

catena-Poly[[bis(acetylacetonato- κ^2O,O')cobalt(II)]- μ -1,3-di-4-pyridylpropane- $\kappa^2N:N'$]: a one-dimensional coordination polymer capable of forming clathrates with prochiral aldehydes

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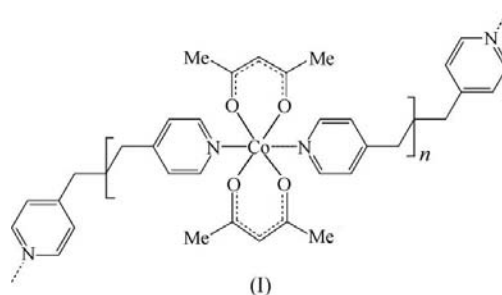
The title compound, $[\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_{13}\text{H}_{14}\text{N}_2)]_n$, forms a coordination polymer in which the Co^{II} centre is located on an inversion centre and the 1,3-di-4-pyridylpropane ligand is located on a twofold axis. The polymeric chains are parallel and are held together by weak intermolecular $\text{C}-\text{H}\cdots\text{O}$ interactions. The complex is intended as a possible host for prochiral aldehydes and ketones, and one clathrate was isolated with *p*-tolylaldehyde.

Comment

There are only a limited number of β -diketonate complexes in the Cambridge Structural Database (CSD, Version 5.30 of November 2008; Allen, 2002) incorporating the 1,3-di-4-pyridylpropane ligand. Except for $(\mu_2$ -1,3-di-4-pyridylpropane)-bis(acetylacetonato)bis(1,10-phenanthroline)dicopper(II) diperchlorate hexahydrate (Madalan *et al.*, 2005) and *catena*-[bis(μ_2 -1,3-di-4-pyridylpropane)tetrakis(1-benzoylacetonato)-dizinc trihydrate] (Han & Zhou, 2008), the published structures appear to be limited to hexafluoroacetylacetonate (hfacac) complexes of manganese, cobalt and copper. The 1,3-di-4-pyridylpropane complexes of manganese hexafluoroacetylacetonate form a number of clathrates with aromatic guest molecules. Bis[$(\mu_2$ -1,3-di-4-pyridylpropane)bis(hexafluoroacetylacetonato)]manganese(II) forms clathrates with benzene (Tabellion *et al.*, 2001*a*), toluene, diphenylmethane, *cis*-stilbene, benzyl alcohol, nitrobenzene and benzonitrile (Tabellion *et al.*, 2001*b*). Two further clathrates are formed by the coordination polymer *catena*-[$(\mu_2$ -1,3-di-4-pyridylpropane)bis(hexafluoroacetylacetonato)manganese(II)] with 1,3-diphenylpropane (Tabellion *et al.*, 2001*b*) and 1,2-diphenylethane (Tabellion *et al.*, 2001*a*). In addition, *catena*-[bis(μ_2 -1,3-di-4-pyridylpropane)tetrakis(hexafluoroacetylacetonato)dibobalt(II)] [hereinafter (II)] forms a clathrate with dimethyl-

formamide (CSD refcode WUTTUA; Seidel *et al.*, 2001). These results indicate that it would be possible to use a similar system to form clathrates with prochiral aldehydes or ketones. If such a clathrate crystallized in one of the Sohncke space groups (Flack, 2003), it would be a possible candidate for use in the absolute asymmetric synthesis (Feringa & Van Delden, 1999) of alcohols. Previous work from our laboratory includes the coordination of prochiral aldehydes to tris(2,6-diphenylphenolato)aluminium (Johansson & Håkansson, 2005), π -coordination by unsaturated aldehyde to copper(I) chloride (Andersson *et al.*, 1986) and the coordination of acetylpyridines to copper(I) halides (Lennartson, Salo & Håkansson, 2005; Lennartson *et al.*, 2006). The principle is that slow crystallization of a stereochemically labile compound may result in an enantiomerically enriched product, a phenomenon known as total spontaneous resolution or crystallization-induced asymmetric transformation (Jacques *et al.*, 1984).

Optical activity in stereochemically labile substances will only exist in the solid state, but can in some cases be transferred to stereochemically inert compounds by a chemical reaction. Hence, tris[(2,6-diphenylphenolato)(*p*-tolylaldehyde)]-aluminium resolved by crystallization-induced asymmetric transformation reacts with solid methylolithium to give 1-(4-methylphenyl)ethanol with an enantiomeric excess (e.e.) of 17% (Johansson & Håkansson, 2005). Since no optically active reagents or catalysts were involved, such reactions may be described as absolute asymmetric synthesis. The self-assembly of a conformationally chiral clathrate from achiral building blocks in solution can proceed to completeness with a theoretical yield of 100% and a theoretical e.e. of 100%. The requirement is that all crystals grow from a single primary nucleus, to ensure that all crystals are of the same enantiomorph. We have observed such an example of high yield in combination with an e.e. close to 100%, *e.g.* in the optical resolution of seven-coordinate enantiomers (Lennartson, Vestergren & Håkansson, 2005). Among the clathrates described above, only one crystallizes in a Sohncke space group, *viz.* (II).



The title compound, (I), was found to crystallize in the centrosymmetric space group $C2/c$, and did not appear to show any tendencies to cocrystallize with dimethyl sulfoxide under the conditions employed. The metal centre is located on an inversion centre and the 1,3-di-4-pyridylpropane ligand is located on a twofold axis which passes through C12 (Fig. 1).

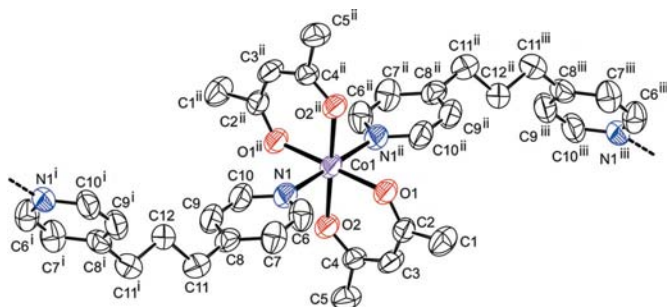


Figure 1

A view of (I), showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted. [Symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $2 - x, 1 - y, 1 - z$; (iii) $1 + x, 1 - y, \frac{1}{2} + z$.]

The coordination geometry around the metal centre is slightly distorted octahedral, with the two bidentate acetylacetonate (acac) ligands forming a plane and two 1,3-di-4-pyridylpropane ligands occupying the remaining two sites in a *trans* arrangement, resulting in the formation of extended one-dimensional zigzag chains (Fig. 1). These features are similar to those in (II), but there are some differences. The deviation from planarity of the $\text{Co}(\text{acac})_2$ unit in (I) is much smaller than in the $\text{Co}(\text{hfacac})_2$ unit in (II). Both chelate rings in (I) are virtually planar [maximum deviation from the least-squares plane formed by atoms $\text{Co1}/\text{O1}/\text{O2}/\text{C2}-\text{C4} = -0.036$ (1) Å]. In significant contrast, the hfacac ligands in (II) are planar excluding the Co, which are out of plane by between 0.414 (1) and 0.200 (1) Å. Moreover, the planes of the two hfacac ligands (again excluding the Co) are tilted at angles of 37.9 (4) and 23.1 (4)° to each other about each Co.

In (I), the 1,3-di-4-pyridylpropane ligand adopts a C_2 -symmetric conformation, since atom C12 is located on a twofold axis with a $\text{C8}-\text{C11}-\text{C12}-\text{C11}^i$ torsion angle of 170.06 (19)° [symmetry code: (i) $1 - x, y, \frac{1}{2} - z$]. The two different 1,3-di-4-pyridylpropane ligands in (II) lack similar symmetry, with corresponding torsion angles of 66.4 (9) and 175.2 (9)°. The 1,3-di-4-pyridylpropane ligand may adopt a wide variety of conformations in the solid state, and essentially achiral conformations have been reported (*e.g.* Jin *et al.*, 2002). As the Co^{II} cation is (unfortunately) located on an inversion centre, each chain is centrosymmetric and achiral. In (II), on the other hand, the whole chain is conformationally chiral.

There is one set of weak intermolecular interactions in (I) (Table 2). Due to the centrosymmetry of (I), each chain interacts with four adjacent chains and the chains run parallel through the unit cell (Fig. 2). Interactions between the chains are weak and could perhaps be disrupted by the introduction of a potential guest molecule. To test this idea, approximately equivalent amounts of $\text{Co}(\text{acac})_2(\text{H}_2\text{O})_x$ and 1,3-di-4-pyridylpropane were dissolved in various prochiral aldehydes and ketones (*p*-tolylaldehyde, acetophenone, benzylacetone, *p*-ethylbenzaldehyde, benzaldehyde, butyraldehyde, salicylaldehyde, capronaldehyde, 3-methoxybenzaldehyde, 2-methoxybenzaldehyde, propiophenone, isopropyl methyl ketone and *tert*-butyl methyl ketone) by gentle heating. In the cases where

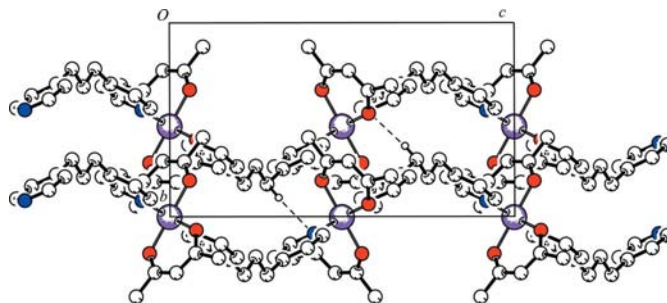


Figure 2

A view along the *a* axis of (I), showing the one-dimensional coordination polymer forming zigzag-shaped chains held together by weak $\text{C}-\text{H}\cdots\text{O}$ interactions (dashed lines). Only those H atoms involved in the interactions are shown. Co centres are shown as large shaded spheres, N atoms as darker shaded small spheres and O atoms as lighter shaded small spheres.

crystals deposited on cooling, the crystals were identified as (I), except in the case of *p*-tolylaldehyde where a clathrate was obtained. The quality of data was only enough to work out the basic molecular structure; the aldehyde molecules are disordered, and the crystals belong to the centrosymmetric space group $C2/c$ and are of no use for absolute asymmetric synthesis. The polymeric chains in the clathrate appear to be similar in conformation to those in (I). It is hoped that other structures may be revealed in future, displaying well ordered keto compounds in a chiral environment.

Experimental

Equimolar amounts of $\text{Co}(\text{acac})_2(\text{H}_2\text{O})_x$ (where *x* was assumed to be 2) and 1,3-di-4-pyridylpropane were heated in dimethyl sulfoxide until a clear solution was obtained. Slow cooling to ambient temperature resulted in light-red crystals of (I).

Crystal data

$[\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_{13}\text{H}_{14}\text{N}_2)]$	$V = 2277.9$ (11) Å ³
$M_r = 455.40$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 14.902$ (4) Å	$\mu = 0.78$ mm ⁻¹
$b = 8.969$ (2) Å	$T = 295$ K
$c = 18.434$ (5) Å	$0.4 \times 0.2 \times 0.1$ mm
$\beta = 112.397$ (9)°	

Data collection

Rigaku R-Axis-IIIC image-plate diffractometer	6897 measured reflections
Absorption correction: multi-scan (CrystalClear; Rigaku, 2000)	1970 independent reflections
$T_{\min} = 0.669$, $T_{\max} = 0.926$	1786 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	140 parameters
$wR(F^2) = 0.118$	H-atom parameters constrained
$S = 0.98$	$\Delta\rho_{\max} = 0.22$ e Å ⁻³
1970 reflections	$\Delta\rho_{\min} = -0.25$ e Å ⁻³

All H atoms were included in calculated positions and refined using a riding model, with $\text{C}-\text{H} = 0.93-0.97$ Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{iso}}(\text{C})$ for methyl H atoms or $1.2U_{\text{iso}}(\text{C})$ for other H atoms.

Table 1

Selected geometric parameters (Å, °).

Co1—O1	2.0512 (15)	Co1—N1	2.2357 (19)
Co1—O2	2.0629 (14)		
O1—Co1—O2	89.56 (6)	O2—Co1—N1	90.40 (6)
O1—Co1—N1	88.89 (7)		

Table 2

Hydrogen-bond 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>
C11 ⁱⁱ —H11B ⁱⁱ ...O1	0.97	2.64	3.612 (3)	173

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

A total of 38 reflections were not collected due to the image-plate system having a cusp of data around the φ rotation axis which cannot be measured. Also, 95 low-angle measured reflections were excluded since these caused saturation of the image plate.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLUTON* (Spek, 2009); 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: GA3125). Services for accessing these data are described at the back of the journal.

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