P(1)—C(30)	1.823 (7)	P(2)—C(40)	1.826 (7)
P(2)—C(50)	1.825 (7)	P(2)—C(60)	1.825 (6)
P(3)—F(1)	1.608 (7)	P(3)—F(2)	1.556 (8)
P(3)—F(3)	1.596 (6)	P(3)—F(4)	1.592 (6)
P(3)—F(5)	1.589 (7)	P(3)—F(6)	1.585 (7)
S—C(5)	1.735 (7)	Cl(1)—C	1.746 (12)
Cl(2)—C	1.828 (13)	Cl(3)—C	1.683 (12)
N—C(1)	1.381 (10)	N—C(5)	1.325 (9)
C(1)—C(2)	1.405 (12)	C(2)—C(3)	1.382 (13)
C(3)—C(4)	1.396 (12)	C(4)—C(5)	1.397 (11)
P(1)—Pt—P(2)	97.4 (1)	P(1)—Pt—S	165.6 (1)
P(2)—Pt—S	97.0 (1)	P(1)—Pt—N	97.8 (2)
P(2)—Pt—N	163.8 (2)	S—Pt—N	68.0 (2)
Pt—P(1)—C(10)	110.1 (2)	Pt—P(1)—C(20)	109.0 (3)
C(10)—P(1)—C(20)	107.5 (3)	Pt—P(1)—C(30)	123.1 (2)
C(10)—P(1)—C(30)	102.6 (3)	C(20)—P(1)—C(30)	103.4 (3)
Pt—P(2)—C(40)	112.9 (2)	Pt—P(2)—C(50)	114.7 (2)
C(40)—P(2)—C(50)	102.1 (3)	Pt—P(2)—C(60)	111.1 (2)
C(40)—P(2)—C(60)	104.1 (3)	C(50)—P(2)—C(60)	111.2 (3)
F(1)—P(3)—F(2)	178.8 (4)	F(1)—P(3)—F(3)	89.1 (3)
F(2)—P(3)—F(3)	91.5 (4)	F(1)—P(3)—F(4)	89.8 (3)
F(2)—P(3)—F(4)	89.6 (4)	F(3)—P(3)—F(4)	178.9 (4)
F(1)—P(3)—F(5)	87.7 (4)	F(2)—P(3)—F(5)	91.3 (4)
F(3)—P(3)—F(5)	89.4 (4)	F(4)—P(3)—F(5)	90.8 (4)
F(1)—P(3)—F(6)	88.6 (4)	F(2)—P(3)—F(6)	92.5 (4)
F(3)—P(3)—F(6)	89.9 (3)	F(4)—P(3)—F(6)	89.8 (4)
F(5)—P(3)—F(6)	176.2 (4)	Pt—S—C(5)	81.3 (2)
Pt—N—C(1)	135.3 (5)	Pt—N—C(5)	101.3 (4)
C(1)—N—C(5)	122.4 (6)	Cl(1)—C—Cl(2)	106.9 (7)
Cl(1)—C—Cl(3)	113.2 (7)	Cl(2)—C—Cl(3)	109.7 (6)
N—C(1)—C(2)	118.6 (8)	C(1)—C(2)—C(3)	119.1 (8)
C(2)—C(3)—C(4)	121.0 (8)	C(3)—C(4)—C(5)	118.0 (8)
S—C(5)—N	108.8 (5)	S—C(5)—C(4)	130.1 (6)
N—C(5)—C(4)	121.0 (7)		

The crystal used for the study was mounted on a glass fiber with epoxy. The diffractometer was controlled by a Data General Nova 4 minicomputer. Triclinic symmetry was suggested from interaxial angles and by Delaunay reduction. Axial lengths were confirmed by comparison with interlayer spacings observed in axial photographs. Backgrounds were estimated from a 96-step peak profile. The data were corrected for decay by scaling on the standard reflections (both decayed similarly). Data were also corrected for Lorentz and polarization effects. Absorption corrections were based on seven reflections spanning a range of 2θ values from 10.75 to 32.63°. Crystal structure solution and refinement were carried out using the *SHELXTL* collection of crystallographic software (Sheldrick, 1985) on a Data General Eclipse S140 minicomputer. The coordinates of the Pt atom were determined from a Patterson map. All remaining non-H atoms were obtained from subsequent difference Fourier maps. The positions of H atoms on the phenyl rings were calculated by using a fixed C—H distance of 0.96 Å. A chloroform solvent molecule was located and refined successfully. All non-H atoms were refined anisotropically.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71779 (38 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1051]

References

Deeming, A. J., Karim, M., Bates, P. A. & Hursthouse, M. B. (1988). *Polyhedron*, **7**, 1401–1403, and references therein.
Shedrick, G. M. (1985). *SHELXTL User's Manual*. Revision 5.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.
Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
Umakoshi, K., Kinoshita, I., Fukui-Yasuba, Y., Matsumoto, K., Ooi, S., Nakai, H. & Shiro, M. (1989). *J. Chem. Soc. Dalton Trans.* pp. 815–819, and references therein.
Wang, S. & Fackler, J. P. Jr (1989). *Inorg. Chem.* **28**, 2615–2619.

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Tris(*tert*-butylcyclopentadienyl)neodymium-μ-chloro-tris(tetrahydrofuran)lithium, $[\mathrm{Nd}(\eta^5\text{-}{}^t\mathrm{BuCp})_3(\mu\text{-Cl})\mathrm{Li(thf)}_3]$

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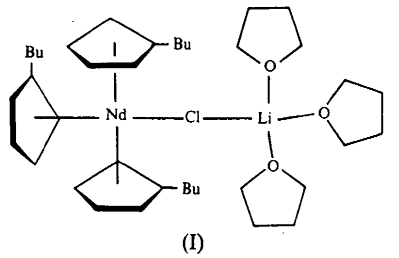
Abstract

The title complex, tris[2(η^5)-*tert*-butylcyclopentadienyl]-μ-chloro-1:2κ^2*Cl*-tris(tetrahydrofuran-1κ*O*)-lithiumneodymium, $[\mathrm{Nd(C_9H_{13})_3}(\mu\text{-Cl})\mathrm{Li(C_4H_8O)_3}]$, consists of the neutral moiety $({}^t\mathrm{BuCp})_3\mathrm{Nd}$ linked to the cation $[\mathrm{Li(thf)_3}]^+$ by a μ-Cl bridge. The Nd atom is coordinated by three η^5-bonded *tert*-butylcyclopentadienyl (^{t}BuCp) ligands and a Cl^- ion to form a slightly deformed tetrahedron. Nd—Cl = 2.797 (2), Li—Cl = 2.345 (9) Å and Nd—Cl—Li = 141.4 (3)°.

Comment

The synthesis and structures of $\mathrm{Cp_3Ln}$ and $\mathrm{Cp_3Ln}L$ complexes (Cp = cyclopentadienyl, Ln = lanthanide, L = neutral ligand) have been reported for all the rare-earth elements (Birmingham & Wilkinson, 1956; Eggers, Kopf & Fischer, 1986). $[\mathrm{Cp_3PrC_4H_9}]^-$ (Jahn, Yünlü, Oroschin, Amberger & Fischer, 1984), $[\mathrm{Cp_3NdC_6H_5}]^-$ (Gao, Shen, Hu, Jin & Lin, 1992) and $[\mathrm{Cp_3LnCH_3}]^-$ (Ln = La, Nd) (Guan, Hu & Shen, 1991) have also been reported. Recently, we described the complex $[(\eta^5\text{-}{}^t\mathrm{BuCp})_3\mathrm{Nd}(\mu\text{-Br})\mathrm{Li(thf)_3}]$ (thf = tetrahydrofuran) (Song, Shen & Jin, 1992) and now report the structure of the analogous species

[(η^5-^{t}BuCp)$_3$Nd(μ-Cl)Li(thf)$_3$] (I) prepared by the reaction of (^{t}BuCp)$_2$NdCl.$n$thf with Li(CH$_2$)(CHCH$_3$)P(CH$_2$CH$_3$)$_2$ in thf. Although the bulk of the ^{t}BuCp$^-$ ion complicates the synthesis of its complexes with early lanthanides such as Pr and Nd (Shen, Qi, Guan & Lin, 1991; Shen, Cheng & Lin, 1991), ligand transfer between metal centres can occur *in situ* (Wayda, 1989). The structure determination of the title complex confirms that it belongs to a new class of heteronuclear dimetal complexes, which also includes [(η^5-^{t}BuCp)$_3$Nd(μ-Br)Li(thf)$_3$], and that it differs from the complexes reported earlier by Rogers & Rogers (1991).



(I)

The Li atom is coordinated by three thf ligands and one Cl$^-$ ion; the Li—Cl distance is 2.345 (9) Å and the mean Li—O distance is 1.92 (1) Å. The Nd—Cl distance [2.797 (2) Å] is in agreement with the corresponding value in [Li(thf)$_2$]$_2$(μ-Cl)$_2$[(η^5-Cp')Nd.thf] (Guan, Shen, Hu, Jin & Wei, 1990; Jin, Hu, Li, Xu & Liu, 1988), but is longer than the Pr—Cl distance of 2.718 (6) Å in [(^{t}BuCp)$_2$PrCl.2thf] (the ionic radii of Pr^{3+} and Nd^{3+} differ by 0.001 Å). The coordination number (10) and steric saturation of Nd^{3+} in the title complex are larger than those of Pr^{3+} in [(^{t}BuCp)$_2$PrCl.2thf], which may explain the longer Ln—Cl bond in the neodymium species.

From the angles listed in Table 2, it can be seen that the Nd, Cl and Li atoms are not collinear and that the three ^{t}BuCp rings are evenly arranged about the Nd centre.

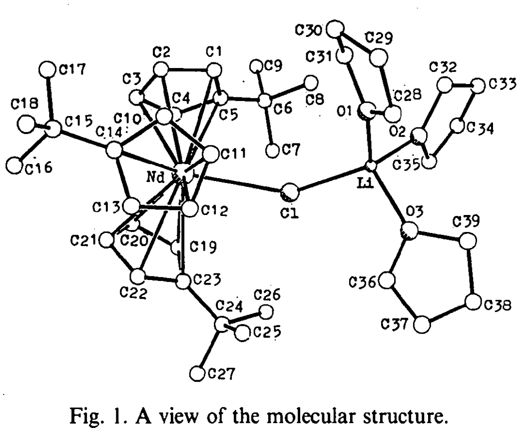


Fig. 1. A view of the molecular structure.

Experimental

Crystal data

[LiNdCl(C$_9$H$_{13}$)$_3$(C$_4$H$_8$O)$_3$]
M_r = 766.56
Monoclinic
$P2_1/n$
a = 12.027 (2) Å
b = 24.220 (7) Å
c = 13.904 (5) Å
β = 92.02 (2)°
V = 4047 (2) Å^3
Z = 4

D_x = 1.25 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 3–12°
μ = 1.381 mm^{-1}
T = 298 K
Quadrilateral
0.50 × 0.45 × 0.38 mm
Violet-red

Data collection

Nicolet $R3m/E$ diffractometer
ω scans
Absorption correction: empirical
$T_{\min}$ = 0.409, $T_{\max}$ = 0.439
7561 measured reflections
7365 independent reflections
4316 observed reflections [$I \geq 3\sigma(I_o)$]

$R_{\rm int}$ = 0.0269
$\theta_{\max}$ = 24°
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 29$
$l = -17 \rightarrow 17$
2 standard reflections monitored every 100 reflections
intensity variation: none

Refinement

Refinement on F
R = 0.038
wR = 0.036
S = 1.48
4316 reflections
458 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.0002F^2]$
$(\Delta/\sigma)_{\max}$ = 0.060
$\Delta\rho_{\max}$ = 0.62 e Å^{-3}
$\Delta\rho_{\min}$ = −0.51 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELXTL* (Sheldrick, 1983)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Nd	0.2889 (1)	0.0432 (1)	0.1947 (1)	0.054 (1)
Cl	0.1345 (1)	0.1143 (1)	0.2755 (1)	0.077 (1)
Li	−0.0500 (8)	0.1170 (4)	0.3242 (7)	0.076 (4)
O(1)	−0.1291 (3)	0.0492 (2)	0.3108 (3)	0.086 (2)
O(2)	−0.1419 (3)	0.1716 (2)	0.2596 (3)	0.092 (2)
O(3)	−0.0516 (3)	0.1385 (2)	0.4587 (3)	0.114 (2)
C(1)	0.1341 (4)	0.0420 (2)	0.0342 (4)	0.071 (2)
C(2)	0.2124 (6)	0.0002 (2)	0.0222 (4)	0.079 (3)
C(3)	0.3127 (6)	0.0239 (3)	0.0019 (4)	0.086 (4)
C(4)	0.2965 (4)	0.0815 (2)	−0.0004 (4)	0.072 (2)
C(5)	0.1859 (4)	0.0933 (2)	0.0178 (3)	0.059 (2)
C(6)	0.1314 (5)	0.1494 (2)	0.0036 (4)	0.083 (3)
C(7)	0.1943 (6)	0.1943 (3)	0.0569 (5)	0.116 (4)
C(8)	0.0123 (5)	0.1486 (3)	0.0376 (5)	0.115 (3)
C(9)	0.1261 (8)	0.1621 (3)	−0.1042 (4)	0.131 (4)
C(10)	0.1827 (5)	−0.0622 (2)	0.2259 (4)	0.083 (3)
C(11)	0.1523 (6)	−0.0253 (3)	0.2975 (6)	0.103 (3)
C(12)	0.2438 (7)	−0.0155 (3)	0.3558 (5)	0.100 (3)
C(13)	0.3303 (6)	−0.0467 (3)	0.3233 (4)	0.090 (3)
C(14)	0.2953 (4)	−0.0759 (2)	0.2431 (4)	0.068 (2)
C(15)	0.3589 (7)	−0.1224 (3)	0.1976 (5)	0.097 (3)
C(16)	0.4795 (9)	−0.1133 (4)	0.1959 (12)	0.332 (12)
C(17)	0.3175 (13)	−0.1350 (5)	0.0988 (7)	0.337 (11)
C(18)	0.3438 (8)	−0.1751 (3)	0.2487 (6)	0.171 (5)

C(19)	0.4485 (4)	0.1313 (3)	0.2097 (4)	0.077 (2)
C(20)	0.4943 (4)	0.0884 (3)	0.1570 (4)	0.084 (3)
C(21)	0.5169 (4)	0.0447 (3)	0.2175 (4)	0.095 (3)
C(22)	0.4885 (4)	0.0611 (2)	0.3090 (4)	0.061 (2)
C(23)	0.4463 (4)	0.1144 (2)	0.3069 (4)	0.061 (2)
C(24)	0.4268 (4)	0.1497 (3)	0.3953 (4)	0.082 (3)
C(25)	0.3586 (6)	0.1204 (3)	0.4686 (4)	0.108 (3)
C(26)	0.3648 (6)	0.2030 (3)	0.3656 (5)	0.120 (4)
C(27)	0.5406 (5)	0.1660 (3)	0.4393 (5)	0.108 (3)
C(28)	−0.1852 (9)	0.0224 (4)	0.3824 (6)	0.146 (4)
C(29)	−0.2335 (7)	−0.0289 (3)	0.3429 (5)	0.119 (4)
C(30)	−0.1870 (8)	−0.0341 (3)	0.2488 (5)	0.124 (4)
C(31)	−0.1527 (7)	0.0213 (3)	0.2219 (4)	0.106 (3)
C(32)	−0.2444 (6)	0.1629 (3)	0.2062 (7)	0.118 (4)
C(33)	−0.2861 (9)	0.2176 (4)	0.1789 (10)	0.172 (6)
C(34)	−0.1925 (9)	0.2538 (5)	0.1848 (9)	0.159 (6)
C(35)	−0.1098 (8)	0.2277 (3)	0.2502 (8)	0.133 (5)
C(36)	0.0357 (7)	0.1403 (7)	0.5165 (6)	0.341 (11)
C(37)	0.0220 (9)	0.1612 (4)	0.6056 (6)	0.186 (6)
C(38)	−0.0742 (9)	0.1938 (4)	0.5878 (8)	0.210 (6)
C(39)	−0.1349 (7)	0.1627 (5)	0.5116 (7)	0.170 (5)

Table 2. *Selected geometric parameters* (Å, °)

Cp indicates the centroid of the *tert*-butylcyclopentadienyl ring.

Li—O(1)	1.90 (1)	Li—O(2)	1.93 (1)
Li—O(3)	1.94 (1)	Cl—Li	2.345 (9)
Nd—Cl	2.797 (2)	Nd—C(1)	2.856 (5)
Nd—C(2)	2.744 (6)	Nd—C(3)	2.746 (5)
Nd—C(4)	2.872 (5)	Nd—C(5)	2.974 (5)
Nd—C(10)	2.894 (5)	Nd—C(11)	2.767 (7)
Nd—C(12)	2.722 (7)	Nd—C(13)	2.850 (6)
Nd—C(14)	2.962 (5)	Nd—C(19)	2.874 (6)
Nd—C(20)	2.769 (5)	Nd—C(21)	2.750 (5)
Nd—C(22)	2.865 (5)	Nd—C(23)	2.965 (5)
Nd—Cl—Li	141.4 (3)	*Cp*(1)—Nd—*Cp*(2)	118.0
Cp(2)—Nd—*Cp*(3)	115.8	*Cp*(3)—Nd—*Cp*(1)	115.7
Cl—Nd—*Cp*(1)	101.0	Cl—Nd—*Cp*(2)	98.2
Cl—Nd—*Cp*(3)	103.7		

The title complex is very sensitive to air and moisture, so all manipulations were performed using Schlenk techniques under Ar. A suitable crystal was chosen and sealed in a glass capillary. The structure was solved by Patterson methods and refined by full-matrix least squares. H atoms were located in idealized positions, 0.96 Å from the parent C atom, and were assigned fixed isotropic displacement parameters, $U = 0.05$ Å^2. All calculations were carried out on an Eclipse S/140 microcomputer with the *SHELXTL* (Sheldrick, 1983) program.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71788 (33 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1076]

References

Birmingham, J. M. & Wilkinson, G. (1956). *J. Am. Chem. Soc.* **78**, 42–44.

Eggers, S. H., Kopf, J. & Fischer, R. D. (1986). *Organometallics*, **5**, 383–385.

Gao, H. R., Shen, Q., Hu, J. Y., Jin, S. C. & Lin, Y. H. (1992). *J. Organomet. Chem.* **427**, 141–149.

Guan, J. W., Hu, J. Y. & Shen, Q. (1991). *Kexue Tongbao*, **7**, 516–518. (In Chinese.)

Guan, J. W., Shen, Q., Hu, J. Y., Jin, Z. S. & Wei, G. C. (1990). *J. Inorg. Chem.* **6**, 221–225. (In Chinese.)

Jahn, W., Yünlü, K., Oroschin, W., Amberger, H. D. & Fischer, R. D. (1984). *Inorg. Chim. Acta*, **95**, 85–104.

Jin, Z. S., Hu, N. H., Li, Y., Xu, X. L. & Liu, G. Z. (1988). *Inorg. Chim. Acta*, **142**, 333–336.

Rogers, R. D. & Rogers, L. M. (1991). *J. Organomet. Chem.* **416**, 201–290.

Sheldrick, G. M. (1983). *SHELXTL User's Manual*. Revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Shen, Q., Cheng, Y. X. & Lin, Y. H. (1991). *J. Organomet. Chem.* **419**, 292–298.

Shen, Q., Qi, M. H., Guan, J. W. & Lin, Y. H. (1991). *J. Organomet. Chem.* **406**, 353–361.

Song, S. P., Shen, Q. & Jin, S. C. (1992). *Polyhedron*, **11**, 2863–2865.

Wayda, A. L. (1989). *J. Organomet. Chem.* **361**, 73–78.

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A 1:2 Addition Compound of Cadmium Bromide with 3-Methyl-4-nitropyridine *N*-Oxide

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Abstract

catena-Poly[bis(3-methyl-4-nitropyridine *N*-oxide-*O*)cadmium-di-μ-bromo], [$Cd(C_6H_6N_2O_3)_2Br_2$], which belongs to a group of potential nonlinear optical materials, crystallizes in the non-centrosymmetric space group *Fdd*2. The Cd atom is octahedrally coordinated to two O atoms from the *trans* 3-methyl-4-nitropyridine *N*-oxide ligands in the axial positions and four Br atoms lying in the equatorial plane. The coordination octahedra form one-dimensional chains along the short *c* axis by edge-sharing through the Br atoms, with each Cd atom located on a crystallographic diad axis.

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