

## *catena*-Poly[[bis(pentane-2,4-dionato- $\kappa^2$ O, $O'$ )cobalt(II)]- $\mu$ -4,4'-methylene-dianiline- $\kappa^2$ N: $N'$ ]

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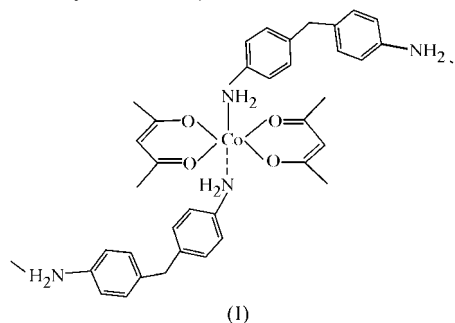
In the title compound,  $[\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_{13}\text{H}_{14}\text{N}_2)]_n$  or  $[\text{Co}(\text{acac})_2(\text{dadpm})]_n$ , where acac is acetylacetonate and dadpm is 4,4'-methylenedianiline, the Co atom is on a centre of symmetry and is octahedrally coordinated by four O atoms from two acac anions and by two N atoms from two dadpm ligands. Each dadpm ligand, which has a twofold axis passing through its methylene C atom, bridges two Co atoms to form a spiral polymeric chain. Neighbouring chains connect *via* hydrogen bonds to form a two-dimensional network.

### Comment

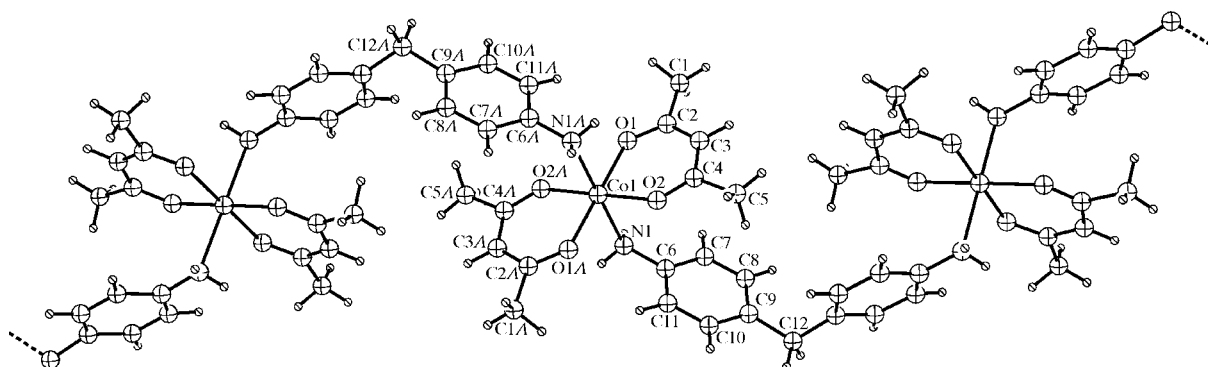
'Spirality' is an important structural feature of great interest in inorganic and coordination chemistry (Constable, 1992; Carina *et al.*, 1993; Lehn, 1995). Much effort has been devoted in recent decades to the design of metal complexes exhibiting spiral, particularly helical, architectures (Constable, 1992; Carina *et al.*, 1993; Lehn, 1995; Zaworotko, 1998). Suitably tailored polydentate ligands, particularly oligopyridines, have

been widely used to coordinate with metals to create spiral oligonuclear complexes and polymers (Hasenknopf *et al.*, 1996; Jung *et al.*, 1998; Abrahams *et al.*, 1999).

Ligands containing amino groups are well known to coordinate with various metals to give coordination polymers (Dickman, 2000; Alcock *et al.*, 1997; Lu *et al.*, 1994). Among these ligands, 4,4'-methylenedianiline (dadpm) has frequently been employed for the construction of coordination polymers, *e.g.* the one-dimensional polymer  $[\text{Cu}_2(\text{dadpm})_2(\text{trans-oxpy})](\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  [*trans-oxpy* is *trans-N,N'*-bis(2-pyridylmethyl)oxamide; Zhang, Kang *et al.*, 2001], the one-dimensional polymer  $[\{\text{Cu}(\text{dadpm})(\text{C}_3\text{H}_4\text{O}_4)\text{Cl}\}\text{Cl}]_2$  ( $\text{C}_3\text{H}_4\text{O}_4$  is malonic acid; Zhang *et al.*, 1999), the three-dimensional polymer  $[\text{Ni}(\text{dadpm})_4(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (Zhang, Lei *et al.*, 2001) and the three-dimensional polymer  $[\text{Cd}(\text{dadpm})_2\text{Cl}](\text{dca})$  (dca is dicyanamide; Luo *et al.*, 2003). We report here the crystal structure of the title cobalt(II) acac-dadpm complex, (I) (acac is acetylacetonate).

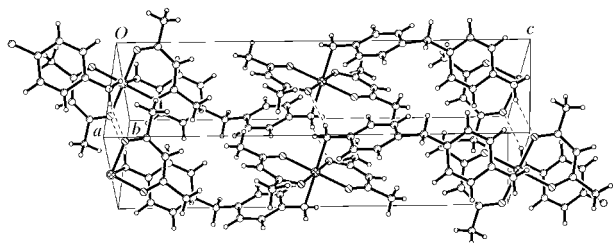


The polymer backbone of (I) is made up of  $\text{Co}(\text{acac})_2$  fragments and bridging dadpm ligands. Each dadpm ligand links two fragments through two Co–N bonds, forming an interesting one-dimensional spiral array of repeating  $\text{Co}(\text{acac})_2(\text{dadpm})$  units stacked along the crystallographic *c* axis (Fig. 1). The Co atom in (I) lies on a centre of symmetry and is coordinated by four O atoms from two chelated acac anions and two N atoms from two different dadpm ligands, forming a distorted octahedral coordination geometry. Four O atoms (O1, O2, O1A and O2A) occupy the equatorial positions, with bond lengths of 2.0672 (12) and 2.0319 (12) Å (Table 1), and two N atoms (N1 and N1A) are located in the axial positions, with a Co1–N1 distance of 2.2201 (17) Å.



**Figure 1**

A view of the polymeric structure of (I), with the atom-labelling scheme. Atoms related by the centre of symmetry at  $(-x, 1-y, 1-z)$  are indicated with the suffix *A*. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

**Figure 2**

A packing diagram for (I), showing the two-dimensional network formed by hydrogen bonds (dashed lines) between the polymeric chains.

The Co1—O bond lengths in (I) are similar to those found in related Co<sup>II</sup>–acac complexes, such as [Co(acac)<sub>2</sub>(pz)] (2.0382 Å; pz is pyrazine; Ma *et al.*, 2001), [Co(acac)<sub>2</sub>(4,4'-bipy)] (2.032 Å; 4,4'-bipy is 4,4'-bipyridine; Ma *et al.*, 2001) and [Co<sub>2</sub>(acac)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>][Co(acac)(H<sub>2</sub>O)<sub>4</sub>](ClO<sub>4</sub>)·EtOH (2.051 Å; McCann *et al.*, 2001). The Co—N bond length of 2.2201 (17) Å in (I) is comparable with that in compounds with similar motifs, such as [Co(hfac)<sub>2</sub>(opda)<sub>2</sub>] (2.2243 Å; hfac is 1,1,1,5,5,5-hexafluoropentane-2,4-dionate and opda is 1,2-phenylenediamine; Dickman, 2000), but longer than those observed in [Co(azpy)(pht)(H<sub>2</sub>O)<sub>3</sub>] (2.188 Å; azpy is 4,4'-azopyridine and pht is *o*-phthalate; Zhu *et al.*, 2003) and [Co(3,3'-azpy)(H<sub>2</sub>O)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub>·3(3,3'-azpy) (2.176 Å; 3,3'-azpy is 3,3'-azopyridine; Li *et al.*, 2001).

There is a twofold axis passing through methylene atom C12 of the dadpm ligand in (I). The dadpm ligand adopts a *trans-gauche* conformation. The dihedral angle between the two phenyl rings in the dadpm ligand in (I) [75.78 (7)°] is smaller than that in [Cd(dadpm)<sub>2</sub>Br](dca) [98.7 (5)°; Luo *et al.*, 2003], but larger than that in [Cd(dadpm)(dca)<sub>2</sub>] [55.3 (2)°; Luo *et al.*, 2003]. The C(Ph)—C—C(Ph) bond angle between the two phenyl groups of dadpm in (I) is 117.0 (2)°, which is slightly larger than the values reported for [CdCl(dadpm)<sub>2</sub>](dca) [115.8 (4)°; Luo *et al.*, 2003], [CdBr(dadpm)<sub>2</sub>](dca) [115.9 (1)°; Luo *et al.*, 2003] and {[CuCl(dadpm)(C<sub>3</sub>H<sub>4</sub>O<sub>4</sub>)Cl]<sub>2</sub>} [114.7 (7)°; Zhang *et al.*, 1999].

The NH<sub>2</sub> groups of the dadpm ligand of (I) interact with the O atoms of acac anions from adjacent chains *via* atom H1A (Table 2), thereby forming a two-dimensional hydrogen-bonded network (Fig. 2). The second atom, H1B, is located 2.51 (3) Å above the Co(acac) group and in contact with an adjacent atom, H1E(1 - x, 1 - y, 1 - z), at 2.37 (4) Å.

## Experimental

An ethanol solution (3.5 ml) of 4,4'-methylenedianiline (0.103 g, 0.1 mmol) was added to [Co(acac)<sub>2</sub>(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>]<sub>2</sub>·6H<sub>2</sub>O (0.035 g, 0.1 mmol) in *N,N*-dimethylformamide (1.5 ml) at room temperature and the resulting mixture stirred for 1 h. The mixture was layered with propan-2-ol and pink plates of (I) were formed (yield 0.023 g, 51% based on Co). The crystal used for the crystal structure determination was obtained directly from the above preparation. Analysis found: C 60.85, H 6.18, N 6.22%; calculated for C<sub>23</sub>H<sub>28</sub>CoN<sub>2</sub>O<sub>4</sub>: C 60.66, H 6.20, N 6.15%. IR (KBr, ν, cm<sup>-1</sup>): 3368 (*w*), 3271 (*w*), 1589 (*s*), 1512 (*s*), 1458 (*s*), 1408 (*s*), 1358 (*w*), 1253 (*m*), 972 (*m*), 760 (*w*), 555 (*w*).

## Crystal data

[Co(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>(C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>)]  
 $M_r = 455.40$   
 Monoclinic,  $P2_1/c$   
 $a = 5.5805$  (5) Å  
 $b = 8.9808$  (9) Å  
 $c = 21.955$  (2) Å  
 $\beta = 94.976$  (3)°  
 $V = 1096.20$  (19) Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 1.380$  Mg m<sup>-3</sup>

Mo K $\alpha$  radiation  
 Cell parameters from 3781 reflections  
 $\theta = 3.6$ – $25.3$ °  
 $\mu = 0.81$  mm<sup>-1</sup>  
 $T = 193$  (2) K  
 Plate, pink  
 $0.36 \times 0.35 \times 0.07$  mm

## Data collection

Rigaku Mercury CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (Jacobson, 1998)  
 $T_{\min} = 0.758$ ,  $T_{\max} = 0.945$   
 10 160 measured reflections

2005 independent reflections  
 1887 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.023$   
 $\theta_{\max} = 25.4$ °  
 $h = -6 \rightarrow 6$   
 $k = -10 \rightarrow 10$   
 $l = -23 \rightarrow 26$

## Refinement

Refinement on  $F^2$   
 $R(F) = 0.031$   
 $wR(F^2) = 0.074$   
 $S = 1.11$   
 2005 reflections  
 195 parameters  
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0316P)^2 + 0.6071P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.20$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.29$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Co1—O2	2.0319 (12)	O1—C2	1.269 (2)
Co1—O1	2.0672 (12)	O2—C4	1.259 (2)
Co1—N1	2.2201 (17)	N1—C6	1.425 (2)
O2—Co1—O1	89.87 (5)	C6—N1—Co1	118.35 (12)
O2—Co1—N1	91.46 (6)	C9 <sup>i</sup> —C12—C9	117.0 (2)
O1—Co1—N1	93.07 (6)		

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

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1A <sup>ii</sup> ···O1 <sup>ii</sup>	0.83 (2)	2.36 (2)	3.155 (2)	159 (2)

Symmetry code: (ii)  $1 - x, 1 - y, 1 - z$ .

All H atoms were placed in geometrically idealized positions and refined with isotropic displacement parameters.

Data collection: *CrystalClear* (Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSK, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1073). Services for accessing these data are described at the back of the journal.

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