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Structure of the Adduct of Bis(*O,O'*-dibutyldithiophosphato)nickel(II) with Imidazole

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Abstract. $[Ni\{(C_4H_9O)_2PS_2\}_2(C_3H_4N_2)_2]$, $M_r = 677{\cdot}53$, monoclinic, $P2_1/n$, $a = 12{\cdot}770\,(0)$, $b = 16{\cdot}756\,(3)$, $c = 17{\cdot}135\,(0)$ Å, $\beta = 111{\cdot}67\,(3)°$, $V = 3407{\cdot}3$ Å^3, $Z = 4$, $D_x = 1{\cdot}321$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 9{\cdot}299$ cm^{-1}, $T = 295$ K, $F(000) = 1432$, $R = 0{\cdot}053$ and $wR = 0{\cdot}061$ for 3284 reflections. The title complex is composed of a distorted octahedron with two imidazole groups in *cis* positions. The planes S(1)S(3)N(1)N(3), NiS(1)S(2)P(1) and NiS(3)S(4)P(2) are nearly mutually perpendicular.

Introduction. Esters of dithiophosphoric acid and its metal chelates show insecticidal, rodenticidal, and fungicidal activities which are believed primarily to result from enzyme inhibition. Salts of the type $[PR_4][(RO)_2PS_2]$ have also been found to display fungicidal and bacteriological activity (Rüfenacht, 1968; Livingstone & Mihkelson, 1970).

A series chelates of phosphate derivatives has been reported (You, Xu, Yu, Liu & Lin, 1986; Liu, Lin, Xu, Yu & You, 1987). Metal chelates in which the metal ion is coordinatively unsaturated can act as Lewis acids (electron acceptors) and form adducts with neutral Lewis bases (electron donors). The physical properties of the chelates and the inability to form adducts with nitrogen heterocycles are influenced by the group *R* of the dialkyldithiophosphate (dtp) ligand. Some attempts have been made to determine the structures of such adducts by overcoming the difficulties in isolating them and their instability in air. In this paper, we report the crystal structure of the title complex.

Experimental. The preparation of $Ni[(C_4H_9O)_2PS_2]_2$ followed the method of You, Xu, Yu, Liu & Lin (1986) and that of Chamberlain & Drago (1979) for the octyl derivative. The resulting purple liquid was identified by its characteristic infrared bands and elemental analysis.

The nickel complex was dissolved in ethanol and imidazole was added dropwise until the solution colour changed from purple to green. The solution was evaporated at room temperature to give green column-shaped crystals. The molecular structure proposed is consistent with elemental anlysis: Calc: C39·00%, H6·55%, N8·27%; Expt: C38·85%, H 6·28%, N8·17%.

A small crystal with dimensions 0·25 × 0·32 × 0·60 mm was selected for data collection. The crystal was coated with a thin layer of paraffin wax to prevent the loss of imidazole. Unit-cell dimensions from measurements of 25 strong reflections in the range $14 < \theta < 18°$.

The intensities of 5371 reflections were obtained on a CAD-4 four-circle diffractometer with Mo $K\alpha$ radiation in the range $1 < \theta < 27°$, in ω–2θ scan mode, of which 3284 unique reflections with $I > 3\sigma(I)$ were used in the structure determination and refinement. *hkl* ranges: *h* − 15 to 14; *k* 0 to 19; *l* 0 to 20. Lp corrections and an empirical absorption correction were applied (transmission factors 0·93–0·99). The structure was solved by the heavy-atom method and refined by a full-matrix least-squares procedure with anisotropic temperature factors. The H atoms were included in idealized positions. Final refinement on *F*, 334 parameters, largest shift/error 0·06. A weighting scheme of the form $w = 4F_o^2/[\sigma^2(F_o^2)]^2$ was used. Final $R = 0{\cdot}053$ and $wR = 0{\cdot}061$. The maximum positive and maximum negative electron densities are 0·606 and $-0{\cdot}275$ e Å^{-3} respectively. Computer program used was *SDP* (B. A. Frenz & Associates Inc., 1985). The scattering factors were from *International Tables for X-ray cyrstallography* (1974). Table 1 gives the atomic coordinates and thermal parameters. The

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Table 1. *Atomic coordinates and thermal parameters*

	x	*y*	*z*	B_{eq}(Å^2)
Ni	0·23709 (5)	0·21599 (4)	0·19108 (4)	5·21 (2)
S1	0·3124 (1)	0·11022 (9)	0·30891 (9)	6·36 (4)
S2	0·0772 (1)	0·20901 (9)	0·24073 (9)	6·99 (4)
S3	0·1683 (1)	0·10109 (8)	0·08545 (9)	6·49 (4)
S4	0·4025 (1)	0·20147 (9)	0·1509 (1)	6·91 (4)
P1	0·1878 (1)	0·1527 (1)	0·33725 (9)	6·77 (4)
P2	0·3206 (1)	0·11008 (9)	0·0842 (1)	6·75 (4)
O1	0·2430 (3)	0·2078 (2)	0·4177 (2)	8·3 (1)
O2	0·1303 (3)	0·0885 (2)	0·3756 (2)	8·9 (1)
O3	0·3232 (4)	0·1110 (3)	−0·0069 (3)	10·2 (1)
O4	0·3820 (3)	0·0275 (2)	0·1171 (3)	9·2 (1)
N1	0·3125 (3)	0·3078 (2)	0·2707 (2)	5·1 (1)
N2	0·3360 (4)	0·4214 (2)	0·3367 (3)	7·0 (1)
N3	0·1521 (3)	0·2938 (2)	0·0961 (2)	5·8 (1)
N4	0·0215 (4)	0·3449 (3)	−0·0130 (3)	8·7 (2)
C1	0·1759 (6)	0·2566 (5)	0·4493 (4)	11·0 (2)
C2	0·2594 (6)	0·3127 (5)	0·5154 (4)	12·9 (2)
C3	0·2109 (7)	0·3679 (6)	0·5484 (6)	15·5 (4)
C4	0·2952 (7)	0·4247 (5)	0·6053 (6)	16·2 (4)
C5	0·0631 (5)	0·0276 (4)	0·3235 (4)	9·7 (2)
C6	0·0199 (6)	−0·0205 (4)	0·3828 (5)	12·6 (3)
C7	−0·0535 (7)	−0·0831 (6)	0·3374 (6)	14·6 (3)
C8	−0·0911 (7)	−0·1335 (6)	0·3951 (6)	16·6 (4)
C9	0·2650 (7)	0·1772 (6)	−0·0630 (5)	15·0 (3)
C10	0·326 (1)	0·2056 (7)	−0·0982 (8)	22·1 (5)
C11	0·2437 (9)	0·2823 (9)	−0·1666 (8)	23·1 (6)
C12	0·310 (1)	0·319 (1)	−0·166 (1)	33·5 (9)
C13	0·4980 (6)	0·0170 (4)	0·1355 (5)	11·2 (3)
C14	0·5444 (6)	−0·0469 (5)	0·2055 (5)	12·4 (3)
C15	0·5501 (7)	−0·0207 (5)	0·2864 (5)	13·6 (3)
C16	0·5916 (7)	−0·0838 (5)	0·3530 (6)	13·6 (3)
C17	0·2642 (4)	0·3730 (3)	0·2798 (3)	6·7 (2)
C18	0·4363 (5)	0·3851 (3)	0·3653 (3)	6·9 (2)
C19	0·4217 (4)	0·3150 (3)	0·3248 (3)	6·0 (1)
C20	0·0498 (5)	0·2855 (3)	0·0415 (3)	7·2 (2)
C21	0·1095 (7)	0·3941 (4)	0·0073 (4)	11·2 (3)
C22	0·1903 (5)	0·3629 (4)	0·0745 (4)	9·2 (2)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Ni—S(1)	2·590 (1)	Ni—N(3)	2·055 (3)
Ni—S(2)	2·488 (1)	S(1)—P(1)	1·961 (2)
Ni—S(3)	2·565 (1)	S(2)—P(1)	1·973 (2)
Ni—S(4)	2·464 (2)	S(3)—P(2)	1·959 (3)
Ni—N(1)	2·046 (3)	S(4)—P(2)	1·966 (2)
S(1)—Ni—S(2)	79·44 (4)	S(2)—Ni—N(3)	92·4 (1)
S(1)—Ni—S(3)	88·19 (5)	S(3)—Ni—S(4)	80·47 (4)
S(1)—Ni—S(4)	92·32 (5)	S(3)—Ni—N(1)	171·6 (1)
S(1)—Ni—N(1)	92·8 (1)	S(3)—Ni—N(3)	88·5 (1)
S(1)—Ni—N(3)	170·8 (1)	S(4)—Ni—N(1)	91·1 (2)
S(2)—Ni—S(3)	95·47 (5)	S(4)—Ni—N(3)	95·6 (1)
S(2)—Ni—S(4)	170·97 (5)	N(1)—Ni—N(3)	91·9 (1)
S(2)—Ni—N(1)	92·9 (2)		

calculated values of selected bond distances and bond angles are given in Table 2.*

Discussion. Fig. 1 shows the configuration of $[Ni\{(C_4H_9O)_2PS_2\}_2(Im)_2]$. An X-ray crystallographic structure determination of the nickel(II) chelate of $Ni[(C_2H_5O)_2PS_2]_2$ (McConnell & Kastalsky, 1967) has shown that the metal ion is planar tetracoordinated, but in polar solvents the Ni^{II} ion is hexacoordinated. Our diadduct of $Ni[(C_4H_9O)_2PS_2]_2$ with imidazole also shows octahedral structure distorted by the influences of the chelate rings in the adduct.

The Ni^{II} ion is coordinated by four S atoms and two *cis* N atoms. The dihedral angles between the planes of S(1)S(3)N(1)N(3) and NiS(1)S(2)P(1), S(1)S(3)N(1)N(3) and NiS(3)S(4)P(2), and NiS(1)S(2)P(1) and NiS(3)S(4)P(2) are 97·76 (6), 87·70 (6) and 92·04 (3)° respectively.

The Ni—S distances are in the range 2·46–2·59 Å, the S—Ni—S bond angles are 79·44 and 80·47° and the S—P—S angles are 113·6 and 111·8° in the same phosphate moiety. These results are comparable with 2·21 Å, 88 and 103° respectively in the square planar complex $Ni[(C_2H_5O)_2PS_2]_2$ (McConnell & Kastalsky, 1967). It is apparent that the steric and electronic effects of the axial imidazole group can destabilize the Ni—S bond leading to an increase in strain in the four-membered P—S—Ni—S ring. It is possible to interpret these results on the basis of a simple electrostatic model. Adduct formation reduces the net positive charge on the N atom and increases the net negative charge on the S atoms. The latter effect results in an increase in the S—P—S angle, while the former effect lengthens the Ni—S distance and decreases the S—Ni—S angle.

In comparison with *cis*-$Ni[(C_4H_9O)_2PS_2]_2$.bpy (You, Xu, Yu, Liu & Lin, 1986), the imidazole

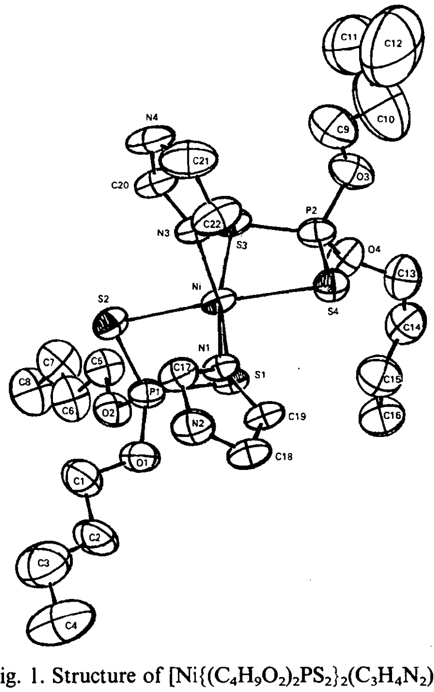

Fig. 1. Structure of $[Ni\{(C_4H_9O_2)_2PS_2\}_2(C_3H_4N_2)_2]$.

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* Lists of structure factors, bond distances and angles, general and refined displacement parameters, least-squares-planes data and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52546 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

adduct is also *cis*-coordinated. The Ni—N distances are 2·046 and 2·055 Å and the S—Ni—S angles in the same dibutyldithiophosphate ligand are 79·44 and 80·47°. These are comparable with those found in Ni[$(C_2H_5O)_2PS_2$].2py (Ooi & Fernando, 1967) and Ni[$(C_4H_9O)_2PS_2$]$_2$.2py (Liu, Lin, Xu, Yu & You, 1987).

The P atoms in the dibutyldithiophosphate ligand have approximate sp^3 hybridization. The N—C and C—C distances and bond angles in imidazole are normal. Thus, this ligand interacts weakly with the metal ion.

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Structure of Bis(*cis*-1,2-cyclohexanediamine)nickel(II) Dibromide

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Abstract. [Ni($C_6H_{14}N_2$)$_2$]Br$_2$, M_r = 478·90, monoclinic, $P2_1/n$, a = 6·1610 (2), b = 20·6379 (15), c = 6·7270 (7) Å, β = 101·329 (5)°, V = 838·7 (1) Å^3, Z = 2, D_x = 1·90 Mg m^{-3}, Mo $K\alpha$ radiation (graphite crystal monochromator, λ = 0·71073 Å), μ = 5·891 mm^{-1}, F(000) = 484, T = 293 K. Final conventional R = 0·022 for 1577 observed reflections and 144 variables. The Ni atom has a square planar coordination given by two *cis*-1,2-cyclohexanediamine ligands. Distances and angles are normal. Distances Ni—N are both equal, within the experimental error, the average being 1·914 (2) Å; the N(1)—Ni—N(2) bite angle is 86·4 (1)°.

Introduction. This structural investigation was undertaken as a part of our work on nickel(II) compounds with *C*-substituted ethylenediamine ligands. In previous communications we have reported crystal and molecular structures of several octahedral and square planar complexes of this family including compounds with tetramethylethylenediamine (Alcalá-Aranda, Fernández, Gómez-Beltrán & Larena, 1977), *trans*-1,2-cyclohexanediamine (Valero-Capilla, Alcalá-Aranda & Gómez-Beltrán, 1980), 2-methyl-1,2-propanediamine (García-Granda & Gómez-Beltrán, 1984*a*), 1,2-ethanediamine (García-Granda & Gómez-Beltrán, 1984*b*), *meso*-1,2-diphenyl-1,2-ethanediamine (García-Granda & Gómez-Beltrán, 1984*c*), 2-methyl-1,2-propanediamine (García-Granda & Gómez-Beltrán, 1986). The structure of the partially oxidized compound, *catena*-(μ-bromo)bis[(1*R*,2*R*)cyclohexanediamine]-nickel 2·77-bromide, a bromide containing the *trans* form of cyclohexanediamine, has been reported (Toftlund & Simonsen, 1984). This paper describes the crystal and molecular structure of a new complex within this series.

Experimental. Yellow crystal, size 0·26 × 0·13 × 0·13 mm. Throughout the experiment Mo $K\alpha$ radiation was used with a graphite crystal monochromator on a Nonius CAD-4 single-crystal diffractometer (λ = 0·71073 Å). The unit-cell dimensions were determined from the angular settings of 25 reflections with θ between 20 and 30°. The space group was determined to be $P2_1/n$ from the systematic absences. The intensity data of 5663 reflections, in *hkl* range (−8, −29, 0) to (8, 29, 9), and θ limits (0 < θ < 30°) were measured, using the ω–2θ scan technique and a variable scan rate with a maximum scan time of 60 s per reflection. The intensity of the primary beam was checked throughout the data

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