

Di- μ -acetato- $O:O'$ -di- μ -acetato- $O,O':O'$ -bis{[(cyclopentadienyl)-tris(dimethylphosphito- P)cobalt- O,O',O'']neodymium(III)}

Soo-Gyun Roh and Jong Hwa Jeong*

Department of Chemistry, Kyungpook National University, Taegu 702-701, Korea
Correspondence e-mail: jeongjh@kyungpook.ac.kr

Received 1 February 2000

Accepted 1 March 2000

Data validation number: IUC0000051

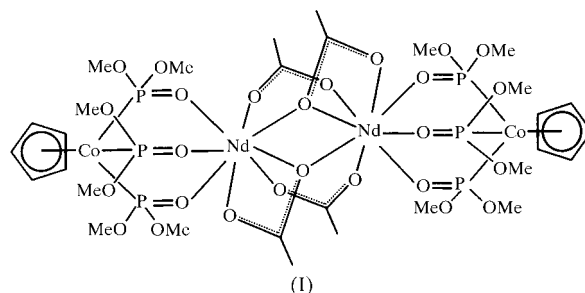
In the title compound, $[[\eta^5\text{-CpCo}\{\text{P}(\text{O})(\text{OMe})_2\}_3]\text{Nd}(\text{O}_2\text{C-CH}_3)_2]_2$, with a centrosymmetric molecule, each Nd atom has an eight-coordination environment, surrounded by a tripodal $\{L_{\text{OMe}} = \text{CpCo}\{\text{P}(\text{O})(\text{OMe})_2\}_3\}$ and four bridging acetato ligands. The coordination geometry around each Nd centre is described as a distorted square-antiprism and the two different types of acetato ligands have $\mu\text{-O:O'}$ - and $\mu\text{-O,O':O'}$ -acetato coordination modes. The Nd—O distances are in the range 2.378 (4)–2.594 (5) Å and the Nd \cdots Nd distance is 3.9913 (6) Å.

Comment

Lanthanide complexes are of considerable interest for their potential application as luminescent probes in systems of biological relevance and as resonance-contrasting agents (Bünzli, 1989). In general, coordination numbers for lanthanide complexes are greater than for transition metal complexes, usually eight or more. The change in coordination number of lanthanoid(III) complexes in solution is of interest in connection with the anomalous behaviour (a double series or S-shaped) in their thermodynamic and physicochemical properties (Lauffer, 1987). Early transition metal and lanthanide complexes containing the O-donor tripodal ligand, $L_{\text{OMe}} = \text{CpCo}\{\text{P}(\text{O})(\text{OMe})_2\}_3$, having stability and high π -donor ability, in comparison with cyclopentadienyl or polytris(pyrazol-1-yl)borate have not been reported extensively yet. In our recent investigation, we have synthesized various compounds such as $(L_{\text{OMe}})_2ML_{1-2}$, $(L_{\text{OMe}})YL_2$ and $[(L_{\text{OMe}})YL_2]_2$ (Cho *et al.*, 1995*a,b*; Kim *et al.*, 1996; Han *et al.*, 1999). The various coordination modes of carboxylate ligands binding to metals, such as *anti* or *syn* monodentate, symmetrical or asymmetrical bidentate chelating and monodentate or bidentate bridging, are of considerable interest in inorganic and organometallic chemistry (Rardin *et al.*, 1991). $[\text{Y}\{\text{HB}(\text{Pz})_3\}(\text{O}_2\text{CCH}_3)_2]_2$ containing bidentate bridging carboxylate and hydrotris(pyrazol-1-yl)borate ligands has

been reported (Reger *et al.*, 1988). $[\text{Zn}(\text{C}_{10}\text{H}_{13}\text{N}_4\text{S})(\text{O}_2\text{CCH}_3)_2]_2$ (Bresolin *et al.*, 1997) and $[\text{Nd}(\text{Phen})(\text{ONO})(\text{O}_2\text{CCH}_3)_2]_2$ (Niu *et al.*, 1997) having bridging and chelating acetato ligands were recently reported. More recently, we have reported $[(L_{\text{OMe}})\text{Y}(\text{O}_2\text{CCH}_3)_2]_2$ having $\mu\text{-O:O'}$ - and $\mu\text{-O,O':O'}$ -acetato coordination modes (Han *et al.*, 1999). $[\text{Nd}_2(\text{Acc}^6)_6(\text{H}_2\text{O})_6](\text{ClO}_4)_6 \cdot 6\text{H}_2\text{O}$ ($\text{Acc}^6 = 1\text{-aminocyclohexane-1-carboxylic acid}$) containing both the monodentate carboxylato and the bridging carboxylato O atoms has been determined by X-ray diffraction (Aparna *et al.*, 1997). $[\{\text{NdL}_2(\text{H}_2\text{O})\}_n][\text{ClO}_4]_{3n} \cdot x\text{H}_2\text{O}$ complexes ($L = N,N'$ -dicarboxymethyl- N,N,N',N' -tetramethyl-1,4-butanediammonium; $x = 0, n$) have been characterized by X-ray crystallography and their structures have a centrosymmetric paddle-wheel-like dimeric subunits and a distorted square antiprismatic geometry (Wei *et al.*, 1997). However, the lack of structural studies in new early lanthanide(III) complexes prompted us to the synthesis and structure of new neodymium(III) complexes containing strongly π -donor tripod and acetate ligands.

We discuss herein the structure of $[\eta^5\text{-CpCo}\{\text{P}(\text{O})(\text{OMe})_2\}_3]\text{Nd}(\text{O}_2\text{CCH}_3)_2$, (I). This molecule possesses an inversion centre. Each Nd atom is surrounded by O1, O2 and O3 of L_{OMe} and O10, O11, O12, O13 and O11ⁱ of acetato having two different coordination modes, $\mu\text{-O:O'}$ and $\mu\text{-O,O':O'}$, and the coordination geometry of Nd at the centre is a distorted square antiprism eight-coordination [symmetry code: (i) $-x, -y, -z$]. The average of Nd—O [2.443 (5) Å] is *ca.* 0.1 Å longer than that [2.345 (5) Å] of isomorphous $[(L_{\text{OMe}})\text{Y}(\text{O}_2\text{CCH}_3)_2]_2$ (Han *et al.*, 1999). The difference between Nd—O11 and Ndⁱ—O11 [2.438 (5) and 2.594 (5) Å, respectively] at the μ_2 -bridging acetato ligand of the title compound is smaller than those [2.370 (5) and 2.707 (3) Å] of $[\text{Nd}(\text{Phen})(\text{ONO})(\text{O}_2\text{CCH}_3)_2]_2$ (Niu *et al.*, 1997), but the distance of Nd \cdots Nd [3.9913 (6) Å] is similar to that [3.974 (1) Å] found in the above Nd complex. O12—C12—O11ⁱ [121.8 (7)°] at the $\mu\text{-O:O'}$ -acetato ligand and O10—C10—O13ⁱ [126.9 (6)°] at the $\mu\text{-O,O':O'}$ -acetato ligand are comparable to the bond angles found in yttrium [120.6 (6) and 126.4 (7)°] and neodymium [120.8 (7) and 129 (2)°] acetato complexes (Han *et al.*, 1999; Niu *et al.*, 1997).



Experimental

All materials used were of reagent grade. NdCl_3 and sodium acetate were purchased from Aldrich, and the $\text{Na}L_{\text{OMe}}$ ligand was prepared according to the literature procedure of Kläui (1979). $^1\text{H NMR}$

spectra were recorded on a Varian 300-NMR spectrometer at ambient temperature and chemical shifts were referenced to the internal standard tetramethylsilane. Elemental analyses were performed in the Chemical Analysis Laboratory of the Korea Basic Science Institute at Kyungpook National University. A mixture of NdCl₃ (0.16 g, 0.64 mmol), NaL_{OMe} (0.30 g, 0.64 mmol) and NaAc (0.10 g, 1.29 mmol) in 25 ml of dry THF was stirred for 2 d at room temperature. The resulting yellow suspension was dried *in vacuo* and extracted with methanol. The yellow solution was slowly evaporated to afford a crop of X-ray quality yellow crystals (0.24 g, 53% based on Nd). Analysis calculated for C₃₀H₅₈Co₂Nd₂O₂₆P₆: C 25.25, H 4.10%; found: C 25.10, H 4.11%. ¹H NMR (CDCl₃): δ 8.84 (*br*, Cp), 3.76 (*br*, OCH₃), -0.62 (*br*, OOCCH₃), -1.12 (*br*, OOCCH₃).

Crystal data

[Co₂Nd₂(C₅H₅)₂(C₂H₃O₂)₄·(C₂H₆O₃P)₆]
M_r = 1426.96
 Monoclinic, *P*₂₁/*a*
a = 14.0685 (9) Å
b = 11.9199 (9) Å
c = 15.7428 (7) Å
 β = 99.541 (4)°
V = 2603.5 (3) Å³
Z = 2
D_x = 1.820 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 11–13°
 μ = 2.851 mm⁻¹
T = 293 (2) K
 Tetragonal rod, yellow
 0.50 × 0.50 × 0.40 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/*2θ* scans
 Absorption correction: ψ scan (*MolEN*; Fair, 1990)
T_{min} = 0.273, *T_{max}* = 0.320
 5598 measured reflections
 4744 independent reflections
 4212 reflections with *I* > 2σ(*I*)
R_{int} = 0.013
 θ_{max} = 25.97°
h = 0 → 17
k = 0 → 14
l = -19 → 19
 2 standard reflections
 frequency: 60 min
 intensity decay: 0.1%

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.044
wR (*F*²) = 0.123
S = 1.027
 4744 reflections
 261 parameters
 H-atom parameters constrained
w = 1/[σ²(*F_o*²) + (0.0677*P*)² + 14.4440*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 2.46 e Å⁻³
 Δρ_{min} = -1.00 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Nd—O1	2.378 (4)	P1—O1	1.503 (4)
Nd—O2	2.388 (4)	P2—O2	1.491 (4)
Nd—O3	2.400 (4)	P3—O3	1.487 (4)
Nd—O10	2.400 (5)	O10—C10	1.248 (8)
Nd—O13	2.419 (5)	O11—C12 ⁱ	1.244 (9)
Nd—O11	2.438 (5)	O12—C12	1.247 (9)
Nd—O12	2.515 (5)	O13—C10 ⁱ	1.249 (8)
Nd—O11 ⁱ	2.594 (5)	C10—O13 ⁱ	1.249 (8)
Co—P2	2.1603 (19)	C10—C11	1.499 (9)
Co—P3	2.1628 (18)	C12—O11 ⁱ	1.244 (9)
Co—P1	2.169 (2)		
O1—Nd—O2	77.67 (16)	O2—Nd—O11	140.59 (17)
O1—Nd—O3	75.43 (16)	O3—Nd—O11	132.43 (17)
O2—Nd—O3	74.51 (16)	O10—Nd—O11	73.38 (19)
O1—Nd—O10	91.2 (2)	O13—Nd—O11	72.71 (18)
O2—Nd—O10	73.23 (17)	O1—Nd—O12	152.86 (16)
O3—Nd—O10	147.03 (16)	O2—Nd—O12	79.57 (19)
O1—Nd—O13	109.52 (19)	O3—Nd—O12	84.42 (19)
O2—Nd—O13	146.29 (17)	O10—Nd—O12	96.3 (2)
O3—Nd—O13	75.70 (15)	O13—Nd—O12	82.2 (2)
O10—Nd—O13	137.18 (17)	O11—Nd—O12	124.45 (16)
O1—Nd—O11	82.68 (15)	O1—Nd—O11 ⁱ	155.24 (15)

O2—Nd—O11 ⁱ	113.31 (15)	P2—Co—P3	90.86 (8)
O3—Nd—O11 ⁱ	128.10 (15)	P2—Co—P1	93.03 (7)
O10—Nd—O11 ⁱ	72.30 (19)	P3—Co—P1	90.30 (7)
O13—Nd—O11 ⁱ	74.30 (18)	O10—C10—O13 ⁱ	126.9 (6)
O11—Nd—O11 ⁱ	75.08 (17)	O11 ⁱ —C12—O12	121.8 (7)
O12—Nd—O11 ⁱ	50.38 (16)		

Symmetry code: (i) -*x*, -*y*, -*z*.

The methoxy O5 and O7 atoms and the methyl C13 atom of the μ-*O,O'*-acetato ligand were disordered and refined on *U_{iso}* with an occupancy factor of 0.5. The Cp ring was constrained as a regular pentagon on *U_{iso}*. H atoms were constrained using a riding model and with *U*(H) fixed at 1.5 (Me) or 1.2 (Cp) times *U_{eq}* of the parent atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *SHELXL97*.

This research has been supported financially by the Basic Science Research Institute Program of Ministry of Education in Korea and a grant of Postdoctoral Program from Kyungpook National University (1999).

References

Aparna, K., Krishnamurthy, S. S., Nethaji, M. & Balaram, P. (1997). *Polyhedron*, **16**, 507–514.
 Bresolin, L., Burrow, R. A., Horner, M., Bermejo, E. & Castineiras, A. (1997). *Polyhedron*, **16**, 3947–3951.
 Bünzli, J.-C. G. (1989). *Lanthanide Probes in Life, Chemical and Earth Sciences*, edited by J.-C. G. Bünzli and G. R. Choppin, ch. 7. Amsterdam: Elsevier.
 Cho, I. Y., Yeo, H. J. & Jeong, J. H. (1995a). *Acta Cryst.* **C51**, 2035–2037.
 Cho, I. Y., Yeo, H. J. & Jeong, J. H. (1995b). *Bull. Korean Chem. Soc.* **16**, 1244–1246.
 Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
 Fair, C. K. (1990). *MolEN*. Enraf–Nonius, Delft, The Netherlands.
 Han, S. H., Roh, S.-G. & Jeong, J. H. (1999). *Polyhedron*, **18**, 3027–3030.
 Kim, N. H., Yeo, H. J. & Jeong, J. H. (1996). *Bull. Korean Chem. Soc.* **17**, 483–485.
 Kläui, W. (1979). *Z. Naturforsch. Teil B*, **34**, 1403–1407.
 Lauffer, R. B. (1987). *Chem. Rev.* **87**, 901–927.
 Niu, S., Yang, Z., Yang, Q., Yang, B., Chao, J., Yang, G. & Shen, E. Z. (1997). *Polyhedron*, **16**, 1629–1635.
 Rardin, R. L., Tolman, W. B. & Lippard, S. J. (1991). *New J. Chem.* **15**, 417–430.
 Reger, D. L., Lindeman, J. A. & Lebioda, L. (1988). *Inorg. Chem.* **27**, 3923–3929.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
 Wei, P.-R., Wu, D.-D., Zhou, Z.-Y., Li, S.-L. & Mak, T. C. W. (1997). *Polyhedron*, **16**, 749–763.