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The Structure of Carbonatobis(di-2-pyridylamine)cobalt(III) Perchlorate

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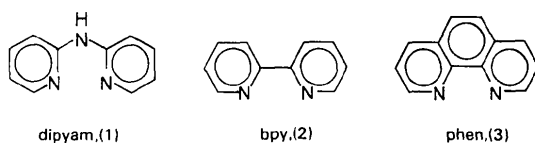
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Abstract. $[\text{Co}(\text{C}_{10}\text{H}_9\text{N}_3)_2(\text{CO}_3)]\text{ClO}_4$, $M_r = 560.8$, monoclinic, $P2_1/n$, $a = 10.983$ (3), $b = 13.640$ (2), $c = 15.548$ (3) Å, $\beta = 93.23$ (1)°, $V = 2325.5$ (9) Å³, $Z = 4$, $D_m = 1.62$ (1), $D_x = 1.60$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.904$ mm⁻¹, $F(000) = 1144$, room temperature, $R = 0.094$ for 2039 reflections. The cation possesses a pseudo-octahedral structure with a bidentate carbonate ligand. The bond lengths and angles are normal, but some short non-bonded distances suggest interligand repulsion. Hydrogen bonds occur between the secondary amine groups and (i) the carbonate ligand of a neighbouring cation and (ii) the partially disordered perchlorate anion.

Introduction. The bidentate ligand di-2-pyridylamine [dipyam, (1)] is unusual in forming an η^2 dioxygen complex $[\text{Co}(\text{dipyam})_2\text{O}_2]^+$ on treatment with hydrogen peroxide (Johnson & Geldard, 1978). An attempt to grow crystals containing this complex yielded the perchlorate salt of the carbonate complex. The crystal structure of this compound is reported, and allows comparison of the structural properties of the ligand dipyam with the analogous 2,2'-bipyridyl [bpy, (2)] and 1,10-phenanthroline [phen, (3)] cobalt (III) carbonate complexes (Niederhoffer, Martell, Rudolf & Clearfield, 1982).



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Experimental. Preparation of crystals: di-2-pyridylamine (previously recrystallized from ethanol), 0.54 g, and cobalt(II) perchlorate hexahydrate, 0.36 g, were dissolved in 150 ml of ethanol:water (2:1) and filtered into a clean flask. 7 ml of 30% hydrogen peroxide were added, and the flask placed in a dewar filled with warm water at 323 K. Over a period of four weeks, red crystals were slowly deposited. Density was measured by flotation.

A parallelepiped 0.18 × 0.15 × 0.30 mm was measured using a Philips PW 1100 diffractometer, $\omega/2\theta$ scan, scan width 1.1°, scan speed 1.8° min⁻¹. Graphite-monochromated Mo $K\alpha$ radiation. 3123 reflections measured ($6 < 2\theta < 44^\circ$; $h = -11, 11$; $k = 0, 14$; $l = 0, 16$). 2717 unique reflections ($R_{\text{int}} = 0.017$) of which 649 were taken as unobserved [$|F_o| \leq 4\sigma(F_o)$ and $|F_o| \leq 8.0$]. Two standard reflections measured every 90 min showed a variation of less than 1.8 $\sigma(I)$, and no correction for change in intensity was applied. Cell parameters from least-squares refinement of 30 centred reflections ($19 \leq 2\theta \leq 30^\circ$). Data corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). All other calculations used a local version of *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) and *ORTEPII* (Johnson, 1976). Scattering factors from *International Tables for X-ray Crystallography* (1974). Least-squares refinement on $|F|$ (block matrix, four blocks) with all H atoms in calculated positions gave final values $R = 0.094$, $wR = 0.135$, $S = 3.08$ for 2039 reflections with $w = 1$ for $|F_o| \leq 48$, $w = (48/|F_o|)^2$ for $|F_o| > 48$. $(\Delta/\sigma)_{\text{max}} = 0.931$. The final difference

Fourier map showed max. and min. of $+0.79$ and $-0.81 e \text{ \AA}^{-3}$.

Discussion. Atomic coordinates and equivalent isotropic temperature factors are given in Table 1, and selected bond lengths, bond angles and short non-bonded distances in Table 2.* Fig. 1 shows the atom numbering and Fig. 2 is a stereoview of the cation.

The cation shows pseudo-octahedral coordination of the cobalt as expected for a complex with three bidentate ligands. There is an approximate twofold axis of symmetry running through Co, C(21) and O(3).

The bond lengths and angles of the complexed carbonate ligand are normal and similar to those for the analogous bpy and phen complexes (Niederhoffer *et al.*, 1982). The average Co—N bond length [1.932 (10) Å] is identical, within experimental error, to

* Lists of structure factors, atomic positional and anisotropic displacement parameters for all atoms and other information in the printed form of the Standard Crystallographic File Structure of Brown (1985) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43664 (51 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates and equivalent isotropic temperature factors, U_{eq} ($\text{\AA}^2 \times 10^3$), with *e.s.d.*'s in parentheses

U_{eq} is the average of the eigenvalues of U.

	x	y	z	U_{eq}
Co	0.23287 (12)	0.17866 (9)	0.97272 (10)	39.7 (6)
Cl	0.2924 (3)	0.54941 (22)	0.85931 (22)	61.6 (12)
N(1)	0.4322 (7)	0.3232 (6)	1.0327 (6)	51 (3)
N(2)	0.2196 (8)	0.3052 (6)	1.0275 (7)	52 (3)
N(3)	0.3702 (7)	0.2290 (6)	0.9126 (6)	45 (3)
N(4)	0.0351 (7)	0.0507 (6)	0.8807 (7)	60 (4)
N(5)	0.2440 (7)	0.0486 (6)	0.9248 (7)	53 (3)
N(6)	0.1138 (7)	0.2110 (6)	0.8820 (6)	48 (3)
O(1)	0.1210 (6)	0.1266 (5)	1.0472 (5)	53 (3)
O(2)	0.3158 (7)	0.1313 (5)	1.0740 (6)	62 (3)
O(3)	0.1926 (8)	0.0626 (6)	1.1729 (6)	80 (4)
O(4)	0.2166 (16)	0.5849 (17)	0.9171 (12)	205 (11)
O(5)	0.2047 (13)	0.5244 (10)	0.7956 (11)	162 (7)
O(6)	0.3581 (14)	0.4772 (14)	0.8889 (18)	259 (13)
O(7)	0.3630 (8)	0.6264 (7)	0.8301 (8)	98 (5)
C(1)	0.3205 (9)	0.3534 (7)	1.0601 (8)	48 (4)
C(2)	0.1087 (10)	0.3414 (8)	1.0491 (9)	59 (5)
C(3)	0.0950 (11)	0.4202 (9)	1.0996 (8)	61 (5)
C(4)	0.2036 (12)	0.4629 (9)	1.1407 (10)	76 (6)
C(5)	0.3141 (11)	0.4311 (8)	1.1159 (8)	56 (4)
C(6)	0.4556 (9)	0.2842 (7)	0.9568 (8)	48 (4)
C(7)	0.3894 (10)	0.2000 (8)	0.8311 (8)	57 (4)
C(8)	0.4946 (13)	0.2219 (11)	0.7909 (9)	76 (6)
C(9)	0.5868 (13)	0.2737 (13)	0.8422 (14)	95 (8)
C(10)	0.5650 (11)	0.3051 (10)	0.9184 (11)	69 (5)
C(11)	0.1450 (10)	0.0001 (7)	0.8972 (8)	54 (4)
C(12)	0.3521 (10)	-0.0005 (8)	0.9300 (8)	59 (5)
C(13)	0.3609 (12)	-0.0978 (9)	0.9125 (11)	80 (6)
C(14)	0.2557 (14)	-0.1481 (9)	0.8840 (11)	82 (6)
C(15)	0.1456 (11)	-0.1013 (9)	0.8795 (11)	82 (6)
C(16)	0.0229 (9)	0.1487 (8)	0.8563 (8)	48 (4)
C(17)	0.1062 (10)	0.3029 (8)	0.8462 (9)	55 (4)
C(18)	0.0142 (10)	0.3339 (8)	0.7907 (8)	58 (5)
C(19)	-0.0850 (10)	0.2690 (10)	0.7740 (9)	65 (5)
C(20)	-0.0803 (9)	0.1759 (9)	0.8075 (8)	57 (4)
C(21)	0.2112 (10)	0.1034 (7)	1.1071 (7)	47 (4)

those found with bpy and phen, but the chelate bite angles [N(2)—Co—N(3) 88.6 (4); N(5)—Co—N(6) 89.0 (4) $^\circ$] are greater than for bpy [83.2 (2) $^\circ$] and phen [84.3 (3) $^\circ$], and are closer to the value of 90° expected for an ideal octahedron. The greater bite angle presumably arises from the six-membered chelate ring in the dipyam complex.

Table 2. Selected bond lengths (Å) and angles ($^\circ$) and short interligand distances (Å) for $[\text{Co}(\text{dipyam})_2\text{CO}_3]^+$

Co—N(2)	1.934 (9)	Co—N(5)	1.931 (8)
Co—N(3)	1.944 (9)	Co—N(6)	1.920 (9)
Co—O(1)	1.875 (8)	Co—O(2)	1.889 (8)
O(1)—C(21)	1.358 (13)	O(2)—C(21)	1.341 (13)
C(21)—O(3)	1.192 (15)		
N(2)—Co—N(3)	88.6 (4)	N(5)—Co—N(6)	89.0 (4)
N(2)—Co—N(6)	93.1 (4)	N(5)—Co—N(3)	94.1 (4)
N(2)—Co—N(5)	176.4 (4)	N(3)—Co—N(6)	94.6 (4)
N(2)—Co—O(1)	89.9 (4)	N(5)—Co—O(1)	87.0 (4)
N(2)—Co—O(2)	89.0 (4)	N(5)—Co—O(2)	88.2 (4)
C(1)—N(1)—C(6)	127.6 (9)	C(11)—N(4)—C(16)	126.2 (9)
O(1)—Co—O(2)	70.0 (3)	O(1)—C(21)—O(2)	106.1 (9)
N(2)...C(17)	3.018 (16)	N(6)...C(2)	3.152 (16)
N(3)...C(12)	3.149 (14)	N(6)...C(7)	3.175 (14)
N(3)...C(17)	3.186 (14)	N(5)...C(7)	3.034 (15)
C(7)...C(12)	3.176 (16)	C(2)...C(17)	3.197 (19)

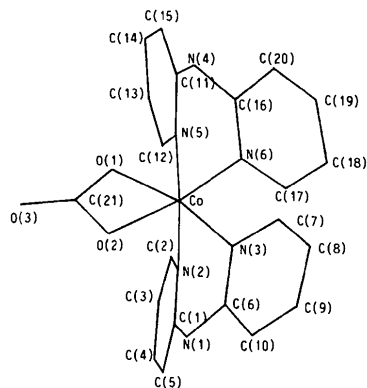


Fig. 1. Line drawing of $[\text{Co}(\text{dipyam})_2\text{CO}_3]^+$ showing numbering of atoms. The perchlorate anion [atoms Cl and O(4) to O(7)] is omitted.

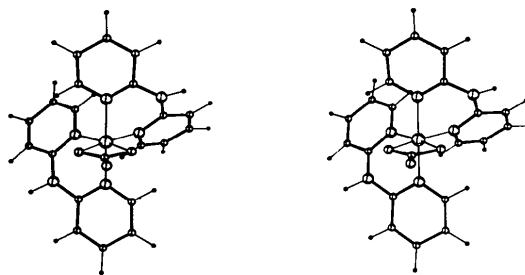


Fig. 2. Stereoview of the cation $[\text{Co}(\text{dipyam})_2\text{CO}_3]^+$.

In contrast to bpy and phen, the dipyam ligand is strongly distorted from planarity. The angles between the least-squares planes through the two pyridyl rings of each ligand are 36.1 (5) and 37.4 (5)° for the two independent dipyam molecules in the complex. These values are similar to those found for dipyam bound to Cu^{II} (Fuller & Jacobson, 1981; Jensen & Jacobson, 1981) and Pd^{II} (Freeman & Snow, 1965). The axis of intersection of the two least-squares planes passes close to the Co atom and the secondary amine N atom, the amine N atom lying in the obtuse and the Co atom in the reflex angle formed by the two planes. The six-membered chelate ring has a boat conformation, and the Co—N bond makes an average angle of 11.5° with the plane of the pyridyl ring.

The unusually intense transitions in the electronic spectrum of [Co(dipyam)₃]³⁺ are thought to arise from ligand–ligand repulsions (Johnson & Geldard, 1979). In the cation [Co(dipyam)₂(CO₃)]⁺, all the C atoms in the 6-position of the pyridyl rings show some interaction with the other dipyam molecule as shown by short non-bonded distances (C—C or C—N distances less than 3.2 Å, Table 2). For the bpy and phen complexes, in contrast, such short interligand distances are found only between the two mutually *cis* pyridyl groups *trans* to the carbonate. This supports the hypothesis of greater interligand repulsion in complexes of dipyam, and may be attributed to the expansion of the chelate ring which moves the C atoms in the 6-position closer to the centre of the complexes and thus nearer to the other ligands.

The H atoms of the secondary amine groups are involved in hydrogen bonding. One is hydrogen bonded

to the terminal O atom of the carbonate of another cation [distance N(4)···O(3) (−*x*, −*y*, 2−*z*) = 3.018 (12) Å]. The other is hydrogen bonded to an O atom of the perchlorate anion [distance N(1)···O(7) (1−*x*, 1−*y*, 2−*z*) = 3.088 (14) Å]. The other O atoms of the perchlorate anion show much larger atomic displacement parameters, and may be considered as disordered, and this is presumably responsible for the relatively high final *R* factor.

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Fluoro-Containing Coordination Compounds of Chromium(III). IV. Structure of Racemic *cis*-Bis(ethylenediamine)difluorochromium(III) Perchlorate

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Abstract. *cis*-[CrF₂(C₂H₈N₂)₂]ClO₄, *M_r* = 309.65, monoclinic, *P*2₁/*c*, *a* = 5.587 (1), *b* = 11.601 (2), *c* = 17.774 (3) Å, β = 98.07 (1)°, *V* = 1140.6 (6) Å³, *Z* = 4, *D_m* = 1.80 (1), *D_x* = 1.803 Mg m^{−3}, *Mo Kα*, λ = 0.71069 Å, μ = 1.19 mm^{−1}, *F*(000) = 636, *T* = 293 K, *R* = 0.052 for 1569 reflections. The Cr atom is in an octahedral environment coordinated by two bidentate ethylenediamines and two F atoms in a *cis* position. Cations are in the *Aδλ* and *Δλδ* enantiomeric

forms. Cr—F and Cr—N bonds are 1.883 (3), 1.882 (3); and from 2.072 (4) to 2.099 (4) Å. Weak N···F hydrogen bonds exist between cations.

Introduction. Structural studies of fluoro-containing chromium(III) coordination compounds are rare. [CrF₂(en)₂]⁺ (en = NH₂—CH₂—CH₂—NH₂) can exist as *trans* and *cis* isomers. Structures of *trans*-[CrF₂(en)₂]ClO₄ and *trans*-[CrF₂(en)₂]Cl were solved