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## Structure of Bis(*N*-methyl-5-nitrosalicylideneaminato)nickel(II)

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**Abstract.**  $[\text{Ni}(\text{C}_8\text{H}_7\text{N}_2\text{O}_3)_2]$ ,  $M_r = 417.00$ , monoclinic,  $P2_1/n$ ,  $a = 20.500$  (4),  $b = 10.266$  (3),  $c = 3.824$  (1) Å,  $\beta = 92.93$  (2)°,  $V = 803.67$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.73$  (by flotation),  $D_x = 1.72$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 21.21$  cm<sup>-1</sup>,  $F(000) = 428$ , room temperature, final  $R = 0.036$  for 1244 observed unique reflections. The title complex has a molecular centre of symmetry and the Ni atom is in square-planar coordination. The molecule has a stepped conformation with a step height of 0.136 Å, measured by the perpendicular distance between planes of best fit through the two benzene rings. The close intramolecular approaches between O(1') ( $-x, -y, -z$ ) and H(81) and H(82) atoms of the methyl group [2.445 and 2.470 Å] possibly influence the conformation of the complex molecule. The Ni—O and Ni—N bond lengths are 1.826 (2) and 1.924 (2) Å, respectively. Within the benzene system, three consecutive bonds are longer [C(6)—C(1) 1.400 (3), C(1)—C(2) 1.411 (3), C(2)—C(3) 1.419 (3) Å] and three shorter [C(3)—C(4) 1.368 (4), C(4)—C(5) 1.396 (4), C(5)—C(6) 1.377 (4) Å]. The two distinctly shorter bonds [C(3)—C(4) and C(5)—C(6)] suggest a quinonoid character of the ring.

**Experimental.** Crystals obtained by slow evaporation of dimethylformamide solution. Crystal dimensions and data collection procedure are given in Table 1. The structure was solved by the heavy-atom method and refined by a full-matrix least-squares procedure

using anisotropic temperature factors for all non-hydrogen atoms. Function minimized  $\sum w(|F_o| - |F_c|)^2$  with weighting scheme given in Table 1. No absorption correction applied. At an intermediate stage in the refinement, difference maps showed peaks at the expected locations of H atoms. In the final rounds of calculations they were positioned on geometrical grounds (C—H = 1.08 Å) and included in the structure factor calculations. Structure solution and refinement performed with modified *SHELX76* (Sheldrick, 1976), molecular geometry calculations with *CSU - Crystal Structure Utility* program (Vicković, 1988). Anomalous-scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations carried out on IBM PC/AT-compatible microcomputer (microprocessor 80386/20 MHz and mathematical coprocessor 80387). Final atomic coordinates are given in Table 2,\* the bond lengths and angles in Table 3. The structure is shown in Fig. 1.

**Related literature.** The structures of a number of the bis(*N*-*R*-salicylideneaminato)nickel(II) complexes reported so far showed that the coordination around

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52713 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Details of data collection and refinement

Crystal form and size (mm)	Olive-green prism 0.52 × 0.14 × 0.08
Reflections for cell constants	20 (2θ ≥ 24°)
Scan speed (° s <sup>-1</sup> )	0.04
Scan width (°)	1.2
Scan mode	θ-2θ
2θ <sub>max</sub> (°)	140
Maximum values of indices	h -24 → 24 k 0 → 12 l 0 → 4
Standard reflections	311, 710, 031
R	0.036
wR	0.041
Weighting scheme: w = k/[σ <sup>2</sup> (F <sub>o</sub> ) + g F <sub>o</sub>   <sup>2</sup> ]	k = 2.3001, g = 0.000128
Independent measured reflections	1264
Observed reflections [I > 3σ(I)]	1244
Refined parameters	135
Max. Δ/σ	0.030
Max. Δρ features (e Å <sup>-3</sup> )	-0.477, +0.265

Table 2. Final atomic coordinates (× 10<sup>4</sup>) and equivalent isotropic thermal parameters (Å<sup>2</sup> × 10<sup>4</sup>)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	U <sub>eq</sub>
Ni	0	0	0	317 (1)
O(1)	96 (1)	1725 (2)	-1014 (5)	423 (4)
O(2)	2036 (1)	5758 (2)	-6619 (9)	915 (10)
O(3)	2596 (1)	4023 (2)	-7253 (7)	690 (7)
N(1)	831 (1)	-460 (2)	-1779 (6)	329 (4)
N(2)	2104 (1)	4582 (3)	-6352 (7)	524 (6)
C(1)	1160 (1)	1744 (2)	-3247 (7)	339 (5)
C(2)	581 (1)	2357 (2)	-2265 (7)	347 (5)
C(3)	523 (1)	3726 (2)	-2676 (8)	446 (6)
C(4)	1021 (1)	4442 (3)	-3955 (8)	459 (6)
C(5)	1590 (1)	3814 (3)	-4900 (8)	415 (6)
C(6)	1664 (1)	2486 (3)	-4573 (7)	376 (6)
C(7)	1243 (1)	363 (2)	-2987 (7)	349 (5)
C(8)	1035 (1)	-1836 (3)	-1929 (8)	424 (6)

the Ni atom as well as the molecular conformation depend upon the N atom and benzene-ring substituents. Both tetrahedral (Fox, Orioli, Lingafelter & Sacconi, 1964; Braun & Lingafelter, 1967; Castellano, Hodder, Prout & Sadler, 1971) and square-planar coordinations of the Ni atom have been found. Square-planar complexes adopt either strictly planar (Stewart & Lingafelter, 1959; Fox & Lingafelter, 1967; Kamenar, Kaitner, Ferguson & Waters, 1990) or stepped molecular conformation (Frasson, Panattoni & Sacconi, 1959; Braun & Lingafelter, 1966; Shkol'nikova, Knyazeva & Voblikova, 1967; Bhatia, Bindlish, Saini & Jain, 1981; Bhatia, Syal, Kashyap, Jain & Brown, 1983; Jones, Waters, Kaitner & Kamenar, 1986; Fernandez, Rosales, Toscana & Tapia T., 1986; Ravikumar, Rajan, Rajaram, Ramalingam & Natarajan, 1986; Britton & Pignolet, 1989; Kamenar, Kaitner, Stefanović & Waters, 1990).

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Table 3. Bond lengths (Å) and angles (°)

Primed atoms are related to unprimed atoms by a centre of symmetry.

Ni—O(1)	1.826 (2)	C(4)—C(5)	1.396 (4)
Ni—N(1)	1.924 (2)	C(5)—C(6)	1.377 (4)
O(1)—C(2)	1.300 (3)	C(6)—C(1)	1.400 (3)
N(1)—C(7)	1.298 (3)	N(1)—C(8)	1.475 (3)
C(1)—C(7)	1.430 (3)	C(5)—N(2)	1.450 (3)
C(1)—C(2)	1.411 (3)	N(2)—O(2)	1.219 (3)
C(2)—C(3)	1.419 (3)	N(2)—O(3)	1.225 (3)
C(3)—C(4)	1.368 (4)		
O(1)—Ni—N(1)	93.2 (1)	C(5)—C(6)—C(1)	119.4 (2)
O(1)—Ni—N(1')	86.8 (1)	C(6)—C(1)—C(2)	120.0 (2)
Ni—O(1)—C(2)	130.9 (2)	Ni—N(1)—C(8)	120.5 (2)
C(2)—C(1)—C(7)	121.5 (2)	C(7)—N(1)—C(8)	114.7 (2)
C(1)—C(7)—N(1)	126.4 (2)	C(4)—C(5)—N(2)	118.8 (2)
C(7)—N(1)—Ni	124.8 (2)	C(6)—C(5)—N(2)	119.6 (2)
C(1)—C(2)—C(3)	118.6 (2)	C(5)—N(2)—O(2)	119.2 (3)
C(2)—C(3)—C(4)	120.8 (2)	C(5)—N(2)—O(3)	118.6 (2)
C(3)—C(4)—C(5)	119.5 (3)	O(2)—N(2)—O(3)	122.2 (2)
C(4)—C(5)—C(6)	121.6 (2)		

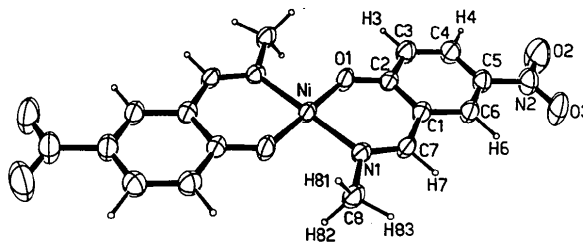


Fig. 1. An ORTEP (Johnson, 1971) view of the molecular structure of the title complex showing the atom-numbering scheme. Ellipsoids at 50% probability level.

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## Tetraethylammonium-hexachlorozirconat und -hexachlorohafnat

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**Abstract.**  $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{ZrCl}_6$ ,  $M_r = 564.45$ , monoclinic,  $C2/c$ ,  $a = 14.071$  (3),  $b = 14.481$  (4),  $c = 13.237$  (2) Å,  $\beta = 90.63$  (2)°,  $V = 2697.1$  (8) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.39$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 9.09$  cm<sup>-1</sup>,  $F(000) = 1168$ ,  $T = 293$  K,  $R = 0.075$  for 1710 unique observed reflexions.  $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{HfCl}_6$ ,  $M_r = 651.72$ ,  $C2/c$ ,  $a = 14.062$  (2),  $b = 14.450$  (2),  $c = 13.237$  (1) Å,  $\beta = 90.65$  (1)°,  $V = 2689.6$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.61$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 42.4$  cm<sup>-1</sup>,  $F(000) = 1296$ ,  $T = 293$  K,  $R = 0.046$  for 1703 observed reflexions. Both compounds are isotopic with  $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{SnCl}_6$ , having octahedral  $[\text{MCl}_6]^{2-}$  ions situated on inversion centres and  $\text{NEt}_4^+$  ions on twofold rotation axes. One half of the  $\text{NEt}_4^+$  ions show positional disorder with two possible orientations such that the terminal C atoms of the ethyl groups coincide for both orientations. According to its lattice parameters,  $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{TiCl}_6$  is also isotopic:  $a = 13.939$  (2),  $b = 14.263$  (2),  $c = 13.103$  (2) Å,  $\beta = 90.89$  (1)°.

**Experimentelles.** Zu einer Lösung von 786 mg  $\text{ZrCl}_4$  (2,5 mmol) in 20 ml wasserfreiem MeCN wurde eine Lösung von 805 mg  $\text{NEt}_4\text{SH}$  (4,9 mmol) in 40 ml MeCN getropft. Unter Freisetzung von  $\text{H}_2\text{S}$  entstand ein hellgelber Niederschlag, dessen genaue Natur noch nicht aufgeklärt werden konnte (laut chemischer Analyse enthält er außer Zr noch  $\text{NEt}_4^+$ -Ionen, Cl und S im Verhältnis 1:1,33:2,75); er wurde abfiltriert. Aus dem Filtrat kristallisierte bei 277 K  $(\text{NEt}_4)_2\text{ZrCl}_6$ .  $(\text{NEt}_4)_2\text{HfCl}_6$  entstand auf die gleiche Art. Die erhoffte Synthese von  $(\text{NEt}_4)_2\text{ZrSCl}_4$  bzw.  $(\text{NEt}_4)_2\text{HfSCl}_4$  gelang auf diesem Wege nicht.

Vierkreisdiffraktometer Enraf-Nonius CAD-4. Gitterparameterbestimmung mit 25 Reflexen  $8 < \theta < 23^\circ$ .  $\omega$ -scan,  $\Delta\omega = (1,9 + 0,35 \tan\theta)^\circ$ , Meßbereich

$\sin\theta/\lambda < 0,572$  Å<sup>-1</sup>,  $0 \leq h \leq 16$ ,  $0 \leq k \leq 16$ ,  $-15 \leq l \leq 15$ . Kontrollreflexe 060, 400, 311 zeigten Intensitätsschwankungen < 1%. Strukturaufklärung durch Patterson-Synthese. Verfeinerung durch Minimieren von  $\sum w(|F_o| - |F_c|)^2$ ,  $w = 1/\sigma^2(F)$  bis  $(\Delta/\sigma)_{\max} < 0,01$ . Keine Extinktionskorrektur. H-Atome nicht berücksichtigt. Rechenprogramme: Sheldrick (1976), Johnson (1965). Atomformfaktoren: Cromer & Mann (1968).  $f'$ ,  $f''$ : Cromer & Liberman (1970). Weitere Angaben siehe in Tabelle 1.

Es sind zwei kristallographisch unabhängige Kationen auf einer zweizähligen Drehachse vorhanden, von denen eines in zwei Orientierungen fehlgeordnet ist; die C-Atome der  $\text{CH}_3$ -Gruppen haben dabei für beide Orientierungen annähernd die gleiche Lage (Fig. 1). Die Atomparameter sind in Tabelle 2,\* Bindungsabstände und -winkel in Tabelle 3 aufgeführt. Wie bei Anwesenheit von fehlgeordneten Teilchen üblich, lassen sich nicht so gute  $R$ -Werte wie bei völlig geordneten Substanzen erreichen; dies gilt insbesondere für die Zr-Verbindung, während sich die Fehlordnung neben dem stärker streuenden Hafnium weniger stark auf den  $R$ -Wert auswirkt.

**Verwandte Literatur.** Isotype Verbindung:  $(\text{NEt}_4)_2\text{SnCl}_6$  (Sowa, Drück & Kutoğlu, 1981; Pabst, Ben Gholzen & Fuess, 1987). Andere Hexachlorozirconate:  $(\text{PPh}_4)_2\text{ZrCl}_6 \cdot 2\text{CH}_2\text{Cl}_2$  (Hartmann,

\* Die Parameter für den anisotropen Temperaturfaktor und die Liste der beobachteten und berechneten Strukturparameter sind beim British Library Document Supply Centre (Supplementary Publication No. SUP 52908: 17 pp.) hinterlegt. Kopien sind erhältlich durch: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.