metal-organic compounds

A new polymorph of a cobalt(III) Schiff base complex exhibits a one-dimensional C—H···O hydrogen-bonded extended structure with helical 2₁ symmetry

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In a new polymorph of acetato(2,2′-{iminobis[(E)-propane-3,1-diylnitrilomethylidyne]}diphenolato)cobalt(III), [Co-$(C_{20}H_{23}N_3O_2)(C_2H_3O_2)$], in the space group $P2_1/c$, the Co^{III} ion is six-coordinate, with unequal Co—O$_{phenolate}$ distances that average 1.908 (12) Å and more similar Co—N$_{imine}$ distances averaging 1.937 (4) Å. The acetate ion occupies the sixth coordination site and forms an intramolecular hydrogen bond (H···O = 1.95 Å) with the Co-bound NH group of the pentadentate chelate. The extended structure is a one-dimensional (aryl)C—H···O(carbonyl) hydrogen-bonded polymer with 2₁ (helical) symmetry and is thus distinct from the simple hydrogen-bonded stack of the $P2_1/n$ polymorph [Matsumoto, Imaizumi & Ohyoshi (1983). *Polyhedron*, **2**, 137–139].

Comment

Cobalt(II) complexes of pentadentate Schiff base ligands formed by condensation of *N*-(3-aminopropyl)propane-1,3-diamine and salicylaldehyde, or their structurally related derivatives, are normally neutral five-coordinate species with a trigonal–bipyramidal coordination geometry (Cini & Orioli, 1982; Zanello *et al.*, 1983). The cobalt(III) analogues, on the other hand, are typically six-coordinate because of the coordination of an anion (Anderson *et al.*, 1998), or a neutral ligand such as *N*-methylimidazole (Kistenmacher *et al.*, 1974; Padden, Krebs, Trafford *et al.*, 2001), at the sixth site. Such systems are attractive for applications that include roles as molecular O₂ transporters (Cini & Orioli, 1981, 1983; Lindblom *et al.*, 1971) and porous O₂/NO sensing polymers (Krebs & Borovik, 1998; Sharma & Borovik, 2000; Padden, Krebs, MacBeth *et al.*, 2001).

As part of a more general project in our laboratory, we have isolated crystals of a new polymorph of the title compound, (I). The first structure of (I) (space group $P2_1/n$) was reported

by Matsumoto *et al.* (1983) with cell constants $a = 16.846$ (4), $b = 9.417$ (2) and $c = 14.032$ (4) Å, and $\beta = 111.29$ (1)°. As discussed below, the present polymorph of (I) has both a clearly different cell and an extended structure different from that of the $P2_1/n$ polymorph.

(I)
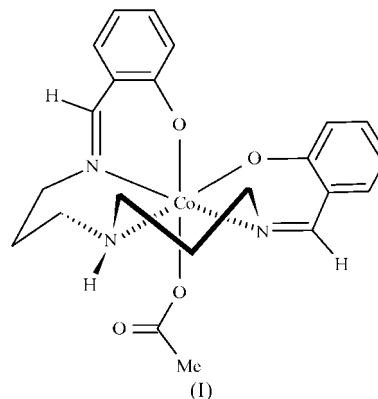
The pentadentate ligand of (I) occupies five of the six coordination sites at the Co^{III} centre, with the phenolate O atoms in a *cis* arrangement (Fig. 1). The two imine N atoms (N1 and N3) are *trans* to each other and the acetate ligand coordinates *trans* to phenolate atom O1. The Co—N$_{imine}$ distances are short [mean 1.937 (4) Å], while the bond to the secondary amine atom (N2) is considerably longer as a result of additional steric strain associated with its sp^3 hybridized geometry (Table 1). The Co—O$_{phenolate}$ distances average 1.908 (12) Å, but differ by more than 4σ. Since atom O1 forms a shorter bond to Co^{III} than atom O2 and is possibly hydrogen bonded to atoms H11B and H13A (Table 1), it is not unlikely that these attractive intramolecular interactions favour a somewhat shorter coordination interaction for this phenolate
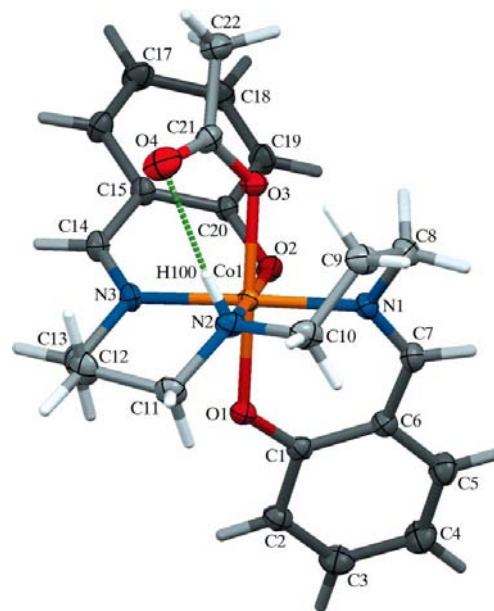

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 70% probability level. H atoms are shown only as the intersections and end-points of bonds represented as cylinders. The most prominent intramolecular hydrogen bond is shown as a dashed line.
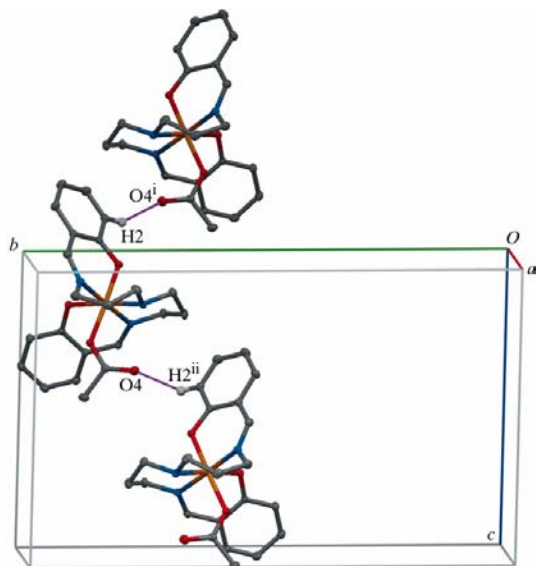
Figure 2
Part of the one-dimensional hydrogen-bonded extended structure of (I), viewed approximately down the *a* axis of the unit cell (full contents have been omitted for clarity). H atoms involved in intermolecular hydrogen bonds are shown as spheres (isotropic displacement parameter radii). All other atoms have displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) $x - 1, \frac{3}{2} - y, z - \frac{1}{2}$; (ii) $1 + x, \frac{3}{2} - y, \frac{1}{2} + z$.]

O atom. It is also likely that the secondary amine donor atom (N2) has a *trans* elongating effect on the Co-bound phenolate atom (O2), particularly as it is a better σ-donor (stronger Lewis base) than the acetate ligand *trans* to O1. Notwithstanding possible differences in the intermolecular interactions for the two phenolate groups, the combined effect of these intramolecular perturbations would account, at least partly, for the significant difference in the Co—O$_{\text{phenolate}}$ bond lengths.

The conformation of (I) is characterized by a hinge-like shape brought about by the non-orthogonal relative orientation of the two benzene rings [dihedral angle = 76.2 (2)°]. The benzene rings are, furthermore, individually canted relative to the mean plane passing through the metal ion and four coplanar ligand donor atoms (N1–N3/O2); the dihedral angles between this plane and the C1–C6 and C15–C20 planes are 66.5 (2) and 39.5 (2)°, respectively.

Somewhat surprisingly, the acetate ligand of (I) is firmly bound to the Co$^{\text{III}}$ ion. We have therefore been unable to substitute the anion in dichloromethane solution by primary amines such as butylamine or benzylamine, even using an excess of these ligands. A possible explanation for the substitution-inert anion, beyond the high ligand field stabilization energy for low-spin Co$^{\text{III}}$, is the fact that it is further anchored within the complex *via* a hydrogen bond between the carbonyl O atom and the amine N atom (Table 2 and Fig. 1). This conclusion is consistent with the fact that an iodo analogue of (I), which is presumably incapable of forming strong intramolecular hydrogen bonds, has been used for the synthesis of the corresponding *N*-methylimidazole adduct (Padden, Krebs, MacBeth *et al.*, 2001).

In the packing of (I), each molecule belongs to an infinite one-dimensional hydrogen-bonded polymer chain generated by the twofold screw axis (Fig. 2). An (aryl)C—H$\cdots$O(carbonyl) interaction occurs between *ortho* atom H2 of one of the phenolate groups and acetate carbonyl atom O4 of a neighbouring molecule (Table 2). In the case of the $P2_1/n$ polymorph, the intermolecular hydrogen bonding is characterized by a longer interaction distance (H$\cdots$O = 2.66 Å) and occurs between the acetate carbonyl O atom of one molecule and the *meta* H atom of a phenolate group of a neighbouring molecule (Matsumoto *et al.*, 1983). This results in a one-dimensional extended structure that is more like a simple hydrogen-bonded stack than a spiral or helix, as it lacks an axis of symmetry.

Despite the unique extended structures and crystal packing arrangements for the two polymorphs of (I), the molecular structures are similar and have virtually equivalent *saturated* chelate ring conformations and coordination group geometries (r.m.s. deviation < 0.05 Å; Fig. 3). The key differences between the molecular structures of the two polymorphs are the relative orientations of the two phenoxy rings and, to a lesser extent, the relative orientations of the acetate ions. More specifically, the dihedral angle between the lower pair of phenoxy rings in Fig. 3 is 8.4 (2)°, while that between the upper right-hand pair of rings is somewhat smaller, at 5.4 (2)°. Interestingly, the two six-membered chelate rings that include the imine N atoms have different conformations in the two polymorphs. One chelate ring has a regular chair conformation (back ring in Fig. 3), while the other chelate ring (left-hand ring) is best described as having a twisted boat conformation. Clearly, the latter twist is required to enable coordination of one of the phenolate O atoms (O1) in an axial position relative to the three N atoms that occupy sites within the equatorial plane about the Co$^{\text{III}}$ ion (Fig. 1).
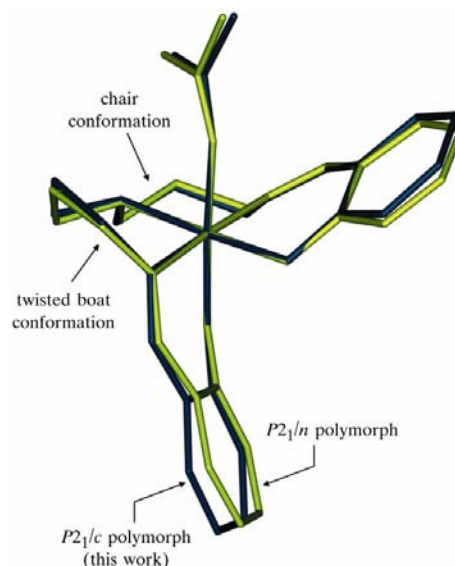

Figure 3
Root-mean-square fit of the present molecular structure of (I) and the $P2_1/n$ polymorph [Co ion and six ligand donor atoms; r.m.s. deviation = 0.033 (4) Å] reported by Matsumoto *et al.* (1983) [Cambridge Structural Database (Allen, 2002) refcode BUWWEV]. Only the bonds are shown (as cylinders) in both structures for the sake of clarity.

metal-organic compounds

Experimental

A new two-step method for the synthesis of (I) was developed. *N*-(3-Aminopropyl)propane-1,3-diamine (4 ml, 30.48 mmol) was dissolved in dry ethanol (25 ml). Salicylaldehyde (6.5 ml, 60.97 mmol) was added slowly to the solution, which turned yellow. On stirring at ambient temperature (30 min), the colour of the solution changed from yellow to bright orange. The solvent was then removed *in vacuo* to yield the ligand (2,2′-{iminobis[(*E*)-propane-3,1-diylnitrilomethylidyne]}diphenol) as an orange oil. UV–vis (CH₂Cl₂, λ_{max}, nm): 255.26, 316.00; IR (KBr pellet, ν, cm^{-1}): 2933 (*m*, C—H), 1631 (*s*, C=N), 1460 (*m*, CH₂), 1278 (*s*, C—O). The ligand (1.0450 g, 3.079 mmol) was dissolved in dry tetrahydrofuran (14 ml, THF). A solution of cobalt(II) acetate (0.7333 g, 2.944 mmol) dissolved in dry methanol (20 ml) was added slowly to the stirred THF solution of the ligand. An immediate colour change from bright yellow to brown occurred. The solution was stirred for *ca* 2 h and then left to stand for 1 h prior to removal of the solvent *in vacuo* to afford a brown powder. Compound (I) was recrystallized from a mixture of CH₂Cl₂ and hexane (1:12) in a test tube over several days (isolated yield 0.7694 g, 57%).

Crystal data

[Co(C₂₀H₂₃N₃O₂)(C₂H₃O₂)]	$V = 2040.6$ (7) Å^3
$M_r = 455.39$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 7.730$ (2) Å	$\mu = 0.88$ mm^{-1}
$b = 20.439$ (3) Å	$T = 100$ (2) K
$c = 13.321$ (2) Å	$0.27 \times 0.17 \times 0.06$ mm
$\beta = 104.169$ (18)°	

Data collection

Oxford Xcalibur2 CCD area-detector diffractometer	Clark & Reid (1995)]
Absorption correction: numerical [*CrysAlis RED* (Oxford Diffraction, 2003), using a multi-faceted crystal model based on expressions derived by	$T_{min} = 0.688$, $T_{max} = 0.904$
	18148 measured reflections
	6468 independent reflections
	5817 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.083$	
$S = 1.05$	
6468 reflections	$\Delta\rho_{max} = 0.50$ e Å^{-3}
276 parameters	$\Delta\rho_{min} = -0.63$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—O1	1.3157 (15)	Co1—N1	1.9318 (11)
C20—O2	1.3157 (15)	Co1—N3	1.9410 (11)
Co1—O1	1.8934 (10)	Co1—N2	1.9950 (11)
Co1—O2	1.9222 (9)	O3—C21	1.2914 (16)
Co1—O3	1.9236 (10)	O4—C21	1.2375 (17)
O1—Co1—O2	91.14 (4)	O3—Co1—N3	93.14 (4)
O1—Co1—O3	176.17 (4)	N1—Co1—N3	177.71 (5)
O2—Co1—O3	85.12 (4)	O1—Co1—N2	92.80 (5)
O1—Co1—N1	92.02 (5)	O2—Co1—N2	175.88 (4)
O2—Co1—N1	88.54 (5)	O3—Co1—N2	90.96 (5)
O3—Co1—N1	88.71 (5)	N1—Co1—N2	90.13 (5)
O1—Co1—N3	86.04 (5)	N3—Co1—N2	91.19 (5)
O2—Co1—N3	90.28 (4)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H100$\cdots$O4	0.91 (2)	1.95 (2)	2.8270 (17)	160.3 (19)
C2—H2$\cdots$O4^i	0.95	2.51	3.372 (2)	150
C8—H8*A*$\cdots$O3	0.99	2.50	2.8496 (18)	100
C11—H11*B*$\cdots$O1	0.99	2.46	2.9658 (19)	111
C13—H13*A*$\cdots$O1	0.99	2.50	2.9183 (18)	105

Symmetry code: (i) $x - 1, -y + \frac{3}{2}, z - \frac{1}{2}$.

The methyl H atoms of the acetate ligand were identified in a difference Fourier synthesis, idealized and refined as part of a rigid rotating group, with C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C). Other H atoms were positioned geometrically and refined using a riding model, with C—H = 0.97 Å and U_{iso}(H) = 1.2U_{eq}(C) for methylene H atoms, and C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic H atoms. Atom H100 attached to N2 (the secondary amine donor atom) was located in a difference Fourier map and refined without constraints.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *WinGX* (Farrugia, 1999); software used to prepare material for publication: *WinGX*.

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