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- (17) The Gaussian exponents in the 52/52 calculations were: (N) s 553.3, 84.91, 19.62, 5.421, 0.4201 and p 2.333, 0.4148; (O) s 736.6, 112.9, 26.04, 7.212, 0.5764 and p 2.333, 0.4148; (B) s 258.4, 40.19, 9.342, 2.579, 0.1900 and p 0.9285, 0.1681; (F) s 948.5, 144.9, 33.46, 9.261, 0.7528 and p 4.190, 0.7106.
- (18) The Gaussian exponents in the 73/73 calculations were: (N) s 1619., 248.7, 57.75, 16.36, 5.081, 0.7797, 0.2350 and p 6.273, 12.82, 0.2974; (O) s 2200., 332.2, 76.93, 21.74, 6.773, 1.103, 0.3342 and p 8.356, 1.719, 0.3814; (B) s 738.0, 114.4, 26.79, 7.723, 2.426, 0.3538, 0.1134 and p 2.713, 0.5336, 0.1251; (F) s 2723., 416.4, 97.73, 27.87, 8.712, 1.396, 0.4209 and p 10.53, 2.168, 0.4785.
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- (24) We have attempted to assign numerical values to Δ_n and Δ_d for N_2O_4 by means of the extended Hückel approximation employing oxygen 2p Slater orbitals oriented parallel to the N-N axis. Within this approximation $\Delta_n = 0.42$ eV and $\Delta_d = 0.17$ eV. We believe that while the Δ_n/Δ_d ratio is probably nearly right these values are too low. As the interatomic separation becomes large single ζ Slater orbitals demonstrate overlap which is increasingly too small relative to that of atomic orbitals expressed in terms of larger basis sets. Compare the single ζ Slater overlaps with those obtained by using the oxygen 2p SCF eigenfunctions expressed in our three p-type Gaussians: with $r = 1.16$ A, overlap $S_{2p_x, 2p_x} = 1STO = 0.319$ ($3GTO = 0.274$); $r = 2.09$, $1STO = 0.063$ ($3GTO = 0.193$); $r = 3.02$, $1STO = 0.005$ ($3GTO = 0.028$).
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Synthesis and Structural Characterization of a New Cyanomanganate(III) Complex, Heptapotassium μ -Oxo-bis[pentacyanomanganate(III)]cyanide

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Abstract: The final product resulting from the reaction of $KMnO_4$ and KCN in saturated aqueous solution is a gold-brown compound $K_7[(CN)_5MnOMn(CN)_5]CN$, as established by a single-crystal X-ray diffraction study. Full-matrix least-squares refinement included anisotropic temperature parameters for all atoms and converged with a final R index (on F) of 0.091. The structure contains the oxo bridged $[Mn_2O(CN)_{10}]^{6-}$ ion, which has $2/m$ crystallographic symmetry with the bridging oxygen atom lying at a center of symmetry. The ion exists in an eclipsed rotameric configuration. The Mn-O distance is relatively short, 1.723 (4) Å. Crystallographically independent potassium ions are coordinated to the nitrogen ends of cyanide groups in trigonal prismatic, octahedral, and square antiprismatic geometries. Crystal data are as follows: orthorhombic; space group $Ibam$; $a = 12.397$ (8), $b = 12.772$ (8), $c = 14.618$ (7) Å (temperature 23°); $Z = 4$; $d_{obsd} = 1.98$, $d_{calcd} = 1.97$ g/cm³. The synthesis, isolation, and physical characteristics of $K_7[Mn_2O(CN)_{10}]CN$ are reported along with spectral and magnetic data. The principal features in the infrared spectrum are cyanide stretching bands centered around 2090 cm⁻¹. The optical absorption spectrum in a KBr pellet consists of a primary band at 370 nm with a prominent shoulder at 410 nm and a weak shoulder at approximately 610 nm. The gold-brown crystals are strongly pleochroic, the crystals being colorless when the E vector is parallel to the long needle axis. This characteristic serves as a convenient means of identification for this substance. At room temperature $K_7[Mn_2O(CN)_{10}]CN$ is diamagnetic.

In 1930 Yakimach¹ reported that the action of KCN on $KMnO_4$ in saturated aqueous solution led to a red crystalline substance of composition $K_4[Mn(CN)_8]$, which decomposed in water giving HCN and MnO_2 . It was suggested, assuming this composition, that the salt was a crystal aggre-

gate of $K_2Mn(CN)_6$ and 2KCN.² Goldenberg,³ in an attempt to prepare this double cyanide of tetravalent manganese, noted that when using Yakimach's preparation, *i.e.*, saturated aqueous $KMnO_4$ (6.7%) and a solution containing 80 g of KCN to 100 g H_2O , a bulky precipitate of

MnO₂ resulted. Upon altering the formulation, however, to 4 ml of saturated KMnO₄ and 5 ml of the KCN solution, Goldenberg obtained brown diamagnetic crystals, which he formulated as K₃Mn₂(CN)₉ · 4KOH.³ He thereby carried out a large scale preparation at ice temperature whereupon "5 g of apparently pure golden brown crystalline plates were obtained."

We have confirmed that the predominant crystalline species formed when saturated aqueous solutions of KCN and KMnO₄ are mixed, and the water evaporated, is a gold-brown compound existing as single or clustered crystals of long thin needles or blades. The most striking physical property of these crystals is their pleochroism as observed by polarized light microscopy. The infrared spectrum of the compound indicates the presence of cyanide, as does the fact that decomposition occurs in water to give manganese dioxide and hydrogen cyanide. These observations, taken together with electronic spectral and magnetic data, serve to distinguish the gold-brown compound from all known cyano complexes of manganese. Although elemental analyses of the compound confirmed the presence of potassium, manganese, oxygen, and cyanide, our attempts to establish the empirical formula of the compound from these analyses were unsuccessful. Thus we undertook a single-crystal X-ray diffraction study of the compound.

This paper reports the synthesis, isolation, and structural characterization of this new compound, heptapotassium μ -oxo-bis[pentacyanomanganate(III)]cyanide.

Experimental Section

A. Synthesis and Isolation. Heptapotassium μ -oxo-bis[pentacyanomanganate(III)]cyanide may be prepared by mixing together saturated aqueous solutions of KCN and KMnO₄ and allowing H₂O to evaporate (25°, 1 atm) until a slurry of crystalline material is obtained. The slurry contains the product as gold-brown needles or blades along with other compounds such as KOCN, red-orange K₃Mn(CN)₆, K₂CO₃, and possibly KHCO₃. Both the yield and crystal quality of the product seem to improve when the reaction is carried out at lower temperatures. In a typical run, 100 ml of saturated aqueous KCN at 4° are added to 50 ml of saturated aqueous KMnO₄, also at 4°. The reddish brown solution is allowed to evaporate (4°, 1 atm) to approximately 50 ml, whereupon gold-brown needles and aggregates may be obtained by decanting the remaining solution. Quantities of several hundred milligrams of product may be isolated, and at this stage relatively pure samples of compound may be obtained by picking out the crystalline impurities under a microscope.⁴

The solid compound is stable in dry air and light and is insoluble in ordinary polar⁵ and nonpolar solvents. The compound rapidly decomposes in water at 20°, forming HCN and a voluminous precipitate of hydrous MnO₂. For instance, a solution of 2 ml of H₂O and 10 mg of compound undergoes visible decomposition within seconds. At 0°, however, the solution appears unchanged for about 40 min.

Distilled H₂O and reagent grade KCN and KMnO₄ were used as starting materials. Attempts to recrystallize the product led to decomposition. Decomposition of the crystals in a He atmosphere sets in at about 270° (TGA data) and melting is not observed. Analytical samples were hand picked, crystal by crystal, but infrared spectral analysis almost always showed impurities, such as H₂O, CO₃²⁻, and HCO₃⁻, that are usually associated with ionic cyanide. The elemental analysis reported represents an average of several analyses performed by Galbraith Laboratories, Inc., Knoxville, Tenn., Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and M-H-W Laboratories, Garden City, Mich. *Anal.* Calcd for K₇Mn₂(CN)₁₁O: K, 39.9; Mn, 16.0; C, 19.3; N, 22.4; O, 2.3. Found: K, 41.8; Mn, 15.5; C, 19.5; N, 21.7; O, 3.0; H, 0.4.

B. Physical Measurements. Electronic absorption spectra were recorded on a Cary Model 17 spectrophotometer, and infrared measurements were made on a Perkin-Elmer 180 spectrophotometer. Both spectral studies used a 1.0-mg sample in a 250 mg, 13 mm diameter KBr disk. Far-infrared spectra were obtained with a

paraffin wax pellet. Magnetic susceptibilities were measured with a Princeton Applied Research FM-1 vibrating sample magnetometer.

C. Collection and Reduction of Intensity Data. Thirty-eight well-formed, but very thin, needle-like crystals, which gave good optical extinction under crossed polarizers, were selected for X-ray analysis. Only one (0.08 × 0.19 × 0.61 mm) proved to be a single crystal and was used in the subsequent X-ray investigation. A series of Weissenberg and precession photographs taken with Mo K α and Cu K α radiations indicated systematic absences of reflections hkl with $h + k + l$ odd, $0kl$ with k odd and $h0l$ with h odd. The crystals were assigned to the orthorhombic system, space group $Iba2$ or $Ibam$. The measured density of the crystal, by flotation in a CHBr₃-*n*-C₆H₁₄ mixture, is 1.98 (3) g/cm³ and the calculated density, assuming four formula units per unit cell, is 1.97 g/cm³.

Sixteen reflections ($2\theta > 20^\circ$) were centered in the counter aperture by varying 2θ , ϕ , and χ in conjunction with the left-right and top-bottom balancing features of the variable receiving aperture. The cell constants and their standard deviations were determined by a least-squares refinement of the 2θ values for these sixteen reflections. The results (Mo K α radiation, λ 0.7107, 23°) are $a = 12.397$ (8), $b = 12.772$ (8), and $c = 14.618$ (7) Å. The corresponding ϕ and χ values for 14 of the reflections were used as input data for the orientation program operating under the CRYM crystallographic computing system.⁶ The independent intensity data set was collected from a single crystal at 23° using a Datex-automated General Electric diffractometer. The crystal was mounted with its c axis approximately parallel to the ϕ axis of the diffractometer.

A total of 567 independent reflections was collected by the θ - 2θ scan technique in the range $4^\circ \leq 2\theta(\text{Mo K}\alpha) \leq 40^\circ$. A check of several high-angle reflections indicated that our settings included the entire peak in the scan. The pulse height analyzer was set for approximately a 90% window centered on the Mo K α peak. A scan rate of 0.5°/min (in 2θ) was used with stationary counter, stationary crystal background counts of 60 sec duration taken at each end of the scan. A symmetric scan range of between 2.0 and 4.0° was adjusted to account for α_1 - α_2 splitting.

Throughout the data collection the intensities of three reference reflections were measured every 60 reflections. There were no signs of crystal decomposition in the X-ray beam.

The values for the observed intensities, I_{obsd} , were derived from the scalar counts using the formula

$$I_{\text{obsd}} = S - \frac{B_1 + B_2}{2} \left(\frac{t}{30} \right)$$

where S is the scan count, B_1 and B_2 are the two background counts, and t is the scan time in seconds. Negative values of I_{obsd} calculated from this formula were set equal to zero. The standard deviation for each reflection was calculated using

$$\sigma^2(I_{\text{obsd}}) = S + \frac{B_1 + B_2}{2} \left(\frac{t}{30} \right)^2 + (0.02S)^2$$

The last term in this equation is an empirical term (Busing and Levy)⁷ which presumably allows for errors not due to counting statistics. The standard deviations calculated in this way were the basis for the weights used in the least-squares refinement. The intensities and their standard deviations were corrected for Lorentz and polarization effects but not for absorption.⁸ The linear absorption coefficient (Mo K α) for this compound is 24.1 cm⁻¹, $\mu t_{\text{max}} = 1.5$. The data were put on an approximately absolute scale with a Wilson plot.⁹ The distribution of the normalized structure factors¹⁰ and application of the zero moment test of Howells, Phillips, and Rogers¹¹ suggested the centric space group $Ibam$, and, in accordance with this, $Ibam$ was assumed for the analysis. Of the 567 reflections collected, 426 obeyed the condition $F^2 > \sigma(F^2)$ and were used in subsequent calculations.

D. Solution and Refinement of the Structure. The approximate coordinates of the manganese atom were readily determined from a three-dimensional Patterson map. Subsequent Fourier and difference Fourier maps were used to locate the potassium, oxygen, carbon, and nitrogen atoms. The positions of the potassium ions suggested further that the space group is $Ibam$ rather than $Iba2$. The function minimized throughout the full-matrix least-squares

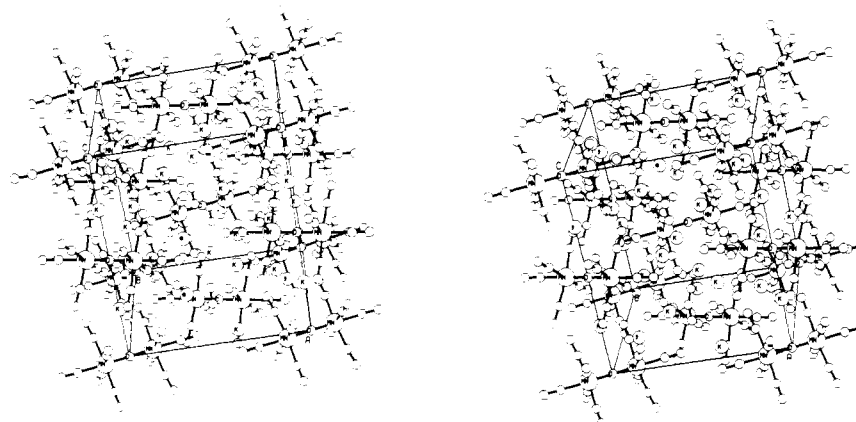


Figure 2. A stereoscopic view of the packing in a unit cell of $K_7[(CN)_5MnOMn(CN)_5]CN$.

Table II. Interatomic Distances (Å) and Angles (deg)^{a,b}

Atoms	Distances	Atoms	Angles
Mn–O	1.723 (4)	C(1)–Mn–C(3)	88.3 (6)
Mn–C(1)	1.999 (17)	C(1)–Mn–C(2)	89.7 (7)
Mn–C(2)	1.974 (17)	C(2)–Mn–C(3)	84.9 (6)
Mn–C(3)	2.056 (27)	Mn–C(1)–N(1)	176.7 (14)
C(1)–N(1)	1.146 (21)	Mn–C(2)–N(2)	177.1 (1)
C(2)–N(2)	1.178 (22)	Mn–C(3)–N(3)	178.0 (21)
C(3)–N(3)	1.130 (36)	O–Mn–C(1)	92.4 (4)
C(4)–N(4)	0.910 (81)	O–Mn–C(2)	94.4 (5)
K(1)–C(4)	2.947 (17)	O–Mn–C(3)	179.0 (7)
K(3)–O	3.654		
K(1)–K(1')	3.552 (8) ^c		

^a See Figure 1 for the atom-labeling scheme. ^b The values in parentheses are estimated standard deviations in the least significant figure(s) as obtained from the least-squares refinement process *via* the inverse matrix. ^c Closest potassium–potassium approach: $K(1')[\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z]$.

[phthalocyanatopyridinemanganese(III)] dipyridinate,¹⁹ which is the only other known binuclear manganese complex containing a linear oxo bridge. In the latter compound, the phthalocyanine groups assume a staggered configuration (49°), which contrasts with our findings for $[Mn_2O(CN)_{10}]^{6-}$. A similar situation of different rotameric configurations but similar M–O distances has been observed for the compounds $[Pt(NH_3)_4]_2[Re_2O_3(CN)_8]$ and $Re_2O_3[S_2CN(C_2H_5)_2]_4$.²⁰

In the present structure, the manganese atoms are displaced out of the MnC_4 (eq) least-squares plane by 0.14 Å toward the oxygen atom. This type of metal–atom displacement has been observed in other six-coordinate complexes containing X_4Mn-O and X_4Mn-N units,²¹ and has been explained as arising from the nonbonded repulsions between the X and the O and N atoms, respectively.²² In the present case, the distances between the oxygen atom and the carbon atoms of the equatorial cyanide groups (2.69 and 2.72 Å for C(1) and C(2), respectively) have an optimum value of approximately 2.7 Å, and about 0.1 Å longer than the $O \cdots C$ distance calculated for O–Mn–C angles of 90°. The present O–Mn–C(1) and O–Mn–C(2) angles are 92.4 (4) and 94.4 (5)°, respectively.

The manganese–carbon distances appear normal and have a mean value of 2.010 (36) Å with essentially no difference between the equatorial and axial distances ($<3\sigma$). The carbon–nitrogen distances have a mean value of 1.151 (47) Å, except for the C(4)–N(4) unit, which has a distance of 0.910 (81) Å. The closest contacts of the potassium ions to the free cyanide are about the same as that in KCN (2.94 Å).²³

Table III. Least-Squares Plane

Atoms defining plane ^a	Equation of plane ^b	Deviations
Mn C(1) N(1) C(2) N(2)	$0.928X + 0.372Y - 1.859 = 0$	Mn, -0.138 ; O, -1.859 ; C(3), $+1.914$; C(1), $+0.004$; N(1), $+0.039$; C(2), -0.043 ; N(2), $+0.070$

^a And equivalent atoms related by x, y, z except for Mn. ^b Defined by the real coordinates X, Y .

A. Crystal Packing. The packing arrangement within crystalline $K_7[Mn_2O(CN)_{10}]CN$ is dominated by the $[Mn_2O(CN)_{10}]^{6-}$ ion and may be described with the aid of a stereoscopic view of the unit cell contents (Figure 2). The structure consists of layers of $[Mn_2O(CN)_{10}]^{6-}$ ions, with the linear Mn–O–Mn units of the ions lying in planes normal to the c axis at $z = 0, \frac{1}{2}$, and 1, and making in-plane angles of 19.5° with respect to the a axis or its projection in the case of $z = \frac{1}{2}$. In a layer, the four nearest neighbor anions, in terms of their Mn–O–Mn units, make angles of $2 \times 19.5^\circ$ with respect to the center anion's Mn–O–Mn unit, thereby orienting nearest in-plane neighbor anions 39° with respect to each other. The layers of $[Mn_2O(CN)_{10}]^{6-}$ ions stack to form columns of anions running parallel to the c axis. In the stack the oxygen atoms are arranged along the center line of the column. The anions are again staggered, alternatingly, 39° with respect to each other along the column. Each binuclear unit therefore has a total of six nearest neighbors, all oriented in the same direction with respect to each other, but all 39° with respect to the center anion in terms of the Mn–O–Mn units.

The alternatingly staggered packing of the binuclear anions gives rise to two nearly regular coordination polyhedra, having vertices occupied by nitrogen atoms from the cyanide groups of the anions and a center occupied by one of the three crystallographically independent potassium ions. From Figure 2 it may be seen that the staggered packing *along a column* gives rise to a slightly distorted square antiprism (39° vs. 45°), whose vertices are composed of four nitrogen atoms from one anion and four nitrogen atoms from an adjacent anion in the column. The relative rotation of the anions by 39° clearly lessens the repulsions between the nonbonded nitrogen atoms, while leaving the oxygen–oxygen distances unaltered. The center of the square antiprism, which lies midway between the oxygen atoms along the center line of the column, is occupied by one of the independent potassium ions, K(3). The eight K(3)–N distances have a mean value of 3.27 (4) Å. The staggered arrange-

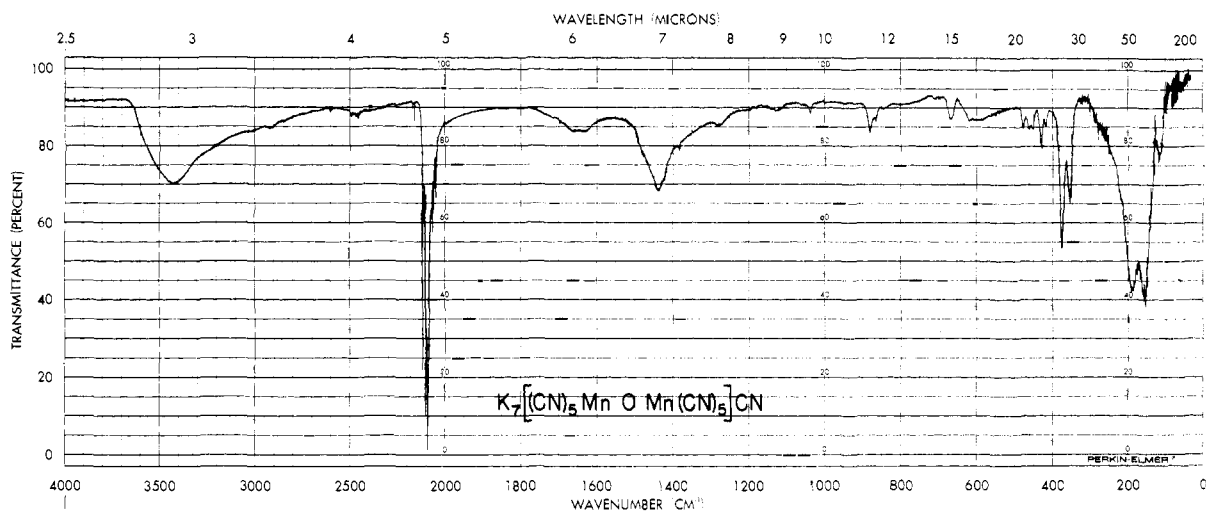


Figure 3. The infrared spectrum of $K_7[(CN)_5MnOMn(CN)_5]CN$: KBr pellet, 4000–300 cm^{-1} ; paraffin wax, 300–33 cm^{-1} .

ment of anions *within a layer* gives rise to a slightly distorted *trigonal prism*, whose vertices are composed of six nitrogen atoms from one, two, and three cyanide groups of three separate anions, respectively. The second independent potassium ion, K(2), is located approximately at the center of this trigonal prism, and the mean value for the six K(2)–N distances is 2.89 (4) Å. To our knowledge, this represents the first instance of a potassium ion in a trigonal-prismatic coordination environment. The triplet of potassium ions is completed by K(1), which is located between the planes of anions; K(1) has a six-coordinate, distorted octahedral geometry composed of the one free cyanide group (equatorial position) and five nitrogen atoms from coordinated cyanide groups. The mean value for the five K(1)–N distances and the one K(1)–CN distance is 2.83 (5) Å. Three of the five nitrogen atoms are furnished from cyanide groups on different anions, whereas two come from cyanide groups of the same anion but attached to different manganese atoms.

Finally, we note that the free cyanide group occupies voids within the crystal lattice and may be viewed as being centrally located within columns of potassium ions (K(1) and K(2)) running parallel to the *c* axis. This situation is readily seen on the front face of the unit cell in Figure 2.

B. Spectral and Magnetic Data. The infrared spectrum of $K_7[Mn_2O(CN)_{10}]CN$ is presented in Figure 3. The dominant features are the main cyanide stretching band at 2090 cm^{-1} and the less intense C–N stretches at 2102, 2117, 2063, 2050, and 2161 cm^{-1} . Other prominent features, which are assigned to Mn–C stretching and bending modes, are the sharp, lower energy bands at 376 and 355 cm^{-1} , the more intense far-infrared features at about 189 and 156 cm^{-1} , and the series of rather sharp bands at 477, 464, 452, 431, 418, and 119 cm^{-1} . Present in the ir spectra of all samples, but of varying intensity with respect to the cyanide features, are the bands at 1450 and 865 cm^{-1} . These bands may be assigned to carbonate and bicarbonate impurities,²⁴ which are believed to adhere to the fibrous or needle-like compound, and which result from the decomposition of cyanide in the presence of CO_2 and H_2O . Additionally, water bands at 3430 and ~ 1650 cm^{-1} are present.

Most oxo bridged binuclear species exhibit a medium to strong intensity absorption band in the 700–900- cm^{-1} region attributable to the asymmetric M–O–M stretching vibration.^{25,26} For instance, this stretching vibration gives rise²⁷ to a prominent band at ~ 890 cm^{-1} in $K_4[O(CN)_4Re-ORe(CN)_4O] \cdot H_2O$,²⁰ and in the oxo bridged manganese(III) phthalocyanine complex $\nu_{as}(M-O-M)$ appears at

820 cm^{-1} .²⁸ The only apparent candidate for $\nu_{as}(M-O-M)$ in the ir spectrum of $K_7[(CN)_5MnOMn(CN)_5]CN$ is a relatively weak band at 880 cm^{-1} , which is not assignable at least to CO_3^{2-} , HCO_3^- , OCN^- , H_2O , or $K_3Mn(CN)_6$. A similarly weak absorption occurs in $K_4[Ru_2OCl_{10}]H_2O$ at 888 cm^{-1} , and its assignment as the Ru–O–Ru asymmetric stretch has been confirmed by ^{18}O labeling.²⁹ In the present case, however, the possibility that the 880- cm^{-1} band represents another impurity has not been ruled out.

The optical absorption spectrum of solid $K_7[(Mn)_2O(CN)_{10}]CN$ in a KBr pellet (300°K) consists of a primary band at 370 nm with a prominent shoulder at 510 nm and a weak shoulder at approximately 610 nm. At 78°K, the major change is a sharpening of the two shoulders. The molar extinction coefficient of the 370-nm peak is estimated to be at least 2×10^3 from the pellet data. It is probable, therefore, that the 370-nm feature represents a ligand-to-metal charge transfer (LMCT) transition. The spectrum of the $[Mn(CN)_5(OH)]^{3-}$ ion would be expected to be similar. In acidic solution, it consists of a set of two bands at 381 and 393 nm and a less intense band at 470 nm in addition to higher energy bands.³⁰ The two bands at 381 and 393 nm are analogous to the 370-nm feature in the present complex.

The thin, needle-like, biaxial crystals of $K_7[Mn_2O(CN)_{10}]CN$, when examined under magnification, are strongly pleochroic. When the *E* vector is parallel to the long needle axis, the crystals are colorless, and when *E* is perpendicular to the needle axis, the color varies from orange (β direction) to orange-brown (γ direction). The strong color can be correlated to the structural orientations of the $[Mn_2O(CN)_{10}]^{6-}$ ions by noting that maximum color (absorption) occurs when the electric vector is in the plane of the Mn–O–Mn units. This strong absorption which occurs when the electric vector is parallel to a component of the M–O–M direction appears to be a general feature of transition metal oxo bridged binuclear complexes.²⁶

At room temperature, the observed gram susceptibility of $K_7[Mn_2O(CN)_{10}]CN$ is -0.205×10^{-6} $g^{-1} cm^3$. After applying a diamagnetic correction of -140×10^{-6} , a net paramagnetism of $+71 \times 10^{-6}$ per mole of Mn is obtained, which represents a μ_{eff}/Mn of 0.41 BM. This value represents an upper limit to the paramagnetism, as the impurities which occur with the compound can be paramagnetic manganese compounds. High-spin Mn(III) compounds commonly have magnetic moments of about 4.9 BM when not antiferromagnetically coupled.³¹ Low-spin Mn(III) com-

pounds are few in number, being limited to the salts of $[\text{Mn}(\text{CN})_6]^{3-}$ and $[\text{Mn}(\text{CN})_5\text{OH}]^{3-}$. The magnetic moment of $\text{K}_3\text{Mn}(\text{CN})_6$ at 300°K is 3.50 BM,³² and that of $\text{K}_3\text{Mn}(\text{CN})_5\text{OH}$ is 2.92 BM.³³ These values are far above the upper limit of 0.46 BM found for $\text{K}_7[\text{Mn}_2\text{O}(\text{CN})_{10}]\text{CN}$. The low effective magnetic moment could arise from antiferromagnetic coupling between the manganese atoms. Antiferromagnetic coupling probably occurs in the oxo bridged Mn(III) phthalocyanine complex, which has a room temperature moment of 0.71 BM.¹⁹ A study of the temperature dependence of the susceptibility of the gold-brown compound is obviously needed, but will not be meaningful until extremely high-purity crystalline material is available.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-7910.

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- (15) Our experimental procedure did not include enclosing the crystal in a sealed capillary, as the surface impurities apparently result from the preparative procedure and not from subsequent exposure to the environment.
- (16) We offer the following explanations of the apparent inconsistencies of the observations made by Yakimach¹ and Goldenberg.³ Yakimach's preparation leads to the synthesis of $\text{K}_7[\text{Mn}_2\text{O}(\text{CN})_{10}]\text{CN}$, which was incorrectly formulated as $\text{K}_4\text{Mn}(\text{CN})_6$ and identified as a red crystalline material. In many of our preparations of $\text{K}_7[\text{Mn}_2\text{O}(\text{CN})_{10}]\text{CN}$, we have observed well-formed red crystals of $\text{K}_3\text{Mn}(\text{CN})_6$. Unless careful microscopic observation of the product is employed, the differences between the red crystals and those of $\text{K}_7[\text{Mn}_2\text{O}(\text{CN})_{10}]\text{CN}$ may go undetected. Also, any contact of this mixture of crystals with H_2O will result in the formation of at least MnO_2 and HCN . Goldenberg's initial attempt to repeat Yakimach's work resulted in what he dismissed as MnO_2 . Again, unless careful microscopic examination of the final product is employed, the initial fine crystals of $\text{K}_7[\text{Mn}_2\text{O}(\text{CN})_{10}]\text{CN}$, which in bulk physically resemble a voluminous precipitate of brown, hydrated MnO_2 , may not be identified correctly. Goldenberg's altered formulation also leads to the synthesis of $\text{K}_7[\text{Mn}_2\text{O}(\text{CN})_{10}]\text{CN}$, as does his large scale preparation at low temperatures, which obviously improves the yield. The resulting gold-brown compound, however, was incorrectly identified as $\text{K}_3\text{Mn}_2(\text{CN})_9 \cdot 4\text{KOH}$. As noted earlier, our attempts to establish the formula of $\text{K}_7[\text{Mn}_2\text{O}(\text{CN})_{10}]\text{CN}$ from elemental analyses were unsuccessful. The fact that impurities are so difficult to eliminate most likely accounts for the variation in the reported formulas.
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