

Structure of Bis(monothiobenzoato-*S*)[ethylenebis(diphenylphosphino)]nickel(II)

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Abstract. $[\text{Ni}(\text{C}_7\text{H}_5\text{OS})_2\{\text{P}_2(\text{C}_2\text{H}_4)(\text{C}_6\text{H}_5)_4\}]$, $M_r = 770$, orthorhombic, $Pna2_1$, $a = 15.842$ (3), $b = 20.283$ (3), $c = 11.017$ (2) Å, $V = 3540.1$ Å³, $Z = 4$, $D_x = 1.37$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.731$ mm⁻¹, $F(000) = 936$, $T = 293$ K, $R = 0.050$, $wR = 0.053$ for 1475 unique reflections. The chromophore is planar NiS_2P_2 . The thiobenzoate ligands are linked only through sulfur with distances $\text{Ni}-\text{S}(1) = 2.218$ (5) and $\text{Ni}-\text{S}(2) = 2.244$ (5) Å. The $\text{Ni}-\text{P}$ bonds are symmetric with distances $\text{Ni}-\text{P}(1) = 2.156$ (5) and $\text{Ni}-\text{P}(2) = 2.157$ (5) Å. There are no $\text{Ni}-\text{O}$ interactions. There are no significant inter- or intramolecular short contacts. The molecular packing in the unit cell is due to van der Waals forces.

Introduction. A great deal of work has been done on the complexation of carboxylic acids with transition-metal ions because of their interesting bonding properties (Oldham, 1968; Bennet, Caulton & Cotton, 1969). Of late, thiocarboxylates have also interested researchers because of their ability to form bridged complexes as well as simple mononuclear complexes (Melson, Crawford & Geddes, 1970; Savant, Gopalakrishnan & Patel, 1970; Savant & Patel, 1971). The presence of soft and hard donor atoms (sulfur and oxygen respectively) in the same ligand increases the possible modes of interaction with soft and hard metal ions. As a border-line acceptor, Ni^{II} interacts with thiocarboxylic acids readily to form complexes (Melson, Crawford & Geddes, 1970). The interaction of Ni^{II} with monothiobenzoic acid (mtbH) results in a dimeric complex, $\text{Ni}_2(\text{mtb})_4(\text{C}_2\text{H}_5\text{OH})$, which has been shown to have NiO_5 and NiS_4 chromophores by crystal structure analysis (Melson, Greene & Bryan, 1970). This complex reacts with a series of Lewis bases to give paramagnetic adducts or substitution products. Nitrogenous bases on interaction with $\text{Ni}_2(\text{mtb})_4(\text{C}_2\text{H}_5\text{OH})$ form paramagnetic octahedral adducts and substituted phosphines on interaction give diamagnetic planar complexes (Goodfellow & Stephenson, 1980). Crystal-structure analyses of complexes involving mtb are very sparse to date. The interaction of $\text{Ni}_2(\text{mtb})_4(\text{C}_2\text{H}_5\text{OH})$ with a chelating phosphine, ethylenebis(diphenylphosphino) (diphos) results in $\text{Ni}(\text{mtb})_2(\text{diphos})$.

Experimental. Reddish-brown $\text{Ni}_2(\text{mtb})_4(\text{C}_2\text{H}_5\text{OH})$ (10 mmol) was dissolved in ethanol (25 ml) and diphos (5 mmol) in dichloromethane (25 ml) was added to the solution and the mixture was left without disturbance. Needle-shaped crystals separated out. Crystal $0.17 \times 0.22 \times 0.35$ mm; Enraf-Nonius CAD-4 diffractometer; cell constants from least-squares analysis of 25 high-angle reflections; θ range 2 to 21°; h : 0 to 15, k : 0 to 20, l : 0 to 11; no absorption correction; insignificant fluctuations in three reflections (400, 040, 036 monitored every hour); 2188 reflections measured, 1475 with $I > 3\sigma(I)$ considered observed; the data showed the following systematic absences; $0kl$ no conditions; $h0l$, $h + l$ odd; $hk0$, k odd; the space group was found to be $P2_1nb$ and was then transformed into $Pna2_1$ to suit the international convention. Structure determined using *SHELX76* (Sheldrick, 1976) and heavy-atom technique. Refinement on F . Sixteen H atoms were fixed by geometrical constraints. The remaining eighteen H atoms appeared in the difference map and their positions were refined. Final $R = 0.050$, $wR = 0.053$, $w = 1.00/[\sigma^2(F_o) + 0.342|F_o|^2]$, non-H atoms anisotropic and H atoms isotropic. The reflections/parameters ratio was 5.2. Final difference Fourier map contained no peak higher than $0.53 \text{ e } \text{Å}^{-3}$. The max. and av. shift/e.s.d. were 3.144 and 0.71 respectively. The high max. shift/e.s.d. value is due to the anisotropic thermal parameters of two ring C atoms, C(39) and C(40), which did not refine as well as the other C atoms. Atomic scattering factors from Cromer & Mann (1968) for non-H atoms and Stewart, Davidson & Simpson (1965) for H; anomalous-dispersion correction factors from Cromer & Liberman (1970).

Discussion. Positional and thermal parameters are listed in Table 1. Bond parameters are given in Table 2.* Fig. 1 shows an *ORTEP* plot (Johnson, 1976) of the molecule. Unlike $\text{Ni}_2(\text{mtb})_4(\text{C}_2\text{H}_5\text{OH})$, $\text{Ni}(\text{mtb})_2-$

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43440 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for the non-H atoms with e.s.d.'s in parentheses

$$U_{\text{eq}} = \frac{1}{3} \sum_{i=1}^3 U_{ii}$$

	x	y	z	U_{eq}
Ni	2437 (1)	2841 (1)	7250	49 (1)
S(1)	1798 (3)	3813 (2)	7571 (5)	61 (3)
S(2)	1326 (3)	2372 (3)	6380 (5)	67 (3)
P(1)	3526 (3)	3167 (2)	8261 (5)	51 (3)
P(2)	3145 (2)	1957 (2)	6371 (5)	54 (3)
C(1)	4276 (10)	2500 (9)	8409 (20)	67 (12)
C(2)	4241 (12)	2070 (8)	7195 (20)	69 (12)
C(3)	4115 (10)	3812 (7)	7490 (14)	71 (14)
C(4)	4889 (13)	4037 (11)	7962 (12)	86 (19)
C(5)	5377 (13)	4493 (13)	7364 (27)	115 (24)
C(6)	5066 (15)	4773 (10)	6291 (31)	118 (24)
C(7)	4347 (20)	4504 (11)	5785 (25)	119 (21)
C(8)	3842 (11)	4017 (10)	6383 (21)	78 (13)
C(9)	3337 (10)	3447 (10)	9779 (10)	58 (13)
C(10)	3218 (13)	3008 (11)	743 (23)	67 (15)
C(11)	3015 (17)	3227 (17)	1840 (22)	90 (18)
C(12)	2843 (13)	3868 (12)	2105 (19)	110 (20)
C(13)	2919 (14)	4337 (11)	1169 (22)	93 (19)
C(14)	3190 (12)	4132 (11)	9986 (22)	73 (15)
C(15)	3122 (12)	1652 (10)	5349 (21)	57 (12)
C(16)	2557 (15)	1143 (12)	4972 (27)	71 (16)
C(17)	2504 (22)	946 (14)	3778 (31)	101 (20)
C(18)	3017 (22)	1187 (17)	2924 (26)	75 (14)
C(19)	3585 (22)	1657 (13)	3262 (19)	73 (15)
C(20)	3656 (13)	1876 (9)	4482 (20)	71 (15)
C(21)	2877 (11)	1305 (11)	7919 (18)	46 (10)
C(22)	2282 (14)	1432 (10)	8838 (24)	78 (14)
C(23)	2166 (14)	914 (15)	9685 (23)	96 (17)
C(24)	2620 (17)	360 (17)	9648 (26)	89 (19)
C(25)	3149 (18)	214 (12)	8760 (24)	105 (20)
C(26)	3283 (11)	706 (10)	7885 (23)	68 (13)
C(27)	1251 (8)	3593 (7)	8870 (12)	58 (10)
O(1)	1275 (6)	3030 (5)	9306 (10)	99 (9)
C(28)	777 (8)	4117 (7)	9525 (13)	64 (11)
C(29)	348 (12)	3961 (8)	583 (17)	82 (13)
C(30)	-86 (12)	4438 (11)	1232 (16)	106 (16)
C(31)	-108 (11)	5092 (9)	796 (17)	90 (12)
C(32)	313 (12)	5239 (10)	9767 (19)	90 (15)
C(33)	754 (11)	4765 (8)	9105 (15)	75 (12)
C(34)	1496 (10)	2638 (8)	4901 (14)	49 (8)
O(2)	2014 (9)	3060 (7)	4645 (12)	67 (7)
C(35)	970 (10)	2313 (8)	3921 (16)	53 (9)
C(36)	522 (11)	1746 (9)	4129 (18)	82 (12)
C(37)	91 (15)	1411 (10)	3166 (19)	96 (14)
C(38)	224 (10)	1625 (11)	2016 (20)	72 (11)
C(39)	695 (14)	2175 (12)	1771 (17)	87 (13)
C(40)	1076 (10)	2531 (10)	2735 (15)	64 (11)

Table 2. Bond lengths (\AA) and bond angles ($^\circ$)

Ni—S(1)	2.244 (5)	Ni—S(2)	2.218 (5)
Ni—P(1)	2.157 (5)	Ni—P(2)	2.156 (5)
P(1)—C(1)	1.80 (1)	P(2)—C(2)	1.78 (2)
S(1)—C(27)	1.73 (1)	S(2)—C(34)	1.73 (1)
C(1)—C(2)	1.59 (2)	P(1)—C(3)	1.81 (1)
C(3)—C(4)	1.40 (2)	C(4)—C(5)	1.37 (3)
C(5)—C(6)	1.40 (4)	C(6)—C(7)	1.38 (3)
C(7)—C(8)	1.43 (3)	C(3)—C(8)	1.36 (2)
P(1)—C(9)	1.79 (2)	C(9)—C(10)	1.39 (3)
C(10)—C(11)	1.32 (3)	C(11)—C(12)	1.35 (4)
C(12)—C(13)	1.40 (3)	C(13)—C(14)	1.43 (3)
C(9)—C(14)	1.42 (3)	P(2)—C(15)	1.78 (2)
C(15)—C(16)	1.42 (3)	C(16)—C(17)	1.37 (4)
C(17)—C(18)	1.33 (4)	C(18)—C(19)	1.36 (4)
C(19)—C(20)	1.42 (3)	C(15)—C(20)	1.35 (3)
P(2)—C(21)	1.80 (2)	C(21)—C(22)	1.40 (3)
C(22)—C(23)	1.41 (3)	C(23)—C(24)	1.33 (4)
C(24)—C(25)	1.32 (3)	C(25)—C(26)	1.40 (3)
C(21)—C(26)	1.37 (2)	C(27)—O(1)	1.24 (1)
C(27)—C(28)	1.48 (1)	C(28)—C(29)	1.38 (2)
C(29)—C(30)	1.38 (2)	C(30)—C(31)	1.41 (2)
C(31)—C(32)	1.34 (2)	C(32)—C(33)	1.39 (2)
C(28)—C(33)	1.39 (2)	C(34)—O(2)	1.21 (2)
C(34)—C(35)	1.51 (2)	C(35)—C(36)	1.37 (2)
C(36)—C(37)	1.43 (2)	C(37)—C(38)	1.35 (3)
C(38)—C(39)	1.36 (3)	C(35)—C(40)	1.38 (2)
S(1)—Ni—S(2)	95.0 (3)	S(1)—Ni—P(2)	174.8 (3)
S(2)—Ni—P(2)	88.4 (3)	S(1)—Ni—P(1)	90.6 (3)
S(2)—Ni—P(1)	171.5 (3)	P(2)—Ni—P(1)	86.5 (2)
Ni—P(1)—C(1)	110 (1)	Ni—P(2)—C(2)	111 (1)
P(1)—C(1)—C(2)	108 (1)	C(1)—C(2)—P(2)	106 (1)
P(1)—C(3)—C(4)	120 (1)	C(3)—C(4)—C(5)	122 (1)
C(4)—C(5)—C(6)	118 (1)	C(5)—C(6)—C(7)	118 (1)
C(6)—C(7)—C(8)	123 (1)	C(7)—C(8)—C(3)	116 (1)
P(1)—C(9)—C(10)	122 (1)	C(9)—C(10)—C(11)	120 (1)
C(10)—C(11)—C(12)	124 (2)	C(11)—C(12)—C(13)	118 (2)
C(12)—C(13)—C(14)	119 (2)	C(9)—C(14)—C(13)	118 (2)
P(2)—C(15)—C(16)	122 (1)	P(2)—C(15)—C(20)	122 (1)
C(15)—C(16)—C(17)	121 (1)	C(16)—C(17)—C(18)	122 (1)
C(17)—C(18)—C(19)	117 (2)	C(18)—C(19)—C(20)	122 (2)
C(19)—C(20)—C(15)	120 (1)	P(2)—C(21)—C(22)	118 (1)
P(2)—C(21)—C(26)	121 (1)	C(21)—C(22)—C(23)	115 (1)
C(22)—C(23)—C(24)	122 (2)	C(23)—C(24)—C(25)	123 (2)
C(24)—C(25)—C(26)	116 (1)	C(25)—C(26)—C(21)	122 (1)
C(26)—C(21)—C(22)	119 (1)	Ni—S(1)—C(27)	97.5 (5)
Ni—S(2)—C(34)	98.6 (6)	S(1)—C(27)—O(1)	122 (1)
S(2)—C(34)—O(2)	122 (1)	S(1)—C(27)—C(28)	118 (1)
S(2)—C(34)—C(35)	116 (1)	O(1)—C(27)—C(28)	119 (1)
O(2)—C(34)—C(35)	120 (1)	C(27)—C(28)—C(29)	119 (1)
C(28)—C(29)—C(30)	121 (1)	C(29)—C(30)—C(31)	119 (1)
C(30)—C(31)—C(32)	118 (1)	C(31)—C(32)—C(33)	122 (1)
C(28)—C(33)—C(32)	119 (1)	C(29)—C(28)—C(33)	118 (1)
C(34)—C(35)—C(36)	122 (1)	C(34)—C(35)—C(40)	117 (1)
C(35)—C(36)—C(37)	121 (1)	C(36)—C(37)—C(38)	117 (1)
C(37)—C(38)—C(39)	122 (1)	C(38)—C(39)—C(40)	119 (1)
C(35)—C(40)—C(39)	119 (1)	C(36)—C(35)—C(40)	119 (1)

(diphos) is monomeric with no short intermolecular Ni—O, Ni—S and Ni—Ni contacts. The molecule is planar with an NiS₂P₂ chromophore. The observed diamagnetism of the complex is in keeping with the structure.

The Ni—S distances in the complex are significantly different [2.244 (5), 2.218 (5) \AA] whereas the two Ni—P distances are almost equal [2.157 (5), 2.156 (5) \AA]. The S(2)—Ni—P(2) angle [90.6 (3)°] is also larger than the S(1)—Ni—P(1) angle [88.4 (3)°]. The asymmetry in the Ni—S distances is due to the packing requirements of the molecule in the crystal. Ni—O(1) and Ni—O(2) distances in the present complex of 2.980 (13) and 2.944 (13) \AA , respectively, show that there is no interaction, whereas in the parent complex the average Ni—O distance is 2.237 (5) \AA indicating a

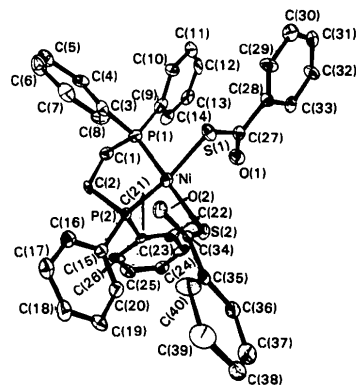


Fig. 1. ORTEP (Johnson, 1976) plot of Ni(mtb)₂(diphos) showing the atom numbering.

strong interaction. The ν_{C-O} of the thiobenzoate moiety in the IR spectrum of $Ni(mtb)_2(diphos)$ occurs at 1590 and 1580 cm^{-1} whereas in $Ni_2(mtb)_4(C_2H_5OH)$ the ν_{C-O} occurs at a much lower frequency of 1508 cm^{-1} due to Ni-O bonding (Goodfellow & Stephenson, 1980).

The Ni-P distances observed in the present complex are shorter than the distances observed in similar compounds (Hope, Olmstead, Power & Viggiano, 1984). Tetrahedral geometry is observed around P atoms and the angles are close to 109° and the P-C distances are normal. The P(1)-C(1)-C(2)-P(2) dihedral angle is -45 (1)° indicating a puckered nature to maintain a planar NiS_2P_2 chromophore. The average S-C bond distance, 1.734 (17) Å, is shorter than the single-bond distance of 1.832 (6) Å (Rout, 1982), indicating a partial delocalization of electrons over the O-C-S moiety. The phenyl rings are planar within 0.01 Å and other bond parameters are normal. There are no significant short contacts. The molecules in the unit cell are held together by van der Waals forces. The present crystal structure confirms the chromophore to be NiS_2P_2 and shows that only S coordination in the parent complex is retained on interaction with diphos.

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(1-2:5-6- η -Cycloocta-1,5-diene)(2,4-dinitrophenyl)(4-methoxyphenyl)platinum(II) (1) and (1-2:5-6- η -Cycloocta-1,5-diene)(2,4-dinitrophenyl)(4-nitrophenyl)platinum(II) (2)

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Abstract. (1): $[Pt(C_6H_3N_2O_4)(C_7H_7O)(C_8H_{12})]$, triclinic, $P\bar{1}$, $a = 6.872$ (4), $b = 11.742$ (4), $c = 13.582$ (5) Å, $\alpha = 71.94$ (4), $\beta = 76.55$ (5), $\gamma = 75.25$ (3)°, $V = 993.4$ Å³, $Z = 2$, $D_x = 1.93$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 67.99$ cm⁻¹, $F(000) = 560$, $T = 295$ K, $R = 0.039$ for 3253 observed reflections. (2): $[Pt(C_6H_3N_2O_4)(C_6H_4NO_2)(C_8H_{12})]$, $M_r = 592.5$, triclinic, $P\bar{1}$, $a = 12.758$ (4), $b = 11.213$ (4), $c = 7.060$ (2) Å, $\alpha = 77.570$ (3), $\beta = 87.44$ (3), $\gamma = 89.32$ (5)° (the Delaunay reduced cell is 11.213, 11.895, 12.758 Å, 90.88, 90.68, 144.58°), $V = 985.3$ Å³, $Z = 2$, $D_x = 2.00$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 68.61$ cm⁻¹, $F(000) = 572$, $T = 295$ K, $R = 0.039$ for 3676 observed reflections. In (1) and (2) C(10) and C(20) of the phenyl rings, the Pt atom and

the midpoints of the coordinated double bonds C(1)=C(2) and C(5)=C(6) are nearly coplanar, the largest deviation from the plane being less than 0.11 Å. In (1) the angle between this plane and the 2,4-dinitrophenyl ring is 81.1°, while it is 86.9° between this plane and the 4-methoxyphenyl ring; in (2) the angles between the above-defined plane and the 2,4-dinitrophenyl or the 4-nitrophenyl ring measure 82.8 and 81.1° respectively (the mean standard deviation for all interplanar angles is 0.9°). In (1) the *ortho*-nitro group is twisted by 12.3° with respect to the phenyl ring, whereas this angle is 29.1° for the *para*-nitro group. In (2) all three nitro groups are nearly coplanar with the phenyl rings to which they are attached; the deviations are 5.9 [N(13)], 8.3 [N(15)] and 6.8° [N(23)]. A structure