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S-, *O*-, *O,O'*- *p*-TOLUENESULFINATO COMPLEXES OF IRON(II), COBALT(II) AND NICKEL(II) WITH POLYDENTATE TRIPOD-LIKE PHOSPHINES. CRYSTAL STRUCTURE OF 1,1,1-TRIS(DIPHENYLPHOSPHINOMETHYL)ETHANE *p*-TOLUENESULFINATOCOBALT(II) PERCHLORATE

C.A. GHILARDI, S. MIDOLLINI and S. MONETI

Istituto Composti di Coordinazione del C.N.R., 27 via G. Guerrazzi, Istituto di Chimica Generale ed Inorganica, 41 via J. Nardi, 50132 Firenze (Italy)

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Summary

Reaction of sodium *p*-toluenesulfinate with iron(II), cobalt(II) and nickel(II) aquo ions in the presence of the poly(tertiary phosphines) 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos), tris(2-diphenylphosphinoethyl)amine (np_3) and tris(2-diphenylphosphinoethyl)phosphine (pp_3) gives five-coordinated *p*-toluenesulfinato complexes of formulae [(triphos)Co(*p*-tolSO_2)]ClO_4 and [LM(*p*-tolSO_2)]BPh_4 (L = pp_3, M = Fe, Co, Ni; L = np_3, M = Co, Ni). The nickel derivatives are diamagnetic with the *p*-toluenesulfinate ligand bonded to the metal through the sulfur atom. The iron and cobalt complexes are paramagnetic, low or high spin, with the *p*-toluenesulfinate ion linked to the metal via one oxygen (np_3 and pp_3 derivatives) or both oxygen atoms (cobalt-triphos derivative).

The structure of [(triphos)Co(*p*-tolSO_2)]ClO_4 has been determined from three-dimensional X-ray data collected by counter methods. The crystals are monoclinic, space group $P2_1/n$ with $a = 20.942(9)$, $b = 9.652(4)$, $c = 22.040(8)$ Å, $\beta = 96.36(5)°$, $d_c = 1.407$ gcm^{-3} for $Z = 4$. Full-matrix least-squares refinements converged at the conventional R factor of 0.063 for 5573 observed reflections. The complex cation has a distorted square pyramidal geometry with the sulfinate group acting as a bidentate ligand through the two oxygen atoms.

Introduction

The poly(tertiary phosphines) 1,1,1-tris(diphenylphosphinomethyl)ethane [$CH_3C(CH_2PPh_2)_3$, triphos], tris(2-diphenylphosphinoethyl)amine

[$N(CH_2CH_2PPh_2)_3$, np$_3$], and tris(2-diphenylphosphinoethyl)phosphine [$P(CH_2CH_2PPh_2)_3$, pp$_3$], form stable 3*d*-metal complexes with mixed sulfur-oxygen ligands such as sulfur dioxide [1], sulfite [2], alkylsulfite [3] and sulfate [4]. We have now found that reaction of iron(II), cobalt(II) and nickel(II) aquo ions with the triphos, np$_3$, or pp$_3$ ligands and sodium *p*-toluenesulfinate gives a series of *p*-toluenesulfinato complexes of formulae [(triphos)Co(*p*-tolSO_2)]ClO_4 and [LM(*p*-tolSO_2)]BPh_4 (L = pp$_3$, M = Fe, Co, Ni; L = np$_3$, M = Co, Ni). The same compounds can be formed by metathetical reaction of the corresponding halide complexes with Na(*p*-tolSO_2).

The complexes are five-coordinate, with the RSO_2^- ion linked to the metal via the sulfur atom (nickel derivatives) or via one oxygen (iron-pp$_3$ and cobalt-np$_3$ and cobalt-pp$_3$ derivatives) or both the oxygen atoms (cobalt-triphos complex).

All the compounds have been characterized by appropriate physical methods. A complete X-ray structure determination has been carried out on the complex [(triphos)Co(*p*-tolSO_2)]ClO_4.

Experimental

All the solvents were purified by standard methods. The ligands triphos [5] and np$_3$ [6] were prepared by previously described methods. The pp$_3$ was purchased from the Pressure Chemical Co., Pittsburgh, Pa., and used without further purification.

Preparation of the complexes

The cobalt and iron derivatives were prepared under dry nitrogen, using deoxygenated solvents.

Synthesis of [LM(p-tolSO$_2$)]BPh$_4$ (L = pp$_3$, M = Fe, Co, Ni; L = np$_3$, M = Co, Ni). A solution of the appropriate metal perchlorate hexahydrate (1 mmol) in 10 ml of ethanol was added to the ligand (1 mmol) in 20 ml of methylene chloride at room temperature. Sodium *p*-toluenesulfinate (1 mmol) and sodium tetraphenylborate (1 mmol) were then added. Concentration at room temperature led to separation of crystals, which were collected on a sintered-glass frit, and washed with ethanol followed by petroleum ether.

These complexes can also be prepared by reaction of the corresponding chloride complexes [LMCl]BPh_4 with sodium *p*-toluenesulfinate.

Synthesis of [(triphos)Co(p-tolSO$_2$)]ClO$_4$. 1 mmol of Na(*p*-tolSO_2) dissolved in 20 ml of ethanol was added to a solution obtained by room temperature mixing of 1 mmol of triphos in 20 ml of acetone and 1 mmol of $Co(ClO_4)_2 \cdot 6\ H_2O$ in 10 ml of ethanol. A brisk stream of nitrogen was passed through the solution until sufficient acetone had evaporated and crystallization began. The crystals were filtered off and washed with ethanol and light petroleum ether.

Physical measurements

Infrared and electronic spectra, conductivity measurements and magnetic susceptibilities were recorded by previously described methods [7]. The analytical, magnetic, and conductivity data of the complexes are reported in Table 1. Tables 2, 3 list the electronic and infrared spectral data, respectively.

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR THE COMPLEXES

Complex	Analysis Found (calcd.) (%) [a]					Λ_M [b] (Ω^{-1} mol^{-1} cm^2)	μ_{eff} (BM) (T(K))
	C	H	S	M	N		
[(pp$_3$)Fe(p-tolSO$_2$)]BPh$_4$	73.20	6.01		4.90		45	2.94
	(73.01)	(5.79)		(4.65)			
[(np$_3$)Co(p-tolSO$_2$)]BPh$_4$ · 0.5 CH$_2$Cl$_2$	71.69	5.51		4.66	1.14	46	4.33
	(71.76)	(5.73)		(4.79)	(1.13)		
[(pp$_3$)Co(p-tolSO$_2$)]BPh$_4$	72.13	6.40		4.55		48	1.97
	(72.82)	(5.78)		(4.89)			
[(triphos)Co(p-tolSO$_2$)]ClO$_4$	61.84	4.95	3.33	6.25		76	1.95
	(61.44)	(4.94)	(3.41)	(6.28)			
[(pp$_3$)Ni(p-tolSO$_2$)]BPh$_4$	72.47	5.57	2.66	5.05		50	diamagnetic
	(72.83)	(5.78)	(2.66)	(4.88)			
[(np$_3$)Ni(p-tolSO$_2$)]BPh$_4$	73.96	5.87	2.60	4.90	1.21	46	diamagnetic
	(73.87)	(5.86)	(2.70)	(4.94)	(1.18)		

[a] Calculated values are given in parentheses. [b] Molar conductance values for nitroethane solutions.

TABLE 2

MAXIMA AND EXTINCTION COEFFICIENTS FOR THE ELECTRONIC SPECTRA OF THE COMPLEXES

Compound	Absorption max (cm^{-1}) (ϵ for soln.)
$[(pp_3)Fe(p\text{-}tolSO_2)]BPh_4$	8230; 19050 [a] 8370(619); 19050(3384) [b]
$[(np_3)Co(p\text{-}tolSO_2)]BPh_4$	10526; 13700; 19300 [a] 10800(166); 13600(366); 19900(1656) [c]
$[(pp_3)Co(p\text{-}tolSO_2)]BPh_4$	9523; 15385; 21070(sh) [a] 9345(253); 16000(536); 21075 [b]
$[(triphos)Co(p\text{-}tolSO_2)]ClO_4$	10309; 19047 [a] 10000(357); 19230(770) [b]
$[(pp_3)Ni(p\text{-}tolSO_2)]BPh_4$	19047; 26300 [a] 18870(4753); 25000(6979) [b]
$[(np_3)Ni(p\text{-}tolSO_2)]BPh_4$	15748; 26316 [a] 16000(3311); 26500(10535) [b]

[a] Solid at room temperature. [b] 1,2-dichloroethane solution. [c] Acetone solution.

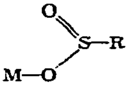
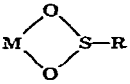
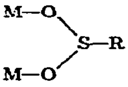
TABLE 3

SELECTED IR DATA (cm^{-1}, NUJOL) FOR THE COMPLEXES

Compound	$\nu_{as}(SO_2)$ or $\nu(SO)$ (cm^{-1})	$\nu_s(SO_2)$ or $\nu_{as}(SOM)$ (cm^{-1})	Coordination type
$[(pp_3)Fe(p\text{-}tolSO_2)]BPh_4$	1095	855	*O*
$[(pp_3)Co(p\text{-}tolSO_2)]BPh_4$	1070	880	*O*
$[(np_3)Co(p\text{-}tolSO_2)]BPh_4$	1090	880	*O*
$[(triphos)Co(p\text{-}tolSO_2)]ClO_4$	915	890	*O*, *O*
$[(pp_3)Ni(p\text{-}tolSO_2)]BPh_4$	1190	1040	*S*
$[(np_3)Ni(p\text{-}tolSO_2)]BPh_4$	1220	1055	*S*

TABLE 4

RANGES OF THE S—O STRETCHING FREQUENCIES OF THE COORDINATED RSO_2 GROUP [a, b]

Anchoring modes of the R—SO_2 group	$\nu_{as}(SO_2)$ or $\nu(SO)$ (cm^{-1})	$\nu_s(SO_2)$ or $\nu_{as}(SOM)$ (cm^{-1})	$\Delta\nu$ (cm^{-1})
 $M-\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}-R$ (I)	1100—1250	1000—1100	
 (II)	1000—1100		100—200
 (III)		800—1000	10—80
 (IV)			

[a] Data from refs. 17 and 18. [b] The values of the $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ stretching frequencies for the $[(C_6H_5)SO_2]Na$ compound are 1020 and 980 cm^{-1}, respectively [19].

TABLE 5

POSITIONAL AND THERMAL PARAMETERS FOR [(triphos)Co(p-tolSO$_2$)]ClO$_4$ [a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	2266(1)	−2734(1)	23(1)	34(1)	30(1)	35(1)	7(1)	5(1)	2(1)
Cl	248(1)	−36(2)	−3150(1)	45(1)	71(1)	56(1)	−5(1)	−1(1)	−5(1)
P(1)	2165(1)	−5010(1)	44(1)	34(1)	31(1)	44(1)	3(1)	6(1)	0(1)
P(2)	3084(1)	−2866(1)	807(1)	35(1)	33(1)	34(1)	4(1)	4(1)	2(1)
P(3)	2928(1)	−2971(2)	−682(1)	40(1)	39(1)	37(1)	6(1)	8(1)	2(1)
S	1526(1)	−704(2)	264(1)	46(1)	40(1)	40(1)	15(1)	3(1)	1(1)
O(1)	1409(2)	−2269(4)	295(2)	47(2)	41(2)	56(2)	12(2)	17(2)	11(2)
O(2)	2107(2)	−705(4)	−108(2)	36(2)	34(2)	61(3)	6(2)	4(2)	9(2)
O(3)	772(3)	681(7)	−2868(3)	81(4)	121(5)	169(7)	−43(5)	−49(4)	4(4)
O(4)	4(4)	−988(8)	−2746(3)	146(6)	166(7)	81(4)	−75(4)	10(4)	15(5)
O(5)	−254(4)	853(8)	−3336(5)	99(5)	122(7)	274(11)	28(7)	−70(6)	−1(5)
O(6)	399(4)	−779(9)	−3643(4)	216(9)	173(8)	174(8)	−59(7)	124(7)	−90(7)
C(1)	4116(3)	−6095(6)	104(3)	50(1)					
C(2)	3540(3)	−5065(6)	80(3)	41(1)					
C(3)	2942(3)	−5863(6)	248(3)	42(1)					
C(4)	3735(3)	−3912(5)	540(3)	39(1)					
C(5)	3409(3)	−4541(6(	−587(3)	43(1)					
C(42)	898(3)	−56(5)	−261(2)	38(1)					
C(43)	690(3)	−757(6)	−802(3)	51(2)					
C(44)	242(3)	−118(6)	−1223(3)	52(2)					
C(45)	−5(3)	1189(6)	−1106(3)	46(1)					
C(46)	201(3)	1853(7)	−566(3)	52(2)					
C(47)	664(3)	1248(6)	−132(3)	41(1)					
C(48)	−486(4)	1869(8)	−1582(4)	72(2)					

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[a] The form of the thermal ellipsoid is $\exp[-2T^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)$ coordinates multiplied by 10^4, temperature factors in Å × 10^3.

X-ray data collection

A well formed violet crystal of dimensions 0.23 × 0.23 × 0.15 mm delimited by the faces (111), (−11 − 1), (101), (100), (001), and the centrosymmetric ones, was mounted in a Philips computer-controlled PW 1100 diffractometer. Cell dimensions determined by least squares refinement of the setting angles of 22 reflections carefully centered are a = 20.942(9), b = 9.652(4), c = 22.040(8) Å, β = 96.36(5)°. The observed density of 1.40 g cm^{-3}, measured by flotation, agrees with the value of 1.407 g cm^{-3} calculated for four formula units of [(triphos)Co(p-tolSO_2)]ClO_4 per cell. The crystals belong to the monoclinic system with extinctions ($h0l$ with $h + l$ odd and $0k0$ with k odd) characteristic of the space group $P2_1/n$. Data collection was carried out using Mo-K_α radiation (λ = 0.7107 Å) monochromatized with a graphite crystal at a take off

TABLE 6

THERMAL AND DERIVED POSITIONAL PARAMETERS OF GROUP ATOMS FOR [(triphos)Co(p-tolSO_2)]ClO_4 [a]

Atom	x	y	z	U (Å^2)
C(6)	1805(2)	−5789(4)	−666(2)	41(1)
C(7)	1941(2)	−7139(4)	−838(2)	55(2)
C(8)	1643(2)	−7683(4)	−1384(2)	69(2)
C(9)	1208(2)	−6878(4)	−1757(2)	75(2)
C(10)	1071(2)	−5528(4)	−1586(2)	73(2)
C(11)	1370(2)	−4984(4)	−1040(2)	52(2)
C(12)	1635(2)	−5695(4)	584(2)	42(1)
C(13)	1837(2)	−6675(4)	1029(2)	60(2)
C(14)	1411(2)	−7158(3)	1424(2)	70(2)
C(15)	782(2)	−6660(4)	1374(2)	71(2)
C(16)	580(2)	−5679(4)	929(2)	67(2)
C(17)	1006(2)	−5196(4)	534(2)	55(2)
C(18)	2847(2)	−3734(4)	1487(2)	37(1)
C(19)	2242(2)	−3381(4)	1649(2)	47(1)
C(20)	2018(2)	−3986(4)	2160(2)	60(2)
C(21)	2399(2)	−4943(4)	2509(3)	71(2)
C(22)	3004(2)	−5296(4)	2347(2)	68(2)
C(23)	3227(2)	−4691(4)	1836(2)	52(2)
C(24)	3521(2)	−1372(3)	1151(2)	39(1)
C(25)	4035(2)	−1577(3)	1601(2)	58(2)
C(26)	4356(2)	−440(3)	1882(2)	67(2)
C(27)	4162(2)	901(3)	1713(2)	59(2)
C(28)	3648(2)	1106(3)	1263(2)	67(2)
C(29)	3327(2)	−31(2)	982(2)	52(2)
C(30)	3501(2)	−1538(4)	−710(2)	46(1)
C(31)	4162(2)	−1757(4)	−675(2)	82(2)
C(32)	4575(2)	−645(4)	−739(2)	99(3)
C(33)	4327(2)	687(4)	−838(2)	80(2)
C(34)	3665(2)	906(4)	−873(2)	72(2)
C(35)	3252(2)	−206(4)	−809(2)	63(2)
C(36)	2501(2)	−2995(4)	−1443(2)	47(1)
C(37)	2624(2)	−3950(4)	−1891(2)	70(2)
C(38)	2255(2)	−3934(4)	−2458(2)	91(3)
C(39)	1763(2)	−2964(4)	−2577(2)	94(3)
C(40)	1641(2)	−2009(4)	−2129(2)	75(2)
C(41)	2010(2)	−2025(4)	−1562(2)	53(2)

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[a] Coordinates multiplied by 10^4, temperature factors by 10^3.

angle of 3.5°. Reflections within $2\theta \leqslant 50°$ were collected using the ω—2θ scan technique with a scan speed of $0.09° \text{ s}^{-1}$ and a scan width determined according to the formula of Alexander and Smith [8], scan range = $A + B \tan\theta$ with $A = 0.74$ and $B = 0.69$. Stationary background measurements were taken before and after each scan for a time equal to half the scan time. The intensities of three reflections measured every two hours showed no variation. After correction for background the intensities were assigned standard deviations calculated as described elsewhere [9] using a value of 0.04 for the instability factor K. 5573 reflections having $I \geqslant 3\sigma(I)$ were considered observed. The data were corrected for Lorentz-polarization effects and an absorption correction using $\mu = 6.4 \text{ cm}^{-1}$ gave transmission factors ranging from 0.85 to 0.72.

Structure determination and refinement

All the calculations were carried out on a SEL 32/70 computer using the SHELX-76 programs [10]. Scattering factors were taken from ref. 11. The structure was solved by the heavy-atom technique. Several Fourier maps showed all the remaining non-hydrogen atoms. Full matrix least squares refinements were carried out, the function minimized being $\Sigma w(|F_0| - |F_c|)^2$. The weights w were taken as $1/\sigma^2(F_0)$. The agreement factors R and R_w are defined as $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ and $R_w = [\Sigma_w(|F_0| - |F_c|)^2/\Sigma_w F_0^2]^{1/2}$. Anisotropic thermal parameters were used only for the heavier atoms. The phenyl rings were treated as rigid groups with $d(\text{C—C}) = 1.395$ Å, each carbon atom being assigned an individual thermal parameter. Hydrogen atoms were included in calculated positions at a distance of 0.95 Å and not refined. Refinements converged at values of 0.063 and 0.072 for R and R_w, respectively. Final positional and thermal parameters are listed in Tables 5 and 6.

Results and discussion

The title complexes were prepared by reaction of sodium p-toluenesulfinate with the metal aquo ions and the appropriate ligand (eq. 1) or with the corresponding halide complexes $[\text{MLX}]^+$ (eq. 2) (L = np$_3$, pp$_3$):

$$[\text{M(H}_2\text{O)}_6]^{2+} + \text{L} + p\text{-tolSO}_2^- \rightarrow [\text{LM}(p\text{-tolSO}_2)]^+ + 6\ \text{H}_2\text{O} \qquad (1)$$

$$[\text{LMX}]^+ + \text{Na}^+(p\text{-tolSO}_2)^- \rightarrow [\text{LM}(p\text{-tolSO}_2)]^+ + \text{NaX} \qquad (2)$$

The solid complexes are air stable; the cobalt and the iron derivatives slowly decompose in oxygenated solutions. All the complexes are soluble in polar organic solvents such as 1,2-dichloroethane, acetone, nitroethane, in which they behave as 1 : 1 electrolytes.

The iron and the cobalt complexes are paramagnetic with μ_{eff} values corresponding to one ($[(\text{pp}_3)\text{Co}(p\text{-tolSO}_2)]\text{BPh}_4$, $[(\text{triphos})\text{Co}(p\text{-tolSO}_2)]\text{ClO}_4$) two ($[(\text{pp}_3)\text{Fe}(p\text{-tolSO}_2)]\text{BPh}_4$) and three ($[(\text{np}_3)\text{Co}(p\text{-tolSO}_2)]\text{BPh}_4$) unpaired electrons, respectively; the nickel derivatives are diamagnetic (Table 1).

Electronic spectral data for the complexes are listed in Table 2. The reflectance spectra are closely similar to the corresponding absorption spectra in 1,2-dichloroethane solution. The spectra of the nickel complexes, which show two bands at 15 748—19 047 cm^{-1} and 26 300 cm^{-1}, are similar to each other, the substitution of the np_3 by the pp_3 ligand causing only a hypsochromic shift of the bands. These spectra are typical of low spin five-coordinated nickel(II) complexes with trigonal-bipyramidal geometry [12].

The electronic spectrum of the compound $[(pp_3)Fe(p\text{-tolSO}_2)]BPh_4$ with bands at 8230 and 19 050 cm^{-1} is quite similar to that of the $[(pp_3)FeBr]BPh_4$ complex, for which a trigonal-bipyramidal geometry has been established by an X-ray analysis [13].

The spectra of the cobalt(II) complexes which exhibit bands in the range 9523—10 309 cm^{-1} and 15 385—19 047 cm^{-1} for the low spin species, and at 10 526, 13 700, and 19 300 cm^{-1} for the high spin one, are suggestive of five-coordinate structures. In particular the spectra of $[(np_3)Co(p\text{-tolSO}_2)]BPh_4$ and $[(pp_3)Co(p\text{-tolSO}_2)]BPh_4$ are fully comparable with those of the trigonal-bipyramidal $[(np_3)CoCl]BPh_4$ compound [14] and of the square-pyramidal $[(pp_3)Co(OH)]BF_4$ [15] compound respectively. The $[(\text{triphos})Co(p\text{-tolSO}_2)]ClO_4$ compound (whose spectrum is similar to those of distorted five-coordinate complexes with P_3O_2 donor set, e.g. $[Co_2(\text{triphos})_2(OH)_2](BPh_4)_2$ or $[(\text{triphos})Co(CH_3COO)]BPh_4$ [16]) is likely to contain the RSO_2^- anion *O,O'*-coordinated to the metal.

The assignment of the binding mode of the sulfinate group is generally made on the basis of the infrared spectroscopic data [17]. Table 3 shows the S—O stretching frequencies of the title complexes; Table 4 lists the ranges of occurence of the S—O stretching frequencies for the principal binding modes of the sulfinate ion. In the case of the nickel complexes the two strong bands at 1190—1220 and 1040—1055 cm^{-1} which are attributable to the $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ stretching vibrations, respectively, are diagnostic of the presence of a sulfinate group *S*-coordinated to the metal (I). The sulfur—oxygen stretching frequencies in the iron and cobalt complexes (Table 3), which are well separated from the *S*-sulfinato bands, are within the range found for the *O*-sulfinato complexes (1100—800 cm^{-1}). In the case of the $[(pp_3)Fe(p\text{-tolSO}_2)]BPh_4$, $[(pp_3)Co(p\text{-tolSO}_2)]BPh_4$ and $[(np_3)Co(p\text{-tolSO}_2)]BPh_4$ complexes the large separation between the $\nu(SO_2)$ modes (240—190 cm^{-1}) is clearly indicative of an unidentate sulfinate group (II); In the case of the $[(\text{triphos})Co(p\text{-tolSO}_2)]ClO_4$ compound, the small separation (25 cm^{-1}) seems to be indicative of bidentate (III) or bridging bidentate (IV) *O*-sulfinato coordination. Such hypothesis is also supported by the spectral UV data. However, the presence of a monodentate *O*-sulfinate group cannot be definitely ruled out on the basis of the IR spectra, since this type of coordination has been established by X-ray analysis even for some complexes with small separations between the $\nu(SO_2)$ frequencies [20].

In order to define precisely the geometry of the *p*-toluenesulfinate group and its binding in the $[(\text{triphos})Co(p\text{-tolSO}_2)]ClO_4$ complex, a complete X-ray analysis has been carried out. The structure of the complex consists of discrete $[(\text{triphos})Co(p\text{-tolSO}_2)]^+$ cations and ClO_4^- anions. The metal atom is surrounded by the three phosphorus atoms of the triphos ligand and by the two oxygen atoms of the sulfinate ion acting indeed as bidentate. Figure 1 shows a perspective view of the cation, and selected bond distances and angles are reported in Table 7. The coordination geometry may be described in terms of a distorted square pyramid with P(2) in the apical position, the main distortion

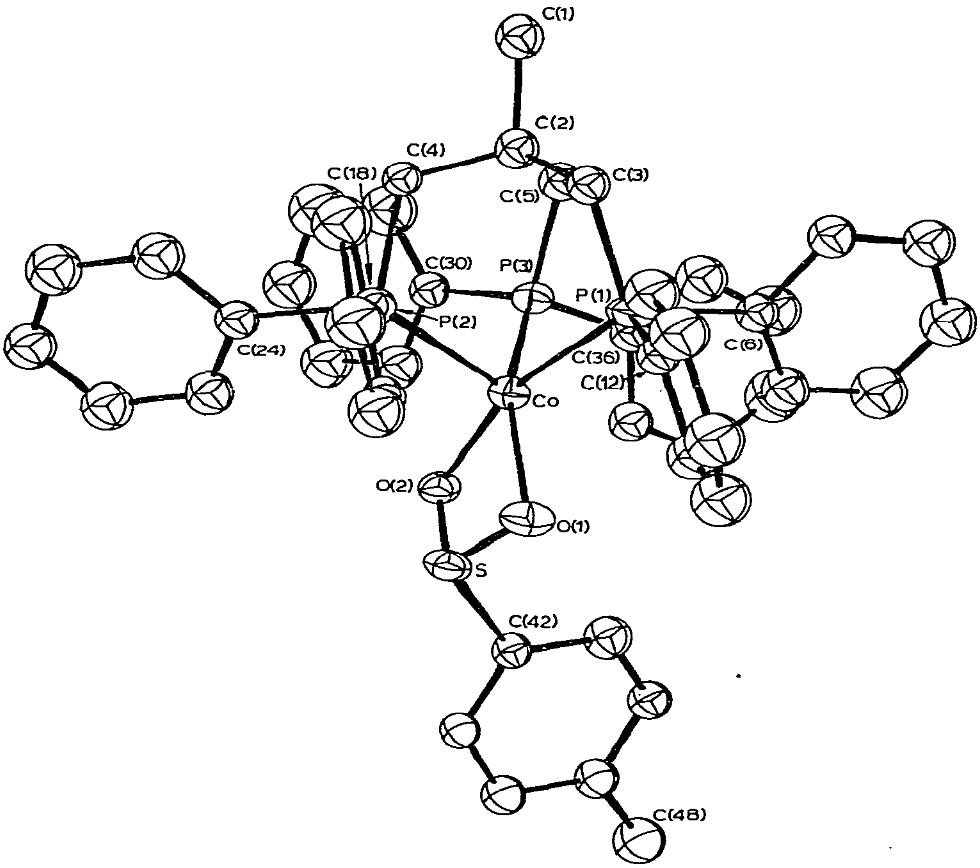

Fig. 1. Perspective view of the $[(\text{triphos})\text{Co}(p\text{-tolSO}_2)]^+$ cation.

being induced by the requirements of the four-membered CoOSO ring. The displacements of the basal donor atoms from their basal least squares plane are 0.09 to 0.12 Å, while the metal atom is 0.36 Å out of the plane towards the apical ligand. The values of the Co—P distances are comparable with those reported for other five-coordinated cobalt(II) compounds where the triphos ligand is involved [4,16,21], but the apical Co—P distance of 2.298(2) is significantly larger than the other basal Co—P distances of 2.208(2) and 2.206(2) Å. Apical lengthening is a common feature for low spin square pyramidal d^7 and d^8 complexes and may be attributed to the steric properties of the d electrons [22].

Concerning the coordination of the sulfinate group, the Co—O distances of 2.004(4) and 2.002(3) Å are practically equivalent. Due to the small bite of the SO_2 group the O—Co—O angle cannot open up much, its value being 71.6(1)°. The CoO_2S fragment is not planar, with the sulfur atom displaced by 0.31 Å out of the CoOO plane. The values of the Co—O distances compare well with those reported for the complex $[(\text{triphos})\text{Co}(\text{CH}_3\text{COO})]^+$ [16], where the (triphos)Co fragment is coordinated by a bidentate acetate group.

TABLE 7

SELECTED BOND DISTANCES (Å) AND ANGLES (deg)

About the metal atom			
Co—P(1)	2.208(2)	Co—O(1)	2.004(4)
Co—P(2)	2.298(2)	Co—O(2)	2.002(3)
Co—P(3)	2.206(2)	Co···S	2.589(2)
P(1)—Co—P(2)	89.6(1)	P(3)—Co—O(1)	152.5(1)
P(1)—Co—P(3)	88.9(1)	P(1)—Co—O(2)	164.1(1)
P(2)—Co—P(3)	92.8(1)	P(2)—Co—O(2)	105.1(1)
P(1)—Co—O(1)	97.2(1)	P(3)—Co—O(2)	96.1(1)
P(2)—Co—O(1)	113.9(1)	O(1)—Co—O(2)	71.6(1)
In the rest of the cation			
S—O(1)	1.533(4)	C(1)—C(2)	1.559(8)
S—O(2)	1.541(4)	C(2)—C(3)	1.549(7)
S—C(42)	1.768(5)	C(2)—C(4)	1.530(7)
P(1)—C(3)	1.835(5)	C(2)—C(5)	1.550(7)
P(1)—C(6)	1.823(4)	C(42)—C(43)	1.399(8)
P(1)—C(12)	1.838(4)	C(43)—C(44)	1.387(8)
P(2)—C(4)	1.845(5)	C(44)—C(45)	1.399(8)
P(2)—C(18)	1.833(4)	C(45)—C(46)	1.377(8)
P(2)—C(24)	1.827(4)	C(46)—C(47)	1.412(8)
P(3)—C(5)	1.820(5)	C(47)—C(42)	1.391(7)
P(3)—C(30)	1.837(5)	C(45)—C(48)	1.521(9)
P(3)—C(36)	1.810(5)		
O(1)—S—O(2)	99.4(2)	Co—P(3)—C(30)	114.2(2)
O(1)—S—C(42)	105.4(2)	Co—P(3)—C(36)	111.7(2)
O(2)—S—C(42)	103.1(2)	C(5)—P(3)—C(30)	106.0(2)
Co—P(1)—C(3)	111.6(2)	C(5)—P(3)—C(36)	107.8(2)
Co—P(1)—C(6)	115.1(2)	C(30)—P(3)—C(36)	103.6(2)
Co—P(1)—C(12)	115.9(2)	S—C(42)—C(43)	121.7(4)
C(3)—P(1)—C(6)	107.3(2)	S—C(42)—C(47)	116.1(4)
C(3)—P(1)—C(12)	105.2(2)	C(43)—C(42)—C(47)	121.9(5)
C(6)—P(1)—C(12)	100.7(2)	C(42)—C(43)—C(44)	118.6(6)
Co—P(2)—C(4)	107.9(2)	C(43)—C(44)—C(45)	120.9(6)
Co—P(2)—C(18)	113.2(2)	C(44)—C(45)—C(46)	119.6(6)
Co—P(2)—C(24)	124.4(2)	C(44)—C(45)—C(48)	119.5(6)
C(4)—P(2)—C(18)	106.7(2)	C(46)—C(45)—C(48)	121.0(6)
C(4)—P(2)—C(24)	102.1(2)	C(45)—C(46)—C(47)	121.2(6)
C(18)—P(2)—C(24)	101.0(2)	C(46)—C(47)—C(42)	117.8(5)
Co—P(3)—C(5)	112.9(2)		
In the anion			
Cl—O(3)	1.384(6)	Cl—O(5)	1.383(6)
Cl—O(4)	1.414(6)	Cl—O(6)	1.367(8)
O(3)—Cl—O(4)	111.4(4)	O(4)—Cl—O(5)	105.9(5)
O(3)—Cl—O(5)	111.2(5)	O(4)—Cl—O(6)	106.9(5)
O(3)—Cl—O(6)	112.2(5)	O(5)—Cl—O(6)	108.9(6)

The geometry around the sulfur atom of the sulfinate group is trigonal pyramidal with angles of 99.4(2), 103.1(2) and 105.4(2)°. The S—O bond distances of 1.533(4) and 1.541(4) Å are fully comparable to the value of 1.541(4) Å reported for the S—O distance involving the oxygen atom linked to the metal in the *O*-sulfinato $[Cu(H_2O)_4(p\text{-tolSO}_2)_2]$ complex [20a]. No significant distortions are present in the aromatic ring of the sulfinate ligand which is not involved in any short contact distance.

The different bonding modes of the sulfinate ligand in our complexes require comment. It is well known that the sulfinate ion can act as a *O*-bonded ligand (hard Lewis base) when it is coordinated to a "hard" metal ion, while it can act as a *S*-bonded ligand (soft Lewis base) towards a "soft" metal ion [17]. In the Ahrland-Chatt-Davies classification [23] iron(II), cobalt(II) and nickel(II) are essentially "hard" metals and generally form M—O bonds with the sulfinate ligands, but these metals can also form *S*-sulfinato complexes in the presence of such coligands which reinforce the "softness" of the metal by increasing the π-back bonding capability of the central ion [24]. Thus it is not surprising that the metal—S bonds are preferred by these nickel complexes. In fact the nickel(II) ion in the $\{Ni(np_3)\}$ and $\{Ni(pp_3)\}$ moieties has been found to act as a "soft" metal when linked to very "soft" bases such as alkyl$^-$ [25], aryl$^-$ [26], stannyl$^-$ [27], H$^-$ [28].

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