Journal of Organometallic Chemistry, 192 (1980) 437—446

SYNTHESIS AND REACTIVITY OF NOVEL CATIONIC ORGANONICKEL(II) COMPLEXES. X-RAY STRUCTURE OF [BIS(2-DIPHENYLPHOSPHINOETHYL)PHENYLPHOSPHINENICKEL-*O*-METHYLSULFINATE]TETRAPHENYLBORATE

C. MEALLI, M. PERUZZINI and P. STOPPIONI *

Istituto Chimica Generale ed Inorganica, Università di Firenze, Laboratorio C.N.R., Via J. Nardi, 39, Florence (Italy)

(Received January 16th, 1980)

Summary

Cationic tetracoordinate nickel(II) compounds containing a nickel—carbon σ bond with general formula [NiR(etp)]Y, (etp = bis(2-diphenylphosphinoethyl)phenylphosphine, $PhP(CH_2CH_2PPh_2)_2$; R = CH_3, $CH_2C_6H_5$, C_6H_5; Y = BPh_4, PF_6) were synthesized by reaction of the complexes [NiX(etp)]Y (X = halogen) with appropriate Grignard reagents.

This type of organometallic complexes undergo insertion of sulfur dioxide into the Ni—C bond with formation of tetracoordinate O-sulfinate derivatives of nickel(II). The structure of $[NiOS(O)CH_3(etp)]BPh_4$ has been determined from three dimensional X-ray data collected by counter methods. The compound crystallized in the triclinic group $P\bar{1}$ with cell dimensions a 16.726(4), b 15.350(4), c 11.632(3) Å, α 66.55(4), β 73.37(4), γ 74.75(4)°, $Z = 2$. The structure was refined by full matrix least-squares methods to a conventional R factor of 0.076. The coordination polyhedron has a distorted square planar geometry. The sulfinate group is linked to the metal through an oxygen atom.

Introduction

In recent years a wide variety of neutral organonickel(II) complexes have been characterized [1]; cationic organometallic nickel(II) derivatives have attracted less attention [2]. The only cationic complex with square planar geometry so far reported has the formulae $[C_6Cl_5Ni(P(CH_3)_3(C_6H_5))(3,5\text{-lutidine})]ClO_4$ [3].

The ability of these compounds to insert small molecules is rather low [4,5,6]; insertion of sulfur dioxide into the Ni—C bond has been reported only for $[(C_5H_5)Ni(PR_3)R']$, which forms S-sulfinate derivatives [7].

With the aim of further investigating the chemistry of cationic organonickel complexes, we have synthesized complexes of formula [NiR(etp)]Y, R = CH_3, $CH_2C_6H_5$, C_6H_5; etp = bis(2-diphenylphosphinoethyl)phenylphosphine, PhP-$(CH_2CH_2PPh_2)_2$; Y = PF_6, BPh_4 and square planar geometry by reaction of [NiX(etp)]Y, X = halogen, with the appropriate Grignard reagents. The above complexes react with sulfur dioxide to give O-sulfinate derivatives. All the complexes have been characterized by conductivity, ^1H NMR and other spectroscopic measurements. The structure of [NiOS(O)CH_3(etp)]BPh_4 has been determined by a complete X-ray analysis.

Experimental section

All solvents were purified by standard methods; the ligand etp was purchased from Strem Chemicals Inc. Danwers (Massachussets) and was used without further purification. The complexes [NiX(etp)]Y (X = halogen; Y = PF_6, BPh_4) were prepared by methods previously described [8]. All the syntheses were carried out under dry nitrogen.

Synthesis of complexes [NiR(etp)]Y (R = CH_3, $CH_2C_6H_5$, C_6H_5; Y = PF_6, BPh_4)

A solution of the appropriate Grignard reagent (1 mmol) in ether was slowly added to a suspension of [NiX(L)]Y (1 mmol) in tetrahydrofuran (40 ml). The resulting slurry was stirred at 0°C for 1 h, then treated with a few drops of water and filtered. The crystalline products were obtained from the filtrate by addition of absolute ethanol and concentration under nitrogen. The compounds were filtered and then washed with absolute ethanol and petroleum ether. The complexes may be recrystallized from methylene chloride-absolute ethanol.

Reaction of sulfur dioxide with [NiR(etp)]Y (R = CH_3, $CH_2C_6H_5$, C_6H_5)

The complexes were placed in a cold trap immersed in a dry ice/acetone bath; dry sulfur dioxide was then condensed into the trap and dissolved the complexes. The addition of sulfur dioxide was stopped immediately after the complete dissolution of the solid. The liquid was removed by allowing the trap to warm to room temperature. The remaining solid was dissolved in methylene chloride; orange crystals of the compounds were obtained by addition of ethanol and concentration in a stream of nitrogen. The complexes were recrystallized from methylene chloride-ethanol.

Physical measurements

Magnetic, conductometric and spectrophotometric (both visible and infrared) measurements were carried out using methods already described [9].

Proton magnetic resonance spectra were recorded with a Varian EM 390 spectrometer. The solutions in deuterated methylene chloride were prepared under nitrogen and then transferred to the sample tube, which was then sealed. Chemical shifts are quoted relative to tetramethylsilane, TMS = 10.00 τ.

Collection and reduction of X-ray intensity data

A well formed crystal with dimensions 0.05 × 0.4 × 0.22 mm was used

TABLE 1

CRYSTAL DATA FOR $[NiOS(O)CH_3(etp)]BPh_4$

$C_{59}H_{56}BNiO_2P_3S$	F.W. 991.6
Crystal system	triclinic
Space group	$P\bar{1}$
Cell dimensions	$a = 16.726$ (4) Å $\alpha = 65.55$ (4)° $b = 15.350$ (4) Å $\beta = 73.37$ (4)° $c = 11.632$ (4) Å $\gamma = 74.75$ (4)°
Volume, V	2568.89 Å^3
Density	obs. 1.28 gcm^{-3} calcd. 1.282 gcm^{-3} for $Z = 2$
Linear absorption coefficient (Mo-K_α)	5.50 cm^{-1}

throughout cell determination and data collection on a Philips's PW 1100 automated diffractometer. By using monochromatized Mo—K_α radiation it was established that the compound crystallized in the triclinic system. The space group $P\bar{1}$ was initially assumed and later confirmed by successful refinement of the structure. The unit cell dimensions were obtained by a least-squares refinement of 20 angular settings. The relevant crystal data are summarized in Table 1. The intensities of 4761 reflections were measured up to $\theta \leqslant 20°$. Of these, 2841 unique reflections which obeyed the condition $I \geqslant 2.5\sigma(I)$ were used in subsequent calculations. The crystal chosen had faces of the form {100}, {010}, {001} and {011}. An absorption correction was applied for this specimen, although the difference between maximum and minimum absorption was less than 5%.

Solution and refinement of the structure

The structure was solved by direct methods and refined by full matrix least squares methods using anisotropic thermal parameters for Ni, P, S, O, B and non-rigid body carbon atoms. Rigid body models were assumed for phenyl groups. (C—C distance = 1.395 Å). The hydrogen atoms were placed geometrically such that C—H was equal to 1.08 Å. Common isotropic temperature factors were used for these hydrogen atoms. The refinement converged to R = 0.076 for the conventional R factor and R_w = 0.075 for the weighted R factor. An analysis of the variance showed little systematic variation of $|F_{obs} - F_{calcd}|$ with either sin θ/λ or F_{obs}. Most calculations were performed by using the SHELX system of programs [10]. The final positional and thermal parameters are listed in Table 2. Important intramolecular bond distances and angles are reported in Table 3.

Results and discussion

The complexes of formula [NiR(etp)]Y, (R = CH_3, $CH_2C_6H_5$, C_6H_5; Y = PF_6, BPh_4), which contain a nickel—carbon σ bond, are synthesized by reaction of the appropriate Grignard reagent with the four coordinate complexes [NiX(etp)]Y (X = halogen). Analytical data for the compounds are listed in Table 4. These derivatives are fairly air stable and are diamagnetic in the solid state; they are readily soluble in polar organic solvents without decomposition

TABLE 2

ATOMIC [a] PARAMETERS FOR THE STRUCTURE OF [NiOS(O)CH_3(etp)]BPh_4 (all quantities × 10^4)

Atom	X	Y	Z	U or U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni	1928 (1)	2483 (1)	2391 (2)	474 (13)	418 (12)	439 (12)	−164 (9)	−95 (10)	−18 (9)
P(1)	1859 (2)	1135 (3)	2210 (4)	403 (26)	513 (26)	517 (26)	−221 (21)	−101 (21)	−21 (20)
P(2)	2851 (2)	2687 (3)	670 (3)	434 (25)	503 (25)	427 (24)	−187 (20)	−111 (20)	−28 (20)
P(3)	2407 (2)	3628 (3)	2565 (3)	553 (26)	445 (25)	360 (24)	−135 (20)	−90 (21)	−15 (20)
S	284 (3)	3062 (3)	3705 (5)	647 (34)	728 (33)	1151 (44)	−546 (32)	169 (31)	−191 (28)
O(1)	1039 (5)	2243 (7)	3923 (9)	468 (63)	775 (72)	723 (73)	−226 (59)	2 (55)	−47 (56)
O(2)	300 (7)	3522 (7)	2283 (12)	886 (92)	872 (84)	1000 (99)	−1 (74)	−96 (77)	62 (67)
C(55)	2502 (8)	1093 (10)	668 (12)	459 (99)	541 (98)	665 (99)	−255 (80)	−123 (81)	−27 (81)
C(56)	3270 (8)	1553 (9)	401 (12)	416 (97)	601 (92)	470 (95)	−247 (76)	−104 (77)	65 (78)
C(57)	3668 (8)	3269 (9)	660 (13)	586 (95)	563 (96)	398 (97)	−156 (82)	−124 (78)	−104 (79)
C(58)	3224 (8)	4105 (9)	1133 (12)	683 (90)	478 (92)	386 (93)	−196 (77)	−79 (75)	−224 (74)
C(59)	−548 (11)	2385 (13)	4277 (17)	1113 (151)	723 (146)	1077 (147)	−353 (121)	33 (124)	−278 (122)
B	6403 (10)	2253 (11)	119 (15)	386 (109)	519 (108)	490 (113)	−205 (91)	−151 (90)	144 (87)
C(1)	819 (6)	954 (6)	2321 (8)	539 (39)					
C(2)	443 (6)	201 (6)	3329 (8)	637 (42)					
C(3)	−389 (6)	131 (6)	3416 (8)	729 (46)					
C(4)	−845 (6)	814 (6)	2495 (8)	758 (48)					
C(5)	−469 (6)	1567 (6)	1487 (8)	871 (52)					
C(6)	363 (6)	1637 (6)	1400 (8)	700 (45)					
C(7)	2335 (6)	106 (7)	3414 (8)	537 (40)					
C(8)	2536 (6)	−802 (7)	3307 (8)	781 (49)					
C(9)	2926 (6)	−1598 (7)	4219 (8)	994 (57)					
C(10)	3114 (6)	−1485 (7)	5238 (8)	867 (52)					
C(11)	2913 (6)	−576 (7)	5345 (8)	862 (52)					
C(12)	2524 (6)	219 (7)	4433 (8)	625 (42)					
C(13)	2399 (5)	3476 (7)	−701 (10)	437 (36)					
C(14)	2870 (5)	3626 (7)	−1950 (10)	695 (46)					
C(15)	2510 (5)	4259 (7)	−3007 (10)	1059 (61)					
C(16)	1679 (5)	4741 (7)	−2817 (10)	1061 (60)					
C(17)	1208 (5)	4591 (7)	−1569 (10)	1021 (59)					
C(18)	1568 (5)	3959 (7)	−511 (10)	717 (46)					
C(19)	2915 (5)	3027 (8)	3937 (11)	539 (39)					

C(20)	2473 (5)	2453 (8)	5105 (11)	967 (57)
C(21)	2868 (5)	1945 (8)	6158 (11)	1081 (62)
C(22)	3705 (5)	2012 (8)	6043 (11)	1012 (57)
C(23)	4147 (5)	2586 (8)	4875 (11)	1206 (67)
C(24)	3752 (5)	3094 (9)	3822 (11)	832 (50)
C(25)	1703 (6)	4675 (7)	2765 (8)	495 (37)
C(26)	1448 (6)	4808 (7)	3941 (8)	897 (54)
C(27)	837 (6)	5598 (7)	4067 (8)	1132 (64)
C(28)	480 (6)	6255 (7)	3016 (8)	967 (57)
C(29)	735 (6)	6122 (7)	1840 (8)	1093 (62)
C(30)	1346 (6)	5332 (7)	1715 (8)	925 (55)
C(31)	6447 (5)	3009 (6)	777 (9)	502 (38)
C(32)	7158 (5)	2937 (6)	1231 (9)	622 (42)
C(33)	7146 (5)	3533 (6)	1874 (9)	757 (47)
C(34)	6423 (5)	4202 (6)	2063 (9)	776 (48)
C(35)	5713 (5)	4274 (6)	1609 (9)	747 (47)
C(36)	5725 (5)	3678 (6)	966 (9)	614 (42)
C(37)	7378 (5)	1591 (7)	—183 (7)	570 (40)
C(38)	7608 (5)	704 (7)	767 (7)	667 (43)
C(39)	8414 (5)	166 (7)	565 (7)	765 (48)
C(40)	8989 (5)	516 (7)	—586 (7)	741 (46)
C(41)	8758 (5)	1403 (7)	—1536 (7)	891 (52)
C(42)	7953 (5)	1940 (7)	—1335 (7)	656 (45)
C(43)	5757 (5)	1453 (6)	1081 (7)	524 (39)
C(44)	5689 (5)	743 (6)	674 (7)	536 (39)
C(45)	5188 (5)	37 (6)	1483 (7)	614 (42)
C(46)	4754 (5)	41 (6)	2700 (7)	726 (46)
C(47)	4822 (5)	750 (6)	3108 (7)	700 (45)
C(48)	5323 (5)	1456 (6)	2298 (7)	581 (41)
C(49)	6069 (5)	2946 (7)	—1313 (10)	534 (39)
C(50)	6494 (5)	3751 (7)	—2080 (10)	734 (46)
C(51)	6319 (5)	4826 (7)	—3301 (10)	926 (55)
C(52)	5745 (5)	4095 (7)	—3754 (10)	895 (53)
C(53)	5346 (5)	3291 (7)	—2986 (10)	862 (51)
C(54)	5522 (5)	2716 (7)	—1766 (10)	659 (43)

---

[a] The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2\,U_{12}hka^*b^* + \ldots)]$.

TABLE 3

SELECTED BOND LENGTHS (Å) AND ANGLES (deg)

Ni—P(1)	2.199 (5)	P(1)—Ni—P(2)	85.0 (2)
Ni—P(2)	2.111 (5)	P(1)—Ni—P(3)	162.4 (2)
Ni—P(3)	2.214 (5)	P(2)—Ni—P(3)	85.5 (2)
Ni—O(1)	1.937 (11)	P(1)—Ni—O(1)	91.2 (4)
Ni . . . S	2.851 (6)	P(2)—Ni—O(1)	175.5 (4)
S—O(1)	1.525 (11)	P(3)—Ni—O(1)	98.7 (4)
S—O(2)	1.501 (14)	O(1)—S—O(2)	108.0 (7)
S—C(59)	1.765 (19)	O(1)—S—C(59)	100.3 (9)
P(1)—C(55)	1.826 (16)	O(2)—S—C(59)	102.4 (9)
P(1)—C(1)	1.793 (12)	C(1)—P(1)—C(7)	108.3 (5)
P(1)—C(7)	1.799 (12)	C(1)—P(1)—C(55)	107.8 (6)
P(2)—C(56)	1.817 (15)	C(7)—P(1)—C(55)	105.1 (6)
P(2)—C(57)	1.815 (15)	C(13)—P(2)—C(56)	104.8 (6)
P(2)—C(13)	1.787 (13)	C(13)—P(2)—C(57)	106.0 (6)
P(3)—C(58)	1.841 (15)	C(56)—P(2)—C(57)	113.0 (7)
P(3)—C(19)	1.807 (13)	C(19)—P(3)—C(25)	107.6 (5)
P(3)—C(25)	1.784 (13)	C(19)—P(3)—C(58)	107.6 (6)
		C(25)—P(3)—C(58)	105.1 (6)
		Ni—P(1)—C(1)	115.8 (4)
		Ni—P(1)—C(7)	109.8 (4)
		Ni—P(1)—C(55)	109.5 (5)
		Ni—P(2)—C(13)	111.0 (4)
		Ni—P(2)—C(56)	111.0 (5)
		Ni—P(2)—C(57)	110.8 (5)
		Ni—P(3)—C(19)	105.7 (4)
		Ni—P(3)—C(25)	120.6 (4)
		Ni—P(3)—C(58)	109.7 (5)

under an inert atmosphere. The complexes behave as 1 : 1 electrolytes in nitroethane solution; these solutions decompose quickly in the air. Spectral data of the solid compounds as well as of their nitroethane solutions are shown in Table 5. An intense band at ca. 2.50 $Å^{-1}$ (ϵ ca. 3500) is present in all the electronic spectra, which are typical of Ni^{II} compounds with square planar geometry. Also the ^1H NMR spectra of the methyl and benzyl derivatives are consistent with square planar geometry in solution, (see Table 4). The signals due to the phenyl group in the phenyl derivative are not detectable because they are hidden by signals of the ligand and the anion.

All the complexes described above dissolve in SO_2 at solid CO_2/acetone temperature to take up a sulfur dioxide molecule and give compounds of the general formula $[NiSO_2R(etp)]Y$ ($R = CH_3, CH_2C_6H_5, C_6H_5$). Analytical data for the compounds are reported in Table 4. These diamagnetic complexes behave as 1 : 1 electrolytes in nitroethane. The electronic reflectance spectra, both in the solid state and in nitroethane (Table 5), show an intense band at ca. 2.40 $Å^{-1}$ (ϵ ca. 3400) typical of nickel(II) in square planar geometry. These compounds show two strong infrared bands attributable to SO stretching frequencies at ca. 1095 and 865 cm^{-1} (Table 4). These two bands may be assigned respectively, to the symmetric and asymmetric stretching vibrations of the sulfur dioxide. The low value of the $\nu(S{-}O)_{as}$ stretching frequency is indicative of a sulfinate group bonded to the metal through an oxygen atom [11]. The chemical shifts of the methyl and benzyl sulfinate are 8.65 and 6.98 τ, respec-

TABLE 4

PHYSICAL CONSTANTS AND ANALYTICAL DATA

Compound	Analyses, found (calcd.) (%)					Λ_M [a] (ohm^{-1} mol^{-1} cm^2)	ν(SO)/(cm^{-1})	Chemical shift [b]
	C	H	Ni	P	S			
[NiCH$_3$(etp)]BPh$_4$	76.2 (76.4)	6.1 (6.1)	6.2 (6.3)	9.9 (10.0)		45		9.83t $J(P_{trans}$—H) = 4 $J(P_{cis}$—H) = 4
[NiCH$_3$(etp)]PF$_6$	55.7 (55.8)	4.9 (4.8)	7.7 (7.8)			47		9.83t $J(P_{trans}$—H) = 4 $J(P_{cis}$—H) = 4
[NiCH$_2$C$_6$H$_5$(etp)]BPh$_4$	77.5 (77.8	6.1 (6.0)	5.6 (5.8)			47		7.88m
[NiCH$_2$C$_6$H$_5$(etp)]PF$_6$	59.4 (59.4)	4.9 (4.9)	7.0 (7.1)	14.7 (14.9)		48		7.88m
[NiC$_6$H$_5$(etp)]BPh$_4$	77.5 (77.7)	6.0 (5.9)	5.7 (5.9)	9.7 (9.9)		47		
[NiC$_6$H$_5$(etp)]PF$_6$	58.8 (58.9)	4.7 (4.7)	7.1 (7.2)			47		
[NiOS(O)CH$_3$(etp)]BPh$_4$	71.2 (71.5)	5.8 (5.7)	5.7 (5.9)	8.6 (8.8)	2.9 (3.0)	46	1097, 865	8.65s
[NiOS(O)CH$_3$(etp)]PF$_6$	51.3 (51.4)	4.6 (4.4)	7.0 (7.2)			47	1097, 865	8.65s
[NiOS(O)CH$_2$C$_6$H$_5$(etp)]BPh$_4$	72.9 (73.1)	5.6 (5.6)	5.4 (5.5)		2.9 (3.0)	48	1095, 867	6.98m
[NiOS(O)CH$_2$C$_6$H$_5$(etp)]PF$_6$	55.0 (55.1)	4.6 (4.5)	6.4 (6.6)			47	1096, 865	6.98m
[NiOS(O)C$_6$H$_5$(etp)]BPh$_4$	73.2 (73.5)	5.7 (5.6)	5.6 (5.6)		2.8 (3.0)	46	1090, 868	
[NiOS(O)C$_6$H$_5$(etp)]PF$_6$	54.5 (54.6)	4.3 (4.4)	6.6 (6.7)			47	1090, 868	

[a] Molar conductance values of ca. 10^{-3} M nitroethane solution at 20°C. [b] Chemical shifts of the alkyl group are relative to TMS = 10.00τ; key: s, singlet; t, triplet; m, multiplet; coupling constants in Hz.

TABLE 5

MAXIMA AND EXTINCTION COEFFICIENTS FOR THE ELECTRONIC SPECTRA

Compound	State [a]	Absorption max (μm^{-1}) (ϵ_M for soln)
$[NiCH_3(etp)]BPh_4$	a	2.63
	b	2.38 (3150)
$[NiCH_3(etp)]PF_6$	a	2.63
	b	2.41 (3100)
$[NiCH_2C_6H_5(etp)]BPh_4$	a	2.33
	b	2.35 (3780)
$[NiCH_2C_6H_5(etp)]PF_6$	a	2.33
	b	2.36 (3650)
$[NiC_6H_5(etp)]BPh_4$	a	2.58
	b	2.63 (3340)
$[NiC_6H_5(etp)]PF_6$	a	2.58
	b	2.64 (3280)
$[NiOS(O)CH_3(etp)]BPh_4$	a	2.38
	b	2.44 (3380)
$[NiOS(O)CH_3(etp)]PF_6$	a	2.41
	b	2.45 (3250)
$[NiOS(O)CH_2C_6H_5(etp)]BPh_4$	a	2.38
	b	2.43 (3630)
$[NiOS(O)CH_2C_6H_5(etp)]PF_6$	a	2.41
	b	2.45 (3570)
$[NiOS(O)C_6H_5(etp)]BPh_4$	a	2.38
	b	2.44 (3550)
$[NiOS(O)C_6H_5(etp)]PF_6$	a	2.41
	b	2.44 (3410)

[a] Key: a, diffuse reflectance spectrum at room temperature; b, nitroethane solution spectrum.

tively. These NMR signals, although detected at lower field than those found for the parent alkyl complexes, are not shifted by the amount expected for S-sulfinate derivatives [12]. Thus, the NMR data also favour the presence of a sulfinate group linked to the metal through an oxygen atom.

Among the three binding modes of an O-sulfinate group to a metal, the most common is that with a single M—O bond, but π bonding of an S—O to the metal or bonding of both oxygen atoms to the metal cannot be ruled out [4a]. A complete X-ray analysis of $[NiSO_2Me(etp)]BPh_4$ has been carried out to assess clearly the geometry of the methyl sulfinate group and its binding mode. The complex consists of $[NiOS(O)CH_3(etp)]^+$ cations and of tetraphenylborate anions. Figure 1 shows a perspective view of the cation. Selected bond distances and angles are down in Table 3. The nickel atom is tetracoordinated by the three donor atoms of the ligand and by the oxygen atom of the methyl sulfinate. An inspection of bond distances and angles involving the metal center shows that the coordination polyhedron has a clearly distorted square planar geometry. Two Ni—P bonds (those involving the terminal phosphorus atoms of the etp ligand) are significantly longer than the bond of the nickel to the central phosphorus atom (2.165(2) av. cf. 2.111(2) Å). The latter short linkage

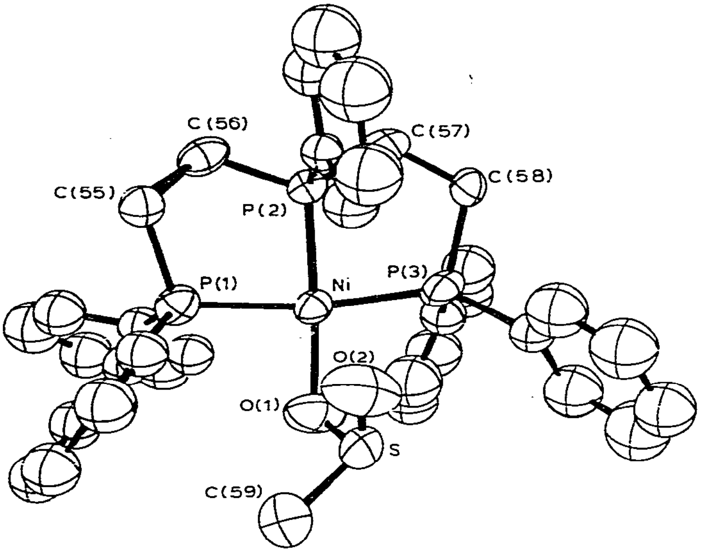

Fig. 1. Molecular structure of the cation $[NiOS(O)CH_3(etp)]^+$.

is *trans* to the short Ni—O bond (1.937(11) Å). Thus, on acount of this symmetry among *trans* linkages, the inner coordination sphere of the complex is better described as diamond shaped rather than square. As already suggested [13], the observed distortion from square planarity is probably caused by the geometric requirements of the etp ligand as well as the steric repulsions of its terminal phenyl groups towards the methyl sulfinate group. The geometry around the sulfur atom of the sulfinate group is the expected trigonal pyramid, and the S—O bond lengths (1.525(11), 1.501(14)) are practically equal to those of the complex $Cu(H_2O)_4(OS(O)C_6H_4Me\text{-}_p)_2$ [14], which represents the only O-sulfinate metal complex whose structure has been reported.

Some other O-sulfinate complexes are known to undergo desulfination [15] or structural rearrangement to the S-sulfinate form [16], especially when heated. Our derivatives, however, are quite stable on warming (in the solid state and in solution) and retain their geometry until they decompose.

The binding mode of the sulfinate group through the oxygen atom may be rationalized [17] in terms of the hard character of the central cation, which prefers to combine with the hard oxygen atom rather than the softer sulfur atom. Evidently the softening influence of the three phosphorus atoms on the metal ion is not sufficient to alter the binding mode of the sulfinate group.

Acknowledgements

Thanks are expressed to Prof. L. Sacconi for continuous interest.

References

1 P.W. Jolly and G. Wilke, The Organic Chemistry of Nickel, Vol. 1, Academic Press, New York, N.Y., 1974.

2 L. Sacconi, P. Dapporto, P. Stoppioni, P. Innocenti and C. Benelli, Inorg. Chem., 16 (1977) 1669.
3 M. Vada, Inorg. Chem., 14 (1975) 1415.
4 (a) A. Wojcicki, Adv. Organomet. Chem., 12 (1974) 31; (b) F. Calderazzo, Angew. Chem., 89 (1977) 305.
5 P. Stoppioni, P. Dapporto and L. Sacconi, Inorg. Chem., 17 (1978) 718.
6 H.F. Klein, Angew. Chem., 85 (1973) 403; H.F. Klein and H.H. Karsch, Chem. Ber., 109 (1976) 2524.
7 M.D. Rausch, Y.F. Chang and H.B. Gordon, Inorg. Chem., 8 (1969) 1355.
8 J.C. Cloyd, D.W. Meek, Inorg. Chim. Acta, 6 (1972) 607.
9 L. Sacconi, I. Bertini and F. Mani, Inorg. Chem., 7 (1968) 1417.
10 G.M. Sheldrick, "SHELX-76" System of Programs, 1976.
11 E. Lidner and G. Vitzthum, Chem. Ber., 102 (1969) 4062; G. Vitzthum and E. Lidner, Angew. Chem., Internat. Ed., 10 (1971) 315.
12 S.E. Jacobson, P. Reich-Rohrwig and A. Wojcicki, Chem. Commun., (1971) 1526; S.E. Jacobson, P. Reich-Rohrwig and A. Wojcicki, Inorg. Chem., 12 (1973) 717 and references therein.
13 C. Mealli and P. Stoppioni, J. Organometal. Chem., 175 (1979) C19.
14 D.A. Langs and C.R. Hare, Chem. Commun., (1967) 853.
15 J. Chatt and D.M.P. Mingos, J. Chem. Soc. A, (1969) 1770.
16 E. König, E. Lindner, I.P. Lorenz and G. Ritter, Inorg. Chim. Acta, 6 (1972) 123.
17 R.G. Pearson, J. Amer. Chem. Soc., 85 (1963) 3533.