Preparation and Structure of Barium Decacyanodicobaltate(II) Tridecahydrate, $Ba_3[Co_2(CN)_{10}]\cdot 13H_2O$. Stereochemical Analysis of the Metal–Metal Bonded $[Co_2(CN)_{10}]^{6-}$ Dimer

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Abstract: The preparation of purple $Ba_3[Co_2(CN)_{10}]\cdot 13H_2O$ (an air-stable salt in striking contrast to the potassium salt) by reaction of an aqueous solution of $Co(NO_3)_2\cdot 6H_2O$ with $Ba(CN)_2$, and its subsequent characterization by single-crystal X-ray diffraction, not only has resolved all doubt regarding the architecture of the heretofore structurally elusive $[Co_2(CN)_{10}]^{6-}$ anion but also has furnished detailed structural parameters for comparison with those of related complexes. This binuclear cobalt anion (of crystallographic site symmetry C_2 relating the two $Co(CN)_5{}^{3-}$ halves to each other) was found to conform ideally to the D_{4d}-$\bar{8}2m$ $Mn_2(CO)_{10}$-type structure stabilized by a Co(II)–Co(II) bond of length 2.798 (2) Å. An unexpected structural feature (which contrasts that in $Mn_2(CO)_{10}$) is the Co–CN(ax) bond length of 1.961 (9) Å being significantly longer by 0.075 Å than the average value of 1.886 (4) Å for the Co–CN(eq) distances which range from 1.876 (8) to 1.896 (8) Å. A comparison of the metal-metal and metal-ligand bond lengths in the $[Co_2(CN)_{10}]^{6-}$ anion with those in the electronically and structurally equivalent $Mn_2(CO)_{10}$ and the $[Co_2(CNCH_3)_{10}]^{4+}$ cation is made, and the differences are rationalized in terms of bonding considerations. The fact that the C–N(ax) bond length of 1.125 (11) Å is 0.04 Å shorter (on the borderline of statistical significance) than the average value of 1.165 (5) Å for the C–N(eq) bond lengths of range 1.159 (9)–1.178 (10) Å is utilized along with the intensity variations of the three infrared-allowed cyanide frequencies to provide a tentative vibrational assignment which is different from the known vibrational assignment of the corresponding infrared carbonyl bands in $Mn_2(CO)_{10}$. $Ba_3[Co_2(CN)_{10}]\cdot 13H_2O$ crystallizes to give a monoclinic unit cell of dimensions a = 9.414 (1) Å, b = 20.831 (4) Å, c = 15.126 (2) Å, β = 93.457 (4)°, and of symmetry $C2/c$. The structural determination and least-squares refinement were based on 1761 independent data ($I > 2\sigma(I)$) collected by counter methods. Although the initial X-ray results indicated the formula as a dodecahydrate, the presence of the 13th water was shown both from complete elemental analysis and from density measurement (*viz.*, ρ_{obsd} = 2.305 (5) g cm^{-3} *vs.* ρ_{calcd} = 2.295 g cm^{-3} for Z = 4) and subsequently substantiated from an anisotropic least-squares model (based on a statistical crystalline disorder of only this crystallographically independent 13th water oxygen atom) which yielded an unweighted R_1 of 3.5% and a weighted R_2 of 5.3%.

The cyanocobalt(II) system in solution has generated widespread interest over a long period of time due to its remarkable catalytic properties in various hydrogenation reactions,[2,3] to its facility in producing scission of small molecules such as H_2,[2-4] Br_2,[5] I_2,[5] H_2O,[6] H_2O_2,[7] $HONH_2$,[7] ICN,[7] and various organic halides,[8,9] and to its unusual ability in forming a variety of bridged complexes, $[(NC)_5Co\text{-}L\text{-}Co(CN)_5]^{6-}$, by coordination with various reagents. Examples of the ligand-bridged species include L being peroxo,[10,11] cyano,[10] Cd(II),[12] Hg(II),[12] Tl(I),[13] $SnCl_2$,[14] SO_2,[14] acetylene,[15] C_2F_4,[16] and p-benzoquinone.[17] Unfortunately, the complexity of this solution chemistry has made it difficult to establish the physiochemical nature and role of the various pentacyanocobalt complexes involved in these reactions. Although optical data show the predominant cobalt(II) cyanide species in solution to be the olive-green $Co(CN)_5{}^{3-}$ monomer, it has been suggested (and not as yet ruled out)[4] that the reactive species involved in the homolytic splitting of molecular hydrogen may not be two $[Co(CN)_5]^{3-}$ monomers but rather the violet $[Co_2(CN)_{10}]^{6-}$ dimer (which is in rapid equilibrium with the monomer).[18,19] From interpretations of the optical and esr spectra of the monomeric $[Co(CN)_5]^{3-}$ anion under a variety of

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[12] H. S. Lim and F. C. Anson, *Inorg. Chem.*, **10**, 103 (1971).

[13] E. C. C. Crouch and J. M. Pratt, *Chem. Commun.*, 1243 (1969).

[14] A. A. Vlček and F. Basolo, *Inorg. Chem.*, **5**, 156 (1966).

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[16] M. J. Mays and G. Wilkinson, *ibid.*, 6629 (1965).

[17] A. A. Vlček and J. Hanzlík, *Inorg. Chem.*, **6**, 2053 (1967).

[18] The recent reactions of aqueous solutions of pentacyanocobaltate(II) with hydrated electrons (generated by pulse radiolysis) led to the detection and characterization of a transient species, pentacyanocobaltate(I), which reacts with water to yield hydridopentacyanocobaltate(III).[19] Since this five-coordinate d^8 $[Co(CN)_5]^{4-}$ anion (which is isoelectronic with $[Mn(CO)_5]^-$, $Fe(CO)_5$, and $[Ni(CN)_5]^{3-}$) is presumed[19] to possess a trigonal-bipyramidal architecture in solution, both its preparation from the square-pyramidal $[Co(CN)_5]^{3-}$ anion and its reaction with water to give the octahedral-like $[Co(CN)_5H]^{3-}$ anion would appear to involve greater geometrical changes than that produced by the reversible transformation between the D_{4d} structure of the $[Co_2(CN)_{10}]^{6-}$ dimer and the two C_{4v} $[Co(CN)_5]^{3-}$ anions.

[19] G. D. Venerable II and J. Halpern, *J. Amer. Chem. Soc.*, **93**, 2176 (1971); G. D. Venerable II, E. J. Hart, and J. Halpern, *ibid.*, **91**, 7538 (1969).

conditions, a ground-state square-pyramidal C_{4v} geometry was proposed for the anion in solution with the unpaired electron placed in an orbital of d_{z^2} symmetry (along the fourfold axis) corresponding to a $^2A_1$ ground state.[20–26]

In 1951 Adamson[27] showed the solid purple complex formed from Co(II) and KCN to have the empirical formula $K_3Co(CN)_5$ rather than $K_4Co(CN)_6$ as previously presumed. Furthermore, the observed diamagnetism of the solid, in contrast to its paramagnetism in aqueous cyanide solution (corresponding to one unpaired electron per cobalt), led Adamson[27] to suggest that pairing of the odd electron per cobalt in the solid state occurs by dimer or polymer formation. From solid-state infrared measurements which showed three strong absorption bands in the terminal cyanide stretching region, Griffith and Wilkinson[28] in 1958 proposed a dimeric structure for the anion analogous to that of the isoelectronic $Mn_2(CO)_{10}$ molecule (whose structure was first reported[29,30] by an X-ray diffraction study in 1957) for which three strong absorption bands (characteristic primarily of terminal carbonyl stretching modes) were also observed. A reinvestigation of the alkali pentacyanocobaltate(II) complexes by Nast and coworkers[31] in 1961 resulted in their isolation of the diamagnetic compounds $K_4H_2[Co_2(CN)_{10}]\cdot 4H_2O$, $K_6[Co_2(CN)_{10}]\cdot 6H_2O$, and $Na_6[Co_2(CN)_{10}]\cdot 4H_2O$.[32] They also suggested from a qualitative analysis of the solid-state infrared spectra that the anion in these compounds has the D_{4d} $Mn_2(CO)_{10}$-type structure.[32] Further spectral evidence for a D_{4d} structure was recently provided from a vibrational study of the $[Co_2(CN)_{10}]^{6-}$ anion as the potassium salt by Griffith and Wickham[33] who, from infrared measurements over a 200–4000-cm^{-1} range and Raman measurements over a 60–2500-cm^{-1} range, showed that the observation of three cyanide stretching frequencies in the Raman spectrum is not inconsistent with the D_{4d} geometry.[34]

Previous attempts by us and others to determine directly (and hence unambiguously) the geometry of the $[Co_2(CN)_{10}]^{6-}$ anion in the solid state (presumed to be the same as that in solution) were unsuccessful primarily because of the lack and instability of suitable single crystals of the potassium and other salts for an X-ray diffraction study. We wish to report here the preparation of a stable alkaline earth hydrated salt of this anion, $Ba_3Co_2(CN)_{10}\cdot 13H_2O$, and its X-ray characterization which provides an important missing link in directly establishing the overall geometry of the anion and in furnishing a unified picture regarding the stereochemical interrelationship between the monomer and dimer in solution. In addition, this work has enabled a comparison of metal–metal and metal–ligand bond lengths of transition metal cyanide complexes with those of the corresponding metal carbonyl and methyl isocyanide complexes and thereby has provided further insight concerning the bonding in these complexes.

Experimental Procedure

Preparation of $Ba_3Co_2(CN)_{10}\cdot 13H_2O$. A nitrogen-degassed solution of $Co(NO_3)_2\cdot 6H_2O$ (7.5 g, 32.7 mmol) in water (*ca.* 125 ml) was slowly added to a 50-ml nitrogen-degassed $Ba(CN)_2$ solution (made by the dissolving of 83 g (438 mmol) of technical $Ba(CN)_2$ in 200 ml of water followed by filtering) at ice-bath temperature. While the green mixture was still near 0°, approximately 50 ml of 95% ethanol was added; the crude crystalline product was filtered under nitrogen, washed with cold alcohol, and dried in a vacuum desiccator. Recrystallization was accomplished by the dissolving of 2 g of crude product in KCN solution (0.5 g of KCN in 40 ml of water) under nitrogen. This solution was immediately sucked into an inverted sintered-glass funnel (used to ensure a minimum of contact with air during the recrystallization process as well as to have the recrystallization proceed from a solution that was fairly free of suspended impurities) and then cooled to ice-bath temperature. This procedure yielded violet needle-shaped crystals.

This compound was initially formulated from the X-ray structural determination as $Ba_3Co_2(CN)_{10}\cdot 12H_2O$. Convincing evidence that the actual formula is $Ba_3Co_2(CN)_{10}\cdot 13H_2O$ not only was established by the following elemental analysis[35] but also substantiated by a comparison of the experimental and calculated densities (*vide infra*) and by a significantly better least-squares refinement of the crystal structure upon inclusion of the 13th water oxygen atom. *Anal.* Calcd for $Ba_3Co_2(CN)_{10}\cdot 13H_2O$ (FW 1024.26): Ba, 40.22; Co, 11.51; C, 11.73; N, 13.67; O, 20.31; H, 2.56. Found:[35] Ba, 40.09; Co, 11.52; C, 11.70, 11.60, 11.65; N, 13.51; O, 20.30, 20.32, 20.25; H, 2.52, 2.50, 2.51. Distinctly poorer agreement is found on the basis of the following formulas. Calcd for $Ba_3Co_2(CN)_{10}\cdot 12H_2O$ (FW 1006.25): Ba, 40.95; Co, 11.71; C, 11.94; N, 13.92; O, 19.08; H, 2.40. Calcd for $Ba_3Co_2(CN)_{10}\cdot 14H_2O$ (FW 1042.28); Ba, 39.53; Co, 11.31; C, 11.52; N, 13.44; O, 21.49; H, 2.71.

Crystal Data and Collection of Intensity Data. Several needle crystals were mounted on glass fibers with epoxy cement and aligned with the needle axis parallel to the spindle axis. Oscillation and Weissenberg photographs exhibited C_{2h}-2/*m* monoclinic symmetry with the b^* symmetry axis (recorded on the zero-level Weissenberg film) perpendicular to the axis of rotation. Owing to an apparent large angular difference between the axis of rotation and its corresponding reciprocal axis, initial attempts to index the upper-level Weissenberg photographs were unsuccessful. This difficulty ultimately was resolved by the utilization of precession photographs to characterize the crystallographic space group symmetry as well as to provide initial lattice parameters. Systematic absences of $\{hkl\}$ with $h + k$ odd and $\{h0l\}$ with l odd indicated the space group to be either *Cc* (C_s^4, No. 9) or *C*2/*c* (C_{2h}^6, No. 15).

For the collection of intensity data a needle crystal of length 0.408 mm and sides 0.145 mm was mounted with the glass fiber perpendicular to the needle axis and coincident with a face diagonal direction such that the unique *b* symmetry axis was parallel to the spindle axis. This crystal was optically aligned about the spindle axis on a General Electric Datex-automated, full-circle diffractometer equipped with a scintillation counter and pulse height analyzer

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(20) J. J. Alexander and H. B. Gray, *J. Amer. Chem. Soc.*, **89**, 3356 (1967).

(21) K. G. Caulton, *Inorg. Chem.*, 7, 392 (1968).

(22) Maher[23] later speculated from additional esr data that there is a possibility that the monomeric anion does not strictly conform to C_{4v} symmetry but rather to C_{2v} symmetry.

(23) J. P. Maher, *J. Chem. Soc. A*, 2918 (1968).

(24) J. M. Pratt and R. J. P. Williams, *ibid.*, 1291 (1967).

(25) The proposal[24] that the green monomeric pentacyanocobaltate(II) anion in aqueous solution is actually a hexacoordinate $[Co(CN)_5(H_2O)]^{3-}$ complex with a water oxygen atom occupying the sixth octahedral site appears as yet not to be unambiguous.[21,26]

(26) J. H. Espenson and J. R. Pipal, *Inorg. Chem.*, 7, 1463 (1968).

(27) A. W. Adamson, *J. Amer. Chem. Soc.*, 73, 5710 (1951).

(28) W. P. Griffith and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 7, 295 (1958).

(29) L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957).

(30) L. F. Dahl and R. E. Rundle, *Acta Crystallogr.*, **16**, 419 (1963).

(31) R. Nast, H. Ruppert-Mesche, and M. Helbig-Neubauer, *Z. Anorg. Allg. Chem.*, **312**, 314 (1961).

(32) The originally presumed potassium salt $K_6[Co_2(CN)_{10}]$,[27] from which the first infrared spectrum (Nujol mull) of the dimeric anion was measured[28] in the 1800–2200-cm^{-1} region, was later reported[31] to be $K_4H_2[Co_2(CN)_{10}]\cdot 4H_2O$.[2] Chadwick and Sharpe[2] mentioned that this latter postassium tetrahydrate salt can be dehydrated over P_2O_5 *in vacuo* at room temperature.

(33) W. P. Griffith and A. J. Wickham, *J. Chem. Soc. A*, 834 (1969).

(34) Although the staggered D_{4d} configuration was assumed to be more likely than the eclipsed D_{4h} one from steric considerations, there is no spectral evidence for this choice over that of D_{4h}.

(35) Meade Microanalytical Laboratory, Amherst, Mass. A single analysis of Ba, Co, and N and triple analyses of C, O, H were carried out on the needle crystals from which sample the particular crystal utilized in the X-ray structural analysis was obtained.

Table I. Positional and Anisotropic Thermal Parameters for $Ba_3Co_2(CN)_{10}\cdot 13H_2O$[a,b]

Atom	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Ba(1)	0	0.0240 (0.3)	$^1/_4$	77 (1)	11 (0.2)	34(0.4)	*c*	18 (0.5)	*c*
Ba(2)	0.2841 (0.5)	0.1805 (0.2)	0.1018 (0.3)	83 (1)	14 (0.2)	26 (0.3)	3 (0.2)	15 (0.3)	2 (0.1)
Co	0.1035 (1)	0.3556 (0.4)	0.3204 (0.6)	47 (1)	11 (0.3)	21 (0.5)	−1 (0.4)	1 (0.6)	−1 (0.3)
C(1)	0.2443 (9)	0.3555 (4)	0.4213 (5)	75 (11)	16 (2)	26 (4)	−2 (4)	5 (6)	1 (2)
N(1)	0.3252 (9)	0.3588 (4)	0.4790 (5)	119 (11)	28 (2)	35 (4)	0.4 (4)	−18 (6)	−0.7 (2)
C(2)	−0.0293 (8)	0.3160 (3)	0.3903 (5)	59 (10)	13 (2)	20 (3)	4 (3)	−6 (5)	−6 (2)
N(2)	−0.1033 (8)	0.2889 (3)	0.4366 (4)	104 (10)	19 (2)	26 (3)	−5 (3)	14 (5)	−1 (2)
C(3)	0.2323 (9)	0.3935 (3)	0.2452 (5)	72 (10)	14 (2)	24 (4)	0.5 (4)	−4 (5)	−6 (2)
N(3)	0.3205 (7)	0.4166 (3)	0.2033 (5)	81 (10)	21 (2)	42 (4)	−12 (4)	17 (5)	−4 (2)
C(4)	0.0413 (8)	0.4386 (4)	0.3515 (5)	62 (11)	19 (2)	32 (4)	−9 (4)	2 (5)	−2 (2)
N(4)	0.0132 (9)	0.4894 (4)	0.3768 (6)	106 (11)	18 (2)	70 (5)	−2 (4)	16 (6)	−11 (3)
C(5)	0.1592 (8)	0.2729 (4)	0.2855 (5)	51 (10)	19 (2)	21 (3)	−9 (4)	4 (4)	3 (2)
N(5)	0.1974 (7)	0.2217 (3)	0.2690 (4)	98 (10)	15 (2)	30 (3)	8 (3)	2 (4)	−3 (2)
O(1)	0.0028 (6)	0.1363 (3)	0.3623 (4)	87 (7)	17 (1)	35 (3)	−3 (3)	−8 (4)	2 (2)
O(2)	0.2884 (6)	0.0740 (3)	0.2262 (4)	91 (8)	19 (1)	57 (4)	0.1 (3)	−9 (4)	4 (2)
O(3)	0.4206 (8)	0.4902 (3)	0.4131 (4)	151 (11)	26 (2)	43 (3)	−9 (3)	13 (5)	4 (2)
O(4)	0.2188 (11)	0.4337 (4)	0.0012 (6)	359 (21)	28 (2)	68 (5)	−17 (5)	79 (8)	−0.9 (3)
O(5)	0.4320 (9)	0.1268 (8)	0.3909 (6)	113 (12)	162 (9)	58 (5)	−38 (8)	17 (6)	−43 (5)
O(6)	0.4074 (12)	0.3075 (5)	0.0872 (11)	231 (18)	61 (4)	298 (17)	−68 (7)	191 (16)	−95 (7)
O(7)[d]	0.2375 (27)	0.0444 (13)	0.3891 (17)	114 (37)	28 (8)	46 (14)	17 (14)	−9 (17)	−12 (8)
O(8)[e]	$^1/_2$	0.2234 (12)	$^1/_4$	14 (21)	42 (8)	217 (29)	*c*	−24 (19)	*c*

[a] The form of the anisotropic temperature factor which is used here is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] The standard deviations in the last significant figure are given in parentheses in this and succeeding tables. [c] For the Ba(1) and O(8) atoms in special positions (4*e*) on twofold axes, β_{12} and β_{23} are required by symmetry to be zero. [d] Corresponds to a crystalline disordered site of the 13th water oxygen atom with an occupancy factor of $^1/_4$. [e] Corresponds to a crystalline disordered site of the 13th water oxygen atom with an occupancy factor of $^1/_2$.

designed to admit 90% of the Zr-filtered Mo Kα radiation. After X-ray alignment, 18 independent reflections were subsequently refined to convergence by the least-squares program ANGSET[36] which furnished cell dimensions $a = 9.414$ (1) Å, $b = 20.831$ (4) Å, $c = 15.126$ (2) Å, and $\beta = 93.457$ (4)°.[37] The volume of the unit cell is 2963.5 Å^3. The experimental density of 2.305 (5) g cm^{-3}, carefully measured by the flotation method, agrees well with the calculated density of 2.295 g cm^{-3} for four $Ba_3Co_2(CN)_{10}\cdot 13H_2O$ species per unit cell.[38] Intensities were collected to a maximum 2θ of 45.0°; the θ–2θ scan technique was utilized with scan speeds of 2°/min and with stationary-crystal–stationary-counter background counts of 15 sec on each side of the peak. The scan width was 1.75° for reflections with $2\theta \leq 10.0$ and 1.50° for the other measured reflections. The formulas used in the data reduction are as follows: $I = S - B(T/t)$, $\sigma(I) = [S + B(T/t)^2 + (0.05I)^2]^{1/2}$, $|F| = (I/Lp)^{1/2}$, and $\sigma(F) = \sigma(I)/2|F|Lp$, where S is the total scan count measured over time T, B the total background count measured over time t, I the integrated intensity, $\sigma(I)$ its standard deviation, and Lp the Lorentz–polarization corrections. The intensities of four standard reflections, sampled throughout the data collection at intervals of every 100 reflections, showed no evidence of either crystal decay or crystal movement. Most of the independent reflections were recorded three times, and none was observed less than twice such that the observed structure factor amplitudes used in the structural determination are a weighted average of at least two observations. From the merged data,[36] 1761 independent reflections for which $I > 2\sigma(I)$ were used in the subsequent structural determination and refinement. Since the transmission coefficients (calculated on the basis of a linear absorption coefficient for Mo Kα radiation of 47.0 cm^{-1}) varied in their extreme range from 0.16 to 0.55, an absorption correction of the intensities was executed[36] prior to the merging of the data.

Determination of the Structure. The solid-state structure of $Ba_3Co_2(CN)_{10}\cdot 13H_2O$ was determined through utilization of the heavy-atom method. On the basis of the presumed formula $Ba_3Co_2(CN)_{10}\cdot xH_2O$ containing an unknown "x" number of molecules, the experimental density indicated for the centrosymmetric space group $C2/c$ that the unit cell contained 12 barium and eight cobalt atoms. An examination of the Harker vectors of a Patterson map[36] yielded interatomic vectors consistent with the 12 Ba^{2+} occupying one eightfold general set of positions (8*f*) and one fourfold special set of positions (4*e*) of crystallographic site symmetry C_2-2. These equivalent positions are as follows: 8*f*, (000; $^1/_2{}^1/_2$0) ± (x, y, z; $\bar{x}$, y, $^1/_2 - z$); 4*e*, (000; $^1/_2{}^1/_2$0) ± (0, y, $^1/_4$).[39] A Fourier synthesis[36] phased on the preliminary Ba^{2+} coordinates revealed the location of a single cobalt atom in the asymmetric part of the unit cell. A series of Fourier syntheses coupled with isotropic least-squares refinement[36] resulted in an R_1 value[40] of 12% for $Ba_3Co_2(CN)_{10}\cdot 8H_2O$ (containing four independent H_2O oxygen atoms occupying eightfold general positions). At this point a Fourier difference map showed only two reasonably sized positive peaks (in the asymmetric unit) which were interpreted as corresponding to two more independent oxygen atoms in general positions. For the resulting formula $Ba_3Co_2(CN)_{10}\cdot 12H_2O$, the R_1 value was lowered to 6.5%. A series of full-matrix, anisotropic least-squares cycles[36] were initiated which refined to convergence at $R_1 = 4.3$ and $R_2 = 7.2\%$.[40–42] Another difference Fourier map showed no positive residuals >1.0 electron/Å^3 except

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(36) (a) A. S. Foust, ANGSET, Ph.D. Thesis (Appendix), University of Wisconsin–Madison, 1970; (b) J. C. Calabrese, SORTMERGE, Ph.D. Thesis (Appendix), University of Wisconsin—Madison, 1971; (c) J. F. Blount, DEAR, an absorption correction program based on a method given by W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 10, 180 (1957); (d) J. F. Blount, "A Three-Dimensional Crystallographic Fourier Summation Program," Ph.D. Thesis (Appendix), University of Wisconsin—Madison, 1965. (e) ORFLSD, a local modification of the program by W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962; (f) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964; (g) D. L. Smith, Ph.D. Thesis (Appendix IV), University of Wisconsin—Madison, 1962.

(37) The uncertainties (given in parentheses) of the lattice parameters obtained from ANGSET are estimates of precision and are unrealistically small on account of the large number of reflections used in the least-squares determination.

(38) The corresponding calculated densities for the assumed formulas $Ba_3[Co_2(CN)_{10}]\cdot 12H_2O$ (2.255 g cm^{-3}) and $Ba_3[Co_2(CN)_{10}]\cdot 14H_2O$ (2.336 g cm^{-3}) do not give as good agreement with the experimental value.

(39) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1965, p 101.

(40) $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100$ and $R_2 = [\Sigma w_i||F_o| - |F_c||^2/\Sigma w_i|F_o|^2]^{1/2} \times 100$. All least-squares refinements were based on the minimization of $\Sigma w_i||F_o| - |F_c||^2$ with the individual weights $w_i = 1/\sigma(F_o)^2$.

(41) Atomic scattering factors used for Co, O, N, and C are from H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964); those of Ba^{2+} are from D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18, 104 (1965). Real and imaginary corrections for anomalous dispersion for Mo Kα radiation were applied in the final least-squares cycles for the Ba^{2+} cations and Co atoms (*i.e.*, $\Delta f' = -0.4$ and $\Delta f'' = 3.0$ for barium; $\Delta f' = 0.4$ and $\Delta f'' = 1.1$ for cobalt).[42]

(42) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1968, p 215.

Table II. Interatomic Distances and Angles

A. Bond Distances (Å) and Angles (deg) for the $Co_2(CN)_{10}^{6-}$ Anion

Co–Co′	2.798 (2)	C(1)–N(1)	1.125 (11)
		C(2)–N(2)	1.163 (9)
Co–C(1)	1.961 (9)	C(3)–N(3)	1.178 (10)
Co–C(2)	1.876 (8)	C(4)–N(4)	1.160 (10)
Co–C(3)	1.886 (8)	C(5)–N(5)	1.159 (9)
Co–C(4)	1.896 (8)		
Co–C(5)	1.884 (8)		
Co′–Co–C(1)	178.4 (2)	C(1)–Co–C(2)	90.2 (3)
Co′–Co–C(2)	88.4 (2)	C(1)–Co–C(3)	92.3 (3)
Co′–Co–C(3)	89.1 (2)	C(1)–Co–C(4)	90.7 (3)
Co′–Co–C(4)	88.7 (2)	C(1)–Co–C(5)	91.8 (3)
Co′–Co–C(5)	88.8 (2)		
Co–C(1)–N(1)	176.4 (8)	C(2)–Co–C(3)	177.2 (3)
Co–C(2)–N(2)	175.0 (7)	C(2)–Co–C(4)	92.0 (3)
Co–C(3)–N(3)	175.0 (7)	C(2)–Co–C(5)	87.8 (3)
Co–C(4)–N(4)	173.6 (8)	C(3)–Co–C(4)	89.3 (3)
Co–C(5)–N(5)	175.9 (7)	C(3)–Co–C(5)	90.8 (3)
		C(4)–Co–C(5)	177.6 (3)

B. Important Nonbonding Interatomic Distances for the $Co_2(CN)_{10}^{6-}$ Anion

C(1)···C(2)	2.718 (11)	C(2)···C(3′)	3.160 (10)
C(1)···C(3)	2.775 (11)	C(3)···C(4)	2.657 (11)
C(1)···C(4)	2.743 (12)	C(3)···C(5)	2.684 (10)
C(1)···C(5)	2.761 (11)	C(3)···C(4′)	3.034 (11)
C(2)···C(5)	2.608 (10)	C(4)···C(4′)	3.122 (16)
C(2)···C(5′)	2.996 (10)	C(5)···C(5′)	3.122 (15)

C. Distances (Å) for Distorted Dodecahedral Geometry about $Ba(1)^{2+}$ and $Ba(2)^{2+}$ Cations

Ba(1)–O(1)	2.890 (6)	Ba(2)–O(4$^{\mathrm{IV}}$)	2.823 (8)
Ba(1)–O(2)	2.950 (6)	Ba(2)–O(5$^{\mathrm{V}}$)	2.894 (9)
Ba(1)–O(3$^{\mathrm{II}}$)[a]	2.714 (6)	Ba(2)–O(6)	2.903 (9)
Ba(1)–N(3$^{\mathrm{II}}$)	2.866 (7)	Ba(2)–N(2$^{\mathrm{I}}$)	2.867 (7)
Ba(2)–O(1$^{\mathrm{I}}$)	2.934 (5)	Ba(2)–N(2$^{\mathrm{VI}}$)	2.845 (6)
Ba(2)–O(2)	2.908 (6)	Ba(2)–N(5)	2.837 (6)

D. Distances (Å) for the Crystalline Disordered 13th H_2O Oxygen Atom about $Ba(1)^{2+}$ and $Ba(2)^{2+}$ Cations

Ba(1)–O(7)	3.006 (26)
Ba(2)–O(8)	3.067 (7)

E. Nonbonding Contacts

(a) The Ten Independent Edges[b] for Distorted Dodecahedron about $Ba(1)^{2+}$

Edge type[c]		
a	O(1)···O(1$^{\mathrm{I}}$)	3.396 (11)
	N(3$^{\mathrm{II}}$)···N(3$^{\mathrm{III}}$)	3.583 (15)
b	O(2)···O(3$^{\mathrm{III}}$)	4.919 (15)
	O(2)···O(3$^{\mathrm{II}}$)	3.295 (10)
m	O(1)···O(3$^{\mathrm{III}}$)	3.244 (8)
	O(2)···N(3$^{\mathrm{II}}$)	3.614 (9)
g	O(1)···O(2)	3.718 (8)
	O(1)···O(2$^{\mathrm{I}}$)	3.248 (9)
	O(3$^{\mathrm{II}}$)···N(3$^{\mathrm{II}}$)	4.242 (12)
	O(3$^{\mathrm{II}}$)···N(3$^{\mathrm{III}}$)	3.450 (9)

(b) The 18 Independent Edges for Distorted Dodecahedron about $Ba(2)^{2+}$

a	O(4$^{\mathrm{IV}}$)···O(2)	3.404 (11)
	O(6)···N(2$^{\mathrm{I}}$)	2.890 (13)
b	O(1$^{\mathrm{I}}$)···N(5)	3.196 (9)
	O(1$^{\mathrm{I}}$)···N(2$^{\mathrm{VI}}$)	5.224 (16)
	O(5$^{\mathrm{I}}$)···N(5)	4.790 (14)
	O(5$^{\mathrm{V}}$)···N(2$^{\mathrm{VI}}$)	3.462 (12)
m	O(1$^{\mathrm{I}}$)···N(2$^{\mathrm{I}}$)	3.536 (8)
	O(5$^{\mathrm{V}}$)···O(6)	4.068 (15)
	O(4$^{\mathrm{IV}}$)···N(2$^{\mathrm{VI}}$)	3.370 (10)
	O(2)···N(5)	3.269 (9)
g	O(4$^{\mathrm{IV}}$)···O(5$^{\mathrm{V}}$)	3.318 (16)
	O(4$^{\mathrm{IV}}$)···O(1$^{\mathrm{I}}$)	3.768 (9)
	O(2)···O(5$^{\mathrm{V}}$)	3.442 (10)
	O(2)···O(1$^{\mathrm{I}}$)	3.248 (9)
	N(2$^{\mathrm{I}}$)···N(2$^{\mathrm{VI}}$)	3.819 (13)
	N(2$^{\mathrm{I}}$)···N(5)	3.477 (9)
	O(6)···N(2$^{\mathrm{VI}}$)	3.035 (13)
	O(6)···N(5)	3.915 (14)

(c) Closest Distances Involving Crystalline Disordered 13th H_2O Oxygen Atom

O(7)···O(1)	2.933 (25)
O(7)···O(2)	2.612 (27)
O(7)···O(5)	2.508 (31)
O(7)···N(1$^{\mathrm{VII}}$)	2.921 (25)
O(7)···N(3$^{\mathrm{II}}$)	3.040 (27)
O(7)···N(4$^{\mathrm{VIII}}$)	2.854 (24)
O(7)···O(4$^{\mathrm{II}}$)	2.878 (30)
O(8)···O(5)	3.028 (21)
O(8)···O(6)	3.105 (22)
O(8)···N(5)	2.880 (7)

(d) Other Nonbonding Distances

N(1)···O(1$^{\mathrm{VII}}$)	2.815 (10)
N(1)···O(6$^{\mathrm{V}}$)	2.964 (12)
N(1)···O(3)	3.065 (10)
N(2)···O(6$^{\mathrm{IX}}$)	3.035 (13)
N(3)···O(6)	3.016 (11)
N(4)···O(2$^{\mathrm{X}}$)	3.062 (10)
N(4)···O(4$^{\mathrm{XI}}$)	3.048 (14)
N(4)···O(5$^{\mathrm{XII}}$)	2.973 (17)
N(5)···O(1)	2.971 (8)
O(2)···O(5)	2.973 (11)
O(3)···O(4$^{\mathrm{XI}}$)	2.846 (10)
O(3)···O(3$^{\mathrm{XIII}}$)	2.973 (14)

[a] The superscripts refer to the following symmetry operations: (I) $\bar{x}, y, {}^1/_2 - z$; (II) ${}^1/_2 - x, y - {}^1/_2, {}^1/_2 - z$; (III) $x - {}^1/_2, y - {}^1/_2, z$; (IV) ${}^1/_2 - x, {}^1/_2 - y, \bar{z}$; (V) $1 - x, y, {}^1/_2 - z$; (VI) ${}^1/_2 + x, {}^1/_2 - y, z - {}^1/_2$; (VII) ${}^1/_2 - x, {}^1/_2 - y, 1 - z$; (VIII) ${}^1/_2 + x, y - {}^1/_2, z$; (IX) $x - {}^1/_2, {}^1/_2 - y, {}^1/_2 + z$; (X) ${}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$; (XI) $x, 1 - y, {}^1/_2 + z$; (XII) $x - {}^1/_2, {}^1/_2 + y, z$; (XIII) $1 - x, 1 - y, 1 - z$. [b] Only ten of the 18 edges of the distorted dodecahedron about $Ba(1)^{2+}$ are independent due to the C_2-2 crystallographic site symmetry. [c] The nomenclature corresponding to the four types of edges (*viz.*, *a*(2), *b*(4), *m*(4), *g*(8)) possessed by a regular D_{2d}-$\bar{4}2m$ dodecahedron is given by J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963). The nonequivalent distances for a given edge type indicate a large distortion from a regular D_{2d} geometry.

for one peak of 1.5 electrons/Å^3 lying on a twofold axis at 0, 0.222, $^1/_4$ and another one of 1.1 electrons/Å^3 located at 0.233, 0.043, 0.393. It is noteworthy that an interpretation of these peaks as possible water oxygen atoms (with assumed occupancy factors of 1.0) results in the formula $Ba_3Co_2(CN)_{10}\cdot 15H_2O$ with $Z = 4$. Since the above coordinates for both of these two peaks are compatible as possible water oxygen atoms in giving rise to reasonable distances to the other atoms, least-squares refinement of both of these peaks as possible oxygen atoms (with assumed complete occupancy) was carried out. Inordinately high isotropic temperature factors of 17 and 38 Å^2 were obtained after three cycles (based on full occupancy of the sites) compared with the much lower isotropic thermal values ranging from 3 to 8 Å^2 (resulting from the previous refinement before conversion from isotropic to anisotropic thermal parameters) for the other six independent water oxygen atoms; hence, it was concluded that full occupancy of both independent sites (corresponding to $x = 15$) provided too much scattering power which necessitated thermal damping. In light of the actual stoichiometry of $x = 13$ based on both the elemental analysis and density measurements, further refinement was performed for the model in which the 13th water oxygen atom was assumed to occupy completely only the fourfold special set (4*e*) of positions (which corresponded to the smaller of the above two isotropic thermal parameters). This model, which utilized aniso-

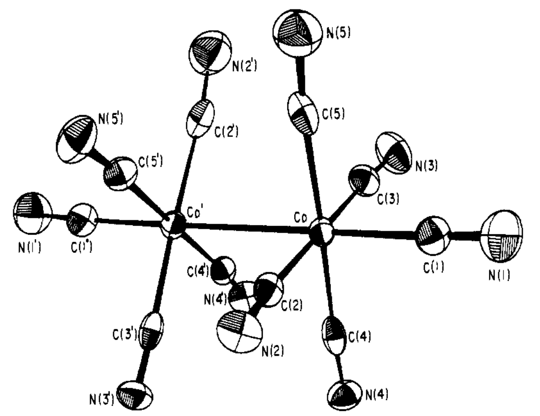

Figure 1. The 50% probability thermal ellipsoids of the $[Co_2(CN)_{10}]^{6-}$ anion which has idealized D_{4d}-$\bar{8}2m$ geometry and crystallographic C_2-2 site symmetry.

tropic thermal parameters for all atoms except initially for the 13th oxygen one, was not deemed satisfactory since the oxygen's isotropic temperature factor decreased only slightly to a still unreasonably high value of 16 Å^2. Upon conversion of it to anisotropic thermal parameters the refinement lowered R_1 to 4.0% and R_2 to 6.1%. However, refinement of a second model based on a statistical crystalline disorder with this 13th water oxygen atom distributed in both positions (with occupancy factors of $^1/_4$ on the eightfold general positions and $^1/_2$ on the fourfold special positions) not only gave reasonable isotropic thermal values of 8 Å^2 for both positions but also after conversion to anisotropic thermal parameters yielded still lower R_1 and R_2 values of 3.5 and 5.3%, respectively, at convergence. Since the R_1 factor ratio for the second model *vs.* the first one is considered significant at the 0.5% level,[43] this second model is assumed to correspond most nearly to the actual situation. This last refinement resulted in a lowering of the esd's of the atomic parameters to values of approximately two-thirds those of the previous esd's based on the initial refinement with $x = 12$.[40,41] A detailed comparison of the initial refinement ($x = 12$) and final refinement ($x = 13$) showed no significant changes in the corresponding atomic coordinates (*i.e.*, <2 esd's). No attempt was made to locate any water hydrogen atoms.

The atomic parameters obtained from the output of the last cycle are listed in Table I.[44] Interatomic distances and bond angles with esd's computed from the full inverse least-squares matrix (which included the uncertainties in the lattice parameters)[36] are presented in Table II. Equations of "best" least-squares planes formed by sets of specified atoms along with the perpendicular distances of these and other atoms from these planes are given in Table III together with appropriate dihedral angles between the normals of these planes.[36]

Results and Discussion

General Description of the Structure. The crystal structure is composed of discrete $[Co_2(CN)_{10}]^{6-}$ anions together with Ba^{2+} cations surrounded by water molecules and cyanide nitrogen atoms. As anticipated, each dimeric anion, located on a crystallographic twofold axis perpendicular to the Co–Co axis, may be considered to ideally conform to a D_{4d}-$\bar{8}2m$ geometry with the two sets of equatorial cyanide ligands in a staggered array (Figure 1). The orientations of the 12 Ba^{2+} cations, four $[Co_2(CN)_{10}]^{6-}$ anions, and 52 water molecules in the monoclinic cell are shown in Figures 2 and 3.

Table III. Equations of Least-Squares Planes, Perpendicular Distances (Å) of Selected Atoms from these Planes, and Dihedral Angles between Normals of Planes[a]

(a) Plane I through C(2), C(3), C(4), and C(5)			
$-0.6456X + 0.0016Y - 0.7637Z + 4.0819 = 0$			
C(2)	+0.000	N(2)	−0.06
C(3)	+0.000	N(3)	−0.08
C(4)	−0.000	N(4)	−0.11
C(5)	−0.000	N(5)	−0.05
Co	−0.041	C(1)	−2.00
(b) Plane II through Co, Co′, C(1), C(2), and C(3)			
$0.3284X - 0.9032Y - 0.2764Z + 7.7993 = 0$			
Co	−0.004	C(1′)	−0.00
Co′	−0.014	N(1′)	−0.05
C(1)	−0.019	N(1)	−0.09
C(2)	+0.018	N(2)	+0.09
C(3)	+0.018	N(3)	+0.04
(c) Plane III through Co, Co′, C(1), C(4), and C(5)			
$0.6999X + 0.4068Y - 0.5871Z + 0.6380 = 0$			
Co	+0.012	C(1′)	+0.02
Co′	−0.014	N(1′)	+0.06
C(1)	−0.019	N(1)	−0.01
C(4)	+0.010	N(4)	+0.02
C(5)	+0.010	N(5)	−0.02
(d) Plane IV through Co, Co′, C(1′), C(2′), and C(3′)			
$0.3284X + 0.9032Y - 0.2764Z - 5.5630 = 0$			
Co	+0.014	C(1)	−0.00
Co′	+0.004	N(1)	+0.05
C(1′)	+0.019	N(1′)	+0.09
C(2′)	−0.018	N(2′)	−0.09
C(3′)	−0.018	N(3′)	−0.04
(c) Plane V through Co, Co′, C(1′), C(4′), and C(5′)			
$0.6999X - 0.4068Y - 0.5871Z + 5.3894 = 0$			
Co	+0.014	C(1)	−0.02
Co′	−0.012	N(1)	−0.06
C(1′)	+0.019	N(1′)	+0.01
C(4′)	−0.010	N(4′)	−0.01
C(5′)	−0.010	N(5′)	+0.02

Dihedral Angles (deg) between Planes	
Plane II and plane IV	50.8
Plane II and plane V	40.6
Plane III and plane IV	40.6
Plane III and plane V	48.0

[a] The equations of the planes and distances were obtained from the Smith plane program.[36] The equation of the plane is expressed in orthogonal coordinates X, Y, Z, which are related to the crystallographic fractional coordinates x, y, z, by the transformations $X = ax + cz\cos\beta$, $Y = by$, $Z = cz\sin\beta$. Unit weights were used in the calculation of the planes.

The existence of analogous binuclear metal complexes also stabilized by only electron-pair metal–metal bonds has been established directly from X-ray studies for the electronically equivalent $[Co_2(CNCH_3)_{10}]^{4+}$ cation,[45] the $[M_2(CO)_{10}]^{2-}$ (M = Cr, Mo) anions,[46] $M_2(CO)_{10}$ (M = Mn,[30] Tc,[47] Re[29]), $Mn_2(CO)_8(PR_3)_2$ (where for the axial PR_3 ligands R = F,[48] C_2H_5[49]), and $Rh_2(DMG)_4(P(C_6H_5)_3)_2$[50] and has been shown indirectly from infrared measurements for the $[W_2(CO)_{10}]^{2-}$ anion,[51] $MnRe(CO)_{10}$,[52] $[MM'(CO)_{10}]^-$ (M = Mn, Re; M′

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(43) W. C. Hamilton, "Statistics in Physical Science," Ronald Press, New York, N. Y., 1964, p 159.

(44) A listing of the structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St. N.W., Washington, D. C. 20036, by referring to code number JACS-72-7654. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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(52) N. Flitcroft, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **3**, 1123 (1964).

Table IV. Comparison of Mean Geometrical Parameters for Electronically Equivalent $M_2(CX)_{10}$ Species

Distances, Å	$[Co_2(CN)_{10}]^{6-}$ (this work)	$[Co_2(CNCH_3)_{10}]^{4+}$ (ref 45)	$Mn_2(CO)_{10}$ (ref 30)	$[Cr_2(CO)_{10}]^{2-}$ (ref 46)	$Tc_2(CO)_{10}$ (ref 47)	$[Mo_2(CO)_{10}]^{2-}$ (ref 46)
M–M	2.798 (2)	2.736 (10)	2.923 (3)	2.97 (1)	3.036 (6)	3.123 (7)
M–C(ax)	1.961 (9)	1.92 (4)	1.792 (14)	1.84 (5)	1.899 (11)	1.90 (5)
M–C(eq)	1.886 (4)	1.87 (3)	1.835 (7)	1.87 (2)	1.995 (6)	1.90 (2)
C(ax)–X(ax)	1.125 (11)	1.15 (6)	1.151 (14)	1.12 (4)	1.205 (13)	1.18 (5)
C(eq)–X(eq)	1.165 (5)	1.16 (4)	1.157 (8)	1.16 (2)	1.121 (8)	1.21 (2)
Bond angles, deg						
C(ax)–M–C(eq)	91.2 (2)	92.3 (6)	93.8 (4)	93 (1)	93.8 (4)	94 (1)
C(eq)–M–C(eq)	90.0 (2)	89.9 (6)	89.8 (4)	86 (1)	89.8 (3)	86 (1)
C(eq)–M–M	88.8 (1)	87.8 (5)	86.2 (2)	87 (1)	86.2 (2)	86 (1)

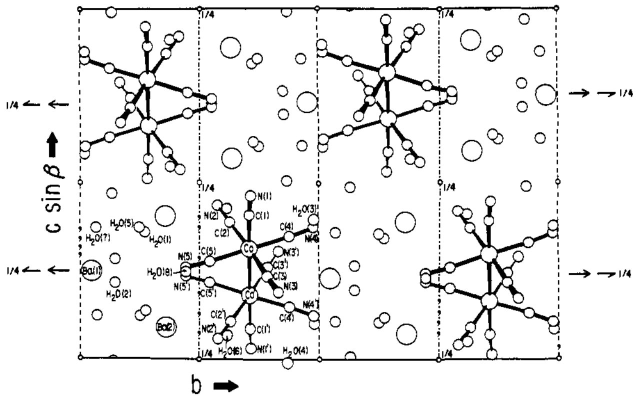

Figure 2. [100] projection of the monoclinic unit cell of symmetry $C2/c$ containing four $Ba_3[Co_2(CN)_{10}]\cdot 13H_2O$ formula species.

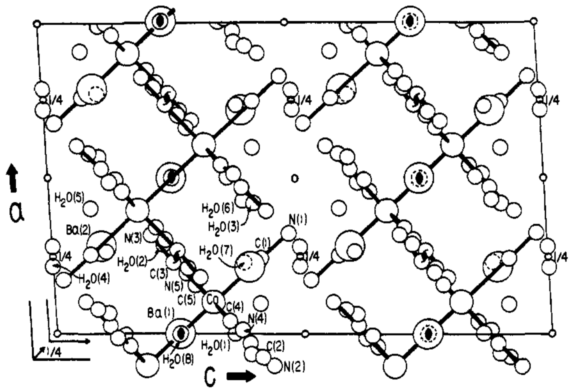

Figure 3. [010] projection showing each of the four $[Co_2(CN)_{10}]^{6-}$ anions and four $Ba(1)^{2+}$ cations per cell lying on a crystallographic twofold axis. The eight $Ba(2)^{2+}$ cations per cell are located in general eightfold positions of $C2/c$.

= Cr, Mo, W),[53] $Mn_2(CO)_8(PR_3)_2$ (where R = C_6H_5, OC_6H_5, p-C_6H_4F, C_2H_5),[54] $Mn_2(CO)_8(As(C_6H_5)_3)_2$,[54] the $[Mn_2(CO)_8X_2]^{2-}$ (X = Cl, Br, I) anions,[55] the $[Re_2(CO)_8I_2]^{2-}$ anion,[56] $Fe_2(CO)_8I_2$,[57] and $Ru_2(CO)_8(SiR_3)_2$.[58] For comparison the structural parameters of several of these complexes are listed in Table IV.

The $[Co_2(CN)_{10}]^{6-}$ Anion. (a) Comparison of Metal–Metal Bond with Those of $Mn_2(CO)_{10}$ and the $[Co_2(CNCH_3)_{10}]^{4+}$ Cation. There are marked departures from D_{4d} geometry in the $[Co_2(CN)_{10}]^{6-}$ anion. The observed dihedral angles (Table III) between planes each formed by the two cobalt atoms, two equatorial carbon atoms, and the axial carbon atom average either 40.6 (4) or 49.4 (4)° compared with an exact value of 45° for strict D_{4d} symmetry. These distortions, which can be rationalized by a torsional rotation of the two $Co(CN)_5{}^{3-}$ moieties about the Co–Co′ bond, may be attributed to crystal packing effects. Nevertheless, the overall geometry of the $[Co_2(CN)_{10}]^{6-}$ anion closely parallels that of $Mn_2(CO)_{10}$. There is an analogous but yet smaller bending of the equatorial (eq) cyanide ligands toward the other half of the anion with the mean Co′–Co–CN(eq) bond angle of 88.8 (2)° nearer 90° than the mean Mn′–Mn–CO(eq) bond angle of 86.2 (2)° in $Mn_2(CO)_{10}$. Consequently, the cobalt atom is perpendicularly displaced by only 0.041 Å out of the mean plane of the four equatorial cyanide carbon atoms in the axial cyanide direction compared to a larger corresponding perpendicular displacement of 0.12 Å for the manganese atom out of the mean plane of the four equatorial carbonyl carbon atoms.[59–61] The minimum C···C contact distance between the two halves of the $[Co_2(CN)_{10}]^{6-}$ anion is 3.00 Å which is the same value obtained in $Mn_2(CO)_{10}$.

The most important structural feature obtained from this X-ray investigation is the Co(II)–Co(II) distance of 2.798 (2) Å. This electron-pair bond length is appreciably shorter than the Mn(0)–Mn(0) bond length of 2.923 (3) Å in $Mn_2(CO)_{10}$ but is significantly longer than the Co(II)–Co(II) bond length of 2.736 (10) Å found[45] in the $[Co_2(CNCH_3)_{10}]^{4+}$ cation of the perchlorate salt.

The smaller metal–metal single-bond distance for the $[Co_2(CNCH_3)_{10}]^{4+}$ cation compared with that for $Mn_2(CO)_{10}$ was attributed by Cotton and coworkers[45] mainly to the smaller size of a Co(II) relative to that of an isoelectronic Mn(0). The decrease of 0.2 Å in the metal–metal distance between $Mn_2(CO)_{10}$ and the $[Co_2(CNCH_3)_{10}]^{4+}$ cation (corresponding to a difference in metal radius of 0.1 Å) is compatible with the metal–

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(57) F. A. Cotton and B. F. G. Johnson, *ibid.*, 6, 2113 (1967).

(58) S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. A*, 2559 (1969).

(59) SCCC calculations by Brown and coworkers[60] recently have indicated that a significant cross-interaction occurs in $Mn_2(CO)_{10}$ between one Mn atom and the equatorial carbonyl ligands coordinated to the other Mn atom and that this cross-interaction is an important factor in the stabilization of the dimer. Similarly, an approximate but nonparameterized MO calculation by Hall and Fenske[61] has indicated in the $M(CO)_{6-x}L_x$ complexes (M = Cr, Mn, Fe; L = Cl, Br, I; x = 1, 2) that the direct donation of electron density from the halogen's σ orbital to the cis carbonyl's π^* orbital is the most important mechanism by which a change in the halogen affects a change in the carbonyl force constant.

(60) D. A. Brown, W. J. Chambers, N. J. Fitzpatrick, and R. M. Rawlinson, *J. Chem. Soc. A*, 720 (1971).

(61) M. B. Hall and R. F. Fenske, *Inorg. Chem.*, 11, 1619 (1972).

metal bond length changes in other analogous dinuclear managanese and cobalt complexes.[62,63] The similar Co–Hg bond lengths in $Hg[Co(CO)_4]_2$ (2.498 (7) and 2.500 (7) Å)[64] and $Hg[Co(CO)_3P(C_2H_5)_3]_2$ (2.499 (5) Å)[65] are 0.11 Å shorter than the Mn–Hg bond length in $Hg[Mn(CO)_5]_2$ (2.610 (2) Å).[66] Furthermore, the presumed Co–Co bond length of 2.66 (1) Å[67–69] in the nonbridged form of $Co_2(CO)_8$ is 0.26 Å shorter than the Mn–Mn bond length in $Mn_2(CO)_{10}$, which leads to a smaller metallic radius for cobalt of 0.13 Å. These data all substantiate the expectation that (even with the neglect of steric effects) the greater nuclear charge of the cobalt atom relative to that of the manganese atom gives rise to a smaller metal radius.

Although metal-metal bond lengths are sensitive to a combination of factors including both steric and electronic effects of the ligands (especially when bridging ones are present), we believe that the observed difference of 0.06 Å between the Co(II)–Co(II) bond lengths in the $[Co_2(CN)_{10}]^{6-}$ anion and $[Co_2(CNCH_3)_{10}]^{4+}$ cation may be rationalized primarily on the basis of the dissimilitudes in the bonding of the isoelectronic isocyanide and cyanide ligands. In particular, on the basis of the evidence cited below we propose that the predominant factor responsible for the larger Co(II)–Co(II) distance in the $[Co_2(CN)_{10}]^{6-}$ anion is the increased negative charge on each cobalt atom such that equilibration of the metal–metal bond occurs at a greater distance in the cyanide complex through increased orbital expansion. These same arguments were utilized[46] to account for the difference in metal-metal distances between the isosteric $[Fe_2(CO)_8]^{2-}$–$Co_2(CO)_8$ (nonbridged) pair and between the isosteric $[Cr_2(CO)_{10}]^{2-}$–$Mn_2(CO)_{10}$ pair.

The limiting factor in the shortness of the metal–metal bond in both the cobalt isocyanide and cyanide dimers is presumably dictated by the nonbonding ligand–ligand repulsions between the two halves of the dimer. Of significance is that steric considerations *per se* lead to the expectation that substitution of $CNCH_3$ ligands for CN^- ones (thereby transmuting the $[Co_2(CN)_{10}]^{6-}$ anion into the $[Co_2[CNCH_3)_{10}]^{4+}$ cation) would give rise to an *increase* rather than the *observed decrease* in the Co(II)–Co(II) bond length. Therefore, it is our contention that the known variations in the metal–ligand electronic character provide a rationale for the observed difference in Co(II)–Co(II) bond lengths. Thus, the greater σ-donor and poorer π-acceptor properties of the cyanide ligands (*vide infra*) should result in an increased electron density on the cobalt atoms in the $[Co_2(CN)_{10}]^{6-}$ anion compared to that in the $[Co_2(CNCH_3)_{10}]^{4+}$ cation. We feel that this shift in electron distribution between the two dimers is reflected in the increased Co(II)–Co(II) bond length in the cyanide complex on account of not only a size expansion of the appropriate cobalt valence orbitals but also greater coulombic repulsions among the equatorial ligands between the two halves of the dimer. These observations are compatible with those of Kaska and coworkers[70] who concluded from the esr and optical properties of the paramagnetic $[Co(CNCH_3)_5]^{2+}$ and $[Co(CN)_5]^{3-}$ monomers as well as from their strongly contrasting chemical behavior that there is increased delocalization of the unpaired electron over the ligand orbitals of the isocyanide monomer with less charge density localized on the cobalt atom.

(b) Axial *vs.* Equatorial Co–CN Distances and Resulting Bonding Implications. The average value of 1.886 (5) Å for the four independent Co–CN(eq) bonds in the $[Co_2(CN)_{10}]^{6-}$ anion compares favorably with mean values of the nonbridged Co–CN(eq) bonds in $(NH_3)_5CoNCCo(CN)_5 \cdot H_2O$ (1.893 (4) Å),[71] and in $K_3[Co(CN)_5(CF_2CF_2H)]$ (1.894 (14) A).[72] It is especially noteworthy that these Co–CN bond lengths are not distinctly longer than the mean values of the Co–$CNCH_3$ bonds reported for the $[Co_2(CNCH_3)_{10}]^{4+}$ cation (1.88 (4) Å)[45] and the trigonal-bipyramidal $[Co(CNCH_3)_5]^{2+}$ cation (1.87 (2) Å),[73] both crystallized as the perchlorate salts. These values are considerably longer than the normal Co–CO distances of range 1.7–1.8 Å found for terminal carbonyl ligands in cobalt carbonyl complexes but are shorter than both the bridging Co–C(alkyl) σ-bond distance of 2.01 Å in $Co_2(CO)_4(tert\text{-}C_4H_9C_2H)_2(HC_2H)$[74] and the *predicted* single-bond distances of range 2.0–2.1 Å based on a radius of 0.77 Å for an aliphatic carbon atom and a halving of typical Co–Co distances in a variety of polynuclear cobalt complexes containing electron-pair Co–Co bonds.

Spectral studies have been interpreted in light of π-acceptor characteristics of the ligands following the trend $CO > CNCH_3 > CN^-$ with σ-bonding characteristics related in exactly the opposite manner (*viz.*, $CN^- > CNCH_3 > CO$),[24,70,75,76] and these trends have

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(62) The estimated ionic crystal radii for octahedrally coordinated Mn^{2+} and Co^{2+} are 0.91 and 0.82 Å, respectively, while the estimated covalent radii of Mn and Co are 1.168 and 1.157 Å, respectively.[63] Since the electronic charge distribution of a given metal atom in a complex does not bear a linear correlation with its formal oxidation state, we feel that the estimated difference between the radii of Mn and Co is best approximated by bond-length comparisons in related complexes without any regard for a dissimilarity in the formal oxidation states of the Mn and Co atoms.

(63) *Cf.* T. Moeller, "Inorganic Chemistry," Wiley, New York, N. Y., 1952, pp 135, 140.

(64) G. M. Sheldrick and R. N. F. Simpson, *J. Chem. Soc. A*, 1005 (1968).

(65) R. F. Bryan and A. R. Manning, *Chem. Commun.*, 1316 (1968).

(66) M. L. Katcher and G. L. Simon, *Inorg. Chem.*, 11, 1651 (1972); W. Clegg and P. J. Wheatley, *J. Chem. Soc. A*, 3572 (1971).

(67) This estimated value is based on the invariance in Co–Co distances for three axially substituted phosphine derivatives of $Co_2(CO)_6$—*viz.*, $Co_2(CO)_6(PX_3)_2$ (where X = n-C_4H_9,[68] OC_6H_5,[69] C_6H_5[69]) which all exhibit equivalent Co–Co bond lengths of 2.66–2.67 Å. An analogous situation of virtually identical Mn–Mn bond lengths exists for $Mn_2(CO)_{10}$ and its axially substituted phosphine derivatives.[46]

(68) (a) J. A. Ibers, *J. Organometal. Chem.*, 14, 423 (1968); (b) R. F. Bryan and A. R. Manning, *Chem. Commun.*, 1316 (1968).

(69) J. A. Molin-Case, A. S. Foust, Jr., and L. F. Dahl, submitted for publication.

(70) M. E. Kimball, D. W. Pratt, and W. C. Kaska, *Inorg. Chem.*, 7, 2006 (1968).

(71) B. Wang, W. P. Schaeffer, and R. E. Marsh, *ibid.*, 10, 1492 (1971).

(72) R. Mason and D. R. Russell, *Chem. Commun.*, 182 (1965).

(73) F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, 4, 318 (1965).

(74) O. S. Mills and G. Robinson, *Proc. Chem. Soc., London*, 187 (1964).

(75) D. F. Schriver and J. Posner, *J. Amer. Chem. Soc.*, 88, 1672 (1966); R. C. Taylor and W. D. Horrocks, Jr., *Inorg. Chem.*, 3, 584 (1964), and references cited therein.

(76) These differences in σ-donating and π-acceptor abilities of $CNCH_3$ and CO relative to CN^- may be readily rationalized by an envisioning of a $CNCH_3$ ligand being formed from a CN^- by the formal addition of a Lewis acid CH_3^+ to the nitrogen lone pair and by a CO ligand being evolved from CN^- by the formal addition of a proton to the nitrogen nucleus. These transmutations result in a substantial stabilization of each of the $CNCH_3$ and CO energy levels relative to its CN^- counterpart with the greatest stabilization occurring for the CO energy levels. Hence, the antibonding $\pi^*(CO)$ and $\pi^*(CNCH_3)$ levels (which are the lowest unoccupied MO's of the free ligands) are depressed much nearer the levels of the filled metal $3d_\pi$ orbitals thereby

been substantiated by Fenske and coworkers[77] from their MO calculations. The fact that the Mn–CO bond length in $Mn_2(CO)_{10}$ is 0.05–0.06 Å shorter than the Co–CN and Co–$CNCH_3$ bond lengths together with the Mn(0) radius being ~0.1 Å larger than the Co(II) radius[62] further emphasizes for a given metal that a M–CO bond length is considerably shorter than either a M–CN or M–$CNCH_3$ bond length. These bond-length comparisons thereby provide strong crystallographic evidence that a carbonyl ligand has considerably greater π-acceptor capability (which would lead to a reduction in M–CO bond length). Although an analogous π-acceptor argument would suggest that the M–$CNCH_3$ bond length should be noticeably shorter than a M–CN one, the composite influence of σ-donor and π-acceptor effects of the CN^- and $CNCH_3$ ligands must largely counterbalance each other with regard to giving rise to analogous equatorial cobalt–ligand distances in the $[Co_2(CN)_{10}]^{6-}$ anion and $[Co_2(CNCH_3)_{10}]^{4+}$ cation.

A completely unexpected structural feature found for the $[Co_2(CN)_{10}]^{6-}$ anion is that the axial Co–C(1) bond length of 1.961 (9) Å is 0.075 Å longer than the average value of 1.886 (4) Å for the Co–CN(eq) distances of range 1.876 (8)–1.896 (8) Å. We believe that this difference (more than $3\sigma_{av}$) is outside of experimental error and hence highly significant. While no indication whatsoever of an analogous bond-length distinction between the axial and equatorial ligands is observed in either $(NH_3)_5CoNCCo(CN)_5 \cdot H_2O$ (1.885 (4) *vs.* 1.893 (2) Å)[71] or the $[Co_2(CNCH_3)_{10}]^{4+}$ cation (1.92 (4) *vs.* 1.87 (3) Å),[45] there is a hint (not of meaningful statistical significance) of a similar trend in $K_3[Co(CN)_5(CF_2CF_2H)]$ (1.927 (14) *vs.* 1.894 (7) Å).[72] These Co–CN distances compare favorably with those of range 1.846 (13)–1.906 (12) Å and average value 1.869 Å found in the octahedral $[Co(CN)_6]^{3-}$ anion of $[Cr(C_2H_8N_2)_3][Co(CN)_6] \cdot 6H_2O$.[78] In complete contrast to the Co–CN(ax) distance being significantly longer than the Co–CN(eq) distances in $Ba_3[Co_2(CN)_{10}] \cdot 13H_2O$, the axial and equatorial M–CO distances show an opposite trend in $Mn_2(CO)_{10}$ (1.792 (14) *vs.* 1.835 (7) Å)[30] which is significantly magnified in $Tc_2(CO)_{10}$ (1.899 (11) *vs.* 1.995 (6) Å);[47] this shorter and presumably stronger M–CO(ax) bond has been rationalized[47] in terms of primarily a variation in π bonding in that the other half of the dimeric molecule being a much poorer π acceptor than a carbonyl ligand will enhance the π-acceptor ability of the carbonyl trans to it to a greater extent than those cis.[79,80] We feel that the observation of a longer M–CN(ax) bond relative to the M–CN(eq) ones in the $[Co_2(CN)_{10}]^{6-}$ anion must be rationalized on the basis that π bonding is no longer the prevailing factor. If only π bonding were important, the opposite trend in bond lengths (*viz.*, that cited above for $Mn_2(CO)_{10}$ and $Tc_2(CO)_{10}$) would be expected. From the hypothesis that a stronger σ-donor ability of a ligand (corresponding to greater metal orbital participation in the σ bond and hence greater "covalency") leads to a decreased metal–ligand distance, one may conclude (in the *absence* of both steric effects and large variations in π bonding) that the σ interaction of the axial Co–CN bond is considerably weaker than that of the equatorial Co–CN bonds. Our premise that NC(ax) $\cdots$ CN(eq) repulsions are not responsible for the longer Co–CN(ax) bond is based mainly on these nonbonding distances (*viz.*, the C(1)$\cdots$C(*n*) distances ($n = 2$-5) given in Table II) not only being longer than the closest NC(eq)$\cdots$CN(eq) contacts but also definitely longer than the OC(ax)$\cdots$CO(eq) distances found in $Mn_2(CO)_{10}$. Furthermore, this notably longer (and hence presumably weaker) M–CN(ax) bond in the $[Co_2(CN)_{10}]^{6-}$ anion cannot be rationalized in terms of a complete domination of σ bonding, since weaker σ donation of the electron pair from the axial CN–ligand to the cobalt relative to that from the equatorial CN–ligands would be expected to produce a weaker and hence longer axial C–N bond due to the metal-coordinated electron pair being somewhat antibonding between the carbon and nitrogen atoms.[77] However, both the infrared spectral intensity data and the C–N bond lengths suggest that the axial C–N bond may be stronger than the equatorial C–N bonds (*vide infra*). These latter observations insinuate a synergic bonding mechanism involving greater π back-bonding from the cobalt to the equatorial cyanides relative to the axial cyanide (in harmony with the shorter Co–CN(eq) distances imparting more $d\pi(Co)$–$\pi^*(CN)$ orbital overlap) such that the larger amount of π^* CN(eq) occupation overcomes the opposite σ-bond variation to give weaker and hence longer C–N(eq) distances. Therefore, in the case of $Ba_3[Co_2(CN)_{10}] \cdot 13H_2O$ we conclude that the longer Co–CN(ax) bond relative to the Co–CN(eq) ones must be rationalized mainly on the basis of strong anisotropic σ-bonding character[81] providing a compensatory effect which outweighs the expected variation in π-back-bonding character found in $Mn_2(CO)_{10}$. The importance of both kinds of interactions has been indicated from a vibrational spectral analysis[82] of $K_3Co(CN)_6$ as well as from MO calculations[77] of transition metal cyanide complexes.

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giving rise to much stronger d_π(metal)–π^*(ligand) back-bonding. Since the energy levels of a ligand 5σ orbital (the highest occupied MO of the free ligand which is primarily on the less electronegative carbon atom of the ligand) in general lies below the metal $3d_\sigma$ levels, an energy stabilization of the $5\sigma(CO)$ and $5\sigma(CNCH_3)$ orbitals relative to the $5\sigma(CN^-)$ one results in less interaction with the metal $3d_\sigma$ orbitals due to greater energy separation. Therefore, much greater σ donation of the lone electron pair in the 5σ orbital on the carbon atom to the metal atom occurs for a cyanide ligand relative to that for either a CO or $CNCH_3$ ligand. The ligand 5σ orbital is antibonding with respect to σ linkage between the ligand atoms such that removal of electron density from this orbital through σ donation to the metal will strengthen the σ bonding between the carbon and adjacent ligand atom.[61,77] Furthermore, Fenske and coworkers[61,77] found from their bonding studies that both the 5σ-donor and π^*-acceptor abilities of a cyanide ligand markedly depend upon the nature of the other ligands in the complex (*viz.*, upon the entire environment). The change of metal from Co(II) to Mn(0) should raise the metal energy levels relative to those of the ligands thereby increasing the π-acceptor and decreasing the σ-donor abilities of the ligands.

(77) R. L. DeKock, A. C. Sarapu, and R. F. Fenske, *Inorg. Chem.*, **10**, 38 (1971), and references cited therein.

(78) K. N. Raymond and J. A. Ibers, *ibid.*, **7**, 2333 (1968).

(79) These arguments are in complete agreement with both the carbonyl force constants and MO calculations presented by Fenske and DeKock[80] for $Mn(CO)_6^+$ and $HMn(CO)_5$ with only slight changes occurring in the 5σ carbonyl orbitals. However, Fenske and Hall[61] showed for $M(CO)_{6-x}L_x$ complexes (M = Cr, Mn, Fe; L = Cl, Br, I; $x = 1, 2$) that both the degree of σ donation from the 5σ orbital and the degree of back-bonding to the π^* orbitals have an important effect on the carbonyl's force constant with a lower 5σ occupation (corresponding to greater σ donation) counteracting a higher 2π occupancy (corresponding to greater π back-bonding).

(80) R. F. Fenske and R. L. DeKock, *Inorg. Chem.*, **9**, 1053 (1970).

(81) The degree of interactions of each cobalt's d_{z^2} orbital with the 5σ orbitals[76] of the five cyanide ligands (but mainly with the axial one) are smaller than those of each cobalt's $d_{x^2-y^2}$ orbital with the four equatorial ligands.

(82) L. H. Jones, *J. Chem. Phys.*, **41**, 856 (1964).

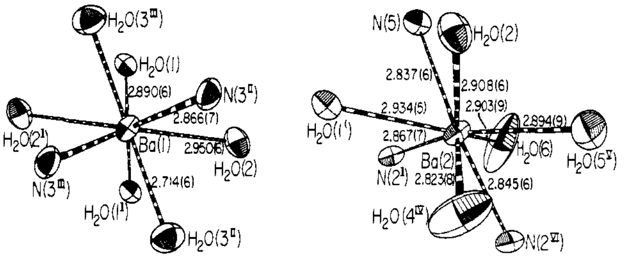

Figure 4. Localized dodecahedral-like coordination sphere (excluding the crystalline-disordered 13th water oxygen atom) about the $Ba(1)^{2+}$ and $Ba(2)^{2+}$ cations. The former cation lying on a crystallographic twofold axis is surrounded by six water oxygen and two cyanide nitrogen atoms, while the latter cation located in a general set of positions is surrounded by five water oxygen and three cyanide nitrogen atoms. All atoms are represented by 50% thermal probability ellipsoids.

(c) **Axial *vs.* Equatorial C–N Bonds.** The axial C–N bond length of 1.125 (11) Å is 0.04 Å shorter (on the border line of statistical significance) than the equatorial C–N bond lengths of range 1.159 (9)–1.178 (10) Å with an average value of 1.165 (5) Å in accord with the presumption of a higher C–N(ax) bond order. This small difference is not either surprising or inconsistent, since C–N bond lengths (as well as C–O and $C–NCH_3$ bond lengths) are known to be relatively insensitive to bond orders in the range 2–3.[83] These results have definite implications with respect to an assignment of the observed solid-state infrared bands obtained for $Ba_3[Co_2(CN)_{10}]\cdot 13H_2O$ in the cyanide stretching region. The three infrared active ligand modes under D_{4d} symmetry are a doubly degenerate e_1 mode and two b_2 modes; $b_2^{(1)}$ is assumed to represent primarily the asymmetric axial ligand stretch, while $b_2^{(2)}$ is assumed mainly to correspond to the asymmetric equatorial ligand stretch.[52,84] The observed frequencies are 2045.8 (s), 2014.7 (vs), and 1983.8 (m) cm^{-1} for $Mn_2(CO)_{10}$[84a,c] and 2130 (m), 2100 (s), and 2073 (vs) cm^{-1} for $Ba_3[Co_2(CN)_{10}]\cdot 13H_2O$.[85] The very intense band in the $Mn_2(CO)_{10}$ spectrum at 2014.7 cm^{-1} has been assigned to the e_1 mode, while the bands at 2045.8 and 1983.8 cm^{-1} correspond to the $b_2^{(2)}$ and $b_2^{(1)}$ modes, respectively.[52,84] This assignment is in accord with the above-mentioned π-bonding effects in $Mn_2(CO)_{10}$—*viz.*, that the axial C–O vibrational frequency is at lower energy than the equatorial C–O one due to increased occupation of the π* orbitals in the axial carbonyl group. In an analogous manner we tentatively assign the very intense band at 2073 cm^{-1} in $Ba_3[Co_2(CN)_{10}]\cdot 13H_2O$ to the e_1 mode. However, in deference not only to the indicated difference between the C–N(ax) and C–N(eq) bond lengths but also to the relative intensities of the three previously given infrared frequencies being different for $Mn_2(CO)_{10}$ and $Ba_3[Co_2(CN)_{10}]\cdot 13H_2O$, we tentatively assign the 2130-cm^{-1} band to the $b_2^{(1)}$ mode and the band at 2100 cm^{-1} to the equatorial $b_2^{(2)}$ mode.[86] Thus, the higher frequency of the axial C–N group is assumed to arise from the reduced $d_\pi(Co)–\pi^*(CN)$ interaction. We feel this tentative assignment is not unreasonable in that the weakest of the three absorption bands in both $Mn_2(CO)_{10}$ and $Ba_3[Co_2(CN)_{10}]\cdot 13H_2O$ would correspond primarily to the asymmetric axial ligand stretching mode, $b_2^{(1)}$.

Stereochemistry of Two Kinds of Ba^{2+} Cations. The air-stable nature of $Ba_3[Co_2(CN)_{10}]\cdot 13H_2O$ in striking contrast to that of the potassium salt may be attributed in large part to relatively stronger interactions existing between the barium cations and the cyanide nitrogen atoms and water molecules. The resulting coordination polyhedron of cyanide nitrogen atoms and 12 crystalline ordered waters of hydration (but excluding the 13th crystalline-disordered water molecule) about each of the two kinds of barium cations may be loosely described as a distorted dodecahedron (Figure 4). Each $Ba(1)^{2+}$ cation, lying on a crystallographic twofold axis, is enclosed by two symmetry-related equatorial nitrogen atoms and six water oxygen atoms, while each $Ba(2)^{2+}$ cation of site symmetry C_1-1 is encompassed by three equatorial nitrogen atoms and five water oxygen atoms. For these distorted dodecahedrons, the Ba^{2+}–N and Ba^{2+}–O distances (Table II) range from 2.837 (6) to 2.866 (7) Å and from 2.714 (6) to 2.934 (5) Å, respectively. Inclusion of the 13th crystallographically disordered water molecule into the coordination sphere gives rise to a possible nine- or ten-coordination about $Ba(1)^{2+}$ (*i.e.*, corresponding to this water oxygen atom, labeled O(7), of occupancy factor $^1/_4$ and its twofold-related mate each being 3.006 (26) Å from $Ba(1)^{2+}$) and a possible nine-coordination about $Ba(2)^{2+}$ (corresponding to this water oxygen atom, labeled O(8), statistically lying with occupancy factor $^1/_2$ at the other site on a twofold axis at 3.067 (7) Å from $Ba(2)^{2+}$). Analogous Ba^{2+}–O and Ba^{2+}–N distances were found recently in crystal structural determinations[87] of two barium cryptate salts, $Ba(C_{18}H_{36}N_2O_6)(SCN)_2\cdot H_2O$ and $Ba(C_{20}H_{40}N_2O_7)(SCN)_2\cdot 2H_2O$; in the first cryptate salt the barium cation is coordinated to ten nitrogen and oxygen atoms, while in the latter salt the barium cation is surrounded by 11 nitrogen and oxygen atoms. Similar Ba^{2+}–O distances were also found in the crystal structural determination[88] of an antibiotic X-537A, $C_{34}H_{54}O_8$, stabilized as a barium salt monohydrate, $Ba(C_{34}H_{53}O_8)_2\cdot H_2O$; in this complex eight oxygen atoms from the two independent antibiotic anions and the water molecule of crystallization are wrapped around the barium cation at Ba^{2+}–O distances of range 2.6–3.1 Å. Comparison of O···O and O···N con-

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[83] In a recent compilation on the structural chemistry of the cyanide group (D. Britton, *Perspect. Struct. Chem.*, 1, 109 (1967)), the C–N distances in a number of accurately determined gas-phase structures of RCN molecules were shown in practically all cases to lie between 1.156 and 1.159 Å; bond lengths in ionic cyanide groups were found in the more accurate crystal structures to be about 1.16 Å, whereas bond lengths for cyanide ligands covalently bridged at both ends were observed to be about 1.13 Å.

[84] (a) D. J. Parker and M. H. B. Stiddard, *J. Chem. Soc. A*, 695 (1966); (b) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 4, 1328 (1965); (c) G. Bor, *Chem. Commun.*, 641 (1969).

[85] Recorded in solid form (KBr pellet) on a Perkin-Elmer 421 infrared spectrometer.

[86] The three infrared active frequencies in the cyanide stretching region reported for $K_6[Co_2(CN)_{10}]$ by Griffith and Wickham[33] are 2117 (m), 2085 (vs), and 2070 (s) cm^{-1}. On the basis of their relative intensities, a tentative assignment of the weakest band at highest frequency to the axial C–N stretching mode ($b_2^{(1)}$) is analogous to the tentative assignment of the highest cyanide frequency measured for $Ba_3[Co_2(CN)_{10}]\cdot 13H_2O$. A considerable variation in these frequencies for different ionic substances containing the $[Co_2(CN)_{10}]^{6-}$ anion is not unexpected in view of similar variations in solid-state infrared frequencies in the carbonyl stretching region found for different salts containing polynuclear metal carbonyl anions.

[87] B. Metz, D. Moras, and R. Weiss, *J. Amer. Chem. Soc.*, 93, 1806 (1971).

[88] S. M. Johnson, J. Herrin, S. J. Liu, and I. C. Paul, *ibid.*, 92, 4428 (1970).

tacts in Table II expectedly indicates hydrogen bonding among the water molecules and between the water molecules and the cyanide nitrogen atoms. This network of hydrogen bonds undoubtedly plays a significant role in stabilizing the crystal.

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