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Synthesis, Properties, and Characterization of Sulfato and Selenato Complexes of Cobalt(II) and Nickel(II) with 1,1,1-Tris(diphenylphosphinomethyl)ethane (p_3). Crystal and Molecular Structures of $Co(p_3)SO_4$ and $Ni(p_3)SeO_4$

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Sulfato and selenato complexes of cobalt(II) and nickel(II) with the ligand 1,1,1-tris(diphenylphosphinomethyl)ethane (p_3) with formulas $M(p_3)SO_4$ and $M(p_3)SeO_4$ have been prepared. The structures of the complexes $Co(p_3)SO_4$ (I) and $Ni(p_3)SeO_4$ (II) have been determined by single-crystal x-ray data collected by counter methods. The compounds crystallize in space group $Pn2_1a$ of the orthorhombic system with four formula units in a cell of dimensions $a = 20.341$ (9), $b = 17.339$ (8), $c = 10.440$ (5) Å (I) and $a = 20.472$ (8), $b = 17.759$ (7), $c = 10.475$ (5) Å (II). Both structures have been refined by least-squares techniques to final R factors of 0.059 (I) and 0.058 (II). The compounds possess a distorted square-pyramidal coordination geometry with the SO_4 and SeO_4 groups coordinating as bidentate ligands to one metal atom. The cobalt complexes are low-spin whereas the nickel complexes are high-spin, in spite of the fact that they have rather similar coordination geometry. This fact is rationalized on the basis of the structural results. The nickel complexes in solution transform almost completely to diamagnetic species. The equilibrium between diamagnetic and paramagnetic species in solution has been investigated by NMR measurements. The IR frequencies of the coordinated SO_4 and SeO_4 groups have been assigned, those of the chelating SeO_4 being reported here for the first time.

Introduction

The tri(tertiary phosphine) ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, p_3, forms stable 3d-metal complexes in combination with a variety of other donor groups. Four-, five-, and six-coordinate complexes of iron, cobalt, and nickel with oxidation numbers +1 and +2 formed by p_3 in the presence of other ligands such as halogen, pseudohalogen, carbon monoxide, hydride, nitrate, acetate, etc., have been described.[1] We now report that cobalt(II) and nickel(II) sulfates and selenates readily react with p_3 in acetone and methanol–ethanol solution to yield complexes with formulas $M(p_3)SO_4$ and $M(p_3)SeO_4$ (M = Co, Ni). Complete x-ray analyses, performed on two of these compounds, show that the sulfate and selenate groups are bonded to the metal through two oxygen atoms. On the basis of the structural results and of the spectral and magnetic properties of the compounds, the coordination geometry of all complexes of the series has been assigned. In spite of the fact that the geometry of coordination is essentially the same for the cobalt and for the nickel complexes, the former are low spin whereas the latter are high spin. This may be accounted for on the basis of the structural results.

There are few structural reports on metal–sulfato complexes. The SO_4 group has been found to coordinate either as a monodentate or as a bidentate ligand.[2] In the latter case it may act either as a monometallic chelating[2b] or as a bimetallic bridging ligand.[2c] In the absence of structural information, IR data have been used[3] to distinguish between monodentate and bidentate sulfate. However, this procedure is neither straightforward nor unambiguous.[4] Bands due to SO_4 in the IR spectra of the present complexes have been assigned and their number and positions have been found essentially to agree with those expected for bidentate SO_4. The IR spectra of the selenato complexes have also been assigned, using comparison with those of the corresponding sulfate compound. The characterization as well as the determination of the structure of these selenato complexes is of interest as no complex containing SeO_4 as a ligand has been reported so far.

The nickel complexes undergo a transformation in solution, producing a predominant concentration of diamagnetic species. The equilibrium between paramagnetic and diamagnetic forms has been investigated by NMR measurements.

Experimental Section

Materials. All solvents were reagent grade. The compounds were prepared in a routine way using degassed solvents under a nitrogen atmosphere. The synthesis of the ligand p_3 appears elsewhere.[5]

Table I. Analytical and Magnetic Data

	Elemental anal., %						μ_{eff} (293 K), μ_B
	C		H		M		
Compd	Calcd	Found	Calcd	Found	Calcd	Found	
$Co(p_3)SO_4$[a]	63.14	63.90	5.04	5.27	7.55	7.55	2.03
$Co(p_3)SeO_4$	59.54	59.01	4.75	5.08	7.13	6.50	2.01
$Ni(p_3)SO_4$	63.16	63.01	5.04	5.04	7.53	7.25	3.01
$Ni(p_3)SeO_4$	59.56	59.37	4.75	4.80	7.10	7.40	3.12

[a] S: 4.50% calcd; 4.03% found.

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

Compd	Absorption max,[a] $cm^{-1} \times 10^3$ (ϵ_M for soln)
$Co(p_3)SO_4$	a: 11.1, 16.5, 22.7 b: 10.8 (562), 16.7 (198), 22.2 sh
$Co(p_3)SeO_4$	a: 11.1, 16.1, 22.2 sh b: 10.8 (446), 16.1 (66), 20.8 (614)
$Ni(p_3)SO_4$	a: 9.7, 13.7, 15.4, 19.3, 26.3 sh b: 11.1 (30), 22.7 (811)
$Ni(p_3)SeO_4$	a: 9.8, 14.2, 18.8, 26.3 sh b: 10.0 (19), 21.7 (730)

[a] Key: a, solid at room temperature; b, 1,2-dichloroethane solution.

Preparation of $Co(p_3)SO_4$ and $Co(p_3)SeO_4$. To a solution of the metal salt (1 mmol) in methanol/ethanol (30 ml, 1:2) the ligand p_3 (1 mmol in 30 ml of acetone) was added. The light brown solution, exposed to a stream of dry N_2 for few minutes, deposited light brown crystals, which were filtered off and washed with ethanol and petroleum ether. Results of elemental analyses are given in Table I.

Preparation of $Ni(p_3)SO_4$ and $Ni(p_3)SeO_4$. The same procedure was followed as for the cobalt derivatives. In order to obtain crystals of the selenato derivative, the brown solution had to be concentrated to a small volume by heating. On cooling, purple crystals precipitated. These were filtered and washed as above. Results of elemental analyses are given in Table I.

Physical Measurements. The physical measurements used were carried out by previously described methods.[6] The NMR spectra of the CD_2Cl_2 solutions were recorded on a Varian CFT-20 spectrometer equipped with an ^1H probe, using the technique of an internal lock on deuterium. The magnetic data are reported in Table I. Table II lists the electronic spectral data and Table III lists the IR frequencies.

Collection and Reduction of X-Ray Intensity Data. Crystals of the cobalt and nickel sulfate and of the nickel selenate compounds are isomorphous with each other. Those of the cobalt selenate are not

Table III. IR Absorptions (cm^{-1}) of Some Sulfate and Selenate Compounds

Compd	ν_3	ν_1	ν_4	Ref
Free SO_4^{2-}	1140	983	613	*a*
$Co(p_3)SO_4$	1235, 1170, 1140	920	640, 600, 570	*b*
$Ni(p_3)SO_4$	1255, 1170, 1150	920	650, 600, 570	*b*
$[Co(en)_2SO_4]Br$	1211, 1176, 1075	993	647, 632	*a*
$Ir(p_3)Cl(SO_4)$	1255, 1145, 1070	895		*c*
Free SeO_4^{2-}	875	833	432	*d*
$Co(p_3)SeO_4$	930, 895	780	495, 450, 390	*b*
$Ni(p_3)SeO_4$	930, 895	790	485, 440, 390	*b*

[a] K. Nakamoto, J. Fujita, S. Tamaka, and M. Kobayashi, *J. Am. Chem. Soc.*, 79, 4904 (1957). [b] Present work; spectra recorded as Nujol mulls. [c] W. O. Siegl, S. J. Lapporte, and J. P. Collman, *Inorg. Chem.*, **10**, 2158 (1971). [d] Reference 3.

isomorphous with the others, although their cell dimensions are close to those of the other complexes (Table IV). Crystals of the compound $Co(p_3)SeO_4$ were of poor quality and did not provide suitable data for accurate structure determination. X-ray structure investigation was undertaken on the compounds $Co(p_3)SO_4$ (I) and $Ni(p_3)SeO_4$ (II), for which suitable crystals were available.

Systematic extinctions for the three isomorphous compounds ($hk0$, h odd; $0kl$, $k + l$ odd; $h00$, h odd; $0k0$, k odd; $00l$, l odd) indicate that the space group is $Pn2_1a$ or possibly $Pnma$ of the orthorhombic system.[7] The first space group was assigned, due to the isomorphism of the present compounds with others formed by p_3, which had been studied previously (see ref 1 and results to be published). Subsequent structure determination proved that this choice was correct. A nonstandard setting, axes b and c being interchanged with respect to ref 7 (equivalent positions: x, y, z; $\bar{x}, {}^1/_2 + y, \bar{z}$; ${}^1/_2 - x, {}^1/_2 + y, {}^1/_2 + z$; ${}^1/_2 + x, y, {}^1/_2 - z$), was adopted in order to match the choice which had been made for an isomorphous compound.[1] Lattice constants at 298 K (Table IV) were determined by least-squares refinement of the angular positions of 24 reflections for the orthorhombic complexes and of 30 reflections for the triclinic one. Density measurements were performed by the flotation method, in a K_2HgI_4 aqueous solution. Data collection was performed with a Philips computer-controlled PW 1100 diffractometer following the procedure described previously;[1] details are given in Table V. Intensities of three standard reflections measured every 100 min did not reveal any systematic trend. Data were processed in the usual way with $\sigma(F_o^2)$ calculated using a value of 0.04 for p.[8] Only reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in subsequent calculations. Corrections for absorption were applied.[9]

Structure Refinement. Fourier syntheses phased with the contributions of atoms of the p_3 ligand and of the metal atom, whose positions were initially assumed from the structure of an isomorphous complex,[1] showed all atoms of the SO_4 (I) and SeO_4 (II) groups. In the course of the subsequent least-squares refinement, carbon atoms were assigned isotropic temperature factors and all other nonhydrogen atoms were refined anisotropically. Hydrogen atoms were introduced into calculated positions as fixed contributions (C–H = 1.00 Å), each with a temperature factor ca. 15% larger than that of the carbon atoms to which it was attached. Methyl hydrogen atoms were located from difference-Fourier syntheses and their positions were idealized to produce a tetrahedral arrangement about the carbon atom, by a least-squares procedure.[9] The quantity minimized in the least-squares method was $\sum w(|F_o| - |F_c|)^2$ and weights w were taken as $1/\sigma^2(F_o)$. Atomic scattering factors were taken from ref 10 and anomalous dispersion terms for the metal, P, S, and Se atoms were included in F_c.[11] As the space group is polar, the y coordinate of one heavy atom was kept fixed during the least-squares cycles. Refinement converged to $R = 0.059$ and $R_w = 0.061$ for I and to $R = 0.058$ and $R_w = 0.055$ for II; the largest shift:error ratio was 0.25 at this point. Refinement performed on the structures, with the sign of the y coordinate changed for all atoms, converged to the significantly higher[12] $R = 0.079$ (I) and 0.062 (II) values, thus allowing an unambiguous assignment of the absolute configuration. This assignment agrees with that previously found for the isomorphous complex.[1] The large difference in R for the two enantiomorphs of the cobalt compound is due to the use of Cu Kα radiation for data collection. The effects of anomalous dispersion under these experimental conditions are large, but they should not affect the structural results in view of the correction applied.[11] A few least-squares cycles in which the anomalous dispersion correction factors were allowed to refine were run as a test. They yielded a $\Delta f''$ value for cobalt somewhat different (by ca. 3σ) from tabulated values[12] but did not produce appreciable shifts in the other parameters. Final ΔF Fourier syntheses failed to show significant features: the highest peaks were close to the heavy-atom positions and had heights of ca. 0.4 e/Å^3 in both structures. The final positional

Table IV. Cell Parameters of the Complexes (Esd's in Parentheses)

Compd	a, Å	b, Å	c, Å	α, deg	β, deg	γ, deg
$Co(p_3)SO_4$	20.341 (9)	17.339 (8)	10.440 (5)	90	90	90
$Co(p_3)SeO_4$	22.60 (4)	18.65 (3)	9.90 (3)	89.7 (1)	102.7 (1)	102.3 (1)
$Ni(p_3)SO_4$	20.412 (10)	17.450 (9)	10.438 (6)	90	90	90
$Ni(p_3)SeO_4$	20.472 (8)	17.759 (7)	10.475 (5)	90	90	90

Table V. Summary of Crystal Data, Intensity Collection, and Refinement

	$Co(p_3)SO_4$	$Ni(p_3)SeO_4$
Formula	$C_{41}H_{39}Co_1O_4P_3S_1$	$C_{41}H_{39}Ni_1O_4P_3Se_1$
Mol wt	779.68	826.36
V, Å^3	3682	3808
Z	4	4
Density, g/cm^3	1.406 (calcd), 1.40 (exptl)	1.441 (calcd), 1.43 (exptl)
Space group	$Pn2_1a$	$Pn2_1a$
Crystal dimensions, mm	0.03 × 0.60 × 0.06	0.08 × 0.34 × 0.12
Crystal shape	Needles, [010] elongated	Needles, [010] elongated
Radiation	Cu Kα (λ 1.5418 Å), graphite monochromatized, Ni filtered	MoKα (λ 0.7107 Å), graphite monochromatized, Zr filtered
μ, cm^{-1}	59.33	16.20
Transmission factors	0.538–0.819	0.816–0.875
Takeoff angle, deg	4.5	4.0
Scan speed	3.0° in 2θ/min	3.0° in 2θ/min
Scan range, deg	1.10 + 0.10 in θ, symmetric	0.80 in θ, symmetric
Background counting[a]	$t_{b_1} = t_{b_2} = {}^1/_2 t_s$	$t_{b_1} = t_{b_2} = {}^1/_2 t_s$
2θ limits, deg	4.0–135.0	4.0–40.0
Final no. of variables	245	245
Unique data used ($F_o^2 > 3\sigma(F_o^2)$)	1498	1344
Error in observn of unit wt, electrons	1.26	1.30
R	5.9	5.8
R_w	6.1	5.5

[a] t_s is total scan time.

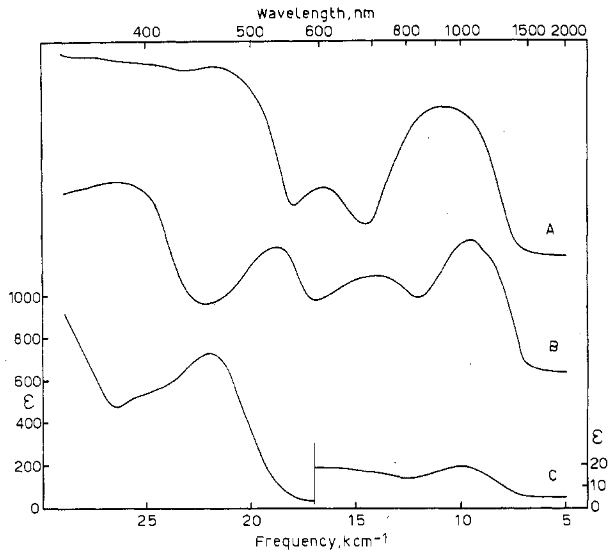

Figure 1. Reflectance spectra of $Co(p_3)SO_4$ (A) and $Ni(p_3)SeO_4$ (B) recorded at liquid nitrogen temperature. Absorption spectrum of $Ni(p_3)SeO_4$ (C) in 1,2-dichloroethane.

and thermal parameters appear in Tables VI and VII. A listing of the observed and calculated structure amplitudes is available.[13]

Results and Discussion

The light brown complexes $Co(p_3)SO_4$ and $Co(p_3)SeO_4$ are stable in air and soluble in common organic solvents, in which they do not conduct. They are paramagnetic, with μ_{eff} close to that expected for one unpaired spin (Table I). They exhibit similar solution and reflectance spectra (Table II, Figure 1) with intense bands at ca. 11 000 and 22 000 cm^{-1} and a weak one at ca. 16 000 cm^{-1}. Substitution of SO_4 by the SeO_4 group produces marked shifts in the IR group frequencies which are discussed below.

The violet complexes $Ni(p_3)SO_4$ and $Ni(p_3)SeO_4$ are air stable and sparingly soluble in common solvents; they do not conduct in 1,2-dichloroethane solution. The solid compounds are paramagnetic (Table I) with μ_{eff} values corresponding to two unpaired electrons. Their reflectance spectra (Table II, Figure 1), which show absorptions at ca. 10 000, 14 000–16 000, 20 000, and 26 000 cm^{-1}, differ markedly from the solution spectra, which exhibit very low absorption at frequencies below 20 000 cm^{-1} and show essentially one strong band at ca. 22 000 cm^{-1}. The IR spectra are similar to those of the corresponding cobalt complexes.

The structures of the isomorphous complexes $Co(p_3)SO_4$ and $Ni(p_3)SeO_4$ consist of isolated molecules in which the metal atom is five-coordinated by the three phosphorus atoms of the p_3 ligand by two oxygen atoms of the sulfate or selenate group, which chelate as bidentate ligands. Figure 2 shows the $Ni(p_3)SeO_4$ molecule. The coordination geometries are similar in the two complexes and may be described in terms of a very distorted square pyramid, with a phosphorus atom P(3) in the apical position. The same type of coordination may be tentatively assigned to the $Co(p_3)SeO_4$ and $Ni(p_3)SO_4$ complexes, in view of their physicochemical properties. In spite of the gross similarity of their structures, the two complexes investigated do exhibit significant differences in the dimensions of their coordination polyhedra. In complex I the apical Co–P(3) distance of 2.291 (5) Å is longer than the other two Co–P distances (2.212 (5), 2.212 (6) Å). A similar trend has been found for the $[Co(CH_3COO)(p_3)]^+$ cation,[1] which is low spin like complex I. On the other hand the apical Ni–P(3) distance of 2.299 (6) Å in the high-spin complex II is shorter than those in the base (2.356 (5), 2.341 (5) Å). The metal atoms lie above the best plane, through the four atoms forming the base of the pyramid, by 0.337 Å (I) and 0.396 Å (II). Hence the lower deviation from the base is found for the low-spin compound, which exhibits some elongation of the apical bond. This agrees with a trend that has been established previously by consideration of a number of square-pyramidal complexes.[14] Metal–ligand distances in the high-spin nickel complex are longer than in the low-spin cobalt one: the average of the Ni–P bonds exceeds that of the Co–P by 0.094 Å. Values of distances and angles about the metal atom in the two complexes are reported in Table VIII and selected values for the rest of the molecule are reported in Table IX.

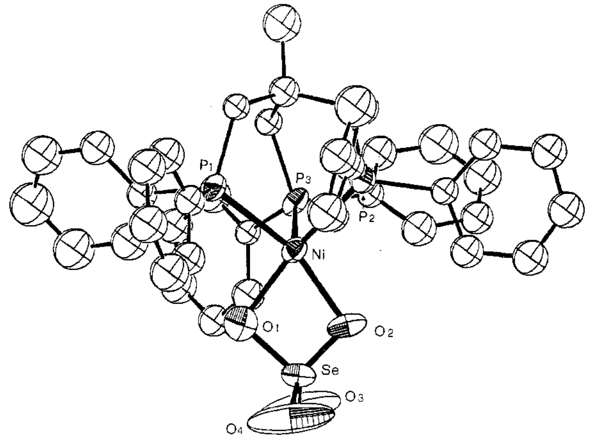

Figure 2. View of the molecular structure of $Ni(p_3)SeO_4$. Thermal ellipsoids are drawn at the 50% probability level.

Dimensions within the p_3 ligand are in the normal range for both complexes, with the exception of values of the P–C–C angles in the aliphatic chains (see below). Distortions from the tetrahedral geometry in the SO_4 group agree with those previously reported[2b] for monometallic chelating sulfate. Distortions in the SeO_4 group are large and irregular and are probably caused by the large size of the Se atom. There are no unusually short intermolecular contacts in the structures.

The magnetic properties of these complexes should be rationalized on the basis of the structural results. In spite of the fact that all the complexes have the same P_3O_2 donor set, to which corresponds a value of the overall nucleophilicity, $\sum n°$, equal to 31.1, a value which belongs to the low-spin range,[14] they are found to possess different spin states: the nickel complexes are high spin, whereas the cobalt ones are low spin. A possible explanation can be found in view of the strict geometric requirements imposed on the coordination by the three ligands, p_3, SO_4, and SeO_4, which are less flexible than those previously used to establish the $\sum n°$ scale.[14]

Considering the nickel complexes first, it should be observed that square-pyramidal low-spin d^8 complexes formed with ligands that are not strong π acceptors quite generally exhibit an appreciable elongation of the apical bond.[14,15] This is rationalized in terms of an anisotropic d-charge distribution for the preponderant strong-field electronic configuration. The geometric requirements of the ligands in the present complexes are definitely incompatible with such an arrangement and favor a symmetrical d-charge distribution, pertaining to different (high-spin) electronic configurations.

For the square-pyramidal low-spin d^7 complexes, on the other hand, the apical elongation is generally small, in keeping with what is found for the $Co(p_3)SO_4$ complex. This can be rationalized by the same sort of arguments invoked for the d^8 compounds.[14,16] Therefore it seems that no factors strongly oppose spin pairing in the d^7 configuration, at variance with the d^8 case. Actually, the low-spin state should be favored, on general grounds, when rigid ligands which impose short metal–donor atom distances are employed. In fact, such geometric conditions prevent the radial expansion which is

Table VI. Positional Parameters and Isotropic Thermal Parameters, with Estimated Standard Deviations in Parentheses

$Co(p_3)SO_4$					$Ni(p_3)SeO_4$				
Atom	x/a	y/b	z/c	10^2B, Å^2	Atom	x/a	y/b	z/c	10^2B, Å^2
Co	−0.0636 (1)	−0.1338	0.0729 (2)		Ni	−0.0639 (1)	−0.1308 (2)	0.0758 (2)	
S	−0.1314 (2)	−0.2509 (3)	−0.0033 (5)		Se	−0.1333 (1)	−0.2539	−0.0066 (2)	
P(1)	0.0404 (2)	−0.1280 (3)	0.1338 (4)		P(1)	0.0467 (2)	−0.1244 (4)	0.1372 (5)	
P(2)	−0.0535 (2)	−0.0161 (2)	−0.0064 (4)		P(2)	−0.0537 (2)	−0.0095 (3)	−0.0094 (6)	
P(3)	−0.0969 (2)	−0.0884 (2)	0.2686 (4)		P(3)	−0.0960 (2)	−0.0846 (3)	0.2710 (5)	
O(1)	−0.0729 (7)	−0.2469 (6)	0.0836 (11)		O(1)	−0.0668 (8)	−0.2427 (9)	0.0883 (17)	
O(2)	−0.1385 (7)	−0.1671 (6)	−0.0281 (14)		O(2)	−0.1375 (9)	−0.1688 (9)	−0.0331 (18)	
O(3)	−0.1840 (7)	−0.2802 (8)	0.0670 (13)		O(3)	−0.1869 (10)	−0.2894 (13)	0.0724 (19)	
O(4)	−0.1185 (8)	−0.2928 (8)	−0.1121 (13)		O(4)	−0.1194 (11)	−0.3010 (13)	−0.1200 (19)	
C(1)	0.038 (1)	0.089 (1)	0.305 (1)	4.5 (5)	C(1)	0.039 (1)	0.088 (1)	0.309 (2)	7.3 (8)
C(2)	0.010 (1)	0.019 (1)	0.235 (1)	3.0 (4)	C(2)	0.010 (1)	0.021 (1)	0.236 (2)	4.7 (6)
C(3)	0.066 (1)	−0.030 (1)	0.182 (1)	2.9 (4)	C(3)	0.068 (1)	−0.026 (1)	0.180 (2)	3.5 (5)
C(4)	−0.035 (1)	0.052 (1)	0.124 (1)	2.7 (4)	C(4)	−0.032 (1)	0.054 (1)	0.121 (2)	3.8 (5)
C(5)	−0.031 (1)	−0.026 (1)	0.334 (1)	3.7 (4)	C(5)	−0.029 (1)	−0.023 (1)	0.332 (2)	3.7 (5)
C(6)	0.066 (1)	−0.188 (1)	0.270 (1)	3.8 (4)	C(6)	0.071 (1)	−0.183 (1)	0.271 (2)	4.6 (6)
C(7)	0.025 (1)	−0.249 (1)	0.304 (2)	5.4 (5)	C(7)	0.035 (1)	−0.241 (1)	0.310 (2)	7.3 (7)
C(8)	0.046 (1)	−0.299 (1)	0.406 (2)	7.4 (6)	C(8)	0.052 (1)	−0.290 (1)	0.413 (3)	8.7 (8)
C(9)	0.105 (1)	−0.286 (1)	0.464 (2)	7.3 (6)	C(9)	0.110 (1)	−0.275 (2)	0.470 (2)	9.7 (9)
C(10)	0.145 (1)	−0.227 (1)	0.428 (2)	8.3 (7)	C(10)	0.148 (1)	−0.216 (1)	0.437 (2)	7.9 (8)
C(11)	0.126 (1)	−0.178 (1)	0.333 (2)	5.8 (5)	C(11)	0.129 (1)	−0.168 (1)	0.340 (2)	6.0 (7)
C(12)	0.098 (1)	−0.158 (1)	0.011 (1)	3.5 (4)	C(12)	0.104 (1)	−0.152 (1)	0.015 (2)	4.7 (6)
C(13)	0.081 (1)	−0.214 (1)	−0.075 (2)	5.9 (5)	C(13)	0.089 (1)	−0.211 (1)	−0.063 (2)	5.8 (7)
C(14)	0.127 (1)	−0.242 (1)	−0.168 (2)	5.0 (5)	C(14)	0.132 (1)	−0.236 (1)	−0.160 (2)	7.4 (8)
C(15)	0.189 (1)	−0.211 (1)	−0.173 (2)	6.6 (6)	C(15)	0.192 (1)	−0.200 (1)	−0.167 (2)	7.4 (8)
C(16)	0.205 (1)	−0.154 (1)	−0.089 (2)	5.5 (5)	C(16)	0.209 (1)	−0.145 (1)	−0.088 (2)	7.0 (7)
C(17)	0.161 (1)	−0.128 (1)	0.003 (1)	4.9 (4)	C(17)	0.166 (1)	−0.122 (1)	0.006 (2)	6.7 (6)
C(18)	0.009 (1)	−0.007 (1)	−0.126 (1)	2.9 (4)	C(18)	0.013 (1)	−0.001 (1)	−0.132 (2)	4.6 (6)
C(19)	0.017 (1)	−0.063 (1)	−0.214 (2)	3.6 (4)	C(19)	0.020 (1)	−0.063 (1)	−0.210 (2)	5.3 (7)
C(20)	0.062 (1)	−0.059 (1)	−0.317 (2)	6.4 (6)	C(20)	0.064 (1)	−0.062 (1)	−0.313 (2)	7.8 (8)
C(21)	0.100 (1)	0.005 (1)	−0.328 (2)	7.7 (7)	C(21)	0.097 (1)	0.004 (1)	−0.322 (2)	6.5 (7)
C(22)	0.093 (1)	0.064 (1)	−0.243 (2)	7.1 (6)	C(22)	0.092 (1)	0.066 (2)	−0.250 (3)	8.9 (9)
C(23)	0.051 (1)	0.058 (1)	−0.144 (2)	5.5 (5)	C(23)	0.049 (1)	0.065 (1)	−0.146 (2)	6.5 (7)
C(24)	−0.121 (1)	0.029 (1)	−0.090 (2)	3.9 (4)	C(24)	−0.119 (1)	0.038 (1)	−0.094 (2)	3.8 (6)
C(25)	−0.164 (1)	−0.013 (1)	−0.164 (2)	5.5 (5)	C(25)	−0.164 (1)	−0.006 (1)	−0.162 (2)	5.6 (7)
C(26)	−0.211 (1)	0.024 (1)	−0.239 (2)	5.9 (5)	C(26)	−0.211 (1)	0.033 (1)	−0.235 (2)	6.5 (7)
C(27)	−0.217 (1)	0.102 (1)	−0.234 (2)	5.9 (6)	C(27)	−0.214 (1)	0.107 (1)	−0.232 (2)	6.7 (7)
C(28)	−0.176 (1)	0.144 (1)	−0.157 (2)	5.2 (5)	C(28)	−0.175 (1)	0.153 (1)	−0.163 (2)	6.4 (7)
C(29)	−0.129 (1)	0.107 (1)	−0.088 (2)	5.4 (5)	C(29)	−0.127 (1)	0.114 (1)	−0.092 (2)	5.1 (6)
C(30)	−0.112 (7)	−0.157 (1)	0.397 (1)	2.8 (4)	C(30)	−0.112 (1)	−0.151 (1)	0.395 (2)	3.2 (6)
C(31)	−0.152 (1)	−0.220 (1)	0.366 (2)	4.4 (5)	C(31)	−0.150 (1)	−0.214 (1)	0.368 (2)	5.4 (6)
C(32)	−0.166 (1)	−0.275 (1)	0.462 (2)	5.8 (6)	C(32)	−0.164 (1)	−0.266 (1)	0.460 (2)	5.0 (6)
C(33)	−0.146 (1)	−0.264 (1)	0.583 (2)	4.7 (5)	C(33)	−0.144 (1)	−0.258 (1)	0.584 (2)	6.7 (7)
C(34)	−0.107 (1)	−0.201 (1)	0.616 (2)	5.9 (5)	C(34)	−0.106 (1)	−0.200 (1)	0.615 (2)	6.3 (7)
C(35)	−0.094 (1)	−0.144 (1)	0.525 (2)	4.3 (5)	C(35)	−0.092 (1)	−0.140 (1)	0.520 (2)	5.9 (6)
C(36)	−0.172 (1)	−0.026 (1)	0.272 (2)	3.6 (4)	C(36)	−0.170 (1)	−0.024 (1)	0.272 (2)	3.7 (5)
C(37)	−0.211 (1)	−0.024 (1)	0.171 (2)	4.6 (5)	C(37)	−0.209 (1)	−0.023 (1)	0.164 (2)	6.3 (7)
C(38)	−0.266 (1)	0.026 (1)	0.171 (2)	5.6 (5)	C(38)	−0.262 (1)	0.028 (1)	0.166 (2)	5.4 (7)
C(39)	−0.278 (1)	0.068 (1)	0.280 (2)	5.7 (5)	C(39)	−0.273 (1)	0.072 (1)	0.269 (2)	7.1 (7)
C(40)	−0.241 (1)	0.065 (1)	0.385 (2)	5.4 (5)	C(40)	−0.238 (1)	0.072 (1)	0.373 (2)	8.1 (8)
C(41)	−0.184 (1)	0.017 (1)	0.384 (2)	5.4 (5)	C(41)	−0.184 (1)	0.021 (1)	0.378 (2)	6.4 (7)

predicted[17] and found[18] to take place in the alternative high-spin state. In this connection it should be observed that the P–C–C angles in the p_3 chains of $Co(p_3)SO_4$ average to the large value of 115.0° and the strains increase in the high-spin nickel complex, where those angles average to 116.8°. In conclusion, the P_3O_2 donor set favors the low-spin state, but this is destabilized by geometric factors in the case of the d^8 configuration.

The reflectance spectra of the two cobalt complexes (Table II, Figure 1) do not change with temperature, except for the usual effects of improved resolution at low temperatures. They are quite similar to each other and to the absorption spectra, indicating that the geometry of the chromophore does not change in solution. They are also similar to the spectra of other five-coordinate low-spin d^7 complexes with trigonal-bipyramidal[19] or distorted geometry.[16] Actually, these spectra are rather insensitive to geometric distortions of the chromophore. This may be rationalized by simple strong-field considerations, as values of the one-electron d-orbital energies, for both idealized geometries of five-coordination, as well as for intermediate geometries, are such that one level lies at distinctly higher energy than the others. Transitions within the lower lying manifold in the d^7 low-spin case produce broad and generally unresolved absorption at frequencies below ca. 10 000–15 000 cm^{-1}. At higher frequencies in the spectrum appear the scarcely resolved bands due to transitions that involve the upper level and which generally overlap with charge-transfer bands.

The reflectance spectra of the two nickel complexes are similar to each other (Table II) and that of $Ni(p_3)SeO_4$ is reported in Figure 1. It shows features which are common to the spectra of both square-pyramidal and trigonal-bipyramidal high-spin d^8 complexes. This should be ascribed to the highly distorted coordination geometry of the present complexes. For the same reason, assignment of transitions in these spectra would be rather involved and is not attempted. From Table II and Figure 1 we can notice that there are d–d transitions at relatively high energy in these d^8 spectra, compared with those of corresponding five-coordinate high-spin complexes.[15,19b] In fact, the strength of the ligand field should be high, due to the nature of the donor set and to the compression of the M–P bonds which is revealed by the strains

Table VII. Anisotropic Thermal[a] Parameters ($\times 10^2$), with Esd's in Parentheses

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
			$Co(p_3)SO_4$			
Co	3.6 (1)	2.1 (1)	3.4 (1)	−0.1 (2)	−0.3 (1)	0.3 (1)
S	7.1 (4)	2.4 (2)	3.8 (2)	−1.2 (2)	0.1 (3)	−0.3 (2)
P(1)	3.4 (2)	2.7 (2)	3.5 (2)	0.2 (3)	−0.4 (2)	0.3 (3)
P(2)	3.2 (2)	2.6 (2)	3.3 (2)	0.2 (2)	−0.1 (2)	−0.1 (2)
P(3)	3.0 (2)	3.1 (2)	3.2 (2)	0.2 (2)	−0.3 (2)	−0.1 (2)
O(1)	9.0 (9)	3.0 (7)	7.2 (9)	−1.4 (7)	−3.0 (8)	1.5 (7)
O(2)	9.8 (1.2)	1.8 (6)	14.7 (1.4)	−0.9 (7)	−5.8 (1.0)	1.1 (7)
O(3)	8.6 (1.1)	7.8 (1.0)	10.0 (1.2)	−4.0 (9)	2.2 (9)	−0.7 (9)
O(4)	16.3 (1.6)	6.9 (9)	6.6 (1.0)	−4.9 (1.0)	1.7 (1.0)	−3.9 (8)
			$Ni(p_3)SeO_4$			
Ni	2.6 (1)	3.9 (2)	3.6 (1)	0.0 (1)	−0.2 (1)	−0.3 (2)
Se	5.0 (1)	3.5 (1)	4.7 (1)	−1.2 (1)	0.4 (2)	−0.6 (2)
P(1)	2.5 (3)	4.2 (4)	5.0 (3)	0.2 (4)	−0.4 (3)	−0.4 (4)
P(2)	2.6 (3)	3.6 (3)	4.8 (3)	0.1 (3)	0.1 (4)	−0.1 (4)
P(3)	2.3 (3)	5.0 (4)	3.2 (3)	0.0 (3)	−0.2 (3)	−0.4 (3)
O(1)	8.3 (1.2)	6.1 (1.2)	16.6 (1.8)	0.2 (1.1)	−5.4 (1.2)	0.0 (1.4)
O(2)	12.0 (1.6)	6.0 (1.2)	16.4 (2.0)	−1.1 (1.1)	−9.1 (1.5)	−3.2 (1.2)
O(3)	16.8 (2.0)	21.8 (2.7)	12.4 (1.7)	−17.5 (2.0)	3.5 (1.6)	−1.6 (1.7)
O(4)	21.9 (2.4)	20.5 (2.6)	11.5 (1.8)	−13.1 (2.0)	5.4 (1.7)	−11.6 (1.8)

[a] The form of the anisotropic thermal factor is $\exp[-2\pi^2(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* \cos\gamma^* + 2B_{13}hla^*c^* \cos\beta^* + 2B_{23}klb^*c^* \cos\alpha^*)]$.

Table VIII. Bond Lengths (Å) and Angles (deg) within the Coordination Polyhedra (Esd's in Parentheses)

	$Co(p_3)SO_4$	$Ni(p_3)SeO_4$
	Lengths	
M-P(1)[a]	2.212 (5)	2.356 (5)
M-P(2)	2.212 (6)	2.341 (5)
M-P(3)	2.291 (5)	2.299 (6)
M-O(1)	1.97 (1)	1.99 (2)
M-O(2)	1.94 (1)	2.01 (2)
	Angles	
P(1)-M-P(2)	88.7 (2)	88.5 (2)
P(1)-M-P(3)	90.6 (2)	90.8 (2)
P(2)-M-P(3)	92.5 (2)	92.1 (2)
P(1)-M-O(1)	96.9 (4)	93.4 (5)
P(1)-M-O(2)	157.0 (4)	153.3 (5)
P(2)-M-O(1)	161.2 (3)	161.0 (5)
P(2)-M-O(2)	98.3 (4)	99.2 (5)
P(3)-M-O(1)	105.3 (4)	106.8 (5)
P(3)-M-O(2)	110.8 (4)	114.2 (6)
O(1)-M-O(2)	70.1 (5)	71.3 (7)

[a] M = Co or Ni.

in the chains of the p3 ligand.

The absorption spectra of the nickel complexes in solution, which are quite different from the spectra of the solids, suggest that there is a predominant concentration of diamagnetic, probably four-coordinate species.[20] A possible explanation is that one of the phosphorus atoms in these species is not coordinated. Square-planar nickel(II) complexes in which p3 chelates with only two phosphorus atoms have been described previously,[21] and a similar mechanism implying the detachment of a phosphorus from the metal has been established by x-ray and NMR measurements for a five-coordinate nickel(II) complex formed with the tripod ligand bis(2-diethylaminoethyl)(2-diphenylphosphinoethyl)amine.[22]

NMR measurements have been performed on the CD_2Cl_2 solutions of the nickel complexes in an attempt to identify the species and possible equilibria existing in these solutions. The spectrum at 303 K (Figure 3) shows upfield and downfield isotropic shifts of the aromatic protons as well as their signal at 7.40 ppm (from TMS). Assignment of the peaks was made on the basis of their intensities and by reference to existing data on tertiary phosphine complexes.[23] In the temperature range 303–253 K the isotropic shifts increase linearly with $1/T$, whereas the position of the peak at 7.40 ppm does not change.

Table IX. Selected Bond Lengths (Å) and Angles (deg) in the Ligands (Esd's in Parentheses)

	$Co(p_3)SO_4$	$Ni(p_3)SeO_4$
	Lengths	
A-O(1)[a]	1.50 (1)	1.70 (2)
A-O(2)	1.48 (1)	1.54 (2)
A-O(3)	1.39 (1)	1.51 (2)
A-O(4)	1.37 (1)	1.48 (2)
	Angles	
O(1)-A-O(2)	97.9 (7)	92.0 (9)
O(1)-A-O(3)	107.9 (8)	108.1 (1.0)
O(1)-A-O(4)	111.9 (9)	112.4 (1.1)
O(2)-A-O(3)	111.9 (8)	117.8 (1.1)
O(2)-A-O(4)	113.2 (8)	114.9 (1.1)
O(3)-A-O(4)	113.0 (9)	110.1 (1.2)
M-O(1)-A	95.1 (6)	95.9 (8)
M-O(2)-A	96.9 (7)	100.7 (9)
M-P(1)-C(3)	112.7 (5)	110.2 (6)
M-P(2)-C(4)	109.8 (5)	107.6 (7)
M-P(3)-C(5)	108.2 (5)	107.7 (6)
P(1)-C(3)-C(2)	114.1 (9)	114.3 (1.2)
P(2)-C(4)-C(2)	115.0 (9)	118.2 (1.3)
P(3)-C(5)-C(2)	115.8 (1.0)	117.8 (1.3)
C(3)-C(2)-C(4)	111.4 (1.2)	109.2 (1.5)
C(3)-C(2)-C(5)	110.6 (1.1)	111.8 (1.5)
C(4)-C(2)-C(5)	112.3 (1.2)	114.0 (1.5)
C(3)-C(2)-C(1)	109.5 (1.2)	108.1 (1.6)
C(4)-C(2)-C(1)	106.0 (1.1)	107.5 (1.6)
C(5)-C(2)-C(1)	106.8 (1.2)	105.8 (1.6)

[a] M = Co or Ni; A = S or Se.

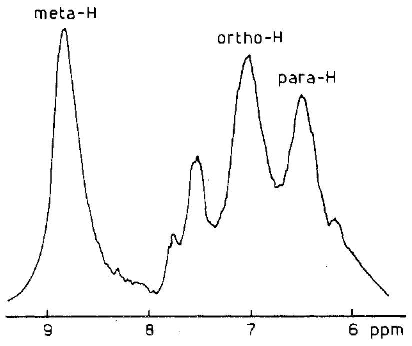

Figure 3. Proton NMR spectrum of aromatic protons of $Ni(p_3)SeO_4$ (ppm from TMS, in CD_2Cl_2 at 303 K).

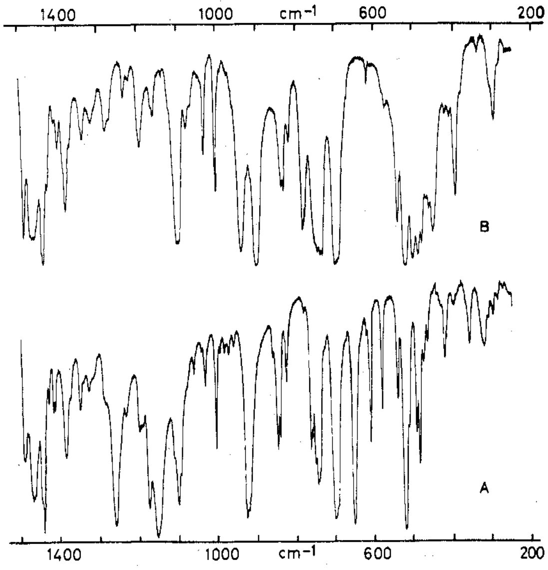

Figure 4. Infrared spectra of $Co(p_3)SO_4$ (A) and $Co(p_3)SeO_4$ (B) recorded as Nujol mulls.

On further lowering of the temperature, the first trend is reversed, and, at the lowest temperatures that may be reached in CD_2Cl_2 solution (ca. 183 K), only one broad signal centered at 7.40 ppm is detected. These results clearly indicate that both diamagnetic and paramagnetic species exist in solution and the concentration of the latter increases in the range 303–253 K, probably due to increase of the average time spent by the phosphorus atoms in the proximity of the metal. However, no simple explanation can be offered for the results at the lower temperatures, which are probably caused by competing processes in solution. The measurements were made difficult by the low solubility of the compounds (ca. 10^{-3} M in CD_2Cl_2, no other suitable solvent being found) and in particular by the low concentration of the paramagnetic form. For the same reason attempts to determine the thermodynamic constants of the equilibrium[22] by measuring the magnetic susceptibility, according to the method described by Evans,[24] were unsuccessful.

The frequencies of infrared bands mainly arising from the sulfate and selenate groups are listed in Table III. Included are the values for the free ions and a few values reported for bidentate sulfate by previous investigators. The IR spectra of the two cobalt derivatives are shown in Figure 4 and those of the corresponding nickel compounds are quite similar (Table III). The bands of the selenate group have been assigned through a comparison between the spectra of the SO_4 and SeO_4 derivatives, taking also into account the frequencies of the free ion modes.

The ν_1 frequency is safely identified for both groups. The three bands originating in C_{2v} symmetry from the ν_4 mode are also clearly identified in the spectra of the sulfates. In the case of the selenates, assignments of these three bands, differing slightly from that proposed in Table III, would also be possible, due to strong absorption in the 400–550-cm^{-1} region. The three ν_3 frequencies are assigned for the sulfates and only two for the selenates: as in the case of the free ions, frequencies of this asymmetric stretching mode are affected most by the change in reduced mass following substitution of S by Se. The IR-allowed ν_2 component, in C_{2v} local symmetry, cannot be safely identified. Actually, the low-energy symmetric bending mode of the free ion would be expected to be significantly perturbed upon coordination. As it appears from Table III, changing the metal atom does not produce significant changes in the spectrum.

Registry No. $Co(p_3)SO_4$, 60746-33-0; $Co(p_3)SeO_4$, 60746-34-1; $Ni(p_3)SO_4$, 60746-35-2; $Ni(p_3)SeO_4$, 60746-36-3.

Supplementary Material Available: Listings of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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