† Dihedral angle between the chelate rings defined by Cu1, O1, N1 and Cu1, O2, N2. ‡ Displacement of C atoms of the ethylene backbone from the coordination plane defined by Cu1, N1, N2.

Notes: (*a*) *N*,*N*′-bis(salicylidene)-1,2-diimino-2-methylpropanecopper(II), (I) (present work); (*b*) nitrobenzene solvate of *N*,*N*′-bis(salicylidene)-1,2-diiminoethanecopper(II), (II) (Hall & Waters, 1960); (*c*) chloroform solvate of *N*,*N*′-bis(salicylidene)-1,2-diiminoethanecopper(II), (III) (Baker, Hall & Waters, 1970*b*); (*d*) chloroform solvate of *N*,*N*′-bis(salicylidene)-1,2-diiminoethanecopper(II), (IV) (Bhadbhade & Srinivas, 1993); (*e*) *N*,*N*′-bis(5-methoxysalicylidene)-1,2-diiminoethanecopper(II), (V) (Bhadbhade & Srinivas, 1993); (*f*) *N*,*N*′-bis(salicylidene)-1,2-diiminopropanecopper(II)–H$_2$O, (VI) (Llewellyn & Waters, 1960); (*g*) *p*-nitrophenol solvate of *N*,*N*′-bis(salicylidene)-1,2-diiminoethanecopper(II), (VII) (Baker, Hall & Waters, 1970*a*); (*h*) *N*,*N*′-bis(5-chlorosalicylidene)-1,2-diiminoethanecopper(II), (VIII) (Bhadbhade & Srinivas, 1993).

The data collection nominally covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 5.89 cm. Coverage of the unique set is over 86% complete to at least 25.6° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analyzing the duplicate reflections; it was found to be negligible. H atoms were placed geometrically and refined with a riding model and with $U_{\rm iso}$ constrained to be 0.08 Å^2.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1145). Services for accessing these data are described at the back of the journal.

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Iodobis(pyridine-*N*)bis(η^5-trimethylsilylcyclopentadienyl)neodymium

DAVID L. CLARK,[a] JOHN C. GORDON,[b] BRIAN L. SCOTT[b] AND JOHN G. WATKIN[b]

[a]*Chemical Science & Technology Division, Mail Stop G739, Los Alamos National Laboratory, Los Alamos, NM 87545, USA, and* [b]*Chemical Science & Technology Division, Mail Stop C346, Los Alamos National Laboratory, Los Alamos, NM 87545, USA. E-mail: jwatkin@lanl.gov*

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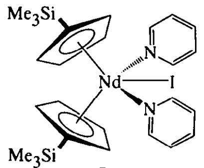
Abstract

The title complex, [NdI(C$_8$H$_{13}$Si)$_2$(C$_5$H$_5$N)$_2$], adopts a typical bent bis(cyclopentadienyl) geometry with one iodide and two pyridine ligands occupying the plane between the cyclopentadienyl moieties. Principal bond lengths include Nd—I 3.1483 (4), Nd—N 2.740 (3) and Nd—C 2.715 (4)–2.824 (3) Å.

Comment

We have been examining the metathesis chemistry of lanthanide triiodides with potassium salts of substituted cyclopentadienyl ligands in order to develop synthetic routes for mono- and bis(cyclopentadienyl) lanthanide complexes without the formation of intermediate salt complexes. Following the reaction of a tetrahydrofuran adduct of neodymium triiodide, [NdI$_3$(thf)$_3$], with two equivalents of KC$_5$H$_4$SiMe$_3$, and subsequent addition of pyridine, we have isolated the title complex, (I), in modest yield.



(I)

The molecule crystallizes in the trigonal space group $R\bar{3}c$, with the Nd and I atoms sitting on a twofold rotation axis. In the solid state, the molecule adopts a typical bent metallocene geometry with one iodide and two pyridine ligands occupying the 'girdle' between the two cyclopentadienyl ligands. The trimethylsilyl groups are oriented above and below the iodide ligand, *i.e.* toward the 'open' face of the metallocene wedge. The Nd—I distance of 3.1483 (4) Å is somewhat shorter than the corresponding distance of 3.287 (1) Å seen in [NdI(thf)$_3$(η-C$_8$H$_8$)] (Kilimann, Schäfer, Herbst-Irmer & Edelmann, 1994). The Nd—N distance to the pyridine ligands of 2.740 (3) Å is comparable to those of 2.668 (5) Å observed in [Nd(py)(η-C$_5$H$_5$)$_3$] (Deacon, Gatehouse, Platts & Wilkinson, 1987) and 2.682 (5) Å in [Nd$_2$(OCH^{i}Pr$_2$)$_6$(py)$_2$] (Barnhart, Clark, Huffman, Vincent & Watkin, 1993). Nd—C distances to the C atoms within the cyclopentadienyl rings range from 2.715 (4) to 2.824 (3) Å and are directly comparable to Nd—C distances observed in other substituted cyclopentadienyl systems (Herrmann *et al.*, 1992; Song, Shen & Jin, 1992; Shen, Cheng & Lin, 1991; Guan, Shen, Jin & Lin, 1994). The distance from the metal center to the centroid of the cyclopentadienyl ligands is 2.493 (2) Å, while the angle between the cyclopentadienyl ring planes is 62.3 (2)°.

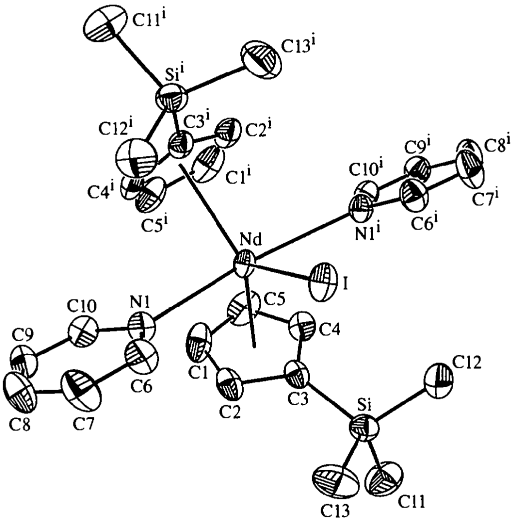


Fig. 1. Molecular structure (50% probability displacement ellipsoids) of [NdI(η-C$_5$H$_4$SiMe$_3$)$_2$(C$_5$H$_5$N)$_2$], with H atoms omitted for clarity. [Symmetry code: (i) $\frac{2}{3}+x-y, \frac{4}{3}-y, \frac{5}{6}-z$.]

Experimental

The title compound was prepared by reaction of [NdI$_3$(thf)$_3$] with two equivalents of potassium trimethylsilylcyclopentadienide in THF, followed by the addition of an excess of pyridine and recrystallization from toluene at low temperature.

Crystal data

[NdI(C$_8$H$_{13}$Si)$_2$(C$_5$H$_5$N)$_2$]
M_r = 703.89
Trigonal
$R\bar{3}c$
a = 27.001 (2) Å
c = 21.525 (4) Å
V = 13590 (3) Å^3
Z = 18
D_x = 1.548 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 24.6–25.0°
μ = 2.836 mm^{-1}
T = 173 K
Prism
0.29 × 0.25 × 0.25 mm
Lavender

Data collection

Siemens *P*4/*PC* diffractometer
ω scans
Absorption correction: empirical (ψ scan; Walker & Stuart, 1983)
$T_{\min}$ = 0.400, $T_{\max}$ = 0.492
6669 measured reflections
1979 independent reflections

1760 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.0321
$\theta_{\max}$ = 22.5°
$h = -18 \rightarrow 29$
$k = -25 \rightarrow 23$
$l = -17 \rightarrow 23$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.012
$wR(F^2)$ = 0.043
S = 1.058
1979 reflections
146 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0146P)^2 + 14.5159P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.002
$\Delta\rho_{\max}$ = 0.252 e Å^{-3}
$\Delta\rho_{\min}$ = −0.316 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

I—Nd	3.1483 (4)	Nd—C4	2.780 (3)
Nd—C1	2.715 (4)	Nd—C5	2.729 (3)
Nd—C2	2.772 (3)	Nd—N1	2.740 (3)
Nd—C3	2.824 (3)		
N1—Nd—I	80.60 (5)		

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93.

This work was performed under the auspices of the Laboratory Directed Research and Development Program. Los Alamos National Laboratory is operated by the University of California for the US Department of Energy under Contract W-7405-ENG-36.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1006). Services for accessing these data are described at the back of the journal.

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Diaquabis(2-quinolinecarboxylato-*N*,*O*)-manganese(II)

Nobuo Okabe and Makiko Koizumi

Faculty of Pharmaceutical Sciences, Kinki University, Kowakae 3-4-1, Higashiosaka, Osaka 577, Japan

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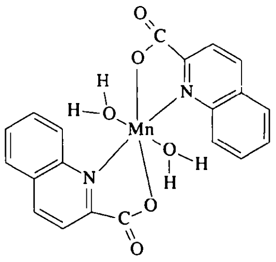
Abstract

The title compound, $[Mn(C_{10}H_6NO_2)_2(H_2O)_2]$, contains a six-coordinate Mn atom at a center of symmetry. The Mn atom displays distorted octahedral coordination. 2-Quinolinecarboxylate anions lie in a *trans* position with respect to one another, forming the equatorial plane, and the water ligands occupy the axial positions. In the equatorial plane, the Mn–ligand distances and the bite angle of the ligand are Mn—O 2.131 (2), Mn—N 2.315 (2) Å and O—Mn—N 74.85 (7)°. In the axial direction, $Mn—OH_2$ 2.185 (2) and O—Mn—N 91.10 (8)°. Molecules are linked by a three-dimensional O—H···O hydrogen-bonding network involving water molecules and carboxylate groups.

Comment

2-Quinolinecarboxylic acid (quinaldinic acid), (I), is one of the final products of tryptophan metabolism and is derived from kynurenic acid (Martin, Mayes & Rodwell, 1983). It inhibits dopamine β-hydroxylase (EC 1.14.17.1), which is a multi-subunit enzyme containing two Cu atoms per subunit (Townes, Titone & Rosenberg, 1990).

2-Quinolinecarboxylic acid is also known to be a potent chelator of copper and other transition metal ions (Martell & Smith, 1974). Accordingly, we have carried out the structure analysis of the chelate compounds of 2-quinolinecarboxylic acid and biologically important metal ions in order to clarify the binding scheme of this metabolite to metal ions. In the present study, the crystal structure of the Mn^{II} complex of 2-quinolinecarboxylic acid, (II), has been determined.



(II)

The structure of the precursor of 2-quinolinecarboxylic acid, kynurenic acid, has been reported (Okabe, Miura & Shimosaki, 1996), and recently the structure of (II) has been reported as the water and ethanol solvate (Haendler, 1996). The molecular structure of (II) with the atom-labeling scheme is shown in Fig. 1. The Mn^{II} atom is coordinated octahedrally by two *trans* quinoline N atoms [Mn1—N1 2.315 (2) Å], by two *trans*-O atoms of the carboxylate groups in position 2 of (I) [Mn1—O2 2.131 (2) Å] and by two *trans*-O atoms of the water molecules [Mn1—O3 2.185 (2) Å]. These Mn^{II}–ligand distances are similar to those values in the water/ethanol solvate [Mn—N 2.324 (3), Mn—O 2.125 (2) and $Mn—OH_2$ 2.209 (3) Å; Haendler, 1996]. The carboxyl group is present in an ionized form and is almost parallel to the quinoline ring plane [O2—C1—C2—N1 −15.4 (3)°]. These conformational features are also observed in the solvated complex (Haendler, 1996). The molecular packing of the crystal

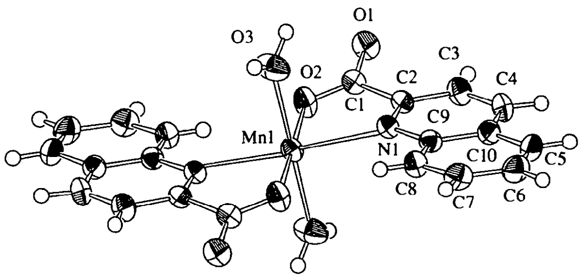


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

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