THE STRUCTURE OF BIS(ISOPROPYLXANTHATO)NICKEL(II)

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The structure of $[Ni(i\text{-}PrXa)_2]$ (i-Pr = i-C_3H_7, Xa = S_2CO^-) was solved by the heavy-atom method and refined anisotropically to $R = 0.044$ for 985 unique observed reflections. The compound crystallizes in the $P2_1/c$ space group with $a = 8.879(2)$, $b = 6.086(1)$, $c = 13.203(3)$ Å, $\beta = 94.74(3)°$, $V = 711.0(3)$ Å^3, $T = 296$ K, $Z = 2$. The molecule contains the NiS_4 chromophore with an approximately planar configuration of the four sulfur atoms around the Ni(II). The Ni atom is located in the centre of symmetry.

The structures of $[Ni(EtXa)_2]$ (Et = C_2H_5, Xa = S_2CO^-) (ref.[1]) and $[Ni(n\text{-}BuXa)_2]$ (n-Bu = n-C_4H_9) (ref.[2]) have been solved. Solution of the structure of $[Ni(i\text{-}PrXa)_2]$ (i-Pr = i-C_3H_7) is the subject of this paper.

EXPERIMENTAL

The complex studied was prepared by reacting $KS_2COi\text{-}C_3H_7$ with $NiCl_2 . 6 H_2O$ (molar ratio 2 : 1) in a mixture of 2-propanol and water. Crystals for X-ray structure analysis were obtained by recrystallization from 2-propanol. Density was determined pycnometrically in an aqueous solution of KI at 23 °C. For $C_8H_{14}NiO_2S_4$ (329.1) calculated: 29.19% C, 4.29% H, 17.84% Ni; found: 28.43% C, 4.53% H, 17.73% Ni.

Preliminary lattice parameters and the space group were determined from Weissenberg photographs. The structure was solved by the heavy-atom method. The F^2 values of all atoms except hydrogens were refined anisotropically by the block-diagonal least-squares procedure. The hydrogen atoms were fixed in the calculated positions and refined isotropically. Application of absorption did not lead to reduction of the *R*-factor and therefore was neglected.

Data collection and structure refinement parameters are summarized in Table I.

RESULTS AND DISCUSSION

Crystals of the compound studied are monoclinic, space group $P2_1/c$ with $a = 8.879(2)$, $b = 6.086(1)$, $c = 13.203(3)$ Å, $\beta = 94.74(3)°$, $V = 711.0(3)$ Å^3, $Z = 2$, $D_m = 1.55$ g cm^{-3}, $D_c = 1.537$ g cm^{-3}, $\mu = 7.24$ mm^{-1}, $F(000) = 340$.

The final atomic coordinates and equivalent isotropic displacement factors of the non-hydrogen atoms are given in Table II. Selected interatomic distances and angles are listed in Table III. The structure is shown in Fig. 1.

The structure is composed of isolated molecules, no evidence of H-bonding was found. The Ni atom which occupies the centre of symmetry is coordinated by four S atoms from two molecules of the ligand in a slightly distorted square-planar arrangement.

While the bond distances Ni–S1 (2.214 Å) and Ni–S2 (2.197 Å) of the complex studied are not very different, the angles S1–Ni–S2 (79.35°) and S1–Ni–S2a (100.65°) differ appreciably, in agreement with refs[1,2].

The deviations of the Ni, S1, S2, C1, O1, C2, C3 and C4 atoms from the "ideal" plane formed by the Ni–S1–S2–C1 atoms are 0.0080, –0.0112, –0.0113, 0.0144, 0.0387, 0.0856, –0.5495 and 1.5051 Å, respectively. This group of atoms deviates sig-

TABLE I
Data collection and structure refinement parameters

Crystal dimensions	0.55 × 0.40 × 0.20 mm
Diffractometer and radiation used	KUMA KM-4, λ(CuKα) = 1.54178 Å
Scan technique	$\omega - 2\theta$
Number and 2θ range of reflections for lattice parameters refinement	25, 78 → 90°, λ(CuKα_1) = 1.54056 Å
Range of *h*, *k* and *l*	–11 → 11, 0 → 7, 0 → 16
Standard reflections and their intenzity fluctuation	2 after every 50 measured, –4%
Total number of reflections measured, 2θ range	1 663, 4 → 163°
Number of unique observed reflections	985
Criterion for observed reflections	$I > 2\,\sigma(I)$
Value of R_{int}	0.025
Function minimized	$\sum w\,(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Weighting scheme	$w = [\sigma^2\,(F_o) + 0.02\,F_o^2]^{-1}$
Parameters refined	98
Values of *R*, *wR* and *S*	0.044, 0.050 and 1.71
Ratio of max. LS shift to e.s.d. (Δ/σ)	0.01
Max. and min. heights in final $\Delta\rho$ map	1.4; –1.4 e Å^{-3}
Source of atomic scattering factors	SDS System (ref.[4])
Programs used	SHELXS86 (ref.[3]), SDS System (ref.[4]), ORTEP (ref.[5])
Computer used	PC AT 386, 486

nificantly from planarity; the sum of the $(D/S)^2$ values for the Ni–S1–S2–C1 atoms is 220.083, the χ^2 value at the 95% probability level is 3.84.

The O1–C1 distance (1.289 Å) is significantly shorter than the O1–C2 distance (1.482 Å). This fact has also been observed for the $[Ni(EtXa)_2]$ and $[Ni(n\text{-}BuXa)_2]$ complexes[1,2] and has been attributed to a partial increase in the multiplicity of the O1–C1 bond in comparison with the O1–C2 bond. Weak bond interactions have been found in the rhomboedric complex $[Ni(EtXa)_2]$ between the Ni atom and the sulfur

TABLE II
Fractional coordinates of the non-hydrogen atoms (. 10^4) and B_{eq} values with e.s.d.'s in parentheses. $B_{eq} = [B_{22} + (B_{11} + B_{33} + B_{13} \cos \beta)/\sin^2 \beta]/3$

Atom	*x*	*y*	*z*	B_{eq}, Å^2
Ni	0	0	0	5.73(2)
S1	–310(1)	2113(1)	–1366.5(4)	6.61(2)
S2	–1928(1)	–1637(1)	–834.9(4)	7.50(2)
O1	–2709(2)	468(3)	–2498(1)	6.3(1)
C1	–1770(2)	400(4)	–1700(2)	5.7(1)
C2	–2613(2)	2250(4)	–3255(2)	6.3(1)
C3	–3281(5)	1266(7)	–4239(2)	9.2(1)
C4	–3473(4)	4205(7)	–2934(3)	8.9(1)

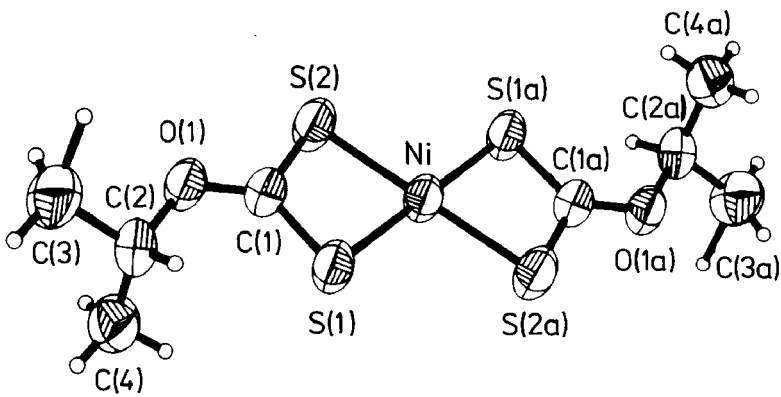

FIG. 1
A perspective view of $[Ni(i\text{-}PrXa)_2]$. The non-hydrogen atoms are represented by thermal ellipsoids at 50% probability level

atoms of the neighbouring molecules (Ni–S = 3.448 Å), whereby the coordination is completed to octahedral. Such interaction, however, was not observed in the monoclinic [Ni(i-PrXa)$_2$] complex.

TABLE III
Selected interatomic distances (Å) and angles (deg)

Atoms	Distances	Atoms	Angles
Ni–S1	2.214(1)	S1–Ni–S2	79.35(2)
Ni–S2	2.197(1)	Ni–S1–C1	83.99(8)
S1–C1	1.693(2)	Ni–S2–C1	84.39(7)
S2–C1	1.699(2)	S1–Ni–S2a	100.65(2)
O1–C1	1.289(3)	S1–C1–O1	128.5(2)
O1–C2	1.482(3)	S2–C1–O1	119.3(2)
C2–C3	1.507(4)	C1–O1–C2	120.4(2)
C2–C4	1.494(5)	S1–C1–S2	112.2(1)
		O1–C2–C3	104.5(2)
		O1–C2–C4	109.4(2)

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