

Structure of a Scandium–Carboxylate Complex: $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sc}(\text{O}_2\text{C})\text{C}_6\text{H}_4\text{CH}_3$

BY MARTIN A. ST. CLAIR AND BERNARD D. SANTARSIERO*

Arthur Amos Noyes Laboratory of Chemical Physics,† California Institute of Technology,
Pasadena, CA 91125, USA

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Abstract. Bis(pentamethylcyclopentadienyl)(*p*-toluato)-scandium, $\text{C}_{28}\text{H}_{37}\text{O}_2\text{Sc}$, $M_r = 450.56$, monoclinic, $P2_1/c$, $a = 16.712(3)$, $b = 10.355(2)$, $c = 15.310(2)$ Å, $\beta = 99.77(1)^\circ$, $V = 2611.0(8)$ Å³, $Z = 4$, $D_x = 1.146$ g cm⁻³, Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å, $\mu = 2.99$ cm⁻¹, $T \approx 290$ K, $F(000) = 968$, $R = 0.077$ for the 2194 reflections with $I > 0$ and 0.050 for the 1521 reflections with $I > 3\sigma$, the goodness-of-fit is 1.79 for the 2395 reflections used in the refinement. The Sc–O bond lengths are equal, 2.172 Å on average, with an $\text{O}_1\text{–Sc–O}_2$ angle of 60.9 (1)°.

Introduction. The reduction of carbon dioxide by insertion into metal–carbon or metal–hydrogen bonds is an important preliminary step in the synthesis of organic molecules derived from carbon dioxide. The insertion of carbon dioxide into the scandium–carbon bond of permethylscandocene-*p*-tolyl, $(\text{C}_5\text{Me}_5)_2\text{Sc–C}_6\text{H}_4\text{–}p\text{-Me}(\text{Me} \equiv \text{CH}_3)$, proceeds smoothly at 195 K to yield the bidentate-chelating carboxylate $(\text{C}_5\text{Me}_5)_2\text{Sc}(\text{O}_2\text{C})\text{C}_6\text{H}_4\text{–}p\text{-Me}$ (St. Clair, 1988). The product is exceptionally stable to air in solution for several days. The insertion of CO_2 into the scandium–aryl bond is reminiscent of CO_2 reactivity with organoaluminium reagents (Ziegler, 1956), and is more facile than with analogous titanium reagents, e.g. Cp_2TiR , $R = \text{alkyl}$ (Klei, Telgen & Teuben, 1981).

Experimental. Single pale-yellow crystals from cold, saturated *n*-pentane solution. Specimen, $0.2 \times 0.3 \times 0.5$ mm, sealed in glass capillary under N_2 . Space group by oscillation and Weissenberg photographs, $P2_1/c$ (systematic absences: $h0l$ for l odd, $0k0$ for k odd). Diffractometry: CAD-4, Mo $K\alpha$ radiation with graphite monochromator. Cell parameters and orientation matrix by least-squares refinement using 25 reflections, $10 < \theta < 20^\circ$. Intensity data: 5840, $\theta < 20^\circ$ ($-h$, $\pm k$, $\pm l$); θ -scan width 1.0° plus dispersion, θ - 2θ scans at $\sim 4^\circ$ (θ) min⁻¹, four check reflections every 3000 s, no unusual variation. No decay or absorption correction,

reflections averaged over $2/m$ Laue symmetry, scaling of F_o by Wilson (1942) plot. Structure derivation: Patterson and density maps. Refinement: full-matrix least squares on F^2 , all 2395 reflections, weights w , $w^{-1} = [s + r^2b + (0.02s)^2]k^4/(\text{Lp})^2$ ($s = \text{scan counts}$, $b = \text{background counts}$, $r = \text{scan-to-background time ratio of } 2.0$, $k = \text{scale factor}$), anisotropic Gaussian amplitudes, analytic atom form factors (*International Tables for X-ray Crystallography*, 1974).

The coordinates of methyl H atoms were determined from difference density maps, and the coordinates of the phenyl H atoms were calculated by assuming planar, trigonal geometry at C:C–H = 1.00 Å, and isotropic $B = 12$ Å²; no H atoms were refined.

CRYRM program library (Duchamp, 1964); final GOF = 1.79 (2395 total, averaged reflections, 281 parameters), $R = 0.077$ (2194 reflections, $I > 0$), $R = 0.050$ (1521 reflections, $I > 3\sigma$), $g(\text{isotropic secondary-extinction parameter}) = 0.24(5) \times 10^{-4}$, maximum peak $0.3 e \text{ \AA}^{-3}$ near Sc in final ΔF map, mean and maximum ratio of shift/e.s.d. in final cycle: 0.01 and 0.02.

Discussion. The coordinates and U_{eq} values of the non-hydrogen atoms are given in Table 1, and selected bond lengths and angles in Table 2.‡ The C_5Me_5 ring centroids (R_1 and R_2) and the two oxygen atoms are arranged pseudotetrahedrally around the Sc atom with average distances of 2.178 Å for Sc– R and 2.172 Å for Sc–O, and average angles of 142.3° for $R_1\text{–Sc–}R_2$ and 60.9° for $\text{O}_1\text{–Sc–O}_2$ (Fig. 1). The Sc–O bond length of 2.172 Å is reasonable, cf. the average Sc–O bond length of 2.199 Å in $(\text{C}_5\text{H}_5)\text{Co}(\mu_2, \eta^1, \eta^1\text{-CO})\text{-}\{\text{C}(\text{CH}_3)\text{O–Sc}(\text{C}_5\text{Me}_5)_2\}$ (St. Clair, Santarsiero & Bercaw, 1989). The Sc–ring centroid parameters are like those of the $(\text{C}_5\text{Me}_5)_2\text{ScMe}$ complex [Sc– R , 2.17 Å; $R_1\text{–Sc–}R_2$, 144° (Thompson, Baxter, Bulls,

‡ Fractional atom coordinates for H atoms, anisotropic Gaussian amplitudes for non-hydrogen atoms, least-squares-planes information, a complete listing of bond lengths and angles, and a listing of structure factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51648 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Author to whom correspondence should be addressed. Present address: MRC of Canada Group in Protein Structure and Function, Department of Biochemistry, University of Alberta, Edmonton, Alberta T6G 2H7, Canada.

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Table 1. Atom coordinates ($\times 10^4$) and U_{eq} values ($\text{\AA}^2 \times 10^3$)
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Sc	2875.3 (5)	213.1 (9)	2142.7 (6)	45.4 (3)
O(1)	1885 (2)	-764 (3)	2618 (2)	53 (1)
O(2)	2628 (2)	663 (3)	3460 (2)	53 (1)
C(1)	2063 (3)	-175 (5)	3348 (4)	48 (2)
C(2)	1615 (3)	-472 (5)	4091 (4)	47 (2)
C(3)	1751 (3)	261 (5)	4856 (4)	60 (2)
C(4)	1351 (4)	-41 (6)	5558 (3)	70 (2)
C(5)	831 (4)	-1082 (6)	5502 (4)	65 (2)
C(6)	683 (3)	-1789 (5)	4723 (5)	73 (2)
C(7)	1088 (4)	-1487 (6)	4022 (4)	65 (2)
C(8)	412 (3)	-1421 (6)	6277 (4)	101 (2)
C(11)	4057 (4)	-832 (7)	1641 (4)	64 (2)
C(12)	4359 (3)	-234 (5)	2451 (6)	70 (2)
C(13)	4021 (4)	-872 (7)	3104 (4)	64 (2)
C(14)	3527 (3)	-1837 (6)	2710 (5)	56 (2)
C(15)	3529 (3)	-1812 (6)	1804 (4)	57 (2)
C(21)	1737 (4)	1096 (6)	1061 (5)	66 (2)
C(22)	1862 (4)	1957 (6)	1767 (4)	60 (2)
C(23)	2623 (5)	2519 (5)	1796 (4)	66 (2)
C(24)	2973 (4)	2035 (7)	1100 (6)	77 (2)
C(25)	2411 (6)	1144 (7)	643 (4)	78 (3)
C(11M)	4391 (4)	-701 (7)	793 (4)	147 (3)
C(12M)	4978 (4)	800 (6)	2624 (6)	174 (4)
C(13M)	4222 (4)	-626 (7)	4089 (4)	136 (3)
C(14M)	3097 (4)	-2822 (6)	3185 (5)	116 (2)
C(15M)	3088 (4)	-2758 (6)	1141 (4)	119 (3)
C(21M)	988 (4)	306 (6)	779 (4)	127 (3)
C(22M)	1277 (4)	2311 (5)	2371 (4)	102 (2)
C(23M)	3023 (4)	3505 (6)	2446 (4)	124 (3)
C(24M)	3716 (4)	2549 (7)	780 (5)	149 (3)
C(25M)	2448 (5)	491 (8)	-230 (4)	165 (4)

Burger, Nolan, Santarsiero, Schaefer & Bercaw, 1987)] or the $(C_5Me_5)_2Sc(C,N-\eta^2-C_5H_4N)$ complex [Sc—R, 2.194 Å, R_1 —Sc— R_2 , 142.1° (Thompson *et al.*, 1987)].

The metrical details of the symmetrically bonded carboxylate ligand are analogous to those of $(C_5H_5)_2TiO_2CC_6H_5$, with Ti—O bond lengths of 2.147 Å and O—Ti—O angle of 60.7° (Clauss, Wilson, Buchanan, Pierpont & Hendrickson, 1983). All atoms of the carboxylate ligand are coplanar, with greatest deviations from the $Sc(CO_2)C_7$ plane for Sc(+0.14 Å) and O₁(-0.13 Å), principally due to a 10° twist about the C₁—C₂ bond (with greatest deviations in the four-atom $ScCO_2$ plane of ± 0.02 Å). The C—O bond lengths are equal: 1.264 (6) and 1.272 (6) Å.

The C_5Me_5 rings are staggered and in close steric contact; the methyl groups are not coplanar with the ring atoms but bent away from Sc, on the average, by 0.13 Å. The greatest deviations are by C(11M) on one ring, 0.34 Å, and C(24M) and C(25M) on the other ring, 0.25 and 0.20 Å. [The shortest $CH_3 \cdots CH_3$ contacts are, in fact, C(11M) \cdots C(24M) 3.55 and C(11M) \cdots C(25M) 3.58 Å.] The ring atoms are each coplanar to within ± 0.01 Å, and coordinate to the Sc in the conventional pentahapto manner. The average C_5Me_5 ring distances, C—C (ring) 1.392 and C—C(Me) 1.503 Å, and C—C phenyl-ring distances, 1.384 Å, are unexceptional.

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Table 2. Selected bond lengths (Å) and angles (°) (averages over chemically equivalent groups)

Group 1			Group 2			Average*		
Sc	O1	2.167 (3)	Sc	O2	2.176 (3)	2.172		
C1	O1	1.264 (6)	C1	O2	1.272 (6)	1.268		
Sc	C11	2.485 (7)	Sc	C21	2.475 (7)	2.479 (3)		
Sc	C12	2.488 (5)	Sc	C22	2.476 (7)			
Sc	C13	2.478 (6)	Sc	C23	2.467 (6)			
Sc	C14	2.475 (6)	Sc	C24	2.494 (8)			
Sc	C15	2.460 (6)	Sc	C25	2.489 (6)			
Sc	R1	2.177	Sc	R2	2.178	2.178		
C2	C3	1.382 (8)	}		1.384 (5)			
C3	C4	1.394 (8)						
C4	C5	1.378 (9)						
C5	C6	1.386 (9)						
C6	C7	1.398 (9)						
C7	C2	1.364 (8)						
C1	C2	1.496 (8)				}	1.392 (3)	
C8	C5	1.516 (9)						
C11	C12	1.401 (10)	C21	C22	1.389 (9)			
C12	C13	1.394 (10)	C22	C23	1.393 (10)			
C13	C14	1.369 (9)	C23	C24	1.392 (11)			
C14	C15	1.387 (10)	C24	C25	1.414 (11)			
C15	C11	1.395 (9)	C25	C21	1.388 (12)			
C11	C11M	1.504 (10)	C21	C21M	1.497 (9)	1.503 (3)		
C12	C12M	1.481 (8)	C22	C22M	1.500 (10)			
C13	C13M	1.511 (8)	C23	C23M	1.501 (9)			
C14	C14M	1.505 (9)	C24	C24M	1.507 (11)			
C15	C15M	1.510 (9)	C25	C25M	1.509 (9)			
O1	Sc	O2	60.9 (1)					
R1	Sc	R2	142.3					
O1	C1	O2	120.4 (5)					
Sc	O1	C1	89.6 (3)	Sc	O2	C1	89.0 (3)	89.3
O1	C1	C2	120.0 (5)	O2	C1	C2	119.6 (5)	119.8
C1	C2	C3	120.0 (5)	C1	C2	C7	120.0 (5)	120.0

* The standard deviation of the average is estimated as

$$| \sum_k^h = 1(d_k - \bar{d})^2 / n(n-1) |^{1/2}$$

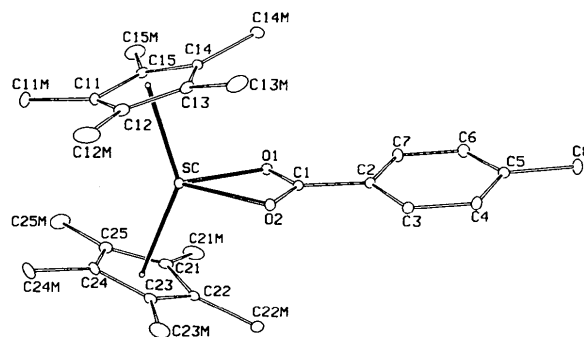


Fig. 1. Molecular structure and labelling scheme; H atoms have been omitted for clarity.

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Structures of *cis*-Amminedichloro(cyclopentylamine)platinum 0.25-Hydrate and Potassium Trichloro(cyclopentylamine)platinate 0.5-Hydrate

BY CHANTAL DION AND ANDRÉ L. BEAUCHAMP

Département de chimie, Université de Montréal, CP 6128, Succ. A, Montréal, Canada H3C 3J7

AND FERNANDE D. ROCHON AND ROBERT MELANSON

Département de chimie, Université du Québec à Montréal, CP 8888, Succ. A, Montréal, Canada H3C 3P8

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Abstract. *cis*-Pt(NH₃)(cyclopentylamine)Cl₂· $\frac{1}{4}$ H₂O, C₅H₁₄Cl₂N₂Pt·0.25H₂O, $M_r = 372.7$, tetragonal, *P4b2*, $a = 11.456$ (4), $c = 16.172$ (6) Å, $V = 2122$ (1) Å³, $Z = 8$, $D_x = 2.333$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 13.83$ mm⁻¹, $F(000) = 1380$, $T = 295$ K, $R = 0.040$ for 725 unique observed reflections. Pt has *cis* square-planar coordination with bond distances Pt–Cl = 2.31 (1), 2.33 (1) Å and Pt–N = 2.02 (3) and 1.99 (2) Å. The C atoms in the cyclopentylamine ligand, especially C(4), show very high thermal motion. The structure is stabilized by hydrogen bonding involving the ammine ligand and the amino group with the chloro ligands. K[Pt(cyclopentylamine)Cl₃] $\cdot\frac{1}{2}$ H₂O, K⁺·C₅H₁₁Cl₃NPt⁻·0.5H₂O, $M_r = 434.7$, monoclinic, *C2/c*, $a = 33.169$ (21), $b = 5.881$ (4), $c = 12.280$ (8) Å, $\beta = 102.45$ (5)°, $Z = 8$, $V = 2339$ (3) Å³, $D_x = 2.468$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 13.13$ mm⁻¹, $F(000) = 1608$, $T = 295$ K, $R = 0.043$ for 1399 unique observed reflections. Pt has square-planar coordination with Pt–Cl = 2.313 (4), 2.309 (4), 2.304 (4) Å, and Pt–N = 2.03 (1) Å. The carbon atoms of cyclopentylamine are disordered and two positions were refined for C(1). The compound crystallizes with a molecule of water located on a twofold axis. The water molecule is exceptionally close to the K⁺ ion [O···K = 2.756 (9) Å]. The compound is stabilized by hydrogen bonds between the amino group and one chloro ligand.

Introduction. Platinum(II) compounds of the type *cis*-PtL₂Cl₂ with *L* = cycloalkylamine are less toxic than cisplatin, *cis*-Pt(NH₃)₂Cl₂ (Braddock, Connors,

Jones, Khokhar, Melzack & Tobe, 1975). A considerable decrease in toxicity was also observed as ring size of the amine increases. The changes in toxicity were postulated to be structure-related (Braddock *et al.*, 1975). The low toxicity of the cyclic amine complexes was suggested to be caused by the great flexibility of the larger rings, allowing orientation of the rings so that they protect the axial positions above and below the platinum plane, thus preventing coordination to the S atoms in the kidney tubules (Lock, Speranzini & Zvagulis, 1980).

The crystal structures of *cis*-Pt(cyclobutylamine)₂Cl₂ (Lock & Zvagulis, 1981) and *cis*-Pt(cyclohexylamine)₂Cl₂ (Lock, Speranzini & Zvagulis, 1980) have confirmed that a few carbon atoms of the rings are in a position to block the two axial sites. However, the crystal structure of *cis*-Pt(cyclopropylamine)₂Cl₂ (Howard-Lock, Lock, Turner & Zvagulis, 1981) has shown that in the solid state the two cyclopropyl rings are on the same side of the platinum coordination plane, leaving the second axial site opened. But in solution there is probably free rotation about the Pt–N bonds and again the two axial positions could be partly blocked.

We have synthesized several platinum(II) compounds containing one NH₃ and one cycloalkylamine ligand, *cis*-Pt(*L*)(NH₃)Cl₂ (Rochon & Kong, 1986), in order to compare the antitumor activity and toxicity of these compounds with those of cisplatin and *cis*-PtL₂Cl₂. The three compounds *cis*-Pt(*L*)(NH₃)Cl₂ with *L* = cyclopropylamine, cyclobutylamine and cyclopentylamine were found to be much more toxic than the