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Crystal and Molecular Structure of Tris(*p*-fluorophenyl isocyanide)bis(trimethyl phosphite)cobalt(I) Tetrafluoroborate, $[Co(CNC_6H_4F)_3\{P(OCH_3)_3\}_2]BF_4$

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The structure of $[Co(CNC_6H_4F)_3\{P(OCH_3)_3\}_2]BF_4$ has been determined using three-dimensional X-ray diffractometer data collected at −40 °C. The pale yellow crystals are orthorhombic, space group *Pnna*, with a = 17.168 (2) Å, b = 17.034 (3) Å, c = 12.051 (2) Å, Z = 4, density (X-ray, −40 °C) = 1.427 g cm^{-3}, and density (measured, 21 °C) = 1.422 g cm^{-3}. The structure was refined by full-matrix least squares using 1372 reflections with $I \geq 2\sigma(I)$ to a final weighted R of 0.088. The coordination around the Co(I) is very nearly trigonal bipyramidal with the complex lying on a twofold crystallographic axis and the phosphite ligands occupying the axial positions. The axial Co–P bond distance is 2.137 (3) Å; the two independent Co–C bond distances are 1.83 (2) and 1.85 (1) Å. The P–Co–P bond angles are 90.3 (1), 90.3 (4), and 89.4 (4)°; the two independent equatorial angles are 115.7 (5) and 122.2 (4)°.

Introduction

Distortions of bond distances and angles from idealized trigonal-bipyramidal geometry have been observed in pentakis(aromatic isocyanide)cobalt(I) compounds including $[Co(CNC_6H_5)_5]ClO_4{\cdot}HCCl_3$,[1] $[Co(CNC_6H_4Cl\text{-}p)_5]BF_4$,[2] $[Co(CNC_6H_5)_5]ClO_4$,[3,4] and $[Co\{CNC_6H_2(CH_3)_3\text{-}2,4,6\}_5]ClO_4$.[5] Recently, trialkyl phosphites have been shown to readily replace aromatic isocyanide ligands in $[Co(CNR)_5]ClO_4$ and $[Co(CNR)_5]BF_4$ to yield $[Co(CNR)_3\{P(OR')_3\}_2]ClO_4$ and $Co(CNR)_3\{P(OR')_3\}_2]BF_4$.[6] On the basis of infrared and ^{59}Co NQR data, Becker[6] predicted these compounds to have strict D_{3h} symmetry in solution but to have distorted trigonal-bipyramidal geometry in the solid state. To learn more about the geometries of these complexes and the extent of distortion, if any, the X-ray structural determination of tris(*p*-fluorophenyl isocyanide)bis(trimethyl phosphite)cobalt(I) tetrafluoroborate, $[Co(CNC_6H_4F\text{-}p)_3\{P(OCH_3)_3\}_2]BF_4$, was undertaken. Also of interest was the linearity of the Co—C≡N and –C≡N—C bonds, found to be bent in the pentakis(phenyl isocyanide) compounds. Additionally, it was hoped that this investigation of the structure at −40 °C would yield improved bond distances and angles for the trimethyl phosphite ligand, which in previous structures was found to have very large thermal motions.

Experimental Section

Collection and Reduction of Data. The compound $[Co(CNC_6H_4F)_3\{P(OCH_3)_3\}_2]BF_4$ was prepared by Dr. C. A. L. Becker in a procedure described elsewhere.[6,7] Crystals were obtained by slow

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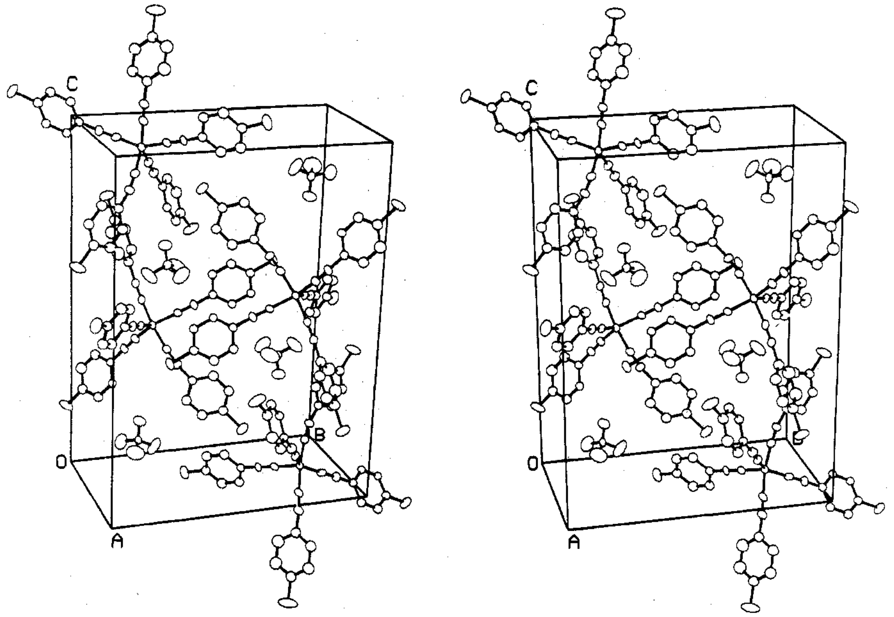

Figure 1. Packing diagram for $[Co(CNC_6H_4F)_3\{P(OCH_3)_3\}_2]BF_4$.

Table I

Mol formula	$[Co(CNC_6H_4F)_3\{P(OCH_3)_3\}_2]BF_4$
Mol wt	757.23
Space group	*Pnna*
Cell constants	
a, Å	17.168 (2),[a] 17.301 (2)[b]
b, Å	17.034 (3),[a] 17.102 (2)[b]
c, Å	12.051 (2),[a] 12.097 (1)[b]
Vol, Å^3	3524.3,[a] 3579.3[b]
Z	4
Density, g cm^{-1}	1.405 (X-ray; room temp) 1.427 (X-ray; −40 °C) 1.422 (measd; room temp)
Cryst dimensions	0.15 × 0.19 × 0.41 mm
μ	6.77 cm^{-1}

[a] At −40 °C; measured on a Syntex $P2_1$; Mo radiation. [b] At room temperature; measured on a GE XRD-5; Cu radiation.

evaporation of a solution in which a mixture of 75% dichlorobenzene and 25% *cis*-1,2-dichloroethylene was used as solvent. The pale yellow crystals generally exhibited the forms {010}, {101}, and {121}. The crystal chosen for data collection measured 0.15 × 0.19 × 0.41 mm, respectively, perpendicular to faces (101), ($\bar{1}01$), and (010).

Data were collected at −40 °C with a Syntex $P2_1$ automatic diffractometer using Mo radiation (λ 0.71069 Å) monochromatized by a graphite crystal. Systematic absences of $h = 2n + 1$ for $hk0$, $h + l = 2n + 1$ for $h0l$, and $k + l = 2n + 1$ for $0kl$ uniquely established the space group to be *Pnna*. The unit cell dimensions and other crystal data are listed in Table I.

The ω-scan technique was employed for data collection with a scan rate, S, varying from 0.5 to 4.0° min^{-1} (directly dependent on peak intensity) with a majority of the 2763 reflections (within the limits, $4 \le 2\theta \le 55°$) measured at the slowest rate. The peaks were scanned over a 1.0° range bisected by the Kα position, accumulating P counts. Background measurements B_1 and B_2 were made on both sides of the peak at displacements of 1.0° from the Kα position each for a time equal to half the total scan time. Net intensity for each peak was calculated as $I = S[P - (B_1 + B_2)]$. Standard deviations in intensities, $\sigma(I)$, and in structure factor amplitudes, $\sigma(F_o)$, were derived directly from counting statistics: $\sigma(I) = S(P + B_1 + B_2)^{1/2}$. The intensities of four standard reflections were measured after every 96 reflections; the intensities of these reflections were constant within experimental errors. Lorentz, polarization, and absorption (μ = 6.77 cm^{-1}, Mo Kα radiation) corrections were applied.

Solution and Refinement of the Structure. The position of the cobalt atom was determined from a three-dimensional Patterson synthesis. An electron density map, phased by the cobalt position, revealed several other atoms; the positions of all other nonhydrogen atoms were found in Fourier maps after several cycles of least-squares refinement of the partial structure. Hydrogen atoms were not located and were not used in the refinement.

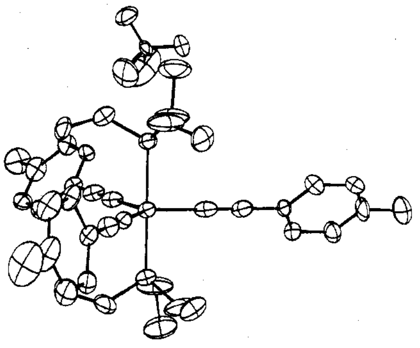

Figure 2. A perspective view of the $Co(CNC_6H_4F)_3\{P(OCH_3)_3\}_2^+$ cation and BF_4^- anion (ORTEP diagram).

Only the 1372 (49.7%) reflections for which $I \ge 2\sigma(I)$ were used in the solution and refinement of the structure; weights for these reflections were assigned as $1/\sigma^2(F_o)$. Full-matrix least-squares refinement[8] of all positional and anisotropic thermal parameters converged at a conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.091 and a weighted $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$ of 0.088. When all 2763 reflections were included, the conventional R was found to be 0.168 and the R_w was 0.094. The largest shift of any parameter in the final cycle of refinement was 0.55σ (in the BF_4^- ion). The largest peak of residual electron density in the final difference map (all reflections included) had a magnitude of 0.85 e/Å^3 and was located near the phosphite ligand.

The atomic scattering factors were those of Cromer and Waber (1965)[9] and the real and imaginary parts of the anomalous dispersion corrections for cobalt and phosphorus were those of Cromer (1965).[10] The final positional and anisotropic thermal parameters of the atoms are shown in Table II. The final observed and calculated structure factor amplitudes for the 2763 reflections are available as supplementary material.

Description of the Structure

The structure consists of discrete $[Co(CNC_6H_4F)_3\{P(OCH_3)_3\}_2]^+$ cations and BF_4^- anions. A stereoscopic crystal packing diagram is shown in Figure 1; the cation–anion pair is shown in Figure 2. The cation has trigonal-bipyramidal geometry with the two phosphite ligands occupying the axial positions. A twofold axis passes through the cation such that there are only three crystallographically independent ligands, one axial and two equatorial. One of the isocyanide ligands is collinear with the twofold axis. The overall coordination

Table II. Final Positional and Thermal Parameters[a] for $[Co(CNC_6H_4F)_3\{P(OCH_3)_3\}_2]BF_4$ with Esd's in Parentheses

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	0.250	0.000	0.245 (1)	4.8 (1)	4.3 (1)	5.7 (1)	0.9 (1)	0.0 (0)	0.0 (0)
C(2)	0.291 (1)	0.083 (1)	0.327 (1)	5 (1)	7 (1)	6 (1)	3 (1)	0 (1)	1 (1)
N(3)	0.314 (1)	0.133 (1)	0.384 (1)	6 (1)	6 (1)	9 (1)	2 (1)	−1 (1)	−1 (1)
C(4)	0.342 (1)	0.191 (1)	0.454 (1)	5 (1)	4 (1)	7 (1)	0 (1)	−2 (1)	−2 (1)
C(5)	0.415 (1)	0.223 (1)	0.432 (1)	5 (1)	7 (1)	16 (2)	−1 (1)	−1 (1)	0 (1)
C(6)	0.440 (1)	0.280 (1)	0.501 (2)	4 (1)	6 (1)	16 (2)	0 (1)	−1 (1)	0 (1)
C(7)	0.391 (1)	0.305 (1)	0.585 (1)	9 (1)	6 (1)	14 (2)	−2 (1)	−5 (1)	−3 (1)
C(8)	0.318 (1)	0.275 (1)	0.607 (1)	7 (1)	6 (1)	12 (1)	−1 (1)	−2 (1)	−1 (1)
C(9)	0.293 (1)	0.215 (1)	0.538 (1)	5 (1)	5 (1)	6 (1)	0 (1)	1 (1)	−1 (1)
F(10)	0.416 (1)	0.364 (1)	0.652 (1)	11 (1)	10 (1)	27 (1)	−2 (1)	−5 (1)	−6 (1)
C(11)	0.250	0.000	0.094 (1)	5 (1)	4 (1)	11 (2)	0 (1)	0 (1)	0 (1)
N(12)	0.250	0.000	−0.001 (1)	6 (1)	6 (1)	6 (1)	1 (1)	0 (1)	0 (1)
C(13)	0.250	0.000	−0.115 (1)	6 (1)	4 (1)	6 (1)	0 (1)	0 (1)	0 (1)
C(14)	0.195 (1)	0.045 (1)	−0.172 (1)	8 (1)	4 (1)	9 (1)	0 (1)	−3 (1)	1 (1)
C(15)	0.195 (1)	0.045 (1)	−0.286 (1)	11 (1)	6 (1)	8 (1)	0 (1)	−4 (1)	0 (1)
C(16)	0.250	0.000	−0.339 (2)	18 (2)	6 (2)	5 (1)	0 (2)	0 (2)	0 (1)
F(17)	0.250	0.000	−0.452 (1)	28 (1)	14 (2)	5 (1)	0 (1)	0 (1)	0 (1)
P(18)	0.139 (0)	0.057 (1)	0.246 (1)	4.9 (2)	5.0 (1)	8.8 (3)	1.3 (1)	1.0 (3)	0.9 (2)
O(19)	0.075 (1)	0.027 (1)	0.168 (1)	5 (1)	12 (1)	39 (2)	3 (1)	−6 (1)	−12 (1)
C(20)	0.059 (1)	−0.050 (1)	0.141 (1)	8 (1)	6 (1)	26 (2)	−2 (1)	−4 (1)	−2 (1)
O(21)	0.102 (1)	0.060 (1)	0.361 (1)	10 (1)	19 (1)	12 (1)	9 (1)	3 (1)	2 (1)
C(22)	0.028 (1)	0.102 (1)	0.391 (2)	11 (1)	15 (2)	29 (3)	6 (1)	6 (2)	−1 (2)
O(23)	0.135 (1)	0.144 (1)	0.216 (1)	8 (1)	8 (1)	37 (2)	3 (1)	3 (1)	8 (1)
C(24)	0.173 (1)	0.180 (1)	0.122 (1)	10 (1)	5 (1)	15 (2)	1 (1)	4 (1)	4 (1)
B	0.092 (1)	0.250	0.750	2 (1)	8 (2)	26 (4)	0 (1)	0 (1)	10 (3)
F(1)	0.143 (1)	0.248 (1)	0.678 (1)	24 (1)	14 (1)	66 (4)	3 (1)	32 (2)	1 (2)
F(2)	0.053 (1)	0.188 (1)	0.765 (1)	7 (1)	8 (1)	37 (2)	−2 (1)	5 (1)	5 (1)

[a] Anisotropic thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{23}kl)] \times 10^3$.

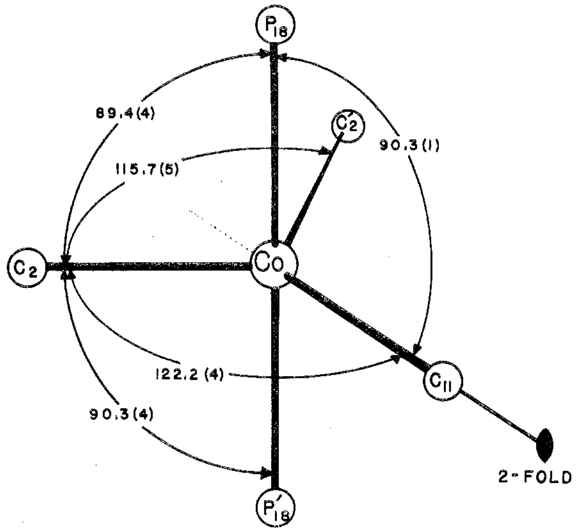

Figure 3. Coordination sphere of the cobalt(I).

geometry, shown in Figure 3, of the $[Co(CNC_6H_4F)_3\{P(OCH_3)_3\}_2]^+$ cation exhibits only minor deviations from D_{3h} symmetry. The axial to equatorial angles are 89.4 (4), 90.3 (1), and 90.3 (4)°. The unique equatorial angles are 122.2 (4) and 115.7 (5)°. All of the Co—C≡N and –C≡N—C bond angles are within 4° of being 180°. Thermal motion in the cation is significant and generally increases with increasing distance from the cobalt position.

The BF_4^- anion is located on another, independent twofold axis. All the atoms in the anion show very high thermal motion, even at −40 °C. The independent B–F distances are 1.23 (2) and 1.27 (1) Å and the F–B–F bond angles are 90 (1), 107 (1), 115 (1), and 118 (1)°.

Discussion

A reversal of the d^0 Muetterties rule,[11,12] which states that the more electronegative substituents prefer axial positions in trigonal-bipyramidal structures, was observed in this compound. This reversal was not unexpected and, in fact, was predicted and observed in the case of the $[Fe(CO)_4CN]^-$ anion by Goldfield and Raymond.[13] Rossi and Hoffmann,[14] on the basis of unified molecular orbital calculations, found that the equatorial σ orbitals place increased electron density at the equatorial positions so that they become more negative than the axial positions and, therefore, are the preferred sites for the more electronegative substituents. A consideration of the π molecular orbitals resulted in the same general conclusions. In summary, they predicted σ- and π-acceptor ligands to prefer equatorial positions and σ and π donors to prefer axial positions. In the title compound the phosphite ligands, σ donors,[15–17] occupy the axial positions, whereas the isocyanide ligands, π acceptors,[16,17] occupy equatorial sites. Other deviations from the Muetterties rule have also been observed.[18–20]

In the observed arrangement each of the five ligands is nearly free of close steric contact. It has, however, been shown in the structure of $NiI_2\{P(OCH_3)_3\}_3$[18] that trimethyl phosphite ligands may occupy both axial and equatorial positions, only 90° apart, without significant deviations from regular trigonal-bipyramidal geometry. The isocyanide ligands could occupy any combination of positions without significant steric interaction. The internal packing arrangement of the atoms in the phosphite ligands may account for the slight distortion of the equatorial angles from strict D_{3h} symmetry. The P–O bonds are approximately staggered relative to the Co–C bonds, an arrangement observed in other phosphite structures. The methoxy groups of the phosphite ligands do not follow each other in the "head-to-tail" manner observed in various degrees in several other compounds;[18,19] rather two of the terminal methyl groups on each ligand are bent inward toward the equatorial plane, whereas the other is bent outward away from that plane. The distances between the three independent methyl carbon atoms and the equatorial plane are 2.54, 2.58, and 4.20 Å, values that compare very well with the distances 2.64, 2.66, and 4.22 Å observed for a similar arrangement in *trans*-$Fe(CO)_3P(OCH_3)_{3_2}$.[21] Because of the orientation of the twofold axis with respect to the phosphite ligand in the title compound, two of the methyl groups closely approach methyl groups on the other side of the equatorial plane, as shown in Figure 4. The proximity of these four methyl groups to the phenyl isocyanide ligands could exert a repulsive force re-

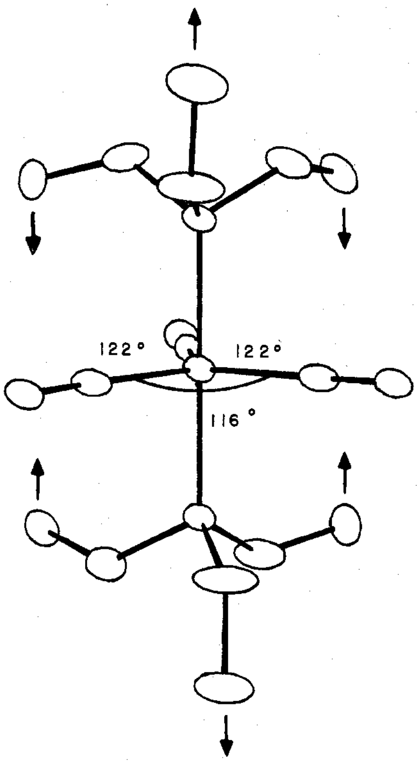

Figure 4. Geometry of the phosphite ligands.

Table III. Deviations of the Equatorial Plane from Planarity (Å)

Equation of Plane: $-0.089P - 0.439Q - 0.000R - 3.856 = 0.000^a$

Co(1)	0.000	N(3)′	−0.005
C(2)	−0.008	C(11)	0.000
C(2)′	0.008	N(12)	0.000
N(3)	0.005		

[a] In angstroms, where *P, Q,* and *R* are directions *a, b,* and *c*; all atoms were given equal weight in the calculation.

Table IV. Bond Distances (Å) in $[Co(CNC_6H_4F)_3\{P(OCH_3)_3\}_2]BF_4$

Co–C(2)	1.85 (1)	C(13)–C(14)	1.40 (1)
Co–C(11)	1.83 (2)	C(14)–C(15)	1.38 (2)
Co–P(18)	2.137 (3)	C(15)–C(16)	1.37 (2)
C(2)–N(3)	1.17 (2)	C(16)–F(17)	1.36 (2)
N(3)–C(4)	1.38 (2)	P(18)–O(19)	1.54 (1)
C(4)–C(5)	1.39 (2)	P(18)–O(21)	1.53 (1)
C(4)–C(9)	1.39 (2)	P(18)–O(23)	1.53 (1)
C(5)–C(6)	1.36 (2)	O(19)–C(20)	1.37 (2)
C(6)–C(7)	1.38 (2)	O(21)–C(22)	1.50 (2)
C(7)–C(8)	1.39 (3)	O(23)–C(24)	1.44 (2)
C(7)–F(10)	1.37 (2)	B–F(1)	1.23 (2)
C(8)–C(9)	1.39 (2)	B–F(2)	1.27 (1)
C(11)–N(12)	1.14 (2)		
N(12)–C(13)	1.37 (2)		

Table V. Bond Angles (deg) for $[Co(CNC_6H_4F)_3\{OCH_3)_3\}_2]BF_4$

C(2)–Co–C(2)′	115.7 (5)	C(14)–C(13)–C(14)′	122 (1)
C(2)–Co–C(11)	122.2 (4)	C(13)–C(14)–C(15)	119 (1)
C(2)–Co–P(18)	89.4 (4)	C(14)–C(15)–C(16)	118 (1)
C(2)–Co–P(18)′	90.3 (4)	C(15)–C(16)–C(15)′	124 (1)
C(11)–Co–P(18)	90.3 (1)	C(15)–C(16)–F(17)	118 (1)
Co–C(2)–N(3)	176 (1)	Co–P(18)–O(19)	119.2 (5)
C(2)–N(3)–C(4)	178 (1)	Co–P(18)–O(21)	113.4 (5)
N(3)–C(4)–C(5)	118 (1)	Co–P(18)–O(23)	118.3 (5)
N(3)–C(4)–C(9)	117 (1)	O(19)–P(18)–O(21)	98.3 (7)
C(5)–C(4)–C(9)	125 (1)	O(19)–P(18)–O(23)	105.5 (7)
C(4)–C(5)–C(6)	117 (1)	O(21)–P(18)–O(23)	99.3 (8)
C(5)–C(6)–C(7)	118 (1)	P(18)–O(19)–C(20)	127 (1)
C(6)–C(7)–C(8)	125 (2)	P(18)–O(21)–C(22)	126 (1)
C(6)–C(7)–F(10)	118 (2)	P(18)–O(23)–C(24)	126 (1)
C(8)–C(7)–F(10)	117 (2)		
C(7)–C(8)–C(9)	116 (1)	F(1)–B–F(1)′	90 (1)
C(8)–C(9)–C(4)	118 (1)	F(1)–B–F(2)	118 (1)
Co–C(11)–N(12)	180	F(2)–B–F(2)′	115 (1)
C(11)–N(12)–C(13)	180	F(2)–B–F(1)′	107 (1)
N(12)–C(13)–C(14)	119 (1)		

sponsible for the slight increase in two of the equatorial angles. Also, these methyl groups are probably responsible for the differences in dihedral angles of the phenyl rings. The phenyl ring lying along the twofold axis and bordered on each side by the closely approaching methyl groups forms an angle of 76.8° with the equatorial plane, whereas the other phenyl rings, bordered only on one side by these methyls, make angles of 48.3°.

The planarity of the atoms in the equatorial plane, as determined by the cobalt atom and the cyano groups, is shown in Table III. Atomic deviations from this plane indicate no significant distortion toward square-pyramidal geometry. The phenyl rings are essentially planar with no deviations from planarity larger than 0.012 Å.

Bond distances and bond angles are listed in Tables IV and V. The Co—C≡N and C≡N—C bond angles deviate only slightly from linearity with values of 176 (1)° and 180° [22] and 178 (1) and 180°,[22] respectively, for the two independent ligands. In previous pentakis structures these bond angles were observed as small as 169 and 165°, respectively. The Co–C distances, 1.83 and 1.85 Å, are consistent with previously determined values.[1-3,5,16] Agreement with other bond distances and angles throughout the structure with accepted values is generally good. Irregular distances and angles in the extremes of the cation and in the BF_4^- anion can be attributed to the high thermal motion which persists even at −40 °C. Comparison of phosphite ligand distances and angles to those listed in a recent compilation[18] of averages for phosphite containing compounds indicates no significant discrepancies. Unfortunately, the extreme thermal motion in this rather loosely constrained ligand made it impossible to determine the bonding parameters of the group any more precisely than had been done in other studies.

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Registry No. $[Co(CNC_6H_4F)_3\{P(OCH_3)_3\}_2]BF_4$, 58592-14-6.

Supplementary Material Available: A listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Spectroscopic and Magnetic Properties of a New Class of Dimeric, Fluoro-Bridged High-Spin Cobalt(II) Compounds Containing Substituted-Pyrazole Ligands

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A new type of dimeric, five-coordinate, high-spin Co(II) compound, containing an asymmetric (CoF_2Co) bridge, is described. The product is formed upon reaction of cobalt(II) tetrafluoroborate with a 4-substituted 3,5-dimethylpyrazole in ethanol solution with triethyl orthoformate added for dehydration. The X-ray structure of one compound in the series, i.e., μ-difluoro-hexakis(3,5-dimethylpyrazole)dicobalt(II) bis(tetrafluoroborate), is described in detail. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.325$ (5) Å, $b = 13.753$ (5) Å, $c = 17.234$ (6) Å, $\beta = 117.92$ (5)°, and $Z = 4$. Single-crystal X-ray diffraction data, complete to $\theta = 26°$ (Mo Kα radiation), were collected with a Nonius CAD-3 automated diffractometer, and the structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques. The final discrepancy index is $R_F = 5.6\%$ for 3084 independent reflections. The symmetry around Co(II) is nearly trigonal bipyramidal. Ligand field spectra of the compounds can be interpreted on the basis of this symmetry. A unique type of hydrogen bonding is observed. This so-called trifurcated hydrogen bonding may cause the observed splitting of the (stretching) vibration at frequencies of the BF_4^- anion and the appearance of "forbidden" bands in the infrared spectra. In all compounds the magnetic-exchange coupling constant between the Co(II) ions is close to zero. The bridging Co–F–Co angle is 98.8 (2)°, in agreement with theories relating the Co–F–Co angle and magnetic exchange.

Introduction

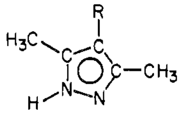
The BF_4^- anion is frequently used in coordination chemistry as a stabilizing counterion in cationic complexes. This ion is comparable in size with the perchlorate ion and has the advantage of not being a potential explosive. The anion is supposed to be stable in both aqueous and nonaqueous solution, although heating or strong bases may cause decomposition.

Recently, it has been shown that, in the presence of strong bases having bulky substituents (such as quinuclidine and 3,5-dimethylpyrazole), decomposition of the BF_4^- anion occurs, resulting in anhydrous metal fluorides for quinuclidine[1] and polymeric products of stoichiometry $MF_2(ligand)_2$ for 3,5-dimethylpyrazole.[2] In the case of 3-hydroxypyridine, a monomeric product $MF_2(ligand)_4$ has been analyzed, with trans fluoride anions.[3] Recently, a molybdenum fluoride coordination compound has been described.[4] Upon reaction of hydrated $Co(BF_4)_2$ with excess 3,5-dimethylpyrazole (and its 4-substituted products) under dehydrating conditions, compounds of empirical formula $Co(ligand)_3BF_5$ are obtained, which appeared to be low-molecular-weight products, with coordinated F^- ions, distorted BF_4^- anions, and Co(II) in a trigonal-bipyramidal geometry.

The present paper describes the spectroscopic and magnetic properties of this class of compounds. The molecular structure of one of these compounds is described in detail. Preliminary reports of this work have appeared.[5]

Experimental Section

Syntheses of the New Compounds. 4-Substituted 3,5-dimethylpyrazoles were prepared by condensation of acetylacetone (or its 3-substituted products) with hydrazine according to standard procedures.[6] In this way products of formula I with R = H (DMPZ), Me (TMPZ), Et (EDMPZ), *n*-Pr (PDMPZ), and benzyl (BDMPZ) were obtained, which were purified by crystallization and characterized by NMR techniques. Cobalt(II) tetrafluoroborate was commercially available as the hydrate. Upon reaction of $Co(H_2O)_6(BF_4)_2$ with the pyrazole ligands in the ratio 1:4 using ethanol as a solvent and an excess of triethyl orthoformate as a dehydrating agent, violet crystals of composition $Co(ligand)_3BF_5$ separate.



I

With smaller amounts of the dehydrating agent or a lower ligand:metal ratio, pink products of formula $Co(ligand)_2F_2$ separate, as described previously.[2] Upon reaction of a 1:3 mixture of $Co(H_2O)_6(ClO_4)_2$ and $Co(H_2O)_6(BF_4)_2$ with DMPZ, a product of composition $Co(DMPZ)_3F(ClO_4)$ can be isolated, which appears to be isomorphous with the corresponding BF_4 compound. The same product can also be prepared from equimolar amounts of $Co(DMPZ)_2F_2$ and $Co(DMPZ)_4(ClO_4)_2$ in $CHCl_3$.

Determination of the Molecular Structure. Violet crystals of $CoF(DMPZ)_3(BF_4)$ were prepared as described above. The nearly octahedrally shaped crystal selected for X-ray analysis measured approximately 0.15 mm along the edges. Weissenberg photographs, taken with Cu Kα radiation, showed monoclinic diffraction symmetry and systematic extinctions of $P2_1/c$. The unit cell dimensions, deduced from measurements on a Nonius automatic single-crystal diffractometer (CAD-3), are $a = 10.325$ (5), $b = 13.753$ (5), $c = 17.234$ (6) Å, and $\beta = 117.92$ (5)° (Mo Kα_1 = 0.70926 Å). The volume of the unit cell is 2162.58 Å^3 and contains four molecules.

The intensities were measured up to $\theta = 26°$ with the θ–2θ scan mode using Mo Kα radiation and a graphite monochromator (monochromator angle 6°). High intensities were reduced by nickel filters. From the 3084 reflections above background, 1664 were significantly ($>2.85\ \sigma(I)$) different from the background intensity. In the reduction of the intensities to structure factors no correction for absorption has been applied ($\mu_{(\mathrm{Mo\ K}\alpha)} = 9.7\ \mathrm{cm}^{-1}$). Crystal data and experimental parameters are summarized in Table I.

The structure was solved by the heavy-atom method and refined by (blocked) full-matrix least-squares calculations using unit weights. The form factors used for Co, F, N, C, and B were obtained from Cromer and Mann[7] and those for H from Stewart et al.[8] In the last difference map a rest density was found, indicating a large thermal motion of the protons of the methyl groups. Therefore, these protons were not placed. Assigned isotropic temperature factors of the remaining hydrogen atoms were not refined. The final conventional

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