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Ambident Nucleophiles
VI[a]. Solution Metal–Ligand Binding Modes in Phosphorodithioate Complexes. A Phosphorus-31 N.M.R. Study

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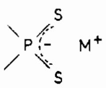
Examination of model compounds enables ionic, unidentate-covalent, and bidentate-covalent metal–ligand binding modes to be distinguished in solution by ^{31}P n.m.r. Solution constitutions are deduced for complexes of the following central ions: Li(I), Na(I), Mg(II), Ca(II), Ba(II), Hg(II), Tl(I), Si(IV), Ge(IV), Sn(IV), Pb(II), P(III), P(V), As(III), Sb(III), Bi(III), S(II), S(I), Se(II), Ag(I), and Th(IV). Solvent effects are described for selected complexes.

Introduction

In previous papers [1, 2] it was demonstrated that ^{31}P chemicals shifts can be used to distinguish between the several possible binding modes of the (1,3)-ambident ligands di-isopropylphosphorothioate, $(RO)_2POS^-$ ($R{=}Me_2CH$ throughout this paper) and di-isopropylphosphoroselenoate, $(RO)_2POSe^-$, to metal ions in solution. The present paper reports an investigation of the metal–ligand binding modes, in solution, of complexes of the ligand di-isopropylphosphorodithioate, $(RO)_2PS_2^-$, hereafter denoted L^-.

Results and Discussion

Four extreme modes of metal–ligand interaction are possible: an essentially ionic interaction in which the two sulphur atoms of the ligand are equivalent, (I); an asymmetrical covalent interaction, (II); a symmetrical covalent interaction, (IIIa); and a bridging form (IIIb) in which the two sulphur atoms are equivalent. The ^{31}P data cannot distinguish between types IIIa and IIIb, but types I, II, and III can be distinguished without ambiguity in the majority of cases.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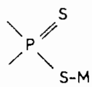
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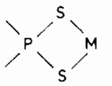
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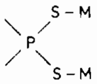
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TABLE I. Chemical Shifts of Model Compounds.

	Compound	$\delta(P)^a$
Type I	L^-K^+	107.49
	$L^-NH_4^+$	107.34
	$L^-NMe_4^+$	109.55
Type II	LH	81.65
	L_2	81.84
	L_3P	81.76[b]
	L_3PO	73.89[c]
	L_3PS	81.50[d]
Type III	L_2Zn	94.30
	L_2Cd	100.78
	L_3In	87.91
	L_2Ni	89.04
	L_2Pd	100.27

[a]Type I in solution in H_2O, remainder in $CDCl_3$ [b]$\delta(P^{III})$ 149.58. [c]$\delta(PO)$ 73.83. [d]$\delta(PS)$ 82.15.

Model Compounds

In order to set up reference points on the scale of ^{31}P chemical shifts for species L_nM, model compounds of unambiguous constitutions are required (Table I). The salts L^-K^+, $L^-NH_4^+$, and $L^-NMe_4^+$ in dilute (0.2 *M*) aqueous solution are taken as representative of type I.

The constitution of L_2 is of type II: a structure determination in the solid state has revealed a zigzag $S_1{=}P{-}S_2{-}S_3{-}P{=}S_4$ chain in which S_1 and S_3 (and S_2 and S_4) are *trans* to one another, and in which the two directly-bonded P–S distances are markedly different in length, $P{-}S_1$ = 1.908 Å and $P{-}S_2$ = 2.072 Å, corresponding to double and single bonds respectively. The compounds L_3P, L_3PO, and L_3PS are assigned constitutions of type II, containing unidentate L, on the basis of their solution

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[a]Part V: C. Glidewell, *J. Organometal. Chem.*, in press.

TABLE II. Diagnostic Chemical Shifts.

Compound	$\delta(P)^a$	Binding Mode
LLi	95.18	III
LNa	111.00	I
L_2Mg	109.23^b	I
	80.54	II
L_2Ca	105.35^c	I
	80.48	II
L_2Ba	106.94^d	I
	80.50	II
L_2Hg	96.24	III
LTl	93.79	III
L_4Si	75.63	II
L_4Ge	74.26	II
L_4Sn	74.00	II
L_2Pb	92.00	III
L_3As	86.10	III
L_3Sb	87.30	III
L_3Bi	92.95	III
L_2S	75.29	II
L_2S_2	74.37	II
L_2Se	80.84	II
LAg	102.84	III
L_4Th	96.62^e	III
	77.09	II

[a] In $CDCl_3$ solution, except LLi, LNa, L_2Mg, L_2Ca, L_2Ba and L_4Th, which were in Me_2CO. [b] Relative intensity 13.3:1.00. [c] Relative intensity 15.6:1.00. [d] Relative intensity 7.60:1.00. [e] Relative intensity 1.00:2.79.

n.m.r. spectra. In L_3P, the unique phosphorus has $\delta(P)$ = 149.58 p.p.m., typical of three-connected phosphorus bound to three sulphur atoms: no high-field resonance typical of a phosphorus atom having a high coordination number was found, so that L must be unidentate. Similarly in both L_3PO and L_3PS, the chemical shift of the unique phosphorus (73.83 and 82.15 p.p.m. respectively) demonstrates the absence of any species in which the coordination number of the unique phosphorus exceeds four. The parent acid LH is also assigned a constitution of type II, since it is scarcely conceivable either that LH is ionised in chloroform solution, or that the proton is two-connected.

The complex L_2Ni is assigned a constitution of type IIIa: the diethyl analogue $[(EtO)_2PS_2]_2Ni$ contains strictly square planar NiS_4 chromophores both in the native complex [4], and in the bis-pyridine adduct $[(EtO)_2PS_2]_2Ni(NC_5H_5)_2$ [5]: its optical spectrum is unchanged on dissolution in a non-complexing solvent, as is that of L_2Pd which is also assigned a type IIIa constitution; in non-complexing solvents, both L_2Ni and L_2Pd are diamagnetic. L_2Zn and L_2Cd are [6] both dimeric in the solid state; in the dimeric L_4M_2 unit (M = Zn, Cd) two of the ligands are of type IIIa and two of type IIIb, but within each ligand the two P–S distances are equal. Molecular weight measurements indicate [7] that these dimeric units persist in solution. Finally, the octahedral [8] L_3In is assigned to this group also.

On the basis of these model compounds, any species having $\delta(P) > 107$ p.p.m. is assigned a constitution of type I, and any species having $\delta(P) < 82$ p.p.m., is assigned a constitution of type II. The limits found for model compounds of type III are (p.p.m.) $87 < \delta(P) < 101$.

Assignments of Constitution

The chemical shifts of a number of complexes are set out in Table II: the spectra of most derivatives were recorded in $CDCl_3$ solution, but complexes of Li^+, Na^+, Mg^{+2}, Ca^{+2}, Ba^{+2}, and Th(IV) were insoluble in $CDCl_3$, and consequently their spectra were recorded in acetone solution.

LLi and LNa each exhibit a single chemical shift, and are assigned constitutions of types III and I respectively: LLi is probably oligomeric, even in acetone solution. L_2Mg, L_2Ca and L_2Ba each exhibit two shifts, the more intense at *ca.* 107 p.p.m. corresponding to a constitution of type I, *i.e.*, an ion pair, and the less intense, at *ca.* 80 p.p.m., corresponding to a type II constitution: unfortunately, these species were insoluble in other organic solvents, while in water only spectra due to aqueous L^- were observed having $\delta(P)$ of *ca.* 107 p.p.m. The type II complex is presumably solvated $L_2M(OCMe_2)_n$ (M = Mg, Ca, Ba), containing (n + 2)-coordinate *M*, where n is probably [9] four for M = Mg, six for M = Ca, and greater than six for M = Ba. The chemical shift of L_2Hg indicates a type III constitution in chloroform solution: in the solid state, this compound forms [10] chains in which the ligands are bidentate but unsymmetrical, having P–S distances of 1.941 Å and 2.015 Å, which may be compared with values of 1.908 Å and 2.072 Å in L_2 [3], and 1.965 Å in $[(EtO)_2PS_2]_2Ni$ [4]. LTl has a type II constitution in chloroform solution: the analogous complex $[(Et_2PS_2)Tl]_2$ is dimeric [11] with symmetrical ligands each coordinated to both thallium atoms. Similarly $[(RO)_2POS]Tl$, for which $\delta(P)$ = 46.76 p.p.m., contains a bidentate ligand [2].

The complexes of Si(IV), Ge(IV) and Sn(IV) each exhibit a single phosphorus chemical shift, in the range characteristic of type II constitutions. By contrast in $[(RO)_2POS]_4Sn$, for which $\delta(P)$ = 36.91 p.p.m., $^2J(PSn)$ = 65.8 and 86.7 Hz, the ligand is bidentate [2]: bidentate ligands are found [2] also in $[(RO)_2POS]_2Sn$ and $[(RO)_2POS]_nSnPh_{4-n}$ (n = 1, 2, 3). In L_2Pb, the chemical shift indicates a type III constitution in chloroform solution: in the solid state this compound forms [12] polymeric chains in which two types of ligand can be discerned, in each of which the two P–S distances are very

TABLE III. Solvent Effects on Chemical Shifts in Some *p*-Metal Complexes.

Solvent	DN[a]		L_2Zn	L_2Hg	L_2Pb	L_3As	L_3Sb	L_3Bi
$CDCl_3$	ca. zero		94.30	96.24	92.00	86.10	87.30	92.95
PhCN	11.9		94.07	b	93.05	84.96	86.59	92.27
Me_2CO	17.0		86.36	b	93.55	84.88	86.25	84.36
DMF	26.6		91.07	95.18	96.58	85.03	87.23	86.79
C_5H_5N	33.1		99.67	97.91	83.99	86.29	87.92	94.87
		Range	13.33	2.73	12.59	1.41	1.67	10.51

[a] Donor numbers, DN, from reference 16. [b] Insoluble.

similar, being 1.982 Å and 2.000 Å in one type of ligand and 1.944 Å and 1.958 Å in the other (*cf.* L_2-Hg [10]).

The bismuth complex L_3Bi exhibits $\delta(P)$ = 92.95 p.p.m. in chloroform solution, and so has a type III constitution in this solvent: this is consistent with its solid-state structure [13] in which the bismuth is six-coordinate, having three Bi–S distances of 2.70 Å and three of 2.87 Å. The arsenic and antimony analogues are probably similar: the closely related ethylxanthates $(EtOCS_2)_3M$ (M = As, Sb) adopt structures of this type in the solid state [14, 15]. The chalcogen species L_2S, L_2S_2, and L_2Se are all assigned type II structures: although it might have been expected that L_2Se contained a square planar SeS_4 fragment, the analogous species $[(RO)_2POX]_2Se$ (X = S, Se) both contain unidentate ligands in solution [2], as does $(Et_2PS_2)_2Se$ in the solid state [16].

Although the chemical schift of LAg, $\delta(P)$ = 102.84 p.p.m., falls outside the established range of type III complexes (although not in the range established for type I species), it is probable that, like $[(RO)_2POX]Ag$ (X = S, Se), this complex is oligomeric and contains bidentate, bridging ligands. The complex L_4Th is insoluble in chloroform: in acetone solution, two chemical shifts are observed. The more intense, having $\delta(P)$ = 77.09 p.p.m., corresponds to a type II constitution in which the ligand is unidentate, while the less intense, with $\delta(P)$ = 96.62 p.p.m. corresponds to a type III constitution in which the ligand is bidentate. Although it is possible that two distinct types of complex exist, having metal coordination numbers of eight and four respectively (apart from coordinated solvent), and whose rate of ligand exchange is slow on the n.m.r. time scale, it seems more likely, in view of the intensity ratio observed, 1:2.79 (≅1:3), of bidentate to unidentate ligands, that each molecular complex contains three unidentate ligands and one bidentate ligand, although, if this is so, the slowness of the unidentate $\rightleftharpoons$ bidentate equilibrium is surprising.

For most metals, the binding mode in chloroform solution of the ligand $(RO)_2PS_2^-$ corresponds with those found [2] for the analogous ligands $(RO)_2POS^-$ and $(RO)_2POSe^-$. The exceptions are: (i) Sn(IV), where $(RO)_2PS_2^-$ is unidentate, but both $(RO)_2POS^-$ and $(RO)_2POSe^-$ are bidentate; (ii) As(III), Sb(III), and Bi(III), where both $(RO)_2PS_2^-$ and $(RO)_2POS^-$ are bidentate, but $(RO)_2POSe^-$ is unidentate; and (iii) Th(IV), where $(RO)_2PS_2^-$ is both unidentate and bidentate, but both $(RO)_2POS^-$ and $(RO)_2POSe^-$ are bidentate only.

In a number of complexes of $(RO)_2POX^-$ (X = S, Se), the coupling $^2J(PM)$ was observed [2], specifically when M = Cd(II), Sn(II), Sn(IV), Se(II), and Te(II). By contrast, in none of the $(RO)_2PS_2^-$ complexes is $^2J(PM)$ observed even when M represents an element in which isotopes of nuclear spin I = ½ are 100% abundant, such as ^1H, ^{31}P, (^{107}Ag + ^{109}Ag), and (^{203}Tl + ^{205}Tl).

Solvent Effects

In Table III are recorded the ^{31}P chemical shifts of selected complexes in a number of solvents which span a wide range of donor number, DN [17]. In the absence of acid–base interactions between solvent and solute which cause a change in the connectivity at phosphorus, solvent effects on phosphorus chemical shifts are very small; typical are the ranges of 1.0 p.p.m. observed [18] for $(MeO)_3PO$, and 2.2 p.p.m. found [19] for Ph_3PMe^+. However when the solvent–solute interactions are such that the connectivity at phosphorus is affected, the chemical shift changes are large; thus for Ph_3PO, $\delta(P)$ ranges [20] from 24.8 p.p.m. in dioxan where it exists at $Ph_3P{=}O$, to 59.8 p.p.m. in 98% sulphuric acid, where it exists as a phosphonium cation $(Ph_3P–OH)^+$. From the data of Table III, it is concluded that no change in the connectivity of the phosphorus occurs between different solvents for L_2Hg, L_3As, or L_3Sb, although it is possible that in L_2Hg, the mercury atom may be complexed in the more strongly donor solvents.

The chemical shifts of both L_2Zn and L_3Bi do not vary smoothly with the DN value of the solvent, but pass through a minimum in a solvent of medium DN, acetone. By contrast, the shift in L_2Pb increases slowly from $CDCl_3$ (Dn *ca.* zero) to DMF (DN = 26.6), in all of which solvents it has a type III consti-

TABLE IV. Solvent Effects on Chemical Shift in LK.

Solvent	$MeNO_2$	MeCN	Me_2CO	H_2O	DMF	DMSO	C_5H_5N
Dielectric constant	35.9	38.0	20.7	81.0	36.1	45.0	12.3
DN	2.7	14.1	17.0	18.0	26.6	29.8	33.1
$\delta(P)$	102.37	111.02	111.57	107.49	104.26	103.18	70.63

TABLE V. Microanalytical Data for New Compounds.

Compound	Found (/%)		Required (/%)	
	C	H	C	H
$LNMe_4$[a]	41.39	9.38	41.79	9.12
LTl	17.24	3.53	17.25	3.38
L_3P	31.47	6.66	32.23	6.31
L_3PO	31.76	5.97	31.48	6.17
L_3PS	32.47	7.10	30.76	6.02
L_3As	30.28	6.17	30.25	5.92
L_3Sb	27.88	5.67	28.39	5.56
L_2Pd	27.18	5.61	27.04	5.30

[a] Nitrogen: found 4.70%; required, 4.87%.

tution: in pyridine (DN = 33.1) the shift decreases markedly and is indicative of a structure close to type II in this strongly donating solvent; only pyridine is able to compete effectively as a donor to Pb(II) with the second sulphur atom of the $(RO)_2PS_2^-$ ligand.

The least intelligible series of solvent shifts is that exhibited by LK (Table IV): there is no obvious correlation either with the DN or with the dielectric constant of the solvent. The shifts exhibit a maximum when the solvent is acetone (*cf.* L_2Zn and L_3Bi), and there is a massive shift in pyridine, some 30 p.p.m. to higher field than in any other solvent. This shift in pyridine is indicative of a type II constitution in this solvent, while those in $MeNO_2$, DMF and DMSO suggest ion pairs, in which the constitution is intermediate between types I and III.

It is possible that further detailed information on the variation with solvent S of the metal–ligand and metal–solvent binding in a complex L_nMS_p could be obtained by using the magnetic resonance of a suitable isotope of M, such as ^{39}K (I = 3/2, 93.1% abundant), ^{199}Hg (I = ½, 16.8%), or ^{207}Pb (I = ½, 22.6%).

A study of the solution constitutions of complexes of the related ligand diethyl dithiocarbamate, $Et_2NCS_2^-$, using ^{13}C n.m.r. is in progress, and will be reported in due course.

Experimental

Proton-decoupled ^{31}P n.m.r. spectra were recorded for 0.2 *M* solutions at 32.19 MHz using a Varian CFT-20 spectrometer, with Fourier transform. The internal reference was D_3PO_4 which also activated the frequency-lock: the isotopic chemical shift $\delta(D_3PO_4) - \delta(H_3PO_4)$ was +0.29 p.p.m. All chemical shifts are reported relative to 85% H_3PO_4: downfield shifts are positive.

$(RO)_2PS_2K$ was prepared from P_4S_{10} [21]: oxidation with bromine in carbon tetrachloride yielded $[(RO)_2PS_2]_2$, and acidification with hydrochloric acid yielded $(RO)_2PS_2H$. Salts of Li^+, Na^+, Mg^{+2}, Ca^{+2}, Ba^{+2}, and NH_4^+ were prepared by neutralisation of $(RO)_2PS_2H$ with the appropriate carbonate, in aqueous solution, followed by evaporation to dryness and extraction with dry acetone: the NMe_4^+ salt was similarly prepared using NMe_4OH. $[(RO)_2PS_2]_2Se$ was prepared by reaction of $(RO)_2PS_2K$ with SeO_2 in aqueous hydrochloric acid [22]: the corresponding Te(II) compound decomposed too rapidly for the determination of its chemical shift, as did the Se(I) species prepared from $(RO)_2PS_2K$ and Se_2Cl_2. Treatment of $(RO)_2PS_2K$ with mercury(I) nitrate in aqueous solution caused the immediate precipitation of metallic mercury. Other complexes were prepared by the methods described previously as A and B, thus:

by method A: Si(IV), Ge(IV), Sn(IV), P(III), P(V), As(III), S(II), S(I);

by method B: Zn(II), Cd(II), Hg(II), In(III), Tl(I), Pb(II), Sb(III), Bi(III), Ni(II), Pd(II), Ag(I), Th(IV).

Microanalytical data for new compounds are recorded in Table V.

References

1 C. Glidewell and E. J. Leslie, *J. Chem. Soc. Dalton,* 527 (1977).
2 C. Glidewell, *Inorg. Chim. Acta, 24,* 255 (1977).
3 S. L. Lawton, *Inorg. Chem., 9,* 2269 (1970).
4 Q. Fernando and C. D. Green, *J. Inorg. Nuclear Chem., 29,* 647 (1967).
5 S. Ooi and Q. Fernando, *Inorg. Chem., 6,* 1558 (1967).
6 S. L. Lawton and G. T. Kokotailo, *Inorg. Chem., 8,* 2410 (1969).
7 I. J. Heilweil, *Am. Chem. Soc., Div. Petroleum Chem., Preprints, 10,* 19 (1965).
8 C. K. Jørgensen, *Acta Chem. Scand., 16,* 1048 (1962).
9 C. Glidewell, *Inorg. Chim. Acta, 15,* 85 (1975).
10 S. L. Lawton, *Inorg. Chem., 10,* 329 (1971).
11 S. Esperas and S. Husebye, *Acta Chem. Scand., 27,* 1827 (1973).
12 S. L. Lawton and G. T. Kokotailo, *Inorg. Chem., 11,* 363 (1972).

13 S. L. Lawton, C. J. Fuhrmeister, R. G. Haas, C. S. Jarman, Jr., and F. G. Lohmeyer, *Inorg. Chem.*, *13*, 135 (1974).

14 G. Carrai and G. Gottardi, *Z. Krist.*, *113*, 373 (1960).

15 G. Gottardi, *Z. Krist.*, *115*, 451 (1961).

16 S. Husebye and G. Helland-Madsen, *Acta Chem. Scand.*, *23*, 1398 (1969).

17 V. Gutmann, "Coordination Chemistry in Non-Aqueous Solutions", Springer-Verlag, Vienna (1968).

18 R. A. Y. Jones and A. R. Katritzky, *Angew. Chem.*, *74*, 60 (1962).

19 S. O. Grim, W. McFarlane, E. F. Davidoff, and T. J. Marks, *J. Phys. Chem.*, *70*, 581 (1966).

20 G. E. Maciel and R. V. James, *Inorg. Chem.*, *3*, 1650 (1964).

21 N. I. Zenlyanskii, O. A. Prib and B. S. Drach, *Zh. Obshch. Khim.*, *31*, 880 (1961).

22 S. Husebye, *Acta Chem. Scand.*, *19*, 1045 (1965).