Bis{2-(dimethylphosphino)ethane-1-thiolato}-nickel(II), -palladium(II), and -platinum(II) Complexes, and Molecular Structure of the Nickel(II) Complex

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Synopsis. Bis{2-(dimethylphosphino)ethane-1-thiolato} complexes of Ni(II), Pd(II), and Pt(II) were newly prepared, and the molecular structure of the Ni(II) complex was determined by X-ray analysis to have a square planar *trans*(*P,P*) geometrical configuration. The ^{1}H, ^{13}C, and ^{31}P NMR spectra of the complexes in $CDCl_3$ indicate a *trans*(*P,P*) structure for the nickel(II) and palladium(II) complexes and a *cis*(*P,P*) one for the platinum(II) complex.

We have been interested in syntheses of metal complexes with multidentate phosphine ligands containing other kinds of donor atoms such as phosphorus and nitrogen[1] or phosphorus and sulfur.[2] This paper describes the preparation of Ni(II), Pd(II), and Pt(II) complexes of $R_2PCH_2CH_2S^-$ ($R=CH_3$: dmsp, $R=C_6H_5$: dpsp), together with an X-ray structure analysis of *trans*-[Ni(dmsp)$_2$]. This type of ligand will be one of the most typical and simple bidentate phosphine ligands with a different donor atom. To our knowledge, however, no complex of dmsp has been known. Analogous dpsp complexes of Ni(II),[3,4] Pd(II),[3] and Pt(II)[3] have been reported, but the preparative procedures for the latter two complexes were not described.

Experimental

The phosphine ligands were handled under an atmosphere of nitrogen until they formed metal complexes. All solvents used for the preparation of ligands and complexes were made oxygen-free by bubbling nitrogen for 20 min immediately before use. 2-(Diphenylphosphino)ethane-1-thiol (Hdpsp) was prepared by the method of Chatt et al.[5] Absorption, and ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Hitachi U3400 spectrophotometer and a R-90H spectrometer, respectively.

Preparation of 2-(Dimethylphosphino)ethane-1-thiol (Hdmsp). To liquid ammonia (100 cm^3) containing small pieces of metallic sodium (2.26 g, 0.1 mol) in a 300 cm^3 three-necked flask was added tetramethyldiphosphane[6] (6.0 g, 0.05 mol) with stirring at −78 °C. After 30 min, ethylene sulfide (5.92 g, 0.1 mol) was added to give a colorless solution. The solution was stirred for another 1 h and evaporated at room temperature to dryness. To the residue was added an aqueous solution (100 cm^3) saturated with ammonium chloride. The phosphine ligand was extracted two times with diethyl ether (100 cm^3). The ethereal solution was dried with anhydrous sodium sulfate (20 g) and then filtered. The filtrate was evaporated under reduced pressure to give a colorless oily product (6.68 g). It was used for the preparation of metal complexes without further purification. The purity of the phosphine ligand was estimated to be 50—70% by the ^{1}H NMR spectrum.

Preparation of Metal Complexes. [Ni(dmsp)$_2$]. To an ethanol solution (40 cm^3) of sodium methoxide (0.24 g, 4.4 mmol) in a schlenk tube were added Hdmsp (crude, 1.35 g) and a 40% aqueous solution (1.28 g) of $Ni(BF_4)_2$ (2.2 mmol) with stirring. The resulting red solution was stirred for several hours and then evaporated under reduced pressure to dryness. The red product was extracted with a small amount of chloroform. Red crystals were formed from the chloroform solution on standing and recrystallized from chloroform. Yield: 0.066 g (10%). Found: C, 31.94; H, 6.73%. Calcd for [Ni(dmsp)$_2$]=$C_8H_{20}P_2S_2Ni$: C, 31.92; H, 6.70%. The complex is soluble in alcohol, acetonitrile, and chloroform, but insoluble in water and diethyl ether.

[Pd(dmsp)$_2$]. The Hdmsp ligand (crude, 0.73 g) was added to a benzene–dichloromethane (1:1) solution (20 cm^3) of palladium(II) acetate (0.52 g, 2.3 mmol). The solution which changed from red brown to yellow in color was stirred for a day and then evaporated under reduced pressure to dryness. Yellow crystals were obtained by the same method as that for the above Ni(II) complex. Yield: 0.084 g (10%). Found: C, 27.46; H, 5.81%. Calcd for [Pd(dmsp)$_2$]=$C_8H_{20}P_2S_2Pd$: C, 27.55; H, 5.78%. The solubility of the complex is similar to that of the Ni(II) complex.

[Pt(dmsp)$_2$]. The Hdmsp ligand (crude, 0.76 g) was added with stirring to an aqueous solution (20 cm^3) of K_2PtCl_4 (0.83 g, 2 mmol), yielding a yellow precipitate. The precipitate dissolved during further stirring (a day). The solution was evaporated under reduced pressure to dryness. To the residue was added a small amount of ethanol to dissolve the desired complex, and the mixture was filtered. White crystals were formed from the filtrate on standing. Yield: 0.123 g (14%). Found: C, 21.94; H, 4.63%. Calcd for [Pt(dmsp)$_2$]=$C_8H_{20}P_2S_2Pt$: C, 22.00; H, 4.61%. The solubility of the complex is similar to that of the Ni(II) complex.

[Ni(dpsp)$_2$]. This complex was prepared according to the method of Marty et al.[4] Recrystallization from a chloroform–ethanol solution gave green crystals. Yield: 0.369 g (67%). Found: C, 61.21; H, 5.14%. Calcd for [Ni(dpsp)$_2$]=$C_{28}H_{28}P_2S_2Ni$: C, 61.22; H, 5.21%.

[Pd(dpsp)$_2$]. To a methanol solution of sodium methoxide (0.10 g, 2.0 mmol) were added Hdpsp (0.78 g, 3.2 mmol) and then a methanol solution (20 cm^3) of Li_2PdCl_4 (1 mmol) which was prepared from $PdCl_2$ (0.177 g, 1 mmol) and LiCl (0.085 g, 2 mmol) in methanol (20 cm^3), yielding a grey-yellow precipitate. The precipitate was recrystallized from a chloroform–ethanol solution to yield orange crystals. Yield: 0.158 g (27%). Found: C, 56.15; H, 4.73%. Calcd for [Pd(dpsp)$_2$]=$C_{28}H_{28}P_2S_2Pd$: C, 56.33; H, 4.83%. The complex is soluble in $CHCl_3$, less soluble in CH_2Cl_2, and insoluble in alcohol, diethyl ether, and water.

[Pt(dpsp)$_2$]. To a methanol solution (15 cm^3) of Hdpsp (0.51 g, 2.1 mmol) and triethylamine (0.21 g, 2.1 mmol) were added an aqueous solution (15 cm^3) of K_2PtCl_4 (0.41 g, 1.0 mmol) with stirring, yielding a lemon-yellow precipitate. The complex was collected by filtration and washed with ethanol and then diethyl ether. Yield: 0.357 g (52%). Found: C, 49.11; H, 4.12%. Calcd for [Pt(dpsp)$_2$]=$C_{28}H_{28}P_2S_2Pt$: C, 49.05; H, 4.12%. The solubility of the complex is similar to that of the Pd(II) complex except that the Pt(II) complex is more soluble in CH_2Cl_2.

Table 1. Positional Parameters ($\times 10^4$) and Equivalent Isotropic Temperature Factors of [Ni(dmsp)$_2$]

Atom	x	y	z	B_{eq}/Å^2
Ni	6112(5)	2510(2)	570(3)	2.5
S(1)	6548(4)	1840(2)	2457(2)	3.9
S(2)	5428(4)	3069(2)	−1338(2)	4.0
P(1)	4664(3)	4234(2)	1252(2)	2.8
P(2)	7613(3)	771(2)	−70(2)	2.9
C(1)	1665(13)	4301(8)	1077(8)	3.7
C(2)	5516(19)	5721(8)	561(11)	5.2
C(3)	5278(16)	4428(9)	2872(8)	4.1
C(4)	5192(17)	3045(9)	3400(7)	4.1
C(5)	10771(14)	750(9)	12(9)	4.3
C(6)	6791(15)	−775(8)	516(9)	4.0
C(7)	6743(14)	674(8)	−1730(8)	3.8
C(8)	6981(18)	1949(10)	−2259(8)	4.9

X-Ray Analysis. A red crystal of [Ni(dmsp)$_2$] with approximate dimensions 0.10×0.10×0.25 mm^3 was used for the data collection. Crystal data: monoclinic, Pn, a=5.897(2), b=10.578(2), c=10.895(1) Å, β=92.83(2)°, V=678.8(3) Å^3, D_x=1.47, D_m=1.50 g cm^{-3}, Z=2, and μ=19.26 cm^{-1}. Diffraction data were collected on a Rigaku AFC-5R diffractometer with graphite Mo $K\alpha$ radiation (λ=0.71069 Å). Within the range $2\theta<60°$, 1571 independent reflections with $|F_o|>3\sigma(|F_o|)$ were obtained. The calculations were carried out on a HITAC M-680H computer at the Computer Center of the Institute for Molecular Science with the program system UNICS III.[7] The absorption correction was made by the DABEX program of the Computer Center Library. The structure was solved by the usual heavy-atom method; the position of Ni was deduced by means of the Patterson synthesis, and all the non-hydrogen atoms were located by the subsequent Fourier synthesis. The positions of all hydrogen atoms were identified in the subsequent difference-Fourier maps. The structure was refined by block-diagonal least squares methods with anisotropic thermal parameters for all non-hydrogen atoms. Final R was 0.040 for 1571 observed unique reflections, and atomic parameters are listed in Table 1. Complete lists of observed and calculated structure factors and anisotropic thermal parameters are deposited as Document No. 9016 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

The structure of [Ni(dmsp)$_2$] was determined by an X-ray diffraction method. Perspective drawings of the complex are shown in Fig. 1. The selected bond distances and angles are given in Table 2. The geometry around the nickel atom is square planar with a *trans*(*P,P*) arrangement. The Ni–P distances, av. 2.166(4) Å, are similar to 2.157(2) Å in the square planar thiolate-bridged dinuclear complex [$Ni_2Br_2(Ph_2PCH_2CH_2S)_2$],[8] and those in some square planar Ni(II)–diphosphine complexes.[9] These distances are somewhat shorter than those in square pyramidal Ni(II) phosphine complexes such as in [Ni(*rac*(*P*)-$CH_3SCH_2CH_2PPhCH_2CH_2PPhCH_2CH_2SCH_3$)$_2$](BF$_4$)$_2$ (average 2.226 Å).[2] The Ni–S distances in [Ni(dmsp)$_2$] are nearly equal to those between the nickel and terminal thiolate sulfur atoms in the square planar dinulear complex [$Ni_2(SCH_2CH_2SCH_2CH_2S)_2$].[10]

Table 2. Bond Distances (l/Å) and Angles (ϕ/°) of [Ni(dmsp)$_2$]

Ni–S(1)	2.178(4)	Ni–S(2)	2.179(4)
Ni–P(1)	2.162(4)	Ni–P(2)	2.171(4)
S(1)–C(4)	1.845(10)	S(2)–C(8)	1.828(11)
P(1)–C(1)	1.771(9)	P(1)–C(2)	1.825(12)
P(1)–C(3)	1.797(9)	P(2)–C(5)	1.860(10)
P(2)–C(6)	1.830(10)	P(2)–C(7)	1.858(9)
C(3)–C(4)	1.574(14)	C(7)–C(8)	1.476(14)
S(1)–Ni–S(2)	175.1(2)	S(1)–Ni–P(1)	88.9(2)
S(1)–Ni–P(2)	89.8(2)	S(2)–Ni–P(1)	92.3(2)
S(2)–Ni–P(2)	89.0(2)	P(1)–Ni–P(2)	178.5(2)
Ni–S(1)–C(4)	105.5(3)	Ni–S(2)–C(8)	105.9(4)
Ni–P(1)–C(1)	114.0(3)	Ni–P(1)–C(2)	117.6(4)
Ni–P(1)–C(3)	111.7(3)	C(1)–P(1)–C(2)	102.4(5)
C(1)–P(1)–C(3)	104.7(4)	C(2)–P(1)–C(3)	105.1(5)
Ni–P(2)–C(5)	114.7(3)	Ni–P(2)–C(6)	121.7(3)
Ni–P(2)–C(7)	105.2(3)	C(5)–P(2)–C(6)	104.8(4)
C(5)–P(2)–C(7)	105.9(4)	C(6)–P(2)–C(7)	103.0(4)
P(1)–C(3)–C(4)	104.2(6)	S(1)–C(4)–C(3)	114.6(7)
P(2)–C(7)–C(8)	107.6(7)	S(2)–C(8)–C(7)	108.5(7)

The bite angles of dmsp are almost the right angle. The chelate rings are puckerd with a gauche conformation (Fig. 1). The dihedral angles of the P–C–C–S moieties are 41.9(1) and 53.0(7)°. One methyl group on the phosphorus takes an axial orientation with respect to the coordination plane and the other an equatorial one.

In Table 3 are listed the ^{1}H, ^{13}C, and ^{31}P NMR spectral data of the complexes in CDCl$_3$. In the ^{1}H and ^{13}C NMR spectra, the square planar [Ni(dmsp)$_2$] com-

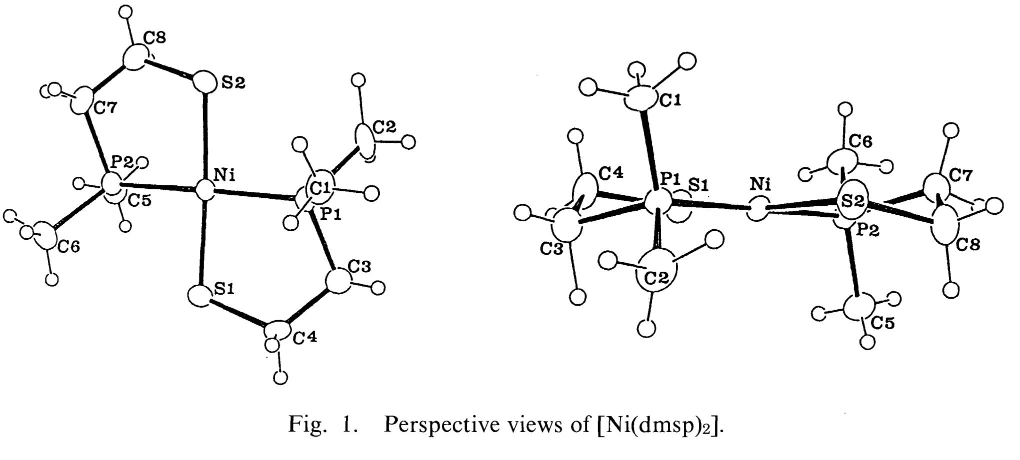

Fig. 1. Perspective views of [Ni(dmsp)$_2$].

Table 3. ^{1}H, ^{13}C, and ^{31}P NMR Spectral Data (δ) in CDCl$_3$[a)]

Complex	^{1}H	^{13}C	^{31}P
[Ni(dmsp)$_2$]	1.43(t, 12H, P-CH$_3$)	12.07(t, P-CH$_3$)	47.00(br.s)
	2.06(m, 4H, -CH$_2$-)	25.82(t, -CH$_2$-)	
	2.56(m, 4H, -CH$_2$-)	39.24(t, -CH$_2$-)	
[Pd(dmsp)$_2$]	1.52(t, 12H, P-CH$_3$)	12.99(t, P-CH$_3$)	42.70(br.s)
	2.12(m, 4H, -CH$_2$-)	26.19(t, -CH$_2$-)	
	2.75(m, 4H, -CH$_2$-)	40.16(t, -CH$_2$-)	
[Pt(dmsp)$_2$]	1.71(d, 12H, P-CH$_3$)	14.41(dd, P-CH$_3$)	30.15(s)
	2.31(m, 4H, -CH$_2$-)	23.98(t, -CH$_2$-)	[^{1}J(Pt-P)=2794 Hz]
	2.79(m, 4H, -CH$_2$-)	42.69(dd, -CH$_2$-)	
[Ni(dpsp)$_2$]	2.36(m, 4H, -CH$_2$-)	25.06(t, -CH$_2$-)	66.5(s)
	2.62(m, 4H, -CH$_2$-)	38.77(t, -CH$_2$-)	
	7.1—7.9(m, 20H, P-C$_6$H$_5$)	128.25(t) 130.39(t) 133.06(t) (P-C$_6$H$_5$)	
[Pd(dpsp)$_2$]	2.1—2.9(m, 8H, -CH$_2$-)	b)	63.13(s)
	7.1—7.9(m, 20H, P-C$_6$H$_5$)		
[Pt(dpsp)$_2$]	2.1—2.9(m, 8H, -CH$_2$-)	23.29(s, -CH$_2$-)	53.39(s)
		42.85(s, -CH$_2$-)	[^{1}J(Pt-P)=2899 Hz]
	6.9—7.9(m, 20H, P-C$_6$H$_5$)	128.02(d) 130.61(d) 133.27(d) (P-C$_6$H$_5$)	

a) References: TMS for ^{1}H and ^{13}C, and 85% H$_3$PO$_4$ for ^{31}P. b) Not defined due to low solubility of the complex.

plex exhibits apparent triplets for the methyl groups, which may be attributed to a so-called virtual coupling[11] in a *trans*(*P,P*) arrangement. The ^{1}H and ^{13}C NMR spectra of [Pd(dmsp)$_2$] are similar to those of [Ni(dmsp)$_2$], indicating a *trans*(*P,P*) arrangement in a square planar complex. On the other hand, [Pt(dmsp)$_2$] exhibits a doublet and a doublet of doublet for the methyl groups in the ^{1}H and ^{13}C NMR spectra, respectively, indicating a *cis*(*P,P*) arrangement.[11,12] The ^{31}P NMR spectrum of the Pt(II) complex also indicates a *cis*(*P,P*) arrangement, exhibiting a large ^{1}J(Pt-P) value which is reasonable for complexes with a *cis*(*P,P*) arrangement.[13]

Schwarzenbach[3] assigned the structures of [M(dpsp)$_2$] (M=Ni(II), Pd(II), Pt(II)) to a *trans*(*P,P*) arrangement. However, the ^{13}C and ^{31}P NMR spectra of the Pt(II) complex strongly suggest a *cis*(*P,P*) arrangement because of doublet signals for the phenyl carbons and the large ^{1}J(Pt-P) value (Table 3). The phenyl carbons of the Ni(II) complex exhibit triplet signals, indicating a *trans*(*P,P*) arrangement. No definite ^{13}C NMR spectrum of the Pd(II) complex was obtained because of low solubility of the complex. However, the spectral pattern of the phenyl protons (7.1—7.9 ppm) of the Pd(II) complex resembles that of the Ni(II) complex with a *trans*(*P,P*) arrangement rather than that of the Pt(II) complex with a *cis*(*P,P*) one.

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