

Table 3. *Hydrogen bonds*

$Y \cdots H-X$ type	$Y \cdots H(\text{\AA})$	$Y \cdots X(\text{\AA})$	$Y \cdots H-X(^{\circ})$
O(2) \cdots H(10 ^m)—N(4 ^m)	2.409	2.911	112.8
O(3) \cdots H(14 ^m)—N(6 ^m)	2.359	3.021	126.4
O(5) \cdots H(10 ^m)—N(4 ^m)	2.050	2.947	156.8
O(6) \cdots H(15 ^m)—N(6 ^m)	2.380	2.953	118.6

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $1/2-x, 1/2+y, 1/2-z$; (iii) $x, y-1, z$; (iv) $-1/2+x, -1/2-y, -1/2+z$. Primed atoms are related by the symmetry center.

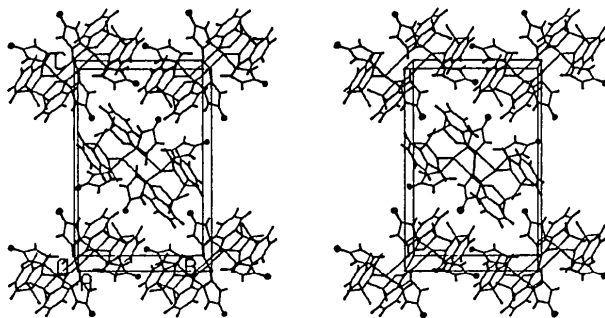


Fig. 2. Packing of the title compound in the unit cell along the a axis.

The two imidazole planes and the eight-membered-ring plane are nearly perpendicular to each other, the values of the dihedral angles being 86.7 (2), 85.8 (3) and 87.7 (2).

As can be seen in Table 3, there are two intermolecular three-center hydrogen bonds between the N—H from the imidazole group and the pair of sulfonyl O atoms of the saccharin ligand. The H atoms involved in these interactions are marked with filled circles in Fig. 2.

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Structure of a Five-Coordinated Nickel Complex: $[\text{Ni}\{(\text{C}_2\text{H}_5\text{O})_2\text{PS}_2\}_2\text{P}(\text{C}_6\text{H}_5)_3]$

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Abstract. Bis(*O,O'*-diethyl dithiophosphato)(triphenylphosphine)nickel(II), $[\text{Ni}(\text{C}_4\text{H}_{10}\text{O}_2\text{PS}_2)_2\text{P}(\text{C}_6\text{H}_5)_3]$, $M_r = 691.45$, triclinic, $P\bar{1}$, $a = 12.985$ (2), $b = 13.748$ (2), $c = 9.389$ (1) Å, $\alpha = 99.58$ (1), $\beta = 99.10$ (1), $\gamma = 84.12$ (1)°, $V = 1627.0$ Å³, $Z = 2$, $D_x = 1.41$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 10.18$ cm⁻¹, $F(000) = 720$, $T = 295$ K, final $R = 0.062$ for 5040 unique observations. The Ni atom in this molecule is coordinated by four

S atoms and one P atom, forming a square pyramid. The triphenylphosphine moiety is planar.

Introduction. $[\text{Ni}\{(\text{RO})_2\text{PS}_2\}_2]$ complexes have attracted broad attention in the study of high fungicidal and bacteriological activity (Livingstone & Mihkelson, 1970). Recently we have studied some reactions of $[\text{Ni}\{(\text{RO})_2\text{PS}_2\}_2]$ and the crystal structures of some adducts (You, Xu, Yu, Liu & Lin, 1986; Liu, Lin, Xu, Yu & You, 1987; Lin, Liu, Xu, Lin & You, 1987; Liu, Lin, Xu, Lin, Yu & You,

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Table 1. Atomic coordinates and equivalent isotropic temperature factors

$$B_{\text{eq}} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2abc\cos\gamma)\beta_{12} + (2accos\beta)\beta_{13} + (2bccos\alpha)\beta_{23}]$$

	x	y	z	B _{eq} (Å ²)
Ni	-0.18385 (5)	0.21358 (4)	0.19286 (6)	3.29 (2)
S(1)	-0.0797 (1)	0.2966 (1)	0.4086 (1)	4.64 (6)
S(2)	-0.0424 (1)	0.2478 (2)	0.0779 (2)	6.77 (9)
S(3)	-0.2505 (1)	0.1168 (1)	0.3420 (2)	5.26 (7)
S(4)	-0.2371 (2)	0.0788 (1)	0.0002 (2)	6.68 (9)
P(1)	0.0251 (1)	0.2940 (1)	0.2774 (2)	4.55 (6)
P(2)	-0.2573 (1)	0.0158 (1)	0.1652 (2)	5.36 (7)
P(3)	-0.31513 (9)	0.33143 (9)	0.1169 (1)	2.82 (4)
O(1)	0.1302 (3)	0.2311 (3)	0.3240 (5)	6.1 (2)
O(2)	0.0794 (3)	0.3926 (4)	0.2904 (5)	6.5 (2)
O(3)	-0.1764 (4)	-0.0768 (3)	0.1895 (6)	7.8 (3)
O(4)	-0.3635 (4)	-0.0340 (4)	0.1236 (7)	8.5 (3)
C(1)	0.1342 (7)	0.1273 (6)	0.309 (1)	9.0 (4)
C(2)	0.2336 (7)	0.0873 (6)	0.388 (1)	8.3 (4)
C(3)	0.0177 (5)	0.4842 (6)	0.265 (1)	7.3 (4)
C(4)	0.0851 (7)	0.5465 (6)	0.214 (1)	8.7 (5)
C(5)	-0.0624 (7)	-0.0609 (7)	0.218 (1)	9.9 (5)
C(6)	-0.0072 (8)	-0.1394 (9)	0.293 (1)	10.4 (6)
C(7)	-0.402 (1)	-0.0880 (8)	0.220 (1)	10.6 (6)
C(8)	-0.498 (1)	-0.041 (1)	0.263 (1)	12.5 (8)
C(11)	-0.4399 (3)	0.3292 (3)	0.1831 (5)	3.1 (2)
C(12)	-0.4895 (4)	0.4124 (4)	0.2555 (6)	4.2 (2)
C(13)	-0.5867 (4)	0.4052 (5)	0.3013 (7)	5.5 (3)
C(14)	-0.6315 (4)	0.3173 (6)	0.2721 (7)	5.6 (3)
C(15)	-0.5825 (5)	0.2337 (5)	0.1991 (8)	5.7 (3)
C(16)	-0.4851 (4)	0.2390 (4)	0.1558 (6)	4.5 (2)
C(21)	-0.2823 (3)	0.4586 (3)	0.1690 (5)	3.1 (2)
C(22)	-0.2809 (4)	0.5206 (4)	0.0648 (6)	4.5 (2)
C(23)	-0.2516 (5)	0.6186 (5)	0.1107 (9)	6.1 (3)
C(24)	-0.2259 (5)	0.6539 (5)	0.2554 (9)	6.0 (3)
C(25)	-0.2266 (4)	0.5929 (5)	0.3596 (8)	5.7 (3)
C(26)	-0.2552 (4)	0.4942 (4)	0.3173 (6)	4.4 (2)
C(31)	-0.3518 (3)	0.3166 (3)	-0.0811 (5)	3.0 (2)
C(32)	-0.4549 (4)	0.3321 (4)	-0.1460 (5)	3.9 (2)
C(33)	-0.4800 (4)	0.3188 (5)	-0.2978 (6)	4.8 (2)
C(34)	-0.4010 (5)	0.2903 (5)	-0.3851 (6)	5.0 (3)
C(35)	-0.2989 (5)	0.2772 (5)	-0.3215 (6)	5.2 (3)
C(36)	-0.2739 (4)	0.2886 (5)	-0.1682 (5)	4.5 (2)

Table 2. Bond distances (Å) and angles (°)

Ni—S(1)	2.433 (2)	O(4)—C(7)	1.44 (1)
Ni—S(4)	2.436 (2)	C(5)—C(6)	1.45 (1)
S(2)—P(1)	1.969 (2)	P(3)—C(21)	1.811 (5)
P(1)—O(1)	1.580 (4)	C(31)—C(32)	1.391 (6)
P(2)—O(4)	1.568 (5)	C(34)—C(35)	1.373 (8)
O(3)—C(5)	1.49 (1)	Ni—S(3)	2.391 (2)
C(3)—C(4)	1.47 (1)	S(1)—P(1)	1.969 (2)
P(3)—C(11)	1.829 (4)	S(4)—P(2)	1.960 (3)
C(31)—C(36)	1.384 (7)	P(2)—O(3)	1.588 (5)
C(33)—C(34)	1.399 (8)	O(2)—C(3)	1.455 (8)
Ni—S(2)	2.395 (2)	C(1)—C(2)	1.48 (1)
Ni—P(3)	2.340 (1)	C(7)—C(8)	1.42 (1)
S(3)—P(2)	1.977 (2)	P(3)—C(31)	1.827 (4)
P(1)—O(2)	1.569 (5)	C(32)—C(33)	1.396 (7)
O(1)—C(1)	1.41 (1)	C(35)—C(36)	1.410 (7)
S(1)—Ni—S(2)	82.06 (6)	S(3)—Ni—S(4)	82.86 (6)
S(1)—Ni—S(4)	157.52 (6)	S(1)—Ni—S(3)	89.76 (5)
S(2)—Ni—S(3)	149.26 (7)	S(2)—Ni—S(4)	93.50 (7)
P(3)—Ni—S(1)	106.22 (5)	P(3)—Ni—S(2)	101.46 (6)
P(3)—Ni—S(3)	109.27 (6)	P(3)—Ni—S(4)	96.26 (6)
Ni—S(1)—P(1)	84.39 (7)	Ni—S(3)—P(2)	83.73 (8)
S(1)—P(1)—O(2)	107.16 (9)	S(1)—P(1)—O(2)	115.6 (2)
S(2)—P(1)—O(1)	113.4 (2)	O(1)—P(1)—O(2)	94.3 (2)
P(1)—O(1)—C(1)	121.1 (4)	P(1)—O(2)—C(3)	120.7 (4)
O(1)—C(1)—C(2)	110.8 (7)	O(2)—C(3)—C(4)	107.5 (6)
Ni—P(3)—C(21)	114.8 (1)	Ni—P(3)—C(31)	113.2 (1)
C(11)—P(3)—C(21)	104.4 (2)	C(21)—P(3)—C(31)	104.8 (2)
P(3)—C(11)—C(12)	122.6 (4)	P(3)—C(11)—C(16)	117.6 (4)
C(12)—C(11)—C(16)	120.4 (4)	C(11)—C(12)—C(13)	119.3 (5)
C(12)—C(13)—C(14)	120.1 (6)	C(13)—C(14)—C(15)	120.9 (5)
C(14)—C(15)—C(16)	119.7 (6)	C(11)—C(16)—C(15)	119.5 (5)

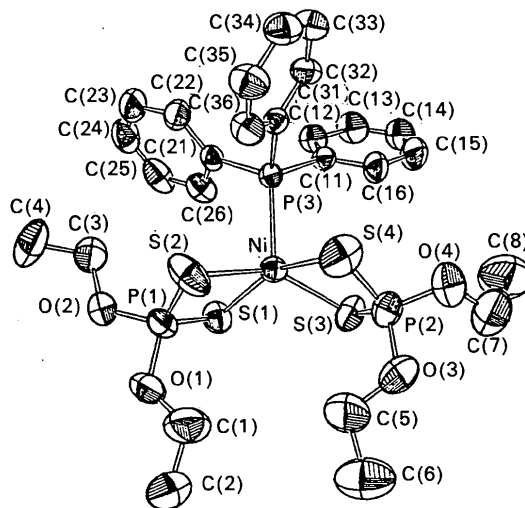


Fig. 1. ORTEP view of the title complex showing the atom numbering and thermal motion ellipsoids (30%).

1990; You, Xu, Xu, Lin, Yu, Lin & Liu, 1990). However, in these complexes the Ni atom has square-planar or octahedral coordination. We now report the crystal structure of [Ni{(C₂H₅O)₂PS₂]₂·PPh₃, in which the Ni atom has a square-pyramidal coordination.

Experimental. Dark-green prismatic crystals were grown from acetone solution. Accurate cell dimensions and crystal orientation matrix determined on an AFC5R diffractometer by a least-squares treatment of the setting angles of 20 reflections in the range $10 < \theta < 15^\circ$, crystal dimensions $0.38 \times 0.42 \times 0.53$ mm; intensities of reflections with indices $h00$ to 17, $k-18$ to 18, $l-12$ to 12 with $2\theta < 55^\circ$ measured; $\omega-2\theta$ scans; ω scan width $(1.470 + 0.400\tan\theta)^\circ$, graphite-monochromatized Mo $K\alpha$ radiation. Intensities of three reflections measured every 200 reflections showed no evidence of crystal decay. 7845 reflections measured, 7514 unique, 5040 with $I \geq 3\sigma(I)$ labelled observed and used in structure solution and refinement; $R_{\text{int}} = 0.029$. Data corrected for Lorentz factor, polarization factor and absorption effects (max. and min. transmission factors 1.327 and 0.722). Gaussian integration grid $6 \times 6 \times 6$.

The crystal structure was solved by the heavy-atom method. Refinement was by full-matrix least-squares calculations, initially with isotropic and then with anisotropic thermal parameters. H atoms not refined. The final cycle of refinement included 343 variable parameters, $R = 0.062$, $wR = 0.083$, goodness-of-fit = 2.24, $w = 1/\sigma^2(F_o)$. Max. shift/e.s.d. = 0.03, density in final difference map ± 0.59 e Å⁻³; no chemically significant features. Scattering factors and anomalous-dispersion corrections of non-H atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations

were performed on a MicroVAX II computer using *TEXSAN* software package (Molecular Structure Corporation, 1985). Atomic coordinates and details of molecular geometry are given in Tables 1 and 2. Fig. 1 is a view of the molecule prepared using *TEXSAN*.*

Discussion. The Ni atom in this crystal has a distorted square-pyramidal coordination with four S atoms of the two diethyldithiophosphates in the square plane and one P atom of triphenylphosphine at the apex; the Ni atom is 0.549 Å above the basal plane of the four S atoms. The lengths of the Ni—S bonds are in the range 2.391 (2) to 2.436 (2) Å, the chelate angles S—Ni—S are 82.06 (6) and 82.86 (6)°. The Ni—S distances are intermediate between four-coordinated Ni complexes (Lin *et al.*, 1987; McConnell & Kastalsky, 1967) and six-coordinated Ni complexes (You *et al.*, 1986; Liu *et al.*, 1987; Liu

et al., 1990; You *et al.*, 1990; Ooi & Fernando, 1967).

In the triphenylphosphine, the P atom is in the three phenyl ring planes; the deviations of C atoms in the same ring from the ring plane are less than 0.014 Å. The dihedral angles between the basal plane consisting of the four S atoms and each of the three phenyl rings are 129.6, 145.2 and 125.7°, respectively.

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* Lists of structure factors, anisotropic thermal parameters, full bond distances and angles not including H atoms, least-squares planes, and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52970 (41 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structures of *cis*- and *trans*-Dichlorodioxobis(triphenylphosphine oxide)-uranium(VI)

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Abstract. *cis*-[UO₂Cl₂(tppo)₂], [UCl₂O₂(C₁₈H₁₅OP)₂]₂, (1), $M_r = 897.52$, monoclinic, $C2/c$, $a = 17.233$ (3), $b = 12.112$ (2), $c = 17.085$ (4) Å, $\beta = 105.90$ (2)°, $V = 3429.7$ Å³, $Z = 4$, $D_x = 1.737$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 47.64$ cm⁻¹, $F(000) = 1736$, $T = 293$ K, $R = 0.040$ for 2855 observed reflections with $I > 3\sigma(I)$. *trans*-[UO₂Cl₂(tppo)₂], [UCl₂O₂(C₁₈H₁₅OP)₂]₂, (2), $M_r = 897.52$, monoclinic, $B2_1$, $a = 10.158$ (11), $b = 18.849$ (17), $c = 19.139$ (14) Å, $\beta = 90.4$ (1)°, $V = 3664.4$ Å³, $Z = 4$, $D_x = 1.638$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 44.74$ cm⁻¹, $F(000) = 1736$, $T = 293$ K, $R = 0.042$ for 2603 observed

reflections with $I > 3\sigma(I)$. In both forms the complex has a distorted octahedral arrangement about the U atom.

Introduction. The uranium(VI) compounds [UO₂X₂(OPR₃)₂] ($X = \text{Cl or Br}$; $R = \text{Me, Et or Ph}$) have been reported (Gans & Smith, 1964) and further studies have included the iodo compound ($X = \text{I}$) (Day & Venanzi, 1966). The compounds were expected to show a near linear arrangement of the uranyl (O—U—O) bonds with the remaining atoms or ligands in the equatorial plane. This allows for *cis* or