Journal of Crystallographic and Spectroscopic Research, Vol. 18, No. 2, 1988

Crystal structure and infrared and electronic spectra of some divalent first series transition metal pentacyanonitrosylmanganates (I)

D. B. SORIA,[1] L. A. GENTIL,[2] and P. J. AYMONINO[3,*]
Programa QUINOR, Quimica Inorgánica, Departamento de Quimica
Facultad de Ciencias Exactas
Universidad Nacional de La Plata
47 Esquina 115, C. C. 962 (1900) La Plata, República Argentina

(Received June 1, 1987)

Abstract

Structural and infrared and electronic spectroscopic studies of the coordination polymers corresponding to the compounds of simplest formulas $M_3^{II}[Mn(CN)_5NO]_2 \cdot nH_2O$ (M = Mn, Co, Ni, Cu, Zn, and n = 8–16) are reported and discussed in comparison with the corresponding nitroprussides. These polymers have a typical face centered cubic unit cell containing $1\frac{1}{3}$ formula units, except for M = Mn where the crystal system is orthorhombic.

Introduction

Beginning with the structural work on Prussian Blue and its analogs performed by Keggin and Miles (1936), a great deal of research has been devoted to coordination polymers containing cyanide ligands as bridging groups. A broad range of compounds having the general composition $M_K^A[M^B(CN)_6]_L \cdot nH_2O$ crystallize in the cubic system (Ludi and Gudel, 1968; Ludi *et al.*, 1970, 1973). Until recently, the structural work performed using x-ray diffraction powder methods was based on the model proposed by Keggin and Miles (1936).

---

[1] Predoctoral fellow of CONICET (Consejo Nacional de Investigaciones Cientificas y Técnicas), República Argentina.
[2] Facultad de Ingenieria, Universidad Nacional de Mar del Plata, República Argentina.
[3] Member of the "Carrera del Investigador Cientifico," CONICET, Republica Argentina.

0277-8068/88/0400-0133$06.00/0

According to it, the polynuclear cyanides with $K = 3$ and $L = 2$ should contain two formula units in the cubic unit cell. However, Ludi and Gudel (1968), based on single crystal studies on $Co_3[Co(CN)_6]_2 \cdot nH_2O$, proposed that the unit cell contains $1\frac{1}{3}$ formula units instead.

Densities predicted by the new model should therefore be distinctly lower than densities corresponding to the Keggin and Miles model as found for $Co_3[Co(CN)_6]_2 \cdot nH_2O$.

The substances studied in this work are also of polymeric nature and have been obtained only as powders due to their extremely low solubilities. These powders show, in general, simple, identical, x-ray diffraction patterns compatible with a cubic face centered unit cell. $Mn_3[Mn(CN)_5NO]_2 \cdot nH_2O$ is an exception because it seems to crystallize in the orthorhombic system. Divalent transition metal nitroprussides are also cubic except the Cu^{2+} salt which seems to be tetragonal (Inoue *et al.*, 1973; Gentil *et al.*, 1976).

The purpose of the present report is to describe the structure and bonding of $M_3^{II}[Mn(CN)_5NO]_2 \cdot nH_2O$ salts on the basis of x-ray diffraction patterns, densities, and infrared and electronic spectra.

Experimental

The compounds of general formula $M_3^{II}[Mn(CN)_5NO]_2 \cdot nH_2O$ were obtained from potassium pentacyanonitrosylmanganate(I) dihydrate which was prepared from potassium hexacyanomanganate(III), hydroxylamine, and potassium cyanide. The compounds were purified according to the published method (Cotton *et al.*, 1959). To aqueous 0.1 M solutions of this salt, 0.1 M solutions of the chlorides or sulfates of first row transition metal divalent cations were slowly added with continuous stirring. The finely divided solids obtained were filtered, washed thoroughly with distilled water, and air dried.

The solid obtained from Fe^{2+} and $[Mn(CN)_5NO]^{3-}$ proved to be extremely sensitive to oxidation, changing color from gray to green. This solid and the product of the reaction between Fe^{2+} and pentacyanonitrosylmanganate(II) will be the subject of a separate report.

Water contents were determined by thermogravimetry, both dynamic (TGA), under flowing nitrogen, and static, by dehydration at 100°C under high vacuum in a drying pistol in the presence of P_4O_{10}.

The x-ray diffraction patterns were recorded with a Philips PW1010 diffractometer using Cu $K\alpha$ radiation.

Densities were determined pycnometrically at 25°C. Considering the zeolitic (labile) character of part of the water content of the compounds, benzene equilibrated with them was first used as the working fluid, and later water and carbon tetrachloride (in equilibrium with the atmosphere) were tried. In all cases the results were the same.

The infrared spectra of the samples between 4000 and 200 cm^{-1} were run in thin KBr disks with a Perkin-Elmer 580B spectrophotometer and attached infrared data station. The anhydrous substances were handled in a glove bag under dry nitrogen.

Electronic reflectance spectra between 300 and 700 nm were obtained with the integrating sphere attachment of a Shimadzu UV-300 Spectrophotometer.

Results and discussion

Hydration water contents, densities, and unit cell constants of the cubic compounds are presented in Table 1. Densities calculated from the two structural models (Keggin and Miles, 1936; Ludi *et al.*, 1973) are also included therein.

It must be pointed out that these sustances and the manganese salt as well show a variable degree of hydration due to the zeolitic nature of part of the water (cf. Ludi *et al.*, 1973).

The x-ray diffraction patterns suggest that these compounds have the f.c.c. unit cell typical of Prussian Blue and its analogs, and the measured densities are in good agreement with the structural model of Ludi *et al.* (1973) belonging to the *Fm3m* space group. In this model, the unit cell of compounds of general formula $M^A_K[M^B(CN)_6]_L \cdot nH_2O$ ($K > L$) is composed of eight small cubes with alternate corners occupied by M^A metal ions and L/K corners by M^B. The CN

Table 1. Hydration degrees, lattice constants, ionic radius, and densities of cubic divalent first series transition metal pentacyanonitrosylmanganates(I)[a]

					d_{calc} (g cm^{-3})	
Compound	n	a (Å)	r_c (Å)[b]	d_{exp} (g cm^{-3})	Ludi and Gudel, 1968, 1973; Ludi *et al.*, 1970	Keggin and Miles (1936)
$Co_3[Mn(CN)_5NO]_2 \cdot nH_2O$	14–16	10.32	0.74	1.73	1.73–1.80	2.59–2.70
$Ni_3[Mn(CN)_5NO]_2 \cdot nH_2O$	14–17	10.24	0.72	1.80	1.76–1.88	2.64–2.83
$Cu_3[Mn(CN)_5NO]_2 \cdot nH_2O$	16–18	10.22	0.69	1.87	1.88–1.94	2.82–2.91
$Zn_3[Mn(CN)_5NO]_2 \cdot nH_2O$	8–9	10.28	0.74	1.64	1.57–1.61	2.36–2.42

[a] For $Mn_3[Mn(CN)_5NO]_2 \cdot nH_2O$ see text
[b] Greenwood, 1968.

groups are situated on the edges of these cubes. Water molecules are of two distinct crystallographic kinds (Herren *et al.*, 1980). Molecules of one type are located in lattice holes due to the anion vacancies and are coordinated to M^A ions. The water molecules of the other type are randomly distributed in the holes of the relatively open crystal framework and behave as zeolitic H_2O.

In the structural model of Keggin and Miles all corners of the small cubes are occupied alternatively by M^A and M^B metal ions, and the $(K-L)$ M^B cations in excess are located inside the small cubes. Hydration water is partly coordinated to these cations and partly has a zeolitic nature.

When $K = L = 1$, there is no alternative and the structure consists of the three-dimensional $\{M^B[M^A(CN)_6]\}$ framework, without voids or cations in excess and with the water molecules located inside the small cubes. Inoue *et al.* (1973) and Gentil *et al.* (1976) have dealt with the nitroprussides of divalent transition metals which have the general formula $M^{II}[Fe(CN)_5NO] \cdot nH_2O$ and shown the expected structural behavior, with the exception of the Cu^{2+} salt which seems to be tetragonal in the hydrated form (Gentil *et al.*, 1976) but cubic when anhydrous.

The thermograms of these nitroprussides suggest that water is lost in a single step, as expected from the identical crystallographic nature of all water molecules. On the contrary, in the present cases, including M = Mn, two DTA features corresponding to water evolution can be detected more or less distinctly as shown by Fig. 1 which shows TGA and DTA results for $Cu_3[Mn(CN)_5NO]_2 \cdot 18H_2O$. The thermograms of the other compounds are similar although the relative heights of the two DTA features are not the same. This fact confirms the existence of two different types of water molecules in these compounds.

The powder x-ray diffraction pattern of $Mn_3[Mn(CN)_5NO]_2 \cdot 8H_2O$ differs from the common pattern shown by the other salts and can be indexed in the orthorhombic system. The cell parameters are $a = 9.85$ Å, $b = 10.2$ Å, $c = 8.22$ Å; and $Z = 1$. The calculated density is 1.40 g cm^{-3} and the observed value is 1.42 g cm^{-3}. It is interesting to note that $Mn[Fe(CN)_5NO] \cdot 2H_2O$ is cubic (Gentil *et al.*, 1976) (see, however, Inoue *et al.*, 1973), while the hexacyanometallates $Mn_3[M(CN)_6]_2 \cdot 8H_2O$ (M = Fe, Ru, Os) are monoclinic (Ludi *et al.*, 1973). Such a diverse behavior of Mn^{2+} has been ascribed to its high spin d^5 configuration and concomitant relatively large ionic radius (Inoue *et al.*, 1973).

Infrared spectra

The infrared spectra of $M_3^{II}[Mn(CN)_5NO]_2 \cdot nH_2O$ compounds are shown in Fig. 2, where the spectrum of $K_3[Mn(CN)_5NO] \cdot 2H_2O$ is also included for comparison. Table 2 gives the wavenumbers and assignments of bands found

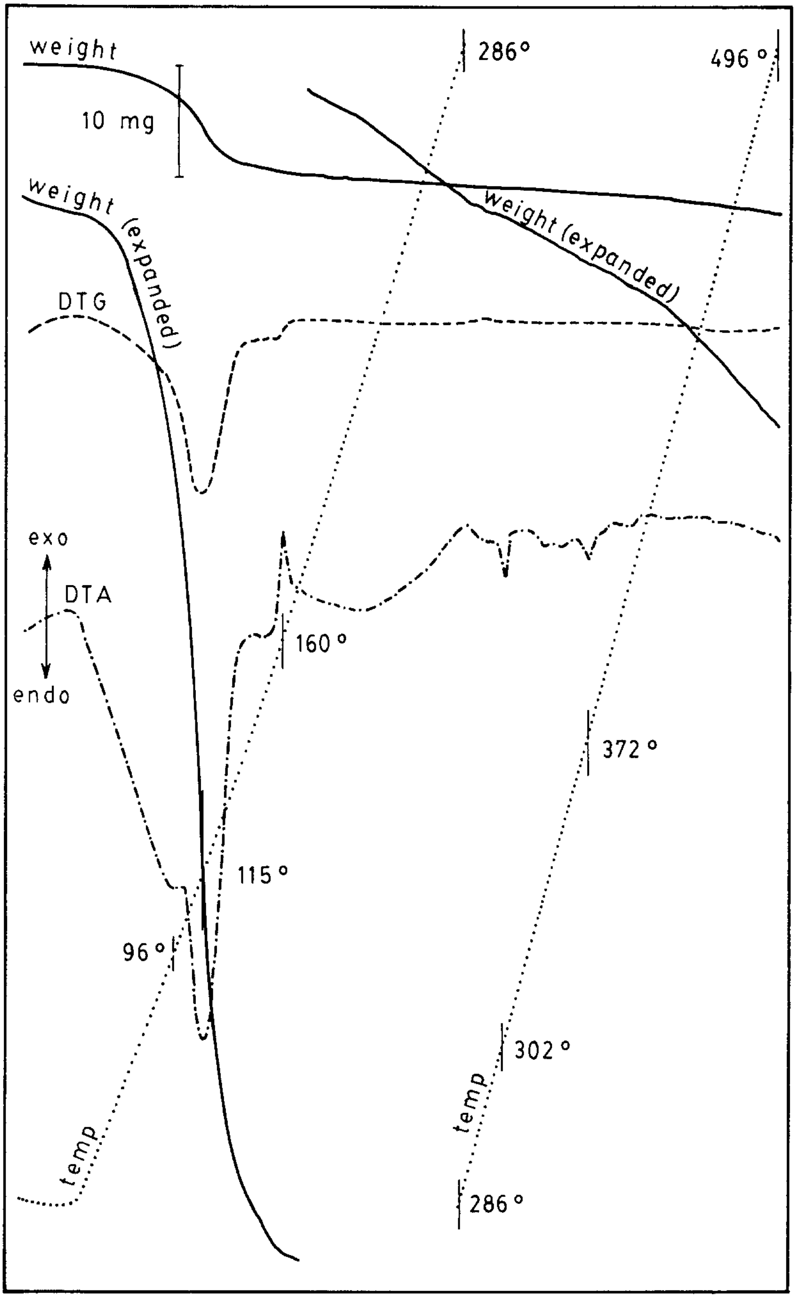

Fig. 1. Thermogram (TGA-DTA) of $Cu_3[Mn(CN)_5NO]_2 \cdot 18H_2O$.

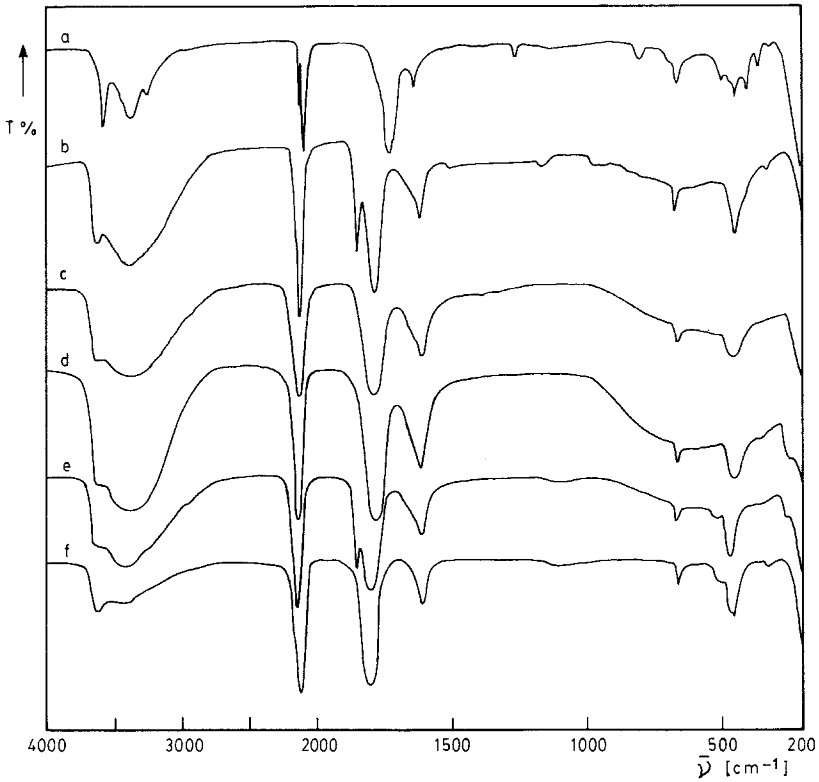

Fig. 2. Infrared spectra of pentacyanonitrosylmanganate(I) salts: (a) K^+; (b) Mn^{2+}; (c) Co^{2+}; (d) Ni^{2+}; (e) Cu^{2+}; (f) Zn^{2+}.

in the room-temperature spectra. It is to be noted that only in the case of the zinc salt was a feature assignable to the M–N stretch found, i.e., a slight shoulder at about 663 cm^{-1}. Cooling of the samples at boiling liquid nitrogen temperature in an RIIC VLT-2 cell did not introduce significant changes in the spectra. They look like type I spectra of M(II) nitroprussides (M = Fe, Co, Ni, Cu) (Gentil *et al.*, 1976). Interestingly, manganese and zinc nitroprusside belong to type II. Recall that there are clear differences between both types of spectra, especially in the water bands (Gentil *et al.*, 1976). These differences are still unexplained. In spite of the unsuccessful attempts to obtain single crystals of some of these nitroprussides (Co, Mn) to get a better insight into their structures, efforts in this direction are continuing.

The anion and water bands are dealt with separately below.

Table 2. Infrared absorption data for hydrated Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} pentacyanonitrosylmanganates(I), including $K_3[Mn(CN)_5NO]\cdot 2H_2O$[a,b]

Compound	νOH	δH_2O	νCN	νNO	δMnNO	δMnCN	νMnC
$Mn_3[Mn(CN)_5NO]_2\cdot nH_2O$	3626(s) 3395(s) 3190(sh)	1658(sh) 1611(m)	2148(m) 2116(s)	1843(m) 1780(s)	666(m)	448(m)	331(w)
$Co_3[Mn(CN)_5NO]_2\cdot nH_2O$	3634(s) 3396(vs) 3210(sh)	1632(sh) 1609(m)	2169(sh) 2125(vs)	1786(vs)	666(m)	459(m)	342(w)
$Ni_3[Mn(CN)_5NO]_2\cdot nH_2O$	3631(s) 3411(vs) 3215(sh)	1642(sh) 1615(m)	2170(sh) 2137(vs)	1780(vs)	666(m)	456(m)	354(w)
$Cu_3[Mn(CN)_5NO]_2\cdot nH_2O$	3625(s) 3442(vs) 3211(sh)	1675(sh) 1606(m)	2176(sh) 2140(vs)	1847(m) 1796(s)	666(m)	466(m)	348(w)
$Zn_3[Mn(CN)_5NO]_2\cdot nH_2O$	3601(vs) 3442(s) 3226(sh)	1634(sh) 1615(m)	2172(sh) 2135(vs)	1804(s)	666(m)	466(m)	340(w)
$K_3[Mn(CN)_5NO]_2\cdot 2H_2O$	3585(vs) (W2) 3572(s) (W1) 3375(sh) (W2) 3351(m) (W1)	1656(w) 1637(m)	2130(s) 2090(vs)	1740(vs) 1730(vs)	670(m) 664(m)	454(m)	318(w)

[a] Soria *et al.*, 1987.

[b] Data in cm^{-1}. vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

Anion bands

Assignments for the anion in Table 2 follow the same line of reasoning given before (Gentil *et al.*, 1976) due to the structural similarity between the $[Mn(CN)_5NO]^{3-}$ and $[Fe(CN)_5NO]^{2-}$ ions (Manoharan and Gray, 1966). The formation of the polymeric transition metal(II) nitroprussides brings about a blue shift of the bands assigned to CN and FeC stretches and FeCN deformations, while the NO and FeN stretches and the FeNO deformation are not affected (Inoue *et al.*, 1973; Gentil *et al.*, 1976). The $M^{II}_3[Mn(CN)_5NO]_2 \cdot nH_2O$ salts show also a blue shift of most of the bands due to the anion, including the NO stretching band which shifts about 40 cm^{-1} in comparison with the potassium salt (Soria *et al.*, 1987). The CN stretch shifts are slightly higher than for nitroprusside. The differences could be due to the higher electron density on the ligands in $[Mn(CN)_5NO]^{3-}$ in comparison with $[Fe(CN)_5NO]^{2-}$ due to the lower formal oxidation state of Mn in comparison with Fe (I vs. II) which allows a greater $M \rightarrow L$ ($d_\pi \rightarrow \pi^*$) charge transfer (Manoharan and Gray, 1966; Fenske and DeKock, 1972; Folkesson, 1974; Wasieleswska, 1986). The formation of M^BCNM^A and M^BNOM^A bridges should therefore affect more the "softer" ligands of $[Mn(CN)_5NO]^{3-}$ than of $[Fe(CN)_5NO]^{2-}$.

The CN stretching wavenumbers in $M^{II}_3[Mn(CN)_5NO]_2 \cdot nH_2O$, from M = Co to Zn, follow the same trend as in the corresponding nitroprussides and reach a maximum for M = Cu. However, for M = Mn the situation is different because $\tilde{\nu}$CN in the nitroprusside is at a maximum while in the pentacyanonitrosylmanganate(I) it is at a minimum. The NO stretch in the pentacyanonitrosylmanganates(I) also parallels the behavior in nitroprussides, including in the Mn^{2+} salt. Surprisingly, νNO for M = Ni presents an anomalous low value. The peculiar behavior of the Cu^{2+} salt among the cubic pentacyanonitrosylmanganates(I) coincides with the fact that it has the smallest unit cell. As mentioned above, $Cu[Fe(CN)_5NO] \cdot 2H_2O$ is tetragonal and one of its unit cell parameters is the lowest found in the transition metal nitroprussides (Gentil *et al.*, 1968, 1976). Also, the smallest cell parameter of $Mn_3[Mn(CN)_5NO]_2 \cdot nH_2O$ ($c = 8.22$ Å) is the shortest for the pentacyanonitrosylmanganates(I). Figure 3 shows graphically correlations between $\tilde{\nu}$CN, $\tilde{\nu}$NO and the cell parameter a for the cubic pentacyanonitrosylmanganates(I).

Water bands

An important result of the neutron diffraction refinement studies performed by Herren *et al.* (1980) is the confirmation of the existence of two crystallographically and chemically distinct kinds of water molecules in Prussian Blue. In one case, the water molecules are coordinated to Fe(III) ions at empty nitrogen sites, and in the other case water molecules are uncoordinated. Part of the latter molecules are isolated, located at the centers of the unit cell octants, and the rest are hydrogen bonded to the coordinated molecules.

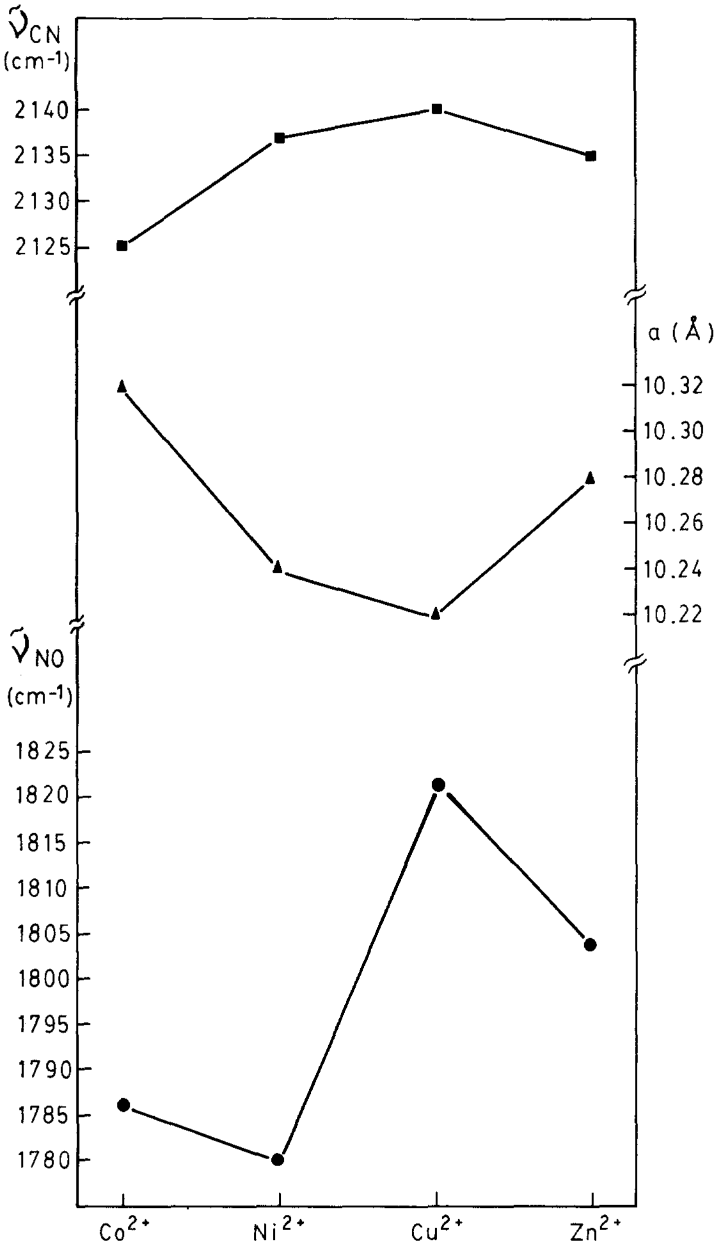

Fig. 3. Correlation between CN and NO stretch wavenumbers and lattice parameter for cubic compounds.

Bands due to the stretches of free and hydrogen-bonded OH groups should be expected therefore in the infrared spectra of the compounds, and this is confirmed by Fig. 2 and Table 2.

For well-known reasons (Falk and Knop, 1973) peaks between 3634 and 3601 cm^{-1} and the broad bands following them, in the region 3442–3396 cm^{-1}, should be assigned to free and hydrogen-bonded OH groups, respectively. Interestingly, the spectrum of the potassium salt shows also similar although narrower main features at slightly lower wavenumbers (3585–3572 and 3375–3351 cm^{-1}) (Soria *et al.*, 1987). In this substance, water molecules seem to be weakly hydrogen bonded to N atoms of CN groups. Also, nitroprussides of group I (Gentil *et al.*, 1976) behave in a similar way because they show their OH bands in the intervals 3653–3644 and 3449–3380 cm^{-1}. The water molecules in those compounds were assumed to be weakly hydrogen bonded to the π electrons of CN and NO groups, although the latter should in fact not be prone to such a bonding if the positive charge assigned to them by Folkesson is correct (Folkesson, 1974). This is precisely not the case for $[Mn(CN)_5NO]^{3-}$ because a negative charge is always assigned to its NO group (Folkesson, 1974; Wasieleswska, 1986).

The H_2O deformation bands in the presently studied compounds are somewhat shifted to lower wavenumbers in comparison with the corresponding bands in the transition metal nitroprussides.

The crystallographic differences between the different types of water molecules contained in the cubic transition metal pentacyanonitrosylmanganates (and by extension in the Mn^{2+} salt) are therefore not big enough to produce a significantly different vibrational behavior. It seems that hydrogen bonding in these compounds is slightly weaker than in the potassium salt.

In the spectra of the anhydrous Ni^{2+} and Co^{2+} salts (see Table 3) the NO stretching bands each split into two peaks of approximately the same intensity. Similar splitting was observed in the group I (Fe^{2+}, Co^{2+}, Ni^{2+}) nitroprussides (Gentil *et al.*, 1976), and it has been suggested that its origin is due to some degree of ordering of the nitroprusside ions and therefore of the NO groupings in the crystal lattice (Gentil *et al.*, 1976; cf. also González *et al.*, 1984). Interestingly, the split bands are shifted toward higher wavenumbers, exactly the opposite behavior observed for the nitroprussides. On the contrary, the CN stretching bands move toward the far infrared, again in the opposite sense as in the nitroprussides (Gentil *et al.*, 1976).

Electronic spectra

The title compounds have a variety of colors, and the electronic spectra show absorptions due to the common anion and to the cations (except Mn^{2+} and Zn^{2+}).

Table 3. Infrared absorption spectra of anhydrous Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} pentacyanonitrosylmanganates(I)[a]

Compound	νCN	νNO	δMnNO	δMnCN	νMnC
$Mn_3[Mn(CN)_5NO]_2$	2154(m)	1836(sh)	666(m)	448(m)	330(w)
	2128(sh)	1800(vs)			
	2110(vs)	1770(sh)			
$Co_3[Mn(CN)_5NO]_2$	2158(s)	1887(s)	663(m)	449(m)	339(w)
	2121(vs)	1787(vs)			
$Ni_3[Mn(CN)_5NO]_2$	2158(s)	1881(s)	660(m)	455(m)	342(w)
	2133(vs)	1796(vs)			
$Cu_3[Mn(CN)_5NO]_2$	2176(sh)	1901(s)	666(m)	467(m)	365(w)
	2139(vs)	1798(vs)			
$Zn_3[Mn(CN)_5NO]_2$	2182(sh)	1845(sh)	666(m)	459(m)	339(w)
	2134(vs)	1807(vs)			
	2026(m)				

[a] Data in cm^{-1}. vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

Distinct color changes occur in the Co^{2+} and Ni^{2+} salts upon dehydration as in the respective nitroprussides, turning in this case from brown to green and violet to brown, respectively.

Table 4 lists data and assignments. The spectrum of the Mn^{2+} salt does not show the very weak $d \rightarrow d$ transition expected for the cation in the visible

Table 4. Electronic reflectance data

Cations	Wavelengths	Assignment to cation[a]
K[a]	405	
	540	
Mn^{2+}	340	[b]
	530	
Co^{2+}(anhydrous)	390	
	560	
	600	$^4T_1(P) \rightarrow {}^4A_2$[c]
Ni^{2+}	370	
	560	
	590	$^3A_{2g} \rightarrow {}^3T_{1g}$
Cu^{2+}	372	
	530	
	560	$^2E_g \rightarrow {}^2T_{2g}$
Zn^{2+}	370	
	520	

[a] The first two bands in each case are assigned to $^1A_1 \rightarrow {}^1A_1$ ($d \rightarrow \pi^*_{NO}$) and $^1A_1 \rightarrow {}^1E$ ($d \rightarrow \pi^*_{NO}$) transitions of the anion, respectively (see text and Manoharan and Gray, 1966).

[b] No band due to the cation was observed (see text and Manoharan and Gray, 1966).

[c] Coordination considered as pseudotetrahedral.

part of the spectrum (Lever, 1984). Figure 4 shows the visible reflectance spectra both of the hydrated and anhydrous Co^{2+} salt. The spectrum of the Zn^{2+} salt is also included to show the anion contribution to the spectra. The spectrum of the hydrated Co^{2+} salt presents two main bands at 400 and 550 nm, approximately, which are assigned to the $^1A_1(2b_2) \rightarrow {}^1A_1(7e)$ and $^1A_1(6e) \rightarrow {}^1E(7e)$ transitions of the anion (cf. Manoharan and Gray, 1966). Also an additional band appears at 580 nm due to a $d \rightarrow d$ transition of the cation located in the pseudooctahedral (mean) environment $N_{10/3}O_{8/3}$. This band corresponds to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition of Co^{2+} in a regular octahedral environment (Lever, 1984). (If the anion were of the $[M(CN)_6]^{3-}$ type, the average coordination around the cations should be N_4O_2 (Ludi and Gudel, 1973) but here we are dealing with $[Mn(CN)_5NO]^{3-}$.)

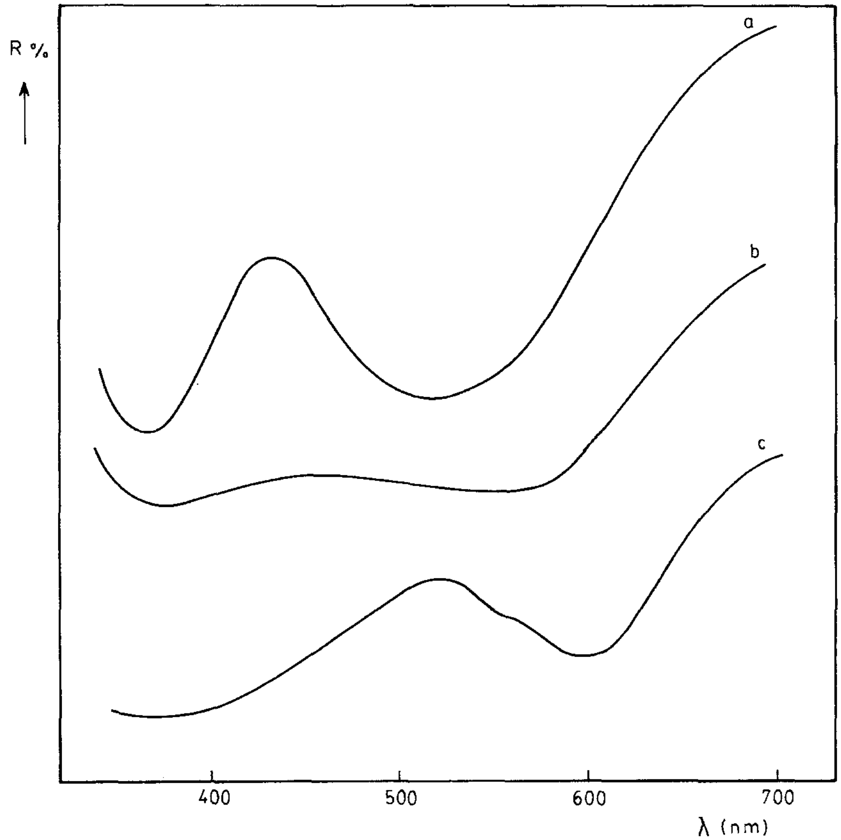

Fig. 4. Electronic reflectance spectra of powdered pentacyanonitrosylmanganate(I) salts: (a) Zn^{2+} (hydrated); (b) Co^{2+} (hydrated); (c) Co^{2+} (anhydrous).

In the anhydrous salt this band shifts to 600 nm due to the reduction in the coordination number of the Co^{2+} ions and perhaps also due to a change of the ligand field strength of the cyanide groups (and perhaps of the NO groups as well) bonded to Co^{2+} through their remote ends.

Interestingly, the salts which show the smallest wavelengths for the ${}^1A_1(2b_2) \rightarrow {}^1E(7e)$ transition of the anion (Cu^{2+} and Zn^{2+}) have the largest wavenumbers for νNO. This is also the case for Mn^{2+}. Dehydration of the Co^{2+} salt brings about, together with the blue shift of the electronic band, also a shift of the IR band in the same direction. As the transitions responsible for these bands involve the NO π^* orbitals, the parallel shifts that they show could be explained by a change in the energy of those orbitals and the concomitant variation in its electronic population (cf. Manoharn and Gray, 1966; Fenske and DeKock, 1972; Wasieleswska, 1986).

Acknowledgements

We express our gratitude to CONICET (Programa QUINOR) and CICPBA, República Argentina, for financial support.

References

Cotton, F., Monchamp, R., Henry, R., and Young, R. (1959) *J. Inorg. Nucl. Chem.* **10,** 28.

Falk, M., and Knop, O. (1973) *Water. A Comprehensive Treatise*, F. Franks, ed. (Plenum Press, New York).

Fenske, R. F., and DeKock, R. L. (1972) *Inorg. Chem.* **11,** 437.

Folkesson, B. (1974) *Acta Chem. Scand. A* **28,** 491.

Gentil, L. A., Baran, E. J., and Aymonino, P. J. (1968) *Z. Naturforsch.* **23,** 1264.

Gentil, L. A., Baran, E. J., and Aymonimo, P. J. (1976) *Inorg. Chim. Acta* **20,** 251.

González, S. R., Aymonino, P. J., and Piro, O. E. (1984) *J. Chem. Phys.* **1,** 625.

Greenwood, N. N. (1968) *Ionic Crystals, Lattice Defects, and Nonstoichiometry* (Butterworths, London).

Herren, F., Fisher, P., Ludi, A., and Halg, W. (1980) *Inorg. Chem.* **19,** 956.

Inoue, H., Iwase, H., and Yanagisawa, S. (1973) *Inorg. Chim. Acta* **7,** 259.

Keggin, K. F., and Miles, F. D. (1936) *Nature (London)* **137,** 577.

Lever, A. B. (1984) *Inorganic Electronic Spectroscopy*, 2nd edn. (Elsevier, Amsterdam).

Ludi, A., and Gudel, H. V. (1968) *Helv. Chim. Acta* **51,** 2006.

Ludi, A., and Gudel, H. V. (1973) *Struct. Bond.* **14,** 1.

Ludi, A., Gudel, H. V., and Ruegg, M. (1970) *Inorg. Chem.* **9,** 2224.

Manoharan, P. T., and Gray, H. B. (1966) *Inorg. Chem.* **5,** 823.

Soria, D. B., Amalvy, J. I., and Aymonino, P. J. (1987) *J. Crystallogr. Spectrosc. Res.* **17,** 139.

Wasieleswska, E. (1986) *Inorg. Chim. Acta* **113,** 115.