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Self-assembly of bis(1,3-diphenylpropane-1,3-dionato-κ^2O,O')bis(thiomorpholine-κN)-cobalt(II)

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Key indicators

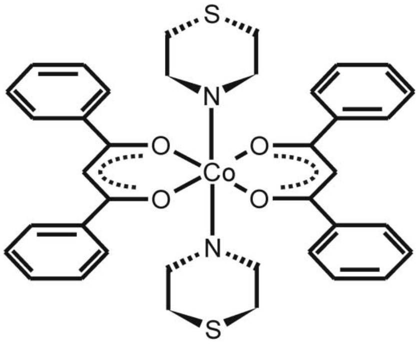
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.059
wR factor = 0.109
Data-to-parameter ratio = 14.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The molecules of the title bis(thiomorpholine) adduct of bis(1,3-diphenylpropane-1,3-dionato)cobalt(II), $[Co(C_{15}H_{12}O_2)_2(C_4H_8NS)_2]$, in the crystal structure are positioned on an inversion center at the intersection of a twofold rotation axis and a perpendicular mirror plane. The two thiomorpholine ligands bond to the octahedral cobalt(II) ion in the axial coordination sites (*trans* configuration).

Comment

Coordinatively unsaturated metal(II) β-diketonates have attracted significant and long-lasting attention as starting materials for vapor-phase deposition of metals and transition-metal based catalysts (Dash & Mohapatra, 1984; Parkanyl *et al.*, 1981; Soldatov *et al.*, 2003). Such complexes have not, however, been studied extensively in terms of supramolecular chemistry and solid-state self-assembly involving weak interactions. Such complexes can be exploited as 'hubs' to explore interactions that steer the self-assembly of molecules in solids (Aakeröy *et al.*, 2005). Such a role is readily achieved through the binding of additional ligands that contain functionalities of interest in molecular self-assembly. Different choices of such additional molecules are expected to result in different solid-state architectures involving transition metal ions. In that context, we report here the crystal structure of the title compound, bis(1,3-diphenylpropane-1,3-dionato)bis(thiomorpholine)cobalt(II), (I).



(I)

Thiomorpholine was selected as a ditopic ligand with one N– and one S-donor atom. This ligand was expected to bind to the metal ion through the N atom and provide a means of achieving the organization of complex molecules in the solid state that is different from that in other bis(1,3-diphenylpropane-1,3-dionato)cobalt(II) complexes, but without significantly disturbing the overall geometry of the 'hub' unit (Aakeröy *et al.*, 2004; Soldatov & Ripmeester, 2001).

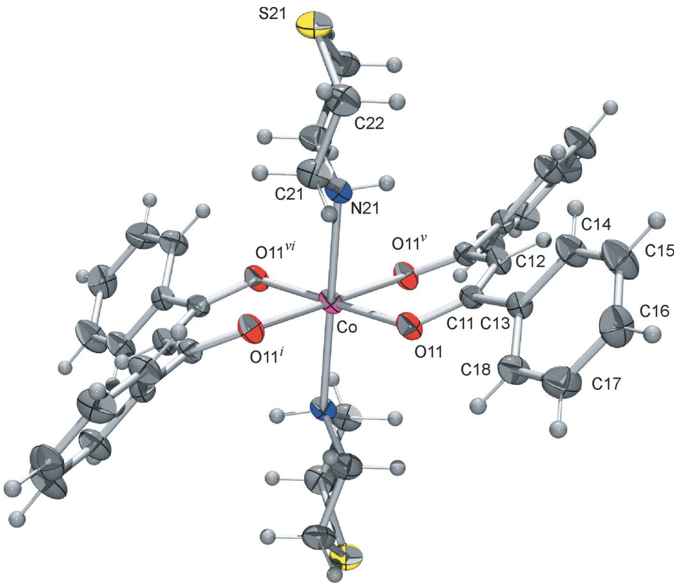


Figure 1
View of the molecular structure of compound (I), showing the atomic numbering scheme and displacement ellipsoids drawn at the 30% probability level. [Symmetry codes: (i) $x, -y, 1 - z$; (v) $1 - x, y, z$; (vi) $1 - x, -y, 1 - z$].

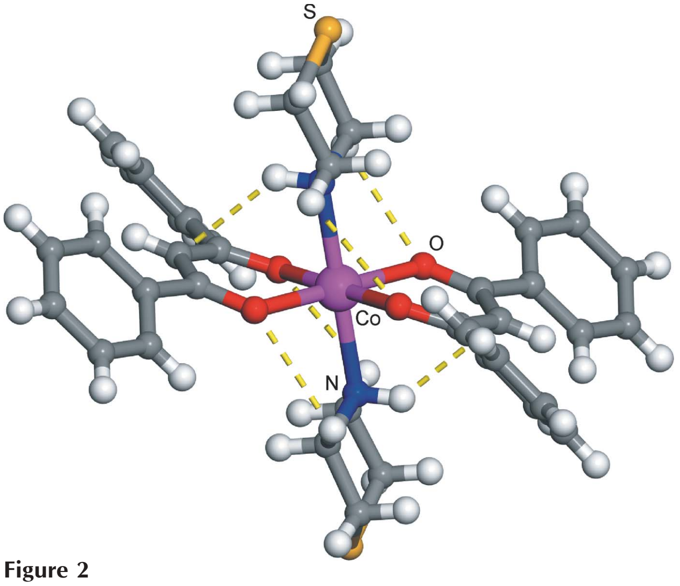


Figure 2
A ball-and-stick representation of compound (I), displaying the intramolecular C—H$\cdots$O and N—H$\cdots\pi$ bonding as dashed lines (see Fig. 1 and Table 1 for details).

Compound (I) possesses C_{2v} symmetry, each molecule being situated on an inversion center at the intersection of crystallographic symmetry elements, *viz*. a mirror plane and a perpendicular twofold rotation axis (Fig. 1). The molecule can best be described as composed of a bis(dibenzoylmethanato)cobalt(II) 'hub' with two thiomorpholine ligands bonded to the cobalt(II) ion in the axial coordination sites (*trans* configuration), thus completing the octahedral coordination of the metal. As anticipated, the thiomorpholine ligand binds to the metal *via* the N-donor atom, and adopts a chair conformation. The chelate ring plane, defined by atoms O11, C11, C12, C11^{v} and O11^{v} [symmetry code: (v) $1 - x, y, z$] of the dibenzoylmethanato ligand is twisted out of the equatorial coordination plane of the metal, defined by atoms O11, Co and O11^{v}, with an interplanar angle of 23.4 (2)°. Such a conformation of the complex is stabilized by four intramolecular C—H$\cdots$O interactions, each involving a methylene group of a thiomorpholine ligand and an O atom of a dibenzoylmethanate ligand. Further stabilization is achieved

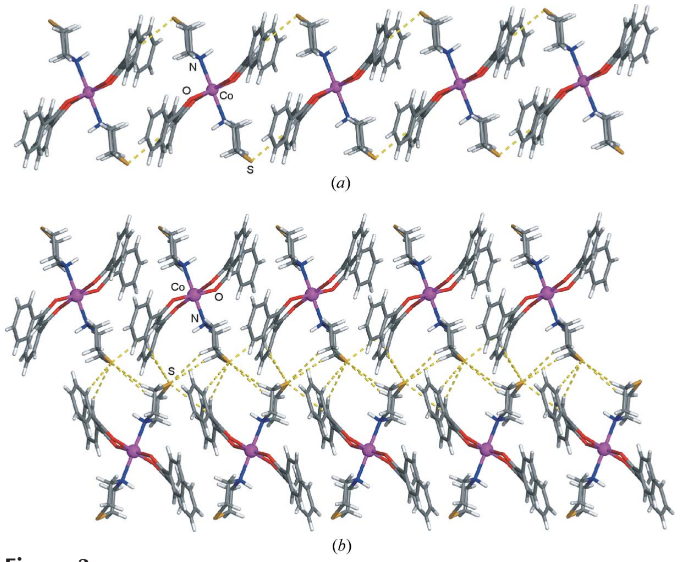


Figure 3
Wireframe representation of (*a*) chains and (*b*) layers that exist in the crystal structure of compound (I). Hydrogen bonds are shown as dashed lines.

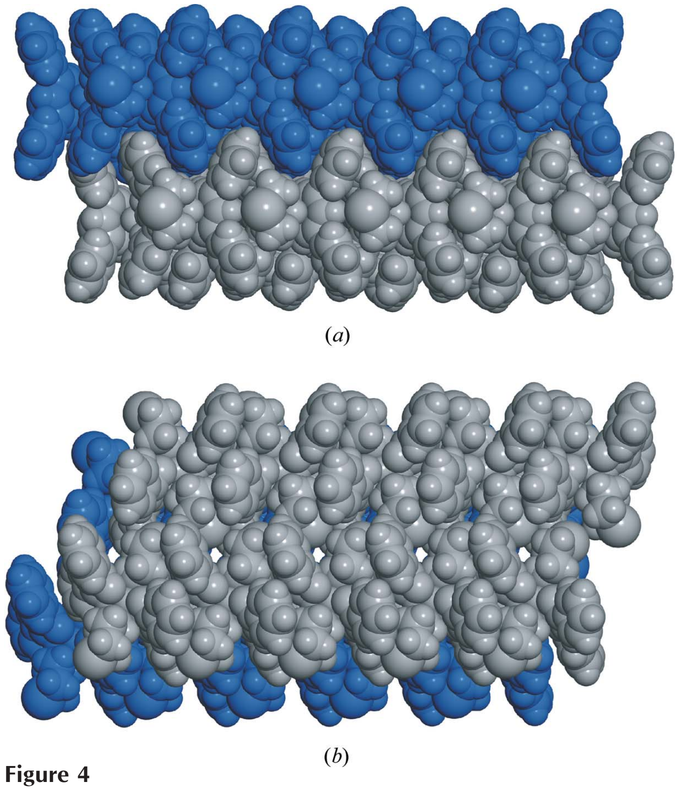


Figure 4
Space-filling representation of two sheets, coloured blue and gray, in the crystal structure of (I); (*a*) view down the *c* axis and (*b*) view down the *a* axis showing the very narrow channels.

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by two intramolecular N—H⋯π interactions (Table 1) that involve the N atom of each thiomorpholine ligand and the π-system of each chelate ring (Fig. 2). In such a conformation, the phenyl groups of the dibenzoylmethanate ligand are twisted out of the chelate ring plane [dihedral angle 32.7 (2)°].

The analysis of the crystal packing reveals that the molecules form chains that propagate in the *b*-axis direction (Fig. 3*a*), and corrugated layers that are parallel to the *ab* plane (Fig. 3*b*). Notably, adjacent layers come together by way of a tongue-in-groove fit involving phenyl groups of molecules that belong to neighboring layers (Fig. 4*a*). The structure displays channels (approximate diameter 1 Å) that run parallel to the *a*-axis direction (Fig. 4*b*).

Experimental

An acetone solution (20 ml) of diaqua(1,3-diphenylpropane-1,3-dionato)cobalt(II) (1 mmol) was overlayed with a solution of thiomorpholine (2 mmol) in diethyl ether (5 ml). The system was left to slowly evaporate while diffusion of the two media took place at room temperature. After a few days, orange plate-like crystals of (I) started to grow on the walls of the reaction vessel.

Crystal data

$[Co(C_{15}H_{12}O_2)_2(C_4H_8NS)_2]$
$M_r = 711.79$
Orthorhombic, *Cmca*
$a = 19.345\ (2)$ Å
$b = 8.1767\ (9)$ Å
$c = 22.104\ (2)$ Å
$V = 3496.4\ (6)$ Å^3
$Z = 4$
$D_x = 1.352$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 2147 reflections
$\theta = 4–54°$
$\mu = 0.65$ mm^{-1}
$T = 295\ (1)$ K
Plate, orange
0.26 × 0.25 × 0.04 mm

Data collection

Oxford Diffraction Xcalibur-3 CCD area-detector diffractometer
ω scans
Absorption correction: analytical (Alcock, 1970)
$T_{min} = 0.825$, $T_{max} = 0.972$
23809 measured reflections

1597 independent reflections
1493 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$
$\theta_{max} = 25.1°$
$h = -22 \rightarrow 22$
$k = -9 \rightarrow 9$
$l = -26 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.109$
$S = 1.33$
1597 reflections
113 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 3.3855P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.2$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C21—H21*A*⋯O11^{i}	0.97	2.82	3.362 (4)	116
N21—H21⋯C12^{i}	0.91	2.62	3.329 (5)	135

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

H atoms were included in calculated positions and treated as riding atoms, with C—H distances of 0.95 Å for phenyl and 0.96 Å for methylene groups, N—H = 0.91 Å, and $U_{iso}(H) = 1.2U_{eq}(C,N)$.

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: *ORTEP-3 for Windows* (Farrugia, 1997), *MERCURY* (Bruno *et al.*, 2002), *RasTop* (Valadon, 2004) and *POVRay* (Persistence of Vision Pty, 2004); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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