Preparation and Structural Characterization of Barium Decacyanodicobaltate(II) Tridecahydrate, $Ba_3[Co_2(CN)_{10}]\cdot 13H_2O$, an Air-Stable Salt of the $[Co_2(CN)_{10}]^{6-}$ Ion

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Abstract: An air-stable salt of the dimeric anion $[Co_2(CN)_{10}]^{6-}$ has been prepared and characterized. The crystal and molecular structure of the salt $Ba_3[Co_2(CN)_{10}]\cdot 13H_2O$ has been determined from single-crystal, three-dimensional, X-ray diffraction data collected by counter methods. The $[Co_2(CN)_{10}]^{6-}$ anion is isoelectronic and isosteric with $Mn_2(CO)_{10}$. The molecular symmetry is $\bar{8}2m$ (D_{4d}). The dimer lies on a crystallographic twofold axis which bisects the Co–Co bond, whose length is 2.794 (2) Å. The average Co–C bond length for the four equivalent equatorial bonds is 1.885 (5) Å as compared with 1.946 (6) Å for the axial bond. This difference in bond lengths and the Co–Co bond length are compared with other isoelectronic complexes of CN^-, CNR, and CO and explained in terms of the relative trans influence of these ligands and the Co–Co bond. The origin of this trans influence is discussed in terms of the relative σ and π bonding strength of the ligands. The equatorial groups are tilted slightly toward the Co–Co bond; the average equatorial C–Co–Co bond angle is 88.8 (2)°. The $[Co(CN)_5]^{3-}$ groups are rotated 4.5° relative to one another about the Co–Co bond from a perfect D_{4d} geometry. The five independent C–N bond lengths are equal to within experimental error and average 1.151 (4) Å. The coordination of the two crystallographically independent barium ions is by the cyanide nitrogen atoms and the water oxygen atoms. Both coordination geometries are approximately Archimedean antiprisms. The Ba–O bond lengths and Ba–N bond lengths range from 2.713 (5) to 2.947 (5) Å and 2.846 (5) to 2.876 (5) Å, respectively. The 13th water molecule in the formula unit is disordered between two positions within the unit cell. These positions are holes at the caps of the Archimedean antiprisms around the two types of barium ions. This is interpreted as a disorder in the structure in which half of both types of barium ions are eight-coordinate and the other half are nine-coordinate monocapped Archimedean antiprisms. The barium cations, $[Co_2(CN)_{10}]^{6-}$ anions, and several of the water molecules are linked by several types of coordination bridges to give a very tight and cross-linked three-dimensional array which presumably explains the unusual stability of this salt to oxidation. In addition to the coordination linkages, there is an extensive network of hydrogen bonds formed between the protons of the water molecules and the nitrogen atoms of the cyanide groups. Several of the hydrogen atoms have been found in difference Fourier maps and were included in the refinement. The ruby-red crystals which crystallize from aqueous solution conform to the space group $C2/c$ with $a = 9.411$ (2), $b = 20.822$ (3), $c = 15.130$ (2) Å; and $\beta = 93.583$ (11)°; $Z = 4$; $\rho_{obsd} = 2.298$ (7) and $\rho_{calcd} = 2.299$ g/cm^3. A total of 6812 reflections were measured, and the symmetry-equivalent forms were averaged. The structure has been refined by full-matrix least-squares methods on F using 3142 independent reflections for which $F^2 > 3\sigma(F^2)$ to give weighted and unweighted R factors of 4.42 and 4.11%, respectively.

The cobalt(II) cyanide system is a problem in coordination chemistry which dates back not just many years but many decades, and yet many of the most important aspects of this chemistry are still not characterized. The unusual aqueous chemistry of the cobalt cyanide complexes appears to have been mentioned first in 1868 by Descamps[2] who noted that hydrogen gas is evolved when aqueous solutions of cobaltous salts and potassium cyanide (in excess) are combined. Seventy-five years later Iguchi[3] found that these solutions would also absorb hydrogen gas and could pass this hydrogen on to other chemical substrates. It is this aspect of the cobalt cyanide system (as a hydrogenation catalyst) that has been the impetus for most of the recent studies. During this early period the complex was usually formulated as the hexacyanide, $[Co(CN)_6]^{4-}$. There was, however, some evidence that a pentacyanide species was predominant; and this formulation was first proposed in 1949 by Hume and Kolthoff from polarographic studies.[4]

The aqueous $[Co(CN)_5]^{3-}$ ion reacts with molecular hydrogen to give the hydride species $[Co(CN)_5H]^{3-}$ [3,5-18] This is apparently the fastest known reaction between hydrogen and a transition metal complex. The isolation of this unstable aqueous metal hydride

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complex has been claimed.[17,19] Although the ion is often written as a hydride of cobalt(III), it will deprotonate to give $[Co(CN)_5]^{4-}$, a cobalt(I) species.[20,21] The pK_a for the hydride is 20 in contrast to that of 7.4 for the isoelectronic neutral carbonyl hydride $Mn(Co)_5H$.[22] In further analogy with metal carbonyl anions, there are complexes in which $[Co(CN)_5]^{4-}$ acts as a ligand, as in $[(NC)_5CoHgCo(CN)_5]^{6-}$.[23] A great many reducing agents other than molecular hydrogen effect the reduction of $[Co(CN)_5]^{3-}$ to the hydride.[9] The rapid formation of the hydride under high pressures of hydrogen has been reported.[24] It has been observed that the $[Co(CN)_5]^{3-}$–$[Co(CN)_5H]^{3-}$ system catalyzes the interchange of deuterium and hydrogen as well as ortho and para hydrogen interconversion.[25–28]

In aqueous solution the cobalt cyanide system is extremely complicated. In excess cyanide solution it is now clear that the primary species is $[Co(CN)_5]^{3-}$, although there is evidence for species with fewer than five cyanide ligands when the $[CN^-]Co$ ratio in solution is less than five.[29a] The solutions change with time, since one of the many insertion reactions of the $[Co(CN)_5]^{3-}$ ion is its reaction with water to give $[Co(CN)_5H]^{3-}$ and $[Co(CN)_5(OH)]^{3-}$.[29b] The decomposition of the hydride to give $[Co(CN)_5]^{3-}$ is the source of hydrogen evolution in cobaltous cyanide solutions. The extensive literature reporting the chemistry of $[Co(CN)_5]^{3-}$ and $[Co(CN)_5H]^{3-}$ has been the subject of an excellent review that covers reports through 1966.[30] The complication of the time dependence of cobalt cyanide solutions can be avoided in some nonaqueous solvents. The catalytic activity of cobalt cyanide complexes in such solvents has been reported recently.[31]

The hydride $[Co(CN)_5H]^{3-}$ as well as $[Co(CN)_5]^{3-}$ reacts with a wide range of chemical substrates. Among the most studied reactions have been those with organic compounds[30,32] although many reactions with inorganic compounds have also been characterized.[23,30,33] The kinetics of the electron-transfer reactions of $[Co(CN)_5]^{3-}$ in such reactions have been reported recently.[34,35]

Although the $[Co(CN)_5]^{3-}$ ion has been the subject of the many studies outlined above, the structure of this ion has continued to be at least in part unknown. The chemical characterization of the cobalt(II) cyanide complex in aqueous solution as $[Co(CN)_5]^{3-}$ was first accomplished by Adamson who also isolated the solid $K_6[Co_2(CN)_{10}]$ and pointed out that the diamagnetism of the salt implied a dimeric structure.[36] In contrast to the emerald green color of fresh aqueous solutions of the $[Co(CN)_5]^{3-}$ monomer, the dimeric salt is a deep violet. Subsequently the following dimer salts also have been prepared: $Na_6[Co_2(CN)_{10}]\cdot 4H_2O$, $K_4H_2[Co_2(CN)_{10}]\cdot 4H_2O$, and $K_6[Co_2(CN)_{10}]\cdot 6H_2O$.[37,38] The structure of $[Co_2(CN)_{10}]^{6-}$ has been assumed to be closely related to that of the isoelectronic compounds $Mn_2(Co)_{10}$[39] and $[Co_2(CNCH_3)_{10}][ClO_4]_4$.[40]

As stated above, the structure of $[Co(CN)_5]^{3-}$ was first characterized by Adamson as five-coordinated. A later paper by Pratt and Williams stated that the aqueous ion is the six-coordinate complex $[Co(CN)_5(OH_2)]^{3-}$.[41] The esr spectrum of $[Co(CN)_5]^{3-}$ in ethylene glycol–water frozen solutions was interpreted in terms of a C_{4v} symmetry for the complex.[42a] Other esr studies of what is apparently $[Co(CN)_5]^{3-}$ have been completed.[42b–f] A reinterpretation of the visible spectrum by Caulton even went so far as to predict the axial-metal-equatorial square-pyramidal bond angle to within 3° based on the four observed ligand-field electronic transitions.[43a] The infrared and Raman spectra of $[Co(CN)_5]^{3-}$ in aqueous methanol solution have also been interpreted in terms of C_{4v} symmetry.[43b] Our interest in the structural chemistry of this and related cobalt cyanide complexes has led to the present study. Since the $[Co_2(CN)_{10}]^{6-}$ ion is the best characterized of the cobalt cyanide species and its molecular parameters are of interest in comparison

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with other metal–metal bonded compounds (particularly $Mn_2(CO)_{10}$ and $[Co_2(CNCH_3)_{10}]^{4+}$), we have begun with its structure determination. A search for crystals of the normally air-sensitive salts of $[Co_2(CN)_{10}]^{6-}$ which would be suitable for diffraction studies has led to the synthesis and characterization of the remarkably stable salt $Ba_3[Co_2(CN)_{10}] \cdot 13H_2O$.[43c]

Experimental Section

Preparation of $Ba_3[Co_2(CN)_{10}] \cdot 13H_2O$. All solutions were kept under an atmosphere of pure N_2. Water to be used in solutions was deaerated by bubbling N_2 through it for at least 30 min. All reagents were reagent grade.

A solution containing 5.89 g (0.12 mol) of NaCN in 50 ml of water and a solution containing 4.76 g (0.02 mol) of $CoCl_2 \cdot 6H_2O$ in 75 ml of water were cooled and combined to give a clear green solution of *ca.* 0.16 *M* $Na_3[Co(CN)_5]$. To this solution was added 7.33 g (0.03 mol) of $BaCl_2 \cdot 2H_2O$ previously dissolved in 50 ml of water. After mixing, 50 ml of 95% ethanol was added and the sealed container placed in an ice bath. After several hours the crystalline red product was removed by suction filtration under N_2. The yield was 7.4 g or 72%. Slow cooling of similar solutions gave large, well-formed crystals which were used in the subsequent diffraction studies. The compound is stable indefinitely in air. *Anal.* Calcd for $Ba_3[Co_2(CN)_{10}] \cdot 13H_2O$ (mol wt 1024.26 g/mol): C, 11.73; H, 2.56; N, 13.67; Ba, 40.23; Co, 11.51; H_2O, 22.8. Found: C, 11.80; H, 2.59; N, 13.68; Ba, 40.42; Co, 11.42; H_2O (by weight loss at 60° under high vacuum), 23.8. These analytical data, the molecular weight as determined from the density and unit cell data, and the subsequent full structure analysis establish the compound as the tridecahydrate. The Ba analysis was gravimetric as $BaSO_4$; Co was determined as $[Co(C_5H_5N)_4](SCN)_2$;[44] H_2O was determined by weight loss (and only H_2O is evolved under these conditions); C, H, and N were determined by standard micro techniques.

Unit Cell and Diffraction Data. A series of precession photographs exhibited Laue symmetry $2/m$ and the absences hkl, $h + k \neq 2n$; and $h0l$, $l \neq 2n$. These absences are consistent with space groups Cc ($C_s{}^4$, No. 9) and $C2/c$ ($C_{2h}{}^6$, No. 15).[45] The latter is correct as proven by the subsequent structure determination.

The data crystal was a small ruby-red needle approximately bounded by the following planes and their reciprocals: 010, 110, and 001. The plane-to-plane distances are, respectively, 0.0105, 0.0105, and 0.0179 cm. The crystal was mounted in a thin-walled glass capillary such that the needle (c) direction was approximately parallel to the ϕ axis of a Picker FACS-1 diffractometer. The lattice constants and orientation angles were determined by a least-squares refinement of the setting and 2θ angles of 12 carefully centered reflections whose 2θ values ranged from 37 to 48°.[46] The X-ray source and diffractometer settings were identical with those used in the subsequent collection of intensity data. The crystal gave ω scan widths at half-height of 0.11–0.12° for several low-angle reflections.

The density of several large crystals was determined by flotation in solutions of CCl_4 and $CHBr_3$. The average density was 2.298 (7) g/cm³ (the standard deviation is calculated from the variance in the range of values). For four formula units of $Ba_3[Co_2(CN)_{10}] \cdot 13H_2O$ per cell, the calculated density is 2.299 g/cm³. The observed and calculated densities, unit cell constants, and other crystal data are summarized in Table I. Intensity data were collected in the θ–2θ scan mode using monochromatic Mo Kα radiation and a scintillation counter. The take-off angle for the X-ray tube was 2.0°, and the Bragg 2θ angle for the highly oriented graphite monochromator crystal was 12.0°. The pulse height analyzer was centered on the Mo Kα peak and was set to admit approximately 90% of the maximum intensity at full window width. The detector was located 33 cm from the source with a receiving aperture of 7 × 7 mm. The 2θ scans were from 0.6° below the Kα_1 peak to 0.6° above the Kα_2 peak at a scan rate of 1.0 deg/min. Copper foil attenuators were automatically inserted in the path of the diffracted beam to keep the count rate for a given reflection below 10,000 counts/sec. One unique form ($\pm h$, $+k$ $+l$) of data was collected out to 2θ = 60°

Table I. Summary of Crystal Data

Molecular formula	$Ba_3[Co_2(CN)_{10}] \cdot 13H_2O$
Molecular weight	1024.26 g/mol
Linear absorption coefficient, μ	47.0 cm⁻¹
Observed density	2.298 (7) g/cm³
Calculated density	2.299 g/cm³
Crystal dimension	0.0105 × 0.0105 × 0.0179 cm
Space group	$C2/c$
Formula units/cell	4
Cell constants[a]	
a	9.411 (2) Å
b	20.822 (3) Å
c	15.130 (2) Å
β	93.583 (11)°
cos β	−0.0625 (2)
Cell volume	2959.0 (11) Å³

[a] Ambient temperature of 23°. Mo Kα_1 radiation, λ = 0.70926 Å.

Two other equivalent forms ($\pm h$, $-k$, $+l$ and $\pm h$, $+k$, $-l$) were collected out to 2θ = 35°.

During the experiment the intensities of the three reflections 002, 060, and 313 were measured as standards every 60 reflections. A maximum change in intensities of approximately 10% from the beginning to the end of the experiment was noted. This change was not isotropic and was corrected as described previously.[47]

The data processing was carried out by our program UCFACS.[48,49] The parameter p, introduced to avoid overweighting strong reflections, was set to 0.04. The corrected intensities were converted to values of F^2 by application of Lorentz and polarization corrections.[49] The value of μ given in Table I gave transmission factors which ranged from 0.55 to 0.66. Since in no case did the calculated absorption correction for F^2 differ by more than 10% from the mean for two equivalent reflections, an absorption correction was not applied. After correcting for the intensity changes of the standards, equivalent reflections were averaged. The 6812 reflections measured gave 4456 independent reflections of which 3142 had $F^2 > 3\sigma(F^2)$. The latter reflections were used in the final refinement. The agreement factor for averaging F^2 is 6.0% which is in reasonable agreement with the final least-squares agreement on F of 4.42%.

Solution and Refinement of the Structure. The structure was solved by application of heavy atom techniques. Full-matrix least-squares refinements on F were used in which the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors.[49] The weighting factor, w, is $4F_o{}^2/\sigma^2(F_o{}^2)$. The atomic scattering factors for neutral Ba, Co, O, N, and C were taken from the values tabulated by Cromer and Mann[50] and those for neutral hydrogen from Stewart, Davidson, and Simpson.[51] Correction for anomalous dispersion effects of the barium and cobalt atoms using both $\Delta f'$ and $\Delta f''$ was included in the calculation of the F's.[52]

The positions of the barium and cobalt atoms were determined from a three-dimensional Patterson map. Subsequent least-squares and difference Fourier calculations located all nonhydrogen atoms.

The last water molecule was found with some difficulty since it is disordered. The total occupancy amounts to four such water molecules per unit cell. Several trial refinements and difference Fourier calculations with all other located atoms showed that the disorder was adequately described by placing one-half of the disordered water molecule on the twofold axis in the crystal and the other one-half on a general position (an occupancy of $^1/_4$). Several water hydrogen atoms were located in a difference Fourier which included only those F's for which sin $\theta/\lambda \leq 0.35$. The positional

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Table II. Positional and Thermal Parameters and Standard Deviations of Nonhydrogen Atoms

Atom	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba_1	0.28398 (4)	0.18034 (2)	0.10172 (2)	78.5 (5)	12.1 (1)	24.5 (2)	2.8 (2)	18.1 (2)	1.5 (1)
Ba_2	0	0.02402 (2)	$^1/_4$	73.6 (6)	9.5 (1)	31.5 (3)	0	19.8 (3)	0
Co	0.10351 (7)	0.35563 (3)	0.32035 (5)	43.4 (8)	9.5 (2)	18.8 (3)	−1.0 (3)	4.9 (4)	−1.5 (2)
C_1	0.2444 (6)	0.3554 (3)	0.4201 (4)	72 (7)	12 (1)	27 (3)	3 (2)	8 (3)	−1 (2)
C_2	−0.0304 (5)	0.3161 (3)	0.3899 (4)	55 (6)	10 (1)	20 (2)	−3 (2)	5 (3)	−3 (1)
C_3	0.2327 (6)	0.3936 (3)	0.2445 (4)	54 (6)	13 (1)	22 (2)	−4 (2)	1 (3)	−5 (2)
C_4	0.0417 (6)	0.4384 (3)	0.3524 (4)	58 (6)	12 (1)	33 (3)	−3 (2)	12 (3)	0 (2)
C_5	0.1589 (5)	0.2734 (3)	0.2862 (3)	50 (6)	15 (1)	16 (2)	−2 (2)	9 (3)	−2 (1)
N_1	0.3244 (6)	0.3586 (3)	0.4798 (4)	110 (8)	24 (2)	36 (3)	0 (3)	15 (4)	0 (2)
N_2	−0.1023 (5)	0.2892 (3)	0.4366 (3)	89 (7)	16 (1)	27 (2)	−7 (2)	14 (3)	−3 (1)
N_3	0.3188 (5)	0.4165 (3)	0.2030 (4)	78 (6)	19 (1)	35 (3)	−13 (2)	15 (3)	−3 (2)
N_4	0.0137 (6)	0.4889 (3)	0.3757 (5)	111 (8)	16 (1)	60 (4)	5 (3)	22 (4)	−5 (2)
N_5	0.1965 (5)	0.2223 (2)	0.2689 (3)	99 (7)	14 (1)	24 (2)	7 (2)	14 (3)	0 (1)
O_1	0.0029 (4)	0.1366 (2)	0.3618 (3)	76 (5)	16 (1)	26 (2)	−6 (2)	−9 (2)	0 (1)
O_2	0.2884 (5)	0.0739 (2)	0.2272 (3)	90 (6)	15 (1)	54 (3)	6 (2)	−7 (3)	−2 (2)
O_3	0.4181 (6)	0.4899 (3)	0.4123 (4)	144 (8)	23 (1)	41 (3)	−3 (3)	11 (3)	8 (2)
O_4	0.2220 (8)	0.4347 (3)	−0.0005 (5)	263 (13)	27 (2)	67 (4)	−7 (4)	66 (7)	3 (2)
O_5	0.4315 (9)	0.1250 (7)	0.3930 (6)	169 (12)	132 (7)	61 (4)	−53 (8)	36 (6)	−35 (5)
O_6	0.4088 (10)	0.3070 (4)	0.0893 (9)	257 (14)	55 (3)	308 (14)	−80 (6)	216 (12)	−103 (6)
$O_7{}^c$	0.2380 (18)	0.0429 (12)	0.3931 (12)	76 (22)	33 (7)	39 (10)	18 (9)	−17 (11)	−18 (6)
$O_8{}^d$	$^1/_2$	0.2243 (10)	$^1/_4$	12 (14)	43 (7)	186 (20)	0	−36 (13)	0

[a] Numbers in parentheses here and in the following tables are the standard deviations in the least significant digits as estimated from the variance–covariance matrix. [b] The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The parameters are tabulated as $\beta_{ij} \times 10^4$. [c] Atom site occupancy is $^1/_4$. [d] Atom site occupancy is $^1/_2$.

parameters for these atoms were refined subject to the constraint that the O–H bond length remain 0.90 Å. The proper application of such constraints in least-squares refinement recently has been described.[53] The thermal parameters of the hydrogen atoms were fixed at 7.39 Å^2, a value determined from a refinement of the overall thermal parameter. There is no evidence of secondary extinction effects.[54] In the final least-squares cycles, all nonhydrogen atoms were refined with anisotropic thermal parameters, and the located hydrogen atoms were refined with a constrained O–H bond length. The position of hydrogen atom H_{81} is on a ridge of electron density, and it oscillated along this ridge. Atom H_{81} was fixed in position for the final refinement. The final agreement factors, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and R_2 (weighted R factor) $= [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$, were 4.11 and 4.42%, respectively. The final error in an observation of unit weight is 1.81. This quantity when computed for classes of reflections is larger at low angles. We ascribe this result to a less than perfect description of the disorder by our model. The final difference Fourier showed no peaks which were more than 26% of the height of a carbon atom peak. The positional and thermal parameters for the nonhydrogen atoms are given in Table II. Table III lists the positional parameters for the hydrogen atoms and Table IV gives the root mean square (rms) amplitudes of vibration of the nonhydrogen atoms along the major axes of the thermal ellipsoids.[55]

Description of the Structure

The structure consists of discrete $[Co_2(CN)_{10}]^{6-}$ anions and two types of crystallographically independent Ba^{2+} cations. The barium cations are coordinated by water and by the nitrogen atoms of some of the cyanide groups in $[Co_2(CN)_{10}]^{6-}$. The entire structure is linked by an extensive system of hydrogen bonds formed between the water molecules and the cyanide nitrogen atoms.

Since there are four formula units per cell, of space group $C2/c$, there are 12 barium atoms and 4 $[Co_2(CN)_{10}]^{6-}$ dimeric anions to place.[45]

Table III. Positional Parameters for Hydrogen Atoms

Atom	x	y	z^a
H_{11}	0.063 (7)	0.149 (5)	0.407
H_{21}	0.330 (9)	0.038 (2)	0.209
H_{22}	0.321 (9)	0.098 (4)	0.274
H_{31}	0.491 (8)	0.468 (4)	0.439
H_{41}	0.303 (6)	0.412 (4)	0.00
H_{42}	0.132 (4)	0.439 (5)	−0.024
H_{51}	0.467 (14)	0.165 (2)	0.393
H_{52}	0.366 (8)	0.145 (5)	0.425
H_{61}	0.417 (11)	0.345 (3)	0.061
$H_{81}{}^b$	0.505	0.247	0.301

[a] The coordinates are constrained such that the O–H bond length is 0.9 Å. See ref 53 for details. [b] Atom position not refined.

Table IV. Root-Mean-Square Amplitudes of Vibration of Nonhydrogen Atoms[a]

	Axis 1	Axis 2	Axis 3
Ba_1	139.4 (6)	160.5 (6)	207.9 (5)
Ba_2	144.5 (8)	147.2 (8)	214.6 (7)
Co	133.3 (12)	138.7 (12)	156.6 (12)
C_1	154 (9)	174 (9)	188 (9)
C_2	133 (9)	150 (9)	172 (9)
C_3	134 (10)	159 (9)	188 (9)
C_4	144 (9)	168 (9)	201 (9)
C_5	122 (10)	156 (9)	185 (9)
N_1	178 (9)	231 (9)	247 (8)
N_2	160 (8)	172 (8)	221 (7)
N_3	152 (8)	193 (8)	236 (8)
N_4	171 (9)	218 (8)	275 (8)
N_5	153 (8)	170 (8)	222 (7)
O_1	149 (7)	184 (6)	211 (6)
O_2	172 (7)	201 (7)	258 (7)
O_3	188 (8)	247 (7)	255 (7)
O_4	211 (8)	253 (9)	376 (9)
O_5	225 (9)	261 (10)	561 (15)
O_6	193 (11)	201 (10)	704 (16)
O_7	157 (29)	171 (28)	317 (29)
O_8	46 (65)	306 (25)	471 (26)

[a] Values are given as 10^3 Å.

The anions lie on the twofold axis (position 4e) with the center of the dimer at 0, 0.3556, $^1/_2$. The first type

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(53) K. N. Raymond, *Acta Crystallogr., Sect. A*, 28, 163 (1972).

(54) W. H. Zachariasen, *ibid.*, 24, 212 (1968).

(55) A listing of structure factors 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-72-7664. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

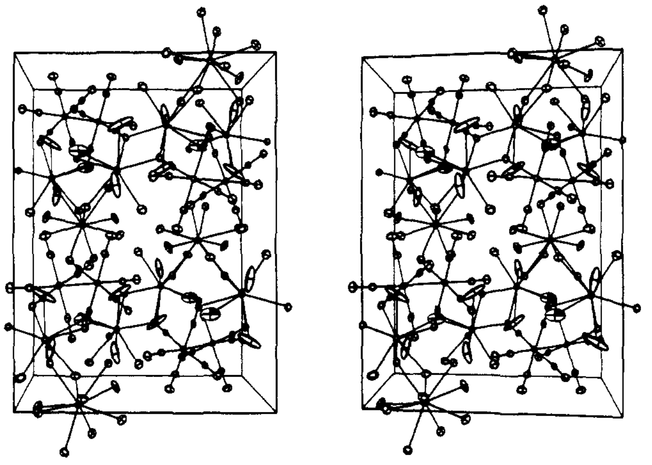

Figure 1. A stereoscopic packing diagram of $Ba_3[Co_2(CN)_{10}]\cdot 13H_2O$. The outline of one unit cell is shown. All of the anions and cations within the unit cell are shown except for the two barium atoms Ba_2 on the back face of the cell. The origin of the unit cell is at the front lower left corner with the vertical axis as *b* and the horizontal axis as *c*. Thermal ellipsoids are drawn at the 30% probability contours. The disordered oxygen atoms are drawn with octant shading.

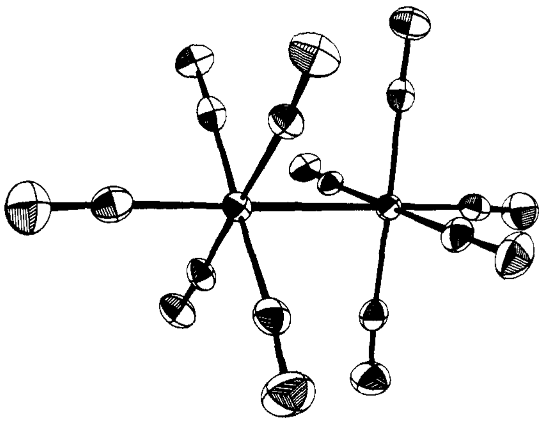

Figure 2. A perspective drawing of the $[Co_2(CN)_{10}]^{6-}$ anion. The crystallographic twofold axis is approximately vertical. The numbering of the cyanide atoms in the left-hand $Co(CN)_5$ unit is: axial, no. 1; top foreground, no. 2; top background, no. 5; trans to no. 2, no. 3; and trans to no. 5, no. 4. The thermal ellipsoids in this and the following drawings are drawn at the 50% probability contours.

of barium, Ba_1, is on the general position 8f and thus represents eight Ba^{2+} ions in the cell. The remaining four ions are of the second type, Ba_2, which lies on the twofold axis (position 4e) at 0, 0.024, $^1/_4$. A stereoscopic crystal packing diagram is shown in Figure 1.

The $[Co_2(CN)_{10}]^{6-}$ Ion. A perspective drawing of the dimer is shown in Figure 2. The structure consists of two square-pyramidal $[Co(CN)_5]^{3-}$ groups joined by a Co–Co bond which is 2.794 (2) Å in length. This and other interatomic distances are given in Table V.

Table V. Distances between Bonded Atoms

Atoms	Distance, Å	Atoms	Distance, Å
CoCo	2.794 (2)	Ba_1N_2	2.876 (5)
CoC_1	1.946 (6)	Ba_1N_2'	2.850 (5)
CoC_2	1.881 (5)	Ba_1N_5	2.846 (5)
CoC_3	1.895 (6)	Ba_1O_1	2.934 (4)
CoC_4	1.892 (6)	Ba_1O_2	2.916 (5)
CoC_5	1.873 (6)	Ba_1O_4	2.842 (7)
C_1N_1	1.141 (8)	Ba_1O_5	2.911 (10)
C_2N_2	1.154 (7)	Ba_1O_6	2.899 (7)
C_3N_3	1.159 (7)	Ba_1O_8	3.071 (6)
C_4N_4	1.144 (8)		
C_5N_5	1.156 (7)	Ba_2N_3	2.877 (5)
		Ba_2O_1	2.890 (5)
Av Co–C	1.885 (5)[a]	Ba_2O_2	2.947 (5)
4 eq[b]		Ba_2O_3	2.713 (5)
Av C–N	1.151 (4)[a]	Ba_2O_7	3.041 (17)
5 cyanides			

[a] See footnote 56. [b] eq = equatorial.

The crystallographically imposed point symmetry of the anion is $C_2(2)$ but the molecular symmetry is very close to D_{4d}-($\bar{8}2m$). The four equatorial Co–C bond lengths average 1.885 (5) Å. The standard deviation in the average (0.005 Å) is that estimated from the variance. This compares reasonably well with the standard deviation estimated from the variance-covariance matrix (0.003 Å) and indicates that the Co–C bond lengths in the equatorial plane are equal within experimental error.[56] The axial Co–C bond length of 1.946 (6) Å is, however, significantly longer than the equatorial bonds. Similarly, the average of all five C–N cyanide bond lengths is 1.151 (4) Å. The standard deviation in the mean as estimated from the variance (0.004 Å) agrees well with that estimated from the variance-covariance matrix (0.004 Å).[56] Although the axial C–N bond is the shortest of the five C–N bonds, it differs from the mean by less than 1.5 standard deviations of an individual bond length and is therefore not significantly different from the equatorial cyanide bonds.

Deviations of the $[Co_2(CN)_{10}]^{6-}$ geometry from D_{4d} symmetry are very small and, especially in the case of bond angles, are presumably due to small distortions imposed by the crystal packing *via* interactions with the barium ions and hydrogen bonding. The Co–Co–C_1 axial bond angle is 178.7 (2)° which is very close to the idealized linear geometry. This and other bond angles are listed in Table VI. The Co–Co–C equatorial bond angles are all nearly 90°. There is, however, a systematic deviation of about 1° such that the equatorial cyanides bend in toward the Co–Co bond. This is again reflected in the axial carbon–cobalt–equatorial carbon bond angles which are all greater than 90° and average about 91°. The Co–C–N bond angles are all linear to within 6°. Variations in the linearity of these cyanide bonds are not regarded as significant and are typical of those in other cyanide structures, as described later.

The ten independent dihedral angles between planes defined by one equatorial carbon atom, the axial carbon atom, and the cobalt atom of the two $[Co(CN)_5]^{3-}$ groups can be divided into two classes. These dihedral angles are given in Table VII. Let us assume a perfect C_{4v} geometry for the $[Co(CN)_5]^{3-}$ units and further assume that the fourfold axis for both units is coincident. There remains one variable parameter which is the rotation around the fourfold axis that is required to bring the first $[Co(CN)_5]^{3-}$ unit into the same orientation as the second. Let us call this angle ϕ. For an

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(56) The average is defined by $\bar{x} = \Sigma_{i=1}{}^n x_i/n$. The standard deviation of an individual observation is defined by $\sigma^2(x_i) = \Sigma_{i=1}{}^n(x_i - \bar{x})^2/(n - 1)$. The standard deviation of the mean is defined by $\sigma^2(\bar{x}) = \sigma^2(x_i)/n$.

Table VI. Angles between Bonded Atoms[a]

Atoms	Angle, deg	Atoms	Angle, deg	Atoms	Angle, deg
$CoCoC_1$	178.7 (2)	$N_2Ba_1N_2'$	84.2 (2)	$N_3Ba_2N_3'$	77.8 (3)
$CoCoC_2$	88.1 (2)	$N_2Ba_1N_5$	74.7 (2)	$N_3Ba_2O_1$	139.4 (2)
$CoCoC_3$	89.0 (2)	$N_2Ba_1O_1$	74.9 (2)	$N_3Ba_2O_1'$	120.2 (2)
$CoCoC_4$	89.1 (2)	$N_2Ba_1O_2$	135.6 (2)	$N_3Ba_2O_2$	141.4 (2)
$CoCoC_5$	89.0 (2)	$N_2Ba_1O_4$	124.3 (2)	$N_3Ba_2O_2'$	76.5 (2)
		$N_2Ba_1O_5$	148.4 (3)	$N_3Ba_2O_3$	79.8 (2)
C_1CoC_2	90.7 (3)	$N_2Ba_1O_6$	60.5 (3)	$N_3Ba_2O_3'$	76.7 (2)
C_1CoC_3	92.2 (3)	$N_2Ba_1O_8$	105.7 (4)	$N_3Ba_2O_7$	132.4 (5)
C_1CoC_4	90.5 (3)	$N_2'Ba_1N_5$	148.9 (2)	$N_3Ba_2O_7'$	61.7 (5)
C_1CoC_5	91.4 (3)	$N_2'Ba_1O_1$	129.4 (2)	$O_1Ba_2O_1'$	71.6 (2)
		$N_2'Ba_1O_2$	138.5 (2)	$O_1Ba_2O_2$	78.9 (1)
C_2CoC_3	176.8 (3)	$N_2'Ba_1O_4$	73.2 (2)	$O_1Ba_2O_2'$	67.7 (2)
C_2CoC_4	91.6 (3)	$N_2'Ba_1O_5$	73.6 (2)	$O_1Ba_2O_3$	71.1 (2)
C_2CoC_5	87.9 (3)	$N_2'Ba_1O_6$	64.2 (3)	$O_1Ba_2O_3'$	138.5 (2)
		$N_2'Ba_1O_8$	107.8 (2)	$O_1Ba_2O_7$	60.0 (4)
C_3CoC_4	89.7 (3)	$N_5Ba_1O_1$	66.9 (2)	$O_1Ba_2O_7'$	106.9 (5)
C_3CoC_5	90.8 (3)	$N_5Ba_1O_2$	69.4 (2)	$O_2Ba_2O_2'$	138.7 (2)
		$N_5Ba_1O_4$	137.8 (2)	$O_2Ba_2O_3$	120.9 (2)
C_4CoC_5	178.0 (3)	$N_5Ba_1O_5$	114.5 (3)	$O_2Ba_2O_3'$	70.8 (2)
		$N_5Ba_1O_6$	85.3 (3)	$O_2Ba_2O_7$	52.8 (4)
CoC_1N_1	176.2 (6)	$N_5Ba_1O_8$	58.4 (2)	$O_2Ba_2O_7'$	120.9 (4)
CoC_2N_2	173.9 (5)	$O_1Ba_1O_2$	67.5 (1)	$O_3Ba_2O_3'$	149.6 (3)
CoC_3N_3	175.2 (5)	$O_1Ba_1O_4$	81.5 (2)	$O_3Ba_2O_7$	68.2 (4)
CoC_4N_4	174.8 (6)	$O_1Ba_1O_5$	136.7 (3)	$O_3Ba_2O_7'$	116.0 (4)
CoC_5N_5	176.8 (5)	$O_1Ba_1O_6$	132.5 (2)	$O_7Ba_2O_7'$	165.2 (9)
		$O_1Ba_1O_8$	122.0 (1)		
$Ba_1O_1'Ba_2$	112.7 (2)	$O_2Ba_1O_4$	73.1 (2)		
$Ba_1O_2Ba_2$	111.6 (2)	$O_2Ba_1O_5$	72.9 (2)		
		$O_2Ba_1O_6$	138.1 (4)		
		$O_2Ba_1O_8$	76.7 (4)		
		$O_4Ba_1O_5$	70.6 (3)		
		$O_4Ba_1O_6$	136.6 (3)		
		$O_4Ba_1O_8$	129.4 (4)		
		$O_5Ba_1O_6$	89.2 (4)		
		$O_5Ba_1O_8$	62.2 (4)		
		$O_6Ba_1O_8$	61.5 (5)		

[a] Ba_1 is bonded to two N_2's which are denoted N_2 and N_2'. Ba_2 is bonded to pairs of atoms since it is on the twofold axis (see Figures 4 and 5).

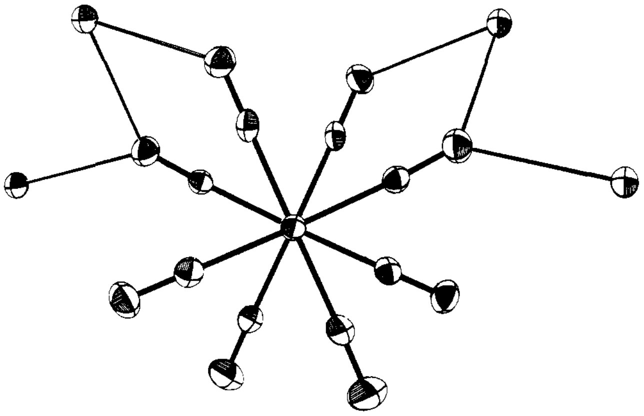

Figure 3. A perspective drawing of the $[Co_2(CN)_{10}]^{6-}$ ion as viewed down the molecular $\bar{8}$ (S_8) symmetry axis. The two types of bridges formed by Ba_1 are also shown. The axial cyanide ligands are not shown. The vertical axis is the crystallographic twofold axis.

Table VII. Dihedral Angles in $[Co_2(CN)_{10}]^{6-}$

Atoms in 1st plane	Atoms in 2nd plane	Angle, deg
C_2CoC_1	C_2CoC_1	51.9 (4)
C_3CoC_1	C_3CoC_1	49.2 (4)
C_4CoC_1	C_4CoC_1	48.7 (4)
C_5CoC_1	C_5CoC_1	47.6 (3)
C_2CoC_1	C_3CoC_1	50.6 (3)
C_4CoC_1	C_5CoC_1	48.2 (3)
C_2CoC_1	C_4CoC_1	39.7 (3)
C_3CoC_1	C_5CoC_1	41.6 (3)
C_3CoC_1	C_4CoC_1	41.0 (3)
C_2CoC_1	C_5CoC_1	40.2 (3)

eclipsed configuration ($\phi = 0$), the cyanide atoms are superimposed in projection down the fourfold axis. The dihedral angles between the $Co(CN)_3$ subunits which contain an axial cyanide are either 0 or 90°. As one $[Co(CN)_5]^{3-}$ unit is rotated from an eclipsed configuration, the values of these two types of dihedral angles become ϕ and $90° - \phi$, respectively. For the D_{4d} symmetry of a perfectly staggered geometry $\phi = 45°$, and all of the dihedral angles of the type under consideration are equal. Of the ten dihedral angles of this type in this structure, four belong to one class and average 40.6 (8)°, and six belong to the remaining class and average 49.4 (7)°.[56] The angle ϕ is therefore 40.6 (4)° or 4.4 (4)° from perfect D_{4d} symmetry. This angle may also be calculated from the dihedral angles between appropriate least-squares planes. There are three such dihedral angles of which one is ϕ and two are $90° - \phi$. The average value of ϕ calculated in this way is 40.5° or 4.5° from D_{4d} symmetry. The relative orientation of the $[Co(CN)_5]^{3-}$ groups can be seen in Figure 3 which shows a view in projection down the molecular fourfold axis.

Equations for the least-squares planes through $Co(CN)_3$ units are presented in Table VIII. All of the

Table VIII. Weighted Least-Squares Planes

	Plane *P*1 of cobalt and eq cyanide atoms[a]	Plane *P*2 of cobalt, ax cyanide, and trans eq cyanide atoms[a]	Plane *P*3 of cobalt, ax cyanide, and trans eq cyanide atoms[a]
Co	0.0010 (7)	−0.0029 (7)	0.0006 (7)
C_1		0.030 (6)	0.001 (6)
C_2	−0.050 (5)	0.004 (5)	
C_3	−0.045 (6)	0.032 (6)	
C_4	−0.035 (6)		−0.019 (5)
C_5	−0.026 (5)		0.002 (5)
N_1		−0.027 (7)	0.000 (6)
N_2	0.025 (5)	0.075 (5)	
N_3	0.023 (6)	0.060 (6)	
N_4	0.043 (7)		−0.002 (6)
N_5	0.020 (5)		−0.013 (5)
A[b]	6.077	3.250	6.680
B	−0.111	−18.760	8.396
C	10.899	−4.304	−9.413
D	4.080	−7.711	0.6615

Angles between Planes[c]

Planes	Angle, deg
*P*1, *P*1′	0.6 (2)
*P*1, *P*2	88.5 (1)
*P*1, *P*2′	89.0 (1)
*P*1, *P*3	89.2 (1)
*P*1, *P*3′	89.0 (1)
*P*2, *P*2′	51.4 (2)
*P*2, *P*3	88.1 (1)
*P*2, *P*3′	40.5 (1)
*P*3, *P*3′	47.6 (2)

[a] Distance in ångströms of individual atoms from the plane. eq = equatorial; ax = axial. [b] Equations for the least-squares planes in monoclinic coordinates of the form $Ax + By + Cz - D = 0$. [c] The primes denote planes of the form $-Ax + By - Cz - D' = 0$, where D' is the new plane-to-origin distance. Thus *P*1 and *P*1′ are twofold related forms of the same plane.

atoms lie within a few hundredths of an ångström of the least-squares planes. The dihedral angles between these planes are also given in Table VIII.

In addition to the rotation angle just described, the degree of departure of the $[Co(CN)_5]^{3-}$ units from C_{4v} symmetry can be measured by the angles between the equatorial plane and the two axial planes (88.5 and 89.2°, respectively) and the angle between the two symmetry-related axial planes (0.6°).

The Ba^{2+} Coordination. The coordination and linkage of the barium ions is shown in Figure 4. The disordered oxygen atoms, O_7 and O_8, are drawn without octant shading to distinguish them from the other atoms. The 13th water molecule has a probability of 25% of being at the general position O_7 and also a probability of 25% of being on the twofold related position O_7'. The remaining 50% probability is that the atom is at the site O_8 which lies on the twofold axis.

There is one disordered water molecule per formula unit of the $[Co_2(CN)_{10}]^{6-}$ salt, or four disordered water molecules per unit cell. These are distributed between two holes in the structure. The holes appear to rearrange slightly when occupied. One hole (the location specified as O_8) lies on the twofold axis between Ba_1 and Ba_1', such that, when occupying this site, it coordinates both ions. There are four such holes per unit cell. The cavity is surrounded by nitrogen and oxygen atoms. None of the interatomic nonbonded distances between O_8 and surrounding atoms are so short that they cannot be explained as a hydrogen bond.

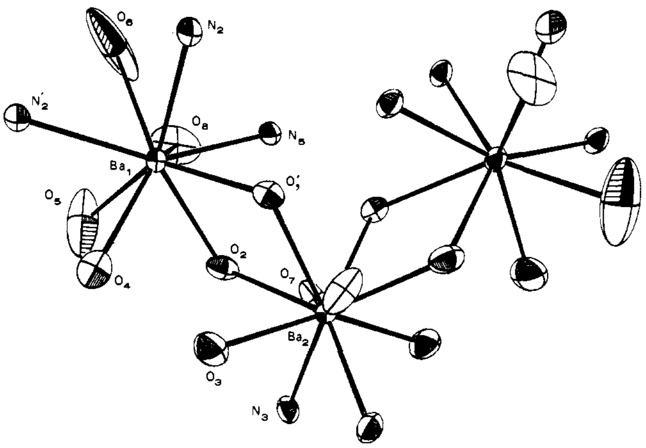

Figure 4. A perspective drawing of the linkage between the coordination polyhedra of the barium ions. The disordered oxygen atoms, O_7 and O_8, are shown without octant shading. The vertical axis is the crystallographic twofold axis.

The second hole (the location specified as O_7) is on a general position near Ba_2. Since the ion Ba_2 is on the twofold axis, there are two holes on either side of Ba_2 related by the twofold axis. These are positions O_7 and O_7'. There are eight such holes per unit cell, again with no surrounding nonbonded distances that cannot be explained by hydrogen bonding.

It is clear from the structure that there is a correlation between the occupancy of sites O_7 and O_8, and some speculation as to this relationship can be made. It seems likely that the disorder of the water molecule is only among the barium coordination sites of one formula unit of the salt. That is, for example, we assume the coordination of one disordered water molecule at O_7 and a second at O_8 for one formula unit of the salt (and the implied absence of coordination of a disordered water for another adjacent formula unit of the salt) is an unlikely event. The disordered water molecule is therefore coordinated at either positions O_7, O_7', or O_8 but not more than one of these positions for a given formula unit of the salt. If the disordered water molecule is ignored, the coordination number for both barium ions is 8. This proposed model would have one other water molecule coordinated to each barium 50% of the time. Thus, for both Ba_1 and Ba_2 the coordination number is 8 for half of the ions in the structure and 9 for the remaining half.

The coordination geometry around each barium ion is approximately that of an Archimedean antiprism. The disordered water molecule coordinates in such a way as to form a monocapped Archimedean antiprism (Figure 5). Except for atom O_3, all of the atoms coordinated to Ba_2 are firmly fixed in space by bonds to other atoms. Although the thermal parameters for atom O_3 are somewhat larger than for the other atoms surrounding Ba_2, there is no evidence that the coordination of the disordered water molecules as a ninth ligand at O_7 causes a significant structural rearrangement. In contrast, atoms O_4, O_5, and O_6 around Ba_1 are all free of bonds to other atoms. Atoms O_5 and O_6 are adjacent to the coordination position O_8 and a pronounced structural change involving these atoms appears to take place upon the coordination of the disordered water molecule to Ba_1 at O_8. This is evidenced by the magnitude and orientations of the thermal ellipsoids of atoms O_5 and O_8.

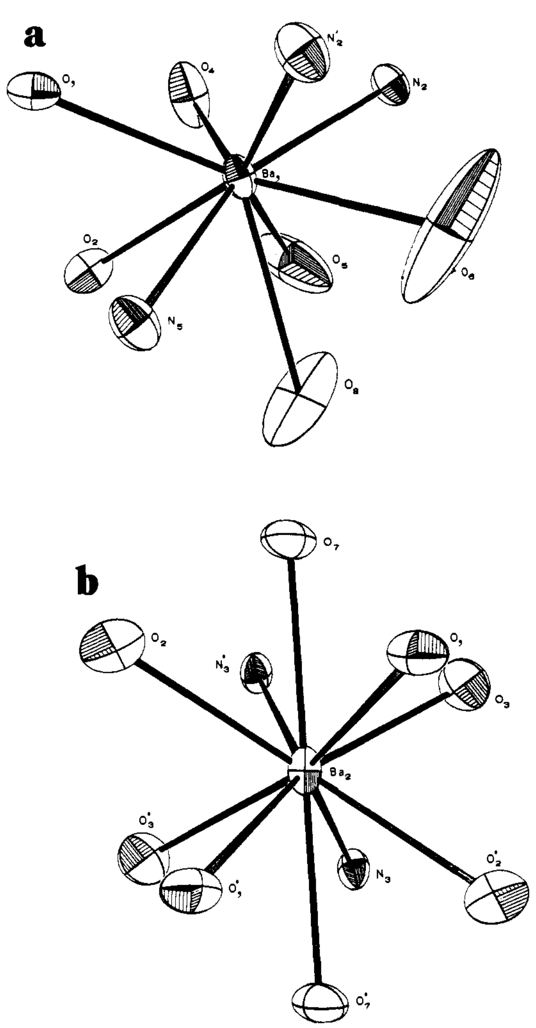

Figure 5. Perspective view of the coordination polyhedra around the barium ions. The vertical axes in both cases are the S_8 symmetry axes of the idealized Archimedean antiprism coordination polyhedron.

Table IX. Least-Squares Planes[a] in Archimedean Antiprisms[b]

Plane	Equation	Atom	Distance from plane, Å
1[c]	$A = 5.87$	N_5	0.079 (5)
	$B = 1.62$	O_2	−0.085 (5)
	$C = 11.13$	O_5	0.306 (11)
	$D = -1.45$	O_6	−0.535 (15)
2	$A = 5.65$	N_2	−0.058 (5)
	$B = 1.27$	N_2'	0.058 (5)
	$C = 1.15$	O_1	0.012 (4)
	$D = 1.73$	O_4	−0.070 (9)
3	$A = 5.57$	N_3'	0.028 (6)
	$B = -1.05$	O_1	0.014 (4)
	$C = 11.57$	O_2	−0.018 (5)
	$D = 4.33$	O_3	−0.028 (6)
4	$A = 5.57$	N_3	−0.028 (6)
	$B = -1.05$	O_1'	−0.014 (4)
	$C = 11.57$	O_2'	0.018 (5)
	$D = 1.45$	O_3'	0.028 (6)

[a] Equations for the least-squares planes in monoclinic coordinates of the form $Ax + By + Cz - D = 0$. [b] Primed notation for atoms forming the antiprisms corresponds to that used in Figures 4 and 5. [c] Planes 1 and 2 are for the atoms coordinated to Ba_1, and planes 3 and 4 are for the atoms coordinated to Ba_2.

The bond lengths and angles for the coordination about the barium ions are in Tables V and VI. The least-squares planes for the Archimedean antiprism geometry are presented in Table IX. The Ba-N bond lengths around Ba_1 are equal and average 2.86 (1) Å. The Ba_1-O bond lengths with the Archimedean antiprisms are also approximately equal and average 2.90 (2) Å.[56] The plane-to-plane distance for the Archimedean antiprism about Ba_1 is 3.18 Å. The plane-to-plane angle is 2.1°. The corresponding values for Ba_2 are 2.88 Å and 5.8°, respectively. The Ba_2-N_3 bond length is 2.877 (5) Å. The Ba_2-O_3 bond length is significantly shorter than the Ba_2-O_1 and Ba_2-O_2 bond lengths. Both of the latter oxygen atoms are bonded to two barium ions, whereas O_3 is bonded to only one Ba_2 ion.

Crystal Packing and Hydrogen Bonding. The three-dimensional structure is a complex network in which bridges between barium cations formed by oxygen atoms and by $[Co_2(CN)_{10}]^{6-}$ anions create infinite chains in several directions. The highly cross-linked and tightly packed nature of this structure presumably explains its unusual stability to oxidation. The barium ions Ba_1 and Ba_2 are bridged by atoms O_1 and O_2 (Figure 4). Pairs of Ba_1 ions related by the inversion center at $^1/_4$, $^1/_4$, 0 are linked by a bridge formed by nitrogen atoms N_2. Since barium ion Ba_2 is bonded to the two-fold related atoms N_3 and N_3' on different $[Co_2(CN)_{10}]^{6-}$ anions, pairs of Ba_2 ions are linked by the $[Co_2(CN)_{10}]^{6-}$ ion. Barium ion Ba_1 is also bonded to N_5 and N_2' such that both nitrogen atoms are in the same $[Co_2(CN)_{10}]^{6-}$ anion. The result is a bridge between the halves of the $[Co_2(CN)_{10}]^{6-}$ anion as shown in Figure 3. There is a large number of close nonbonded contacts between nitrogen and oxygen atoms which suggest the presence of hydrogen bonding. The location of over two-thirds of the hydrogen atoms makes it possible to provide a partial description of the hydrogen bonding. The description given is for only those hydrogen atoms that are considered to be located with confidence and are involved in obvious hydrogen bonds. Close nonbonded contacts are presented in Table X.

Table X. Nitrogen-Oxygen Distances

Atoms	Distance, Å	Atoms	Distance, Å
N_1O_1	2.811 (7)	N_4O_2	3.064 (8)
N_1O_3	3.067 (8)	N_4O_4	3.070 (10)
N_1O_5	3.193 (8)	N_4O_4	3.207 (9)
N_1O_6	2.980 (8)	N_4O_5	2.954 (15)
N_1O_7	2.897 (9)	N_4O_7	2.855 (18)
N_2O_6	2.910 (11)	N_5O_1	2.967 (7)
N_2O_6	3.055 (11)	N_5O_1	3.186 (7)
N_3O_4	3.178 (10)	N_5O_8	2.889 (5)
N_3O_6	3.009 (9)		
N_3O_7	3.037 (11)		

The axial nitrogen N_1 forms a strong hydrogen bond to O_1 *via* H_{11} and a weak bond to O_5 *via* H_{52}. A number of other short interatomic distances involving N_1 are observed which may be weak hydrogen bonds. The coordination of nitrogen N_2 to two barium ions makes formation of a strong hydrogen bond unlikely, but the N_2-O_6 distance is short (2.91 Å). The interactions of nitrogen N_3 are similarly ambiguous with one short interaction to O_6 of 3.01 Å.

Table XI. Summary of Some Co–C and C–N Cyanide Bond Lengths in Cobalt(III) Cyanide Complexes[a]

Compound	Co–C, Å	C–N, Å	Ref
$K_3[Co(CN)_6]$[b]	1.89	1.15	*e*
$D_3[Co(CN)_6]$[b]	1.883 (9)	1.147 (10)	*f*
$[Cr(en)_3][Co(CN)_6] \cdot 6H_2O$	1.869 (12)	1.155 (8)	*g*
$Cs_2Li[Co(CN)_6]$	1.90 (2)	1.16 (2)	*h*
$[Co(((NH_2CH_2CH_2)_2NCH_2)_2)][Co(CN)_6] \cdot 2H_2O$	1.92 (2)	1.14 (3)	*i*
$[(NH_3)_5Co\text{-}NC\text{-}Co(CN)_5]$	1.890 (4)	1.146 (7)	*j*
$K_3[Co(CN)_5(CF_2CHF_2)]$	1.894 (14)[c] 1.927[d]		67
$Ba_3[Co_2(CN)_{10}] \cdot 13H_2O$	1.885 (5)[c] 1.946 (6)[d]	1.151 (4)	This study

[a] Much earlier X-ray studies of $K_3[Co(CN)_6]$ and $Cd_3[Co(CN)]_6$ have been omitted from the table. The Co–C bond lengths reported in both cases are not reliable. [b] Neutron diffraction study. [c] Equatorial bond. [d] Axial bond. [e] Y. Okaya, R. Pepinsky, Y. Takeuchi, H. Kuroya, A. Shimada, P. Gallitelli, N. Stemple, and A. Beevers, *Acta Crystallogr.*, **10**, 798 (1957). [f] H. U. Güdel, A. Ludi, P. Fischer, and W. Hälg, *J. Chem. Phys.*, **53**, 1917 (1970). [g] K. N. Raymond and J. A. Ibers, *Inorg. Chem.*, **7**, 2333 (1968). [h] A. Wolberg, *Acta Crystallogr., Sect. B*, **25**, 161 (1969). [i] A. Muto, F. Marumo, and Y. Saito, *ibid.*, **26**, 226 (1970). [j] B. Wang, W. P. Schaefer, and R. E. Marsh, *Inorg. Chem.*, **10**, 1492 (1971).

Nitrogen atom N_4 is surrounded by several oxygen atoms with short nonbonded distances. There is a bond to O_2 *via* H_{21} and to O_4 *via* H_{42}. Although there is one short interaction between nitrogen N_5 and O_1 (2.97 Å), there is no direct evidence of hydrogen bonds formed between N_5 and proton donors in the structure.

Discussion of the Structure of $[Co_2(CN)_{10}]_6^-$

We regard the difference between the axial Co–C bond length, 1.946 (6) Å, and the average equatorial Co–C bond length, 1.885 (5) Å, as highly significant. Because of the basicity of the highly charged $[Co_2(CN)_{10}]^{6-}$ anion,[37] one possibility that cannot be ignored is that the axial cyanides are protonated and one of the oxygen atoms around the barium ions is present as OH^- rather than H_2O. The short Ba_2–O_3 bond length, 2.714 (5) Å, would make O_3 a plausible candidate for a hydroxide ion, but we see no evidence in the difference Fourier map for a hydrogen bound to atom N_1 at a distance of approximately 1 Å. We therefore conclude that the differences in bond length must be explained by differences in bonding between axial and equatorial sites of the $[Co_2(CN)_{10}]^{6-}$ anion for otherwise equivalent cyanide ligands. The difference, 0.061 (8) Å, is more than seven times its standard deviation as estimated from the variance-covariance matrix. Perhaps more important is the excellent agreement between the equatorial Co–C bond lengths, which establishes the degree of confidence that can be assigned to the difference between the axial and equatorial bond lengths.

Ground state as well as kinetic trans effects are well established, and, although the two are often observed together, a given ligand can cause one and not the other.[57] Basolo and Pearson have restricted use of the term "trans effect" to reaction rate phenomena.[58] The term "trans influence" has been used by Venanzi to describe ground-state phenomena such as changes in metal–ligand bond lengths.[59] Fenske and coworkers have carried out calculations on a series of octahedral manganese d^6 carbonyl and cyanide complexes.[60] These calculations have shown that differences in bonding for carbonyl complexes involve primarily rearrangements of the π-antibonding orbital participation of the metal and ligand. In contrast, for cyanide complexes, changes in the bonding involve rearrangements of both σ- and π-orbital participation. Calculations by Gray indicate that π bonding by cyanide in the ion $[Co(CN)_6]^{3-}$ is relatively unimportant when compared to σ bonding.[61] Vibrational data of Jones[62] and Gray[63] for $[M(CN)_6]^{3-}$ complexes are consistent with this and show that the order of π^*-orbital participation in the bonding is greater for Fe than for Co.

A recent study by Gray of the electronic spectra of a series of $[Co(CN)_5X]^{3-}$ complexes has shown that for X = SCN^-, NCS^-, N_3^-, and $NCSe^-$ there is no π bonding in the Co–X bond.[64] All of these studies indicate that when interpreting the Co–C bond lengths in $[Co_2(CN)_{10}]^{6-}$ most of the differences in bonding between axial and equatorial positions must be explained in terms of σ-bonding rearrangements.

If metal–ligand bond lengths are a criterion for choice of oxidation state, we may formally regard the cobalt atoms in $[Co_2(CN)_{10}]^{6-}$ as d^6, Co(III). This is because the equatorial average Co–C bond length of 1.885 (5) Å agrees very well with those found in $[Co(CN)_6]^{3-}$ and related complexes. A number of recent structure reports have provided bond lengths for comparison, and these are summarized in Table XI. The agreement between the average Co–C equatorial bond lengths in $[Co_2(CN)_{10}]^{6-}$ and those in $[(NH)_3)_5CoNCCo(CN)_5]$ is particularly striking and implies a marked similarity in the bonding.

A simple view of the $[Co_2(CN)_{10}]^{6-}$ anion regards it as just another $[Co(CN)_5X]$ complex of Co(III) in which X = $Co(CN)_5$. That is, the sixth ligand for the two equivalent $Co(CN)_5$ units is the electron pair of the Co–Co bond. This bond has a pronounced trans influence which, as described above, must be due primarily to rearrangement of the σ bonds formed by the cobalt atom. The Co–Co bond is almost certainly entirely σ in character. Its trans influence can be compared with those of a number of metal–metal bonds in such

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Table XII. A Comparison of Some Bond Lengths in Compounds Isoelectronic[a] with $[Co_2(CN)_{10}]^{6-}$ and Other Related Compounds

Complex	M–M bond, Å	M–C ax, Å[b]	M–C eq, Å[b]	Ref
$Mn_2(CO)_{10}$	2.923 (3)	1.792 (14)	1.83 (1)	39
$Tc_2(CO)_{10}$	3.036 (6)	1.899 (11)	2.00 (1)	65
$Re_2(CO)_{10}$	3.02 (1)			*d*
$[Cr_2(CO)_{10}]^{2-}$	2.97 (1)	1.84 (6)	1.87 (4)	*e*
$[Mo_2(CO)_{10}]^{2-}$	3.123 (7)	1.90 (5)	1.90 (6)	*e*
$[Co_2(CNCH_3)_{10}][ClO_4]_4$	2.736 (10)	1.92 (4)	1.87 (2)	40
$Ba_3[Co_2(CN)_{10}]\cdot 13H_2O$	2.794 (2)	1.946 (6)	1.885 (5)	This study
$Mn(CO)_5H$		1.822 (12)	1.853 (12)	*f*
$(CO)_5MnFe(CO)_4Mn(CO)_5$		1.805 (10)	1.855 (10)	*g*
$Mn(CO)_5(Sn(CH_3)_3)$		1.82 (2)	1.80 (3)	*h*
$Mn(CO)_5(Sn(C_6H_5)_3)$		1.79 (4)	1.75 (4)[c]	*i*
$Mn(CO)_5(h^5\text{-}C_5H_5Mo(CO)_3)$		1.70 (3)	1.77 (2)	*j*
$(CO)_4CoSn(C_6H_5)_2Mn(CO)_5$		1.79 (4)	1.84 (2)	*k*
$[(CO)_5CrHCr(CO)_5]^-$		1.82 (2)	1.88 (3)	*e*
$[(CO)_5CrICr(CO)_5]^-$		1.86 (7)	1.82 (2)	*l*

[a] Isoelectronic is used here in a comparison of valence shell configurations. [b] When these are average values, the standard deviation in the mean has been calculated as described in footnote 56. [c] The standard deviation quoted in this case is for an individual observation. The very large number of independent Mn–C bond lengths in this structure precludes the calculation of a realistic standard deviation by the formula given in footnote 56. [d] L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957). [e] L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7312 (1970). [f] S. J. La Placa, W. C. Hamilton, J. A. Ibers, and A. Davison, *Inorg. Chem.*, **8**, 1928 (1969). [g] P. A. Agron, R. D. Ellison, and H. A. Levy, *Acta Crystallogr.*, **23**, 1079 (1967). [h] R. F. Bryan, *J. Chem. Soc. A*, 696 (1968). [i] H. P. Weber and R. F. Bryan, *Acta Crystallogr.*, **22**, 822 (1967). [j] B. P. Biryukov and Yu. T. Struchkov, *Zh. Struct. Khim.*, **9**, 655 (1968). [k] B. P. Biryukov, O. P. Solodova, and Yu. T. Struchkov, *ibid.*, **9**, 228 (1968). [l] L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7327 (1970).

isoelectronic complexes as $Mn_2(CO)_{10}$, $[Cr_2(CO)_{10}]^{2-}$, and $[Co_2(CNCH_3)_{10}]^{4+}$. It is well established that the bond order of these metal–metal bonds is one. For example, the Tc–Tc bond length in $Tc_2(CO)_{10}$ is 3.036 (6) Å[65] while the much shorter bond length of 2.13 (1) Å in the $[Tc_2Cl_8]^{3-}$ ion is regarded as a multiple bond.[66]

Although only minimally significant when compared to the bond length errors, the axial Co–C bond in $[Co_2(CNCH_3)_{10}][ClO_4]_4$, 1.92 (4) Å, is longer than the average equatorial Co–C bond length, 1.87 (2) Å. These and other bond distances are compared in Table XII. Whereas the axial metal–carbon bonds in the cobalt cyanide and isocyanide compounds are *longer* than the equatorial bonds, the *reverse* is true in the group VIIa carbonyls. This relative elongation in the cobalt cyanides can be explained as due to a Co–Co σ bond which competes with the trans cyanide for the σ-bonding e_g metal orbitals ($d_{x^2-y^2}$ and d_{z^2}). As judged from the trans bond lengthening, the Co–Co bond seems to have about the same trans influence as the cobalt alkyl bond in $K_3[Co(CN)_5(CF_2CHF_2)]$[67] (see Table XI). Both Co–Co and Co–alkyl bonds are stronger σ bonds than the Co–C bond to cyanide. As described earlier, changes in bonding for metal cyanides are largely a function of rearrangement of the σ bonds for the complex. If a cyanide is removed from $[Co(CN)_6]^{3-}$ and replaced with $[Co(CN)_5]^{4-}$, the cyanide trans to the changed ligand position experiences a greater competition for σ bonding to the metal e_g orbitals. As a result, the bonding character in the metal–cyanide bond decreases, and the antibonding character increases. In contrast, if one performs a similar imaginary experiment with $[Mn(CO)_6]^+$, the replacement of CO by $[Mn(CO)_5]^-$ causes the trans carbonyl to experience greater competition for σ bonding to the e_g orbitals but much less competition for π bonding to the t_{2g} orbitals. As noted earlier, the primary factor which causes changes in metal–carbon bond order in carbonyls is the metal-to-ligand π bonding, and hence the trans bond strength is increased by the trans influence of the Mn–Mn bond.

None of the other entries in Table XII counter the argument just presented. In all of the compounds tabulated of the type $M(CO)_5X$, the ligand X is a much weaker π-bonding ligand than CO. Unfortunately, the experimental errors in most of the bond lengths are too large to allow a significant comparison of the axial and equatorial bond lengths. Even so, there is a very pronounced trend when all of the complexes are compared as a group, and in those cases where the esd's are small the axial bond lengths are always *shorter* than the equatorial.

A comparison of metal–metal bond lengths is also given in Table XII. The only two bonds that can be directly compared are the two Co–Co bonds. We ascribe the longer Co–Co bond in $[Co_2(CN)_{10}]^{6-}$ to the increased charge density throughout the complex and a resultant increase in non- and antibonding interactions. The $[Co_2(CNCH_3)_{10}]^{4+}$ cation can be thought of as the product of the addition of ten CH_3^+ ions to the $[Co_2(CN)_{10}]^{6-}$ anion. Two things occur with this addition. The first is a concentration of the electron density for the whole complex and a withdrawal of electron density from the metal center of the complex. The second is a decrease in the strength of the Co–C bond since isocyanides are intermediate in bonding properties between CN^- and CO. The latter phenomenon is the trans interaction argument described above but applied to the Co–Co bond. This argument can also be applied to a comparison with the Mn–Mn bond. The radius of the Mn ion is about 0.1 Å larger than that of Co;[40] thus the Mn–Mn bond length of 2.92 Å would predict a Co–Co bond length of 2.72 Å, all else being equal. This distance is still shorter than the other two Co–Co bond lengths and is consistent with the much weaker σ-bond strength of CO as compared to CNR or CN^-. The order of Co–C bond lengths is 2.72, 2.74, and 2.79 Å for the Co–Co–CO (hypothetical), Co–Co–CNR, and Co–

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Co–CN ligand arrangements, respectively. This order directly parallels the expected trend in trans interaction.

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Conformational Analysis. XVIII.[1] Force Field Calculations of Conformational Equilibria of Group IV Organometallic Compounds

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Abstract: Force field calculations of two conformations of CH_3MH_3, two of $(CH_3)_2MH_2$, two of $(CH_3)_3MH$, three of $CH_3CH_2MH_3$, four of $CH_3CH_2CH_2MH_3$, four of $CH_3MH_2CH_2CH_3$, two of $(CH_3)_2MHCH_2CH_3$, two of $(CH_3)_2MHCH(CH_3)_2$, four of $(CH_3CH_2)_2MH_2$, and two of $C_6H_{11}MH_3$ for two series of compounds where M is germanium and tin have been done. Comparisons are made with the previously reported silicon analogs. The parameters for the force field functions are chosen so that the calculated structures and torsional barriers of CH_3MH_3, $(CH_3)_2MH_2$, and $(CH_3)_3MH$ are consistent with the available microwave data. The remaining calculated structures and conformational energies await experimental tests. The conformations of germanium and tin compounds are predicted to be controlled by hydrogen–hydrogen nonbonded attractive terms and thus join silicon compounds in manifesting unique conformational properties in contrast to those of hydrocarbons.

It was reported in a recent paper[2] from this laboratory that force field calculations of the conformational energies of organosilicon compounds successfully predict their conformational properties as determined by nmr spectroscopy. This paper illustrated that the conformational concepts based on carbon compounds are not directly comparable to their silicon analogs. Attractive van der Waals interactions stabilize the gauche conformation of 2-silabutane with respect to the anti conformation. Other compounds containing the 2-silabutane structural unit such as 2-methyl-2-silabutane, 2,3-dimethyl-2-silabutane, and 3-silapentane exhibit the same ordering of conformational energies. In view of the successful extension of force field calculations to hydrocarbons containing silicon as a heteroatom, it was logical to consider the organogermanes and organostannanes. Lead compounds containing lead–hydrogen bonds are sufficiently unstable to have precluded the determination of the necessary physical properties with which to parameterize the force field equations. Accordingly, lead compounds are excluded from this study.

Force Field Calculations

The classical model used in this study involves the calculation of the strain energy, E_s, of the conformation which is defined as the sum of energy terms given in eq 1. The individual terms are the energies associated with bond stretching, bond angle deformations, bond torsions, and nonbonded interactions. The force field can be viewed as two harmonic potentials involving bonded atoms and two nonbonded potentials. The harmonic potentials are given by eq 2 and 3. For

$$E_s = E_r + E_\theta + E_\phi + E_{nb} \qquad (1)$$

$$E_r = \sum {}^1/_2 k_r (l - l_0)^2 \qquad (2)$$

$$E_\theta = \sum {}^1/_2 k_\theta (\theta - \theta_0)^2 \qquad (3)$$

each bond or bond angle, the l_0 and θ_0 values are selected to represent "strain free" values. The individual force constants k_r and k_θ are calculated or estimated from normal coordinate analysis of the infrared and Raman spectra of representative molecules.

The torsional potential is given by eq 4 for the threefold barrier involved in the molecules of interest. The

$$E_\phi = \sum {}^1/_2 k_\phi (1 + \cos 3\phi) \qquad (4)$$

dihedral angle is given by ϕ and the barrier height by k_ϕ.

The Hill function given in eq 5 is used to account for the attractive and repulsive van der Waals forces.

$$E_{nb} = \sum \epsilon \{-2.25\alpha^{-6} + 8.28 \times 10^5 \exp(-\alpha/0.0736)\} \qquad (5)$$

Energy minimization was achieved by utilizing the method of Boyd.[3] When the root-mean-square deviation of the coordinate position was less than 0.002 Å the iterative process was terminated.

Two additional programs were placed prior to the minimization method in order to decrease the labor of preparing the input data. A molecule builder program calculates the coordinates of the molecules and

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[1] This research was supported by Grants GP-9231 and GP-33423 from the National Science Foundation.

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