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References and Notes

(1) A. Davison, N. Edelstein, R. H. Holm, and A. A. Maki, *J. Amer. Chem. Soc.*, **85**, 2029 (1963).
(2) R. Eisenberg, *Progr. Inorg. Chem.*, **12**, 295 (1970).
(3) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 219 (1968).
(4) A. L. Balch and R. H. Holm, *J. Amer. Chem. Soc.*, **88**, 5201 (1966).
(5) G. S. Hall and R. H. Soderberg, *Inorg. Chem.*, **7**, 2300 (1968).
(6) F. Röhrscheid, A. L. Balch, and R. H. Holm, *Inorg. Chem.*, **5**, 1542 (1966).
(7) A. L. Balch, F. Röhrscheid, and R. H. Holm, *J. Amer. Chem. Soc.*, **87**, 2301 (1965).
(8) A. L. Balch and J. E. Parks, *J. Amer. Chem. Soc.*, **96**, 4114 (1974).
(9) M. G. Miles, M. B. Hursthouse, and A. G. Robinson, *J. Inorg. Nucl. Chem.*, **33**, 2015 (1971).
(10) F. R. Hartley, "The Chemistry of Platinum and Palladium," Wiley, New York, N.Y., 1973, pp 462–463.
(11) S. D. Ittel, Ph.D. Thesis, Northwestern University, Evanston, Ill., 1974.
(12) J. W. Lauher and J. E. Lester, *Inorg. Chem.*, **12**, 244 (1973).
(13) D. Cahen, J. R. Hahn, and J. R. Anderson, *Rev. Sci. Instrum.*, **44**, 1567 (1973).
(14) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967); R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).
(15) In addition to various local programs for the CDC 6400 computer, modified versions of the following programs were employed: Zalkin's FORDAP Fourier summation program, Busing and Levy's ORFFE error function program, and Johnson's ORTEP thermal ellipsoid plotting program. Our full-matrix least-squares program NUCLS, in its nongroup form, closely resembles the Busing–Levy ORFLS program. Our absorption program is AGNOST.
(16) D. T. Cromer and J. T. Waber, "International Tables for X-ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.2A; D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(17) See paragraph at end of paper regarding supplementary material.
(18) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N.Y., 1960, p 362.
(19) J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 36 (1940).
(20) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N.Y., 1968, pp 259–265.
(21) K. A. Jensen, *Z. Anorg. Allg. Chem.*, **231**, 365 (1937).
(22) R. D. Gilliard and G. Wilkinson, *J. Chem. Soc.*, 2835 (1964).
(23) R. A. Walton, *Can. J. Chem.*, **46**, 2347 (1968).
(24) J. R. Halden and N. C. Baenziger, *Acta Crystallogr.*, **9**, 194 (1956).
(25) F. R. Hartley, "The Chemistry of Platinum and Palladium," Wiley, New York, N.Y., 1973, pp 490–519.
(26) B. R. Penfold and W. N. Lipscomb, *Acta Crystallogr.*, **14**, 589 (1961).
(27) K. Plumlee and J. A. Ibers, unpublished work.
(28) H. Behrens and A. Muller, *Z. Anorg. Allg. Chem.*, **341**, 124 (1965).
(29) W. Geiger, Southern Illinois University, and M. Suchanski, Northwestern University, personal communication.
(30) D. Cahen, Ph.D. Thesis, Northwestern University, Evanston, Ill., 1973.

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Structure of the Chloroform Adduct of Pentakis(phenyl isocyanide)cobalt(I) Perchlorate, [Co(CNC$_6$H$_5$)$_5$]ClO$_4$·HCCl$_3$[1]

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The structure of [Co(CNC$_6$H$_5$)$_5$]ClO$_4$·HCCl$_3$ has been determined from three-dimensional X-ray diffraction data collected by counter methods. The coordination geometry around the d^8 Co(I) ion is approximately square pyramidal. The complex is situated on a mirror plane. The apical Co–C bond distance is 1.88 (3) Å; the two independent basal Co–C bond distances average 1.83 (2) Å. The trans C$_{\text{basal}}$–Co–C$_{\text{basal}}$ bond angle is 156.5 (10)°. There is no coordination in the position trans to the apical ligand. For a series of five-coordinate complexes of d^8 ions there is a strong correlation between the relative bond lengths of these complexes and the distance of the central metal ion from the basal plane; as the bond lengths become equal, the metal ion moves out of the basal plane. Comparison of the geometries of the cobalt(I) and cobalt(II) pentakis(phenyl isocyanide) complexes gives a direct measurement of the structural effects of a one-electron oxidation–reduction. The yellow, needlelike crystals of [Co(CNC$_6$H$_5$)$_5$]ClO$_4$·HCCl$_3$ conform to space group $P2_1/m$ (C_{2h}^2) with $a = 10.849$ (8) Å, $b = 17.741$ (14) Å, $c = 11.396$ (9) Å, and $\beta = 121.00$ (3)°; $Z = 2$; $\rho_{\text{calcd}} = 1.40$ and $\rho_{\text{obsd}} = 1.39$ g/cm^3. The structure has been refined with full-matrix least squares using 647 reflections with $F^2 > 2\sigma(F^2)$ to a final weighted R factor of 8.7%.

Introduction

Isocyanide complexes of cobalt and other transition metals have received much interest in recent years. The general area has been reviewed by Malatesta and Bonati[3] and more recently by Treichel.[4] Of immediate interest are the cobalt(I) and cobalt(II) isocyanide complexes because of their structural relationship to the analogous pentacoordinate cyanide complex [Co(CN)$_5$]$^{3-}$. Although the dimer of the [Co(CN)$_5$]$^{3-}$ ion has been known for years and has recently been structurally characterized,[5] the monomer has eluded isolation until very recently.[6] Relatively little structural data are available for a comparison of the isocyanide and cyanide complexes of cobalt. Cotton, Dunne, and Wood have reported the structures of the trigonal-bipyramidal [Co(CNCH$_3$)$_5$]$^+$ ion[7] and the corresponding dimer[8] [Co$_2$(CNCH$_3$)$_{10}$]$^{4+}$. More recently, the structure of the cobalt(II) complex [Co(CNC$_6$H$_5$)$_5$]$^{2+}$ has been determined;[9] a discussion of the different forms of the cobalt(II) phenyl isocyanide system is presented in the structure report[9] and elsewhere.[10-13] Structure analysis of the [Co(CNC$_6$H$_5$)$_5$]$^{2+}$ and [Co(CNC$_6$H$_5$)$_5$]$^+$ ions presents an opportunity to follow the structure and bonding changes in these pentacoordinate transition metal complexes as a one-electron oxidation–reduction takes place. For this reason and for the additional comparisons to be made with other pentacoordinate d^8 complexes, the structure of [Co(CNC$_6$H$_5$)$_5$]ClO$_4$·HCCl$_3$ was undertaken.

Experimental Section

Preparation of [Co(CNC$_6$H$_5$)$_5$]ClO$_4$·HCCl$_3$. All preparative operations involved were carried out under dry nitrogen atmosphere using Schlenk apparatus. All solvents were reagent grade and deaerated with N$_2$ before use.

A mixture of [Co(CNC$_6$H$_5$)$_5$](ClO$_4$)$_2$[9,14] (0.139 g, 1.80 × 10^{-4} mol) and Na$_2$SO$_3$ (0.024 g, 1.9 × 10^{-4} mol) in an ethanol slurry (20 ml) was stirred for several hours at room temperature. As the reduction of the Co(II) salt proceeded, the blue suspension slowly changed to a clear yellow solution. The reaction mixture was filtered to remove excess Na$_2$SO$_3$; the yellow filtrate was reduced in volume by vacuum evaporation and then cooled to −15°. The bright yellow crystalline powder of [Co(CNC$_6$H$_5$)$_5$]ClO$_4$ was collected and dried under N$_2$ atmosphere.

A small amount of the dry [Co(CNC$_6$H$_5$)$_5$]ClO$_4$ product was

Table I. Summary of Crystal Data

Molecular formula	$[Co(CNC_6H_5)_5]ClO_4 \cdot HCCl_3$
Mol wt	793.39
Space group	$P2_1/m$
Cell constants[a]	
a	10.849 (8) Å
b	17.741 (14) Å
c	11.396 (9) Å
β	121.00 (3)°
Cell vol	1880.2 Å^3
Formula units/cell	2
Calcd density	1.40 g/cm^3
Obsd density	1.39 g/cm^3
Crystal dimensions	0.012 × 0.016 × 0.027 cm
Linear absorption coeff, μ	7.96 cm^{-1}

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

dissolved in chloroform and placed in a Schlenk vessel connected with a glass U tube to another Schlenk vessel containing diethyl ether. As the ether vapor slowly diffused and condensed in the chloroform solution, yellow crystals of $[Co(CNC_6H_5)_5]ClO_4 \cdot HCCl_3$ suitable for use in X-ray diffraction studies were deposited.[15] The crystals are stable in air in the absence of solvent but slowly lose their solvent of crystallization over long periods of time.

Anal. Calcd for $[Co(CNC_6H_5)_5]ClO_4 \cdot HCCl_3$ (mol wt 793.39): C, 54.50; H, 3.30; N, 8.83; Cl, 17.87. Found: C, 54.72; H, 3.43; N, 8.83; Cl, 18.06.

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 $P2_1$ (C_2^2, No. 4) and $P2_1/m$ (C_{2h}^2, No. 11).[16] As shown by the subsequent solution of the structure, $P2_1/m$ is the correct space group.

Intensity data were collected on an automated Picker FACS-1 four-circle diffractometer as previously described.[17-19] The data crystal was a yellow needle approximating a regular parallelepiped with dimensions 0.012 × 0.016 × 0.027 cm. The crystal was mounted in a thin-walled glass capillary with the needle 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 eight carefully centered reflections. The crystal gave ω scan widths at half-height of 0.08° for several low-angle reflections. The density of several crystals was determined by the flotation method in toluene–carbon tetrachloride solutions. The measured density was 1.39 g/cm^3; the calculated density is 1.40 g/cm^3 for two formula units per cell. Crystal data are summarized in Table I.

Solution and Refinement of the Structure. The structure was solved by a combination of heavy-atom techniques and direct methods of phasing.[20] Full-matrix least-squares refinements were carried out for the 647 reflections with $F^2 > 2\sigma(F^2)$.[21-24] The positions of the Co and the Cl from the perchlorate were found from the three-dimensional Patterson map. Further phasing was accomplished using the program MULTAN.[20] The solution with the greatest absolute figure of merit determined the positions of 14 atoms. Subsequent difference Fourier and least-squares calculations located the remainder of the nonhydrogen atoms.

The phenyl rings were refined as rigid groups with a C–C bond length of 1.395 Å. All nongroup atoms were refined anisotropically, while group atoms were assigned isotropic thermal parameters. Due to the low resolution of the data set, the C–N bond lengths for the three crystallographically independent phenyl isocyanide ligands were constrained, as discussed elsewhere,[25,26] to be 1.16 Å. After all of the nonhydrogen atoms had refined, the phenyl hydrogens were positioned assuming an ideal D_{6h} geometry for the phenyl rings. The C–H bond distance was fixed at 1.0 Å with a thermal parameter fixed at 1 Å^2 plus the thermal parameter of the carbon atom to which that hydrogen atom was bonded. In addition, the H atom for the chloroform was positioned assuming sp^3 bonding at 1.0 Å from the C atom with a thermal parameter of 8.0 Å^2. With the fixed contribution of all the H atoms, the structure refined to R_1 = 10.3% and R_2 = 8.7%.[27] The final error in an observation of unit weight is 1.94. The relatively large residuals are due to the large thermal motion in the structure. The final difference Fourier showed no peak greater than 0.38 e/Å^3 (approximately 10% of a carbon atom). Table II gives the positional and thermal parameters for the nongroup atoms. Group parameters and isotropic thermal parameters for the individual group

Table II. Positional Parameters and Anisotropic Thermal Parameters (×10^3) for the Nongroup Atoms in $[Co(CNC_6H_5)_5]ClO_4 \cdot HCCl_3$

	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0.1255 (5)[b]	$^1/_4$	0.9121 (5)	11.8 (9)	3.30 (26)	12.2 (9)	0	3.7 (8)	0
Cl$_1$	0.0006 (16)	$^1/_4$	0.4530 (15)	17.5 (25)	8.7 (9)	16.0 (26)	0	9.7 (22)	0
O$_1$	0.927 (3)	0.1853 (14)	0.448 (3)	67 (8)	7.5 (14)	104 (12)	−9.2 (27)	67 (9)	−9.7 (29)
O$_2$	0.133 (5)	$^1/_4$	0.563 (5)	46 (10)	26 (5)	37 (11)	0	17 (9)	0
O$_3$	0.036 (4)	$^1/_4$	0.348 (4)	58 (10)	9.0 (19)	35 (8)	0	31 (8)	0
Cl$_2$	0.7401 (13)	0.1722 (7)	0.9838 (11)	63 (3)	20.1 (11)	31.0 (25)	17.1 (15)	19.5 (24)	1.2 (12)
Cl$_3$	0.5509 (14)	$^1/_4$	0.0337 (16)	24.1 (28)	14.8 (12)	44 (4)	0	16.0 (27)	0
C$_{Cl}$[c]	0.717 (4)	$^1/_4$	0.057 (4)	15 (8)	12 (4)	7 (7)	0	−5 (6)	0
C$_1$	0.932 (3)	$^1/_4$	0.771 (3)	24 (9)	3.2 (17)	12 (8)	0	6 (7)	0
N$_1$	0.8149 (27)	$^1/_4$	0.6764[d]	6 (5)	5.9 (16)	11 (5)	0	1 (4)	0
C$_2$	0.2067 (25)	0.1774 (14)	0.8595 (26)	9 (4)	4.3 (16)	11 (5)	−0.6 (21)	2 (4)	−0.4 (21)
N$_2$	0.2579 (26)	0.1323 (13)	0.8244[d]	27 (5)	5.3 (15)	23 (4)	0.5 (20)	17 (4)	−4.0 (20)
C$_3$	0.1198 (26)	0.1772 (13)	0.0247 (22)	12 (4)	2.5 (14)	9 (5)	0.8 (20)	−2 (4)	0.7 (20)
N$_3$	0.1295 (26)	0.1296 (11)	0.0987[d]	30 (5)	2.2 (11)	17 (4)	0.1 (19)	11 (4)	2.3 (16)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Standard deviations of the least significant figures are given here and in subsequent tables in parentheses. [c] The carbon of the chloroform molecule. [d] Determined by constraining the cyanide distance to 1.16 Å.

Table III. Group Parameters

Group Orientation[a]

Group	x_c	y_c	z_c	δ	ϵ	η
Ph$_1$	0.5271 (19)	$^1/_4$	0.4727 (19)	0	0	2.884 (22)
Ph$_2$	0.3718 (11)	0.0245 (8)	0.7347 (11)	1.02 (4)	−2.056 (18)	2.42 (4)
Ph$_3$	0.1191 (8)	0.0137 (7)	0.2509 (9)	3.304 (10)	−2.947 (16)	1.265 (11)

Thermal Parameters,[b] Å^2

Phenyl group, n	C$_{n1}$	C$_{n2}$	C$_{n3}$	C$_{n4}$	C$_{n5}$	C$_{n6}$
1	4.6 (9)	10.3 (13)	10.5 (14)	5.9 (10)	9.7 (13)	9.0 (12)
2	7.2 (8)	12.1 (10)	15.3 (13)	11.9 (10)	18.8 (15)	19.1 (16)
3	4.6 (6)	8.2 (8)	10.3 (9)	8.8 (8)	9.6 (9)	7.9 (8)

[a] x_c, y_c, and z_c are the fractional coordinates of the group center; the angles δ, ϵ, and η (in radians) have been defined previously: R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965); S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.*, 87, 2581 (1965); *Acta Crystallogr.*, **18**, 511 (1965). [b] Isotropic thermal parameters for the individual group atoms.

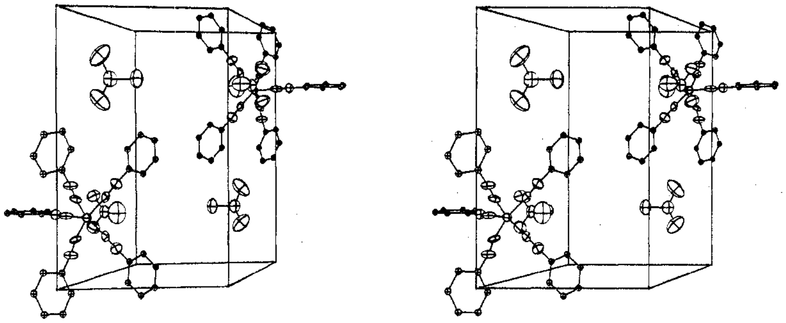

Figure 1. Stereoview of the packing and unit cell contents of $[Co(CNC_6H_5)_5][ClO_4]{\cdot}HCCl_3$. The vertical axis is *b*, and *c* is in the plane of projection.

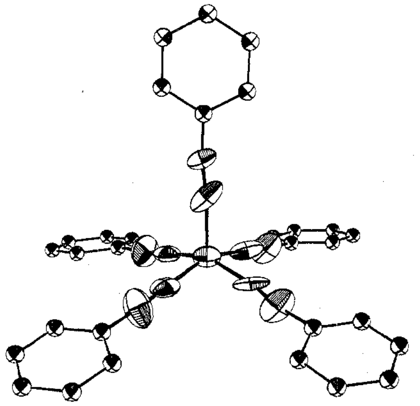

Figure 2. Perspective view of the $[Co(CNC_6H_5)_5]^+$ ion. The crystallographic mirror plane lies in the plane of projection.

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

Atom	Axis 1	Axis 2	Axis 3
Co	217 (9)	229 (9)	282 (9)
Cl_1	259 (25)	283 (20)	373 (20)
O_1	298 (33)	389 (33)	730 (40)
O_2	415 (57)	483 (59)	647 (57)
O_3	346 (52)	380 (41)	505 (45)
Cl_2	383 (16)	392 (14)	688 (15)
Cl_3	318 (20)	479 (22)	486 (20)
C_{Cl}	117 (112)	393 (73)	442 (65)
C_1	227 (60)	241 (83)	352 (63)
N_1	152 (65)	287 (49)	307 (41)
C_2	184 (45)	263 (49)	275 (55)
N_2	187 (51)	338 (33)	369 (32)
C_3	147 (68)	207 (53)	350 (47)
N_3	162 (51)	301 (33)	374 (28)

atoms are listed in Table III. Table IV lists the root-mean-square (rms) amplitudes of vibration of the nongroup atoms derived from the anisotropic thermal motion.[28]

Description of the Structure

The crystal structure consists of discrete $[Co(CNC_6H_5)_5]^+$ cations, ClO_4^- anions, and chloroform molecules. A stereoscopic crystal packing diagram is given in Figure 1. The $[Co(CNC_6H_5)_5]^+$ ion, shown in Figure 2, has square-pyramidal geometry. The square pyramid is situated on the mirror plane such that there are only three crystallographically independent ligands: two basal and one apical. The atoms of the apical phenyl isocyanide, including all phenyl atoms, are constrained to be on the mirror plane. The apical Co–C distance is 1.88 (3) Å, and the average basal Co–C distance is 1.84 (2) Å. These bond distances and others are listed in Table V. The overall geometry of the $[Co(CNC_6H_5)_5]^+$ ion shows only very minor deviations from C_{4v} symmetry. The four basal carbon atoms form almost a perfect square. The Co atom lies 0.37 (2) Å above the plane formed by the basal carbons. This elevation above the plane is evident in the C_2–Co–C_3 angle of 156.5 (10)° and the average C_{apical}–Co–C_{basal} angle of 101.8 (14)°. All of the phenyl isocyanide C–N–C angles as well as the Co–C–N bond angles are within 7° of being linear. The thermal motion of the carbon atoms on all the phenyl rings tends to increase with the distance from the nitrogen atom to which the ring is bound.

Table V. Bond Distances (Å) and Angles (deg) in $[Co(CNC_6H_5)_5]ClO_4{\cdot}HCCl_3$[a]

	Distances		
Co–C_1	1.878 (27)	N_1–C_{11}	1.381
Co–C_2	1.828 (21)	N_2–C_{21}	1.346
Co–C_3	1.843 (20)	N_3–C_{31}	1.335
Co–N_1	3.035 (15)	Cl_1–O_1	1.384 (22)
Co–N_2	2.988 (21)	Cl_1–O_2	1.331 (41)
Co–N_3	2.998 (15)	Cl_1–O_3	1.425 (34)
C_{Cl}–Cl_2	1.696 (27)		
C_{Cl}–Cl_3	1.682 (44)		
	Angles		
C_1–Co–C_2	103.7 (11)	C_1–N_1–C_{11}	172.9
C_1–Co–C_3	99.9 (11)	C_2–N_2–C_{22}	177.5
C_2–Co–C_3'	156.5 (10)	C_3–N_3–C_{33}	173.0
C_2–Co–C_3	86.0 (12)	O_1–Cl_1–O_2	110.8 (17)
C_2–Co–C_2'	89.6 (17)	O_1–Cl_1–O_3	111.5 (16)
C_3–Co–C_3'	88.9 (17)	O_1–Cl_1–O_1'	112.0 (25)
Co–C_1–N_1	174.3 (31)	O_2–Cl_1–O_3	99.5 (26)
Co–C_2–N_2	178.9 (25)	Cl_2–C_{Cl}–Cl_2'	109.0 (30)
Co–C_3–N_3	173.4 (28)	Cl_2–C_{Cl}–Cl_3	109.9 (16)

[a] C–N distances constrained to be 1.16 Å.

The ClO_4^- anion is also situated on the mirror plane roughly equidistant between the axial and two equatorial ligands. The relationship between the ClO_4^- and the $[Co(CNC_6H_5)_5]^+$ ion is illustrated by the stereoscopic diagram in Figure 1. The perchlorate atoms show very high thermal motion, and the refined Cl–O distances are shorter than the expected 1.41 Å.[29]

The chloroform solvent of crystallization lies on the crystallographic mirror plane. The Cl atoms show very high thermal motion. The observed C–Cl distances are slightly shorter than the standard value of 1.76 Å.[30] As illustrated in Figure 1, the chloroform occupies a hole in the structure and is far from both the ClO_4^- and $[Co(CNC_6H_5)_5]^+$ ions. The closest distance to the ClO_4^- anion is 3.97 Å (distance between Cl_2 and O_3), and the closest distance between the chloroform and the cation is 3.45 Å (Cl_3 to C_2 distance).

Discussion

Most of the atoms in the structure exhibit very high thermal motion, and the resultant high standard deviations in the Co–C bond lengths limit conclusions based on small differences in bond lengths. As noted in Table V, the N_1–C_{11} bond distance of 1.38 Å is larger than the average of the equivalent basal distances, 1.34 Å. These distances are expected to be the same. Since the phenyl rings were refined as rigid groups, the relative positions of the bonding phenyl carbon and the Co are probably more accurate than just the Co–C bond distances. The Co–C_{21} and Co–C_{31} distances agree very well at 4.332 and 4.331 Å,

Table VI. Comparison of Geometry of the Square-Pyramidal $[Co(CNC_6H_5)_5]^+$, $[Co(CNC_6H_5)_5]^{2+}$, and $[Ni(CN)_5]^{3-}$ Ions

	$[Co(CNC_6H_5)_5]^{+}$ [a]	$[Co(CNC_6H_5)_5]^{2+}$ [b]	$[Ni(CN)_5]^{3-}$ [c]
M–C_{apical},[d] A	1.88 (3)	1.95 (1)	2.14 (1)
M–C_{basal}(av), A	1.84 (2)	1.84 (1)	1.89 (1)
Trans basal C–M–C(av), deg	156.5 (9)	169.8 (4)	161.5 (2)
C_{basal}–M–C_{apical}(av), deg	101.8 (14)	95.0 (3)	99
M–basal plane, A	0.37	0.16	0.30

[a] This study. [b] Reference 9. [c] Reference 34. [d] M is the metal atom.

respectively, whereas the Co–C_{11} distance is over 0.08 Å longer at 4.414 Å. Assuming an ideal C–N bond length of 1.16 Å and a nitrogen to phenyl carbon bond length of 1.36 Å[31] (total distance 2.52 Å), "corrected" Co–C distances of 1.89, 1.81, and 1.81 Å for Co–C_1, Co–C_2, and Co–C_3, respectively, are calculated. Thus, the Co–C bond distances in this structure agree well with those reported for other cobalt isocyanide structures, including $[Co(CNCH_3)_5]^+$,[7] $[Co_2(CNCH_3)_{10}]^{4+}$,[8] and $[Co(CNC_6H_5)_5]^{2+}$.[9]

Since the cobalt(I) methyl isocyanide complex, $[Co(CNCH_3)_5]^+$, has a trigonal-bipyramidal geometry, one might also expect the corresponding cobalt(I) phenyl isocyanide to be the same. While this is not the case for $[Co(CNC_6H_5)_5]ClO_4 \cdot HCCl_3$, a recent preliminary report of the structure of pentakis(*p*-chlorophenyl isocyanide)cobalt(I) tetrafluoroborate[32] shows its geometry to be trigonal bipyramidal. Since the metal ion is constant, the difference in geometry of these complexes must be ascribed to the relative π acidities of the ligands or steric effects, including packing interactions. Phenyl isocyanide is a stronger π acid than methyl isocyanide.[4] Although stronger π bonding has been cited as favoring square-pyramidal (SP) *vs.* trigonal-bipyramidal (TBP) geometries,[33] the existing data indicate the *opposite* correlation. Thus $Fe(CO)_5$ is a trigonal bipyramid while complexes in which π bonding is less important begin to assume square-pyramidal structures. The overall bond order in the TBP $[Ni(CN)_5]^{3-}$ ion is greater than in the SP form.[34,35] This is also consistent with qualitative molecular orbital considerations. In any case, neither correlation is consistent with the series methyl isocyanide (TBP), phenyl isocyanide (SP), and *p*-chlorophenyl isocyanide (TBP) which are listed here in order of their apparent increasing π acidity. The differences in energy of the TBP and SP structures is probably small enough in these complexes to allow crystal-packing forces or solution environments to determine the predominant structure. A similar phenomenon occurs in another d^8 complex, pentacyanonickelate(II). The $[Ni(CN)_5]^{3-}$ ion has been found to have both trigonal-bipyramidal[34] and square-pyramidal[34,35] geometry. These different geometries have been ascribed to the effects of packing forces in the individual crystalline compounds. The square-pyramidal geometry of the $[Co(CNC_6H_5)_5]^+$ complex can be inferred from its solid-state ir spectrum as discussed by Becker.[15] A similar analysis has been reported for the $[Ni(CN)_5]^{3-}$ salts and solutions.[36]

Knowledge of the structures of $[Co(CNC_6H_5)_5](ClO_4)_2 \cdot {}^1/_2Cl(CH_2)_2Cl$[9] and $[Co(CNC_6H_5)_5]ClO_4 \cdot HCCl_3$ provide an unusual opportunity to compare the detailed geometry of two square-pyramidal complexes of the same metal and ligands, differing only in their respective oxidation states. The structural parameters of the $[Co(CNC_6H_5)_5]^+$ and $[Co(CNC_6H_5)_5]^{2+}$ ions are compared in Table VI. One would expect a lengthening of the apical Co–C bond distance in going from a d^7 to d^8 square-pyramidal complex, since the additional electron in the d_{z^2} antibonding orbital would tend to weaken the apical Co–C bond as compared to the basal Co–C bonds (Figure 3). As shown in Table VI, the apical bond for the d^8 complex is *shorter* than that for the d^7 complex. This apparent anomaly can be resolved by examining the gross geometry of the two complexes. The overall geometric parameters of the $[Co(CNC_6H_5)_5]^+$, $[Co(CNC_6H_5)_5]^{2+}$, and $[Ni(CN)_5]^{3-}$ ions are compared in Table VI. With the Co atom only 0.16 Å above the basal plane of carbon atoms in the Co(II) complex (less than half the distance of the Co(I) complex) and the C_{apical}–Co–C_{basal} angle of 95.0 (3)° compared to 101.8 (14)° in the Co(I) species, it is evident that the Co(II) complex has deviated from the geometry of usual square-pyramidal complexes. This observation has been explained by the proximity of one of the ClO_4^- anions in the approximate sixth position. The coordination is thus intermediate between five and six, causing a change in the structure toward an octahedral geometry.[9] As discussed by Sacconi, a lengthening of the metal–apical ligand bond distance is observed for most Co(II) square-pyramidal complexes as the apical angle is reduced from 100 to 90°.[37] This correlation is also observed in the $[Co(CNC_6H_5)_5]^{2+}$ cation.

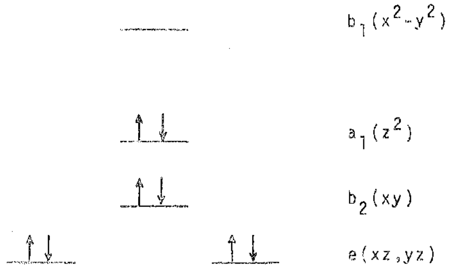

Figure 3. Idealized ligand field diagram for the square-pyramidal d^8 $[Co(CNC_6H_5)_5]^+$ complex (C_{4v} symmetry).

A change in the effective coordination number and the geometry will alter the energy levels of the idealized diagram in Figure 3. For this reason the differences in expected Co–C_{apical} bond lengths can no longer be compared solely on the basis of the diagram. The small elongation of the Co–C_{apical} bond distance compared to the Co–C_{basal} distances in the Co(I) complex can be attributed primarily to slight effects of the d_{z^2} antibonding orbital. The $[Ni(CN)_5]^{3-}$ complex, which exhibits a typical square-pyramidal geometry, has an axial Ni–C bond length that is much longer than the basal bond lengths (see Table VI). This remarkable difference between the two d^8 complexes, $[Ni(CN)_5]^{3-}$ and $[Co(CNC_6H_5)_5]^+$, indicates that the d_{z^2} orbital is much more strongly antibonding in $[Ni(CN)_5]^{3-}$ than in the Co(I) complex. The geometry of the cobalt(I) isocyanide complex also indicates that it is much more covalently bonded than the nickel(II) cyanide. The phenyl isocyanide ligand is a better π acceptor than cyanide; thus the Co–C bond length here (1.84 Å) is less than in a typical cobalt cyanide (1.89 Å).[5] This is structural evidence that π bonding between the highly reduced Co(I) ion and the phenyl isocyanide ligand increases the overall bond order. The result is an approach to an idealized square-pyramidal complex in which the apical and basal bond orders are approximately equal.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals

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References and Notes

(1) This work was first reported at the 165th National Meeting of the American Chemical Society, Dallas, Tex., April 1973. For the other papers in this series see ref 5, 6, and 9.
(2) National Defense Education Act Title IV Fellow, 1970–1973.
(3) L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals," Wiley, New York, N.Y., 1969.
(4) P. M. Treichel, *Advan. Organometal. Chem.*, **11**, 21 (1973).
(5) L. D. Brown, K. N. Raymond, and S. Z. Goldberg, *J. Amer. Chem. Soc.*, **94**, 7664 (1972).
(6) L. D. Brown and K. N. Raymond, *J. Chem. Soc., Chem. Commun.*, 910 (1974).
(7) F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, **4**, 318 (1965).
(8) F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, **3**, 1495 (1964).
(9) F. Jurnak, D. R. Greig, and K. N. Raymond, submitted for publication.
(10) J. M. Pratt and P. R. Silverman, *Chem. Commun.*, **3**, 117 (1967).
(11) J. M. Pratt and P. R. Silverman, *J. Chem. Soc. A*, 1280 (1967).
(12) J. P. Maher, *J. Chem. Soc. A*, 2918 (1968).
(13) C. A. L. Becker, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., April 1971, No. 85.
(14) L. Malatesta and A. Sacco, *Z. Anorg. Allg. Chem.*, **273**, 247 (1953).
(15) Another preparation has been reported: C. A. L. Becker, *J. Inorg. Nucl. Chem.*, **35**, 1875 (1973).
(16) "International Tables for X-ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1969.
(17) The programs used for the PDP8/I computer were those written by Busing and Levy, as modified by the Picker Corp.
(18) E. N. Duesler and K. N. Raymond, *Inorg. Chem.*, **10**, 1486 (1971).
(19) Intensity data were collected in the θ–2θ scan mode with a scan rate of 2°/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 4 sec each were taken at the start and end of each scan. 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 angle for the graphite monochromator was 12.16°. The detector was located 32 cm from the source and had a 7 × 7 mm receiving aperture. The pulse height analyzer was set to a 95% window centered on the Mo $K\alpha$ peak. Intensity data for the unique form $\pm h,+k,+l$ were collected to a 2θ angle of 35°, above which there were no significant intensity data. An equivalent form ($\pm h,k,-l$) was collected out to $2\theta = 30°$. During the data collection the intensities of the 100, 022, and 040 reflections were measured as standards after every 50 reflections. The standards showed only a small random variation of less than ± 3% throughout the experiment. The data were processed as described in ref 18 with a parameter p, introduced to prevent overweighting strong reflections, chosen as 0.04. Equivalent reflections were averaged.
(20) In addition to local programs for the CDC 7600 computer, modifications of the following programs were used: Ibers' NUCLS, a group least-squares version of the Busing–Levy ORFLS program; Zalkin's FORDAP Fourier program; ORFFE, a function and error program by Busing, Martin, and Levy; Johnson's ORTEP thermal ellipsoid plot program; MULTAN, a direct-methods program by Main, Woolfson, and Germain.
(21) 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 Co, Cl, O, N, and C were taken from the tabulations of Cromer and Mann.[22] Hydrogen scattering factor values were those calculated by Stewart, Davidson, and Simpson.[23] Corrections for anomalous dispersion effects for Co were made using the $\Delta f'$ and $\Delta f''$ values of Cromer.[24]
(22) D. T. Cromer and B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
(23) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(24) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(25) K. N. Raymond, *Acta Crystallogr., Sect. A*, **28**, 163 (1972).
(26) S. Z. Goldberg and K. N. Raymond, *Inorg. Chem.*, **12**, 2923 (1973).
(27) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.
(28) See paragraph at end of paper regarding supplementary material.
(29) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1969.
(30) P. N. Wolfe, *J. Chem. Phys.*, **25**, 976 (1956).
(31) N. L. Ferguson, "Modern Structural Theory of Organic Chemistry," Prentice-Hall, Englewood Cliffs, N.J., 1963.
(32) S. H. Simonsen and W. C. Bryson, Abstracts, 29th Southwest Regional Meeting of the American Chemical Society, El Paso, Tex., Dec 1973, No. 184.
(33) J. S. Wood, *Progr. Inorg. Chem.*, **16**, 227 (1972).
(34) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 1362 (1968).
(35) F. A. Jurnak and K. N. Raymond, *Inorg. Chem.*, **13**, 2387 (1974).
(36) A. Terzis, K. N. Raymond, and T. G. Spiro, *Inorg. Chem.*, **9**, 2415 (1970).
(37) L. Sacconi, *Coord. Chem. Rev.*, **8**, 351 (1972).

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Synthesis and Structural Characterization of Sodium Tetra-μ-sulfato-dirhenate(III) Octahydrate

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A compound of composition $Na_2Re_2(SO_4)_4 \cdot 8H_2O$ is obtained in about 90% yield from the reaction of $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ with Na_2SO_4 and H_2SO_4 in $(CH_3OCH_2CH_2)_2O$. The pale blue substance is air sensitive. It is soluble in water and in the more polar organic liquids. Recrystallization from a 10:1 mixture of methanol and 48% aqueous HBF_4 yielded blue-green crystals suitable for X-ray structure determination. Crystal data are as follows: space group $P2_1/n$; unit cell dimensions $a = 7.739\ (1)$ Å, $b = 13.212\ (3)$ Å, $c = 11.077\ (2)$ Å, $\beta = 100.58\ (1)°$, $V = 1113.3\ (4)$ Å^3, $Z = 2$. Using 1331 reflections for which $I > 3\sigma(I)$ in the range $0° < 2\theta < 50°$ the structure was solved and refined anisotropically to $R_1 = 0.042$ and $R_2 = 0.052$. The structure contains $Re_2(SO_4)_4^{2-}$ ions which lie on crystallographic centers of symmetry and have virtual symmetry C_{4h}. They are essentially similar to the $Mo_2(SO_4)_4^{4-}$ ions previously described. The bridging sulfato ligands are appreciably distorted, with S–O distances of 1.54 (1) Å for coordinated oxygen atoms and 1.43 (1) Å for noncoordinated oxygen atoms and with O–S–O angles ranging from 104 to 117°. There are coaxially coordinated water molecules at an Re–O distance of 2.28 (1) Å, while the average of the eight Re–O(sulfate) distances is 2.01 (1) Å. The Re–Re distance is 2.214 (1) Å, which is very similar to those in other species containing quadruply bonded pairs of Re(III) atoms. The compound is very reactive and may serve as a useful starting material for the preparation of other complexes of Re_2^{6+}.

Introduction

The existence of a quadruple bond was first recognized in a dirhenium(III) compound, namely, a salt of $Re_2Cl_8^{2-}$, about a decade ago.[1–3] Since then a great variety of ligand-exchange reactions in which the quadruply bonded Re_2^{6+} core remains intact have been carried out. In some of these, the Cl^- ligands are partly or wholly replaced by bidentate bridging ligands. These have been, in most cases, carboxylato ions,[4–7] although more recently we have prepared and structurally characterized compounds with $Ph_2PCH_2PPh_2$ and $PhNC(Ph)NPh^-$ as bridging ligands.[8] Still, the number of bridging ligands which are known to occur in Re_2^{6+} complexes is less than for Mo_2^{4+} and Cr_2^{4+} species, where xanthate ions,[9] CO_3^{2-} ions,[10] and sulfate ions[11] have all been found. In an effort to see if similar complexes of Re_2^{6+} can be prepared, we have studied the reaction of $Re_2Cl_8^{2-}$ with sulfate-containing media, and the new compound $Na_2Re_2(SO_4)_4 \cdot 8H_2O$ has been isolated and structurally characterized.

Experimental Section

Preparation. $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ was prepared according to a