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Acta Cryst. (1999). C55, 328–330

(3,7-Diethyl-3,7-diazanonane-1,9-dithiolato-*S*,*N*,*N*′,*S*′)nickel(II)

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(*Received 26 May 1998; accepted 30 September 1998*)

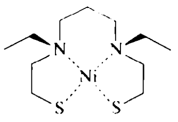
Abstract

The electroneutral title complex, (3,7-diethyl-3,7-diazanonane-1,9-dithiolato-*S*,*N*,*N*′,*S*′)nickel(II), [$Ni(C_{11}H_{24}N_2S_2)$], contains a distorted square-planar arrangement of two N- and two S-donor atoms around the Ni^{II} centre in a *cis*-type fashion.

Comment

Nickel(II) complexes with polyfunctional sulfur/nitrogen ligands have been thoroughly investigated (Musie *et al.*, 1996; Darensbourg *et al.*, 1995; Tuntulani *et al.*, 1992; Colpas *et al.*, 1990) because of their importance as starting materials for the synthesis of heterometallic complexes (Osterloh *et al.*, 1996; Drew *et al.*, 1980; Schneider, 1997). Such heterometallic compounds are of current interest as models for the active sites of nickel-containing metalloenzymes (Cammack, 1988).

Crystals of the title compound, (I), consist of discrete (3,7-diethyl-3,7-diazanonane-1,9-dithiolato-*S*,*N*,*N*′,*S*′)-nickel(II) molecules that belong to the point group C_s in their idealized forms. There is no evidence for intermolecular Ni···S or Ni···Ni interactions. The diethyl-3,7-diazanonane-1,9-dithiolate ligand is bonded to the Ni^{II} centre in a tetradentate manner. The coordination of nickel can be described as distorted square planar with significant deviation from planarity, as indicated by the average of all six valence angles (117.2°). The arrangement of the N_2S_2 donor set in a *cis*-type fashion leads to *X*—Ni—*X* valence angles that differ by 13.8° on going from X = N to X = S. The N and S atoms define a very flat tetrahedron around the Ni atom. As a result, the planes containing the NiS_2 and NiN_2 fragments subtend an angle of 6.95 (2)°. Due to the tetrahedral distortion of the coordination geometry, the sum of the four acute valence angles around Ni exceeds 360° (experimental value 360.4°). Very similar angular distortions have been observed in the chemically related complex (3,7-dimethyl-3,7-diazanonane-1,9-dithiolato)nickel(II) (Colpas *et al.*, 1990), where the average valence angle of nickel is 117.6°.



(I)

The metal–ligand arrangement is a polycyclic system with five- and six-membered chelate subunits. The six-membered chelate ring is formed by coordination of the propylene-bridged N-donor functions to the Ni centre, and it adopts the chair conformation. The basal plane of the chair is defined by N1, N2, C3 and C5, which are exactly coplanar [within 0.0001 (9) Å], in accordance with the idealized symmetry properties of the molecule. Atoms C4 and Ni are displaced in opposite directions from this plane by 0.722 (2) and 0.730 (2) Å, respectively. Both ethyl groups are on the same side of the plane, resulting in different configurations of the N atoms [N1(*S*) and N2(*R*)]. The title compound thus appears in the *meso* form. The two five-membered chelate rings that contain the S-donor functions adopt envelope-like arrangements with C2 and C6 in the flap positions. The Ni—S and Ni—N bonds (mean bond distances 2.174 and 2.018 Å, respectively) are unexceptional in length and comparable to those of related complexes in the literature (Colpas *et al.*, 1990; Mills *et al.*, 1990).

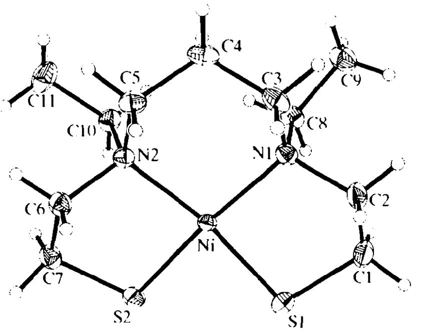


Fig. 1. The structure of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 35% probability level and H atoms are shown as spheres of arbitrary radii.

Experimental

All operations were performed under a dinitrogen atmosphere in a glove box. Compound (I) was synthesized according to the method of Osterloh (1997): *N*,*N*′-diethyl-*N*,*N*′-bis(2-mercaptoethyl)-1,3-diaminopropane (1 g, 4 mmol) was added to a solution of Ni^{II}-acetylacetonate (1 g, 4 mmol) in tetrahydrofuran (THF; 30 ml). The violet solid thus formed was filtered off, washed (THF) and dried *in vacuo* (1.00 g, 81%). Single crystals suitable for X-ray diffraction studies were obtained by slow diffusion of ether into a saturated solution of (I) in acetonitrile. A crystal was mounted on a glass capillary with silicone grease and quickly transferred to the cold nitrogen stream. ^1H NMR (500 MHz, CD_3CN; p.p.m.): 0.89 (*t*, 6H, C9H_3, C11H_3), 1.43 (*m*, 2H, C3H_2, C5H_2), 1.52 (*m*, 1H, C4H_2), 1.74 (*m*, 1H, C4H_2), 1.97 (*m*, 2H, C3H_2, C5H_2), 2.56 (*m*, 6H, C2H_2, C6H_2, C1H_2, C7H_2), 2.86 (*m*, 2H, C2H_2, C6H_2), 3.36 (*m*, 2H, C8H_2, C10H_2), 3.67 (*m*, 2H, C8H_2, C10H_2); ^{13}C NMR (125 MHz, CD_3CN; p.p.m.): 5.08 (C9, C11), 22.53 (C4), 22.87 (C3, C5), 44.74 (C8, C10), 55.29 (C1, C7), 64.36 (C2, C6).

Crystal data

$[Ni(C_{11}H_{24}N_2S_2)]$
$M_r = 307.15$
Monoclinic
$P2_1/n$
$a = 9.674\,(2)$ Å
$b = 8.482\,(2)$ Å
$c = 17.446\,(4)$ Å
$\beta = 104.81\,(2)°$
$V = 1384.0\,(5)$ Å^3
$Z = 4$
$D_x = 1.474$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 18 reflections
$\theta = 10$–$20°$
$\mu = 1.681$ mm^{-1}
$T = 150$ K
Column
0.65 × 0.24 × 0.21 mm
Violet

Data collection

Siemens *P*4-*RA* diffractometer
ω scans
Absorption correction: ψ scan (*SHELXTL-Plus*; Sheldrick, 1990)
$T_{min} = 0.639$, $T_{max} = 0.703$

2723 reflections with $F > 4\sigma(F)$
$R_{int} = 0.014$
$\theta_{max} = 27°$
$h = -12 \rightarrow 0$
$k = 0 \rightarrow 10$
$l = -21 \rightarrow 22$

3191 measured reflections
3014 independent reflections

1 standard reflection every 99 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.024$
$wR(F^2) = 0.058$
$S = 1.086$
3014 reflections
148 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0283P)^2 + 0.6577P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.290$ e Å^{-3}
$\Delta\rho_{min} = -0.420$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0025 (3)
Scattering factors from *SHELXL*93

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

Ni—N2	2.0169 (14)	Ni—S1	2.1724 (6)
Ni—N1	2.0201 (15)	Ni—S2	2.1757 (6)
N2—Ni—N1	98.00 (6)	N2—Ni—S2	88.62 (4)
N2—Ni—S1	171.51 (4)	N1—Ni—S2	171.49 (4)
N1—Ni—S1	89.59 (5)	S1—Ni—S2	84.20 (2)

The structure was solved by direct methods and subsequent difference Fourier synthesis. H atoms were taken from the difference Fourier synthesis, recalculated to idealized positions, and allowed to ride on their parent atoms using a common isotropic displacement parameter.

Data collection: *P*3 *Diffractometer Control Program* (Siemens, 1991). Cell refinement: *P*3 *Diffractometer Control Program*. Data reduction: *XDISK* in *P*3 *Diffractometer Control Program*. Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL*93.

Financial support from the Deutsche Forschungsgemeinschaft, the Bundesminister für Bildung, Wissenschaft, Forschung und Technologie (BMBF), and the Fonds der Chemischen Industrie is gratefully acknowledged. JS thanks the Stiftung Stipendienfonds des Verbandes der Chemischen Industrie for a Kekulé fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1315). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C55, 330–332

The first manganese(II) compound with the saccharinate ligand present both in the complex cation and as the counter-ion: [Mn(bipy)$_2$(sac)(H$_2$O)]$^+$·sac$^-$

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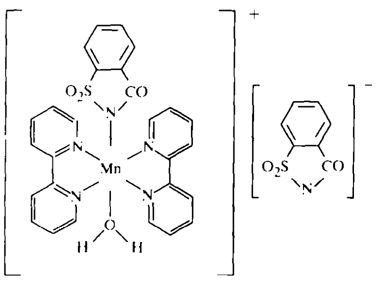
(*Received 19 February 1998; accepted 20 October 1998*)

Abstract

The structure of the title compound, aqua[1,2-benzisothiazol-3(2*H*)-onato 1,1-dioxide-*N*]bis(2,2′-bipyridine-*N*,*N*′)manganese(II) 1,2-benzisothiazol-3(2*H*)-onate 1,1-dioxide, [Mn($C_7H_4NSO_3$)($C_{10}H_8N_2$)$_2$(H_2O)]($C_7H_4NSO_3$), consists of [Mn(bipy)$_2$(sac)(H$_2$O)]$^+$ cations (bipy = 2,2′-bipyridine; sac = saccharinate, $C_7H_4NO_3S$) and non-coordinated saccharinate (sac$^-$) anions. The Mn^{II} ion constitutes the centre of a slightly distorted octahedron, with the water molecule hydrogen bonded to the N atom in the saccharinate counter-ion.

Comment

1,2-Benzisothiazol-3(2*H*)-one 1,1-dioxide, commonly known as saccharin, is widely used as a sweetening agent (Haider *et al.*, 1985). Research on the crystal structures of metal saccharinate (sac) complexes has been very extensive in the last 15 years, partly due to their potential effectiveness in biological systems (Haider *et al.*, 1983; Li *et al.*, 1991; Zhang, 1994). The synthesis and crystal structures of the metal complexes [*M*(sac)$_2$(H$_2$O)$_4$]·2H$_2$O, with *M* = Fe, Co, Ni (Haider *et al.*, 1983), Cu (Haider *et al.*, 1983; Ahmed *et al.*, 1981), Mn (Kamenar & Jovanovski, 1982), Zn, Cd (Haider *et al.*, 1984), Cr (Cotton *et al.*, 1984) or V (Cotton *et al.*, 1986), have all been reported. More recently, several structures have been described for various related species also containing bidentate pyridine ligands, such as 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen). These include examples where all the saccharinate ligands are attached to the metal {[Hg(bipy)(sac)$_2$]; Hergold-Brundić *et al.*, 1989}, where they are present simply as the counter-ion {[Cu*L*(bipy)]sac·2H$_2$O (*L* = 2-formylpyridine thiosemicarbazonate) (Ainscough *et al.*, 1990), [Mn(H$_2$O)$_2$phen$_2$]sac$_2$·H$_2$O (Li, Chen *et al.*, 1993) and [Fe(phen)$_3$]sac$_2$·4H$_2$O (Li, Wei *et al.*, 1993)} or, for some Cu complexes only, where they occur in both the cation and anion {[Cu(bipy)$_2$(sac)]sac·3H$_2$O (Li *et al.*, 1991), [Cu(bipy)$_2$(sac)]sac·2H$_2$O (Hergold-Brundić *et al.*, 1991) and [Cu(phen)$_2$(sac)]sac·2H$_2$O (Zhang *et al.*, 1994)}. These last three complexes all exhibit distorted five-coordinate trigonal-bipyramidal structures for the cations. The title compound, (I), is the first manganese(II) compound with the saccharinate ligand present both in the complex cation and as the counter-ion.



(I)

The structure of the complex consists of cation chains composed of [Mn(bipy)$_2$(sac)(H$_2$O)]$^+$ units, and non-coordinated saccharinate anions. One of the independent structural units is shown in Fig. 1, together with the atom-numbering scheme. In the cation, the Mn—N$_{bipy}$ average bond length is 2.259 (9) Å, with one of the bipy ligands (coordinating through N2 and N3) exhibiting rather more asymmetry in these bonds than the other. The Mn—N$_{sac}$ bond length of 2.228 (4) Å compares with 2.281 (1) Å in [Mn(sac)$_2$(H$_2$O)$_4$]·2H$_2$O (Kamenar & Jovanovski, 1982). Bond angles about Mn clearly show some distortion from idealized octahedral geometry [N5—Mn—O7 163.11 (14), N1—Mn—N3 168.06 (14) and N2—Mn—N4 168.69 (14)°], probably as a consequence of the steric restrictions imposed by the bipy chelate rings. The water molecule which completes the coordination about Mn appears to participate in hydrogen bonding to the N atom of the corresponding saccharinate anion (Fig. 1), with an N···H distance of 1.77 (5) Å. Even so, the Mn—O length of 2.127 (3) Å is significantly shorter than