

**[*N,N'*-(4-Methyl-4-azaheptane-1,7-diyl- $\kappa$ N)bis(4-methoxysalicylidene-iminato- $\kappa^4$ O,*N,N',O'*)]cobalt(II) ethanol hemisolvate**

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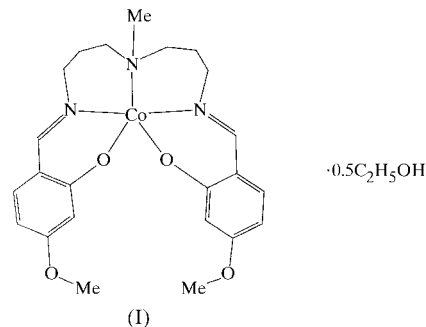
The title compound,  $[\text{Co}(\text{C}_{23}\text{H}_{29}\text{N}_3\text{O}_4)] \cdot 0.5\text{C}_2\text{H}_6\text{O}$  or  $[\text{Co}^{\text{II}}\{(\text{4-MeO-sal})_2\text{Medpt}\}] \cdot 0.5\text{CH}_3\text{CH}_2\text{OH}$  [ $(\text{4-MeO-sal})_2\text{Medpt}$  is *N,N'*-(4-methyl-4-azaheptane-1,7-diyl)bis(4-methoxysalicylideneiminate)], obtained through the reaction of  $\text{H}_2[(\text{4-MeO-sal})_2\text{Medpt}]$  and  $\text{Co}(\text{CH}_3\text{COO})_2$  in refluxing ethanol under an atmosphere of ultrapure nitrogen, has the usual pseudo-trigonal-bipyramidal coordination arrangement previously found for this class of  $(\text{sal})_2\text{Rdpt}$  compounds. The O—Co—O bond angle [ $120.4(1)^\circ$ ] is significantly smaller than the corresponding values previously found for most non- $\text{O}_2$ -bound  $[\text{Co}^{\text{II}}\{(\text{sal})_2\text{Medpt}\}]$ -type molecules (observed range  $126.9$ – $138.6^\circ$ ), whereas the equatorial Co—N bond [ $2.185(3) \text{ \AA}$ ] is relatively long.

**Comment**

Cobalt compounds able to react reversibly with dioxygen have captured the attention of several research groups over the past three decades (Rybak-Akimova *et al.*, 1997, and references therein) and many structural studies have been performed on the parent cobalt complexes,  $[\text{CoL}]$ , as well as on some dioxygen adducts,  $[\text{CoL}(\text{O}_2)]$  (Cini & Orioli, 1983, 1981; Huie *et al.*, 1979). The *L* ligand is a Schiff base in most cases and belongs to the  $\text{H}_2(\text{sal})_2\text{en}$  or  $\text{H}_2(\text{sal})_2\text{Medpt}$  families (Anderson *et al.*, 1998; Boca *et al.*, 1998; Kingma *et al.*, 1993; Polishchuk *et al.*, 1991; Ready & Jacobsen, 1999; Sato *et al.*, 1999). It has been observed that small structural changes to the cobalt complexes upon oxygenation correspond to relatively low activation energies for dioxygen binding (Rybak-Akimova *et al.*, 1997). On the other hand, it has been found that the pentacoordinate cobalt complexes of the  $(\text{sal})_2\text{Medpt}$  family span a wide range of values for the O—Co—O bond angle, which measures the cavity through which the entering dioxygen molecule approaches the metal (Boca *et al.*, 1998, and references therein; Cini & Orioli, 1983, 1982).

On the basis of this reasoning, and as a continuation of the synthetic work and structural studies performed by this group

over the past two decades, single crystals of the title compound, (I), have been prepared from deaerated ethanol solutions and analysed *via* X-ray diffraction, and the results are reported here. The reactivity of (I) with dioxygen in dimethyl sulfoxide solution, determined *via* electrochemical methods, was reported previously by Zanello *et al.* (1983).



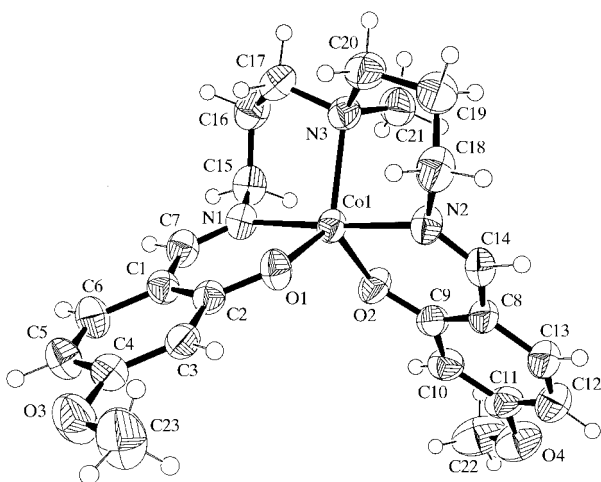
The complex molecule is represented in Fig. 1 and selected geometrical parameters are listed in Table 1. The coordination sphere has the usual trigonal-bipyramidal arrangement found for this type of complex, where the oxygen donors from the sal moiety and the  $\text{Nsp}^3$  donor from the dtp chain are considered as occupying the equatorial positions, and the  $\text{Nsp}^2$  donors are at the apical positions. The Co—O bond distances are equal to within one s.u. and average  $1.977(2) \text{ \AA}$ , in agreement with the values previously found for analogous complexes (Boca *et al.*, 1998, and references therein). The axial Co— $\text{Nsp}^2$  bond lengths are also equal to within one s.u. and average  $2.060(3) \text{ \AA}$ , a value which compares well with the corresponding lengths for analogous complexes. The equatorial Co— $\text{Nsp}^3$  bond length found in (I),  $2.185(3) \text{ \AA}$ , follows the trend already noted for this class of compounds, but it is the largest such value observed so far; the range found in the literature varies from  $2.123(2)$  (Boca *et al.*, 1998) to  $2.170(9) \text{ \AA}$  (Cini & Orioli, 1982).

The  $\text{N1—Co—N2}$  bond angle of  $176.9(1)^\circ$  is close to the ideal value ( $180^\circ$ ) for the axial donors of a trigonal bipyramid. The bond angles involving one equatorial and one axial donor are also close to the ideal value of  $90^\circ$ ; the largest deviation in (I) is  $1.9(1)^\circ$  for  $\text{N2—Co—O1}$ . These angles are in good agreement with the values reported previously for analogous complexes. Interestingly, the  $\text{N3—Co—O1}$  [ $124.7(1)^\circ$ ] and  $\text{N3—Co—O2}$  [ $115.0(1)^\circ$ ] bond angles differ by *ca*  $10^\circ$ . This can be compared with the small value [ $120.4(1)^\circ$ ] of the  $\text{O1—Co—O2}$  bond angle.

It must be noted that the solid-state molecular structures of metal complexes of  $(\text{sal})_2\text{Medpt}$ -type dianions usually show two distinct sets, of three atoms each, around the  $\text{Nsp}^3$  donor (Boca *et al.*, 1998; Cini & Orioli, 1982; Cini, 1983, 1986). Once this type of disorder occurs, the equatorial set of donors (atoms O1 and O2) has an almost strict  $C_2$  symmetry around the  $\text{N3—Co}$  vector. By contrast, the present structure does not have any detectable disorder around N3, the equatorial set of donors is far from  $C_2$  symmetry, the  $\text{O1—Co—O2}$  bond angle is narrow and the Co—N3 bond distance is long. The only other example of an X-ray structure for a cobalt complex from

the (sal)<sub>2</sub>Medpt family which has no disorder around N3 is the non-dioxygenated molecule of [Co{(sal)<sub>2</sub>Medpt}(O<sub>2</sub>)]·[Co{(sal)<sub>2</sub>Medpt}]·2C<sub>6</sub>H<sub>6</sub> (Cini & Orioli, 1983), where the O1—Co—O2 bond angle is also narrow, at 120.4 (7)°.

In conclusion, it seems that once the Co—N3 bond becomes shorter, the ligand forces the O1—Co—O2 angle to open. Furthermore, the short Co—N3 vector and the disorder around N3 seem to be related. These effects on the geometric parameters of cobalt complexes with (sal)<sub>2</sub>Rdpt-type dianions can be due to specific electronic contributions from the ligand itself (tuned by the substituents), or can arise from several types of intermolecular forces or from both these sources. Of course, much more work, both experimental and theoretical, is needed to clarify the matter.



**Figure 1**  
The molecular structure of the [Co<sup>II</sup>[(4-MeO-sal)<sub>2</sub>Medpt]] cation in (I) showing 30% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii and the solvent molecule has been omitted for clarity.

An analysis of the crystal packing in (I) shows several short O···H—C contacts which can be considered hydrogen-bond-type interactions (Table 2) (Taylor & Kennard, 1982). Selected examples are: C14—H14···O3(*x*, −*y*,  $\frac{1}{2}$  + *z*) = 2.71 Å, C12—H12···O4(1 − *x*, −*y*, 1 − *z*) = 2.62 Å and C22—H22C···O1E( $\frac{1}{2}$  + *x*, *y* −  $\frac{1}{2}$ , *z*) 2.46 Å.

## Experimental

Crystals of (I) were obtained as dark-brown prisms from an absolute ethanol solution under an atmosphere of ultrapure nitrogen, following the procedure reported previously by Zanello *et al.* (1983).

### Crystal data

[Co(C<sub>23</sub>H<sub>29</sub>N<sub>3</sub>O<sub>4</sub>)]·0.5C<sub>2</sub>H<sub>6</sub>O  
*M<sub>r</sub>* = 493.46  
 Monoclinic, C2/c  
*a* = 16.793 (1) Å  
*b* = 13.685 (2) Å  
*c* = 21.244 (1) Å  
 $\beta$  = 92.11 (1)°  
*V* = 4878.8 (8) Å<sup>3</sup>  
*Z* = 8

*D<sub>x</sub>* = 1.335 Mg m<sup>−3</sup>  
 Mo *K*α radiation  
 Cell parameters from 42 reflections  
 $\theta$  = 5–18°  
 $\mu$  = 0.74 mm<sup>−1</sup>  
*T* = 293 (2) K  
 Prism, brown  
 0.4 × 0.3 × 0.2 mm

### Data collection

Siemens P4 diffractometer  
 $\omega$  scans  
 Absorption correction: empirical  
 via  $\psi$  scan (North *et al.*, 1968)  
*T<sub>min</sub>* = 0.766, *T<sub>max</sub>* = 0.863  
 6080 measured reflections  
 5067 independent reflections  
 3250 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.017  
 $\theta_{\text{max}}$  = 26.5°  
*h* = −1 → 21  
*k* = −1 → 17  
*l* = −26 → 26  
 3 standard reflections  
 every 97 reflections  
 intensity decay: none

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.049  
*wR*(*F*<sup>2</sup>) = 0.144  
*S* = 1.03  
 5067 reflections  
 308 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0751P)^2 + 2.313P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.45 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$

**Table 1**  
Selected geometric parameters (Å, °).

Co1—O1	1.976 (2)	O4—C11	1.371 (5)
Co1—O2	1.979 (2)	O4—C22	1.412 (6)
Co1—N2	2.057 (3)	N1—C7	1.279 (4)
Co1—N1	2.062 (3)	N1—C15	1.467 (4)
Co1—N3	2.185 (3)	N2—C14	1.277 (4)
O1—C2	1.314 (4)	N2—C18	1.469 (4)
O2—C9	1.318 (4)	N3—C21	1.479 (4)
O3—C4	1.362 (4)	N3—C17	1.490 (4)
O3—C23	1.430 (5)	N3—C20	1.493 (4)
O1—Co1—O2	120.38 (10)	C7—N1—Co1	126.4 (2)
O1—Co1—N2	91.91 (10)	C15—N1—Co1	114.5 (2)
O2—Co1—N2	90.28 (10)	C14—N2—C18	117.6 (3)
O1—Co1—N1	89.05 (10)	C14—N2—Co1	125.1 (2)
O2—Co1—N1	91.81 (10)	C18—N2—Co1	117.3 (2)
N2—Co1—N1	176.87 (11)	C21—N3—C17	110.4 (3)
O1—Co1—N3	124.65 (10)	C21—N3—C20	110.4 (3)
O2—Co1—N3	114.97 (10)	C17—N3—C20	105.6 (3)
N2—Co1—N3	88.59 (11)	C21—N3—Co1	108.4 (2)
N1—Co1—N3	88.41 (11)	C17—N3—Co1	110.7 (2)
C2—O1—Co1	129.3 (2)	C20—N3—Co1	111.4 (2)
C9—O2—Co1	127.9 (2)	C6—C1—C2	118.4 (3)
C4—O3—C23	118.3 (3)	C6—C1—C7	117.5 (3)
C11—O4—C22	118.4 (3)	C2—C1—C7	124.1 (3)
C7—N1—C15	119.0 (3)	O1—C2—C3	118.0 (3)

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C14—H14···O3 <sup>i</sup>	0.93	2.71	3.601 (7)	162
C12—H12···O4 <sup>ii</sup>	0.93	2.62	3.498 (7)	158
C21—H21B···O4 <sup>iii</sup>	0.96	2.67	3.582 (7)	159
C22—H22C···O1E <sup>iv</sup>	0.96	2.46	3.226 (9)	137

Symmetry codes: (i) *x*, −*y*,  $\frac{1}{2}$  + *z*; (ii) 1 − *x*, −*y*, 1 − *z*; (iii) *x* −  $\frac{1}{2}$ ,  $\frac{1}{2}$  + *y*, *z*; (iv)  $\frac{1}{2}$  + *x*, *y* −  $\frac{1}{2}$ , *z*.

All the H atoms of the complex molecule were set in calculated positions and allowed to ride on their respective parent atoms during refinement, with *U<sub>iso</sub>*(H) constrained to be 1.2*U<sub>eq</sub>* of the parent atom. The H atoms of the disordered solvent molecule were not included.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS* and *XEMP* (Siemens, 1994); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-32* (Farrugia, 1998); software used to prepare material for publication: *CIFTAB* (Sheldrick, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1142). Services for accessing these data are described at the back of the journal.

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