.8, and 10.5%, respectively. In the case of the first two models, however, quite unreasonable interatomic distances were obtained: Co–C, 2.25–2.31 Å; C–N, 0.71–0.73 Å; the temperature factor B of the interstitial Mn at 8c was between 8 and 9 Å^2.

The structure of the Prussian Blue analog $Mn_3[Co(CN)_6]_2 \cdot xH_2O$ can adequately be described as a three-dimensional framework of the two octahedral coordination units CoC_6 and $MnN_4(H_2O)_2$, the formula of the latter complex showing an average composition. The resulting interatomic distances follow (Å): Co–C, 1.865 (2); C–N, 1.136 (3); Mn–N, 2.209 (2); Mn–O_1, 2.391 (6). Four Mn are at the position 4a of the face-centered unit cell shown in Figure 1. One-third of the Co(4b), C(24e), and N(24e) positions are not occupied by these atoms. It is assumed that these vacancies occur completely at random leaving thus the high symmetry of space group O_h^5-Fm3m. A similar statistical distribution was postulated in the old model for the interstitial metal ions at 8c. The inequivalence of the two lattice points 4a (4 Mn) and 4b ($2^2/_3$ Co) is illustrated qualitatively by a line through the three-dimensional Fourier map along the edge of the unit cell (Figure 2).

Evidence for Co–C–N linkage is also obtained from electronic spectra[9] in conjunction with results of neutron diffraction data of $K_3Co(CN)_6$[19] and $D_3Co(CN)_6$.[20] The existence of Co–C–N–Mn bridges building up the three-dimensional framework is demonstrated by the position of the CN stretching frequency in the infrared spectra.[9,10]

The structure of $Mn_3[Co(CN)_6]_2 \cdot xH_2O$ contains water molecules which are distinguished with respect to their crystallographic position as well as with respect to their bonding. Eight molecules (O_1) replace one-third of the nitrogen atoms, thus being part of the coordination octahedron of Mn. Eight other water molecules (O_2) randomly distributed on a general position around 8c can be described as zeolitic water situated in the holes of the relatively open Co–C–N–Mn framework. The two different water molecules are connected by hydrogen bonds. The shortest O_1–O_2 distances of 2.67 (2), 2.72 (3), 2.80 (3), and 2.90 (3) Å are in agreement with hydrogen-bond lengths deduced from the infrared spectrum of $Mn_3[Co(CN)_6]_2 \cdot xH_2O$. Stretching frequencies ν(OH) are observed as a broad band at 3200–3400 cm^{-1} leading to O_1–H–O_2 distances of 2.7–2.9 Å.[21]

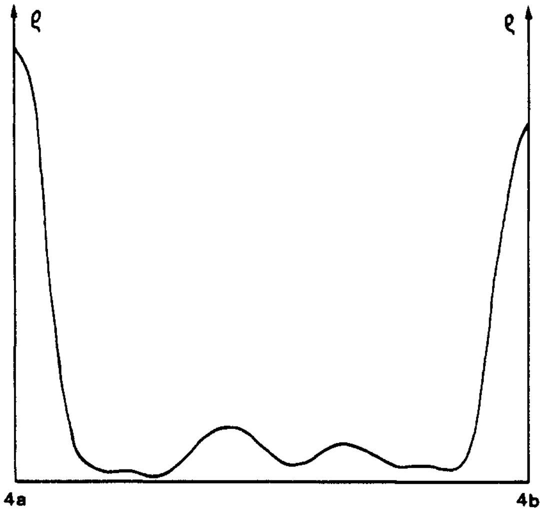

Figure 2.—Section along (100) through a three-dimensional Fourier map of $Mn_3[Co(CN)_6]_2 \cdot xH_2O$.

The total of 16 water molecules per cell corresponds to the composition $Mn_3[Co(CN)_6]_2 \cdot 12H_2O$. Analytical data and density (*cf.* Table III) indicate a somewhat higher amount of water. The difference Fourier map computed with the final parameters showed indeed a small diffuse peak in the neighborhood of 4b, the fourfold position occupied by $2^2/_3$ Co. Structure factor calculations with $2^2/_3$ Co and $1^1/_3$ O in 4b, however, gave a value of R of 11.3% compared with 10.5% without O in 4b. The accuracy of our intensity data is not considered as sufficient to allow a precise crystallographic location of one (or more) water molecule in addition to the 16 molecules per cell. We are therefore basing our results on the composition $Mn_3[Co(CN)_6]_2 \cdot 12H_2O$. It must be emphasized, however, that there exists a rather broad range of hydration which is in complete agreement with the zeolitic nature of part of the water.

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