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A dimeric cobalt(II)–suberate complex with 3-aminopyridine

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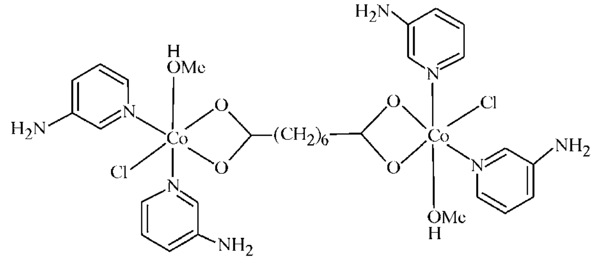
The title complex, μ-octane-1,8-dioato-bis[bis(3-aminopyridine)chloro(methanol)cobalt(II)], $[Co_2(C_8H_{12}O_4)Cl_2(C_5H_6N_2)_4(CH_4O)_2]$, is located on a crystallographic centre of inversion. The coordination around each of the Co centres is distorted octahedral, involving two N, three O and one Cl atom. Discrete dimers are connected in a three-dimensional arrangement through N—H···O, N—H···Cl and O—H···O hydrogen-bond interactions.

Comment

Carboxylate ligands are one of the most widely used class of bridging ligands in coordination chemistry. The versatility of the carboxylate group is illustrated by a variety of coordination modes in which it connects metal centres, the most common being the so-called *syn–syn*, *syn–anti* and *anti–anti* modes. The versatility can be enhanced by ligands that contain more than one carboxylate group (di-, tri- and polycarboxylates). Among them, α,ω-aliphatic dicarboxylates are interesting not just because they contain two terminal functional carboxylate groups, but also by the fact that these two groups are linked by flexible alkyl chains which by their conformational freedom offer a greater degree of structural diversity. In recent years our research has been devoted to the synthesis and structural analysis of metal complexes with monocarboxylates and different aminopyridines (see, for example, Lah, Giester, Lah *et al.*, 2001; Lah, Giester, Šegedin *et al.*, 2001; Lah *et al.*, 2002; Kozlevcar *et al.*, 2004). As a part of our ongoing project, we have extended our investigations to metal complexes with saturated α,ω-aliphatic dicarboxylates. We report here the synthesis and crystal structure of a dimeric Co^{II} complex with anions of suberic acid (octane-1,8-dioic acid) and 3-aminopyridine and discuss its structure in terms of the known structurally characterized metal–suberate complexes.



(I)

Despite our attempts to prepare a new coordination polymer of higher dimensions, the title compound, (I) (Fig. 1), exists as a centrosymmetric dimer in which the suberate dianion (SA) connects two cobalt ions with both carboxylate groups simultaneously adopting chelating bidentate modes. The coordination around the metal centre is completed by two 3-aminopyridine ligands coordinated through endocyclic N atoms, a chloride anion and a methanol molecule (Table 1). Thus, each Co centre has a distorted octahedral geometry. The central C atoms of the alkyl chain adopt a *trans* conformation [C2—C3—C4—C4^i = 178.6 (2)°; symmetry code: (i) $-x + 2$, $-y$, $-z + 1$], while the C1—C2—C3—C4 torsion angle of −64.3 (3)° indicates *gauche* geometry. The presence of several

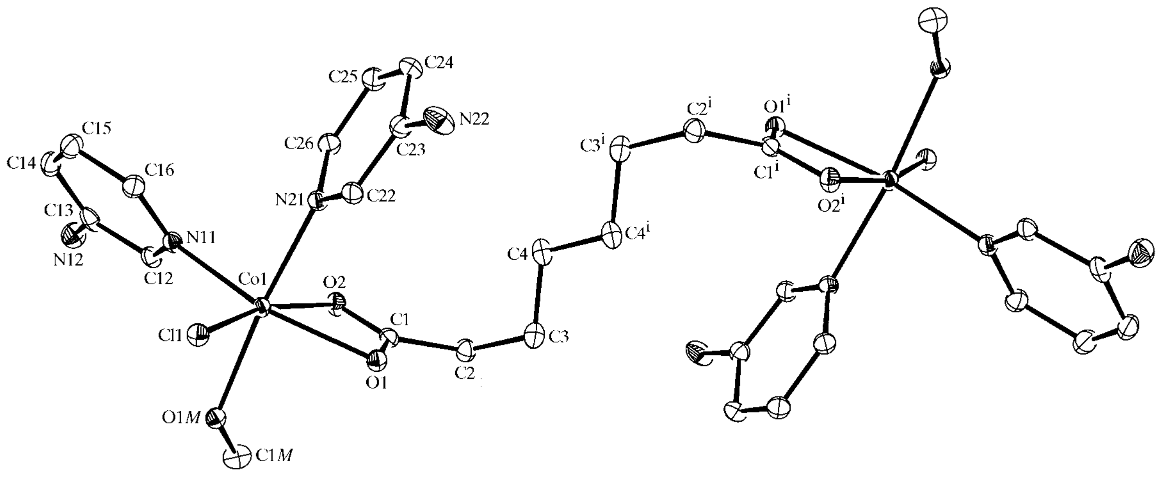


Figure 1
The dimeric structure of (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry code: (i) $-x + 2$, $-y$, $-z + 1$.]

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hydrogen-bond donors and acceptors anticipates a complex hydrogen-bonding scheme. Apparently, the orientation of the 3-aminopyridine ligands and the location of the amino groups on *meta* positions prevent the formation of intramolecular hydrogen bonds. However, both crystallographically independent amino groups and the methanol molecule are involved, as donors, in the formation of hydrogen bonds. One of the amino groups (N12) donates both H atoms to the Cl atoms of two different neighbouring dimeric units. Taking into account a centre of symmetry, the result is the formation of an eight-membered ring. The second amino group (N22) participates in hydrogen bonding with one H atom only, which is in contact with the carboxylate O atom of an adjacent molecule (Fig. 2). The two-dimensional layers that are formed by the hydrogen-bond contacts including the NH_2 groups are further connected into a three-dimensional arrangement through O—H···O interactions between methanol and carboxylate O atoms of neighbouring units (Fig. 3); see Table 2 for details of the hydrogen bonding.

A search of the Cambridge Structural Database (Version 5.27 with August 2006 update; Allen, 2002) gave 26 hits for transition metal complexes with coordinated suberic acid or its anions (either hydrogen suberate or suberate dianions). Most of them (18) are polymers with dimensions varying from one-dimensional to three-dimensional. Only eight examples of structures with discrete entities are known, *viz.* three manganese dimers (Zheng & Lin, 2001; Zheng, Lin & Kong, 2003), a zinc monomer and dimer (Wei *et al.*, 2002), a copper monomer and dimer (McCann *et al.*, 1995; Devereux *et al.*, 1999), and one example of a cobalt dimer (Zheng & Kong, 2003). There is one feature common to all these discrete structures; they all contain additional bifunctional N-ligands (1,10-phenanthroline or 2,2′-bipyridine) that by chelation occupy two coordination sites and are large enough to prevent further interactions with larger ligands in the directions to polymer formation. The above-mentioned cobalt dimer has $[Co_2(SA)_2(phen)_2(H_2O)_2]$ stoichiometry. The two cobalt ions, in a severely distorted octahedral environment, are linked by two SA dianions that serve as tridentate ligands, with one of the carboxylate groups involved in chelation and the second coordinated in a monodentate fashion. The remaining coordination sites on Co are occupied by phenanthroline N atoms and water molecules. The related system of oxalates as the first from the homologous series of α,ω-dicarboxylates and aminopyridines has already been investigated in cobalt, nickel and copper complexes (Castillo *et al.*, 2001). However, the structures of none of the reported complexes resemble that of (I); all the reported compounds are polymers.

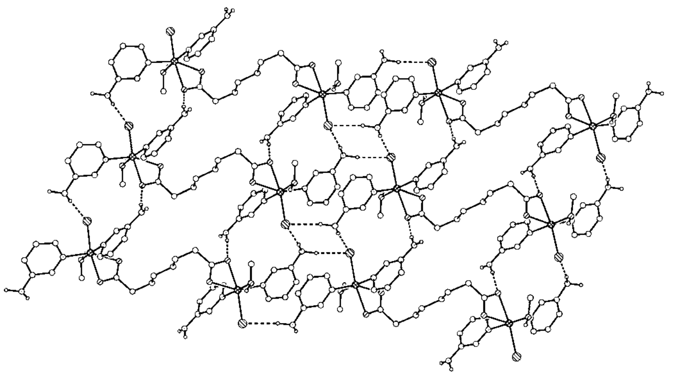

Figure 2
Two-dimensional layers in (I) formed by hydrogen bonds involving NH_2 groups. C-bound H atoms have been omitted.

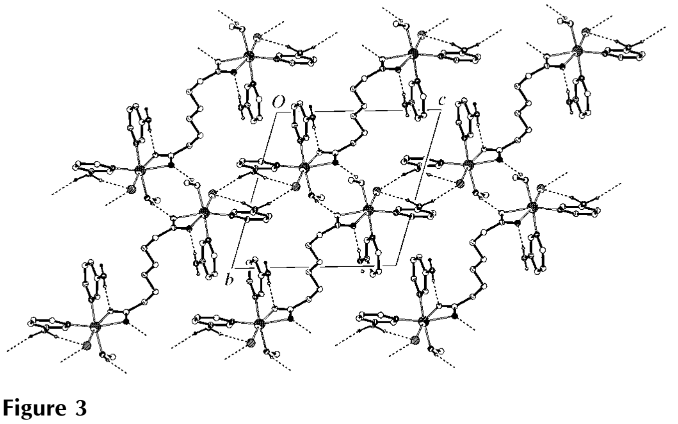

Figure 3
A packing diagram of (I), viewed along the *a* axis, showing the complete hydrogen-bonding scheme. C-bound H atoms have been omitted.

Experimental

$CoCl_2\cdot6H_2O$ (0.40 g, 1.68 mmol) and suberic acid (0.29 g, 1.67 mmol) were combined in methanol (7.0 ml). The resulting pink mixture was stirred for 20 min. 3-Aminopyridine (0.20 g, 2.13 mmol) was added and the resulting deep-blue solution was stirred for 1 h and then filtered. On cooling of the filtrate to 278 K, the colour changed from blue to violet. The change of colour upon cooling/heating is reversible. On standing at 278 K, violet prismatic crystals formed in 66% yield.

Crystal data

$[Co_2(C_8H_{12}O_4)Cl_2(C_5H_6N_2)_4(CH_4O)_2]$
$M_r = 801.49$
Triclinic, $P\bar{1}$
$a = 7.3955$ (2) Å
$b = 11.2390$ (3) Å
$c = 11.7463$ (3) Å
$\alpha = 104.505$ (1)°
$\beta = 106.052$ (1)°
$\gamma = 95.888$ (1)°
$V = 892.73$ (4) Å^3
$Z = 1$
$D_x = 1.491$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.13$ mm^{-1}
$T = 150$ (1) K
Prism, violet
0.12 × 0.12 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
ω scans at κ=55°
6468 measured reflections
3599 independent reflections
3185 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 26.3°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.072$
$S = 1.07$
3599 reflections
238 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0222P)^2 + 0.7104P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.81$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Co1—N11	2.1070 (16)	Co1—O1	2.1662 (13)
Co1—O1*M*	2.1466 (15)	Co1—O2	2.1887 (14)
Co1—N21	2.1470 (17)	Co1—Cl1	2.3793 (5)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*M*—H1*M*···O1^{i}	0.75 (3)	1.98 (3)	2.683 (2)	156 (3)
N22—H22*A*···O2^{ii}	0.83 (3)	2.13 (3)	2.952 (3)	175 (3)
N12—H12*A*···Cl1^{iii}	0.98 (3)	2.41 (3)	3.375 (2)	169 (3)
N12—H12*B*···Cl1^{iv}	1.04 (3)	2.40 (3)	3.430 (2)	169 (3)

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $x+1, y, z$; (iii) $x-1, y, z$; (iv) $-x+1, -y+1, -z$.

The hydoxy H atom (H1*M*) and the H atoms of the amino groups (H12*A*, H12*B*, H22*A* and H22*B*) were found in a difference Fourier map and were refined freely. All other H atoms were placed in geometrically calculated positions (C—H = 0.93–0.97 Å) and were refined using a riding model.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; 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); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3064). Services for accessing these data are described at the back of the journal.

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