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# Structural Characterization of the Pentakis(phenyl isocyanide)cobalt(II) Ion in the Salt of $[Co(CNC_6H_5)_5][ClO_4]_2\cdot{}^1/_2ClCH_2CH_2Cl$

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The crystal and molecular structure of the green form of the $[Co(CNC_6H_5)_5]^{2+}$ cation has been determined at 23° from three-dimensional X-ray diffraction data collected by counter methods. The perchlorate salts of the $[Co(CNC_6H_5)_5]^{2+}$ cation exists in three forms, each with a different color and unique chemical properties. The geometry of the green form reported here can be described as a square pyramid in which the average $C_{apical}$–Co–$C_{basal}$ angle has decreased to 95.0° as a result of weak coordination by a perchlorate ion below the basal plane of the complex. The distance between the perchlorate oxygen and cobalt atoms is 2.594 (10) Å. The apical Co–C bond, 1.950 (11) Å, is longer than the average basal Co–C bond length, 1.843 (13) Å. The effect of coordination in the sixth ligand position and the properties of the three color forms of $[Co(CNC_6H_5)_5]^{2+}$ are discussed. Pentakis(phenyl isocyanide)cobalt(II) perchlorate–hemi-1,2-dichloroethane forms deep green crystals in the monoclinic space group $P2_1/c$ with $a = 10.336$ (2) Å, $b = 13.939$ (6) Å, $c = 27.143$ (7) Å, and $\beta = 95.589$ (11)°. For four formula units in the cell, the calculated density is 1.40 g cm$^{-3}$; the observed density is 1.38 g cm$^{-3}$. For 2358 independent reflections with $F^2 > 3\sigma(F^2)$, the full-matrix least-squares refinement converged to a final weighted $R$ factor of 9.3%.

## Introduction

Low-spin complexes of Co(II) exhibit a wide range of configurations which are four-, five-, or six-coordinate. With the stereochemically simple cyanide and isocyanide ligands, Co(II) forms pentacoordinated structures as well as dimeric structures in which the cobaltous environment is essentially octahedral with a metal–metal bond.[1] The complex $[Co(CNC_6H_5)_5]^{2+}$ as the perchlorate salt forms three species of different colors: light blue, dark green, and bright yellow. The reason for the color change has not been clearly established. It has been ascribed either to a stereochemical change in geometry from $C_{4v}$ to $D_{3h}$ symmetry[2] or to the solvation of a square-pyramidal complex in the sixth ligand position.[3,4] The geometries of the various forms of the $[Co(CNC_6H_5)_5]^{2+}$ cation are of interest since they are presumably isostructural with the green and yellow forms of the $[Co(CN)_5]^{3-}$ anion[5] and the blue form of the $[Co(CNCH_3)_5]^{2+}$ cation.[4] Although the geometries of the latter complexes have been extensively studied in solution, the assigned structures are not clearly established with the exception of the recently characterized yellow form of the $[Co(CN)_5]^{3-}$ anion, which is strictly five-coordinate and square pyramidal.[5]

The chemical literature of the $[Co(CNC_6H_5)_5]^{2+}$ cation is confusing because the various forms were not distinguished chemically until 1971. Sacco[6] first reported the preparation of $[Co(CNC_6H_5)_5][ClO_4]_2$ as a blue-green powder in 1954 and suggested that the cation was five-coordinate. In 1967, Pratt and Silverman[3,4] isolated blue and yellow powders as well as a green solution of the $[Co(CNC_6H_5)_5][ClO_4]_2$ salt. The yellow powder was obtained by drying the blue form and this transformation was reversible in a moist atmosphere. Pratt and Silverman postulated that the hydrated blue powder is a six-coordinate structure with water as the sixth ligand and that the yellow powder of the anhydrous $[Co(CNC_6H_5)_5][ClO_4]_2$ salt has a square-pyramidal five-coordinate geometry. In 1968 Maher[7] obtained green solutions of this salt in methylene chloride and concluded from the ESR spectrum that the cation structure is five-coordinate with $C_{4v}$ symmetry. In 1971, Becker[8] isolated a green powder with the formula $[Co(CNC_6H_5)_5][ClO_4]_2\cdot{}^1/_2ClCH_2CH_2Cl$ as well as the blue and yellow powders previously reported. He concluded that the geometry of the blue form has square-pyramidal ($C_{4v}$) symmetry and the yellow form is trigonal bipyramidal ($D_{3h}$). To clarify some of the often contradictory structural inferences drawn in this area, the crystal structure determination of the green form, $[Co(CNC_6H_5)_5][ClO_4]_2\cdot{}^1/_2ClCH_2CH_2Cl$, was undertaken.

## Experimental Section

**Preparations.** A blue-green powder of pentakis(phenyl isocyanide)cobalt(II) perchlorate was prepared according to the method of Sacco.[6] Green crystals of the pentacoordinated complex were grown by vapor pressure equilibration of ether with a 1,2-dichloroethane solution of the Co(II) compound. Under vacuum at 35°, the green crystals powder to a yellow form of the compound. The weight loss of 5.8% corresponds to the loss of 0.47 mol of 1,2-dichloroethane per mole of cobalt. The green crystals were also reversibly converted to a blue powder by exposure to a moist atmosphere. The increase in the weight accompanying the transformation from green to blue was not determined precisely. Infrared spectra of the green crystals as a Nujol mull were recorded on a Perkin-Elmer 421 grating infrared spectrometer. Infrared isocyanide stretching frequencies were found at 2220 (s) and 2200 (m) cm$^{-1}$ and perchlorate bands at 1050 (s), 1069 (m), 1090 (s), and 1112 (sh) cm$^{-1}$.

The preparation of the reactant, cobalt(II) perchlorate, is described in the literature.[9] The phenyl isocyanide ligand was prepared according to a modification of the method of Hertler and Corey.[10] The final product of the original method yields equal amounts of pyridine and phenyl isocyanide. The phenyl isocyanide was extracted from the mixture with carbon tetrachloride and washed three times with cold water. Most of the carbon tetrachloride solvent was removed at slightly reduced pressures. The residue was distilled at 10-mm pressures and pure phenyl isocyanide was collected between 20 and 30°.

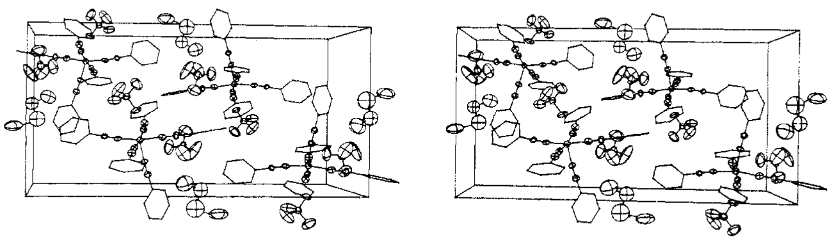

**Figure 1.** Stereoscopic packing diagram of the unit cell of $[Co(CNC_6H_5)_5][ClO_4]_2 \cdot {}^1/_2ClCH_2CH_2Cl$. The horizontal axis is $c$ and the vertical axis is $b$.

**Table I.** Crystallographic Data for Pentakis(phenyl isocyanide)cobalt(II) Perchlorate–Hemi-1,2-dichloroethane

| | |
|---|---|
| Formula | $[Co(CNC_6H_5)_5][ClO_4]_2 \cdot {}^1/_2ClCH_2CH_2Cl$ |
| Space group | $P2_1/c$ |
| Cell constants[a] | |
| $a$ | 10.336 (2) Å |
| $b$ | 13.939 (6) Å |
| $c$ | 27.143 (7) Å |
| $\beta$ | 95.589 (11)° |
| $V$ | 3892.0 Å$^3$ |
| Calcd density | 1.40 g cm$^{-3}$ |
| Obsd density (flotation in $C_6H_5Cl$–$CCl_4$) | 1.38 g cm$^{-3}$ |
| Absorption coeff (Mo K$\alpha$) | 6.68 cm$^{-1}$ |

[a] Ambient temperature 23°. Mo K$\alpha_1$ $\lambda$ 0.70926 Å.

**Diffraction Analysis.** All crystals used for X-ray studies were sealed in thin-walled glass capillaries under a nitrogen–dichloroethane atmosphere. Precession photographs revealed extinctions of $0k0$, $k \neq 2n$, and $h0l$, $l \neq 2n$, and Laue symmetry of $2/m$, implying the monoclinic space group $P2_1/c$.[11] The cell constants, $a$ = 10.336 (2) Å, $b$ = 13.939 (6) Å, $c$ = 27.143 (7) Å, and $\beta$ = 95.589 (11)°, were determined by a least-squares refinement of the diffractometer setting angles for 12 carefully centered reflections. The experimental density of 1.38 g cm$^{-3}$ was determined by flotation in chlorobenzene and carbon tetrachloride. It agrees satisfactorily with the calculated density of 1.40 g cm$^{-3}$, assuming four molecules per unit cell. The pertinent crystallographic data are summarized in Table I.

Intensity data were collected by automated diffraction techniques.[12] The data were extensively checked for errors and reduced to values of $F^2$ after correcting for Lorentz and polarization effects.[13] In the calculation of $\sigma(F^2)$, a parameter $p$ of 0.06 was introduced to avoid overweighting strong reflections.[14] Since the calculated transmission factors ranged from 0.70 to 0.86, an absorption correction was not applied. The 4557 measured reflections were averaged to give 3639 unique reflections of which 2359 had $F^2 > 3\sigma(F^2)$. The latter were used in all least-squares refinements.

**Solution and Refinement of Structure.** The positions of the cobalt atom and two chlorine atoms of the perchlorate ions were determined from a three-dimensional Patterson synthesis. The structure was then solved by standard heavy-atom techniques.[13,15] In all subsequent refinements, the C–N bond distance was constrained to be 1.16 Å by methods previously described.[19] The phenyl ring atoms were refined as a group with a C–C bond distance of 1.397 Å[20] and a C–C–C angle of 120°. The thermal motion of each atom of the group was refined anisotropically.

The oxygen atoms of both perchlorate groups exhibit large thermal motion. Evidence for partial but not complete rotation about the perchlorate chlorine atoms was found in difference Fourier maps. Several attempts were made to refine each of the strongly anisotropic perchlorate groups as two groups with partial occupancy. However, these disorder models did not significantly lower $R_1$ or improve the perchlorate bond distances. In subsequent refinements, the oxygen atoms were treated as fully occupied, despite the large thermal parameters that resulted. The dichloroethane solvent molecule lies on an inversion center and is disordered. It was treated as a group with a C–C distance of 1.490 Å and a Cl–C bond of 1.781 Å.[20] Approximate group orientation angles were calculated from reasonable peak positions in the Fourier map. In subsequent refinements, group origin and orientation angles were refined. After several cycles, the atomic coordinates to which the group refined were held constant and the individual chlorine atoms were refined anisotropically and the carbon atoms, isotropically. The center of symmetry of the solvent molecule is not located on the space group inversion center, so the model must be considered as two groups with 50% occupancy each. The ten highest peaks in the final difference Fourier map ranged from 0.33 to 0.46 e/Å$^3$ and were not located near the solvent molecule. All nonhydrogen atoms except the dichloroethane carbon atoms were refined anisotropically. The positions of the phenyl hydrogen atoms were calculated and included as fixed contributions to the calculated structure factor. The structural parameters of the $[Co(CNC_6H_5)_5]^{2+}$ cation were not sensitive to changes in the various models for disorder of the perchlorate anions and solvent molecule. The final discrepancy factors are $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.071$ and $R_2 = [\sum w(\Delta F)^2/\sum w(F_o)^2]^{1/2} = 0.093$. The final error in an observation of unit weight (defined by $[\sum w(\Delta F)^2/(N_o - N_v)]^{1/2}$) is 2.69. The final positional and thermal parameters of the nonhydrogen atoms are given in Tables II and III. Table IV lists the positional parameters for the hydrogen atoms.[21]

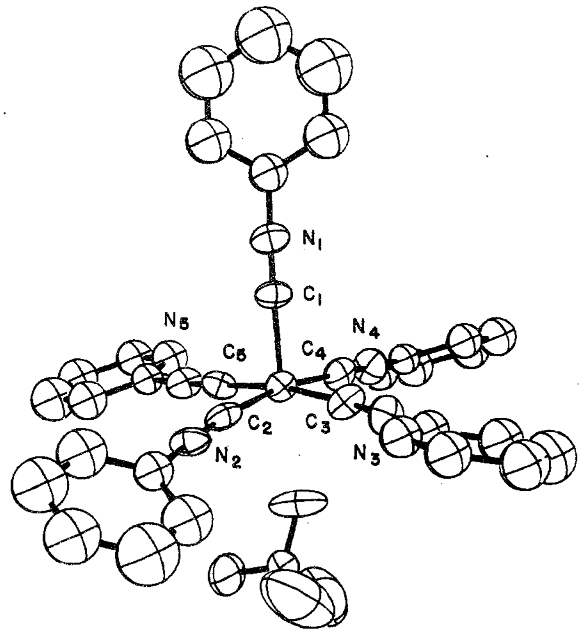

**Figure 2.** Perspective drawing of the square-pyramidal $[Co(CNC_6H_5)_5]^{2+}$ cation with a perchlorate ion below the basal plane. The shapes of all atoms represent 50% probability contours of the thermal motion.

## Description of the Structure and Discussion

The structure consists of discrete $[Co(CNC_6H_5)_5]^{2+}$ ions surrounded by two types of perchlorate ions. Only one of the perchlorate groups is sufficiently close to the Co(II) cation to interact with its coordination sphere. The dichloroethane solvent molecule is disordered about a center of symmetry and does not exhibit close intermolecular contacts. With the absence of hydrogen bonding, the ions are loosely packed with respect to one another. A stereoscopic view of the unit cell is shown in Figure 1. Bond lengths and angles are given in Tables V and VI. The root-mean-square amplitudes of vibrations along the principal axes of the thermal ellipsoids are in Table VII. The orientations of the ellipsoids are illustrated in the figures.

**Table II.** Positional and Thermal Parameters for the Anisotropic Atoms in $[Co(CNC_6H_5)_5][ClO_4]_2 \cdot {}^1/_2 ClCH_2CH_2Cl$ at 23°

| Atom | $10^4x$ | $10^4y$ | $10^4z$ | $10^4\beta_{11}$[a] | $10^4\beta_{22}$ | $10^4\beta_{33}$ | $10^4\beta_{12}$ | $10^4\beta_{13}$ | $10^4\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Co | 846 (2)[b] | 3224 (1) | 3287 (6) | 61 (2) | 43 (1) | 13 (3) | −4 (1) | 5 (6) | −5 (6) |
| $C_1$ | 1451 (12) | 1925 (8) | 3446 (5) | 68 (16) | 36 (10) | 16 (3) | −3 (10) | 8 (5) | 6 (4) |
| $C_2$ | 1295 (12) | 3279 (10) | 2651 (4) | 80 (17) | 28 (9) | 18 (3) | −10 (10) | 5 (6) | 1 (5) |
| $C_3$ | 2423 (11) | 3800 (9) | 3451 (5) | 83 (19) | 44 (10) | 15 (3) | −6 (12) | 17 (6) | −4 (4) |
| $C_4$ | 304 (12) | 3423 (10) | 3921 (4) | 55 (16) | 48 (11) | 19 (3) | −10 (10) | 1 (6) | −2 (5) |
| $C_5$ | −811 (11) | 2839 (9) | 3085 (5) | 58 (17) | 49 (10) | 13 (3) | 13 (11) | 6 (5) | 6 (4) |
| $N_1$ | 1731 (10) | 1150 (8) | 3567 | 79 (14) | 43 (9) | 17 (2) | 10 (9) | 13 (4) | 9 (4) |
| $N_2$ | 1634 (10) | 3407 (7) | 2262 | 110 (15) | 36 (8) | 13 (2) | 7 (8) | 18 (5) | 4 (3) |
| $N_3$ | 3422 (11) | 4185 (8) | 3513 | 63 (14) | 64 (9) | 18 (2) | −11 (9) | 3 (5) | −2 (4) |
| $N_4$ | −118 (12) | 3523 (8) | 4298 | 125 (17) | 66 (9) | 11 (2) | −10 (9) | 16 (5) | −1 (4) |
| $N_5$ | −1879 (10) | 2583 (7) | 2980 | 43 (13) | 48 (8) | 20 (2) | 5 (9) | 5 (5) | 3 (3) |
| $Cl_1$ | 3984 (6) | 2760 (5) | 4722 (2) | 173 (8) | 104 (5) | 17 (9) | −5 (5) | −2 (2) | −6 (2) |
| $Cl_2$ | −305 (4) | 5740 (3) | 2855 (2) | 132 (6) | 51 (3) | 15 (7) | −2 (3) | −12 (2) | 2 (1) |
| $O_1$ | 4626 (19) | 2686 (14) | 4321 (6) | 440 (8) | 278 (23) | 35 (4) | 149 (23) | 65 (10) | 14 (7) |
| $O_2$ | 2816 (19) | 2385 (18) | 4672 (8) | 216 (27) | 333 (30) | 70 (6) | −35 (24) | −16 (11) | −54 (11) |
| $O_3$ | 4583 (17) | 2527 (21) | 110 (9) | 240 (29) | 482 (41) | 67 (6) | −81 (26) | −8 (11) | −129 (13) |
| $O_4$ | 3764 (29) | 3705 (18) | 4797 (9) | 841 (79) | 162 (21) | 77 (77) | 26 (34) | 117 (20) | −20 (11) |
| $O_5$ | 5 (10) | 4967 (7) | 3151 (4) | 180 (16) | 47 (7) | 32 (2) | 27 (8) | 42 (5) | 18 (4) |
| $O_6$ | 874 (20) | 6168 (15) | 2659 (7) | 328 (31) | 253 (22) | 54 (5) | −76 (23) | −25 (10) | 66 (9) |
| $O_7$ | −1050 (14) | 5525 (8) | 2500 (5) | 384 (28) | 77 (10) | 47 (4) | −12 (12) | −108 (9) | 7 (5) |
| $O_8$ | −794 (21) | 6459 (13) | 3129 (6) | 629 (52) | 160 (16) | 35 (4) | 193 (24) | −53 (11) | −26 (7) |
| $EtCl_1$ | −749 | 818 | 4533 | 453 (50) | 265 (26) | 92 (9) | 12 (31) | 60 (18) | 19 (13) |
| $EtCl_2$ | 1047 | −1113 | 5639 | 646 (65) | 139 (16) | 115 (9) | −107 (25) | 76 (20) | −3 (11) |

[a] The form of the temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Numbers in parentheses are the estimated standard deviations in the least significant digits.

**Table III.** Positional and Thermal Parameters for the Isotropic Nonhydrogen Atoms in $[Co(CNC_6H_5)_5][ClO_4]_2 \cdot {}^1/_2 ClCH_2CH_2Cl$ at 23°

| Atom | $10^4x$ | $10^4y$ | $10^4z$ | $B$, A$^2$ |
|---|---|---|---|---|
| | | Phenyl Rings | | |
| $C_{11}$ | 2091 (10) | 256 (7) | 3720 (4) | 5.0 |
| $C_{12}$ | 1537 (10) | −538 (10) | 3465 (4) | 7.1 |
| $C_{13}$ | 1882 (13) | −1464 (8) | 3625 (5) | 9.9 |
| $C_{14}$ | 2780 (14) | −1596 (7) | 4040 (5) | 10.7 |
| $C_{15}$ | 3334 (11) | −802 (11) | 4294 (4) | 10.7 |
| $C_{16}$ | 2990 (11) | 124 (9) | 4134 (4) | 6.9 |
| $C_{21}$ | 2127 (11) | 3559 (8) | 1828 (3) | 4.6 |
| $C_{22}$ | 2967 (12) | 4332 (7) | 1782 (4) | 7.6 |
| $C_{23}$ | 3504 (11) | 4489 (8) | 1334 (5) | 10.9 |
| $C_{24}$ | 3203 (12) | 3871 (10) | 933 (4) | 8.5 |
| $C_{25}$ | 2364 (12) | 3097 (9) | 979 (4) | 8.8 |
| $C_{26}$ | 1826 (10) | 2941 (7) | 1426 (5) | 7.4 |
| $C_{31}$ | 4627 (7) | 4574 (7) | 3543 (4) | 4.8 |
| $C_{32}$ | 5108 (10) | 5104 (8) | 3959 (3) | 6.0 |
| $C_{33}$ | 6351 (11) | 5504 (7) | 3982 (3) | 8.3 |
| $C_{34}$ | 7115 (8) | 5374 (8) | 3589 (4) | 6.8 |
| $C_{35}$ | 6635 (9) | 4844 (8) | 3172 (3) | 5.7 |
| $C_{36}$ | 5391 (10) | 4444 (7) | 3150 (3) | 5.0 |
| | | Phenyl Rings | | |
| $C_{41}$ | −580 (9) | 3649 (7) | 4724 (3) | 3.9 |
| $C_{42}$ | −1926 (8) | 3711 (7) | 4734 (3) | 5.6 |
| $C_{43}$ | −2452 (6) | 3887 (7) | 5182 (4) | 6.8 |
| $C_{44}$ | −1631 (10) | 4000 (7) | 5620 (3) | 6.2 |
| $C_{45}$ | −285 (9) | 3937 (7) | 5610 (3) | 6.4 |
| $C_{46}$ | 241 (6) | 3762 (7) | 5162 (4) | 5.0 |
| $C_{51}$ | −3140 (7) | 2275 (7) | 2888 (4) | 3.9 |
| $C_{52}$ | −3894 (9) | 2087 (7) | 3278 (3) | 5.4 |
| $C_{53}$ | −5199 (9) | 1830 (7) | 3178 (3) | 5.9 |
| $C_{54}$ | −5751 (7) | 1760 (8) | 2687 (4) | 6.6 |
| $C_{55}$ | −4998 (10) | 1948 (8) | 2296 (3) | 8.2 |
| $C_{56}$ | −3692 (10) | 2205 (7) | 2397 (3) | 6.1 |
| | | Solvent Atoms | | |
| $EtC_1$ | 5000 | 378 | 5057 | 18 (2) |
| $EtC_2$ | 5000 | 48 | 5116 | 27 (6) |

A perspective view of the $[Co(CNC_6H_5)_5]^{2+}$ cation is shown in Figure 2. The geometry of the isocyanide complex is a square pyramid. The apical Co–C distance is 1.950 (11) Å and the basal Co–C distances range from 1.826 (11) to 1.882 (12) Å. Important angles include the average trans basal C–Co–C angle of 169.8 (4)° and the average $C_{apical}$–Co–$C_{basal}$ angle of 95.0 (3)°. The cobalt atom lies above the basal plane, 0.16 Å from the plane of the four carbons and 0.31 Å from the plane of the four nitrogen atoms. An oxygen atom of one perchlorate ion is situated in an approximate sixth coordination site of the cation. The oxygen atom, $O_5$, is located 2.594 (10) Å from the cobalt atom below the basal plane. The $O_5$–Co–$C_1$ angle is 175.3 (5)° and the average $O_5$–Co–$C_{basal}$ angle is 85.0 (2)°. The equations for best weighted least-squares planes through various combinations of atoms are given in Table VIII.[21]

The isocyanide groups are linearly coordinated to the cobalt atom. The average Co–C–N angle is 174.6 (6)° and the average C–N–$C_{phenyl}$ angle is 176.4 (10)°. The N–$C_{phenyl}$ bond distances range from 1.308 (9) to 1.368 (11) Å. The basal phenyl planes are tilted from 11.9 to 33.1° from the plane of the basal carbons and are related by an approximate fourfold axis. Other dihedral angles between the phenyl groups and various planes are given in Table IX.[21]

With the exception of the two oxygen atoms, $O_5$ and $O_6$, closest to the cation below the basal plane, the oxygen atoms of both perchlorate ions exhibit large thermal motion. The $Cl$–$O_2$ bond distances average 1.404 (6) Å for $O_5$ and $O_6$ and 1.323 (6) Å for the $O_7$ and $O_8$ atoms which exhibit the larger thermal anisotropy. The O–Cl–O angles vary from 99.3 (13) to 114.9 (7)° in this perchlorate ion. The second perchlorate ion is located between the apical isocyanide ligand and the third and fourth basal ligands. The $Cl_1$–O bond distances for this perchlorate ion range from 1.236 (17) to 1.355 (22) Å and the O–$Cl_1$–O angles range from 103.7 (15) to 115.1 (14)°. The average Cl–O bond distance of 1.404 Å for the oxygen atoms which exhibit the smallest thermal motion compares well with the average Cl–O bond distance of 1.43 Å found in $HClO_4 \cdot H_2O$.[23] The remaining Cl–O bond average of 1.31 Å is considerably shorter than 1.43 Å. This difference may be

**Table IV.** Positional Parameters for the Hydrogen Atoms in $[Co(CNC_6H_5)_5][ClO_4]_2\cdot{}^1/_2ClCH_2CH_2Cl$

| Atom[a] | $10^3x$ | $10^3y$ | $10^3z$ |
|---|---|---|---|
| Phenyl Ring 1 | | | |
| H$_2$ | 88 | −45 | 316 |
| H$_3$ | 152 | 203 | 344 |
| H$_4$ | 306 | −223 | 415 |
| H$_5$ | 395 | −86 | 459 |
| H$_6$ | 331 | 723 | 431 |
| Phenyl Ring 2 | | | |
| H$_2$ | 321 | 473 | 207 |
| H$_3$ | 413 | 500 | 130 |
| H$_4$ | 358 | 396 | 61 |
| H$_5$ | 212 | 265 | 69 |
| H$_6$ | 120 | 238 | 145 |
| Phenyl Ring 3 | | | |
| H$_2$ | 455 | 523 | 424 |
| H$_3$ | 666 | 596 | 426 |
| H$_4$ | 796 | 573 | 358 |
| H$_5$ | 715 | 477 | 289 |
| H$_6$ | 504 | 404 | 287 |
| Phenyl Ring 4 | | | |
| H$_2$ | −250 | 366 | 443 |
| H$_3$ | −341 | 398 | 519 |
| H$_4$ | −200 | 417 | 594 |
| H$_5$ | 30 | 403 | 593 |
| H$_6$ | 121 | 371 | 517 |
| Phenyl Ring 5 | | | |
| H$_2$ | −351 | 216 | 362 |
| H$_3$ | −575 | 172 | 346 |
| H$_4$ | −670 | 161 | 262 |
| H$_5$ | −542 | 194 | 195 |
| H$_6$ | −318 | 239 | 212 |

[a] Temperature factors for the hydrogen atoms are chosen to be 3.0 Å$^2$.

**Table V.** Bond Distances (Å) for $[Co(CNC_6H_5)_5][ClO_4]_2\cdot{}^1/_2ClCH_2CH_2Cl$

| Bond | Distance | Bond | Distance |
|---|---|---|---|
| Co–C$_1$ | 1.950 (11) | Co–C$_{11}$ | 4.455 (10) |
| Co–C$_2$ | 1.831 (11) | Co–C$_{21}$ | 4.322 (10) |
| Co–C$_3$ | 1.833 (12) | Co–C$_{31}$ | 4.332 (8) |
| Co–C$_4$ | 1.882 (12) | Co–C$_{41}$ | 4.342 (8) |
| Co–C$_5$ | 1.826 (11) | Co–C$_{51}$ | 4.360 (7) |
| Co–O$_5$ | 2.594 (10) | | |
| Av basal Co–C | 1.843 (13)[a] | | |
| Co–N$_1$ | 3.106 (11) | N$_1$–C$_{11}$ | 1.351 (14) |
| Co–N$_2$ | 2.986 (4) | N$_2$–C$_{21}$ | 1.344 (11) |
| Co–N$_3$ | 2.989 (11) | N$_3$–C$_{31}$ | 1.355 (14) |
| Co–N$_4$ | 3.040 (6) | N$_4$–C$_{41}$ | 1.304 (10) |
| Co–N$_5$ | 2.985 (10) | N$_5$–C$_{51}$ | 1.380 (13) |
| Cl$_1$–O$_1$ | 1.332 (14) | Cl$_2$–O$_5$ | 1.396 (9) |
| Cl$_1$–O$_2$ | 1.311 (19) | Cl$_2$–O$_6$ | 1.413 (18) |
| Cl$_1$–O$_3$ | 1.236 (17) | Cl$_2$–O$_7$ | 1.327 (11) |
| Cl$_1$–O$_4$ | 1.355 (22) | Cl$_2$–O$_8$ | 1.319 (15) |
| Fixed Bond Lengths | | | |
| Cyanide C–N | 1.160 | Solvent C–C | 1.490 |
| Phenyl C–C | 1.397 | Solvent Cl–C | 1.781 |

[a] See ref 22.

**Table VI.** Bond Angles (deg) for $[Co(CNC_6H_5)_5][ClO_4]_2\cdot{}^1/_2ClCH_2CH_2Cl$

| Atoms | Angles | Atoms | Angles |
|---|---|---|---|
| C$_1$–Co–C$_2$ | 98.2 (6) | Co–C$_1$–N$_1$ | 174.2 (11) |
| C$_1$–Co–C$_3$ | 95.4 (6) | Co–C$_2$–N$_2$ | 172.8 (12) |
| C$_1$–Co–C$_4$ | 93.0 (6) | Co–C$_3$–N$_3$ | 174.3 (11) |
| C$_1$–Co–C$_5$ | 93.7 (5) | Co–C$_4$–N$_4$ | 175.0 (12) |
| C$_2$–Co–C$_3$ | 84.8 (6) | Co–C$_5$–N$_5$ | 176.7 (10) |
| C$_2$–Co–C$_4$ | 168.8 (6) | C$_1$–N$_1$–C$_{11}$ | 178.1 (11) |
| C$_2$–Co–C$_5$ | 92.6 (6) | C$_2$–N$_2$–C$_{21}$ | 175.3 (21) |
| C$_3$–Co–C$_4$ | 92.9 (6) | C$_3$–N$_3$–C$_{31}$ | 173.5 (10) |
| C$_3$–Co–C$_5$ | 170.8 (6) | C$_4$–N$_4$–C$_{41}$ | 179.0 (13) |
| C$_4$–Co–C$_5$ | 88.0 (6) | C$_5$–N$_5$–C$_{51}$ | 176.3 (8) |
| O$_5$–Co–C$_1$ | 175.3 (5) | O$_5$–Co–C$_4$ | 82.3 (5) |
| O$_5$–Co–C$_2$ | 86.5 (5) | O$_5$–Co–C$_5$ | 86.7 (4) |
| O$_5$–Co–C$_3$ | 84.4 (5) | Cl$_2$–O$_5$–Co | 135.6 (7) |
| O$_1$–Cl$_1$–O$_2$ | 114.3 (13) | O$_5$–Cl$_2$–O$_6$ | 108.2 (9) |
| O$_1$–Cl$_1$–O$_3$ | 115.1 (14) | O$_5$–Cl$_2$–O$_7$ | 114.9 (7) |
| O$_1$–Cl$_1$–O$_4$ | 107.6 (13) | O$_5$–Cl$_2$–O$_8$ | 110.9 (9) |
| O$_2$–Cl$_1$–O$_3$ | 109.7 (15) | O$_6$–Cl$_2$–O$_7$ | 111.1 (11) |
| O$_2$–Cl$_1$–O$_4$ | 103.7 (15) | O$_7$–Cl$_2$–O$_8$ | 99.3 (13) |
| O$_3$–Cl$_1$–O$_4$ | 105.3 (18) | O$_7$–Cl$_2$–O$_8$ | 111.3 (10) |

**Table VII.** Root-Mean-Square Amplitudes of Vibration (Å) in $[Co(CNC_6H_5)_5][ClO_4]_2\cdot{}^1/_2ClCH_2CH_2Cl$

| Atom | Min | Intermed | Max |
|---|---|---|---|
| Co | 0.176 (3) | 0.206 (3) | 0.217 (3) |
| CoC$_1$ | 0.17 (3) | 0.20 (2) | 0.25 (2) |
| CoC$_2$ | 0.16 (3) | 0.21 (2) | 0.26 (2) |
| CoC$_3$ | 0.17 (3) | 0.20 (2) | 0.27 (2) |
| CoC$_4$ | 0.16 (3) | 0.22 (2) | 0.26 (2) |
| CoC$_5$ | 0.16 (3) | 0.20 (2) | 0.25 (2) |
| CoN$_1$ | 0.18 (2) | 0.21 (2) | 0.26 (2) |
| CoN$_2$ | 0.17 (2) | 0.19 (2) | 0.27 (2) |
| CoN$_3$ | 0.18 (2) | 0.25 (2) | 0.26 (2) |
| CoN$_4$ | 0.17 (2) | 0.25 (2) | 0.28 (2) |
| CoN$_5$ | 0.15 (2) | 0.22 (2) | 0.27 (2) |
| Cl$_1$ | 0.239 (7) | 0.305 (7) | 0.329 (7) |
| Cl$_2$ | 0.217 (7) | 0.228 (6) | 0.275 (6) |
| O$_1$ | 0.28 (2) | 0.41 (2) | 0.61 (2) |
| O$_2$ | 0.31 (2) | 0.46 (2) | 0.63 (3) |
| O$_3$ | 0.24 (2) | 0.41 (2) | 0.80 (3) |
| O$_4$ | 0.36 (3) | 0.48 (3) | 0.71 (3) |
| O$_5$ | 0.18 (2) | 0.23 (2) | 0.40 (2) |
| O$_6$ | 0.31 (2) | 0.41 (2) | 0.60 (2) |
| O$_7$ | 0.20 (2) | 0.28 (2) | 0.56 (2) |
| O$_8$ | 0.28 (2) | 0.34 (2) | 0.65 (3) |
| EtCl$_1$ | 0.46 (3) | 0.50 (2) | 0.61 (3) |
| EtCl$_2$ | 0.33 (2) | 0.57 (3) | 0.68 (3) |

attributed to error introduced by the high correlation of the positional parameters with the large motion of these oxygen atoms.

The 1,2-dichloroethane solvent molecule is the trans rotamer and is located slightly off a crystallographic inversion center. The Cl–C and the C–C bond distances were held constant at 1.781 and 1.490 Å, respectively. The closest intermolecular contact is 3.52 Å between Cl4 and N4.

The presence of the perchlorate ion below the basal plane of the $[Co(CNC_6H_5)_5]^{2+}$ ion causes a significant distortion of the usual square-pyramidal geometry in which the apex–M–base angle is about 100–103°. The basal ligands are bent away from the perchlorate ion, forming a C$_{apical}$–Co–C$_{basal}$ angle of 95.0 (3)° and the cobalt atom lies 0.16 Å above the basal plane of carbon atoms. Although the cation coordination appears to be nearly octahedral, the Co–O$_5$ distance of 2.59 Å is too long to be considered a full bond. The bond order for the Co–O$_5$ bond is approximately 0.1 using Pauling's equation[24] and 1.97 Å as the distance of a Co–O single bond.[25] This distance is significantly shorter than 2.77 Å, the sum of the van der Waals radius of 1.40 Å for oxygen[24] and the covalent radius of 1.37 Å for Co(II).[26] According to ligand field calculations the apical ligand–metal bond should undergo an elongation as the apex–M–base angle distorts from 100 to 90°.[27,28] Such an elongation is observed. The basal Co–C distances compare well to the average basal Co–C bonds of 1.84 Å in the $[Co(CNC_6H_5)_5]^+$ cation[29] and 1.81 Å in $[Co(CNC_6H_4CH_3)_4]I_2$.[30] The bond shortening has been ascribed to the $\pi$-bonding capabilities of the phenyl isocyanide ligand. The geometries of the d$^7$ and d$^8$ five-coordinate cyanide and isocyanide complexes have been compared in other papers in this series.[5,29] In the present case we wish to concentrate on just the changes in geometry that accompany the oxidation of $[Co(CNC_6H_5)_5]^+$ to $[Co(CNC_6H_5)_5]^{2+}$. Although the basal bond lengths are equal (1.84 Å), the change from the axial Co–C bond length for the Co(I) complex (1.88 Å)[29] to that for the Co(II) complex (1.95 Å) is at first surprising, since an increase in oxidation state almost always results in a shorter metal–ligand bond length. Apparently the decrease in $\pi$ back-bonding that accompanies the change from Co(I) to Co(II) results in a loss of bond order that more than offsets any change in bond length due to a decrease in the metal ion size. This is substantiated by the bond lengths in the coordinative isoelectronic $[Co(CN)_5]^{3-}$ ion,[5] in which the axial and basal Co–C bonds are 0.05 Å longer than in $[Co(CNC_6H_5)_5]^{2+}$.

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**Registry No.** $[Co(CNC_6H_5)_5][ClO_4]_2\cdot{}^1/_2ClCH_2CH_2Cl$, 56195-62-1.

**Supplementary Material Available.** Tables VIII and IX, showing the parameters for several best weighted least-squares planes and dihedral angles of the cation, respectively, and a table listing the observed and calculated structure factors 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 AIC50225C-11-75.

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