edges are probably minimized in this configuration, especially with respect to the *mmmm* stereoisomer with the same N and O arrangement. In the dodecahedral bis(nitrilotriacetato)zirconate(IV) anion[56] and M(AA'-B_2)$_2$ system the two nitrogen atoms are positioned at the A sites as predicted from electronic considerations, while the π-donor acetato oxygens are linked to the metal at the B and remaining A sites across m (2.62 Å), g (2.78 Å), and a (2.68 Å) edges. This variation in edge length emphasizes the strong influence which coordination sphere geometry exerts on ligand bite. Hoard's point that the NTA^{3-} ligand makes "maximal use of short ring spans" is well taken.[58]

The various parameters affecting eight-coordination stereochemistry seem to be of nearly equal value. The more stable systems, therefore, should be the result of a number of concurring effects. For instance, the stereochemistries discussed above could have been rationalized in terms of just ligand constraint effects; *i.e.*, the tungsten complex is *mmmm* (N at B, O at A) because (1) steric restrictions imposed by the ligand will not permit *mmmm* (N at A, O at B) and (2) the dodecahedral g edges and the antiprismatic s and l edges are longer and less favored than the m edges in the configuration actually found. Similar arguments could be made for the other complexes. Therefore, further investigations are in progress in these laboratories to test some of the predictions cited herein. Hopefully, we can shortly place the π-bonding effect as well as other steric considerations on a more quantitative basis.

Acknowledgments.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Atomic Energy Commission for support of this research. Discussions and help from a number of persons at Brookhaven National Laboratories, particularly S. J. La Placa and J. S. Ricci, Jr., discussions with Professors J. L. Hoard and O. Lindqvist, and constructive criticism by the referees have been useful and are deeply appreciated.

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

The Crystal Structure of Manganese(II) Hexacyanoruthenate (II) Octahydrate, $Mn_2[Ru(CN)_6]\cdot 8H_2O$

BY MAX RÜEGG, ANDREAS LUDI,* AND KONRAD RIEDER

Received November 25, 1970

The crystal structure of manganese(II) hexacyanoruthenate(II) octahydrate, $Mn_2[Ru(CN)_6]\cdot 8H_2O$, has been determined from three-dimensional X-ray data using integrated Weissenberg photographs. The polynuclear cyanide crystallizes in the monoclinic space group C_{2h}^5-$P2_1/n$. The unit cell dimensions are $a = 9.488$ (2), $b = 12.494$ (2), $c = 7.606$ (3) Å, $\beta = 98.8$ (1)°. The measured density is 1.90 g/cm^3; the calculated value is 1.90 g/cm^3 with two formula units per cell. Least-squares refinement gave a final R factor of 5.4% for 1476 reflections. Ruthenium is coordinated by six cyanide ions in a slightly distorted octahedron. The average Ru–C and C–N distances are 2.028 (6) and 1.160 (8) Å. All cyano groups are bonded through nitrogen to manganese. Each Mn is coordinated by three nitrogen atoms and three water molecules. Two such distorted octahedra of the facial form are linked together to form a binuclear unit $Mn_2N_6(H_2O)_4$ by sharing one edge, two water molecules acting as bridging ligands. The distance between the two Mn is 3.705 (1) Å. Average Mn–N and Mn–O bond lengths are 2.150 (6) and 2.304 (6) Å. Eight waters of crystallization are connected by hydrogen bonds to the coordinated water molecules. The distances between the different oxygen atoms are between 2.73 and 3.23 Å.

Introduction

The most common structure of the polynuclear transition metal cyanides is the cubic face-centered unit cell of the Prussian blue analogs.[1] In a recent paper we have reported a single-crystal study of manganese(II) hexacyanocobaltate(III) hydrate, a typical member of the cubic cyanides.[2] It was shown that this structure is characterized by fractional occupancies of certain crystallographic positions and that the water molecules are present as coordinated as well as zeolitic water. Compounds with the same simple cubic X-ray pattern are obtained by the reaction of a hexacyanometalate(III) with a variety of divalent metal ions.[1,2] Equally sparsely soluble precipitates result when the tervalent metal ion in the cyano complex is replaced by a divalent one, *e.g.*, Fe(II), Ru(II), and Os(II). The hexacyanometalate(II) salts of nickel and copper still belong to the cubic system.[3] The X-ray pattern of the corresponding manganese and also cobalt salts, however, cannot be assigned anymore to the cubic system. Since we could obtain single crystals in the case of manganese(II) hexacyanoruthenate(II) we concentrated our studies of noncubic Prussian blue analogs on this compound.

The ambident coordination of the cyanide ion in manganese(II) hexacyanoruthenate(II) is demonstrated by the position of the CN stretching frequency. This vibration mode is observed at 2077 cm^{-1} in the polynuclear compound[4] and at 2048 cm^{-1} in the mononuclear $Ru(CN)_6^{4-}$ complex ion.[5] This frequency shift is characteristic for carbon- and nitrogen-bonded

---

(1) B. M. Chadwick and A. G. Sharpe, *Advan. Inorg. Chem. Radiochem.*, **8**, 83 (1966).

(2) A. Ludi, H. U. Güdel, and M. Rüegg, *Inorg. Chem.*, **9**, 2224 (1970).

(3) D. F. Shriver, S. A. Shriver, and S. E. Anderson, *ibid.*, **4**, 725 (1965).

(4) K. Rieder, Lizentiatsarbeit, Universität Bern, 1969.

(5) W. P. Griffith and G. T. Turner, *J. Chem. Soc. A*, 858 (1970).

cyanide ions.[6] Since no splitting of the CN stretching frequency is observed, it is assumed that all cyanide ions are equivalent, *i.e.*, acting as ambident ligands.

The electronic transitions of the $Ru(CN)_6^{4-}$ complex ion are observed in the ultraviolet region of the reflectance spectrum of $Mn_2[Ru(CN)_6]\cdot 8H_2O$.[4,7] Very weak bands are observed in the visible part. These absorptions at 18, 22, 24.1, and 27.8 kK are characteristic for nitrogen and oxygen coordinated manganese(II) in an octahedral environment.[8] By stoichiometric reasons there are only three nitrogen atoms available for each manganese(II) ion. Water molecules must therefore be present as ligands in the coordination sphere of Mn.

Manganese(II) hexacyanoruthenate(II) octahydrate represents a novel structural type of the polynuclear transition metal cyanides. In connection with our studies of transition metal cyanides it was therefore of interest to solve the structure of this compound.

Experimental Section

Almost colorless crystals of $Mn_2[Ru(CN)_6]\cdot 8H_2O$ were grown by the procedure previously described[2] using dilute aqueous solutions of $K_4Ru(CN)_6$[9] and $MnCl_2\cdot 4H_2O$. C, H, and N analyses were performed by the analytical laboratory of Dr. A. Wander A.G., Bern. The amount of water was furthermore determined thermogravimetrically. *Anal.* Calcd for $Mn_2[Ru(CN)_6]\cdot 8H_2O$: C, 14.1; H, 3.1; N, 16.4; H_2O, 28.2. Found: C, 14.1; H, 3.0; N, 16.4; H_2O, 27.6.

The needleshaped crystals were approximately square prisms and showed very sharp extinctions under the polarizing microscope.

Infrared spectra of the solid compound have been recorded with a Beckman IR-9 using KBr disks and Nujol mulls (400–4000 cm^{-1}).

Absorption correction, Patterson function, and the first-refinement calculations were carried out with Engel's programs on the GE-BULL Gamma 30 computer.[10] A modified version of the Busing–Levy ORFLS and the Johnson ORTEP programs were used on a CDC 6500.

Unit Cell Data and Collection of Intensities

Weissenberg photographs showed the crystals of $Mn_2[Ru(CN)_6]\cdot 8H_2O$ to belong to the monoclinic system. The systematic absences $h0l$, $h + l \neq 2n$, and $0k0$, $k \neq 2n$, are consistent with the space group C_{2h}^5-$P2_1/n$. We prefer this description rather than the conventional setting,[11] because in $P2_1/n$ the needle axis of the crystal coincides with the c axis.

The cell parameters were determined by a least-squares treatment of high-angle $hk0$ and $h0l$ reflections from Si-calibrated Weissenberg photographs (21°, λ(Cu $K\alpha_1$) 1.5405 Å, λ(Cu $K\alpha_2$) 1.5443 Å, λ(Cu $K\beta$) 1.3922 Å, a_0(Si) = 5.4308 Å): a = 9.488 (2), b = 12.494 (2), c = 7.606 (3) Å, β = 98.8 (1)°. The density obtained by flotation in bromoform–bromobenzene is 1.90 ± 0.01 g/cm³. On the basis of two $Mn_2[Ru(CN)_6]\cdot 8H_2O$ formula units per cell the calculated value is 1.90 g/cm³.

A needleshaped crystal of dimensions 0.17 × 0.038 × 0.038 mm was mounted along the needle axis (c). Integrated equiinclination Weissenberg photographs were recorded of the six zones $hk0$–$hk5$ with Ni-filtered Cu Kα radiation using the multiple-film technique (four films). The intensities were determined with a recording microdensitometer. Of the total of 1476 independent reflections 191 were unobserved. These unobserved reflections were assigned two-thirds of the intensity of the weakest reflection on the corresponding film. The intensity data were reduced to F^2 by applying Lorentz–polarization factors and absorption corrections using the cylindrical approximation. The linear absorption coefficient for Cu Kα is μ = 193.4 cm^{-1}. The interlevel scaling $hk0$–$hk5$ was accomplished by calculating a Wilson plot for each level.

Solution and Refinement of the Structure

Since the unit cell contains two formula units of $Mn_2[Ru(CN)_6]\cdot 8H_2O$ and the order of the space group $P2_1/n$ is four the ruthenium atoms occupy one of the twofold special positions with site symmetry $\bar{1}$. Mn, C, N, and O are at general positions ($\pm(x, y, z)$; $(^1/_2 \pm x, 1/2 \mp y, 1/2 \pm z)$) where the carbon and nitrogen atoms are divided into three and the oxygen atoms into four structurally inequivalent sets. The reflections with $h + k + l = 2n$ are systematically stronger than the ones with an odd sum. We therefore place Ru in position 2a (0, 0, 0; $^1/_2$, $^1/_2$, $^1/_2$).

Trial coordinates for Mn were obtained from a three-dimensional Patterson function. For the first structure factor calculation only the contribution of the two metal atoms was considered. The atomic scattering factors tabulated by Ibers[12] for C, N, O, Mn, and Ru were used, the effect of anomalous dispersion being neglected for the first calculations. In the final steps of the refinement the real and imaginary parts of anomalous scattering by Mn and Ru were included.[13]

The first calculation gave an R factor of 37% ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; F_o is the observed and F_c the calculated structure factor). A difference Fourier map revealed the positions of all the nonhydrogen atoms. The positional and thermal parameters of Ru, Mn, O, N, and C obtained from this difference Fourier map were refined by isotropic least-squares treatment using block matrix notations. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ taking Cruickshank's weighting scheme[14] $w = (a + |F_o| + b|F_o|^2)^{-1}$ with a = 4.0 and b = 0.011. Unobserved reflections were included with the same weighting function. After two cycles the value of R was 20%. At this point the scale factors of the levels $hk0$–$hk5$ were adjusted such that $\Sigma|F_c| = \Sigma|F_o|$ for each level. Four more cycles of isotropic refinement and a readjustment of the scale factors reduced the R factor to 6.5%. In the next step the atoms were allowed to vibrate anisotropically. After three cycles the value of R was 6.0%. In all subsequent calculations the effect of anomalous dispersion for Mn and Ru was included. The full-matrix least-squares refinement was carried out first with isotropic thermal parameters. The resulting values of R and RW were 6.0% and 9.2% ($RW = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$). With anisotropic thermal motion the full-matrix least-squares refinement converged to values of R and RW of

---

(6) D. F. Shriver, *Struct. Bonding (Berlin)*, **1**, 32 (1965).

(7) J. J. Alexander and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 4260 (1968).

(8) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962.

(9) W. P. Griffith, "The Chemistry of the Rarer Platinum Metals," Interscience, New York, N. Y., 1967.

(10) P. Engel, Abteilung für Kristallographie, Universität Bern, unpublished work.

(11) "International Tables for X-Ray Crystallography," Vol. 1, Kynoch Press, Birmingham, 1952.

(12) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol 3, Kynoch Pres, Birmingham, 1968, Table 3.3.1A.

(13) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(14) D. W. J. Cruickshank, *et al.*, in "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," Pergamon Press, Oxford, 1961, p 32.

TABLE I

POSITIONAL AND THERMAL PARAMETERS FOR $Mn_2[Ru(CN)_6] \cdot 8H_2O$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	0	0	0	285 (8)	156 (5)	453 (29)	3 (3)	63 (9)	−5 (4)
Mn	6276 (1)	947 (1)	4226 (2)	498 (12)	263 (6)	726 (38)	16 (5)	111 (13)	22 (8)
C_1	5812 (6)	3512 (5)	4794 (10)	471 (60)	325 (38)	330 (195)	−33 (37)	152 (74)	−10 (55)
C_2	6337 (6)	5556 (5)	3382 (10)	540 (64)	271 (35)	315 (198)	−51 (36)	166 (76)	24 (54)
C_3	3523 (7)	4661 (5)	2848 (11)	559 (66)	245 (37)	449 (210)	−36 (40)	23 (79)	−40 (58)
N_1	6215 (7)	2639 (5)	4659 (10)	851 (72)	301 (38)	1303 (190)	58 (39)	340 (83)	6 (58)
N_2	7147 (7)	5857 (5)	2494 (11)	761 (73)	397 (40)	1243 (201)	42 (41)	417 (89)	86 (60)
N_3	2638 (6)	4450 (5)	1690 (10)	526 (64)	389 (39)	1025 (195)	35 (37)	−127 (86)	−59 (57)
O_1	4535 (6)	919 (5)	1952 (10)	845 (70)	768 (48)	1212 (189)	−299 (42)	−134 (80)	287 (62)
O_2	4271 (5)	845 (4)	5811 (8)	679 (54)	244 (26)	535 (139)	110 (29)	63 (59)	88 (40)
O_3	2408 (7)	2293 (5)	3992 (10)	1226 (80)	408 (38)	2536 (201)	220 (43)	103 (95)	262 (66)
O_4	9579 (7)	2948 (4)	3900 (9)	1241 (74)	405 (36)	1132 (165)	−140 (40)	181 (78)	−163 (53)

[a] The positional and thermal parameters with their standard deviations have been multiplied by 10^4 and 10^5, respectively. The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

5.4% and 8.3%, respectively.[15] Since we have applied a fixed weighting function the weights are certainly not on an absolute scale. The error in an observation of unit weight is 0.38. During the final cycle no positional parameter was shifted more than 60% of its standard deviation. By Hamilton's criterion[16] the introduction of anisotropic thermal motion represents a significant improvement.

Table I lists the final atomic parameters. Because the individual layers have been rescaled during the isotropic refinement, the thermal parameters in the c direction have rather large standard deviations.

A difference Fourier map calculated with the final set of structure factors showed small peaks up to 0.5 $e^-/Å^3$, the background fluctuations being of the same order of magnitude. Trial calculations including the eight crystallographically independent sets of hydrogen atoms did not lead to an improvement of R and RW. The precision of our photographic data is not considered as sufficient to allow an exact determination of the hydrogen positions in the presence of the heavy atoms Ru and Mn. No further attempt therefore was made to locate the hydrogen atoms.

Description of the Structure

The structure of $Mn_2[Ru(CN)_6] \cdot 8H_2O$ is characterized by a three-dimensional connection of ruthenium and manganese by cyanide ions. There are no discrete complex ions but elements Ru–C–N–Mn leading to a three-dimensional framework where all cyano groups are present as ambident ligands.

The coordination geometry of Ru, its site symmetry being $\bar{1}$, is given by a slightly distorted octahedron. The average distance Ru–C is 2.028 Å. This value can be compared with the distance Ru–C of 2.01 Å in the structure of *cis*-$Ru(CO)_4I_2$.[9] The present average C–N distance of 1.160 Å lies well within the range of C–N distances given by Britton for a variety ofcya no compounds.[17]

Since all the cyano groups are linked through nitrogen to manganese, it is evident from the stoichiometry that each Mn must have three nitrogen atoms in its coordination sphere. Sixfold coordination is achieved by three water molecules in such a way that a distorted $MnN_3(H_2O)_3$ octahedron of the facial configuration is formed. Average bond lengths are 2.150 Å for Mn–N and 2.304 Å for Mn–O. In the structure of $Mn_3[Co(CN)_6]_2 \cdot xH_2O$ with a $MnN_4(H_2O)_2$ group the corresponding distances are 2.21 and 2.39 Å, respectively.[2]

Whereas in the lattice of $Mn_3[Co(CN)_6]_2 \cdot xH_2O$ the metal positions are occupied alternatively by Mn and Co, the sequence of the metal ions in the present structure is Ru–Mn–Mn–Ru. Two $MnN_3(H_2O)_3$ groups are connected to a binuclear complex by sharing one edge. The two bridging ligands are represented by two water molecules. The two Mn atoms and the two oxygen atoms of the bridging water molecules lie in one plane, the center of the connecting line Mn–Mn being a center of symmetry (position 2c; $^1/_2$, 0, $^1/_2$; 0, $^1/_2$, 0). The two Mn atoms are separated by 3.705 Å; the distance between the oxygen atoms of the two bridging water molecules is 2.90 Å. This binuclear complex can be formulated as $Mn_2N_6(H_2O)_4$.

The principal interatomic distances and angles are given in Table II, the root-mean-square amplitudes of vibration in Table III. Figure 1 shows a perspective drawing of the $Ru(CN)_6$ group. The amplitudes of

TABLE II

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (DEG)

Atoms	Distances, Å	Atoms	Angle, deg
Ru–C1	2.027 (5)	C1–Ru–C2	89.14 (25)
Ru–C2	2.024 (6)	C1–Ru–C3	88.22 (22)
Ru–C3	2.034 (6)	C2–Ru–C3	89.65 (29)
Ru–N1	3.191 (5)	N1–Mn–N2	100.63 (26)
Ru–N2	3.187 (6)	N1–Mn–N3	96.78 (15)
Ru–N3	3.185 (6)	N1–Mn–O1	95.87 (17)
		N1–Mn–O2	86.11 (26)
Mn–Mn	3.705 (1)	N1–Mn–O2′	162.23 (52)
Mn–N1	2.141 (5)	N2–Mn–N3	98.14 (27)
Mn–N2	2.140 (6)	N2–Mn–O1	91.42 (28)
Mn–N3	2.170 (6)	N2–Mn–O2	170.3 (13)
Mn–O1	2.206 (6)	N2–Mn–O2′	96.84 (16)
Mn–O2	2.410 (4)	N3–Mn–O1	162.42 (55)
Mn–O2′	2.297 (4)	N3–Mn–O2	87.87 (25)
		N3–Mn–O2′	83.77 (12)
C1–N1	1.165 (8)	O1–Mn–O2	80.87 (25)
C2–N2	1.163 (8)	O1–Mn–O2′	80.46 (12)
C3–N3	1.152 (9)	O2–Mn–O2′	76.15 (17)
O2–O2′	2.904 (6)	Ru–C1–N1	176.9 (15)
		Ru–C2–N2	177.5 (18)
		Ru–C3–N3	176.3 (14)
		Mn–N1–C1	162.6 (11)
		Mn–N2–C2	164.1 (21)
		Mn–N3–C3	169.8 (9)
		Mn–O2–Mn	103.84 (12)

---

(15) A listing of structure factor amplitudes and a table of all distances less than 3.5 Å will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

(16) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

(17) D. Britton, *Perspect. Struct. Chem.*, **1**, 109 (1967).

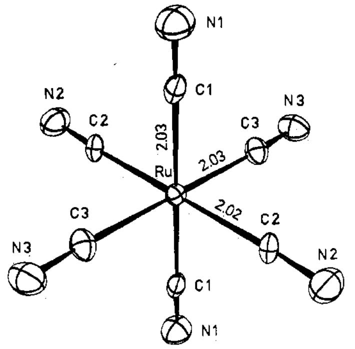


Figure 1.—A perspective drawing of the Ru(CN)$_6$ group in $Mn_2[Ru(CN)_6]\cdot 8H_2O$ down one of the molecular trigonal axes.

TABLE III

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)

Atom	Min	Intermed	Max	Atom	Min	Intermed	Max
Ru	0.109	0.112	0.114	N2	0.152	0.173	0.211
Mn	0.140	0.144	0.151	N3	0.135	0.170	0.197
C1	0.090	0.143	0.162	O1	0.164	0.173	0.281
C2	0.086	0.141	0.161	O2	0.109	0.141	0.182
C3	0.110	0.139	0.161	O3	0.153	0.246	0.278
N1	0.150	0.175	0.208	O4	0.154	0.195	0.240

thermal motion in the direction of the Ru–C and C–N bonds are as expected smaller than the ones perpendicular to these bonds. Furthermore the nitrogen atoms have greater amplitudes than the carbon atoms illustrating the greater strength of the M–C bond compared with the linkage M–N. A perspective view of the binuclear $Mn_2N_6(H_2O)_4$ is displayed in Figure 2.

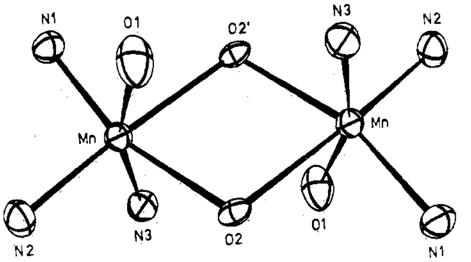
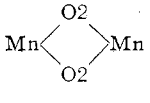


Figure 2.—A perspective drawing of the binuclear $Mn_2N_6(H_2O)_4$ group in $Mn_2[Ru(CN)_6]\cdot 8H_2O$.

One can see the greater thermal motion of the "private" (O1) relative to the bridging (O2) water molecules. Again the amplitudes of O2 perpendicular to the



$$\mathrm{Mn}\overset{\mathrm{O2}}{\underset{\mathrm{O2}}{\langle\,\rangle}}\mathrm{Mn}$$

plane are greater than the ones within the plane.

The binuclear unit $Mn_2N_6(H_2O)_4$, each Mn having two shared and one "private" water molecules, represents a peculiar type of coordination. The tendency to act as a bridging ligand in oligo- and polynuclear complexes is quite familiar for OH^- and O^{2-}. No structures of transition metal compounds, however, seem to be known where two metal ions have one or more water molecules as common ligands.[18]

Our determination of the structure of $Mn_2[Ru(CN)_6]_2\cdot 8H_2O$ did not reveal the positions of the hydrogen atoms. One has to consider also the possibility that the shared ligands are OH^- ions and that the protons are attached to the zeolitic water molecules giving H_3O^+ ions. Additional information concerning this point is furnished by the infrared spectrum (Figure 3).

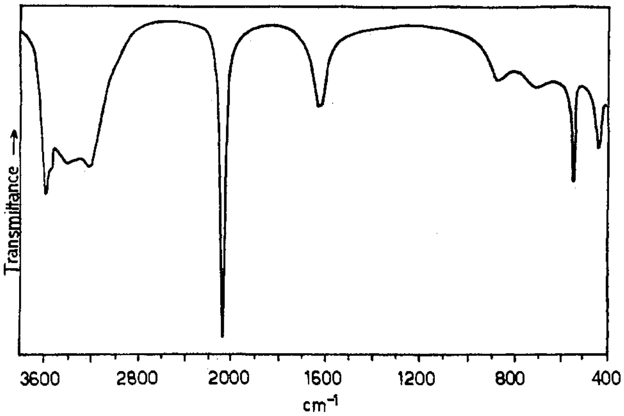


Figure 3.—The infrared spectrum of $Mn_2[Ru(CN)_6]\cdot 8H_2O$.

The sharp bands at 2077 and 552 cm^{-1} are readily assigned to the CN and RuC stretching vibrations[5] whereas the absorption at 450 cm^{-1} is attributed to the MnO stretching and MnOMn bending mode.[19] The rocking and wagging vibrations of the coordinated water molecules are observed as rather broad bands at 865 and 720 cm^{-1}.[19] The broad band centered at 1620 cm^{-1} represents the bending vibration of water and the combination of bands between 3150 and 3600 cm^{-1} is due to OH stretching modes. In particular there is no evidence for an absorption around 1100 cm^{-1} where the hydronium ion gives rise to a very strong band. This strong band appears at 1160 cm^{-1} in the spectrum of $(H_3O)(NO_3)$ and at 1135 cm^{-1} in that of $(H_3O)(HSO_4)$.[20] The existence of discrete H_3O^+ ions in the lattice of $Mn_2[Ru(CN)_6]\cdot 8H_2O$ can thus be excluded, confirming the formulation of the two bridging ligands as water molecules.

A packing diagram showing the RuC$_6$ and $Mn_2N_6(H_2O)_4$ groups is displayed in Figure 4. Figure 5 shows a projection of the structure on the (001) plane indicating the linkage of the two different metal ions by cyanide bridges.

In addition to the water molecules belonging to the coordination sphere of manganese eight more water molecules are situated in the holes of the relatively open Ru–C–N–Mn framework. Hydrogen bonds are assumed to connect these zeolitic molecules to the coordinated ones. A list of the shortest possible hydrogen bonds is given in Table IV. O–H···O distances can also be estimated from the position of the OH stretching frequencies in the infrared spectrum. The broad OH stretching absorption in the spectrum of $Mn_2[Ru(CN)_6]\cdot 8H_2O$ shows band maxima at 3190, 3290, 3370, 3520, and 3570 cm^{-1}. The application of empirical rules[21,22] leads to O–H···O distances of 2.7, 2.75, 2.8,

---

(18) C. K. Jørgensen, "Inorganic Complexes," Academic Press, London and New York, 1963.

(19) D. M. Adams, "Metal–Ligand and Related Vibrations," Edward Arnold, London, 1967; K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Interscience, New York, N. Y., 1970.

(20) R. Savoie and P. A. Giguère, *J. Chem. Phys.*, **41**, 2698 (1964).

(21) K. Nakamoto, M. Margoshes, and R. E. Rundle, *J. Amer. Chem. Soc.*, **77**, 6480 (1955).

(22) K. D. Schubert, *Z. Chem.*, **7**, 320 (1967).

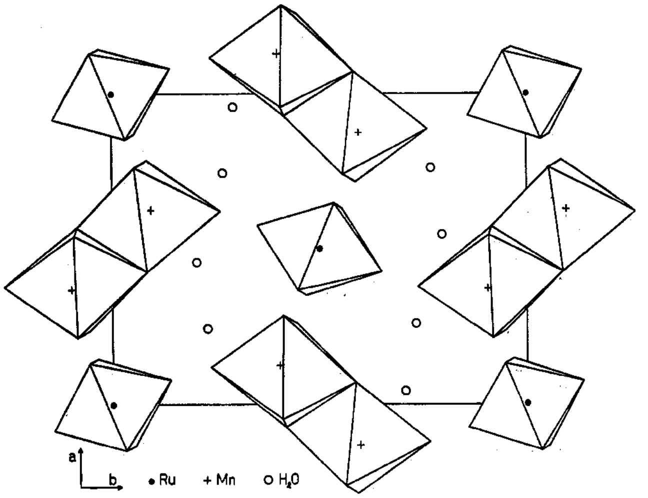


Figure 4.—Packing diagram of the RuC_6 and $Mn_2N_6(H_2O)_4$ groups in $Mn_2[Ru(CN)_6]\cdot 8H_2O$.

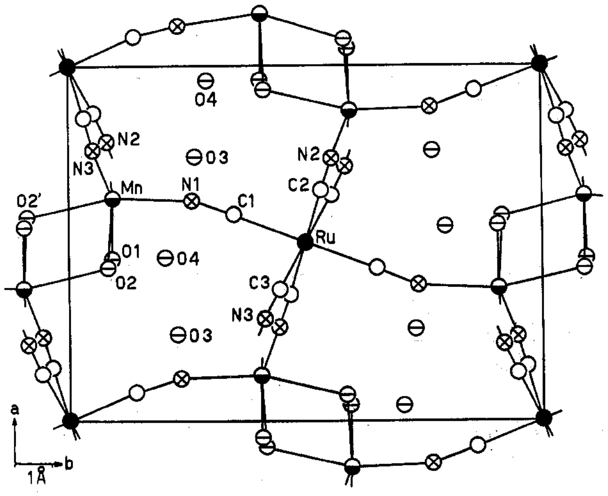


Figure 5.—A projection of the structure of $Mn_2[Ru(CN)_6]\cdot 8H_2O$ on the (001) plane.

TABLE IV
SHORTEST DISTANCES O–O (Å) BETWEEN COORDINATED AND ZEOLITIC WATER MOLECULES AND SOME RELATED ANGLES (DEG)

O1–O4	2.734 (9)	O1–O4–O3	105.68 (33)
O2–O3	2.751 (7)	O1–O4–O2	115.49 (10)
O2–O4	2.777 (8)	O2–O3–O4	138.11 (32)
O3–O4	2.796 (7)	O3–O2–O4	92.75 (14)
O1–O3	3.226 (8)	O3–O1–O4	103.23 (21)

2.9, and >3.0 Å, the last distance corresponding to a very weak hydrogen bond. The angles between three oxygen atoms which are assumed to participate in hydrogen bonds (Table IV) agree well with the values given by Hamilton and Ibers.[23] Since all the nitrogen atoms are bonded to Mn, O–H···N bonds are very unlikely and have therefore not been considered.

The relationship between this monoclinic structure and the cubic one of the Prussian blue analogs is not very obvious. The extension of the model obtained from the investigation of $Mn_3[Co(CN)_6]_2\cdot xH_2O$ leads theoretically to a cubic cell of space group *Fm3m* with an edge of about 10 Å having two formula units of manganese(II) hexacyanoruthenate(II).[2] Position 4a (0, 0, 0) would be occupied by four Mn; position 4b ($^1/_2$, $^1/_2$, $^1/_2$), by only two Ru. This small occupancy is considered as responsible for the realization of the noncubic structure of this compound. We still can draw a comparison between the two structures if we replace in the lattice of $Mn_2[Ru(CN)_6]\cdot 8H_2O$ the binuclear $Mn_2N_6(H_2O)_4$ group by a hypothetical MN_6 unit and distort the monoclinic cell such that it becomes cubic. The resulting idealized cell can be described as cubic face centered with four Ru at 4a and four M at 4b. Whereas this comparison emphasizes the ambident linkage by the cyanide ion, the striking coordination behavior of the water molecules in the monoclinic polynuclear cyanide cannot be seen anymore.

Acknowledgments.—We are indebted to Dr. D. Schwarzenbach and Dr. P. Fischer for many helpful discussions and to Mr. A. Egli for performing the C, N, and H analyses. We thank Professor W. Nowacki and Dr. P. Engel for using their microdensitometer and their programs. This work was supported by the Schweizerischer Nationalfonds and the Entwicklungsfonds Seltene Metalle.

(23) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968.