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 Trivalent Transition Metal Cyanides. Crystal Structures of $Cs_2LiM(CN)_6$ (M = Cr, Ir)[1]

R. R. RYAN and B. I. SWANSON*

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The M(III) transition metal hexacyanides $Cs_2LiM(CN)_6$ (M = Cr, Ir) have been prepared, and their crystal structures determined. Both salts are noncubic at room temperature and undergo a phase change to the cubic space group *Fm*3*m* at high temperatures. The final *R* values, for the high-temperature data, are 2.5 and 2.8% (149 and 179 observed reflections) for Cr(III) and Ir(III), respectively. The unit cell dimensions are a = 10.780 (2) and 10.720 (3) Å for Cr(III) and Ir(III) at 108 and 168°, respectively. Comparison of the data obtained here and those obtained earlier for $Cs_2LiM(CN)_6$ (M = Mn, Fe, Co) salts shows significant M–C bond length decreases in proceeding from Cr(III) to Co(III) and from Ir(III) to Co(III). The results are discussed in terms of trends in the M–CN σ and π bonding as a function of the metal. Trends in the positional and thermal parameters are used to discuss the lattice instability for the Cr(III) and Ir(III) salts.

Introduction

Considerable interest has been focused on characterizing the M–L σ and π bonding in transition metal complexes which contain π-acceptor ligands. The primary goal in these studies has been to define clearly the role of the metal in M–L dπ–pπ* bonding. Infrared and Raman spectroscopy, combined with detailed vibrational analysis, has successfully been used to obtain experimental bonding parameters for simple binary carbonyl[2] and mixed carbonyl-nitrosyl[3] complexes. Vibrational spectroscopic techniques have also been extensively used to study transition metal–cyano complexes.[4] Unfortunately, the ionic nature of cyano complexes precludes the possibility of isolating and sampling these complexes in nonperturbing environments. It is not possible to observe all of the infrared-active fundamentals using aqueous solutions.[5] The strong intermolecular interactions present in crystalline solids are equally troublesome, as they perturb the internal modes of vibration, thereby obscuring the desired intramolecular forces.[6] Vibrational analysis of crystalline solids, where lattice modes and intermolecular interactions are included, shows promise.[7] However, studies of this type have not yet been applied to an isostructural series where the metal atom is varied.

In a recent structural study of $Cs_2LiM(CN)_6$ (M = Mn, Fe, Co)[8] we have been able to observe significant bond length changes which can be correlated with M–CN σ- and π-bonding trends. The $Cs_2LiM(CN)_6$ salts are particularly amenable to a study of this type, since they are isostructural, all crystallizing in the high-symmetry space group *Fm*3*m*. Since they are isostructural, we do not expect differences in crystal packing, which may obscure the discussion of bonding using bonding length comparisons.

Initial efforts extending this study to the Cr(III) and Ir(III) salts were not successful. The Cr(III) salt exhibits very weak tetragonal reflections at room temperature, which are consistent with the noncentric space group $P4_22_12$. Efforts to solve the structure of Cr(III) in the tetragonal phase have not yet been successful. The Ir(III) salt exhibits an *Fm*3*m* diffraction pattern at room temperature. However, a final difference Fourier shows residual electron density around the C and N positions. In addition, the Ir(III) salt is not optically isotropic at room temperature.

Both salts were observed to become optically isotropic at elevated temperatures. Preliminary crystallographic data indicated that at high temperatures, the Cr(III) and Ir(III) salts were isostructural with the manganese, iron, and cobalt analogs. The present study is concerned with the high-temperature structures for $Cs_2LiCr(CN)_6$ and $Cs_2LiIr(CN)_6$.

Experimental Section

The preparation of the dicesium lithium salts has been described earlier.[8] The tripotassium salt $K_3Cr(CN)_6$ was obtained using the usual literature method[9] and $K_3Ir(CN)_6$ was obtained commercially from Automergic Chemetals Co. Crystals were grown at room temperature by slow evaporation of aqueous solutions.

Crystals of both salts were examined optically as a function of temperature using a Zeiss polarizing microscope. The temperature of the crystals was controlled using a Mettler FP2 microthermal apparatus. The Cr(III) compound was observed to become isotropic at *ca.* 75°. Crystals of the Cr(III) salt which were twinned at room temperature were also studied. Interestingly, the room-temperature extinction patterns of twinned crystals were reproduced if the crystals were first heated above the phase change and then cooled to room temperature. This apparent memory persisted even when the crystals were annealed at 300° for 2 hr.

The $Cs_2LiIr(CN)_6$ complex exhibits a rainbow pattern characteristic of a highly twinned (or strained) crystal. The iridium salt was found to become optically isotropic at *ca.* 145°. Neither salt could be supercooled.

Precession photographs (Mo Kα) at room temperature showed the Cr(III) crystal to be tetragonal with systematic absences indicating the space group $P4_22_12$. The Ir(III) salt exhibits cubic diffraction at room temperature with absences indicating the space group *Fm*3*m*. In spite of the fact that none of the crystals were optically isotropic, we were unable to find a crystal of the Ir(III) salt which exhibited *Fm*3*m* forbidden reflections. We were unable to grow a crystal of the Ir(III) salt which was optically isotropic at room temperature either by annealing at high temperatures or by repeatedly going through the phase change. Precession photographs of $Cs_2LiCr(CN)_6$ taken at 80° showed absences consistent with the space group *Fm*3*m*. Long-exposure Precession photographs at this temperature showed no tetragonal reflections.

The Cr(III) and Ir(III) crystals were aligned on an automatic Picker four-circle diffractometer, both at room temperature and at the temperature of interest for data collection (108 and 168°, respec-

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

[1] This work performed under the auspices of the U. S. Atomic Energy Commission.

[2] See, for example, L. H. Jones, R. S. McDowell, and M. Goldblatt, *J. Chem. Phys.*, 48, 2663 (1968); *Inorg. Chem.*, 8, 2349 (1969); L. H. Jones, R. S. McDowell, M. Goldblatt, and B. I. Swanson, *J. Chem. Phys.*, 57, 2050 (1972).

[3] L. H. Jones, R. S. McDowell, and B. I. Swanson, *J. Chem. Phys.*, 58, 3757 (1973).

[4] L. H. Jones, M. N. Memering, and B. I. Swanson, *J. Chem. Phys.*, 54, 4666 (1971), and references therein.

[5] There is also some question about solvent–solute interactions for cyano complexes dissolved in water. Intermolecular interactions in aqueous solutions affect the internal $M(CN)_6^{3-}$ molecular vibrations and there is no way of including such interactions in a normal-mode calculation.

[6] B. I. Swanson and L. H. Jones, *J. Chem. Phys.*, 53, 3761 (1970); *Inorg. Chem.*, 13, 313 (1974).

[7] B. I. Swanson and L. H. Jones, *J. Chem. Phys.*, 55, 4174 (1971).

[8] B. I. Swanson and R. R. Ryan, *Inorg. Chem.*, 12, 283 (1973).

[9] J. H. Bigelow, *Inorg. Syn.*, 2, 203 (1946).

tively). The temperature of the crystal was controlled using a Nonius low-temperature cryostat which has been modified for use on the Picker diffractometer. The temperature (detected using an iron-constantan thermocouple positioned in the N_2 flow at the tip of the nozzle) could be controlled at ±2°. In each case, 12 reflections were centered and their setting angles used in a least-squares refinement of cell parameters and the orientation matrices. No constraints were imposed on the cells in the least-squares refinements. Within the limits of error, the refined cells were found to be consistent with cubic symmetry, with the exception of Cr(III) at room temperature where a tetragonal cell was confirmed. The systematic absences observed using Precession methods were checked by collecting peak height data for the primitive cubic cell out to 25° in 2θ (peak counting for 10 sec, background 2 sec) for Ir(III) and Cr(III) at high temperatures and for Ir(III) at room temperatures. No $Fm3m$ forbidden reflections were observed. During these preliminary studies the crystals were repeatedly taken through the phase change. For the Cr(III) complex it was noted that the unique tetragonal axis was *always* oriented the same when the crystal was allowed to cool to room temperature.

The room-temperature cell constants and their standard deviations for Cr(III) and Ir(III) are $a = 7.600$ (3), $c = 10.778$ (3), and $a = 10.653$ (3) Å, respectively. The high-temperature cell constants and their standard deviations are 10.780 (2) and 10.720 (3) Å for Cr(III) and Ir(III), respectively. It should be noted that the room-temperature tetragonal Cr(III) cell is closely related to the high-temperature cubic cell, both in intensity relationships and cell constants (for the tetragonal cell $\sqrt{2}\,a = 10.748$ Å). Mosaic structures of the crystals were checked by ω and 2θ scans for several reflections at those temperatures where data were collected. Peak widths at half-heights never exceeded 0.3°.

Data were collected for both crystals at temperatures well above their respective phase changes [108° for Cr(III) and 168° for Ir(III)]. One octant of data was collected for each crystal, using Mo Kα radiation, a 3.5° takeoff angle, and a single-crystal graphite monochromator. Data were collected to 70° in 2θ. A symmetric θ-2θ scan (1°/min) range of 2° (plus α_1-α_2 dispersion) was used. The background was counted for 20 sec at each end of the scan range. Of the 183 and 180 reflections measured, totals of 140 and 179 with intensity above 3σ ($I \geqslant 3\sigma(I)$) were observed and used in the structure determinations for Cr (108°) and Ir (168°), respectively. Here I is the intensity after background correction and $\sigma(I) = [(T + B) + (0.015(T - B))^2]^{1/2}$ where T is the total count and B is the estimated background. The intensity of standard reflections, counted after every 25 reflections, showed no significant change during data collection for either of the data sets. The temperature fluctuated by no more than ±2° in either data collection experiment.

Both data sets were corrected for Lorentz and polarization effects, and absorption corrections were made using the Busing and Levy method[10] using Larson, Cromer, and Roof's version of Burnham's program.[11] For the Cr(III) and Ir(III) crystals the calculated transmission factors were in the ranges 0.441-0.376 and 0.152-0.052, respectively.

Refinement of Structures

Wolberg's structure[12] was used as a starting model for full-matrix least-squares refinements. The function minimized was $\Sigma w^2(|F_o| - |F_c^*|)^2$ where w^2 is the weight defined by $1/\sigma^2(F_o)$ and

$$F_c^* = kF_c/\left\{1 + 2g\left(\frac{e^2}{mc^2V}\right)^2 Lp \times \left[\frac{(1 + \cos^2 2\alpha)(\cos^2 2\alpha + \cos^4 2\theta)}{(\cos^2 2\alpha + \cos^2 2\theta)^2}\right]^2 F_c^2\right\}^{1/4}$$

in which k is a scale factor, Lp is the Lorentz-polarization correction, g is the extinction coefficient,[13] and F_c is the structure factor calculated in the usual way.

The structures were refined in the centric space group $Fm3m$ to unweighted R factors of 2.5 and 2.8% for Cr(III) and Ir(III), respectively (here $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$). Extinction coefficients, g, were included in the refinements, and anisotropic temperature parameters were refined for C and N atoms. Neutral atom scattering factors[14] were used for all atoms, and the M and Cs atoms were corrected for anomalous dispersion.[15] The final errors in an observation of unit weight are 2.02 and 3.5 for Cr(III) and Ir(III), respectively.

Final difference-Fourier maps show the usual residuals around the M and Cs atom positions. No significant electron density remained around the C and N atom positions. The final positional parameters, temperature factors, and extinction coefficients are presented in Table I.

Discussion

The structures for the $Cs_2LiM(CN)_6$ salts are quite similar to those found for Prussian Blue complexes.[16] The hexacyanide moiety, $M(CN)_6^{3-}$, occupies a site of O_h symmetry at the origin of the unit cell while the Cs atoms occupy the tetrahedral holes at ($^1/_4$, $^1/_4$, $^1/_4$) and ($^3/_4$, $^3/_4$, $^3/_4$). The Li atom occupies the O_h site at ($^1/_2$, $^1/_2$, $^1/_2$) as does the M(II) atom in $M^{II}_3[M^{III}(CN)_6]_2 \cdot xH_2O$.[16]

The interatomic distances for the Cr(III) and Ir(III) salts are presented in Table II, along with the corresponding values found earlier for the Mn(III), Fe(III), and Co(III) salts.[8] The M-C bond lengths, after correction for thermal motion, are presented in Table III.

The M-C bond lengths show a monotonic decrease in proceeding from Cr through Co and a significant increase in proceeding from Co to Ir. The total M-C change in the series Cr through Co (0.160 (5) Å) is large and significant, as are the successive bond length changes (Cr → Mn, 0.070 (6) Å).[8] The Ir M-C bond length increase compared to Co is also large and significant (0.134 (11) Å).

A comparison of the M-C bond length changes in $Cs_2LiM(CN)_6$ complexes and the M(III) ionic radii is presented in Figure 1.[17] In the series Cr → Co the M-C bond length is seen to decrease nearly twice as much as the M(III) ionic radii ($\Delta R_{MC} = 0.160$ (4) Å, $\Delta R_{M(III)} = 0.090$ Å). Clearly an ionic bonding model, where the bond lengths are predicted from ionic radii, does not provide an adequate description of the bonding in these transition metal cyanides. This disparity between ionic radii and the observed M-C bond lengths is expected, since the ionic radii were obtained from complexes where dπ-pπ^* bonding was not possible.[17]

The comparison which should be made here is that between the M-C bond lengths in cyano complexes (where dπ-pπ^* bonding is important) and the corresponding bond lengths for metal alkyls, where only M←L σ bonding is important. This would provide a means of separating the M-C σ-bonding contribution from that of the M-C π bonding. Unfortunately, accurate structural data for the desired metal alkyls (where the metal is in the +3 formal oxidation state) do not exist.

In the absence of structural data for M-C σ-bonded systems, we have resorted to equating the changes in ionic radii to those M-C bond length changes which would be expected for σ-bonded systems. In cyano complexes where dπ-pπ^* bonding is unimportant (KCN etc.) the cyanide group is considered a pseudohalide. Since the ionic radii are estimated from halides and oxides, it is reasonable to expect that

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Table I. Final Least-Squares Parameters for $Cs_2LiM(CN)_6$

M		z^a	$\mu_z{}^b$	$\mu_x = \mu_y{}^b$	$\mu_{Li}{}^c$	$\mu_{Cs}{}^c$	$\mu_M{}^c$	g
Cr	C	0.1898 (4)	0.180 (5)	0.237 (3)	0.203 (9)	0.263 (1)	0.157 (1)	8 (1) × 10^{-6}
	N	0.2954 (4)	0.174 (5)	0.350 (4)				
Mn	C	0.1853 (3)	0.164 (10)	0.216 (6)	0.145 (16)	0.232 (2)	0.144 (3)	
	N	0.2926 (4)	0.166 (10)	0.327 (8)				
Fe	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)				
Co	C	0.1797 (3)	0.145 (8)	0.165 (4)	0.170 (17)	0.205 (1)	0.121 (2)	
	N	0.2881 (3)	0.145 (8)	0.242 (5)				
Ir	C	0.1868 (10)	0.180 (10)	0.242 (7)	0.26 (3)	0.287 (1)	0.167 (1)	1.6 (2) × 10^{-5}
	N	0.2926 (12)	0.196 (12)	0.341 (11)				

[a] C and N atoms are in special position 24e: 0, 0, z. [b] Rms amplitude of vibration in Å. [c] Li, Cs, and M occupy special positions $^1/_2$, $^1/_2$, $^1/_2$; $^1/_4$, $^1/_4$, $^1/_4$; and 0, 0, 0, respectively.

Table II. Interatomic Distances (Å) for $Cs_2LiM(CN)_6$

	M				
Atoms	Cr	Mn	Fe	Co	Ir
C-N	1.138 (6)	1.145 (6)	1.148 (5)	1.148 (5)	1.134 (16)
M-C	2.046 (4)	1.976 (4)	1.926 (3)	1.886 (3)	2.003 (10)
Li-N	2.206 (4)	2.212 (5)	2.212 (3)	2.213 (3)	2.223 (12)
Cs-N	3.842 (1)	3.798 (1)	3.762 (1)	3.733 (1)	3.817 (1)
Cs-C	3.866 (1)	3.834 (1)	3.805 (1)	3.783 (1)	3.850 (1)

Table III. M-C Bond Lengths (Å) Corrected for Thermal Motion Assuming Rigid-Body Motion for the Octahedron[a]

	M-C		Δ(M-C)	
M	Uncor	Cor	Uncor	Cor
Cr	2.046	2.058		
			0.070	0.071
Mn	1.976	1.987		
			0.050	0.053
Fe	1.926	1.934		
			0.040	0.042
Co	1.886	1.892		
			−0.117	−0.123
Ir	2.003	2.015		

[a] D. W. J. Cruickshank, *Acta Crystallogr.*, 9, 757 (1956).

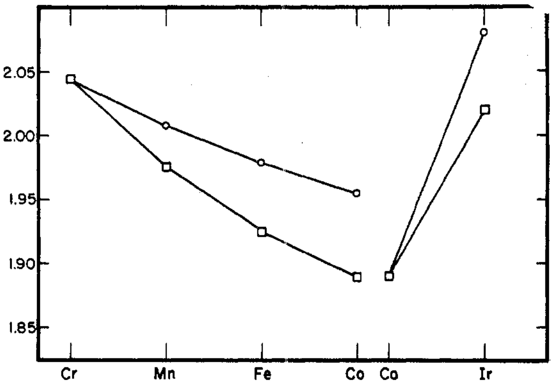

Figure 1. Changes in the scaled M(III) ionic radii[16] (○) and the M(III)-C bond lengths for $Cs_2LiM(CN)_6$ (□) as a function of atomic number. Here the M(III) ionic radii have been scaled to the Cr-C bond length for comparisons in the series and to the Co-C bond length for comparisons in the group.

changes in M-X bond lengths (*i.e.*, the M(III) ionic radii) will provide good estimates of the expected changes resulting from variations in M-CN σ bonding. The major difficulty in such a comparison is the possible synergistic enhancement of the M-C σ bonding as a result of M-CN dπ-pπ* bonding trends within the transition series under discussion. Thus, the correlation of M(III) ionic radii and the M-C bond lengths presented in Figure 1 provides only a crude partition of M-CN σ- and π-bonding effects.

The M-C bond length in the series Cr → Co is changing twice as fast as the M(III) ionic radii. We conclude that changes in the M-CN π bonding (plus, perhaps, some synergistic effects) are occurring about as fast as changes in M-CN σ bonding. The nonlinear changes in M-C bond lengths in the series Cr → Co are interesting. The change in going from Cr to Mn (0.070 (6) Å) is significantly larger than that observed for Fe → Co (0.040 (4) Å).

While the change in M(III) ionic radii is not linear (Figure 1), it does not entirely account for the nonlinear change in M-C bond lengths in going across the series.

The nonlinear change in M-C bond lengths could arise from two sources.

(1) For a *linear* increase in bond order one expects a *smaller decrease* in the bond lengths as the bonds are shortened (assuming a Badger rule type relationship between bond length, d, and force constant, K, $d \propto 1/\sqrt[3]{K}$). This is reflected in the slight nonlinearity of the change in M(III) ionic radii in the series Cr → Co. Interestingly, if the change in M(III) ionic radii in the Cr → Co series is doubled, the change in M-C bond lengths is nearly reproduced.

(2) The nonlinear change in M-C bond lengths may result from a nonlinear increase in dπ-pπ* bonding; that is, dπ-pπ* bonding increases more at the Cr end of the series than at the Co end. This is reasonable since the metal d orbitals will be stabilized as Z_{eff} increases in the series Cr → Co. Since the metal d orbitals are lower in energy than the pπ* levels on the CN^- moiety, an increase in Z_{eff} (a stabilization or decrease in energy of the d orbitals) results in a greater separation of the metal d orbitals and the pπ* level on CN^-. Thus, dπ-pπ* overlap is decreased. In the series Cr → Co the increase in M-C bond order expected from an increase in the number of d electrons may be partially offset by a decrease in dπ-pπ* overlap.

It is not possible to separate these two effects with the present data. However, it is our feeling that both the nonlinear response in bond length as bond order is varied linearly and a possible nonlinear increase in dπ-pπ* as Z_{eff} increases contribute to the observed trends in M-C bond lengths.

Going down the cobalt group the change of ionic radii still reflects the change in M-C bond length for a σ-bonded system. However, the change in ionic radii does not reflect the change in σ-bond strength. However, the difference in M-C bond length and M(III) ionic radii still provides a measure of the effect of changes in M-CN π bonding in the M-C bond length. The increase in M(III) ionic radii in going from Co(III) to Ir(III) (0.205 Å)[18] is substantially larger

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[18] Unfortunately the ionic radius of Ir(III) has not been firmly established, the value quoted being based on analysis of powder pattern intensities.

than the increase in M-C bond length (0.117 (11) Å). If the ionic radius of Ir(III) is to be believed and the assumption that the radius change from Co to Ir reflects the change in σ bonding is valid, then this structure provides evidence for substantial increase in dπ-pπ^* bonding proceeding down the cobalt group. This is reasonable, since the dπ orbitals for Ir(III) are assumed to be closer in energy to the CN$^-$ π^* orbitals than are those of Co(III). Vibrational studies have, however, been interpreted[19,20] in terms of simultaneous increase in both σ- and π-bonding effects for the transition metal cyanides as well as for the carbonyls.[2,3]

The C-N bond lengths for all of the $Cs_2LiM(CN)_6$ complexes are the same within the limits of error. The apparent shortening of the C-N bond lengths for the Cr(III) and Ir(III) salts results from excessive thermal motion of the N atoms. Because of this relative inaccuracy of the CN distance, it is not possible to make a definitive statement concerning trends in C-N bonding. As was stated earlier,[8] the absence of a change in the C-N bond lengths tends to support the suggestion[20] that the M-CN σ- and π-bonding changes have offsetting effects on the C-N bond strength.

The $Cs_2LiM(CN)_6$ structures exhibit high Cs atom thermal motion (the mean-square amplitudes of vibration are given in Table II). In all five structures the Cs atom nearest neighbor distances (Cs-N) are significantly larger than the combined atomic radii (3.24 Å).[21] The Li-N bond lengths, on the other hand, are all comparable to the combined Li and N atomic radii (2.1 Å).[21] Assuming the usual coulombic interaction potential, the large size of the Cs hole results in a weaker Cs^+-CN^- interaction and high Cs thermal motion. This abnormally weak interaction also accounts for the high N thermal motion perpendicular to the Li-N bond. The large Cs hole also results in lattice instability for the cubic phase; as the lattice constant increases, the cubic lattice becomes unstable with respect to movement of the Cs atom and rearrangement of the $M(CN_6)^{3-}$ moieties to reduce the Cs hole size.

In this connection, it is interesting to note the monotonic increase in Cs thermal motion, perpendicular mean amplitudes for N and C atoms, and lattice size in proceeding from Co to Mn (Table I). Since the C-N and Li-N bond lengths do not change, changes in the lattice constant and the Cs hole sizes are determined by the M-C bond length changes. As the M-C bond lengths increase in going from Co to Mn, the Cs hole sizes also increase. At some point between Cr(III) and Mn(III), the holes become too large and the lattice relaxes to the more stable tetragonal phase. Interestingly, the monotonic change in thermal motion does not hold in going from Mn to Cr if the rms amplitudes of vibration observed for $Cs_2LiCr(CN)_6$ at 108° are corrected to room temperature (assuming a classical dependence, $\langle a^2 \rangle = kTC$ where C is the compliance constant[22]). This anomaly is not clearly understood. It is anticipated that the Mn(III) → Co(III) salts will also exhibit phase changes below room temperature.

The $Cs_2LiCr(CN)_6$ $Fm3m \rightarrow P4_22_12$ phase change is intriguing in that the crystal remains single as it goes to the lower symmetry phase and the direction of the tetragonal axis is always the same. Work is under way to characterize these unusual phase changes.

The following conclusions were reached with regard to M-CN σ and π bonding. (1) The M-CN π bonding is increasing at about the same rate as M-CN σ bonding in the series Cr → Co. (2) There is evidence for substantial increase in M-CN π bonding in going down the cobalt group. (3) The M-C bond lengths in the series Cr → Co are changing more rapidly at the Cr(III) end of the series.

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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 INORG-74-1681.

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