Co-ordination Properties of Methylenebis(diphenylphosphine chalcogenides) with Cobalt(II), Nickel(II), and Palladium(II) [1]

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Methylenebis(diphenylphosphine sulphide) (sps) and the analogous diselenide (sepse) form stable tetrahedral and pseudotetrahedral cobalt(II) and nickel(II) complexes, whereas, methylenebis(diphenylphosphine oxide) forms octahedral complexes. The ligand field strength of sps is comparable to that of the trimethylphosphine chalcogenides and greater than that of sepse. The β values of sps and sepse, as well as the corresponding trimethylphosphine chalcogenide ligands, are similar and significantly lower than those of the phosphine oxides. These results are interpreted in terms of the electronic properties of the P=S and P=Se linkages. Palladium(II) complexes of sps and sepse were isolated and confirm the ' Class b ' behaviour of these ligands.

ALTHOUGH numerous studies have been reported[2] on the co-ordination properties of phosphine oxides, little work had been done with phosphine sulphides and selenides[3] until the initial investigations in this laboratory.[4–6] Since 1966 a number of metal complexes of phosphine sulphides and selenides have been reported,[7–15] particularly with ' Class b ' metals.[16] Only recently have the first cobalt(II) and nickel(II) complexes of phosphine sulphides and selenides been reported.[17–19]

Bidentate phosphine oxides of the general formula $R_2P(O)CH_2P(O)R_2$ are superior to the corresponding monodentate phosphine oxides for extracting metal ions from solution.[20] We have investigated the similar bidentate ligands, methylenebis(diphenylphosphine sulphide) and the corresponding selenide, in order to utilize the chelate effect to form stable complexes of cobalt(II) and nickel(II). A comparison of the co-ordination properties of a complete series of phosphine chalcogenides with the same metal has been reported only once previously;[18] thus, we also investigated the metal complexes of the analogous phosphine oxide. Methylenebis(diphenylphosphine oxide) complexes of alkali[21] and alkaline earth metals[22] as well as copper(II)[23] and neodymium(III)[24] have been studied, however cobalt(II) and nickel(II) complexes, although mentioned,[25] have not been characterized.

This paper describes the cobalt(II) complexes of the complete series of methylenebis(diphenylphosphine-chalcogenides), the nickel(II) complexes of the oxide and sulphide ligands, and the palladium(II) complexes of the sulphide and selenide ligands.

EXPERIMENTAL

Syntheses of the Ligands.—Bis(diphenylphosphino)-methane (5·0 g, 0·013 mol) was added to an excess of hydrogen peroxide in benzene, an excess of sulphur in benzene, and an excess of KSeCN in acetonitrile[26] to give crystalline, white solids of methylenebis(diphenylphosphine oxide) (opo), the disulphide (sps), and the diselenide (sepse), respectively. Yields and m.p. were 82% and 177—179°,[27] 85% and 174—175°,[28] and 75% and 183—184°,[28] respectively (Found: C, 66·9; H, 5·1; S, 14·55. Calc. for $C_{25}H_{22}P_2S_2$: C, 66·95; H, 4·95; S, 14·3. Found: C, 55·55; H, 4·1; Se, 29·3. Calc. for $C_{25}H_{22}P_2Se_2$: C, 55·35; H, 4·1; Se, 29·1%).

Preparation of the Complexes.—All synthetic operations and handling of complexes were performed under a dry nitrogen atmosphere. Reagent grade solvents and anhydrous metal salts were used without further purification.

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Acetonitrile complexes of the metal perchlorates were synthesized and used as anhydrous metal reagents.[29]

$[Co(opo)_3](ClO_4)_2$.—The cobalt perchlorate complex was prepared by adding opo (0·42 g, 1·0 mmol) in dichloromethane (20 ml) to $[Co(CH_3CN)_6](ClO_4)_2$ (0·25 g, 0·5 mmol) in nitromethane (20 ml). The solution remained pink in colour; then anhydrous diethyl ether (*ca.* 10 ml) was added. Pink crystals formed over a period of 16 h; these were collected on a filter and dried (75%). The other metal perchlorate complexes were prepared in a similar manner.

$[Co(opo)_3][CoX_4]$ (X = Br or I).—The cobalt bromide and iodide complexes were prepared by adding opo (1·0 mmol) in dichloromethane (20 ml) to the appropriate cobalt halide (1·0 mmol) in tetrahydrofuran (THF) (50 ml). Fine crystals began to form after a few minutes; these were collected and dried (98 and 91%, respectively). A similar procedure was used to prepare the other metal halide complexes. In some cases, diethyl ether or hexane was added to initiate crystal formation. Some of the palladium complexes were recrystallized from dimethylformamide–ethanol.

Physical properties and elemental analyses for the complexes, all of which were satisfactory, are deposited with the N.L.L. as Supplementary Publication SUP 20670 (7 pp.).*

Characterization Measurements.—I.r. spectra, conductance measurements, and magnetic measurements were obtained as previously described.[19] The observed magnetic susceptibility values were corrected for diamagnetism using Pascal's constants [30] except for the diamagnetic contributions of opo, sps, and sepse which were determined experimentally as −247, −179, and -362×10^{-6} c.g.s.u., respectively. Details of the electronic absorption spectra and the magnetic susceptibility data are included in the Supplementary Publication.

Spectral parameters for tetrahedral and pseudotetrahedral cobalt(II) complexes

Compound	Δ/cm^{-1} [a]	ν_2/cm^{-1}	ν_3/cm^{-1}	$\beta = B'/B$ [b]	μ_{eff} [c]	$-\lambda$	Ref.
$Co[(Ph_2PSe)_2CH]_2$	3560	6195	14,205	0·67	4·68	186?	28
$[Co(Me_2N)_3PS)_4](ClO_4)_2$	3620	6208	14,270	0·66	4·59	162	19
$[Co(Ph_3PO)_4](ClO_4)_2$	3680	6240	16,300	0·82	4·53	147	36
$[Co(Me_3PO)_4](ClO_4)_2$	3800	6600	16,890	0·83	4·56	164	17
$[Co(Me_3PS)_4](ClO_4)_2$	3890	6690	14,400	0·65	4·31	105	17
$[Co(Me_3PSe)_4](ClO_4)_2$	3800	6500	13,810	0·61	4·40	130	18
$Co[(Ph_2PS)_2CH]_2$	3804	6539	14,974	0·70	4·56	169	28
$[Co(sps)_2](ClO_4)_2$	3900	6655	14,460	0·65	4·45	140	*e*
$Co(sepse)Cl_2$	3340	5810	15,170	0·75	4·60	155	*e*
$Co(sepse)Br_2,\frac{1}{2}(THF)$	3180	5560	14,040	0·69	4·52	131	*e*
$Co(sps)Br_2$	3270	5690	14,610	0·72	4·52	132	*e*
$Co(sepse)I_2,\frac{3}{4}(THF)$	3030	5220	13,470	0·66	4·53	127	*e*
$Co(sps)I_2,\frac{1}{2}(THF)$	3260	5650	13,710	0·66	4·54	138	*e*

[a] Values ±150 cm^{-1}. B (free ion) = 967 cm^{-1}. [c] In B.M. ±0·03 B.M. [d] In cm^{-1}, ±15 cm^{-1}, λ (free ion) = −172 cm^{-1}. [e] This work.

RESULTS

Even though the ligand opo and the various metal halides were mixed in a 1 : 1 mole ratio in attempts to obtain complexes with the same stoicheiometry and structure as the sps and sepse complexes, the elemental analyses and conductivity values indicate that opo displaces all the halide atoms from one metal ion to form an octahedral cation which was isolated as the complex $[M(opo)_3][MX_4]$. Analogous six-co-ordinate complexes are formed with the dioxide ligand $(C_4H_9)_2P(O)CH_2P(O)(C_4H_9)_2$; [31] however, in the latter case the ligand was present in excess. Interestingly, the ethane analogue of opo, $Ph_2P(O)CH_2CH_2P(O)Ph_2$, forms four-co-ordinate tetrahedral complexes of cobalt(II), *e.g.*, $CoLX_2$.[32]

The ligand field strength modulus, Δ, and the effective value of the Racah interelectronic repulsion term, B', for the sps and sepse cobalt complexes were determined according to published methods.[33,34]. The value for ν_3 was determined from the electronic spectrum of the solid complex suspended in a Nujol mull.[33,35] The position of the ν_2 transition was determined from solid state spectra either by averaging the two bands in the 5000—7000 cm^{-1} region or by using the maximum of the principal band observed in this region. The spectral parameters and magnetic moments for the sps and sepse cobalt(II) complexes are collected in the Table, along with data for other tetrahedral and pseudotetrahedral cobalt(II) complexes.

The magnetic moments of the octahedral $[M(opo)_3]^{2+}$ cations in the $[M(opo)_3][MX_4]$ complexes (M = Co or Ni) were determined by subtracting the molar susceptibility of $(Bu^n{}_4N)_2CoBr_4$,[36] $(Bu^n{}_4N)_2CoI_4$,[36] and $(Et_4N)_2NiBr_4$ [37] (which had been corrected for diamagnetism and for t.i.p. of the cobalt anions) from the total molar susceptibility of the complexes corrected only for the diamagnetism of $[M(opo)_3]^{2+}$.

DISCUSSION

Infrared Spectra.—The i.r. spectrum of methylenebis(diphenylphosphine oxide) contains two strong peaks at 1192 and 1205 cm^{-1} which are assigned to the P–O stretching frequency (literature [21a,27] 1190 and 1204 cm^{-1}).

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20, items less than 10 pp. supplied as full-size copies.

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The P–O absorption in the nickel and cobalt complexes is shifted to lower energy by *ca.* 40 cm^{-1} and appears as a semi-broad band centred at 1160 cm^{-1}. This is good evidence that the ligand is bonded to the metal through the oxygen atoms.[38]

The P–S stretching frequency in methylenebis(diphenylphosphine sulphide) is assigned to the band at 628 cm^{-1}, based on P–S assignments for triphenyl- and diphenylmethyl-phosphine sulphides. The i.r. spectra of the sps–metal complexes are all very similar with the peak at 628 being shifted *ca.* 50 cm^{-1} to lower energy. The shift of the P–S stretching frequency to lower energy on co-ordination, as in the case of the opo complexes, indicate that the ligand sps is bonding to the metal through the sulphur atoms.

Unambiguous assignment of the P–Se stretching frequency in methylenebis(diphenylphosphine selenide) is impossible owing to the presence of a number of medium to strong absorptions in both the parent phosphine and the other two dichalcogenides between 450 and 550 cm^{-1}, where the P–Se stretching frequency is expected.[5,26] The i.r. spectra of the sepse metal complexes are essentially the same as that of the free ligand and indicate that the ligand remains intact upon co-ordination. Even though direct evidence for bonding *via* the selenium atoms is lacking, there are no other sites for co-ordination without altering the structure of the free ligand. The i.r. spectra seems to preclude the latter possibility. Moreover, the elemental analysis of the palladium bromide complex contained the theoretical amount of selenium.

The i.r. spectra of the metal perchlorate complexes also display bands characteristic of the T_d anion, indicating that the perchlorate ions are not co-ordinated.[39]

Six-co-ordinate opo Complexes.—The electronic spectrum of $[Co(opo)_3](ClO_4)_2$ is typical of weak field octahedral cobalt(II) complexes. The band at 18 380 and the shoulder at 20 510 cm^{-1} are assigned to the $^4T_{1g} \longrightarrow {}^4T_{1g}(P)$ and $^4T_{1g} \longrightarrow {}^4A_{2g}$ transitions, respectively in agreement with $[CoL_3](ClO_4)_2$ complexes of the similar chelating ligands $(C_3H_7O)_2P(O)CH_2P(O)(OC_3H_7)_2$ [32] and $(Me_2N)_2P(O)N(CH_3)P(O)(NMe_2)_2$.[40] The electronic spectra of the $[Co(opo)_3][CoX_4]$ complexes show characteristic absorption bands for both the tetrahedral and octahedral cobalt(II) ions. Both the cobalt bromide and iodide complexes contain a lower intensity band at 18 200 and 18 300 cm^{-1} which corresponds to the $^4T_{1g} \longrightarrow {}^4T_{1g}(P)$ transition in the $[Co(opo)_3](ClO_4)_2$ complex. The magnetic data for the $[Co(opo)_3][CoX_4]$ complexes also provide support for the presence of an octahedral $[Co(opo)_3]^{2+}$ cation. The magnetic moments of these complexes, after subtracting the contribution of the $[CoX_4]^{2-}$ anions, were found to be 4·94 and 4·97 B.M., in good agreement with the experimental magnetic moment of 5·00 B.M. for the $[Co(opo)_3]^{2+}$ ion in the perchlorate complex.

As with the cobalt halides, opo forms the mixed octahedral–tetrahedral nickel(II) complex $[Ni(opo)_3][NiBr_4]$. The high intensity and complexity of the $NiBr_4^{2-}$ spectrum obscurs the low intensity bands of the octahedral nickel(II) cation, but the magnetic moment of the complex, after subtracting the contribution due to the tetrahedral $NiBr_4^{2-}$ anion, is 3·22 B.M., which agrees with other octahedral nickel(II) complexes.

Four-co-ordinate sps and sepse Complexes.—The sps and sepse cobalt halide complexes are non-electrolytes in nitromethane and are formulated as the monomeric moieties $Co(sps)X_2$ and $Co(sepse)X_2$ whose electronic spectra and magnetic moments support a pseudo-tetrahedral structure about the cobalt(II) ion. The i.r. spectra and analytical data for $Co(sps)I_2$, $Co(sepse)Br_2$, and $Co(sepse)I_2$ indicate that THF is apparently trapped in the crystal lattice of these complexes. The $Co(sepse)Cl_2$ complex also analysed for $Co(sepse)Cl_2,\frac{1}{2}(THF)$ and showed bands in the i.r. due to THF. However, after the complex was heated overnight at 56° *in vacuo*, these extra bands disappeared and the complex analysed for $Co(sepse)Cl_2$. The same procedure was performed on the above three THF-containing complexes, but little or no THF was removed.

The cobalt perchlorate complex of sps is a bi-univalent electrolyte and its electronic spectrum, as well as magnetic moment, suggests a tetrahedral cobalt(II) complex. The Δ value from the spectra of $[Co(sps)_2]^{2+}$ is 3900 cm^{-1}. The spectrochemical effect of sps is remarkably high when one considers that the similar monodentate, triphenylphosphine sulphide, shows no interaction with cobalt(II) in similar solvents. Likewise, the ligand field strength of sepse is also high and is comparable to $(Me_2N)_3PS$ or triphenylphosphine oxide.

The 'rule of average environment' [41] may be applied satisfactorily to these Co(bidentate)X_2 complexes, as the calculated and experimental values generally agree within 200 cm^{-1}. Utilizing 3130, 2850, and 2645 cm^{-1} for the Δ values of $CoCl_4^{2-}$, $CoBr_4^{2-}$, and CoI_4^{2-} anions,[36] respectively, the Δ value of sepse in the tetrahedral $Co(sepse)_2^{2+}$ complex is 3490 cm^{-1}. The β values for phosphine sulphide and selenide complexes of cobalt(II) are all low and approximately the same (Table), suggesting that the polarisability of the P=X groups and the covalency of the cobalt–sulphur and cobalt–selenium bonds are very similar in all the complexes. The β values are much lower than for the analogous phosphine oxide complexes, which reflect the much higher polarisability of the P=S and P=Se groups.

Although the Δ values for various ligands in tetrahedral cobalt(II) complexes are not sufficiently accurate to permit placing these ligands in an exact spectro-

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chemical series, the relative position of the ligands to each other can be seen. The position of sps and sepse in such a spectrochemical series is: $I^- < Br^- < Cl^- <$ sepse $\sim (Me_2N)_3PS \sim Ph_3PO < Me_3PO \sim Me_3PSe \sim$ sps. Likewise, the order of β values gives a nephelauxetic series: sepse $\sim (Me_2N)_3PS \sim Me_3PS \sim Me_3PSe \sim$ sps $\sim$ $I^- < Br^- \sim Cl^- < Ph_3PO \sim Me_3PO$.

Palladium(II) *Complexes*.—The palladium complexes of sps and sepse are non-electrolytes in DMF and exhibit electronic spectra typical of square planar palladium(II) complexes. The position of the lowest energy electronic transition has been suggested[6] as a means of comparing the spectrochemical effect of various ligands toward palladium(II). Thus, the relative order observed in palladium chloride complexes is: $(Me_2N)_3PS < Ph_3PSe \sim Ph_3PS <$ sepse $\sim$ sps. For comparison, the order of ligand–palladium interaction developed by displacement reactions is $Cl^- < Br^- <$ Ph_3PS, $Ph_3PSe < I^- <$ sps $< SCN^-$. As can be seen, the ordering of the two series is quite comparable.

Nickel(II) *Complexes*.—The nickel halide complexes of sps are monomeric, non-electrolyte $Ni(sps)X_2$ complexes. As with some of the cobalt halides, the nickel bromide complex is formulated as $Ni(sps)Br_2,\frac{1}{2}(THF)$. The nickel iodide complex crystallizes with 0·5 mole of dichloromethane trapped in the crystal lattice. The electronic spectra of the sps–nickel halide complexes are similar to those of known pseudotetrahedral nickel(II) complexes. The magnetic moments for $Ni(sps)Br_2,\frac{1}{2}(THF)$ and $Ni(sps)I_2,\frac{1}{2}(CH_2Cl_2)$ are somewhat lower than those reported for most pseudotetrahedral nickel(II) complexes, but they are comparable to other phosphine chalcogenide nickel(II) complexes.[18,42]

The $[Ni(sps)_2]ClO_4)_2$ complex does not appear to fit a tetrahedral nickel(II) complex. Although conductivity and analytical data indicate that the complex contains the $[Ni(sps)_2]^{2+}$ cation, the electronic spectra and extinction coefficients, as well as magnetic moment, seem to preclude a tetrahedral structure. The electronic spectral data are more compatible for square-planar nickel(II). However, the magnetic moment of 2·82 B.M. would suggest a structure intermediate between a square plane and tetrahedron. Similar reasoning has been used for the $[Ni(Ph_3PO)_4](ClO_4)_2$ complex.[43]

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