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Structural Characterization of the Pentacyanocobaltate(II) Anion in the Salt $[NEt_2(i\text{-}Pr)_2]_3[Co(CN)_5]$

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The structure analysis of the salt $[NEt_2(i\text{-}Pr)_2]_3[Co(CN)_5]$ has been determined by single-crystal X-ray diffraction techniques. The square-pyramidal $[Co(CN)_5]^{3-}$ anion in this *yellow* form of the complex is truly five-coordinate with no axial interaction in the sixth ligand position; comparison with the green form of the isoelectronic $[Co(CNC_6H_5)_5]^{2+}$ cation would indicate that the *green* form of the $[Co(CN)_5]^{3-}$ ion as observed in aqueous solution, among others, *is* weakly coordinated in the sixth position. The yellow $[Co(CN)_5]^{3-}$ anion has an apical Co–C bond distance of 2.010 (16) Å and an average basal Co–C distance of 1.893 (8) Å. The C–N distances were constrained to be 1.15 Å. The trans C_{basal}–Co–C_{basal} bond angle is 164.7 (4)°. The cobalt atom lies 0.251 (7) Å above the plane of the basal carbon atoms. The yellow, prism-like crystals of $[NEt_2(i\text{-}Pr)_2]_3[Co(CN)_5]$ conform to space group $P2_1/m$ with $a = 17.766$ (6) Å, $b = 10.674$ (4) Å, $c = 10.676$ (4) Å, and $\beta = 105.85$ (1)°. For $Z = 2$, $\rho_{calcd} = 1.15$ g/cm³ and $\rho_{obsd} = 1.14$ g/cm³. There is a structural disorder, which involves the alkylammonium cations, that is only partially resolved. Intensity data were collected by an automated diffractometer (Mo Kα monochromatic radiation) and solved by the heavy-atom technique; for 1498 reflections with $F^2 > 3\sigma(F^2)$, the structure refined to $R_1 = 9.6\%$ and $R_2 = 11.0\%$.

Introduction

The question of the structure of the pentacyanocobaltate(II) anion has provoked much debate over the past two decades since Adamson[2] characterized it as a pentacoordinate species in aqueous solution. It is intriguing that such a relatively simple, easily synthesized complex has eluded structural characterization for so long. The primary reason for this is the tendency of this complex to dimerize, converting the green (in aqueous solution) d^7 ion to the deep violet $[Co_2(CN)_{10}]^{6-}$ dimer whose structure was recently characterized[3,4] and which satisfies the 18-electron rule. The extensive literature of the pentacyanocobaltate ion has been reviewed elsewhere.[5,6] Much of this work is concerned with hydrogenation of organic compounds using $[Co(CN)_5]^{3-}$ or its hydride as a catalyst.[6-8]

Since previous efforts at isolating the monomeric $[Co(CN)_5]^{3-}$ species in crystalline form for X-ray studies were unsuccessful, other techniques, primarily ESR and uv–visible spectroscopy, were used to characterize the anion. Both the ESR spectrum of ethylene glycol–water frozen solutions[9] and the visible spectrum[10,11] of aqueous solutions of $[Co(CN)_5]^{3-}$ have been interpreted in terms of C_{4v} symmetry for the anion. In addition, ESR studies of irradiated $K_3[Co(CN)_6]$ also indicated C_{4v} symmetry for the ion present (presumed to be $[Co(CN)_5]^{3-}$).[12-18] Pratt and Williams[19] suggested that the anion in aqueous solutions was actually hexacoordinate with a weakly coordinated water molecule in the sixth position (with the C_{4v} symmetry maintained). Gray and coworkers argued that the anion was instead a true pentacoordinate species since the visible spectrum for the aqueous $[Co(CN)_5]^{3-}$ solution and that for the irradiated $K_3[Co(CN)_6]$ are virtually identical.[12]

The first report of a solid containing the $[Co(CN)_5]^{3-}$ anion described a white powder precipitated from a green solution of $Li_3[Co(CN)_5]$ in ethanol.[20] Recently, a yellow form of pentacyanocobaltate in dimethylformamide (DMF) solution was reported, and a yellow solid was also obtained.[21] Our search for crystals suitable for X-ray studies led to the diethyldiisopropylammonium salt. We report here the crystal and molecular structure of $[NEt_2(i\text{-}Pr)_2]_3[Co(CN)_5]$, a salt of the yellow form of the pentacyanocobaltate(II) anion.[22]

Experimental Section

Preparation of $[NEt_2(i\text{-}Pr)_2]_3[Co(CN)_5]$. All preparative operations were carried out under dry nitrogen using glass Schlenk apparatus. All solvents were reagent grade, deoxygenated with N_2 before use, and stored under N_2 and Type 3A Linde molecular sieves.

The $[NEt_2(i\text{-}Pr)_2]I$ starting material was made by treating 97 g (0.75 mol) of *N,N*-diisopropylethylamine (Aldrich) with 140 g (0.90 mol) of iodoethane. The reaction mixture was refluxed in methanol for several days; yield 103 g of $[NEt_2(i\text{-}Pr)_2]I$ (48%). The iodide salt was converted to $[NEt_2(i\text{-}Pr)_2]^+CN^-$ by anion-exchange chromatography. The anhydrous methanol CN^- exchange column was prepared according to Solodar.[23] A 1 *M* methanol solution of 100 g (0.35 mol) of $[NEt_2(i\text{-}Pr)_2]I$ was slowly washed down the column with anhydrous methanol. The eluent was collected (approximately 1500 ml), and the methanol was removed by rotoevaporation. The solid residue was collected on a filter and washed three times with ethyl acetate and twice with diethyl ether. The extremely hygroscopic white solid was stored under vacuum in a P_2O_5 desiccator; yield 20 g of $[NEt_2(i\text{-}Pr)_2]CN$ (31%).[24]

A dimethylformamide (DMF) solution of $[NEt_2(i\text{-}Pr)_2]_3[Co(CN)_5]$ was prepared by treating 2.42 g (0.0133 mol) of $[NEt_2(i\text{-}Pr)_2]CN$ with 0.325 g (0.0025 mol) of anhydrous $CoCl_2$ in approximately 15 ml of DMF. The deep yellow ca. 0.2 *M* solution was slowly cooled to −20° to yield yellow crystals of $[NEt_2(i\text{-}Pr)_2]_3[Co(CN)_5]$. These crystals are extremely hygroscopic and oxygen sensitive. They decompose within a few seconds if exposed to the atmosphere. The yellow $[NEt_2(i\text{-}Pr)_2]_3[Co(CN)_5]$ solution slowly decomposes at room temperature over a period of 10–20 hr to a blue-green color even under a dry N_2 atmosphere. Presumably, the decomposition is due to the slow reaction of the $[NEt_2(i\text{-}Pr)_2]^+$ cation with the small equilibrium quantity of free CN^- ion to yield a tertiary amine and a nitrile.

Unit Cell and Diffraction Data. A series of precession photographs showed that the crystal was monoclinic and exhibited the absences $0k0$, $k \neq 2n$. These absences are consistent with space groups $P2_1$ and $P2_1/m$; as shown later, the latter is correct. Of a large number of the crystals examined by the precession method, most were found to be twinned, resulting in an apparently tetragonal cell. The virtually identical values of the *b* and *c* constants probably contributed to the large number of twinned crystals that were found. The data crystal, as described later, was not twinned.

Intensity data were collected on an automated Picker FACS-1 four-circle diffractometer.[25,26] The data were processed as described previously[28] with a parameter *p*, introduced to prevent overweighting strong reflections, chosen as 0.04. Equivalent reflections were averaged. The *R* factor for averaging is 3.1%. The density of several crystals was determined by the flotation method in toluene–carbon tetrachloride solutions. The measured density is 1.14 g/cm³; the calculated density is 1.15 g/cm³ for two formula units per cell. Crystal data are summarized in Table I.

Solution and Refinement of Structure. The structure was solved by standard Patterson and difference Fourier techniques.[25] Full-matrix least-squares refinements were carried out for the 1498 reflections with $F^2 > 3\sigma(F^2)$.[29-32] The positions of the Co, two cyanide carbons, two cyanide nitrogens, and the nitrogen for one of the cations were found from the three-dimensional, origin-removed, sharpened Patterson map. Subsequent difference Fourier and least-squares calculations located the remainder of the nonhydrogen atoms. The individual atoms were refined anisotropically with the exception of C_{17}, C_{27}, C_{35}, C_{36}, and C_{38}. These atoms did not refine well with the anisotropic model used. Due to positional disorder imposed by the crystallographic mirror plane, some of the atoms of the cations have partial occupancy in their refinement. This is because the cations are closely related to a

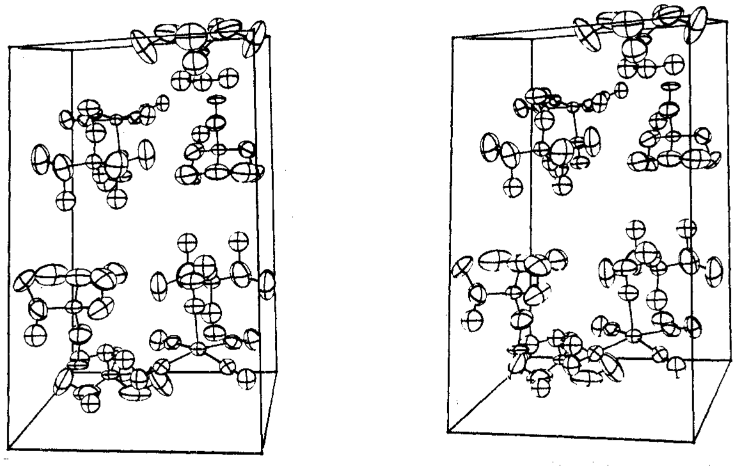

Figure 1. Stereoscopic packing diagram of the $[NEt_2(i\text{-}Pr)_2]_3[Co(CN)_5]$ structure. The vertical axis is *a*, and *b* is the horizontal axis. The origin is at the left rear bottom corner of the cell. The individual atoms are drawn at 30% probability contours of the thermal motion.

Table I. Summary of Crystal Data

Molecular formula	$[N(C_2H_5)_2(C_3H_7)_2]_3[Co(CN)_5]$
Mol wt	663.95
Space group	$P2_1/m$
Cell constants[a]	
a	17.766 (6) Å
b	10.674 (4) Å
c	10.676 (4) Å
β	105.85 (1)°
V	1947.5 Å^3
Formula units/cell	2
Calcd density	1.15 g/cm^3
Obsd density	1.14 g/cm^3
Crystal dimensions	0.030 × 0.032 × 0.038 cm
Linear absorption coeff, μ	4.36 cm^{-1}

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

tetraneopentylammonium structure, such that facile disorder occurs between methyl and proton substituents.

The C–N bond lengths for the three crystallographically independent cyanides were constrained to be 1.15 Å. The need for such constraints with low-resolution data sets has been discussed before.[33,34] After all of the nonhydrogen atoms had refined, no peaks corresponding to reasonable hydrogen atomic positions were found in a difference Fourier map. Since the hydrogens were apparently "smeared out" by the high thermal motion and positional disorder in the cations, the final refinement was made without any hydrogen atom contribution. The structure refined to R_1 = 9.6% and R_2 = 11.0%.[35] The relatively large final *R* factor is due to the disorder and high thermal motion in the three cations. During the final stages of refinement, when various models for the disorder in the cations were being tried, the geometry of the $[Co(CN)_5]^{3-}$ anion was not significantly affected. The final difference Fourier showed no peak greater than 0.9 e/Å^3 (approximately 20% of a carbon atom). Table II gives the positional and thermal parameters for the nongroup atoms. Table III lists the root-mean-square (rms) amplitudes of vibration of the individual atoms derived from the anisotropic thermal motion.[36]

Description of the Structure

The crystal structure consists of discrete $[Co(CN)_5]^{3-}$ anions and $[NEt_2(i\text{-}Pr)_2]^+$ cations. As illustrated in the stereoscopic crystal packing diagram in Figure 1, the anion and all three cations are situated on a mirror plane. The square-pyramidal $[Co(CN)_5]^{3-}$ anion, shown in Figure 2, is truly pentacoordinate with no atoms in the vicinity of the sixth ligand position trans to the apical cyanide. The atoms of the apical cyanide are constrained to be on the mirror plane, while the two independent basal ligands are off the mirror plane. The apical Co–C distance is 2.010 (16) Å, and the average basal Co–C distance is 1.893 (8) Å. These bond distances and others are listed in Tabel IV. The Co atom lies 0.251 (7) Å above the plane formed by the four basal carbons, resulting in a C_2–Co–C_3 angle of 164.7 (4)° and an average C_{apical}–Co–C_{basal} angle of 97.6 (8)°. As expected, all of the Co–C–N bond angles are virtually linear. These and other bond angles are listed in Table V.

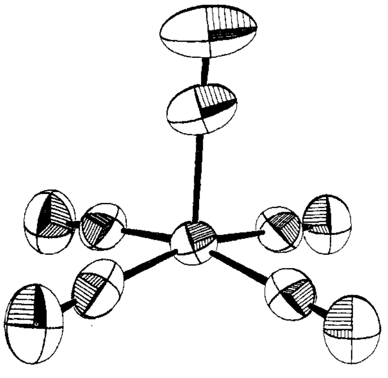

Figure 2. Perspective drawing of the square-pyramidal pentacyanocobaltate(II) anion in $[NEt_2(i\text{-}Pr)_2]_3[Co(CN)_5]$. The mirror plane is the plane of projection such that the cyanide carbon atom C_3 is in the foreground and C_2 is in the background. The individual atoms are drawn at 40% probability contours of the thermal motion.

The three $[NEt_2(i\text{-}Pr)_2]^+$ cations exhibit high thermal motion and some positional disorder about the mirror plane. The presence of the disorder is not surprising upon examination of a model of the $[NEt_2(i\text{-}Pr)_2]^+$ ion. The gross geometry of the cation appears almost spherical with no free rotation of the ethyl and isopropyl groups. There are two possible conformers of the cation (both are present in the structure); in both of these the ethyl and isopropyl groups can partially disorder with one another.

The first cation has an ethyl group and an isopropyl group on the mirror plane, while the remaining ethyl and isopropyl groups are disordered on either side of the mirror plane with C_{17} having an occupancy of only $^1/_2$. The disorder has the appearance of an ordered ethyl group plus half of a third carbon.

The second cation has one ethyl group on the mirror plane. Both atoms of the second ethyl group, C_{22} and C_{27}, refine very near the mirror plane with half-occupancy. The two isopropyl groups are symmetry related by the mirror plane and fairly well ordered although the thermal motion of one of the methyl carbons, C_{26}, is highly anisotropic.

The atoms of the third cation have the highest thermal motion of all. Again, one ethyl group is on the mirror plane. In addition, there is an ethyl–isopropyl disorder across the mirror plane very similar to that described for the first cation. In this case C_{37} is the carbon with half-occupancy. The most severely disordered group is the final isopropyl group on the

Table II. Positional and Thermal Parameters ($\times 10^4$) for the Atoms in $[NEt_2(i\text{-}Pr)_2]_3[Co(CN)_5]$

	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	.22394(10)[b]	1/4	.90279(18)	41.0(8)	139.9(25)	132.0(26)	0	21.9(10)	0
C_1	.3401(9)	1/4	.9853(17)	51(8)	220(24)	262(29)	0	39(13)	0
N_1	.4065(9)	1/4	.0341[c]	53(7)	327(28)	450(37)	0	23(14)	0
C_2	.2005(5)	.3767(10)	.0108(9)	53(5)	140(14)	128(14)	-6(6)	16(6)	6(11)
N_2	.1846(6)	.4534(9)	.0747[c]	92(5)	152(13)	175(14)	2(6)	44(7)	-3(10)
C_3	.2184(6)	.1273(10)	.7729(10)	58(5)	178(17)	167(16)	24(7)	48(8)	36(14)
N_3	.2107(7)	.0541(10)	.6912[c]	119(7)	184(15)	201(16)	27(8)	78(9)	10(12)
N_4	.6676(6)	1/4	.0827(11)	41(5)	167(17)	178(16)	0	19(8)	0
N_5	.3249(8)	1/4	.4305(13)	74(7)	181(19)	156(18)	0	45(9)	0
N_6	.9576(9)	1/4	.7362(17)	33(6)	230(25)	227(25)	0	46(11)	0
C_{11}	.5803(9)	.0905(15)	.9233(18)	92(8)	320(26)	461(35)	-74(12)	-5(14)	-135(24)
C_{12}	.6612(9)	.1206(15)	.0074(17)	91(9)	288(23)	443(34)	1(11)	-2(14)	-168(26)
C_{13}	.6057(14)	1/4	.167(3)	84(13)	501(62)	486(59)	0	103(23)	0
C_{14}	.8202(9)	1/4	.1412(20)	28(6)	281(28)	373(35)	0	58(12)	0
C_{15}	.7513(12)	1/4	.1847(21)	71(10)	316(35)	299(34)	0	-21(17)	0
C_{16}	.6059(11)	.1137(2)	.2309(23)	119(11)	547(43)	603(46)	26(17)	100(18)	403(41)
C_{17}	.7109(19)	.1951(29)	.873(3)	16.2(12)[d]					
C_{21}	.1719(14)	1/4	.3435(20)	108(13)	407(45)	204(29)	0	-1(16)	0
C_{22}	.3970(20)	.205(5)	.677(4)	132(20)	465(156)	334(55)	-28(33)	95(28)	88(67)
C_{23}	.3337(15)	.1312(23)	.3519(21)	192(18)	377(39)	388(36)	54(21)	102(19)	-66(33)
C_{24}	.3105(15)	.0121(18)	.4122(25)	247(21)	194(24)	636(58)	4(17)	134(27)	83(32)
C_{25}	.2475(27)	1/4	.4704(44)	299(36)	294(42)	814(104)	0	389(55)	0
C_{26}	.4237(26)	.1391(33)	.374(7)	309(34)	702(76)	3290(359)	207(40)	872(106)	336(122)
C_{27}	.380(3)	.197(5)	.563(6)	21.0(21)[d]					
C_{31}	.0110(11)	.1361(31)	.7522(27)	82(9)	697(65)	599(57)	-76(21)	90(19)	-264(51)
C_{32}	.0168(18)	-.0157(20)	.2338(28)	261(24)	355(38)	669(66)	-170(27)	171(32)	-141(40)
C_{33}	.9318(18)	1/4	.8722(37)	118(18)	400(47)	439(60)	0	97(29)	0
C_{34}	-.0054(21)	1/4	-.0136(26)	142(19)	558(64)	247(37)	0	61(21)	0
C_{35}	.8555(31)	1/4	.625(6)	25.7(16)[d]					
C_{36}	.885(4)	.146(6)	.574(6)	26.4(23)[d]					
C_{37}	.0189(17)	.179(4)	.581(4)	74(14)	764(160)	455(67)	11(29)	94(26)	-138(73)
C_{38}	.833(7)	1/4	.748(14)	31(5)[d]					

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[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell)]$.

[b] Standard deviations of the least significant figures are given here and in subsequent tables in parentheses.

[c] Determined by constraining the C-N distance to 1.15 Å.

[d] Isotropic temperature factor (x 1).

mirror plane. Carbon atom C_{35} (bonded to the nitrogen) is on the mirror plane. The other two atoms are disordered with C_{36} off the mirror plane and C_{38} on the mirror. Both of these atoms were refined at half-occupancy.

The high thermal motion and disorder has a marked effect on the bond lengths in the cations. The N–C and C–C bond lengths are expected to be 1.48 and 1.54 Å, respectively.[37] For the first cation N–C distances averaged 1.59 Å; the average for the C–C distances was about 1.51 Å. For the second cation these distances averaged 1.56 and 1.57 Å, respectively. For the third cation, there was a very wide range of distances due to the poor refinement of some of the carbon atoms. These interatomic distances and others are given in Table IV. Table V lists the bond angles in the cations.

Discussion

In addition to resolving a continuing controversy, the structure determination of the yellow form of the $[Co(CN)_5]^{3-}$ ion completes our study of pentacoordination in metal cyanide and isocyanide complexes. The pentacyanonickelate(II) anion, until now the only structurally characterized pentacyanide, has been studied in three different salts.[38,39] In all three, the $[Ni(CN)_5]^{3-}$ anion is a square pyramid, although one of the salts has a distorted trigonal-bipyramidal anion as well.[38] Table VI compares the pertinent bond lengths and angles of the $[Co(CN)_5]^{3-}$ anion to those of $[Ni(CN)_5]^{3-}$. Both complexes have the same type of ligand, the same charge, and virtually the same metal ionic radii for the 2+ oxidation state (0.74 and 0.72 Å for Co^{2+} and Ni^{2+}, respectively).[40] In addition, neither complex has a weakly coordinated ligand below the basal plane. Although the $M-C_{basal}$ bond lengths are the same for both ions, the $M-C_{apical}$ distances differ by more than 0.1 Å. If the bonding is assumed to be dominantly σ in character, this is readily explained. The additional electron in the d_{z^2} antibonding orbital of the d^8 $[Ni(CN)_5]^{3-}$ tends to weaken, and therefore lengthen, the apical M–C bond to an even greater extent than that for the d^7 $[Co(CN)_5]^{3-}$. In contrast, the same effect is not observed for the d^7 [Co-

Table III. Root-Mean-Square Amplitudes of Vibration along Principal Axes (Å × 10^3)

Atom[a]	Axis 1	Axis 2	Axis 3
Co	244 (3)	265 (3)	284 (3)
C_1	270 (21)	356 (20)	375 (21)
N_1	280 (18)	433 (18)	502 (20)
C_2	260 (14)	274 (13)	299 (14)
N_2	295 (13)	300 (12)	369 (11)
C_3	246 (15)	275 (14)	360 (15)
N_3	284 (13)	321 (12)	433 (12)
N_4	245 (15)	309 (16)	313 (14)
N_5	269 (16)	324 (17)	332 (16)
N_6	196 (23)	349 (19)	366 (20)
C_{11}	253 (18)	475 (17)	557 (20)
C_{12}	309 (19)	373 (15)	576 (23)
C_{13}	312 (29)	512 (31)	538 (32)
C_{14}	179 (23)	401 (20)	448 (21)
C_{15}	286 (27)	430 (23)	463 (27)
C_{16}	291 (22)	414 (20)	740 (27)
C_{21}	310 (21)	428 (23)	483 (25)
C_{22}	337 (37)	478 (38)	533 (81)
C_{23}	366 (22)	494 (23)	562 (25)
C_{24}	319 (21)	569 (25)	616 (26)
C_{25}	375 (32)	413 (27)	729 (37)
C_{26}	285 (30)	653 (38)	1312 (57)
C_{31}	319 (20)	464 (26)	715 (32)
C_{32}	334 (21)	559 (28)	705 (32)
C_{33}	388 (32)	477 (28)	491 (35)
C_{34}	352 (27)	459 (29)	570 (35)
C_{37}	290 (31)	467 (38)	678 (86)

[a] Atoms refined isotropically are not included.

Table IV. Bond Distances in $[NEt_2(i\text{-}Pr)_2]_3[Co(CN)_5]$[a]

Atoms	Distance, Å	Atoms	Distance, Å
Co-C_1	2.010 (16)	C_{11}-C_{12}	1.51 (2)
Co-C_2	1.896 (11)	C_{12}-C_{17}	2.04 (4)
Co-C_3	1.892 (11)	C_{13}-C_{16}	1.61 (2)
Co-N_1	3.160 (15)	C_{14}-C_{15}	1.42 (3)
Co-N_2	3.046 (8)	C_{21}-C_{25}	1.63 (5)
Co-N_3	3.041 (8)	C_{22}-C_{27}	1.57 (6)
N_4-C_{12}	1.59 (2)	C_{23}-C_{24}	1.53 (3)
N_4-C_{13}	1.60 (3)	C_{23}-C_{26}	1.55 (4)
N_4-C_{15}	1.59 (2)	C_{31}-C_{32}	1.40 (3)
N_5-C_{23}	1.55 (2)	C_{31}-C_{37}	1.92 (5)
N_5-C_{25}	1.55 (3)	C_{33}-C_{34}	1.41 (3)
N_5-C_{27}	1.59 (6)	C_{35}-C_{36}	1.40 (6)
N_6-C_{31}	1.52 (3)	C_{35}-C_{38}	1.48 (12)
N_6-C_{33}	1.64 (3)		
N_6-C_{35}	1.88 (5)		

[a] C-N distances constrained to be 1.15 Å in the $[Co(CN)_5]^{3-}$ anion.

Table V. Bond Angles in $[NEt_2(i\text{-}Pr)_2]_3[Co(CN)_5]$

Atoms	Angle, deg	Atoms	Angle, deg
C_1-Co-C_2	95.9 (4)	C_{11}-C_{12}-N_4	114.4 (12)
C_1-Co-C_3	99.4 (5)	C_{11}-C_{12}-C_{17}	100.9 (15)
C_2-Co-C_3'	164.7 (4)	N_4-C_{12}-C_{17}	91.9 (13)
C_2-Co-C_3	88.6 (4)	N_4-C_{13}-C_{16}	108.5 (12)
C_2-Co-C_2'	91.1 (6)	C_{16}-C_{13}-C_{16}'	129.9 (29)
C_3-Co-C_3'	87.6 (6)	N_5-C_{15}-C_{14}	120.3 (17)
Co-C_1-N_1	179.1 (14)	C_{24}-C_{23}-N_5	111.9 (17)
Co-C_2-N_2	178.5 (9)	C_{24}-C_{23}-C_{26}	111.4 (24)
Co-C_3-N_3	176.2 (11)	N_5-C_{23}-C_{26}	97.2 (26)
		N_5-C_{25}-C_{21}	111.4 (27)
C_{12}-N_4-C_{12}'	121.1 (16)	N_5-C_{27}-C_{22}	113.2 (35)
C_{12}-N_4-C_{13}	108.7 (9)	C_{32}-C_{31}-N_6	121.2 (18)
C_{12}-N_4-C_{15}	105.8 (8)	C_{32}-C_{31}-C_7	116.0 (24)
C_{13}-N_4-C_{15}	105.8 (15)	N_6-C_{31}-C_{37}	84.8 (23)
C_{23}-N_5-C_{23}'	109.6 (21)	N_6-C_{33}-C_{34}	114.8 (23)
C_{23}-N_5-C_{25}	112.2 (14)	C_{36}-C_{35}-C_{36}'	105 (7)
C_{23}-N_5-C_{27}	93.6 (22)	C_{36}-C_{35}-N_6	81 (4)
C_{25}-N_5-C_{27}	97.8 (25)	C_{36}-C_{35}-C_{38}	124 (4)
C_{31}-N_6-C_{31}'	105.9 (20)	C_{38}-C_{35}-N_6	84 (6)
C_{31}-N_6-C_{33}	102.5 (15)		
C_{31}-N_6-C_{35}	122.4 (12)		
C_{33}-N_6-C_{35}	96.2 (24)		

Table VI. Comparison of Geometry of d^7 and d^8 Square-Pyramidal Complexes

	$[Co(CN)_5]^{3-}$[a]	$[Ni(CN)_5]^{3-}$[b]	$[Co(CNC_6H_5)_5]^{2+}$[c]	$[Co(CNC_6H_5)_5]^{+}$[d]
M-C_{apical},[e] Å	2.010 (16)	2.14 (1)	1.95 (1)	1.88 (3)
M-C_{basal}(av), Å	1.894 (8)	1.89 (1)	1.84 (1)	1.84 (2)
trans basal C-M-C(av), deg	164.7 (4)	161.5 (2)	169.8 (4)	156.5 (9)
C_{basal}-M-C_{apical}(av), deg	97.6 (8)	99	95.0 (3)	101.8 (14)
M-basal plane, Å	0.25	0.30	0.16	0.37

[a] This study. [b] Reference 39. [c] Reference 41. [d] Reference 42. [e] M is the metal atom.

$(CNC_6H_5)_5]^{2+}$ and the d^8 $[Co(CNC_6H_5)_5]^+$ ions (see Table VI), because the greater π-bonding ability in the phenyl isocyanide ligand relative to cyanide and the weak coordination of ClO_4^- to the Co(II) complex reverse the structural effects which are due to only the σ bonding in the square-pyramidal complexes. There is a slight increase in the C_{apical}-M-C_{basal} angle in going from $[Co(CN)_5]^{3-}$ to $[Ni(CN)_5]^{3-}$. This trend is in the opposite direction to that discussed by Sacconi[43] in which a lengthening of the M-C apical bond in Co(II) and Ni(II) square-pyramidal complexes is accompanied by a *decrease* in the apical angle toward 90°.

Several years ago Pratt and Williams[19] argued that the green aqueous cyanide solutions of cobalt(II) actually contained a hexacoordinate species $[Co(CN)_5(OH_2)]^{3-}$, based on comparisons of spectra of related cobalt isocyanide complexes. Caulton[10] and Gray[9,12] argued strongly against this formulation, based on uv-visible and ESR studies which were favorably interpreted in terms of a purely five-coordinate C_{4v} symmetry. With the appearance of a yellow form of the $[Co(CN)_5]^{3-}$ ion, reevaluation of the earlier arguments seemed necessary. Now that the yellow form of the $[Co(CN)_5]^{3-}$ ion is shown to be a truly five-coordinate ion with C_{4v} symmetry, the geometry of the green form remains in question. Since all of the earlier studies were unanimous in their interpretation of C_{4v} symmetry for the ion and since no strong evidence exists for D_{3h} symmetry in any cobalt(II) pentacyanide or isocyanide complex, a trigonal-bipyramidal geometry for the green $[Co(CN)_5]^{3-}$ ion is unlikely. The recently completed structure of the green form of the isoelectronic $[Co(CNC_6H_5)_5]^{2+}$ shows a square-pyramidal complex with a weakly coordinated ClO_4^- in the sixth position.[41] There is also a yellow form of the $[Co(CNC_6H_5)_5]^{2+}$ anion.[44] From the similarity of the absorption spectra, there is a direct structural parallel between the green and yellow forms of the $[Co(CNC_6H_5)_5]^{2+}$ and $[Co(CN)_5]^{3-}$ ions. This would imply that the green form of $[Co(CN)_5]^{3-}$ is weakly coordinated in the sixth axial position with a solvent molecule and, in the case of aqueous solutions, could be formulated as $([Co(CN)_5]{\cdot}H_2O)^{3-}$ to distinguish it from a true hexacoordinate species. The weak coordination in the sixth position will tend to lower the apical angle of $[Co(CN)_5]^{3-}$ from 97.6 (8)° (for the yellow form) to about 95°, the value reported for the green $[Co(CNC_6H_5)_5]^{2+}$ (see Table VI).[41] Caulton[10] concluded that an apical angle of 95° in conjunction with a weakly coordinated solvent was an alternative to his interpretation of the uv-visible spectrum of the aqueous $[Co(CN)_5]^{3-}$ system. In the latest ESR study[15] of irradiated $K_3[Co(CN)_6]$, the authors concluded that their results are best interpreted with an apical angle close to 95° for the square-pyramidal $[Co(CN)_5]^{3-}$ ion. Presumably the ion in these crystal host studies must have some type of weak axial interaction from nitrogen atoms of cyanide ligands of adjacent $[Co(CN)_6]^{3-}$ anions. This would explain the similarities of the ion generated in irradiated $K_3[Co(CN)_6]$ and aqueous $[Co(CN)_5]^{3-}$.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50224K-11-75.

References and Notes

(1) NDEA IV Fellow, 1970–1973.

(2) A. W. Adamson, *J. Am. Chem. Soc.*, **73**, 5710 (1951).

(3) L. D. Brown, K. N. Raymond, and S. Z. Goldberg, *J. Am. Chem. Soc.*, **94**, 7664 (1972).

(4) G. L. Simon, A. W. Adamson, and L. F. Dahl, *J. Am. Chem. Soc.*, **94**, 7654 (1972).

(5) B. M. Chadwick and A. G. Sharpe, *Adv. Inorg. Chem. Radiochem.*, **8**, 83 (1966).

(6) J. Kwiatek, *Catal. Rev.*, **1**, 37 (1967).

(7) J. Kwiatek and J. K. Seyler, *Adv. Chem. Soc.*, **70**, 207 (1968).

(8) J. Kwiatek and J. K. Seyler, *J. Organomet. Chem.*, **3**, 421 (1965).

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

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

(11) D. Guenzburger, A. O. Caride, and E. Zuleta, *Chem. Phys. Lett.*, **14**, 239 (1972).

(12) F. D. Tsay, H. B. Gray, and J. Danon, *J. Chem. Phys.*, **54**, 3760 (1971).

(13) W. C. Lin, C. A. McDowell, and D. J. Ward, *J. Chem. Phys.*, **49**, 2883 (1968).

(14) W. C. Lin, C. A. McDowell, and D. J. Ward, *J. Chem. Phys.*, **56**, 1018 (1972).

(15) R. J. Booth and W. C. Lin, *J. Chem. Phys.*, **61**, 1226 (1974).

(16) M. C. R. Symons and J. G. Wilkinson, *J. Chem. Soc. A*, 2069 (1971).

(17) M. C. R. Symons and J. G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1086 (1972).

(18) A. O. Caride, S. I Zanette, and J. Danon, *J. Chem. Phys.*, **52**, 4911 (1970).

(19) J. M. Pratt and R. J. P. Williams, *J. Chem. Soc. A*, 1291 (1967).

(20) G. Pregaglia et al., *Discuss. Faraday Soc.*, 110 (1968).

(21) D. A. White, A. J. Solodar, and M. M. Baizer, *Inorg. Chem.*, **11**, 2160 (1972).

(22) A preliminary report of this structure has been published: L. D. Brown and K. N. Raymond, *J. Chem. Soc., Chem. Commun.*, 910 (1974).

(23) A. J. Solodar, *Synth. Inorg. Met.-Org. Chem.*, **1**, 141 (1971).

(24) Further experimental details are available: L. D. Brown, Ph.D. Dissertation, University of California, Berkeley, Calif., 1974.

(25) The programs used for the PDP8/I computer were those written by Busing and Levy, as modified by Picker Corp. In addition to local programs for the University of California at Berkely CDC 6400 and the Lawrence Berkeley Laboratory CDC 7600 computers, the following programs or modifications were used: Zalkin's FORDAP Fourier program; Ibers' NUCLS, a group least-squares version of the Busing–Levy ORFLS program; ORFFE, a function and error program by Busing and Levy; Johnson's ORTEP, a thermal ellipsoid plot program; FAME, a structure factor normalization program by Dewar; and MULTAN, a direct methods program by Main, Woolfson, and Germain.

(26) The data crystal was a yellow prism with approximate dimensions 0.030 × 0.032 × 0.038 cm. The crystal was mounted in a thin-walled glass capillary with the a axis nearly parallel to the ϕ axis of the diffractometer. The unit cell constants and crystal orientation were determined by a least-squares refinement using the setting angles for 12 carefully centered reflections. The crystal gave ω scan widths at half-height of 0.08–0.14° for several low-angle reflections. The data were collected in the θ–2θ scan mode with a scan rate of 1°/min from 0.65° below the $K\alpha_1$ peak to 0.65° above the $K\alpha_2$ peak. Stationary-crystal, stationary-counter background counts of 10 sec each were taken at the start and end of each scan.[27] Intensity data for the unique form $\pm h,+k,+l$ were collected to a 2θ angle of 40°, above which there were no significant intensity data. Two equivalent forms ($\pm h,k,-l$ and $\pm h,-k,l$) were collected out to $2\theta = 35°$. During the data collection the intensities of the 500, 040, and 003 reflections were measured as standards after every 80 reflections. The standards showed only a small random variation of less than ±2% throughout the experiment.

(27) Copper foil attenuators were automatically inserted if the counting rate approached 10^4 counts/sec. The takeoff angle for the X-ray tube was 2° and the Bragg 2θ angle for the graphite monochromator was 12.16°. The detector was located 32 cm from the source and had a 7 × 7 mm receiving aperature. The pulse-height analyzer was set to a 95% window centered on the Mo $K\alpha$ peak.

(28) E. N. Duesler and K. N. Raymond, *Inorg. Chem.*, **10**, 1486 (1971).

(29) In all refinements the function minimized was $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting factor, w, is $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for the nonhydrogen atoms were taken from the tabulations of Cromer and Mann.[30] Hydrogen scattering factor values were those calculated by Stewart, Davidson, and Simpson.[31] Corrections for anomalous dispersion effects for Co were made using the $\Delta f'$ and $\Delta f''$ values of Cromer.[32]

(30) D. T. Cromer and B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

(31) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(32) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

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

(34) S. Z. Goldberg and K. N. Raymond, *Inorg. Chem.*, **12**, 2923 (1973).

(35) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. The error in an observation of unit weight is defined as $[\sum w((|F_o| - |F_c|)^2)/(N_o - N_v)]^{1/2}$.

(36) Supplementary material.

(37) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1969.

(38) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 1362 (1968).

(39) F. A. Jurnak and K. N. Raymond, *Inorg. Chem.*, **13**, 2387 (1974).

(40) L. Pauling, "Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 518.

(41) F. A. Jurnak, D. R. Greig, and K. N. Raymond, *Inorg. Chem.*, preceding paper in this issue.

(42) L. D. Brown, D. R. Greig, and K. N. Raymond, *Inorg. Chem.*, **14**, 645 (1975).

(43) L. Sacconi, *Coord. Chem. Rev.*, **8**, 351 (1972).

(44) (a) J. M. Pratt and P. R. Silverman, *Chem. Commun.*, 117, (1967); (b) J. M. Pratt and P. R. Silverman, *J. Chem. Soc. A*, 1280 (1967).