ω–2θ scans
Absorption correction:
ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.592$, $T_{max} = 0.699$
3280 measured reflections
3065 independent reflections

$R_{int} = 0.0364$
$\theta_{max} = 30°$
$h = -26 \rightarrow 26$
$k = 0 \rightarrow 20$
$l = -10 \rightarrow 0$
3 standard reflections every 150 reflections intensity decay: 1.9%

Refinement

Refinement on F
$R = 0.0406$
$wR = 0.0511$
$S = 1.044$
1824 reflections
142 parameters
H atoms fixed with $U(H) = 1.2U_{eq}(C)$

$w = 1/[\sigma^2(F_o) + 0.00087|F_o|^2]$
$(\Delta/\sigma)_{max} = 0.083$
$\Delta\rho_{max} = 0.97$ e Å^{-3}
$\Delta\rho_{min} = -1.15$ e Å^{-3} (close to Pt1)
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Pt1—N1	2.020 (7)	Pt1—N2	2.043 (8)
N1—Pt1—N1^{i}	80.9 (4)	N2—Pt1—N2^{i}	82.1 (5)
N1—Pt1—N2	98.5 (3)		

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

Table 2. *Contact distances (Å)*

N1···C3^{i}	3.61 (1)	C2···C3^{ii}	3.60 (1)
C1···C3^{i}	3.65 (1)	C4···C5^{ii}	3.55 (1)
C1···C4^{ii}	3.68 (1)	C5···C5^{iii}	3.61 (2)

Symmetry codes: (i) $x, -y, z - \frac{1}{2}$; (ii) $x, -y, \frac{1}{2} + z$; (iii) $-x, -y, 1 - z$.

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku Corporation, 1995). Cell refinement: *Rigaku/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *MITHRIL*90 (Gilmore, 1990). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

This work was supported by a Grant-in-Aid for Scientific Research (No. 08640712) from the Ministry of Education, Science, Sports and Culture, Japan.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1148). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 840–843

A Water-Bridged Dinuclear Complex of Cobalt(II), Pyridine and Stearic Acid

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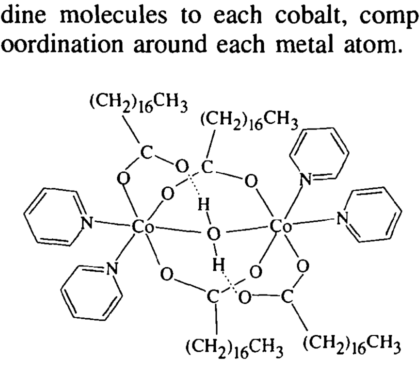
(*Received 9 August 1996; accepted 10 February 1997*)

Abstract

In the crystal structure of μ-aqua-1:2κ^2O-tetrapyridine-1κ^2N,2κ^2N-bis(μ-stearato)-1κ^2O:2κ^2O'-bis(stearato)-1κO,2κO-dicobalt(II), $[Co_2(C_{18}H_{35}O_2)_4(C_5H_5N)_4(H_2O)]$, hydrogen bonding [with an O···O distance of 2.564 (5) Å] between the H atoms of the bridging water and the non-metal-bonding O atoms of the monodentate stearic acid molecules, stabilizes the dimeric core complex and consequently limits chain packing and conformation options. The structure is a member of a rare class of compounds, the well crystallized metallic salts of long-chain fatty acids. The structure also bears a remarkable similarity to built-up Langmuir–Blodgett films of metal carboxylates.

Comment

During the course of a literature search investigation of the recrystallization methods for transition metal carboxylates or metallic soaps, early reports were found on the synthesis of long-chain metal soap complexes with pyridine (Koenig, 1914; Lawrence, 1939). Koenig synthesized an addition product of dry cobalt stearate and pyridine by cooling a heated saturated solution of the metal soap in pyridine. He reported that the precipitate consisted of rose-coloured crystalline plates containing stoichiometric amounts of pyridine, which effloresced slowly to a pink amorphous powder. The title compound, (I), was obtained during a repeat synthesis and its structure is reported here. The complex exhibits a dinuclear centre with the two hexacoordinated Co atoms bridged by an O atom from a water molecule and by two carboxylate groups from stearic acid molecules. Monodentate binding of a further carboxylate group and two pyridine molecules to each cobalt, completes the sixfold coordination around each metal atom.



(I)

The long hydrocarbon chains are remarkably well ordered and coordinate in a mono- and bidentate fashion. The monodentate chains extend from each cobalt in a regular near-planar zigzag or all-*trans* conformation, whereas the bidentate groups (with axes parallel to the monodentate chains) depart from the all-*trans* conformation by rotation around a single bond (C102—C103), resulting in a *gauche* conformation of the hydrocarbon tail near its headgroup [C101—C102—C103—C104 −64.8 (7)°]. The tilt of the chains is about 45° with respect to the layer spacing when viewed along the [100] direction (< 10° along [010]) and the chains interleave or 'interdigitate' fully (see packing diagrams deposited with the supplementary material). The chains pack with axes approximately parallel to each other in an HS2 subcell (Abrahamsson, Dahlén, Löfgren & Pascher, 1978), where chains with parallel zigzag planes are arranged in pleated sheets and adjacent pleated sheets have planes arranged in an almost perpendicular orientation. However, the plane of the zigzag is slightly distorted, with small (< 0.2 Å) helical twisting occurring along the long axis of the chain, with adjacent planes having the opposite sense of twist. This helicity results in a slight effective shortening of the chains relative to a perfect all-*trans* packing length.

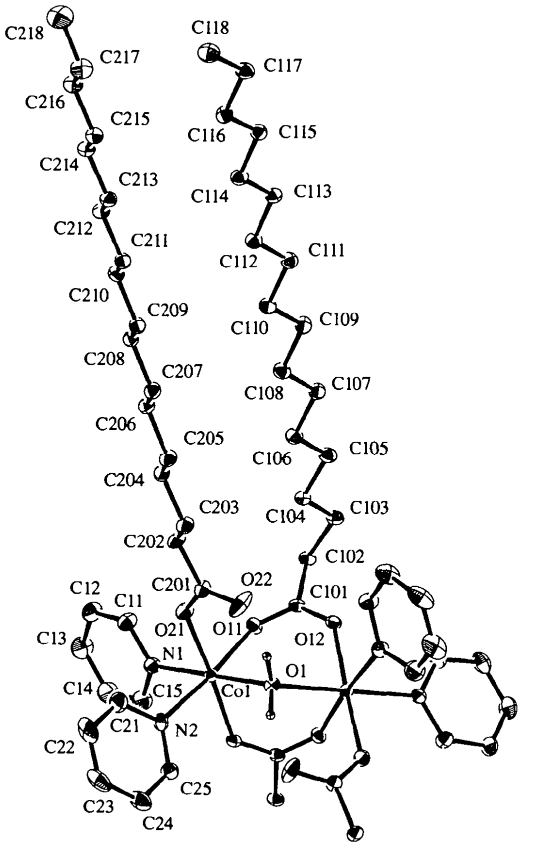


Fig 1. View of the title compound showing the labelling of all non-H atoms. Displacement ellipsoids are shown at 50% probability levels. Water H atoms are shown as circles of arbitrary radii. The C-atom chains of the symmetry-related stearic acid molecules extending downwards from the carboxylate groups are not shown. There is a hydrogen bond from O1 to O22.

Somewhat analogous structures have been reported in the literature. For example the structure of the 1,3-diglyceride of 3-thiadodecanoic acid (Larsson, 1963) shows an alternation of chain-tilt direction either side of the monolayer headgroup, as seen here. Hybl &

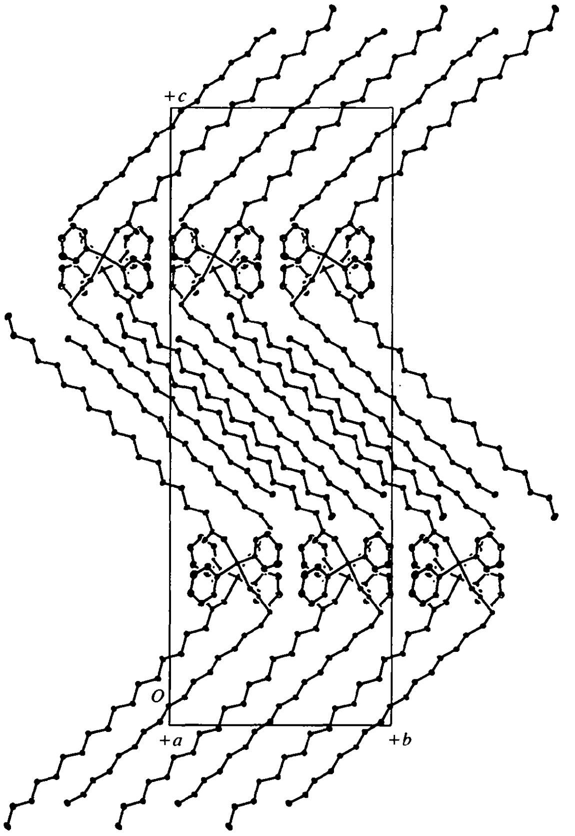


Fig 2. The structure viewed down the *a* axis.

Dorset (1971) reported the non-interdigitating structure of the 1,3-diglyceride of 11-bromoundecanoic acid with similar alternation of chain tilt. Lomer & Perera (1974*a*,*b*) reported the structures of copper decanoate and octanoate, respectively, each structure having a monolayer headgroup sandwiched between hydrocarbon layers. Stephens & Tuck-Lee (1969) reported the structure of a multilayer crystal of lead stearate built up by the Langmuir–Blodgett technique. They found hydrocarbon chains projecting either side of the layer of Pb atoms in the basal plane. Interdigitation of chains anchored on separate but adjacent headgroup layers have also been shown in the crystal structures of octadecyl-2-methylglycerophosphorylcholine (Pascher, Sundell, Eibl & Harlos, 1986), and glycosylphytosphingosine and unsaturated mixed triglycerides (Larsson, 1994).

The stable rigid dimeric core resulting from the cross-linking effect of the hydrogen bonds, combined with its steric demands upon the chains to pack *via* interdigitation, are thus implicated in the high crystallinity and ease of formation of this complex, in contrast to less constrained salts of fatty acids that crystallize with difficulty (*e.g* the metallic soaps). Analogous crystalline addition products of pyridine with Cu, Mn, Co and Ni stearates, myristates and laurates were easily formed and preliminary interpretation reveals that these are also layer structures.

Experimental

Cobalt stearate was synthesized *via* double decomposition in ethanolic water of a 0.02 *M* solution of sodium stearate with a *ca* 0.05 *M* solution of $CoCl_2.6H_2O$ at 333 K in a 2.05:1 molar ratio. The purple precipitate of cobalt stearate was washed with boiling H_2O and partially dried in air for a short time. 5 g of the moist cobalt soap was added to 400 ml toluene and water was removed by distillation at the boiling point of toluene. Upon reheating, the gel liquified and the solution was dried overnight. About 2 g of the product was dissolved in 300 ml of pyridine. After boiling, the dark-red mother liquor was decanted off and allowed to dry slowly overnight, yielding rose-coloured clusters of tabular crystals. The crystals were air dried and stored under refrigeration prior to X-ray diffraction analysis.

Crystal data

$[Co_2(C_{18}H_{35}O_2)_4(C_5H_5N)_4$-
$(H_2O)]$
$M_r = 1586.18$
Monoclinic
$C2/c$
$a = 13.214\ (3)$ Å
$b = 16.145\ (2)$ Å
$c = 44.872\ (2)$ Å
$\beta = 91.039\ (9)°$
$V = 9571\ (1)$ Å^3
$Z = 4$
$D_x = 1.101$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 37.7$–$45.5°$
$\mu = 3.12$ mm^{-1}
$T = 213\ (1)$ K
Irregular
0.28 × 0.24 × 0.16 mm
Pale red

Data collection

Rigaku AFC-6*R* diffractometer
$\omega/2\text{-}\theta$ scans
Absorption correction: empirical based on azimuthal (ψ) scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.232$, $T_{\max} = 0.607$
7801 measured reflections
7421 independent reflections

3667 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.080$
$\theta_{\max} = 60.17°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 18$
$l = -50 \rightarrow 50$
3 standard reflections every 150 reflections intensity decay: negligible

Refinement

Refinement on F
$R = 0.051$
$wR = 0.061$
$S = 2.306$
3667 reflections
487 parameters
H atoms not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.019F_o^2)^2]$

$(\Delta/\sigma)_{\max} = 0.0172$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Co1—O1	2.160 (3)	Co1—O21	2.063 (4)
Co1—O11	2.105 (4)	Co1—N1	2.135 (5)
Co1—O12^{i}	2.030 (4)	Co1—N2	2.200 (5)
O1—Co1—O11	93.1 (1)	O11—Co1—N2	175.1 (2)
O1—Co1—O12^{i}	88.9 (1)	O12^{i}—Co1—O21	176.2 (2)
O1—Co1—O21	91.7 (1)	O12^{i}—Co1—N1	90.6 (2)
O1—Co1—N1	179.0 (2)	O12^{i}—Co1—N2	87.2 (2)
O1—Co1—N2	90.1 (2)	O21—Co1—N1	88.8 (2)
O11—Co1—O12^{i}	96.6 (2)	O21—Co1—N2	89.0 (2)
O11—Co1—O21	87.2 (2)	N1—Co1—N2	90.7 (2)
O11—Co1—N1	86.1 (2)	Co1—O1—Co1^{i}	112.7 (2)

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

The θ-scan width used was $(1.10 + 0.30\tan\theta)°$ at a speed of $16°$ min^{-1} (in ω). The weak reflections were rescanned a maximum of four times and the counts accumulated to ensure good counting statistics. Stationary background counts were made on each side of the reflection with a 2:1 ratio of peak to background counting time. H atoms were fixed at ideal positions with C—H 0.96 Å and $U_{\rm iso} = 1.2U_{\rm eq}$(C). Absorption corrections were obtained from semi-empirical ψ-scan measurements. This was not the method of choice, however. A face-indexed analytical correction would have been much more suitable in view of the chemical nature and size of μ for this crystal. Unfortunately, due to possible decomposition through loss of pyridine, a precautionary measure of coating the crystal in araldite was taken, making identification of the crystal faces impossible.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992*b*). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994) and *DIRDIF*92 (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1127). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 843–845

cyclo-Tetrakis(μ-oxo)tetrakis[iodo(η^5-methylcyclopentadienyl)titanium(IV)]

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(*Received 13 May 1996; accepted 6 June 1996*)

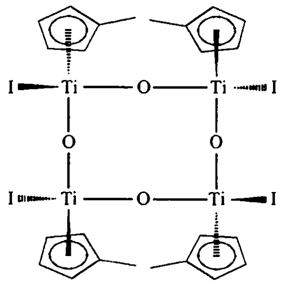
Abstract

The title compound, $[Ti_4I_4O_4(C_6H_7)_4]$, displays the same geometric features as the analogous chloro complex; the central eight-membered (Ti–O)$_4$ ring deviates appreciably from planarity. The cyclopentadienyl and iodo ligands lie alternately above and below the ring. Approximate twofold symmetry is observed. The Ti—I and Ti—O bond lengths lie in the ranges 2.657 (4)–2.673 (4) and 1.763 (15)–1.845 (15) Å, respectively.

Comment

In the following discussion some comparable values for the known chloro(methylcyclopentadienyl) complex $[(MeC_5H_4)TiClO]_4$ (Petersen, 1980) are given in square brackets where applicable.

The 'backbone' of the title compound, (I) (Fig. 1), is formed by an eight-membered ring consisting of four O and four Ti atoms. The iodo and methylcyclopentadienyl ligands lie alternately above and below this ring.



(I)

In contrast to the corresponding chloro complex (Petersen, 1980), the iodo complex possesses no crystallographic C_2 symmetry along either of the vectors O2···O4 or O1···O3, or perpendicular to the ring. Nevertheless, there is an approximate twofold axis along the vector O2···O4. If the methyl groups are ignored (C26 and C36 point into the ring, and C16 and C46 point away from it), the approximate symmetry increases to 222.

In both complexes, the eight-membered ring deviates appreciably [mean deviation in (I) is 0.200 Å] from planarity. It is folded in (I) along the Ti1···Ti3 and Ti2···Ti4 axes giving two pairs of planes, *i. e.* Ti1–O1–Ti2–O2–Ti3 (mean deviation 0.065 Å) and Ti1–

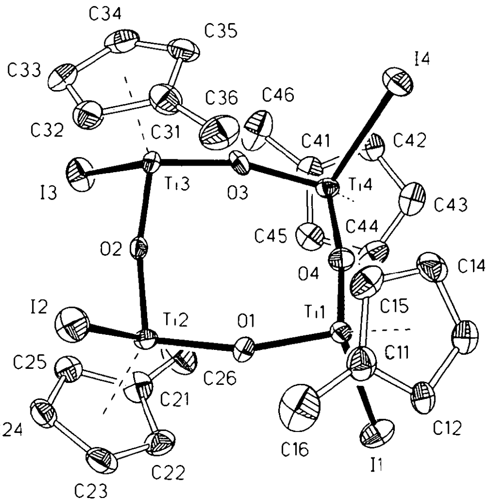


Fig. 1. The molecule of the title compound in the crystal. Radii are arbitrary. Displacement ellipsoids are plotted at the 50% probability level.