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Synthesis and Properties of Sulfur-Bonded Alkylsulfito Complexes of Cobalt(II) and Nickel(II) with Poly(tertiary phosphines). Crystal Structure of $[Ni(SO_2(OC_2H_5))N(C_2H_4P(C_6H_5)_2)_3]BF_4 \cdot 0.5C_2H_5OH \cdot 0.5H_2O$

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Sulfur dioxide reacts with cobalt(II) and nickel(II) aquo ions and the poly(tertiary phosphine) ligands tris(2-diphenylphosphinoethyl)amine, np$_3$, and tris(2-diphenylphosphinoethyl)phosphine, pp$_3$, in methanol or ethanol solution forming five-coordinated alkylsulfito complexes of the general formula $[M(SO_2(OR))L]Y$ (R = CH_3 or C_2H_5 and $Y^- = BF_4^-$ or BPh_4^-). The complexes are low spin with the $SO_2(OR)$ group S bonded to the metal. The structure of $[Ni(SO_2(OC_2H_5))(np_3)]BF_4 \cdot 0.5C_2H_5OH \cdot 0.5H_2O$ has been determined from three-dimensional x-ray data collected by counter methods. The compound crystallizes in the monoclinic space group *I*2/*a* with eight formula units in a cell of dimensions $a = 34.435$ (20) Å, $b = 9.088$ (3) Å, $c = 28.672$ (7) Å, and $\beta = 90.24$ (5)°. The structure was refined by full-matrix least-squares methods to the conventional *R* factor of 0.078. The coordination geometry is a distorted trigonal bipyramid with the sulfur atom of the ethylsulfito group in an axial position. Bond distances and angles of interest are Ni–P = 2.31 (2) Å (average), Ni–S = 2.130 (3) Å, Ni–N = 2.070 (8) Å, and S–Ni–N = 178.0 (4)°.

Introduction

Sulfur dioxide reacts with transition metal complexes in four different ways:[1] (1) addition of SO_2 to a coordinatively unsaturated metal center, (2) substitution of another coordinated ligand, (3) addition to another coordinated ligand, (4) insertion of SO_2 into a transition metal–carbon bond with formation of MSO_2R moieties having different types of structures.

We have found that SO_2 gas, at room temperature and atmospheric pressure, reacting with methanolic or ethanolic solutions of $[Co(H_2O)_6]^{2+}$ or $[Ni(H_2O)_6]^{2+}$ and of poly(tertiary phosphines) like tris(2-diphenylphosphinoethyl)amine, np$_3$, or tris(2-diphenylphosphinoethyl)phosphine, pp$_3$, yields alkylsulfito metal complexes of general formula $[M(SO_2(OR))L]Y$, where R = CH_3 or C_2H_5 and $Y^- = BF_4^-$ or BPh_4^-. The complexes are five-coordinated and the $SO_2(OR)$ group, formed by the reaction of SO_2 with the solvent alcohol, is S bonded to the metal. The same complexes can be obtained by reaction of sodium or ammonium alkylsulfite with solutions of the metal salts and phosphines.

All complexes have been characterized by appropriate physical methods. A complete structure determination of the complex $[Ni(SO_2(OC_2H_5))(np_3)]BF_4 \cdot 0.5C_2H_5OH \cdot 0.5H_2O$ has been carried out.

Experimental Section

Reagents. All solvents were of reagent grade quality and were used without further purification. The ligand np$_3$ was prepared by the method previously described.[2] The ligand pp$_3$ was purchased from the Pressure Chemical Co., Pittsburgh, Pa., and was used without further purification.

Preparation of the Complexes. All the reactions were carried out under dry nitrogen, using deoxygenated solvents.

$[Ni(SO_2(OR))(np_3)]BF_4 \cdot 0.5ROH \cdot 0.5H_2O$ (R = CH_3, C_2H_5). The ligand np$_3$ (1.5 mmol) in 10 mL of CH_2Cl_2 was added to a solution of $[Ni(H_2O)_6](BF_4)_2$ (1 mmol) in 20 mL of the appropriate alcohol (methanol or ethanol). When sulfur dioxide was bubbled into the solution, at room temperature, a deep blue color immediately appeared. After bubbling of SO_2 for a further 2 min the resulting solution was concentrated in a stream of nitrogen. The blue crystals which formed were filtered off and washed with the appropriate alcohol and then with petroleum ether. The compounds were recrystallized from a methylene chloride–alcohol mixture.

The same complexes can also be prepared by adding 1.2 mmol of $NH_4[SO_2(OR)]$[3] to a solution obtained by mixing 1 mmol of $[Ni(H_2O)_6](BF_4)_2$ in 20 mL of alcohol and 1 mmol of np$_3$ in 10 mL of CH_2Cl_2.

$[Ni(SO_2(OR))(pp_3)]BPh_4$ (R = CH_3, C_2H_5). These compounds were prepared as the np$_3$ derivatives, adding to the solution an equimolar amount of $NaBPh_4$.

$[Co(SO_2(OC_2H_5))(L)]BPh_4$ (L = np$_3$, pp$_3$). The compounds were prepared with a method analogous to that used for the above compounds starting from $[Co(H_2O)_6](BF_4)_2$.

Physical Measurements. The physical measurements were executed by previously described methods.[4] The analytical, magnetic, and conductivity data of the complexes are reported in Table I; Table II lists the electronic spectral data.

Collection and Reduction of X-Ray Intensity Data. The compound crystallizes as blue rectangular flat prisms. A sample of dimensions 0.54 × 0.16 × 0.04 mm was mounted so that its longest dimension was approximately parallel to the φ axis of a Philips computer-controlled PW 1100 diffractometer. Cell constants and the Bravais lattice were determined as described elsewhere.[5] The unit cell dimensions are $a = 34.435$ (20) Å, $b = 9.088$ (3) Å, $c = 28.672$ (7) Å, and $\beta = 90.24$ (5)°. The observed density of 1.38 g cm^{-3} measured by flotation agrees with the value of 1.392 g cm^{-3} calculated for eight formula units of $[Ni(SO_2(OC_2H_5))(np_3)]BF_4 \cdot 0.5C_2H_5OH \cdot 0.5H_2O$ per cell. The extinctions hkl for $h + k + l = 2n + 1$ and $h0l$ for $h = 2n + 1$ suggest the space group *I*2/*a* or *Ia*.

Data collection was carried out using Cu Kα (λ 1.5418 Å) radiation monochromatized with a graphite crystal at a takeoff angle of 3.0°. Reflections within $2\theta \leq 120°$ were collected using the ω–2θ scan technique. The scan range was calculated according to the formula of Alexander and Smith,[6] scan range = $A + B \tan \theta$, with $A = 0.6$ and $B = 0.28$. The scan speed was 0.07°/s; stationary background measurements were taken before and after each scan for a time equal to half the scan time. The intensities of three standard reflections measured every 100 min showed no systematic trend.

After correction for background the intensities were assigned standard deviations calculated as described elsewhere[7] using the value of 0.05 for the instability factor *K*. A total of 3299 reflections having $I \geq 3\sigma(I)$ were considered observed and included in the following calculations. An absorption correction by numerical method[8] was applied, the absorption coefficient being 25.2 cm^{-1}. The transmission coefficients ranged from 0.634 to 0.901.

Solution and Refinement of the Structure. The Patterson synthesis successfully interpreted in the space group *I*2/*a* showed the position of the nickel and of the sulfur atom. Successive Fourier synthesis showed the positions of all the other atoms of the cation and of the tetrafluoroborate anion. Full-matrix least-squares refinements were then undertaken, the function minimized being $\sum w(|F_o| - |F_c|)^2$. The weights w were taken as $w = 1/\sigma^2(F_o)$. The agreement factors R and R_w are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. The scattering factors for neutral Ni, S, P, F, O, N, C, and B are those calculated by Cromer and Waber,[9] while those for H were taken from Stewart, Davidson, and Simpson.[10] The real and imaginary corrections for the anomalous dispersion reported by Cromer[11] for Ni, S, and P were applied. Anisotropic thermal parameters were used only for the heavier atoms. Two cycles of refinements lowered the *R* factor to 0.11.

A difference Fourier map calculated in order to localize the solvent molecules, whose presence was inferred from the analytical and infrared data, showed several diffuse peaks whose electronic density

Table I. Analytical and Physical Data of the Complexes

Compd	Color	% calcd			% found			μ_{eff}, μ_B (293 K)	Λ_M,[a] cm^2 Ω^{-1} mol^{-1}
		C	H	M	C	H	M		
$[Co(SO_2(OC_2H_5))(np_3)]BPh_4$[b]	Green	71.57	5.92	5.16	71.85	5.88	4.96	2.39	44
$[Co(SO_2(OC_2H_5))(pp_3)]BPh_4$[c]	Brown	70.53	5.83	5.09	70.39	6.14	4.90	2.25	46
$[Ni(SO_2(OCH_3))(np_3)]BF_4 \cdot 0.5CH_3OH \cdot 0.5H_2O$[d]	Blue	56.83	5.26	6.39	57.09	5.32	6.10	Diam	84
$[Ni(SO_2(OC_2H_5))(np_3)]BF_4 \cdot 0.5C_2H_5OH \cdot 0.5H_2O$[e]	Blue	57.47	5.47	6.24	57.38	5.58	6.15	Diam	85
$[Ni(SO_2(OCH_3))(pp_3)]BPh_4$	Red	70.35	5.73	5.13	69.85	5.64	4.75	Diam	45
$[Ni(SO_2(OC_2H_5))(pp_3)]BPh_4$	Red	70.54	5.83	5.07	70.69	5.68	4.96	Diam	45

[a] Molar conductance of a ca. 10^{-3} M solution in nitroethane at 20 °C. Reference values in nitroethane are 51 for $(n\text{-}Bu_4N)BPh_4$ and 97 for $(n\text{-}Bu_4N)PF_6$. [b] Calcd: N, 1.23. Found: N, 1.08. [c] Calcd: P, 10.70; S, 2.77. Found: P, 10.60; S, 2.53. [d] Calcd: N, 1.52. Found: N, 1.59. [e] Calcd: N, 1.49; S, 3.41. Found: N, 1.48; S, 3.32.

Table II. Maxima and Extinction Coefficients for the Electronic Spectra of the Complexes

Compd	Absorption max,[a] μm^{-1} (ϵ_M for soln)
$[Co(SO_2(OC_2H_5))(np_3)]BPh_4$	a 0.605, 0.94, 1.67 sh, 2.12 sh, 2.45 sh b 0.65 sh, 0.99 (110), 1.6 (506)
$[Co(SO_2(OC_2H_5))(pp_3)]BPh_4$	a 0.69 sh, 1.01, 2.0 sh, 2.5 sh b 0.72 sh, 1.02 (150), 1.92 sh, 2.5 (1307)
$[Ni(SO_2(OCH_3))(np_3)]BF_4 \cdot 0.5CH_3OH \cdot 0.5H_2O$	a 1.78, 2.32 sh b 1.72 (5070)
$[Ni(SO_2(OC_2H_5))(np_3)]BF_4 \cdot 0.5C_2H_5OH \cdot 0.5H_2O$	a 1.78, 2.32 sh b 1.72 (5259), 2.3 sh
$[Ni(SO_2(OCH_3))(pp_3)]BPh_4$	a 2.0 b 2.0 (6030)
$[Ni(SO_2(OC_2H_5))(pp_3)]BPh_4$	a 2.0 b 2.02 (5790)

[a] Key: a, solid at room temperature; b, nitroethane solution.

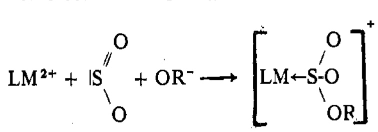
was about one-half to one-third that of the average electron density of a carbon atom. One peak was attributed to the solvating water molecule; the others in the proximity of the twofold axis were interpreted as the ethanol group disordered and overlapping over two sites related by the twofold axis. The atoms of the ethanol group were all treated as carbon atoms with a population parameter of 0.5 which is the highest possible from symmetry considerations and yields satisfactory agreement with the elemental analysis (Table I). Also the oxygen atom of the water molecule was allotted a population parameter of 0.5. Three cycles of refinements gave reasonable results for the oxygen atom of the water molecule but yielded very poor bond distances for the ethanol atoms which were introduced in the following calculation as a fixed contribution, with positional parameters from the difference Fourier map. The hydrogen atoms were introduced in calculated positions (C–H = 1.0 Å) with temperature factors 15% larger than those of the carbon atoms to which they are attached and were not refined. The refinement converged at $R = 0.078$ and $R_w = 0.094$. A final difference Fourier map showed residual electronic density in the region of the tetrafluoroborate anion. Furthermore thermal parameters and bond distances and angles in the anion are indicative of either disorder or thermal motion. Groups such as tetrafluoroborate and perchlorate are often affected by similar problems,[12] and the calculation was concluded at this point since any further chemical information we could have obtained could not be justified by the computing cost. The standard deviation of an observation of unit weight is 1.84. Final positional and thermal parameters are listed in Tables III and IV.

Results and Discussion

In any explanation of the formation of the alkylsulfite complexes, the ability, which we have previously shown,[12e,13-15] of the tri(tertiary phosphines) np_3 and pp_3 to act as proton acceptors forming phosphonium cations of the type np_3H^+, pp_3H^+, etc., undoubtedly plays a significant role. Thus, although different reaction mechanisms can be formulated, in every case the overall reaction must be written

$$[M(H_2O)_6]^{2+} + SO_2 + ROH + L(excess) \rightarrow [M(SO_2(OR))L]^+ + LH^+ + 6H_2O$$

Also the presence of the unsaturated metal centers must be of primary importance. The fact that they can act as electron acceptors may well induce a net displacement of negative charge, thereby facilitating the formation of the sulfito ester and its coordination to the metal



If alkaline alkylsulfites, i.e., $[SO_2(OR)]^-$ ions, are used as reagents, obviously the complexes are directly formed.

The nickel complexes are stable in air, either in the solid state or in solution in polar anhydrous solvents like methylene chloride or nitroethane. The cobalt derivatives quickly decompose in air and their solutions in the above solvents are stable only in an SO_2 atmosphere.

All complexes behave as 1:1 electrolytes in nitroethane solution (Table I).

Table III. Atomic Parameters[a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	1223 (1)	722 (2)	1326 (1)	458 (10)	233 (9)	483 (10)	−51 (8)	22 (8)	5 (8)
S	821 (1)	−1027 (3)	1216 (1)	463 (16)	270 (14)	552 (16)	−58 (12)	3 (13)	3 (12)
P(1)	1200 (1)	492 (3)	2137 (1)	477 (17)	322 (15)	455 (16)	−21 (13)	4 (13)	36 (13)
P(2)	1684 (1)	−457 (3)	898 (1)	507 (17)	320 (16)	538 (18)	−26 (14)	98 (14)	−19 (14)
P(3)	809 (1)	2522 (3)	1030 (1)	614 (19)	235 (14)	472 (16)	38 (13)	13 (14)	16 (13)
F(1)	3454 (3)	1710 (11)	1329 (3)	1353 (77)	1474 (85)	1393 (75)	658 (69)	−326 (60)	−131 (65)
F(2)	2913 (3)	2100 (20)	965 (4)	1073 (75)	4262 (220)	1837 (105)	253 (111)	−719 (71)	−1342 (128)
F(3)	2960 (3)	2851 (17)	1683 (4)	1698 (102)	3123 (167)	1285 (87)	526 (112)	44 (74)	−629 (100)
F(4)	3262 (7)	3707 (22)	1202 (9)	4134 (310)	2365 (201)	4417 (338)	1004 (212)	43 (259)	−46 (209)
O(1)	469 (2)	−877 (7)	1482 (2)	467 (42)	476 (44)	745 (49)	−72 (37)	63 (37)	56 (39)
O(2)	996 (2)	−2471 (7)	1254 (2)	586 (46)	291 (40)	811 (51)	−7 (36)	−42 (38)	27 (38)
O(3)	705 (2)	−791 (7)	683 (2)	703 (49)	505 (44)	570 (45)	−100 (41)	−61 (37)	−64 (38)
N	1629 (2)	2374 (8)	1426 (3)	571 (56)	258 (44)	508 (51)	−121 (42)	−21 (42)	−3 (40)

[a] All quantities ×10^4. The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + \ldots)]$. F_{rel}(scale factor) = 4.8857.

Table IV. Atomic Parameters[a]

Atom	*x*	*y*	*z*	*U*, Å^2
C(1)	1665 (3)	2784 (12)	1937 (4)	553 (29)
C(2)	1658 (3)	1445 (11)	2250 (3)	503 (28)
C(3)	2027 (3)	1894 (12)	1269 (4)	578 (30)
C(4)	2013 (3)	1077 (12)	813 (4)	574 (30)
C(5)	1511 (3)	3725 (12)	1157 (4)	553 (29)
C(6)	1092 (3)	4094 (12)	1229 (3)	560 (29)
C(7)	1230 (3)	−1219 (11)	2469 (3)	471 (27)
C(8)	964 (3)	−2296 (13)	2393 (4)	616 (31)
C(9)	987 (3)	−3676 (13)	2639 (4)	663 (33)
C(10)	1272 (4)	−3842 (14)	2953 (4)	738 (36)
C(11)	1540 (4)	−2780 (14)	3044 (4)	735 (36)
C(12)	1515 (3)	−1435 (13)	2799 (4)	638 (32)
C(13)	841 (3)	1550 (11)	2458 (3)	464 (26)
C(14)	474 (3)	1713 (13)	2283 (4)	627 (32)
C(15)	190 (4)	2532 (15)	2524 (4)	801 (38)
C(16)	297 (4)	3174 (14)	2935 (4)	720 (35)
C(17)	658 (3)	3005 (13)	3124 (4)	669 (33)
C(18)	935 (3)	2196 (12)	2886 (4)	575 (30)
C(19)	1628 (3)	−1277 (12)	332 (4)	560 (29)
C(20)	1717 (3)	−591 (14)	−85 (4)	722 (34)
C(21)	1661 (4)	−1331 (15)	−509 (4)	831 (40)
C(22)	1515 (4)	−2732 (15)	−529 (4)	776 (38)
C(23)	1430 (4)	−3412 (15)	−125 (4)	779 (37)
C(24)	1482 (3)	−2738 (12)	307 (4)	602 (31)
C(25)	1984 (3)	−1814 (11)	1200 (3)	447 (26)
C(26)	2316 (4)	−2360 (14)	990 (4)	742 (36)
C(27)	2537 (4)	−3387 (16)	1242 (5)	836 (40)
C(28)	2440 (4)	−3870 (14)	1667 (4)	766 (37)
C(29)	2110 (4)	−3311 (14)	1866 (4)	712 (35)
C(30)	1878 (3)	−2305 (12)	1635 (4)	538 (28)
C(31)	776 (3)	2800 (11)	404 (3)	467 (26)
C(32)	556 (3)	3909 (13)	209 (4)	624 (32)
C(33)	546 (3)	4174 (13)	−264 (4)	683 (33)
C(34)	764 (4)	3345 (15)	−551 (4)	770 (37)
C(35)	990 (4)	2239 (15)	−379 (5)	889 (40)
C(36)	997 (3)	1958 (14)	110 (4)	705 (34)
C(37)	317 (3)	2940 (12)	1202 (4)	541 (29)
C(38)	214 (4)	4287 (14)	1402 (4)	744 (36)
C(39)	−177 (4)	4509 (15)	1510 (4)	862 (41)
C(40)	−445 (4)	3527 (15)	1435 (4)	818 (38)
C(41)	−362 (4)	2175 (15)	1233 (4)	791 (38)
C(42)	29 (3)	1919 (13)	1121 (4)	632 (32)
C(43)	432 (4)	−1876 (16)	484 (5)	895 (42)
C(44)	402 (4)	−1573 (18)	−5 (5)	1123 (51)
B	3098 (6)	2293 (25)	1304 (7)	1330 (73)
O(4)	2620 (11)	653 (46)	2240 (13)	2703 (174)
C(45)	2010	3430	−40	1500
C(46)	2250	4370	100	1500
C(47)	2420	4500	100	1500

[a] All quantities ×10^4.

The nickel complexes are diamagnetic while the cobalt complexes have values of μ_{eff}, at room temperature, which are consistent with a doublet ground state (2.25–2.39 μ_B).

The molecular structure of the complex $[Ni(SO_2(OC_2H_5))(np_3)]BF_4 \cdot 0.5C_2H_5OH \cdot 0.5H_2O$ consists of the $[Ni(SO_2(OC_2H_5))(np_3)]^+$ cation, BF_4^- anions, and solvating molecules of C_2H_5OH and H_2O. Figure 1 shows a perspective view of the cation. Selected bond distances and angles are reported in Table V. The nickel atom is five-coordinated by the four donor atoms of the ligand and by the sulfur atom of the $SO_2(OC_2H_5)$ group. The coordinating geometry is a fairly regular trigonal bipyramid. Distortions from the idealized geometry are apparent from the mean value of the N–Ni–P angles, 87.2 (2)°,[17] and from the deviation from 120° of the equatorial angles. Similar distortions have been found in low-spin nickel complexes containing tripod ligands.[18,19] The Ni–S bond distance of 2.130 (3) Å is shorter than the sum of the covalent radii of the nickel and sulfur atom (2.19 Å)[20] suggesting a percentage of double bond character. On the contrary the Ni–N bond distance of 2.070 (7) Å is larger than the value of 1.965 (10) Å reported for the low-spin complex $[NiCl(np_3)]PF_6$ where the same np_3 ligand is involved.[19] This can probably be ascribed to a trans effect produced by the sulfito group. A difference of 0.089 (4) Å between cis and trans distances has been found for the complex $[(NH_3)_5CoSO_3]^+$.[21] The S–O bond distances of the terminal oxygen atoms are, as expected, significantly shorter than the $S-OC_2H_5$ bond length (1.443 (4) average vs. 1.594 (7) Å). Also the O–S–O angles reflect the nonequivalence of the three

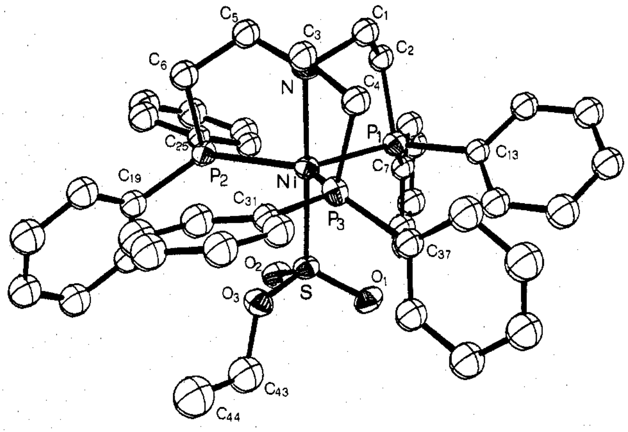


Figure 1. Perspective view of the $[Ni(SO_2(OC_2H_5))(np_3)]^+$ cation.

Table V. Selected Bond Distances (Å) and Angles (deg)

About the Metal Atom			
Ni–S	2.130 (3)	Ni–P(3)	2.327 (3)
Ni–P(1)	2.335 (3)	Ni–N	2.070 (8)
Ni–P(2)	2.279 (3)		
S–Ni–P(1)	93.2 (1)	P(1)–Ni–P(3)	113.8 (1)
S–Ni–P(2)	91.3 (1)	P(2)–Ni–P(3)	124.1 (1)
S–Ni–P(3)	94.3 (1)	N–Ni–P(1)	87.4 (2)
S–Ni–N	178.0 (4)	N–Ni–P(2)	86.8 (2)
P(1)–Ni–P(2)	121.4 (1)	N–Ni–P(3)	87.3 (2)
In the Rest of the Cation			
S–O(1)	1.439 (7)	P(2)–C(25)	1.83 (1)
S–O(2)	1.447 (7)	P(3)–C(6)	1.82 (1)
S–O(3)	1.594 (7)	P(3)–C(31)	1.82 (1)
O(3)–C(43)	1.48 (2)	P(3)–C(37)	1.81 (1)
C(43)–C(44)	1.43 (2)	N–C(1)	1.52 (1)
P(1)–C(2)	1.83 (1)	N–C(3)	1.51 (1)
P(1)–C(7)	1.83 (1)	N–C(5)	1.50 (1)
P(1)–C(13)	1.82 (1)	C(1)–C(2)	1.51 (1)
P(2)–C(4)	1.81 (1)	C(3)–C(4)	1.50 (1)
P(2)–C(19)	1.80 (1)	C(5)–C(6)	1.50 (1)
Ni–S–O(1)	113.5 (3)	C(19)–P(2)–C(25)	101.9 (5)
Ni–S–O(2)	113.3 (3)	Ni–P(3)–C(6)	96.4 (3)
Ni–S–O(3)	101.6 (3)	Ni–P(3)–C(31)	119.6 (3)
O(1)–S–O(2)	113.4 (4)	Ni–P(3)–C(37)	128.4 (4)
O(1)–S–O(3)	106.6 (4)	C(6)–P(3)–C(31)	103.4 (5)
O(2)–S–O(3)	107.2 (4)	C(6)–P(3)–C(37)	104.5 (5)
S–O(3)–C(43)	116.0 (7)	C(31)–P(3)–C(37)	100.7 (5)
O(3)–C(43)–C(44)	107.0 (1.1)	Ni–N–C(1)	111.3 (6)
Ni–P(1)–C(2)	95.8 (3)	Ni–N–C(3)	111.3 (6)
Ni–P(1)–C(7)	126.5 (3)	Ni–N–C(5)	110.0 (6)
Ni–P(1)–C(13)	118.9 (3)	C(1)–N–C(3)	106.8 (7)
C(2)–P(1)–C(7)	105.2 (4)	C(1)–N–C(5)	108.4 (7)
C(2)–P(1)–C(13)	104.3 (4)	C(3)–N–C(5)	109.0 (7)
C(7)–P(1)–C(13)	102.9 (4)	N–C(1)–C(2)	112.0 (8)
Ni–P(2)–C(4)	98.5 (4)	C(1)–C(2)–P(1)	107.0 (7)
Ni–P(2)–C(19)	127.5 (4)	N–C(3)–C(4)	112.1 (8)
Ni–P(2)–C(25)	117.1 (3)	C(3)–C(4)–P(2)	106.3 (7)
C(4)–P(2)–C(19)	105.3 (5)	N–C(5)–C(6)	111.7 (8)
C(4)–P(2)–C(25)	103.3 (5)	C(5)–C(6)–P(3)	107.2 (7)
In the Anion			
B–F(1)	1.34 (2)	B–F(3)	1.29 (2)
B–F(2)	1.17 (2)	B–F(4)	1.43 (2)
F(1)–B–F(2)	119 (2)	F(2)–B–F(3)	124 (2)
F(1)–B–F(3)	117 (2)	F(2)–B–F(4)	100 (2)
F(1)–B–F(4)	90 (2)	F(3)–B–F(4)	88 (2)

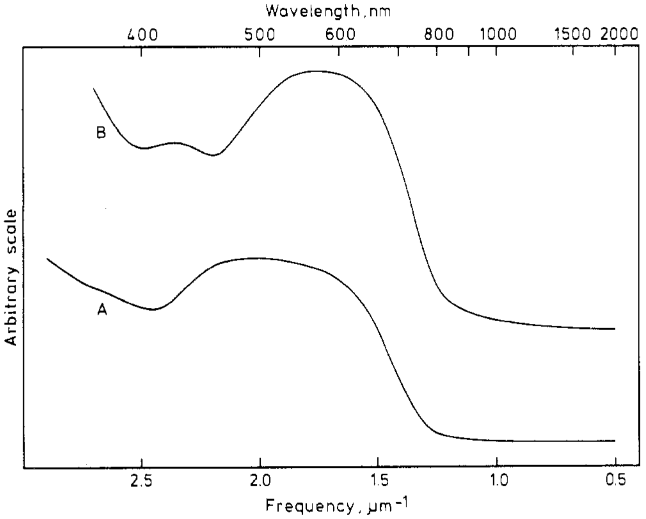


Figure 2. Solid-state spectra (arbitrary scale) of $[Ni(SO_2(OC_2H_5))(pp_3)]BPh_4$ (A) and $[Ni(SO_2(OC_2H_5))(np_3)]BF_4\cdot 0.5C_2H_5OH\cdot 0.5H_2O$ (B).

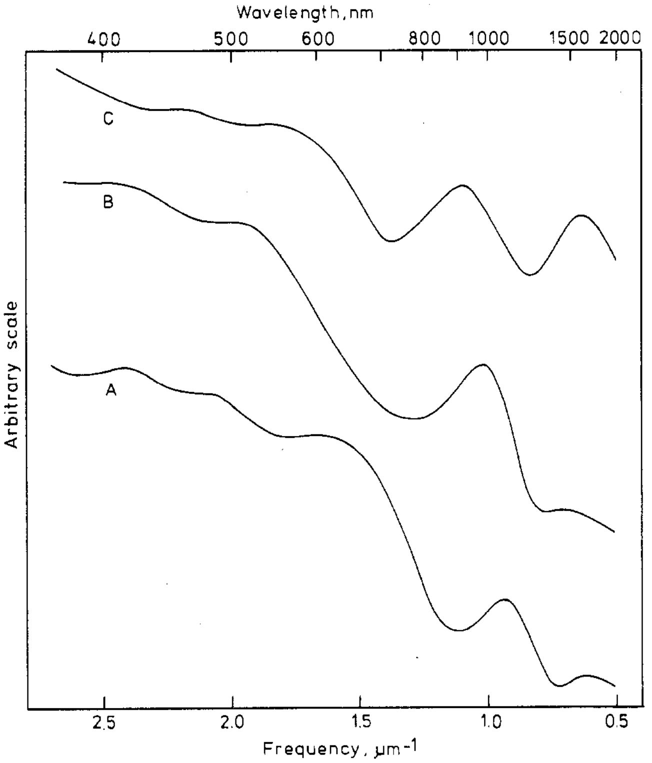


Figure 3. Solid-state spectra (arbitrary scale) of $[Co(SO_2(OC_2H_5))(np_3)]BPh_4$ (A), $[Co(SO_2(OC_2H_5))(pp_3)]BPh_4$ (B), and $[Co(SCH_3)(np_3)]BPh_4\cdot(CH_3)_2O$ (C).

oxygen atoms; such distortions can be accounted for by the larger bond order of the terminal S–O bond compared to that of S–OR in terms of electron pair repulsions.

The oxygen atom of the solvating water molecule lies 2.82 Å from the closest fluorine atom (F(4)) of the tetrafluoroborate anion. This value lies between the values of the sum of the van der Waals radii of fluorine and oxygen as reported by Bondi (2.99 Å)[22] and Pauling (2.75 Å)[20] and may be indicative of a weak hydrogen-bonding interaction. This hypothesis is consistent with the IR spectra of the complexes $[Ni(SO_2(OR))(np_3)]BF_4\cdot 0.5ROH\cdot 0.5H_2O$ which show two slightly broad bands at 3650 and 3550 cm^{-1} attributable to the asymmetric and symmetric O–H stretching vibrations of the solvating water, respectively. There are no unusual contact distances between the ions and the solvent molecules.

The complexity of the IR spectra makes the identification of all the bands relating to the S–O and S–OR vibrations impossible. Nonetheless the two strong bands at 1208–1228 and 632–637 cm^{-1} can safely be attributed to the alkylsulfito group $SO_2(OR)$ and may tentatively be assigned to the ν_{as}(S–O) and ν_s(S–OR) stretching vibrations, respectively.[23]

The electronic reflectance spectra are similar to the corresponding absorption spectra in nitroethane (Table II). Substitution of the np_3 ligand by pp_3 does not produce significant changes in the general feature of the spectra but only a blue shift of the bands is observed. The spectra of the nickel complexes (Figure 2) with an intense band at 1.7–2.0 μm^{-1} and a second much weaker band above 2.3 μm^{-1}, which in the pp_3 derivatives is masked by charge-transfer bands, are closely related to those of the trigonal-bipyramidal complexes $[NiLX]^+$ (L = np_3, pp_3; X = halide) previously described.[2,24] The two bands can be assigned to $e''^4e'^3a'_1 \leftarrow e''^4e'^4$ and $e''^3e'^4a'_1 \leftarrow e''^4e'^4$ transitions, respectively.

The spectra of the cobalt complexes (Figure 3) with absorptions at 0.6–0.72, 0.94–1.0, 1.6–2.0, and ca. 2.5 μm^{-1} (Table II) are fully comparable to the spectrum of the low-spin distorted trigonal-bipyramidal complex $[Co(SCH_3)(np_3)]BPh_4$.[15]

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Registry No. $[Co(SO_2(OC_2H_5))(np_3)]BPh_4$, 63301-46-2; $[Co(SO_2(OC_2H_5))(pp_3)]BPh_4$, 63340-26-1; $[Ni(SO_2(OCH_3))(np_3)]BF_4$, 63301-48-4; $[Ni(SO_2(OC_2H_5))(np_3)]BF_4\cdot 0.5C_2H_5OH\cdot 0.5H_2O$, 63301-51-9; $[Ni(SO_2(OCH_3))(pp_3)]BPh_4$, 63301-53-1; $[Ni(SO_2(OC_2H_5))(pp_3)]BPh_4$, 63301-55-3.

Supplementary Material Available: A listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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