Contribution from the Chemistry Department, University of Texas, Austin, Texas 78712
and Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87544

Bonding in Divalent Transition Metal Cyanides. Crystal Structure of Cs$_2$MgFe(CN)$_6$[1]

B. I. SWANSON,* S. I. HAMBURG, and R. R. RYAN

Received December 18, 1973 AIC30905K

Single crystals of the highly insoluble divalent transition metal cyanide Cs$_2$MgFe(CN)$_6$ have been prepared and its crystal structure has been determined. The dicesium magnesium salt, which is isostructural with the trivalent hexacyanides Cs$_2$LiM(CN)$_6$ (M = Cr, Mn, Fe, Co, Ir), crystallizes in the cubic space group *Fm*3*m* with a lattice constant of a = 10.446 (3) Å. The strong Mg–NC interaction present in the Cs$_2$MgFe(CN)$_6$ salt closely parallels the strong M–NC interactions in Prussian Blue compounds. Interestingly, no zeolitic or coordinated water is found in single crystals of Cs$_2$MgFe(CN)$_6$ in contrast to the Prussian Blue complexes. The final R value based on intensities, including all 165 reflections, is 2.8%. Comparison of the Fe(II)–C bond length obtained here with the Fe(III)–C bond length in Cs$_2$LiFe(CN)$_6$ shows a significant shortening in going from Fe(III) to Fe(II). Trends in the M–C bond lengths are used to discuss the changes in M–CN π bonding as a function of the number of d electrons and effective nuclear charge.

Introduction

We have been interested in characterizing the bonding in transition metal cyanides using X-ray crystallographic[2] and vibrational spectroscopic techniques.[3] Structural parameters obtained from X-ray crystallographic studies on the isostructural series Cs$_2$LiM(CN)$_6$ (M = Cr, Mn, Fe, Co, Ir) have been used successfully to probe the M–CN σ and π bonding in trivalent metal cyanides.[2] The encouraging results obtained for the M(III) transition metal cyanides have prompted us to extend these studies to the divalent cyanides. Comparison of M–C bond lengths for the trivalent and divalent cyano complexes should help clarify the role that the metal oxidation state plays in determining M–CN σ and π bonding.

In order to eliminate the possibility of packing differences it is desirable to study salts which are isostructural with the *Fm*3*m* Cs$_2$LiM(CN)$_6$ complexes.[4] The obvious choices are the dicesium magnesium salts, Cs$_2$MgM^{II}(CN)$_6$, since the ionic radii of Mg^{2+} and Li$^+$ are nearly the same.[5] Unfortunately, the Cs$_2$MgFe(CN)$_6$ salt is highly insoluble and single crystals could not be obtained using conventional crystal growth methods.[6] In addition, Kuznetsov, Popova, and Seifer could not obtain the Cs$_2$MgFe(CN)$_6$ free from water.[6] The same problem persists for Prussian Blue salts of the type Cs$_2$M^{II}Fe(CN)$_6$ (M^{II} = Zn, Cd, Mn, Co, Ni, Pb).[7] The strong M^{II}–N bond renders the salt highly insoluble and water cannot be excluded from the lattice during the rapid precipitation.

One possible means of obtaining single crystals of highly insoluble salts is to allow the ions to diffuse together slowly through an appropriate medium. In this regard, the success of Ludi, *et al.*, in obtaining crystals of Prussian Blue compounds is encouraging.[8] It seemed likely that through slow nucleation one might obtain single crystals which were free of lattice water. In order to slow the migration of Mg^{2+} and Fe(CN)$_6$$^{4-}$ ions, we selected a gel diffusion growth method.[9] The present report concerns the preparation of single crystals of Cs$_2$MgFe(CN)$_6$ and the determination of its crystal structure.

Experimental Section

Single crystals of Cs$_2$MgFe(CN)$_6$ were grown by slow diffusion of Mg^{2+} and Fe(CN)$_6$$^{4-}$ ions through silica gel. The gel was prepared from sodium metasilicate at a density of 1.04 g/cm^3 with a 0.05 *M* concentration of CsCl. The silicate CsCl solution was then filtered through a Millipore microfilter (Haup 04700) in order to remove solid contaminants which might act as sites of nucleation. The filtrate was acidified to a pH of 7.0 using 3 *M* HNO$_3$. The silicate solution was then added to a U tube and quickly thermostated in a water bath to 40°. After allowing 2 days for gelation, 10 ml of 0.05 *M* solution of MgCl$_2$ was carefully added to one side of the U tube while 10 ml of 0.05 *M* K$_4$Fe(CN)$_6$ was added to the other side.

Contact between Mg^{2+} and Fe(CN)$_6$$^{4-}$ occurred at *ca.* 2 months as verified by the appearance of a pale yellow band. After 4 months at 40° the band had grown to *ca.* 2 cm and the contents were examined. The gel was separated from the material in the yellow band by repetitive washing in NH$_4$OH solutions. The yellow solid was dried and examined optically. The yellow solid consisted of microcrystals with nearly perfect cubic habit and an edge size of up to 0.040 mm. It should be noted that many different experiments were attempted with variation in the concentrations of the reactants, pH of the gel, gel density, and temperature. The procedure outlined above was the most successful. The sodium metasilicate was obtained as a crystalline solid from Baker. The K$_4$Fe(CN)$_6$ and MgCl$_2$ were also obtained from Baker while the CsCl was obtained from Matheson Coleman and Bell. The purity of the K$_4$Fe(CN)$_6$ was checked by observing the CN stretch region in the infrared spectrum. No evidence was found for Fe(CN)$_6$$^{3-}$.

X-Ray measurements were made on a crystal with the shape of a cube 0.040 mm on an edge. Precession photographs showed the crystals to have extinctions consistent with the cubic space group *Fm*3*m* (and its noncentric analogs). The cell constant as determined by refinement to the setting angles of 12 high-order reflections (measured on an automatic Picker four-circle diffractometer) is 10.446 (3) Å.

Because of the extremely small size of the crystal, an entire hemisphere of data was collected. Pertinent data collection parameters were as follows: takeoff angle 3.5°, graphite monochromator, 2° θ–2θ scans to 70° at 1°/min, 40-sec background counts at each end of the scan, and Mo Kα_1 radiation. Of the 165 reflections so measured (after averaging over the hemisphere) 100 were judged observed according to the criterion $I \geqslant 3\sigma(I)$ where I is the intensity corrected for background and $\sigma(I) = [(T + B) + [0.015(T - B)]^2]^{1/2}$, T being the total count and B the estimated background. Intensities for two standard reflections monitored after every 25 intensity measurements showed no significant change during the data collection process. Absorption corrections were made using the method of

---

* To whom correspondence should be addressed at the University of Texas.

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) B. I. Swanson and R. R. Ryan, *Inorg. Chem.*, 12, 283 (1973); (b) R. R. Ryan and B. I. Swanson, *ibid.*, 13, 1681 (1974).

(3) B. I. Swanson and L. H. Jones, *Inorg. Chem.*, 13, 313 (1974); *J. Chem. Phys.*, 53, 3761 (1970); 55, 4174 (1971).

(4) The structure of K$_4$Fe(CN)$_6$·xH$_2$O has been determined: V. A. Pojpelov and G. S. Zndunov, *Russ. J. Phys. Chem.*, 21, 405, 521, 879 (1947). However, polytypism and twinning obscure the structural parameters.

(5) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, 25, 925 (1969).

(6) U. G. Kuznetsov, Z. V. Popova, and G. B. Seifer, *Zh. Neorg. Khim.*, 15, 2418 (1970).

(7) U. G. Kuznetsov, Z. V. Popova, and G. B. Seifer, *Zh. Neorg. Khim.*, 15, 2105 (1970).

(8) A. Ludi, H. U. Gudel, and M. Ruegg, *Inorg. Chem.*, 9, 2224 (1970); M. Ruegg, A. Ludi, and K. Reider, *ibid.*, 10, 1773 (1971).

(9) See, for example, Z. Blonk, W. Brenner, and Y. O'Kammota, *Mater. Res. Bull.*, 3, 555 (1968).

Table I. Final Least-Squares Parameters for $Cs_2MgFe(CN)_6$ and $Cs_2LiFe(CN)_6$

M		z^a	$\mu_z{}^b$	$\mu_x = \mu_y{}^b$	$\mu_{M'}{}^c$	$\mu_{Cs}{}^c$	$\mu_M{}^c$
Fe(II)	C	0.1820 (7)	0.142 (60)	0.150 (46)	0.106 (36)	0.227 (20)	0.138 (26)
	N	0.2910 (7)	0.144 (65)	0.219 (53)			
Fe(III)	C	0.1822 (3)	0.153 (8)	0.188 (5)	0.167 (12)	0.216 (1)	0.131 (2)
	N	0.2908 (3)	0.153 (8)	0.273 (6)			

[a] C and N atoms are in special position 24e: 0, 0, *z*. [b] Rms amplitude of vibration in Å. M' = Mg for $Cs_2MgFe(CN)_6$ and Li for $Cs_2LiFe(CN)_6$. [c] M', Cs, and M occupy special positions $^1/_2$, $^1/_2$, $^1/_2$; $^1/_4$, $^1/_4$, $^1/_4$; and 0, 0, 0, respectively.

Busing and Levy.[10,11] Transmission factors varied from 0.76 to 0.80.

Wolberg's structure was used as a starting model for full-matrix least-squares refinements.[12] Because of the large number of unobserved reflections, the function minimized was $\Sigma w^2(F_o^2 - KF_c^2)^2$ where $w = 1.0/\sigma(F_o^2)$ and K is a scale constant.[13] All reflections were included in the refinement. Neutral atom scattering factors with appropriate dispersion terms were used.[14] The final R_1 value ($R_1 = \Sigma|F_c^2 - F_o^2|/\Sigma F_o^2$) was 0.028. The final R_1 value for those reflections for which $F_o^2 > 2\sigma(F_o^2)$ is 0.025 and the conventional R value ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) for this population is 0.031. Refinements made including an extinction parameter showed extinction to be unimportant for this problem. The standard deviation for an observation of unit weight was 1.65. The final difference Fourier map showed the usual residuals around the Cs and Fe atoms; peaks elsewhere did not exceed 0.5 e/Å^3. Final parameters are given in Table I.

Discussion

The structure for the $Cs_2MgFe(CN)_6$ salt is the same as that discussed in the preceding article for $Cs_2LiM(CN)_6$. Again, the structure is quite similar to that found in Prussian Blue complexes of the type $M^{II}{}_3[M^{III}(CN)_6]_2 \cdot xH_2O$ with Mg^{2+} replacing the M^{II} atom in the O_h site at ($^1/_2$, $^1/_2$, $^1/_2$).[15] The tetrahedral holes are occupied by Cs atoms in $Cs_2MgFe(CN)_6$ rather than water as is found for Prussian Blue compounds.

The bond lengths observed for $Cs_2MgFe(CN)_6$ are compared with those observed for the Fe(III) salt $Cs_2LiFe(CN)_6$ found earlier (Table II).[2a] The most noticeable change in going from Fe(III) to Fe(II) is the significant decrease in the M-C bond length ($\Delta R_{MC} = -0.026$ (8) Å). It is interesting to compare this M-C bond length change with the change in ionic radii ($\Delta R_{Fe(III)\rightarrow Fe(II)} = +0.060$ Å).[5] Using the arguments developed earlier, a change in ionic radii in going from Fe(III) to Fe(II) provides a measure of the change in M-C σ bonding. The increase in ionic radii of 0.060 Å implies a large decrease in M-C σ bonding which can be expected on the basis of a decrease in the effective nuclear charge. The observed *decrease* in the M-C bond in going from Fe(III) to Fe(II) indicates that the loss of M-C bond order as a result of decreased M-C σ bonding is more than offset by the increase in M-CN π bonding. The combined change (0.086 Å) is a crude measure of the increase in π back-bonding. The combined change in the present case is similar to the total change attributed to M-CN π bonding in going from Cr(III) to Co(III) or from Co(III) to Ir(III). The evidence presented here agrees with the conclusions reached by Jones using intensity data for the F_{1u} symmetry CN stretch.[16]

Table II. Interatomic Distances (Å) for $Cs_2MgFe(CN)_6$ and $Cs_2LiFe(CN)_6$

Atoms	Fe(II)	Fe(III)	ΔR(Fe(III) → Fe(II))
C-N	1.138 (10)	1.148 (5)	−0.010 (11)
Fe-C	1.900 (7)	1.926 (3)	−0.026 (8)
M'-N (M' = Li, Mg)^a	2.182 (7)	2.212 (3)	−0.030 (8)
Cs-N^b	3.720 (1)	3.762 (1)	−0.042 (1)
Cs-C^b	3.758 (1)	3.805 (1)	−0.047 (1)

[a] The Li^+ and Mg^{2+} ions occupy the octahedral site at ($^1/_2$, $^1/_2$, $^1/_2$) and are surrounded by six N atoms. [b] The Cs atom is surrounded by 12 CN groups. The next nearest neighbor to Cs is greater than 5 Å away.

Table III. Changes in Bond Distances Compared to the Infrared Extinction Coefficients[16]

	σ^a	ϵ^b
Cr(III)^{2b}		232
	0.035	
Mn(III)^{2a}		584
	0.020	
Fe(III)^{2a}		1062
	0.015	
Co(III)^{2a}		1748
	0.088	
Ir(III)^{2b}		1920
Fe(III)		1062
	0.086	
Fe(II)		4600

[a] $\sigma = \Delta R_{MC} - \Delta R_I$, where ΔR_{MC} is the change in M-C bond distances and ΔR_I is the change in ionic radii. [b] In mol^{-1} l. cm^{-1}.

This comparison is summarized in Table III. Notice the close parallel between bond distance changes (attributable to π back-bonding) and extinction coefficients among the M(III) transition metal compounds. The comparison going from Fe(III) to Fe(II) is especially striking.

It is interesting to compare the π back-bonding observed here (as measured by the changes in M-C bond length and M^{n+} ionic radii) with that observed in going from Fe(III) to Co(III) (0.015 Å).[2a] As Fe(II) and Co(III) are isoelectronic, we should be able to separate the effect of the number of electrons (6 in both cases) from that of changing the effective nuclear charge. Clearly, there is more increase in M-CN π bonding in going from Fe(III) to Fe(II) than from Fe(III) to Co(III). Therefore, a decrease in effective nuclear charge (Z_{eff}) leads to enhanced M-CN π bonding, as has been suggested by Jones. This is expected, since a decrease in Z_{eff} will result in a destabilization of the metal d orbitals and, consequently, bonding with the π^* level on the CN^- moiety is enhanced (assuming that the metal d orbitals are lower in energy than are the π^* levels in CN^-).[17]

It is generally felt that the carbonyl ligand is a much better π acceptor than the cyanide ligand. Certainly, if one compares $Cr(CO)_6$ with $Cr(CN)_6{}^{3-}$, this is true. However, a more valid comparison would be that of isoelectronic complexes where the number of d electrons and the effective

---

(10) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).

(11) A. C. Larson, D. T. Cromer, and R. B. Roff, Jr., Report LA-3043, Los Alamos Scientific Laboratory, Los Alamos, N. M., 1964.

(12) A. Wolberg, *Acta Crystallogr., Sect. B*, **25**, 161 (1969).

(13) F. L. Hirshfeld and D. Rabinovich, *Acta Crystallogr., Sect A*, **29**, 510 (1973).

(14) "International Tables of X-Ray Crystallography," Vol. 4, Kynoch Press, Birmingham, England, in press.

(15) See, for example, A. Ludi and G. U. Gudel, *Struct. Bonding (Berlin)*, **14**, 1 (1973).

(16) L. H. Jones, *Inorg. Chem.*, **2**, 777 (1963).

(17) H. B. Gray and N. A. Beach, *J. Amer. Chem. Soc.*, **85**, 2922 (1963).

nuclear charge are the same. While it is possible to find cyano complexes and metal carbonyls where the metal electron configurations are the same (for example, $Cr(CO)_6$ and $Co(CN)_6{}^{3-}$), it is difficult to find complexes where the effective nuclear charges are also the same.[18] The work presented here indicates that both effective nuclear charge and numbers of d electrons are important in determining $d\pi$-$p\pi^*$ bonding. The higher $d\pi$-$p\pi^*$ bonding generally observed in carbonyls is not entirely a result of the inherent difference in the π-acceptor strengths of CO and CN^-. This difference results, in part, from differences in the metals of the complexes being compared.[18]

The C-N bond length change in going from Fe(III) to Fe(II) (−0.010 (11) Å) is not statistically significant. In view of the decrease in M-C σ bonding one expects a decrease in the C-N bond order and an *increase* in the C-N bond length. The decrease in C-N bond order is dramatically shown by the decrease in CN stretching frequencies.[19] The failure of X-ray crystallographic measurements to detect changes in C-N bond order (a rather substantial change in this case) is not surprising, as the bond length for a strong bond is generally insensitive to subtle changes in bond order. This simply points to the utility of vibrational data in supplementing structural data to study bonding trends in these compounds.

It is interesting to compare the thermal motion observed in $Cs_2MgFe(CN)_6$ with that found for $Cs_2LiFe(CN)_6$[2a] (the root-mean-square amplitudes of vibration are given in Table I). The Cs hole size is slightly reduced in going from Fe(III) to Fe(II) (see Table II). However, the Cs thermal motion is about the same. The thermal motion of the Cs atom is abnormally large, as was the case in the $Cs_2LiM(CN)_6$ salts. Again, this is a direct result of the large Cs hole size; the combined Cs and N atomic radii are 3.24 Å[20] as compared with a Cs-N distance of 3.72 Å.

There is a substantial decrease in the thermal motion of the C and N atoms perpendicular to the C-N bond. This, coupled with the decrease in the Li → Mg thermal motion, suggests that the strong Mg-N bond is responsible for tying down the CN^- group. The decrease in the M′-N bond lengths (M′ = Li → Mg) is about what is expected from the difference in M′ ionic radii (0.74 Å for Li^+ and 0.72 Å for Mg^{2+}).[5]

One interesting feature of $Cs_2MgFe(CN)_6$ is that, in spite of its high insolubility and tendency to trap lattice water,[6,7] single crystals can be obtained free of zeolitic water. The absence of residuals in the final difference Fourier and the low thermal parameters observed for all of the atoms in $Cs_2MgFe(CN)_6$ virtually rule out the possibility of zeolitic water. Raman and infrared data for $Cs_2MgFe(CN)_6$ support this conclusion.[19]

As was the case in $Cs_2LiM(CN)_6$ where the Li-N bond determined the packing, the Mg-N bond is the dominant interaction holding the lattice together for $Cs_2MgFe(CN)_6$. The insolubility of $Cs_2MgFe(CN)_6$ is no doubt a direct result of the strength of the Mg-N bond. This strong M^{II}-N interaction is the same strong interaction which is present in Prussian Blue type compounds,[8,15] and the $Cs_2M^{II}Fe(CN)_6$ complexes can be considered a model system for the Prussian Blue compounds. The absence of zeolitic water in $Cs_2MgFe(CN)_6$ is encouraging and suggests that $Cs_2MFe(CN)_6$ (M = Mn^{II}, Co^{II}, Cr^{II}, Fe^{II}, Co^{II}, Zn^{II}, etc.) can also be prepared free of water. This is a distinct advantage over normal Prussian Blue complexes (which cannot be obtained free of water) since zeolitic and coordinated water lead to disorder which obscures the bond length information.[8] In addition, the presence of large Cs atoms in the tetrahedral sites precludes the possibility of H_2O filling these sites in the lattice. The $Cs_2MFe(CN)_6$ complexes should yield structures free of zeolitic water, as is the case in the present study, and should be amenable to a detailed study of bonding using X-ray crystallographic methods.

In conclusion, it has been possible to prepare a Prussian Blue model compound free of lattice water.[6] There is a significant decrease in the Fe-C bond length in going from Fe(III) to Fe(II), inferring that the decrease in M-CN σ bonding is offset by a large increase in M-CN π bonding. A comparison of the π bonding increase observed in the series Fe(III) → Fe(II) with that observed for Fe(III) → Co(III) indicates that the effective nuclear charge is more important in determining M-CN π bonding than is the number of d electrons.

Acknowledgment. The aid of Al Larsen and helpful suggestions of Lew Jones are gratefully acknowledged.

Registry No. $Cs_2MgFe(CN)_6$, 19496-94-7.

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 INORG-74-1685.

---

(18) The cyano carbonyls $Mn(CO)_5CN$, $Mn(CO)(CN)_5{}^{4-}$, etc. do provide a series where the effective nuclear charges are similar: R. L. DeKock, A. C. Sarapu, and R. F. Fenske, *Inorg. Chem.*, 10, 38 (1971).

(19) B. I. Swanson, unpublished results.

(20) J. C. Slater, *J. Chem. Phys.*, 41, 3199 (1964).