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Structure of Homochiral Carbonylchloro(3-trifluoroacetylcamphorato)platinum(II)

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Abstract. Carbonylchloro[1,7,7-trimethyl-3-(trifluoroacetyl)bicyclo[2.2.1]heptan-2-onato-*O,O'*]platinum(II), $[\text{Pt}(\text{Cl})(\text{CO})(\text{C}_{12}\text{H}_{14}\text{F}_3\text{O}_2)]$, $M_r = 505.76$, monoclinic, $P2_1$, $a = 11.035$ (4), $b = 7.216$ (2), $c = 9.824$ (3) Å, $\beta = 99.61$ (3)°, $V = 771.3$ Å³, $Z = 2$, $D_x = 2.177$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 8.929$ mm⁻¹, $F(000) = 474$, $T = 298$ K. Final $R = 0.043$ for 1595 independent reflections [$F_o > 3\sigma(F_o)$]. The unit cell contains two homochiral complex molecules. The Pt atoms form zigzag columns along [010] with coplanar stacking of the Pt coordination plane with a Pt—Pt distance of 4.118 (1) Å.

Introduction. The propensity of many square-planar coordination compounds of Rh^I, Ir^I and Pt^{II} to form linear metal chains in the solid state is well known. Dicarbonyl(3-trifluoroacetylcamphorato)rhodium(I) and dicarbonyl(3-trifluoroacetylcamphorato)iridium(I) form one-dimensional metal chains in the crystalline state in the racemic form but not as pure enantiomers (Schurig, 1981; Pille, 1985). Starting from racemic 3-trifluoroacetylcamphor we have prepared carbonylchloro(3-trifluoroacetylcamphorato)platinum(II) (1), which crystallizes as a conglomerate of enantiomers. The crystal structure of one of the isolated enantiomers is described.

Experimental. The title compound was prepared from $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O}$ ($\text{C}_2\text{H}_4 = \text{ethene}$) and the barium salt of racemic 3-trifluoroacetylcamphor (Schurig, 1972) under an N₂ atmosphere in ethanol. After filtration and evaporation of the solvent the residue was redissolved in diethyl ether followed by the bubbling of carbon monoxide through the solution. Crystallization from diethyl ether/*n*-hexane at 253 K yielded short yellow needles (Scheer, 1990).

A single crystal of approximate dimensions 0.3 × 0.15 × 0.15 mm was used for the data collection. Lattice constants were determined from 22 reflections in the θ range $10^\circ \leq 2\theta \leq 23^\circ$ on a Syntex P1 diffractometer. 2010 reflections were measured with the ω -scan technique ($hkl, \bar{h}kl$; $0 \leq h \leq 14$, $0 \leq k \leq 9$, $-12 \leq l \leq 12$; $3^\circ \leq 2\theta \leq 55^\circ$). Three standard reflections measured at constant intervals showed no significant changes in intensities. The data were corrected for Lorentz and polarization effects, empirical absorption correction (ψ scan) with 11 hkl reflections (Sheldrick, 1987), min. and max. transmission factors 0.085 and 0.131, leading to 1595 unique reflections with $F_o > 3\sigma(F_o)$ ($R_{\text{int}} = 0.021$, 235 unobserved). The structure was solved by direct methods (Sheldrick, 1986). Refinement on F with anisotropic parameters and H atoms in geometrically calculated positions (Sheldrick, 1976) converged at $R = 0.0433$, $wR = 0.0345$, $w = k/\sigma(F_o)^2$, k determined by least squares, max. shift/e.s.d. in final cycle < 1, extinction correction as in *SHELX76*: 8.7×10^{-4} ,

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Table 1. Atomic positional and thermal parameters for (1)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
Pt(1)	0.03662 (4)	0.25000	1.09941 (4)	0.0602 (2)
Cl(1)	0.1119 (3)	0.270 (3)	0.8968 (4)	0.087 (2)
C(1)	0.191 (2)	0.290 (5)	1.194 (2)	0.09 (1)
O(1)	0.288 (1)	0.300 (5)	1.254 (1)	0.18 (2)
O(2)	-0.0294 (7)	0.286 (2)	1.2790 (8)	0.048 (4)
C(2)	-0.144 (1)	0.251 (7)	1.283 (1)	0.057 (4)
C(3)	-0.195 (1)	0.240 (9)	1.416 (1)	0.085 (9)
C(4)	-0.111 (1)	0.283 (7)	1.546 (1)	0.070 (9)
C(5)	-0.243 (2)	0.006 (4)	1.395 (3)	0.078 (8)
C(6)	-0.338 (4)	-0.006 (5)	1.301 (4)	0.085 (9)
C(7)	-0.355 (1)	0.211 (3)	1.243 (1)	0.059 (8)
C(8)	-0.318 (1)	0.320 (2)	1.376 (1)	0.062 (5)
C(9)	-0.409 (1)	0.292 (4)	1.481 (1)	0.069 (8)
C(10)	-0.310 (5)	0.520 (6)	1.362 (5)	0.22 (4)
C(11)	-0.242 (1)	0.266 (6)	1.172 (1)	0.062 (5)
C(12)	-0.230 (1)	0.284 (4)	1.037 (1)	0.050 (6)
C(13)	-0.344 (2)	0.29 (1)	0.921 (2)	0.11 (2)
F(1)	-0.426 (3)	0.389 (7)	0.946 (2)	0.21 (2)
F(2)	-0.394 (4)	0.119 (5)	0.915 (4)	0.26 (2)
F(3)	-0.317 (1)	0.342 (3)	0.810 (1)	0.17 (1)
O(3)	-0.130 (1)	0.281 (4)	0.9852 (6)	0.055 (5)

Table 2. Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

Pt(1)—Cl(1)	2.286 (3)	C(6)—C(7)	1.66 (4)
Pt(1)—C(1)	1.82 (2)	C(7)—C(8)	1.53 (2)
Pt(1)—O(2)	2.035 (7)	C(7)—C(11)	1.57 (2)
Pt(1)—O(3)	1.998 (8)	C(8)—C(9)	1.57 (2)
C(1)—O(1)	1.14 (2)	C(8)—C(10)	1.46 (2)
C(2)—O(2)	1.29 (2)	C(11)—C(12)	1.36 (2)
C(2)—C(3)	1.51 (2)	C(12)—C(13)	1.55 (2)
C(2)—C(11)	1.41 (2)	O(3)—C(12)	1.29 (2)
C(3)—C(4)	1.48 (2)	F(1)—C(13)	1.23 (6)
C(3)—C(5)	1.77 (7)	F(2)—C(13)	1.32 (8)
C(3)—C(8)	1.47 (3)	F(3)—C(13)	1.25 (4)
C(5)—C(6)	1.29 (5)	Pt(1)—Pt(1)*	4.118 (1)
C(1)—Pt(1)—Cl(1)	89.2 (4)	C(8)—C(7)—C(11)	98.0 (1)
C(1)—Pt(1)—O(2)	88.8 (5)	C(3)—C(8)—C(7)	97 (2)
C(1)—Pt(1)—O(3)	164 (2)	C(3)—C(8)—C(9)	116 (2)
Cl(1)—Pt(1)—O(2)	168.9 (7)	C(7)—C(8)—C(9)	113 (2)
Cl(1)—Pt(1)—O(3)	86.4 (2)	C(3)—C(8)—C(10)	110 (3)
O(2)—Pt(1)—O(3)	92.5 (3)	C(7)—C(8)—C(10)	116 (3)
O(1)—C(1)—Pt(1)	175 (4)	C(9)—C(8)—C(10)	104 (2)
C(2)—O(2)—Pt(1)	120 (1)	C(2)—C(11)—C(7)	102 (2)
O(2)—C(2)—C(3)	123 (2)	C(2)—C(11)—C(12)	125 (1)
O(2)—C(2)—C(11)	126 (2)	C(7)—C(11)—C(12)	132 (1)
C(3)—C(2)—C(11)	108.6 (9)	C(11)—C(12)—C(13)	121 (1)
C(2)—C(3)—C(4)	117 (2)	O(3)—C(12)—C(11)	128 (1)
C(2)—C(3)—C(5)	96 (3)	O(3)—C(12)—C(13)	111 (1)
C(4)—C(3)—C(5)	116 (4)	F(1)—C(13)—F(2)	104 (3)
C(2)—C(3)—C(8)	102 (2)	F(1)—C(13)—F(3)	106 (5)
C(4)—C(3)—C(8)	125 (3)	F(1)—C(13)—C(12)	113 (3)
C(5)—C(3)—C(8)	96 (2)	F(2)—C(13)—F(3)	114 (4)
C(3)—C(5)—C(6)	110 (2)	F(2)—C(13)—C(12)	108 (5)
C(5)—C(6)—C(7)	102 (3)	F(3)—C(13)—C(12)	111 (2)
C(6)—C(7)—C(8)	101 (2)	C(12)—O(3)—Pt(1)	123.2 (7)

* Atom on the position $\bar{x}, \frac{1}{2} + y, \bar{z}$, related by a 2₁ axis.

199 parameters, max. residual electron density 1.32 e Å⁻³. Scattering factors for Pt⁰ were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV), others as supplied by *SHELX*. Diagrams were drawn with *SHELXTL-Plus* (Sheldrick, 1987).

Table 1 contains atomic parameters for (1). Bond distances and angles are given in Table 2. Although the single crystals are of perfect shape, the reflections measured were considerably broader than expected resulting in relatively high e.s.d.'s.*

Fig. 1 shows the molecular structure of (1), and Fig. 2 contains a stereoscopic view of the unit cell (view along [001]).

Discussion. The Pt atom in (1) is bonded to two O atoms of the 3-trifluoroacetylcamphor ligand, to the C atom of the carbonyl group and to the Cl atom in an essentially square-planar geometry. The two homochiral molecules in the unit cell are connected by the 2₁ axis forming stacks of molecules with coplanar arrangements of the platinum coordination plane (Fig. 2). The metal atoms are separated by a Pt—Pt distance of 4.118 Å forming a zigzag metal chain along the *b* axis.

The crystal structure of (1) is similar to that of homochiral dicarbonyl(3-trifluoroacetyl-1*R*-camphorato)rhodium(I) which also crystallizes in the space

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53611 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

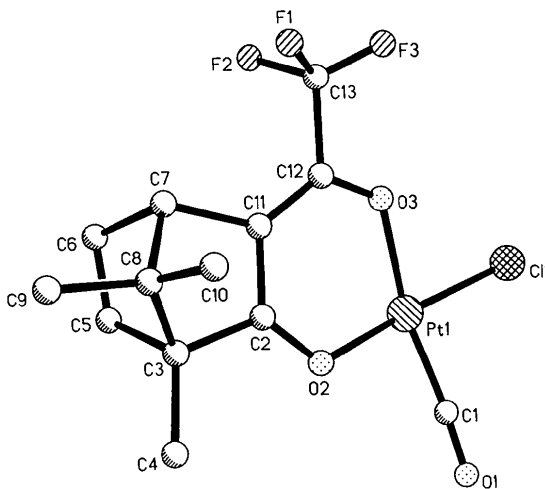


Fig. 1. Molecular structure of (1).

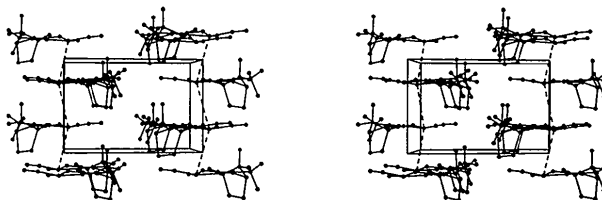


Fig. 2. Stereoscopic view of the unit cell (view along [001]).

group $P2_1$ with an Rh—Rh distance of 4.32 Å (Schurig, 1983).

While racemic dicarbonyl(3-trifluoroacetylcamphorato)rhodium(I) and dicarbonyl(3-trifluoroacetylcamphorato)iridium(I) form dichroic solids containing one-dimensional metal chains with a $(-1R-1R-1S-1S)_\infty$ alternating arrangement of the ligands, in the unit cell of (1) only homochiral molecules are present. Thus, upon crystallization of racemic carbonylchloro(3-trifluoroacetylcamphorato)platinum(II), not the racemate but pure enantiomers are formed as a conglomerate. Of the two possible geometric isomers, only that with a *trans* relationship between Cl(1) and O(2) is present in the crystal.

The formation of a racemic columnar structure, stabilized by a short Pt—Pt contact, as in the case with Rh^I or Ir^I, is not observed.

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Structure of a Five-Coordinate Copper(II) Hexaaza Macrotricyclic Complex: Chloro(1,3,6,9,11,14-hexaazatricyclo[12.2.1.1^{6,9}]octadecane)copper(II) Perchlorate

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Abstract. $[\text{CuCl}(\text{C}_{12}\text{H}_{26}\text{N}_6)]\text{ClO}_4$, $M_r = 452.7$, orthorhombic, $P2_12_12$, $a = 14.124$ (11), $b = 9.837$ (4), $c = 6.570$ (4) Å, $V = 912.8$ (2) Å³, $Z = 2$, $D_x = 1.647$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 14.9$ cm⁻¹, $F(000) = 470$, $T = 291$ K, $R = 0.059$ for 649 reflections with $I \geq 3\sigma(I)$. The Cu ion is coordinated to four N atoms of the macrocycle and a Cl⁻ ion to form a distorted square-pyramidal geometry. The cation possesses crystallographic twofold symmetry through the Cu—Cl bond. The Cu ion lies 0.316 (1) Å above the basal coordination plane. The Cu—N [2.043 (8) and 2.022 (8) Å] and Cu—Cl [2.483 (4) Å] coordination bond distances are normal. Two 1,3-diazacyclopentane ring moieties of the ligand are in the same direction as the Cl⁻ ligand and are almost perpendicular to the ruffled 14-membered macrocycle. The perchlorate anion which is on the twofold symmetry axis is statistically disordered in two positions.

Introduction. Macrocylic complexes show enhanced thermodynamic and kinetic stabilities and the

characteristic properties inaccessible to complexes with non-cyclic chelate ligands. They are often prepared by metal template reactions because they provide selective and high yielding routes to the complexes of new ligands. Recently, the structure of a four-coordinate Ni^{II} complex $\{[\text{Ni}(L)]\text{Cl}_2 \cdot 2\text{H}_2\text{O}\}$ of a hexaaza macrotricyclic ligand 1,3,6,9,11,14-hexaazatricyclo[12.2.1.1^{6,9}]octadecane (*L*) has been reported (Suh, Shin, Kang, Lah & Chung, 1989). *L* is unique in that the hexaaza macrocycle acts as a tetradentate ligand. Here we report the crystal structure of a five-coordinate Cu^{II} complex $\{[\text{Cu}(L)\text{Cl}]\text{ClO}_4\}$ (Suh, Kang & Chung, 1990).

Experimental. Title complex synthesized by the template condensation reaction of diethylenetriamine and formaldehyde in the presence of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Suh *et al.*, 1990). Blue crystals recrystallized from hot aqueous solution. Crystal ca 0.3 × 0.3 × 0.6 mm, Rigaku AFC diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $2\theta \leq 52^\circ$, ω - 2θ scan, scan speed 2° min⁻¹ in 2θ , ω -scan width $(2.3 + 0.3\tan\theta)^\circ$ which is rather large due to split peaks, background measured for 10 s on either side of the peak; cell parameters by least-squares fit to observed 2θ values for 20 centered reflections with $14 \leq 2\theta \leq$

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