Instrumental Achievements

Crystal and Molecular Structures of *trans*-Nickel(II)-bis[(*O*-propyl^n)-(*p*-methoxyphenyl)dithiophosphonate]

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Dithiophosphonate complexes have found important applications in medical, industrial and agricultural fields. Some types of dithiophosphonate compounds have been effectively utilized as insecticide derivatives and anti-oxidants. Monoesters of dithiophosphonic acids are well-known bidentate ligands, and various complexes of these chelating agents have been studied. For example, the crystal structure of some dithiophosphonate derivates, such as [(*O*-isopropyl)(Et)PS_2]$_2$Ni, [(O-Et)(*p*-$MeOC_6H_4$)PS_2]$_2$Ni and [AuS_2P(*p*-$MeOC_6H_4$)($OSiPh_3$)]$_2$, have been previously determined.[1-3]

The study reported here is part of a project aimed at providing a better understanding of the stereochemistry of dithiophosphonate derivates. To this end, *trans*-Ni(II)-bis[(*O*-propyl^n)-(*p*-methoxyphenyl)dithiophosphonate] (Fig. 1) was prepared and investigated.

The ammonium salt of the ligand, ammonium *O*-propyl^n-(*p*-methoxyphenyl)dithiophosphonate was prepared by the reaction of 2,4-bis(*p*-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide with 1-propanol.[4] A 4.6 g (16.70 mmol) sample of the ligand was dissolved in 100 mL of glacial acetic acid; to this solution, 83.5 mL of a Ni(II) acetate solution in acetic acid was added dropwise in about 30 min. The title compound crystallized out directly from the reaction mixture. The crystals, m.p. 380 K was used for X-ray studies without recrystallization.

A single crystal of suitable size and quality was used in collecting 3D intensity data on a CAD-4 diffractometer with Mo K_α radiation. The crystal data, data collection and refinement parameters are given in Table 1.

The crystal structure of the title compound consists of a discrete centrosymmetric NiL_2[L: *O*-propyl^n-(*p*-methoxyphenyl)-dithiophosphonate] unit in which one crystallographically independent L molecule coordinates the central nickel atom as

Table 1 Crystal and experimental data

Formula:	[$C_{20}H_{28}NiO_4P_2S_4$]
Formula weight	= 581.39
Space group:	$P\bar{1}$ (No: 2)
Crystal system:	triclinic Z = 1
a = 6.4944(7)Å	α =76.439(8)˚
b = 7.6682(7)Å	β =77.111(9)˚
c = 13.686(2)Å	γ = 83.145(8)˚
V= 644.3(1)Å^3	
D_x= 1.787 g/cm^3	
μ(Mo K_α)= 1.247 mm^{-1}	
T = 293 K	
Color: purple	
Radiation Mo K_α (λ = 0.71073 Å)	
θ_{max} = 30.40˚	
Absorption correction: empirical Ψ scan	
No. of reflection = 3901	
No. of reflection used = 3098 ($I > 2\sigma(I)$)	
R = 0.0532	
R_w = 0.1738	
$(\Delta\rho)_{max}$ = 0.933 Å^{-3}	
$(\Delta\rho)_{min}$ = –0.899 Å^{-3}	
Measurement: Enraf-Nonius CAD-4	
Program system: SHELX97	
Structure determination: SHELXS97	
Refinement: full matrix least-square SHELXL97	
Treatment of hydrogen atoms: geometric calculation	

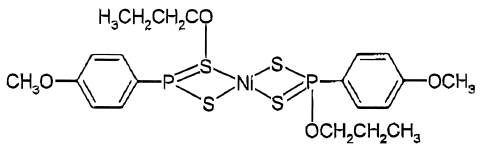

Fig. 1 Chemical diagram of the complex.

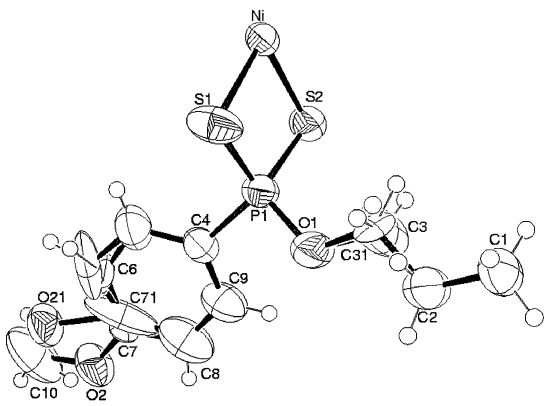

Fig. 2 An ORTEP III view of the discrete complex.

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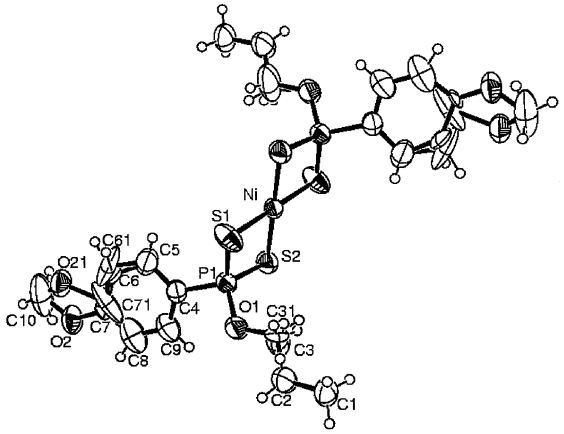

Fig. 3 An ORTEP III view of the centrosymmetric NiL_2.

an *S*,*S*′-bidentate ligand. Figures 2 and 3 show ORTEP III views of the discrete and complete complex molecule with the adopted numbering scheme. Tables 2 and 3 list the structural results. The nickel atom is coordinated by four sulfur atoms provided by the two bidentate ligands in a slightly distorted square arrangement. The P atom deviates from the coordination plane by 0.0765(8)Å.

The L ligand is affected by disorder, which can be essentially described by a deformation of the phenyl ring, the methoxy group and big thermal parameters of the C3 atom. The positions of these atoms have been refined with different occupancy factors. The two positions of each disordered atom are distinguishable (Table 2).

The small differences between the two P–S and the two Ni-S bond lengths indicate a noticable extent of delocalization in the P–Sp bonds of the PS2 group.[2]

The molecular geometry was effected by the C5–H5··S1, C9–H9··O1 and C3–H32··S2 intramolecular hydrogen bonds; the donor-acceptor distances ranged from 2.902(5) to 3.442(5)Å.

Table 2 Final atomic coordinates, equivalent isotropic thermal parameters (Å^2) and occupancy factor

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}	Occupancy factor
Ni	0.5	0.5	0	3.48(1)	1
S1	0.6708(2)	0.7492(1)	-0.06662(7)	5.85(3)	1
S2	0.3733(1)	0.5465(1)	-0.14317(6)	4.74(2)	1
P1	0.5492(1)	0.7603(1)	-0.19041(6)	4.07(2)	1
O1	0.4179(4)	0.9420(3)	-0.2259(2)	6.31(8)	1
O2	1.1336(7)	0.7482(7)	-0.5891(3)	6.2(1)	0.66
O21	1.277(1)	0.680(1)	-0.5274(6)	6.1(3)	0.34
C1	-0.0712(7)	1.2177(5)	-0.1350(4)	6.5(1)	1
C2	0.1157(8)	1.1436(7)	-0.2051(4)	7.5(1)	1
C3	0.223(2)	0.995(2)	-0.1632(9)	13.0(5)	0.77
C31	0.247(3)	1.010(2)	-0.1479(8)	3.2(3)	0.23
C4	0.7433(5)	0.7573(4)	-0.3055(2)	4.16(7)	1
C5	0.9457(6)	0.6840(6)	-0.3027(4)	6.1(1)	1
C6	1.059(2)	0.682(3)	-0.4054(8)	4.1(3)	0.32
C61	1.106(1)	0.673(2)	-0.391(1)	9.8(5)	0.68
C71	1.019(2)	0.736(2)	-0.4752(6)	9.8(5)	0.67
C7	1.021(1)	0.752(2)	-0.5044(6)	2.5(2)	0.33
C8	0.820(1)	0.8190(9)	-0.4902(4)	8.3(2)	1
C9	0.6866(7)	0.8217(6)	-0.4010(3)	6.0(1)	1
C10	1.334(1)	0.676(1)	-0.6036(8)	10.9(3)	1

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\boldsymbol{a}_i \boldsymbol{a}_j)$.

Table 3 Some geometrical parameters with estimated standard deviations (Å, °, °)

Ni-S1	2.2251(9)	S2-P1	2.008(1)
Ni-S2	2.2283(9)	P1-O1	1.577(2)
S1-P1	2.004(1)	P1-C4	1.787(3)
Ni-S1-P1	85.20(4)	S2-Ni-S1	88.34(3)
Ni-S2-P1	85.01(4)	P1-O1-C3	121.6(4)
S1-P1-O1	114.7(1)	P1-O1-C31	118.4(5)
S1-P1-C4	114.2(1)	P1-C4-C5	121.4(3)
S2-P1-O1	113.2(1)	P1-C4-C9	119.9(3)
Ni-S1-P1-S2	2.11(4)	S1-P1-C4-C5	24.3(3)
Ni-S1-P1-O1	124.7(1)	S1-P1-C4-C9	-159.2(3)
Ni-S1-P1-C4	-121.0(1)	S2-P1-O1-C3	50.1(8)
Ni-S2-P1-O1	-125.7(1)	S2-P1-C4-C5	-91.7(3)
Ni-S2-P1-C4	120.9(1)	S2-P1-C4-C9	84.7(3)
S1-P1-O1-C3	-65.5(8)		

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