

Bis(ethylmethyldithiophosphinato)nickel(II)

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Abstract. $[\text{Ni}(\text{C}_3\text{H}_8\text{PS}_2)_2]$, $\text{C}_6\text{H}_{16}\text{NiP}_2\text{S}_4$, monoclinic, $C2/m$, $Z = 2$, $M_r = 337.1$, $a = 11.817(2)$, $b = 9.058(2)$, $c = 6.826(1)$ Å, $\beta = 104.51(1)^\circ$, $D_m = 1.59$, $D_x = 1.58$ Mg m $^{-3}$, $\mu(\text{Mo } K\alpha) = 2.11$ mm $^{-1}$, $R = 0.036$. The molecule reveals point symmetry $2/m$, the ethyl and methyl groups being *trans* with respect to the plane of the four-coordinated Ni atom.

Introduction. The title compound is related to a Ni^{II} complex reported recently (Wunderlich & Wussow, 1979). Introductory remarks concerning dithiophosphinato and dithiophosphato complexes of Ni^{II} of the type $\text{Ni}(\text{S}_2\text{PR}^1\text{R}^2)$ are given in the same paper. A review of these complexes was given by Wasson, Woltermann & Stoklosa (1973). The preparation of the title compound was reported by Diemert & Kuchen (1977), who also supplied a sample for the structure determination. Blue needles limited by only six faces, indexed (210), (120), (210), (120), (201), and (201), were grown from 2-propanol. The crystals tend to be twinned but this can be recognized optically. Systematic absences yielded three possible space groups: $C2$, Cm , and $C2/m$ which with $Z = 2$ require point symmetries of the complex 2 , m , and $2/m$. From model considerations all three symmetries are possible. The refinement of the structure confirmed $C2/m$.

The intensities of all symmetry-independent reflections with $2 \leq 2\theta \leq 70^\circ$ were measured on an automated diffractometer (Syntex P2₁) with Mo $K\alpha$ radiation, a crystal monochromator, and an ω -scan technique. The set of data contained 1636 reflections of which 1104 were classified as observed ($I \geq 1.96\sigma_I$). The phase problem was solved by the Patterson function; the structure, including all H atoms with isotropic temperature factors, was refined (56 variables) to $R = 0.036$ (0.061) and $R_w = 0.033$ (0.036) for the observed (all) reflections. Weights were derived from counter statistics by $1/w = \sigma_F^2 + 0.0001F^2$. Scattering factors were taken from Cromer & Waber (1974), those of Ni being corrected for anomalous dispersion. Because of the low R obtained no further refinement was attempted in the space groups of lower symmetry. All calculations were performed with the

Table 1. Positional parameters with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Ni	0	0	0
S	0.10182 (4)	0.17107 (5)	0.20677 (7)
P	0.18867 (6)	0	0.36378 (10)
C(1)	0.3429 (3)	0	0.3726 (5)
C(2)	0.1830 (4)	0	0.6243 (5)
C(3)	0.3712 (4)	0	0.1682 (6)
H(1)	0.374 (2)	0.085 (3)	0.449 (4)
H(2)	0.221 (2)	−0.077 (3)	0.690 (4)
H(3)	0.106 (4)	0	0.623 (7)
H(4)	0.457 (5)	0	0.181 (7)
H(5)	0.340 (2)	0.086 (3)	0.105 (4)

system EXTL (Syntex) on an Eclipse computer (Data General). Table 1 contains the final parameters.*

Discussion. The molecule shows a *trans* configuration with the Ni atom at a $2/m$ position. The mirror plane is occupied by the Ni and P atoms, and the ethyl as well as the methyl group. Fig. 1 shows all bond lengths and angles between non-hydrogen atoms. The geometry of the H atoms is in the expected range and is not reported. Because of the symmetry, the Ni atom is coplanar with the four adjacent S atoms in an almost perfect square. The geometry of the central NiS_4P_2 group is in agreement with similar Ni^{II} complexes. Bis(diethyldithiophosphinato)nickel(II) (Shetty & Fernando, 1969) reveals the same point symmetry; however, the mirror plane is occupied by the Ni, S and P atoms. With respect to the unequal substituents at the P atom, this arrangement of the mirror plane is impossible in the present structure. The distances Ni—S of 2.234 and S—P of 2.013 Å are in the usual range for comparable structures except one short Ni—S distance of 2.212 Å in a Ni^{II} complex of ethyldithiophosphonic

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34957 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

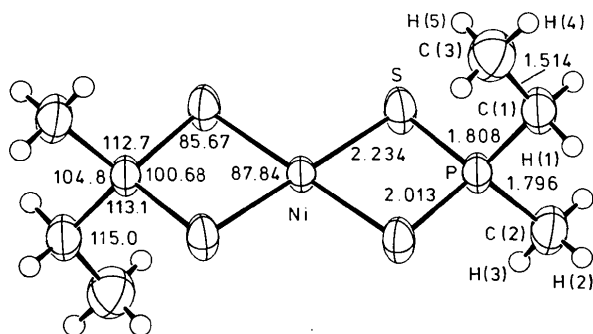


Fig. 1. Molecule of $[\text{Ni}(\text{C}_3\text{H}_8\text{PS}_2)_2]$ in arbitrary crystallographic orientation with thermal ellipsoids at 50% probability (ORTEP II; Johnson, 1976), bond lengths (Å), and bond angles ($^\circ$). Values not given are related by the point symmetry $2/m$ of the molecule. H atoms are shown with radii of 1.0 \AA^2 . The e.s.d.'s are: Ni-S, S-P 0.001; P-C 0.003; C-C 0.005 Å; angles in the four-membered ring 0.02–0.03; other angles 0.1–0.2 $^\circ$.

acid (Arora, Hayes & Fernando, 1978). The P atom is 0.1 Å out of the NiS_4 plane and reduces the distance between Ni and the ethyl group. The tetrahedral

configuration around the P atom is distorted (Fig. 1). The ethyl group shows the expected staggered conformation.

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{2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene}nickel(II) Monohydrate Diperchlorate (β Form)

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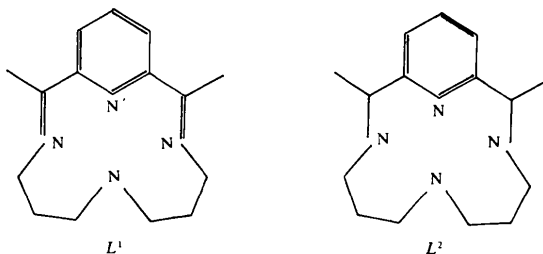
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Abstract. $\text{C}_{15}\text{H}_{26}\text{N}_4\text{Ni}^{2+} \cdot 2\text{ClO}_4^- \cdot \text{H}_2\text{O}$, $[\text{Ni}(\text{C}_{15}\text{H}_{26}\text{N}_4)](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, $M_r = 538$, triclinic, $P\bar{1}$, $a = 9.230$ (8), $b = 8.768$ (9), $c = 14.734$ (13) Å, $\alpha = 112.5$ (1), $\beta = 87.7$ (1), $\gamma = 93.7$ (1) $^\circ$, $U = 1099 \text{ \AA}^3$, $Z = 2$, $D_m = 1.61$ (2), $D_c = 1.62 \text{ Mg m}^{-3}$, $F(000) = 560$. Mo $K\alpha$ radiation $\lambda = 0.7107 \text{ \AA}$, $\mu = 1.18 \text{ mm}^{-1}$. The Ni atom in the complex occupies an approximately square-planar environment [Ni–N 1.95 (1), 1.82 (1), 1.95 (1), 1.95 (1) Å]. In axial positions there are two perchlorate O atoms at 2.78 (2) and 3.29 (2) Å. 2306 independent reflections above background have been refined to $R = 0.077$.

Introduction. The condensation of 2,6-diacetylpyridine with 3,3'-diaminopropylamine in the presence of nickel(II) salts produces the macrocyclic complex

$[\text{NiL}^1]^{2+}$ which was first isolated as the perchlorate salt (Curry & Busch, 1964). Reduction of $[\text{NiL}^1]^{2+}$ under mild conditions gave rise to $[\text{NiL}^2]^{2+}$ (Karn & Busch, 1969). Two forms of this latter cation were isolated, namely a red β form and a yellow α form in the ratio of ca 10:1. Stereochemical considerations and the properties of the derivatives formed indicated that the β form had the *meso* structure. The structure of the α form has



† Deceased.

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