Complexes with Sulphur and Selenium Donor Ligands. Part IV.† Reaction of Some Bidentate Phosphorus and Arsenic Donors with Bis-(*OO'*-dimethyl phosphorodithioato)nickel(II), and the Crystal Structure of [1-(Diphenylarsino)-2-(diphenylphosphino)ethane](*O*-methyl phosphorodithioato)nickel(II)—Benzene (2/1)

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The reaction of $Ni[S_2P(OMe)_2]_2$ with $Ph_2P{\cdot}C_2H_4{\cdot}AsPh_2$ in benzene–dichloromethane gives $[S_2PO(OMe)]$-$(Ph_2P{\cdot}C_2H_4{\cdot}AsPh_2)Ni,0{\cdot}5C_6H_6$. The crystal structure of this compound has been determined by Patterson and Fourier methods from three-dimensional X-ray photographic data. Crystals are monoclinic, space group $P2_1/c$, with $a = 9{\cdot}30(1)$, $b = 17{\cdot}37(1)$, $c = 20{\cdot}13(1)$ Å, $\beta = 108{\cdot}87(2)°$, $Z = 4$. Refinement by least-squares methods gave a conventional R of $0{\cdot}09$ for 3852 independent non-zero reflections.

The nickel atom is co-ordinated in an approximately square-planar configuration of chromophore [NiS$_2$PAs], the sulphur donor being the novel ligand $[S_2PO(OMe)]^{2-}$. Features of the molecular geometry are discussed.

The same reaction is given by 1,2-bis(diphenylphosphino)ethane but not by the arsino-analogue, which instead gives a poorly characterised 1:1 adduct with $Ni[S_2P(OMe)_2]_2$.

BIS(DIALKYL PHOSPHORODITHIOATO)- and bis(dialkyl-phosphinodithioato)-nickel(II) complexes, $Ni[S_2P(OR)_2]_2$ and $Ni(S_2PR_2)_2$, readily form five- and six-co-ordinate complexes with nitrogen-donor ligands in non-aqueous solution.[1] The latter are easily separated as solids and their spectral properties and stereochemistry have been reported.[2] The five-co-ordinate complexes do not normally give stable solids and only $Ni[S_2P(OMe)_2]_2$-(2,9-dimethylphenanthroline), a distorted trigonal bipyramid, and $Ni(S_2PEt_2)_2$(quinoline), a distorted square pyramid, have been fully characterised by crystal-structure analysis.[3]

Few complexes of these [NiS$_4$] chromophores are known with donor ligands other than nitrogen, except for $Ni[S_2P(OEt)_2]_2(PPh_3)$, which is believed to have a square-based pyramidal high-spin configuration on the basis of magnetic moment and electronic spectra.[4]

We report the reactions between the bidentate ligands $Ph_2P{\cdot}C_2H_4{\cdot}PPh_2$ (dpe), the mixed phosphino-arsino-analogue (dpae), and the diarsine (dae) with $Ni[S_2P(OMe)_2]_2$. The intention was to prepare five-

co-ordinate complexes with donor-atom sets S_3P_2, S_3PAs, and S_3As_2, *i.e.* having one of the phosphorodithioate ligands unidentate, analogous to the S_3N_2 donor set of $Ni[S_2P(OMe)_2]_2(2,9$-dimethylphenanthroline).[3] However, it was found that dpe and dpae replace one of the two phosphorodithioate groups in the complex resulting in a loss of a methyl group from the remaining phosphorodithioate. The crystal structure of the complex with dpae obtained by this reaction has been determined.

EXPERIMENTAL

$Ni[S_2P(OMe)_2]_2$ was prepared by addition of nickel chloride hexahydrate to a solution of P_2S_5 in excess of methanol, which was then heated under reflux under nitrogen[5] and recrystallised several times before use. The ligands dpe, dpae, and dae (Strem Chemicals) were not further purified.

[1-*(Diphenylarsino)*-2-*(diphenylphosphino)ethane*](*O*-methyl phosphorodithioato)*nickel*(II)–*benzene* (2/1).—The ligand dpae (0·237 g, 0·5 mmol) in CH_2Cl_2 (50 ml) was added to $Ni[S_2P(OMe)_2]_2$ (0·18 g, 0·5 mmol) in dichloromethane (50

† Part III, preceding paper.

[1] C. K. Jørgensen, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1571; J. R. Angus, G. M. Wolterman, W. R. Vincent, and J. R. Wasson, *ibid.*, 1971, **33**, 3041.

[2] S. E. Livingstone and A. E. Mihkelson, *Inorg. Chem.*, 1970, **9**, 2545.

[3] P. S. Shetty and Q. Fernando, *J. Amer. Chem. Soc.*, 1970, **92**, 3964.

[4] N. Yoon, M. J. Incorvia, and J. I. Zink, *J.C.S. Chem. Comm.*, 1972, 499.

[5] C. Furlani, A. A. G. Tomlinson, P. Porta, and A. Sgamellotti, *J. Chem. Soc. (A)*, 1970, 2929.

ml), when the violet solution immediately became orange. Benzene (25 ml) was added and the mixture set aside overnight. Orange prisms of the *complex* were washed with benzene and dried *in vacuo* (Found: C, 53·0; H, 4·4; As, 11·1; Ni, 8·7; P, 9·7; S, 9·6. $C_{30}H_{30}AsNiO_2P_2S_2$ requires C, 52·8; H, 4·4; As, 11·0; Ni, 8·6; P, 9·1; S, 9·4%).

The presence of half a molecule of benzene of crystallisation was confirmed by thermogravimetry (wt. loss, 146—156 °C: Found, *ca.* 6·2. Calc. 5·75%).

This reaction carried out in acetone solutions gave the same compound, but without acetone of crystallisation (Found: C, 49·3; H, 4·3; As, 11·5; Ni, 8·9; P, 9·5; S, 9·6. $C_{27}H_{27}AsNiO_2S_2P_2$ requires C, 50·4; H, 4·2; As, 11·65; Ni, 9·13; P, 9·63; S, 9·97%).

[1,2-*Bis(diphenylphosphino)ethane*](*O-methyl phosphorodithioato*)*nickel*(II).—A similar procedure with $Ph_2P \cdot C_2H_4 \cdot PPh_2$ gave well developed orange *prisms* (Found: C, 53·0; H, 4·5; Ni, 9·8; P, 15·5; S, 10·65. $C_{27}H_{27}Ni O_2P_3S_2$ requires C, 54·0; H, 4·5; Ni, 9·8; P, 15·52; S, 10·68%).

All the compounds are air-stable, insoluble in water, and soluble in acetone, chloroform, and benzene. The colour of the solution (1 : 1 molar ratio) did not immediately change to orange when reaction was carried out in benzene.

Reaction of 1,2-*Bis(diphenylarsino)ethane with* $Ni[S_2P-(OMe)_2]_2$.—Addition of dae to $Ni[S_2P(OMe)_2]_2$ in acetone, dichloromethane, or benzene gave no visible colour change and the only change in optical spectrum consisted in a slight lowering in intensity of the bands due to the initial nickel(II) complex. Evaporation of the solutions to dryness gave mainly the starting products, but a very small amount of a green crystalline compound could be separated under the microscope. The reaction is not reproducible and depends on the rate of evaporation of solvent. Nevertheless, sufficient product was separated for elemental analyses for carbon and hydrogen, and for the optical spectrum to be recorded (Found: C, 44·0; H, 4·0. Calc. for $C_{27}H_{27}As_2NiO_2PS_2$: C, 47·2; H, 4·0. Calc. for a 1 : 1 complex $C_{30}H_{36}As_2NiO_4P_2S_4$: C, 42·0; H,4·2%). It was not possible to remove completely all impurities due to starting products, and the compound immediately dissociates in solution in acetone, benzene, dichloromethane, or ethanol.

Physical Measurements.—Electronic spectra were recorded on Beckmann DK 2A and Shimadzu MPS 50L spectrophotometers. Magnetic susceptibility measurements were made by the Gouy method using $HgCo(CNS)_4$ as tube calibrant. Thermal analyses were performed on a Du Pont thermal analyser under nitrogen.

Crystal Structure of $Ni[S_2PO(OMe)](Ph_2P \cdot C_2H_4 \cdot AsPh_2)$

Crystal Data.—$C_{30}H_{30}AsNiO_2S_2P_2$, $M = 682·28$, Monoclinic, $a = 9·30$ (1), $b = 17·37$ (1), $c = 20·13$ (1) Å, $\beta = 108·87$ (2)°, $U = 3076·8$ Å³, $D_m = 1·49$ (1) (by flotation), $Z = 4$, $D_c = 1·47$, $F(000) = 1396$. Space group $P2_1/c$ (C_{2h}^5, No. 14) from systematic absences: $0k0$, $h0l$, for k and l odd, respectively. $\mu(Cu-K_\alpha) = 45·8$ cm⁻¹.

Cell dimensions were determined by superimposing zinc oxide lines [6] on zero-layer Weissenberg photographs about the *a* and *b* axes, and applying an improved version of Christ's method.[7]

Reflections from both $Cu-K_{\alpha 1}$, when possible (λ taken as 1·540562 Å), and $Cu-K_\alpha$ radiation (λ = 1·5418 Å) were

used in calculating lattice parameters, and error limits given are maximum estimates. The *X*-ray intensities were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs taken about the *a* (0—7*kl*) and *b* (*h*0—4*l*) axes. A prismatic crystal *ca.* 0·1 × 0·1 × 0·2 mm was used for data collection. The intensities of 3852 independent reflections were recorded with Ni-filtered Cu-K_α radiation (λ = 1·5418 Å) and were corrected for Lorentz and polarisation effects and spot size of the upper layers. No absorption or extinction corrections were applied. Observed structure amplitudes were placed on a common scale.[8]

Structure Determination and Refinement.—The structure was solved by means of three-dimensional Patterson and Fourier syntheses and refined by block-diagonal least-squares analysis. The non-hydrogen atoms were refined

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$) of the non-hydrogen atoms, with standard deviations in parentheses

Atoms	x	y	z
Ni	2954(2)	2511(1)	2197(1)
S(1)	3645(3)	2865(2)	3310(1)
S(2)	1888(3)	1480(2)	2480(1)
P(1)	2709(3)	1860(2)	3483(1)
O(1)	4029(9)	1281(5)	3895(4)
C(1)	5258(17)	1113(8)	3673(8)
O(2)	1656(10)	1921(6)	3892(4)
As	2203(1)	2244(7)	1040(6)
C(2)	3235(11)	2974(6)	616(5)
C(3)	3396(13)	3735(7)	1000(5)
P(2)	3975(2)	3568(1)	1965(1)
C(4)	3466(11)	4470(6)	2328(6)
C(5)	2057(13)	4826(7)	1962(6)
C(6)	1634(16)	5474(8)	2264(9)
C(7)	2512(16)	5772(7)	2885(7)
C(8)	3845(15)	5415(8)	3237(7)
C(9)	4329(13)	4760(6)	2960(6)
C(10)	6080(11)	3545(6)	2281(5)
C(11)	6917(13)	4202(7)	2261(8)
C(12)	8504(17)	4160(9)	2540(10)
C(13)	9205(15)	3501(9)	2806(8)
C(14)	8410(14)	2862(8)	2841(7)
C(15)	6802(11)	2871(7)	2573(6)
C(16)	63(11)	2396(6)	621(5)
C(17)	−640(12)	2237(6)	−72(5)
C(18)	−2229(13)	2279(7)	−366(6)
C(19)	−3081(13)	2474(9)	65(7)
C(20)	−2369(16)	2643(11)	754(7)
C(21)	−781(12)	2598(8)	1055(5)
C(22)	2444(12)	1286(6)	629(5)
C(23)	1961(15)	617(7)	875(7)
C(24)	2064(21)	−82(8)	535(8)
C(25)	2533(20)	−109(9)	−27(8)
C(26)	2942(21)	557(10)	−273(9)
C(27)	2910(18)	1255(8)	48(7)
C(28)	237(19)	4395(9)	−354(8)
C(29)	1119(10)	5078(10)	−291(8)
C(30)	868(18)	5632(9)	40(9)

with isotropic temperature factors to R 0·14. After correction of a few indexing errors and a rescaling of the data, a further four cycles of isotropic refinement were carried out and gave R 0·13. At this point the hydrogen atoms were included at calculated positions (assuming C–H 1·00). Four cycles of least squares with anisotropic temperature factors for the 38 non-hydrogen atoms and isotropic

[7] G. Mazzone, A. Vaciago, and M. Bonamico, *Ricerca sci.,* 1963, **33**, 1113.

[8] W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *Acta Cryst.,* 1965, **18**, 129.

[6] A. Cimino, G. Mazzone, and P. Porta, *Z. phys. Chem.,* 1964, **41**, 154.

thermal and positional parameters for the 30 hydrogen atoms fixed, reduced R to 0·09. A successive cycle of refinement indicated no shifts $>0·25$ σ, and refinement was considered to be concluded. The quantity minimised in the least-squares analyses was $R = \Sigma w(k|F_o| - |F_c|)^2$ where the weighting factor $w = [a + bk|F_o| + c(kF_o)^2]^{-1}$, with $a = 3·0$, $b = 1·0$, $c = 0·004$.

A final difference-Fourier synthesis, calculated from final atomic parameters, confirmed the correctness of the structure since ρ was *ca.* zero at the sites of all atoms [σ(ρ) $= 0·24$ eA^{-3} for the structure as a whole].

Atomic scattering factors were taken from ref. 9 for nickel, arsenic, sulphur, phosphorus, oxygen, and carbon (the first four being corrected for the real part of anomalous dispersion),[10] and from ref. 11 for hydrogen. Final atomic and anisotropic thermal parameters, with their estimated standard deviations, for all non-hydrogen atoms are given in Tables 1 and 2. Calculated and assumed

TABLE 2

Anisotropic thermal parameters * ($\times 10^4$) of the non-hydrogen atoms, with estimated standard deviations in parentheses

Atoms	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ni	119(2)	36(1)	22(1)	−9(2)	33(1)	2(1)
S(1)	188(4)	42(1)	23(1)	−14(3)	35(3)	−4(1)
S(2)	191(5)	50(1)	27(1)	−63(4)	46(3)	0(1)
P(1)	151(4)	48(1)	24(1)	−9(3)	42(2)	10(1)
O(1)	184(14)	48(3)	45(3)	8(11)	25(10)	21(5)
C(1)	238(26)	41(5)	64(6)	25(18)	27(19)	−3(9)
O(2)	197(14)	80(5)	35(3)	−15(13)	89(10)	10(6)
As	151(2)	44(0)	27(0)	−4(1)	41(1)	−3(1)
C(2)	131(15)	48(4)	25(3)	−1(12)	45(10)	2(5)
C(3)	185(18)	41(4)	29(3)	−26(14)	36(11)	6(6)
P(2)	63(2)	23(1)	17(0)	0(2)	18(2)	2(1)
C(4)	129(15)	32(3)	37(3)	3(11)	46(11)	4(5)
C(5)	146(18)	48(5)	43(4)	29(14)	35(13)	−5(7)
C(6)	203(23)	49(5)	65(6)	49(18)	80(18)	−12(9)
C(7)	228(22)	40(4)	53(5)	26(16)	107(17)	0(7)
C(8)	210(22)	53(5)	46(4)	−60(17)	78(16)	−35(8)
C(9)	178(18)	39(4)	39(3)	−21(13)	34(12)	−12(6)
C(10)	106(14)	36(4)	36(3)	10(11)	36(10)	−4(5)
C(11)	115(17)	45(5)	76(7)	1(14)	69(16)	16(9)
C(12)	190(24)	60(7)	79(8)	−34(20)	101(22)	−15(12)
C(13)	154(20)	79(8)	52(5)	30(20)	58(16)	−23(10)
C(14)	164(19)	64(6)	41(4)	54(17)	51(14)	17(8)
C(15)	108(14)	51(5)	38(3)	32(13)	59(11)	3(6)
C(16)	119(14)	44(4)	28(3)	23(12)	41(9)	14(5)
C(17)	145(16)	42(4)	27(3)	8(13)	35(10)	−5(5)
C(18)	156(18)	53(5)	34(3)	21(15)	27(12)	5(7)
C(19)	127(18)	71(7)	46(4)	8(17)	35(13)	24(9)
C(20)	189(23)	98(9)	39(4)	39(4)	87(16)	17(10)
C(21)	128(16)	77(7)	26(3)	52(16)	41(10)	2(7)
C(22)	156(17)	44(4)	26(3)	24(13)	35(10)	−6(5)
C(23)	226(23)	40(4)	43(4)	−16(16)	63(15)	−2(7)
C(24)	384(38)	43(5)	49(5)	12(23)	92(22)	−12(9)
C(25)	343(34)	51(6)	55(6)	10(22)	87(22)	−52(10)
C(26)	368(39)	61(7)	63(7)	29(25)	183(26)	−22(11)
C(27)	314(29)	50(5)	48(5)	4(20)	159(19)	−24(8)
C(28)	304(31)	51(6)	53(6)	74(22)	12(20)	−1(9)
C(29)	254(27)	67(8)	55(6)	51(23)	−1(19)	35(11)
C(30)	232(25)	56(6)	62(6)	21(20)	−11(20)	18(10)

* In the form: $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$.

isotropic temperature factors for hydrogen atoms are in Table 3, and observed and calculated structure factor tables have been deposited as Supplementary Publication No. SUP 20915 (14 pp., 1 microfiche).* Bond angles

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

TABLE 3

Fractional co-ordinates ($\times 10^4$) for hydrogen atoms

Atoms *	x	y	z
H(1a)	5783	775	4088
H(1b)	5955	1543	3652
H(1c)	5002	801	3236
H(2a)	4271	2783	651
H(2b)	2633	3059	110
H(3a)	2408	4015	842
H(3b)	4194	4057	893
H(5)	1358	4603	1514
H(6)	688	5751	2009
H(7)	2182	6234	3086
H(8)	4508	5630	3690
H(9)	5308	4499	3228
H(11)	6405	4688	2048
H(12)	9105	4625	2518
H(13)	333	3486	2998
H(14)	8942	2375	3059
H(15)	6229	2396	2592
H(17)	−574	2091	−541
H(18)	−2174	2135	−835
H(19)	−4209	2487	−127
H(20)	−2424	2793	1226
H(21)	−827	2751	1524
H(23)	1603	634	1293
H(24)	1699	−570	714
H(25)	2589	−610	−258
H(26)	3347	538	−679
H(27)	3147	1746	−162
H(28)	394	3937	−632
H(29)	1494	6116	92
H(30)	1936	5101	−517

* Numbered according to the carbon atoms to which they are bonded; isotropic temperature factor taken as 6·0 Å^2.

TABLE 4

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

(a) Distances

Ni−S(1)	2·209(3)	O(1)−C(1)	1·39(2)
Ni−S(2)	2·210(4)	As−C(2)	1·95(1)
Ni−As	2·253(2)	As−C(16)	1·91(1)
Ni−P(2)	2·185(3)	As−C(22)	1·90(1)
S(1)−P(1)	2·032(4)	C(2)−C(3)	1·51(2)
S(2)−P(1)	2·024(4)	P(2)−C(3)	1·86(1)
P(1)−O(1)	1·597(8)	P(2)−C(10)	1·85(1)
P(1)−O(2)	1·47(1)	P(2)−C(4)	1·85(1)

Mean C−C ^{a} 1·38 ± 0·04

(b) Angles

S(1)−Ni−S(2)	88·4(1)	Ni−As−C(22)	126·0(3)
As−Ni−P(2)	87·9(1)	Ni−P(2)−C(3)	110·8(4)
Ni−S(1)−P(1)	86·2(1)	Ni−P(2)−C(4)	116·2(4)
Ni−S(2)−P(1)	84·4(1)	Ni−P(2)−C(10)	113·1(3)
S(1)−P(1)−S(2)	98·9(2)	As−C(2)−C(3)	109·0(8)
S(1)−P(1)−O(1)	109·3(4)	C(2)−As−C(16)	107·9(4)
S(1)−P(1)−O(2)	115·6(4)	C(2)−As−C(22)	103·6(5)
S(2)−P(1)−O(1)	107·0(4)	C(16)−As−C(22)	100·4(4)
S(2)−P(1)−O(2)	118·5(4)	C(2)−C(3)−P(2)	110·1(7)
P(1)−O(1)−C(1)	122·7(9)	C(3)−P(2)−C(4)	104·8(5)
Ni−As−C(2)	106·7(3)	C(3)−P(2)−C(10)	106·2(5)
Ni−As−C(16)	111·0(3)	C(4)−P(2)−C(10)	105·0(4)

Mean C−C−C ^{b} 120 ± 3°

(c) Intermolecular contacts

O(2)−H(28) ^{c}	2·29	
O(2)−H(2b) ^{c}	2·32	

^{a} Mean C−C bond lengths within benzene rings; σ *ca.* 0·02 Å for each C−C distance. ^{b} Mean C−C−C angles within benzene rings; σ *ca.* 1° was observed for each C−C−C angle. ^{c} H(28) and H(2b) are bonded to C(28) and C(2) (see Figure 1).

9 D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.
10 D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.
11 H. P. Hanson, F. Herman, J. D. Lea, and S. Skilmann, *Acta Cryst.*, 1964, **17**, 1040.

and distances within the crystal-chemical unit of the complex and for the benzene of crystallisation are shown in Table 4, together with significant intermolecular contacts. Table 5 reports the equations of various planes

TABLE 5

Equations of planes, in the form $Ax + By + Cz = D$, referred to the crystallographic axes, and, in square brackets, deviations (Å) of atoms from the planes

Plane (I): $0.855x - 0.496y - 0.134z = 0.442$
[Ni -0.037, S(1) 0.019, S(2) 0.000, As 0.018, P(2) -0.001]

Plane (II): $0.659x + 0.586y - 0.660z = -3.565$
[C(4) -0.010, C(5) 0.004, C(6) 0.006, C(7) -0.010, C(8) 0.004, C(9) 0.006]

Plane (III): $-0.345x + 0.273y + 0.961z = -4.150$
[C(10) 0.006, C(11) 0.000, C(12) -0.010, C(13) 0.013, C(14) -0.007, C(15) -0.002]

Plane (IV): $0.147x + 0.963y - 0.259z = -3.694$
[C(16) 0.001, C(17) 0.000, C(18) -0.006, C(19) 0.011, C(20) -0.010, C(21) 0.004]

Plane (V): $0.788x - 0.139y + 0.313z = -1.860$
[C(22) -0.016, C(23) 0.020, C(24) -0.010, C(25) -0.006, C(26) 0.011, C(27) 0.001]

Dihedral angles (°) between planes:

(I)–(II)	78.36	(I)–(IV)	67.33
(I)–(III)	72.82	(I)–(V)	33.56

and the dihedral angles between them. Figure 1 shows a projection of one asymmetric unit within the cell on the bc plane.
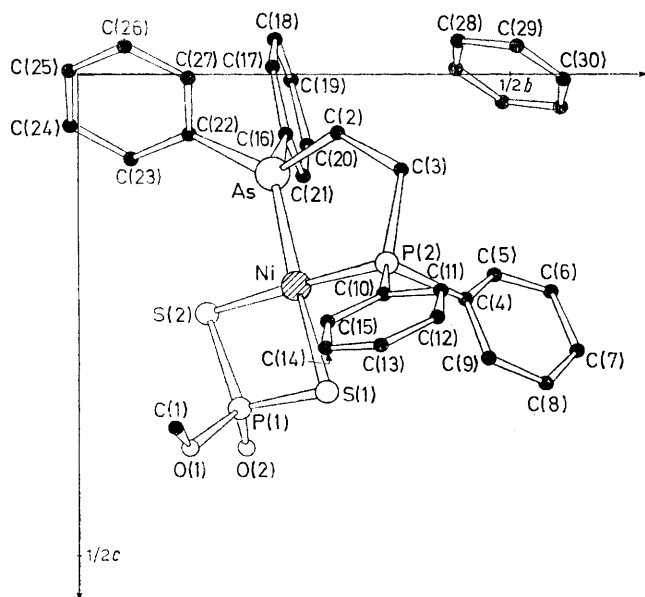

FIGURE 1   Projection on the bc plane of one asymmetric unit

Calculations were carried out on the Univac 1108 computer of Rome University. Intensity corrections, scaling,

Wilson plot, Fourier syntheses, and interatomic distances and angles were calculated using the programs of ref. 12. Programs by Carruthers and Spagna [13] were used for structure-factor calculations and least-squares refinement. Least-squares planes and dihedral angles between planes were calculated by use of a program by Spagna.[14]

RESULTS

The structure of Ni[S$_2$PO(OMe)](dpae), apart from the intermolecular contacts relating to O(2) (Table 4), consists of discrete unimolecular units with no non-hydrogen intermolecular contacts <3.5 Å. The arrangement around the nickel atom is planar [plane (I), Table 5], the maximum deviation being 0.037 Å for nickel.

The Ni–S distances seem a little shorter than is usually found [15–19] for bis(dialkyl phosphorodithioato)- and bis-(dialkylphosphinodithioato)-nickel(II) complexes [2.210(4) compared to 2.23 Å, Table 6] while S–P distances are

TABLE 6

S–Ni and S–P Distances for bis(dialkyl phosphorodithioato)- and bis(dialkylphosphinodithioato)-nickel(II) complexes

Complex	S–Ni	S–P
Ni(S$_2$PMe$_2$)$_2$ [a]	2.229(5)	1.997(7)
	2.242(5)	2.018(7)
Ni[S$_2$P(OMe)$_2$]$_2$ [b]	2.219(2)	1.984(2)
	2.225(2)	1.979(2)
Ni[S$_2$P(OEt)$_2$]$_2$ [c]	2.230(4)	1.986(6)
	2.236(4)	1.993(5)
Ni(S$_2$PEt$_2$)$_2$ [d]	2.23(1)	2.00(1)
	2.22(1)	2.01(1)
Ni(S$_2$PPh$_2$)$_2$ [e]	2.234(5)	2.006(8)
	2.242(5)	2.022(8)

[a] Ref. 15.   [b] Ref. 16.   [c] Ref. 17.   [d] Ref. 18.   [e] Ref. 19.

perhaps a little longer, $2.024(5)$ compared to 2.00 Å. This is as expected for bonding by the $\cdot$PS$_2{}^{2-}$ grouping compared with the more important valence bond form $\cdot\overset{+}{P}S_2{}^{2-}$ of the dialkyl phosphoro- and dialkylphosphino-dithioates (the other valence-bond formulation $\cdot$PS$_2{}^-$, of the latter is believed to be much less important). The S–Ni–S angle [88.39(0.12)°] is the same as that found in Ni[S$_2$P(OMe)$_2$]$_2$.[16]

The P–O [$1.597(8)$] and P=O [$1.474(11)$ Å] distances are in good agreement with literature values, e.g. in the recent structural redetermination of P$_4$O$_{12}{}^{4-}$ mean P–O is 1.607 and mean P=O 1.469 Å.[20]

There are no other structural data for complexes of dpae. However, the Ni–P distance (2.185 Å) is in agreement with those in (π-methylallyl)Ni(dpe)Br, $2.178(4)$ and $2.180(4)$ Å,[21] and longer than those found in tri-phenylphosphine complexes, e.g. (π-C$_5$H$_5$)Ni(PPh$_3$)(C$_6$F$_5$) $2.145(4)$ Å.[22] This may reflect weaker nickel–phosphorus back-donation in the present complex. The Ni–As distance [$2.253(2)$ Å] is significantly shorter than in Ni[o-phenylenebis(dimethylarsine)]$_2$I$_2$ [$2.284(2)$ and

[12] J. R. Carruthers, A. Domenicano, and R. Spagna, unpublished work.
[13] J. R. Carruthers and R. Spagna, unpublished work.
[14] R. Spagna, unpublished work.
[15] M. Jones, G. B. Ansell, and J. J. Katz, Acta Cryst., 1969, B25, 1939.
[16] V. Kastalsky and J. F. McConnell, Acta Cryst., 1969, B25, 909.
[17] V. Kastalsky and J. F. McConnell, Acta Cryst., 1967, 22, 853.
[18] P. S. Shetty and Q. Fernando, Acta Cryst., 1969, B25, 1294.
[19] P. Porta, A. Sgamellotti, and N. Vinciguerra, Inorg. Chem., 1970, 7, 2625.
[20] D. A. Koster and A. J. Wagner, J. Chem. Soc. (A), 1970, 435.
[21] M. R. Churchill and T. A. O'Brien, J. Chem. Soc. (A), 1970, 206.
[22] M. R. Churchill and T. A. O'Brien, J. Chem. Soc. (A), 1968, 2970.

2·302(2) Å],[23] as expected for a square-planar structure compared to a tetragonal octahedral structure. Although Ni–As is also much shorter than given by the Pauling covalent radius [Ni(square) + As(tetrahedral), 1·22 + 1·18 = 2·40 Å], it would be oversimplifying to impute this to M → L backbonding, as pointed out by recent n.m.r. work for the M–P bond.[24]

The As–C(sp^2) [1·91(1) and 1·90(1) Å] and As–C(sp^3) distances [1·95(1) Å] are shorter than those in bis-[o-phenyl-enebis(dimethylarsine)]NiI$_2$. The difference between them (ca. 0·04 Å) agrees with that between the covalent radii of sp^2 and sp^3 hybridised carbon atoms.[18] However, the errors in these bond distances are relatively large. In fact the P–C(sp^2) and P–C(sp^3) distances do not follow this correlation at all well. The mean C–P–C angle within dpae (105·6°) is significantly lower than the ideal tetrahedral angle, as is also the mean C–As–C angle (105·2°). A similar effect has been found in several triphenylphosphine complexes.[22]

There are short intermolecular contacts between C(28) of the benzene molecule of crystallisation and O(2) of the P=O group of another molecule of the complex in the unit cell. This may explain the high temperature needed to drive off the benzene (see Experimental section).

In the molecule as a whole two conformations are theoretically possible, depending on whether the P–C(sp^3) bonds are arranged (A) with the carbon atom pointing in the same direction as the P=O bond of the phosphoro-dithioate, with respect to the plane of the molecule, or (B) with the As–C(sp^3) carbon atom on the same side as the P=O bond.

(A)   (B)
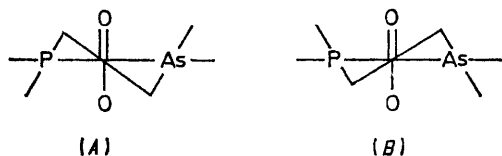
The structure determination has shown that (A) is the form present, presumably partially owing to the short contacts between the P=O oxygen atom, O(2), and the hydrogen atom, H(2b), of dpae.

DISCUSSION

The crystal structure determination has established that addition of dpae to Ni[S$_2$P(OMe)$_2$]$_2$ takes place through replacement of one [S$_2$P(OMe)$_2$]$^-$ ligand by dpae and elimination of a methyl group from the other to give [S$_2$PO(OMe)]$^{2-}$. A similar elimination has been reported to be formed from several reactions of alkyl- and aryl-phosphines with Pd[S$_2$P(OEt)$_2$]$_2$,[25] but this is the first example with nickel(II) or a bidentate ligand.

From chemical and spectroscopic evidence Stephenson et al.[26] suggested that elimination of the methyl group in bis(O-alkyl dithiocarbonato)platinum occurred via a nucleophilic attack by a displaced $^-$S$_2$COR group on the ionic intermediate [(R$_3$P)$_2$Pt(S$_2$COR)]$^+$. A similar

mechanism may be suggested for the present reaction (Scheme).

Attempts to separate the possible intermediates (I) or (II) by addition of excess of light petroleum for (I), or addition of BPh$_4^-$ for (II), were unsuccessful. In addition, conductivity measurements on an acetone solution of Ni[S$_2$P(OMe)$_2$]$_2$ and dpae (1 : 1) gave no evidence for the presence of ionic species. However, the tendency of (non-polar) benzene to inhibit the reaction relative to (polar) acetone or dichloromethane would agree with initial in-plane attack by the phosphorus atom. Triphenylphosphine itself does not substitute S$_2$P(OMe)$_2^-$ in Ni[S$_2$P(OMe)$_2$]$_2$, but gives a 1 : 1 adduct, probably owing to its lower basicity compared with dpae. This is in agreement with the fact that dae does not give the reaction, and supports in-plane attack by the phosphorus atom of dpae.

(I)

(II)

Ni[S$_2$PO(OMe)] (dpae)
+
MeS$_2$P(OMe)$_2$

SCHEME
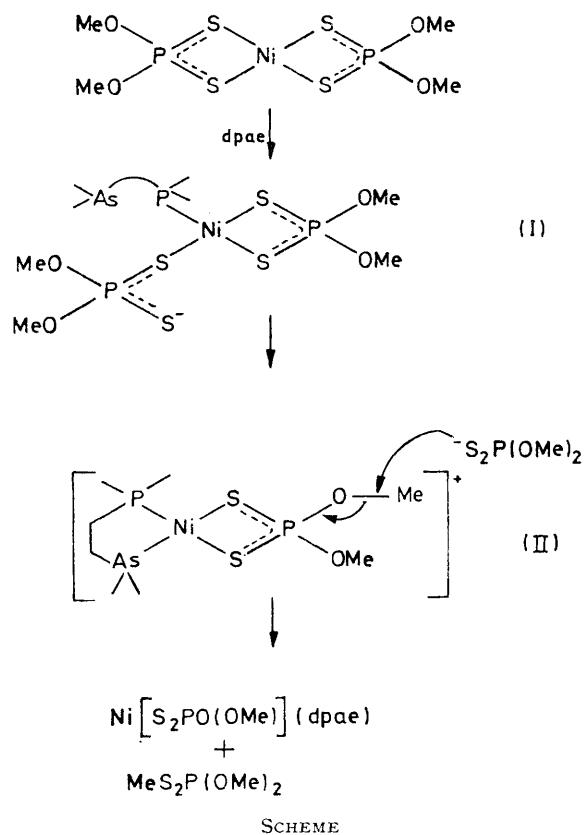
In contrast to dpae, 2,9-dimethyl-1,10-phenanthroline reacts with Ni[S$_2$P(OMe)$_2$]$_2$ to give a 1 : 1 complex in which one phosphorodithioate group is unidentate.[3]

The foregoing points indicate that the flexible back-bone structure of dpae may be important in giving rise to replacement rather than addition, and that there may exist some transition state between (I) and (II) such that the outgoing phosphorodithioate ligand is

[23] N. C. Stephenson, Acta Cryst., 1964, 17, 592.
[24] W. Levason and C. A. McAuliffe, Adv. Inorg. Chem. Radio-chem., 1972, 14, 173.

[25] J. P. Fackler and W. C. Seidel, Inorg. Chem., 1969, 8, 1631.
[26] J. M. C. Alison and T. A. Stephenson, J. Chem. Soc. (A), 1973, 254.

' channelled ' under the plane of the molecule towards the remaining ligand, by the steric hindrance of the phenyl groups attached to arsenic. A preliminary crystal structure of a species similar to (I), with a
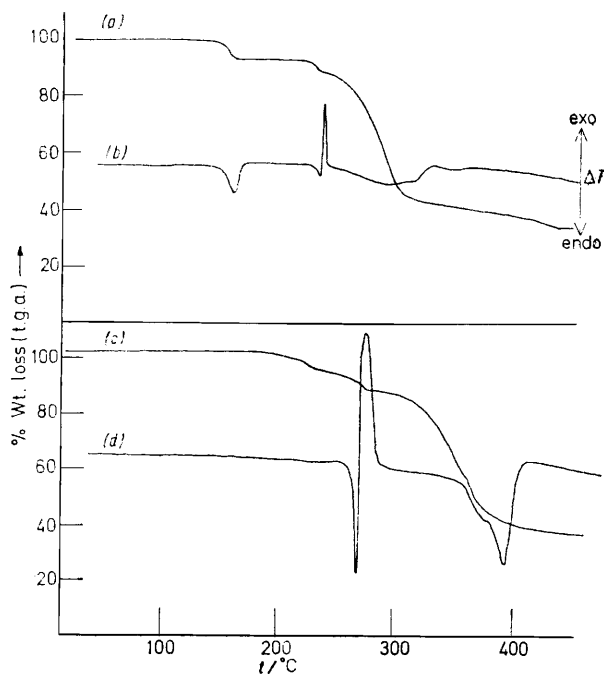

FIGURE 2   T.g.a. [(a) and (c)] and d.t.a. curves [(b) and (d)]

unidentate $^-S_2PPh_2$ group having its free sulphur atom folded under the molecular plane, has been reported.[27]

Chemical analysis and electronic spectra show that a similar reaction occurs between dpe and $Ni[S_2P(OMe)_2]_2$. The electronic spectra of both $Ni[S_2PO(OMe)](dpae)$ and its dpe analogue are uninformative, and consist of a single, well defined band at ca. 25 kK, together with possibly two shoulders at lower energy (Table 7) which are more evident in reflectance spectra. Spectra identical to those in the solid state are given by acetone solutions of $Ni[S_2P(OMe)_2]_2$ with excess of dpae or dpe (1 : 5 molar). This indicates that further substitution, of $[S_2PO(OMe)]^{2-}$ does not occur, presumably because of steric hindrance to further reaction caused by the phenyl groups attached to phosphorus and arsenic. Although the environment of the nickel(II) atom is of lower symmetry in $Ni[S_2PO(OMe)](dpae)$ than in $Ni(dpae)Cl_2$, the band intensities in the electronic spectra are higher in the latter, ε 1·7 $\times$ 10^3 at $\bar{\nu} = 21\cdot6$ kK (Table 7).[28]

[27] J. M. C. Alison and T. A. Stephenson, J. Chem. Soc. (A), 1971, 3690.

The $[S_2PO(OMe)]^{2-}$ group in $Ni[S_2PO(OMe)](dpae)$ appears to be very stable thermally. Thermal measurements (Figure 2) show that, after loss of benzene of crystallisation, decomposition does not occur until 225 °C, and involves the dpae : wt. loss at 265 °C, ca. 3·7%; calc. for $-C_2H_2$, 3·8%. This is followed by complicated rearrangements (exothermic peak at ca. 240 °C in the d.t.a.

TABLE 7

Optical spectra (kK; ε, 1 mol^{-1} cm^{-1})

$Ni[S_2PO(OMe)](dpae)$	(a) 24·4, 19·2sh, ca. 16·1sh
	(b) 24·7(760), ca. 19sh
$Ni[S_2PO(OMe)](dpe)$	(a) 25·6, 22·7sh, ca. 16·0sh
	(b) 25·5(724), ca. 20·0sh
$Ni[S_2P(OMe)_2]_2(dae)$	(a) ca. 30·3, ca. 25·5sh, 19·6, 13·7, 9·4

^{a} Reflectance. ^{b} Acetone solution.

curve) and decomposition of most of the ligand (ca. 45% at 310 °C). Although the d.t.a. curve of the dpe analogue is very similar, the t.g.a. curve is too complicated for definite evidence of loss of acetylene.
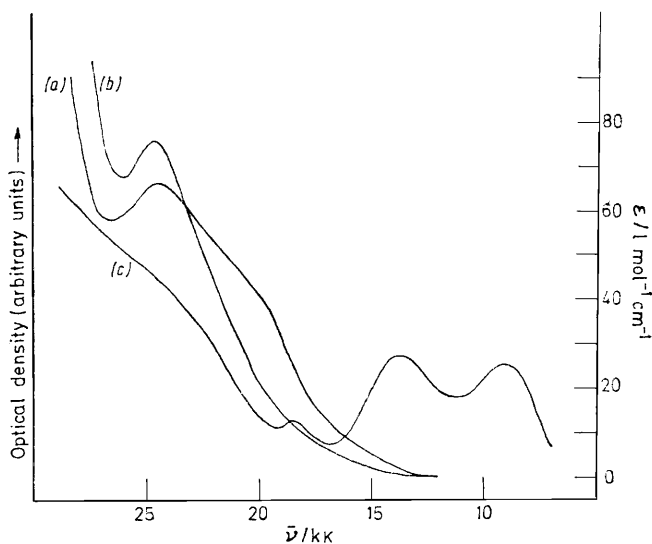

FIGURE 3   Electronic spectra: (a) $Ni[S_2PO(OMe)](dpae)$,-$0\cdot5C_6H_6$ (reflectance); (b), $Ni[S_2P(OMe)_2]_2$-dpae (1 : 1) (acetone solution); and (c), $Ni[S_2P(OMe)_2]_2(dae)$ (reflectance)

The paramagnetism ($\mu \gtrsim 2\cdot3$ B.M., sample impure) and form of the reflectance spectrum of $Ni[S_2P-(OMe)_2]_2(dae)$ would suggest this to be a high-spin, five-co-ordinate, structure (see Figure 3).

[28] G. R. Van Hecke and W. DeW. Horrocks, Inorg. Chem., 1966, 5, 1968.