

arship and university exchange programme (KJ) and the Callery Chemical Company for a generous gift of  $B_{10}H_{14}$ .

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1502). Services for accessing these data are described at the back of the journal.

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## Bis[di-2-pyridylmethanediolato(1-)-*N,O,N'*]cobalt(III) Perchlorate Trihydrate

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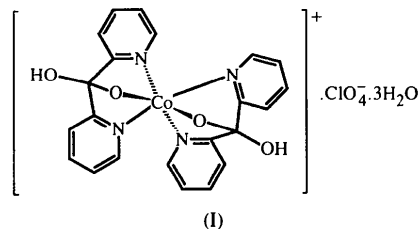
(Received 27 August 1997; accepted 10 October 1997)

## Abstract

In the title compound,  $[Co(C_{11}H_9N_2O_2)_2]ClO_4 \cdot 3H_2O$ , the metal atom is *N,O,N'*-chelated by the two di-2-pyridylmethanediolato anions with distorted octahedral  $CoN_4O_2$  geometry. The Co—O bonds [1.876(1) and 1.879(1) Å] are *cis* to each other.

## Comment

Di-2-pyridyl ketone undergoes hydrolysis when reacted with transition metal ions to form polynuclear di-2-pyridyl ketal complexes (Byers *et al.*, 1985; Wang *et al.*, 1986). The diol can be deprotonated and in complexes, the anion binds through the N, O and *N'* atoms (Baggio *et al.*, 1993; Deveson *et al.*, 1996; Tangoulis *et al.*, 1996). The title complex, (I), which has the Co atom in the +3 oxidation state, was obtained in an attempt to prepare a cobalt(II) complex containing di-2-pyridyl ketone and betaine ligands.



The complex consists of discrete monomeric cations, perchlorate anions and lattice water molecules. The  $Co^{III}$  atom is surrounded by four N atoms and two O atoms of the two tridentate ligands in a distorted octahedral  $CoN_4O_2$  arrangement, with the greatest distortion from octahedral geometry being displayed by the angles N1—Co1—N4 and O3—Co1—N4. The Co—N bond lengths [1.929(1)–1.944(1) Å] are similar to those (1.994–2.098 Å) found in the di-2-pyridyl ketal complexes of nickel(II) and copper(II) reported by Wang *et al.* (1986). In these complexes, the pair of metal–oxygen bonds are in a *trans* alignment. On the other hand, the Co—O bonds in the title complex are mutually *cis*; thus, the title complex presents an unusual mode of binding of this tridentate ligand to a metal centre.

The structure is consolidated by an extensive three-dimensional hydrogen-bonding network which involves the lattice water molecules, the hydroxy groups of the

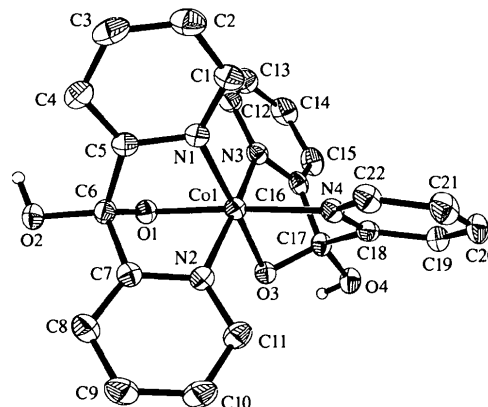


Fig. 1. ORTEP (Johnson, 1976) plot of the title cation with 35% probability displacement ellipsoids. H atoms bonded to C atoms are not included.

organic ligands and the perchlorate anions. Pairs of adjacent cations are also bridged by pairs of hydrogen bonds from the O4 hydroxy atoms to the O3 atoms of the adjacent cation.

O1—Co1—O3	95.13 (5)	O3—Co1—N4	81.40 (5)
O1—Co1—N1	82.46 (5)	N1—Co1—N2	89.74 (5)
O1—Co1—N2	83.03 (5)	N1—Co1—N3	96.45 (6)
O1—Co1—N3	90.15 (5)	N1—Co1—N4	101.02 (6)
O1—Co1—N4	176.44 (5)	N2—Co1—N3	170.13 (6)
O3—Co1—N1	177.58 (6)	N2—Co1—N4	96.15 (6)
O3—Co1—N2	89.99 (5)	N3—Co1—N4	90.22 (6)
O3—Co1—N3	83.51 (5)		

## Experimental

Di-2-pyridyl ketone (1.0 mmol) was dissolved in water (2 ml) and the solution was mixed with an aqueous solution containing Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.0 mmol), betaine (1.0 mmol) and NaClO<sub>4</sub> (1.0 mmol). The mixture was heated to 333 K and stirred briefly. Red blocks were formed after a few days. The Co<sup>II</sup> starting reagent had been oxidized by air; a more common procedure for synthesizing Co<sup>III</sup> complexes involves oxidation by hydrogen peroxide (Chen *et al.*, 1996).

### Crystal data

[Co(C<sub>11</sub>H<sub>9</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub>·  
3H<sub>2</sub>O

*M<sub>r</sub>* = 614.83

Triclinic

*P* $\bar{1}$

*a* = 8.6342 (3) Å

*b* = 11.6080 (5) Å

*c* = 13.384 (1) Å

$\alpha$  = 91.988 (5)°

$\beta$  = 108.291 (5)°

$\gamma$  = 95.861 (3)°

*V* = 1263.8 (1) Å<sup>3</sup>

*Z* = 2

*D<sub>x</sub>* = 1.616 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Mo *K*α radiation

$\lambda$  = 0.71073 Å

Cell parameters from 25  
reflections

$\theta$  = 12–13°

$\mu$  = 0.853 mm<sup>-1</sup>

*T* = 298 (2) K

Block

0.36 × 0.36 × 0.36 mm

Red

### Data collection

Enraf–Nonius CAD-4  
diffractometer

$\omega$  scan

Absorption correction:

$\psi$  scan (North, Phillips  
& Mathews, 1968)

*T<sub>min</sub>* = 0.682, *T<sub>max</sub>* = 0.736

4760 measured reflections

4435 independent reflections

3838 reflections with

*I* > 2σ(*I*)

*R<sub>int</sub>* = 0.012

$\theta_{\max}$  = 25°

*h* = 0 → 10

*k* = -13 → 13

*l* = -15 → 15

3 standard reflections

frequency: 60 min

intensity decay: 2.5%

### Refinement

Refinement on *F*<sup>2</sup>

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.033

*wR*(*F*<sup>2</sup>) = 0.083

*S* = 1.061

4435 reflections

388 parameters

H atoms riding

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0356*P*)<sup>2</sup>  
+ 0.98*P*]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

( $\Delta/\sigma$ )<sub>max</sub> = 0.098

$\Delta\rho_{\max}$  = 0.532 e Å<sup>-3</sup>

$\Delta\rho_{\min}$  = -0.361 e Å<sup>-3</sup>

Extinction correction: none

Scattering factors from

*International Tables for  
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Co1—O1	1.879 (1)	Co1—N4	1.944 (1)
Co1—O3	1.876 (1)	O1—C6	1.389 (2)
Co1—N1	1.941 (1)	O2—C6	1.389 (2)
Co1—N2	1.929 (1)	O3—C17	1.409 (2)
Co1—N3	1.936 (1)	O4—C17	1.376 (2)

Table 2. Hydrogen-bonding geometry (Å, °)

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
O1W—H1WA···O5 <sup>i</sup>	0.90	2.09	2.960 (5)	164
O1W—H1WA···O7 <sup>ii</sup>	0.90	2.24	2.976 (7)	139
O1W—H1WB···O3W	0.93	1.85	2.7669 (19)	170
O2—H2H···O1W	0.97	1.75	2.7060 (18)	167
O2W—H2WA···O4	0.96	1.94	2.8901 (18)	169
O2W—H2WB···O2 <sup>ii</sup>	0.94	2.02	2.929 (2)	163
O4—H4H···O3 <sup>ii</sup>	0.83	1.81	2.6411 (14)	175
O3W—H3WA···O5 <sup>iii</sup>	0.92	2.29	3.199 (5)	172
O3W—H3WA···O6 <sup>iii</sup>	0.92	2.58	3.169 (9)	122
O3W—H3WA···O8 <sup>iii</sup>	0.92	2.07	2.982 (8)	170
O3W—H3WB···O2W <sup>iii</sup>	0.90	1.94	2.834 (3)	173

Symmetry codes: (i) 1 - *x*, 2 - *y*, 1 - *z*; (ii) 1 - *x*, 1 - *y*, 1 - *z*; (iii) *x*, *y*, *z* - 1.

The O atoms in the perchlorate anion are disordered over two positions (70 and 30% occupancies) and were refined with geometric restraints. H atoms were located in a difference electron-density map and were allowed to ride on their parent atoms with fixed isotropic displacement parameters of 0.08 Å<sup>2</sup>.

Data collection: CAD-4 VAX/PC (Enraf–Nonius, 1988). Cell refinement: CAD-4 VAX/PC. Data reduction: Xtal3.0 (Hall & Stewart, 1990). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1036). Services for accessing these data are described at the back of the journal.

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### *trans*-Dichlorotri(cyclohexyl)arsenic(V)

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#### Abstract

The title molecule, [AsCl<sub>2</sub>(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>], has a distorted trigonal-bipyramidal geometry with three equatorial cyclohexyl groups and axial Cl atoms. The As—C distances [1.990 (2), 1.988 (2) and 1.981 (3) Å] differ slightly, and the equatorial angles C—As—C are 117.35 (10), 117.60 (10) and 123.26 (8)°. The angle subtended at arsenic by the axial Cl atoms is 178.60 (2)°, but the chlorine separation distances [2.4957 (7) and 2.3029 (7) Å] differ substantially. The As atom lies out of the plane of the equatorial C atoms, suggesting a contribution from the ionic structure, [As(cyclo-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>Cl]<sup>+</sup>.Cl<sup>−</sup>.

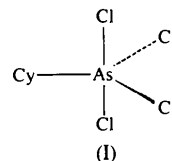
#### Comment

Compounds of the type ER<sub>3</sub>X<sub>2</sub> obtained by halogen (X<sub>2</sub>) oxidation of triorgano derivatives of Group 15 elements, ER<sub>3</sub>, are usually considered to have trigonal-bipyramidal structures and this geometry is found for the phosphorus compounds PPh<sub>3</sub>F<sub>2</sub> (Weller *et al.*, 1991; Doxsee *et al.*, 1992) and P(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>F<sub>2</sub> (Sheldrick, 1975). However, an alternative four coordinate 'spoke' structure, R<sub>3</sub>P···X—X, is observed when R = Ph and X = Br (Bricklebank *et al.*, 1992) or I (Godfrey *et al.*, 1991), but the corresponding chloride, PPh<sub>3</sub>Cl<sub>2</sub>, belongs to a third structural type with a dimeric [Ph<sub>3</sub>PCl<sup>+</sup>···Cl<sup>−</sup>···Cl<sup>−</sup>···PPh<sub>3</sub>]Cl<sup>−</sup> structure (Godfrey *et al.*, 1996).

The first two structural types are represented when the central element is arsenic, *i.e.* trigonal-bipyramidal geometry for AsPh<sub>3</sub>F<sub>2</sub> (Augustine *et al.*, 1975), AsPh<sub>3</sub>Br<sub>2</sub> (Bricklebank *et al.*, 1995), As(neopentyl)<sub>3</sub>Br<sub>2</sub> (Pazik & George, 1989), AsMe<sub>3</sub>Cl<sub>2</sub> (Hursthouse & Steer, 1971) and the four-coordinate spoke structure for AsPh<sub>3</sub>I<sub>2</sub> (McAuliffe *et al.*, 1987; Bricklebank *et al.*, 1995). An ionic structure, [AsMe<sub>3</sub>Br]<sup>+</sup>.Br<sup>−</sup>, has been suggested for AsMe<sub>3</sub>Br<sub>2</sub> (Hursthouse & Steer, 1971).

Trigonal-bipyramidal structures appear to be the norm when the central atom is either antimony or bismuth, for example, SbPh<sub>3</sub>X<sub>2</sub>, where X = Cl or Br (Begley & Sowerby, 1993), and BiR<sub>3</sub>Cl<sub>2</sub>, where R = Ph (Hawley & Ferguson, 1968) or *p*-tolyl (Chen *et al.*, 1993), but the geometry is slightly distorted towards the rectangular-pyramidal alternative for SbPh<sub>3</sub>I<sub>2</sub> (Bricklebank *et al.*, 1994).

We have recently prepared tricyclohexylarsenic dichloride, (I), and because few five-coordinate arsenic(V) structures are known and there are a number of possible geometries for this stoichiometry, we have determined its crystal structure.



The X-ray structure (Fig. 1) establishes that the compound is trigonal bipyramidal, with organic groups in equatorial and Cl atoms in axial positions, rather than adopting the four-coordinate 'spoke' alternative.

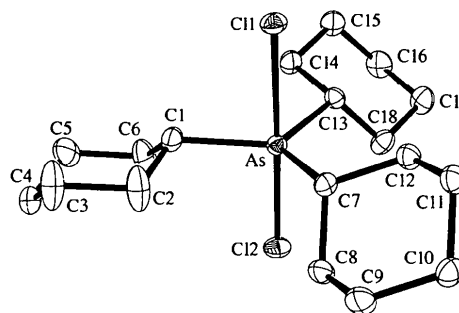


Fig. 1. A view of a molecule of the title compound with the atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces and H atoms are shown as small spheres of arbitrary radii.

The geometry about arsenic (Table 1) is, however, distorted with two of the As—C separations effectively equal [1.990 (2) and 1.988 (2) Å], while the third is shorter [1.981 (3) Å]; again two of the equatorial angles are effectively equal [117.4 (1) and 117.6 (1)°] with the third increased to 123.26 (8)°. The equatorial angles