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The Secondary Explosive Tetraammine-*cis*-bis(5-nitro-2*H*-tetrazolato-*N*^{2})cobalt(III) Perchlorate at 293 and 213 K

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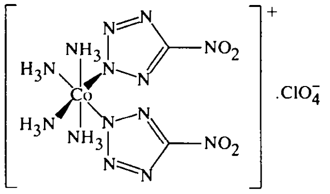
Abstract

For the title compound, (*OC*-6-22)-[Co(CN$_5$O$_2$)$_2$(NH$_3$)$_4$]ClO$_4$, the structure determination confirms the *cis* relationship of the two ring ligands deduced from NMR and shows that these ligands involve N-2 bonding to the Co atom. The accompanying low-temperature study suggests several O atoms of the ClO$_4^-$ ion are slightly disordered rather than having large thermal displacements.

Comment

As part of an effort to elucidate fundamental properties of various substituted-tetrazolato cobalt perchlorate secondary explosives (low impact sensitivity compounds which undergo a deflagration-to-detonation transition, DDT, under the appropriate confinement) (Lieberman, 1983, 1985; Graeber & Morosin, 1983), the title compound, BNCP, proved to be a more powerful explosive and undergoes DDT more rapidly than pentaammine(5-cyanotetrazolato-*N*^{2})cobalt(III) perchlorate, CP, used in national defense applications since 1979. More recently CP detonators have been used in oil-field completion work. The electron-withdrawing characteristics of substituents on the five-membered ligand ring alter the bonding capabilities and hence the nature of these energetic compounds (Graeber & Morosin, 1981).



BNCP

Initially the structure determined at room temperature [compound (1); coordinates deposited] yielded large anisotropic displacements for O7 and O8 of the perchlorate ion. This resulted in us performing a low temperature study which is in close agreement with that at room temperature; the corresponding displacement values were not proportionately reduced compared to those for the remainder of the structure, which is consistent with possible slight disorder, as found recently in other perchlorates (Lu, Chen & Chung, 1993; Chen, Liu, Mao, Hang & Tang, 1995).

The octahedrally coordinated Co atom consists of four Co—NH$_3$ bonds, average 1.951 (5) Å, and two

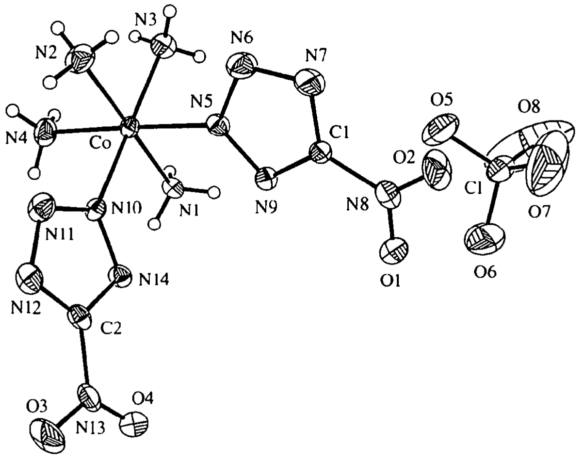


Fig. 1. The molecular structure of the BNCP cation at 213 K showing the numbering scheme and 50% probability displacement ellipsoids.

slightly shorter Co—N bonds for the *cis*-tetrazolato ligands, 1.930 (5) Å. This is consistent with the ^1H NMR spectrum which showed two equivalent ammine proton resonances at 3.79 and 4.29 p.p.m. Good agreement between the values for the intra-ligand bond lengths is obtained.

Experimental

The synthesis of BNCP was carried out by reacting the precursors tetraamminecarbonatocobalt(III) nitrate (Schlessinger, 1960, 1962) and sodium 5-nitrotetrazolate dihydrate (Lee & Coburn, 1983) in $HClO_4$ (pH ~1.8) at 353–363 K for 2 h. Extreme care should be taken in handling these compounds.

Compound (1)

Crystal data

$[Co(CN_5O_2)_2(NH_3)_4]ClO_4$
$M_r = 454.59$
Monoclinic
$P2_1/n$
$a = 10.031\,(2)$ Å
$b = 10.547\,(2)$ Å
$c = 14.861\,(3)$ Å
$\beta = 109.09\,(3)°$
$V = 1485.8\,(6)$ Å^3
$Z = 4$
$D_x = 2.032$ Mg m^{-3}
$D_m = 2.031$ Mg m^{-3}
D_m measured by gas pycnometry

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10–20°$
$\mu = 1.414$ mm^{-1}
$T = 293\,(2)$ K
Prismatic
0.31 (mount axis) × 0.27 × 0.25 mm
Yellow–orange

Data collection

Siemens *P*3 diffractometer
$\theta–2\theta$ scans
Absorption correction: none
10 540 measured reflections
2635 independent reflections
2289 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.039$

$\theta_{\rm max} = 25.06°$
$h = -11 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -17 \rightarrow 17$
2 standard reflections every 50 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.138$
$S = 1.08$
2635 reflections
274 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0897P)^2 + 1.9448P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = -0.02$
$\Delta\rho_{\rm max} = 1.19$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.53$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (2)

Crystal data

$[Co(CN_5O_2)_2(NH_3)_4]ClO_4$
$M_r = 454.59$
Monoclinic
$P2_1/n$
$a = 9.946\,(7)$ Å
$b = 10.542\,(5)$ Å
$c = 14.820\,(7)$ Å
$\beta = 108.68\,(4)°$
$V = 1472.0\,(15)$ Å^3
$Z = 4$
$D_x = 2.051$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8–18°$
$\mu = 1.427$ mm^{-1}
$T = 213\,(2)$ K
Prismatic
0.31 × 0.27 × 0.25 mm
Yellow–orange

Data collection

Siemens *P*3 diffractometer
$\theta–2\theta$ scans
Absorption correction: none
3709 measured reflections
1749 independent reflections (measurements incomplete, see below)
1431 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.024$
$\theta_{\rm max} = 25.03°$
$h = -11 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -17 \rightarrow 17$
2 standard reflections every 50 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.116$
$S = 1.03$
1749 reflections
274 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0733P)^2 + 2.7371P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.020$
$\Delta\rho_{\rm max} = 0.72$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.42$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

The low-temperature structure does not have a complete unique data set; data were initially acquired using a different cell and the crystal was lost during subsequent recollection employing overlapping shells in 2θ. The largest residual peaks (0.7 e Å^{-3}) in the difference Fourier map are primarily associated with the ClO_4 disorder. The five largest peaks are approximately 1.3–1.6 Å from the Cl atom, the next two are near the Co atom (1.0–1.3 Å), and several subsequent smaller peaks are also near these two atoms at similar distances. Attempts to refine these data using multiple regular tetrahedra proved unsatisfactory. The H-atom positions were obtained from the difference Fourier map and then for each cycle restrained as ammine groups with variable N—H [0.822 (13) Å] and Co—H [2.355 (10) Å] lengths, and a fixed H—N—H angle (107°) in further refinements [an isotropic $U = 0.078\,(7)$ and $0.063\,(7)$ Å^2 for the 293 and 213 K structures, respectively, was constrained equally for all H atoms], resulting in a reduction of the *R* values by 0.008. The final H-atom coordinates were examined for consistency with their initial coordinates as well as with respect to the hydrogen-bonding network formed. The hydrogen bonds, $H\cdots X$, span 2.34–2.67 Å with the longer distances in pairs suggesting bifurcated bonds. The structure was solved by Fourier methods and refined using *SHELXTL-Plus* (Sheldrick, 1991). Final refinement for CIF files was with *SHELXTL* (Sheldrick, 1994).

For both compounds, data collection: *SHELXTL-Plus*; cell refinement: *SHELXTL-Plus*; data reduction: *SHELXTL-Plus*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1330). Services for accessing these data are described at the back of the journal.

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Dicarbonyl(η^5-cyclopentadienyl)(pyrrolyl-*N*)iron(II)

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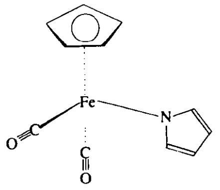
Abstract

The crystal structure of the title compound, $[Fe(C_5H_5)(C_4H_4N)(CO)_2]$, shows a discrete molecular structure with a distorted tetrahedral geometry about the Fe atom. The bond angles between the ligands in the tripod and the Fe—$Cp_{centroid}$ vector range from 121.9 to 123.7 (3)°, and the angles between the tripod ligands range from 90.5 (4) to 96.0 (4)°. The mean Fe—$C_{carbonyl}$ and Fe—C_{Cp} distances are 1.776 (4) and 2.098 (16) Å, respectively [Fe—$Cp_{centroid}$ 1.722 (4) Å], and the Fe—$N_{pyrrole}$ distance is 1.962 (3) Å. The Cp and pyrrole rings are both planar (maximum deviations of 0.007 and 0.006 Å, respectively). The rotational orientation of the Cp ring with respect to the tripod ligands is approximately eclipsed with respect to the Fe—$N_{pyrrole}$ bond [N(1)—Fe(1)—$Cp_{centroid}$—C(8) −3.1°]. The dihedral angle between the pyrrole ring and the N(1)—Fe(1)—$Cp_{centroid}$ plane is 73.7°.

Comment

Dicarbonyl(η^5-cyclopentadienyl)(pyrrolyl-*N*)iron(II), (I), was first reported in 1967 (Pauson & Quazi, 1967). The compound displays interesting chemical behavior, including the ability to undergo a reversible ‘ring-slip’ process to yield azoferrocene (Zakrzewski & Giannotti, 1990). Recently, we have shown that (I) reacts with chemical oxidants to form novel electronically conducting polymers (Martin, Dotson, Litterer, Hanks & Veas, 1996). The reactivity of (I) was explained and the structure of the resulting polymer was predicted based on force-field and semi-empirical quantum mechanical calculations. In this report, we present single-crystal diffraction data which is entirely consistent with our predicted minimum-energy gas-phase structure.



(I)

Compound (I) has the familiar ‘three-legged piano-stool’ structure (see Fig. 1). The bonding distances and angles for CO and η^5-C_5H_5 (Cp) coordination are similar to those observed in other related complexes. Average values based on a large number of carbon monoxide–iron complexes and cyclopentadienyl–iron complexes are: Fe—$C_{carbonyl}$ = 1.78 (3), C—O = 1.14 (2), Fe—C_{Cp} = 2.08 (3), Fe—$Cp_{centroid}$ = 1.71 (4), and C—C in Cp = 1.40 (3) Å (Orpen *et al.*, 1989). Corresponding values for compound (I) are: Fe—$C_{carbonyl}$ = 1.776 (4), C—O = 1.138 (4), Fe—C_{Cp} = 2.10 (2), Fe—$Cp_{centroid}$ = 1.72 (2), and C—C in Cp = 1.41 (1) Å. The Fe—$N_{pyrrole}$ distance is also within the range of values reported for this type of compound where *X* is a nitrogen ligand [1.961 (4) Å for *X* = 1,2,3-triazole (Antipin *et al.*, 1983), 1.970 (7) Å for *X* = benzimidazole (Nesmeyanov *et al.*, 1977) and 1.956 (3) Å for *X* = phthalimidato (Bukowska-Strzyzewska, Tosik, Woka & Zakrzewski, 1994)].

The gas-phase minimum-energy structure for (I) has been calculated using both *ZINDO* and molecular mechanics methods (Martin *et al.*, 1996), and there is