# Preparation and Characterisation of Dithiophosphinato-complexes of Yttrium and the Lanthanoids

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Hydrated lanthanoid(III) chlorides react with salts of dithiophosphinic acids in hot ethanolic solution to form the corresponding neutral tris or anionic tetrakis complexes, $[Ln(S_2PR_2)_3]$ ($R = C_6H_{11}$) and $[Ln(S_2PR_2)_4]^-$ (R = Me, OEt, or $C_6H_{11}$) respectively. The product of the reaction is sterically controlled. Displacement reactions with $PPh_3O$ to give mixed complexes are described. The characterisation, structures, and spectral properties of all the isolated complexes are discussed. The lanthanoid–sulphur bond is compared with transition-metal–sulphur bonds

THE existence of dithiocarbamato-complexes of the lanthanoids had been postulated for many years,[1,2] but the first well characterised examples of this class were not reported until 1968,[3-5] further characterisation being reported in 1977.[6] The isolation of this type of complex demonstrated that the co-ordination of sulphur-donor ligands to lanthanoid ions was stronger than had previously been expected; however, the present knowledge of this type of co-ordination remains limited. In order to explore the field more fully we have extended this work to another class of sulphur donors, the dithiophosphinates, $[R_2PS_2]^-$, and report our results herein. Preliminary details of this work have been published,[7] as have the results of some related structural investigations.[8-10]

## EXPERIMENTAL †

Hydrated lanthanoid(III) chlorides were prepared from the commercial oxides (Fluka) and aqueous hydrochloric acid followed by repeated evaporation *in vacuo* to remove excess of acid and drying over $CaCl_2$. The free dithiophosphinate ligands were prepared by the indicated literature methods.[11] The compounds $PPh_3O$, $[PPh_4]Br$, and $[AsPh_4]Cl$ (Fluka) were used without further purification. Solvents were purified by standard literature methods.[12]

Electronic spectra were recorded in $C_2H_4Cl_2$ solution with a Beckmann Acta V spectrometer. Solid-state reflectance spectra were obtained with a Perkin-Elmer MPF-4 spectrometer. Infrared spectra (200—4 000 $cm^{-1}$) were recorded as Nujol mulls with a Perkin-Elmer PE-577 instrument. Hydrogen-1 n.m.r. spectra were obtained from $CDCl_3$ solutions (where not indicated to the contrary) using a Bruker WP-60 spectrometer. Mass spectra were recorded with an A.E.I. MS 30 instrument operating at 70 eV.‡ Molecular weights were determined in acetone solution by use of a Knauer osmometer. Elemental analyses (C, H, and S) were by Herr W. Manzer, ETH Zurich. The metal content was determined in aqueous alcohol or aqueous acetone solution by titration with ethylenediaminetetra-acetate (edta) to a Xylenol Orange end-point in the presence of urotropine.

In the following procedures, Ln = La—Lu (excluding Pm) and Y and *n* = 6 or 7.

*Preparations*.—$[AsPh_4][Ln\{S_2P(OEt)_2\}_4]$. The compounds $LnCl_3{\cdot}nH_2O$ (1 mol) and $Na[S_2P(OEt)_2]$ (4 mol) were stirred in boiling ethanol for 10 min. Tetraphenylarsonium chloride (1 mol) was added and the heating continued for another 10 min. The hot solution was filtered and the filtrate evaporated to dryness on a rotary evaporator. The solid residue was extracted with several portions of hot benzene or cold chloroform, and the solution again evaporated to dryness. The crude product was recrystallised from ethanol–isopropyl alcohol mixtures (the proportion of isopropyl alcohol increasing with atomic number). The crystalline product was filtered off, washed with ethanol–isopropyl alcohol followed by diethyl ether, and dried *in vacuo*. The final recrystallisation and filtration for the complexes of Er—Lu and Y were carried out under nitrogen. Yields were 60—90%.

$Na[Ln\{S_2P(OEt)_2\}_4]$.—The method used was similar to the above with omission of the $[AsPh_4]Cl$. However, in this case the hot benzene extract was filtered, concentrated, and then allowed to cool and crystallise. The product was filtered off, washed with benzene, and dried *in vacuo*. The manipulations for La—Tb were carried out rapidly in the air and for Dy—Er a nitrogen atmosphere was used. The analogues of Tm—Lu and Y could not be prepared due to their high solubility in benzene. Yields were from 95 (La) to 18% (Er). We note that substitution of diethyl ether for ethanol and/or benzene gives reduced yields of the same product.

$[PPh_4][Ln(S_2PMe_2)_4]$. The procedure used was a modification of that for $[AsPh_4][Ln\{S_2P(OEt)_2\}_4]$ but it was advantageous to work in a nitrogen atmosphere. The extraction step was carried out with a dry ethanol–isopropyl alcohol mixture, and crystallisation was as before. The

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† Details of starting quantities, yields, and elemental analyses are available as Supplementary Publication No. SUP 22158 (11 pp.). See Notice to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

‡ Throughout this paper: 1 eV ≈ $1.60 \times 10^{-19}$ J.

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yields were 35—60%. The complexes of Yb, Lu, and Y were never obtained pure.

*Reactions of* $LnCl_3{\cdot}nH_2O$.—*With* $[NH_4][S_2P(C_6H_{11})_2]$. (*i*) The compound $LnCl_3{\cdot}nH_2O$ (1 mol) was allowed to react with $[NH_4][S_2P(C_6H_{11})_2]$ (4 mol) in hot ethanol in the presence of $[AsPh_4]Cl$ for 20 min. After solvent removal the product was extracted with $C_2H_4Cl_2$. The crude oil obtained on evaporation was crystallised by addition of acetone. The products were identified as $[AsPh_4][Ln\{S_2P(C_6H_{11})_2\}_4]$ for Ln = La—Nd.

(*ii*) The compounds $LnCl_3{\cdot}nH_2O$ (1 mol) and $[NH_4][S_2P(C_6H_{11})_2]$ (3 mol) were dissolved in sufficient hot ethanol to give a clear solution, and heating was continued for 20 min. On cooling and standing for several hours at room temperature a crystalline product identified as the neutral complex $[Ln\{S_2P(C_6H_{11})_2\}_3]$ (Ln = Pr or Nd) was filtered off in high yield, washed with ethanol and diethyl ether, and dried *in vacuo*. For Ln = Sm—Lu and Y under the same conditions a microcrystalline product precipitated almost immediately and was isolated in the same manner.

*With* $[NH_4][S_2P(OPh)_2]$. The compound $LnCl_3{\cdot}nH_2O$ (Ln = La or Eu) (1 mol) was allowed to react with $[NH_4][S_2P(OPh)_2]$ (3 mol) in boiling ethanol for 15 min. The solvent was removed and the product extracted with diethyl ether. Evaporation and recrystallisation from 2-methylbutan-1-ol–light petroleum gave moderate yields of $[NH_4][Ln\{S_2P(OEt)_2\}_4]$. Repeating the reaction with $[NH_4][S_2P(OPh)_2]$ (4 mol) in the presence of $[AsPh_4]Cl$ (Ln = La or Pr) with benzene extraction and crystallisation from ethanol gave moderate yields of the known $[AsPh_4][Ln\{S_2P(OEt)_2\}_4]$.

*Reactions of* $Na[Ln\{S_2P(OEt)_2\}_4]$ *with* $PPh_3O$.—(i) Ln = La—Pr. The salt $Na[Ln\{S_2P(OEt)_2\}_4]$ (1 mol) dissolved in hot ethanol was added to $PPh_3O$ (3 mol) also in hot ethanol. After concentrating, the solution was cooled to 0 °C for 12 h. The resulting crystals were filtered off, washed with ethanol and diethyl ether, and dried *in vacuo*.

(*ii*) Ln = Nd—Lu *and* Y. The same procedure as above was used with $PPh_3O$ (4 mol). For Tm—Lu and Y, the uncrystallised crude sodium salt (oil) was used for reasons given previously. Changing the stoicheiometry of the reaction does not change the nature of the product, but reduces the normally high yield.

All the isolated complexes gave satisfactory elemental analyses (C, H, S, and Ln).

## RESULTS AND DISCUSSION *

Hydrated chlorides of the tervalent lanthanoids and yttrium react with dithiophosphinate salts, $[R_2PS_2]^-$ (R = Me, OEt, or $C_6H_{11}$) in hot ethanolic solution to form neutral tris and anionic tetrakis complexes. The

$$Ln^{3+} + 3[R_2PS_2]^- \longrightarrow [Ln(S_2PR_2)_3] \; (R = C_6H_{11}) \quad (1)$$

$$Ln^{3+} + 4[R_2PS_2]^- \longrightarrow [Ln(S_2PR_2)_4]^- \; (R = Me, OEt, \text{ or } C_6H_{11}) \quad (2)$$

neutral tris complexes may be crystallised or precipitated from the ethanol solution. The anionic tetrakis complexes may be isolated as their sodium (R = OEt), tetraphenylarsonium (R = OEt or $C_6H_{11}$), or tetraphenylphosphonium salts (R = Me) (details are given in the Experimental section).

The sodium salts of the tetrakis complexes are all hygroscopic. For all the other complexes, the lighter members of the series are quite stable in the air but the heavier members are attacked by humidity. The methyl derivatives are more sensitive to moisture than the others; however, the hydrated chlorides may still be used as starting materials. A comparison of the present synthetic methods with those used to prepare the similar dithiocarbamato complexes [3-6] suggests that the dithiophosphinates are less moisture sensitive. All the tetrakis complexes are moderately soluble in dry polar solvents, the solubility increasing with atomic number. In contrast, although the tris complexes of Pr and Nd are moderately soluble in ethanol, all the other tris complexes are insoluble in all the common solvents.

The elemental analyses are in good agreement with our proposed formulation of the isolated complexes. Molecular weights determined by osmometry in acetone solution (using $Na[BPh_4]$ to calibrate the apparatus) for several examples of the sodium salts of the tetrakis complexes show that dissociation occurs in this solvent (Table 1). Errors are due mainly to slight hydrolysis as the measurements were carried out in the air. The absence of co-ordinated solvent in the crystallised solids was demonstrated by i.r. spectroscopy and later by the crystal structure described below.

TABLE 1

Molecular weights determined for $Na[Ln\{S_2P(OEt)_2\}_4]$

| Ln | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb |
|---|---|---|---|---|---|---|---|---|
| Found | 437 | 415 | 419 | 430 | 431 | 456 | 400 | 404 |
| Calc.* | 451.4 | 452.0 | 452.4 | 454.1 | 457.1 | 457.9 | 460.6 | 461.4 |

* For a 1 : 1 dissociation of the salt.

Although Brown and his co-workers [3,4] reported the isolation of both the tris- and tetrakis-(diethyldithiocarbamato)-complexes of the lanthanoids, Siddall and Stewart [5] only observed the formation of the tetrakis-(di-isobutyldithiocarbamato) analogues. In the case of the dithiophosphinates, we believe that the nature of the product is largely determined by steric effects, a bulky ligand favouring a lower co-ordination number. Both the methyl and ethoxy-ligands form the anionic tetrakis complexes, and we have not characterised any other species with these two ligands. The case of the bulkier cyclohexyl ligand is more complicated however. With the light ions (La—Nd) which have large ionic radii it is possible to accommodate four ligands and form the anionic complexes. For La and Ce, the tetrakis complexes are formed exclusively; however, reaction of Pr and Nd with 3 mol of ligand leads to isolation of the neutral tris complexes. For the smaller lanthanoids (Sm—Lu and Y) only the tris complexes are formed under all conditions.

The observation that the tris complexes (R = $C_6H_{11}$) of Pr and Nd slowly crystallise from solution, whereas the heavier analogues (Sm—Lu and Y) precipitate almost

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* In the following discussion, Ln = La—Lu (excluding Pm) and Y.

immediately, coupled with marked differences in their i.r. spectra, suggests that there are two different structure types. It is quite conceivable that the less-soluble heavier members are polymeric with bridging dithiophosphinate groups. In a preliminary attempt to compare the two types, we recorded the mass spectra of the complexes of Pr and Sm. The results suggest that, in fact, both complexes are monomeric, no peaks with *m/e* larger than the molecular ion being observed (see below). However, *X*-ray powder-diffraction patterns showed that there were definitely two structure types. We recently carried out single-crystal *X*-ray studies on the tris complexes of Pr and Sm which show that both are six-co-ordinate monomers.[10] The co-ordination polyhedra are both trigonal prisms distorted by a twist about the three-fold axis. The two structure types are distinguished by the presence of an additional rotation of one ligand about its two-fold axis in the praseodymium complex which does not exist in the samarium analogue.

We recently determined the crystal structure of $[PPh_4][Pr(S_2PMe_2)_4]$ and showed that, in the solid state, the rare-earth metal ions are co-ordinated to eight sulphur atoms in a distorted square-antiprismatic arrangement.[8] This is a more symmetric arrangement than was found for the co-ordination polyhedron of the neptunium(III) tetrakis(diethyldithiocarbamate) anion [4] and its lanthanum analogue.[6] The square antiprism is also the preferred geometry by ligand–ligand repulsion considerations.[13] We presume that the eight co-ordination is preserved in solution because solid-state and solution absorption spectra are identical within experimental error, and because exchange between the free and complexed ligand is slow on the n.m.r. time scale in acetone or in $CD_2Cl_2$ solution at room temperature.

Some indication of the stability of the Ln–S bond in the vapour phase may be obtained from the mass spectra of $[Pr\{S_2P(C_6H_{11})_2\}_3]$ and the samarium analogue. In both cases the parent peak is observed, plus peaks due to the loss of one or two cyclohexyl groups. The most important peak in the two spectra corresponds to the loss of one dithiophosphinate ligand. This indicates an appreciable stability under electronic impact, and also thermally as the samples were heated to 140 °C. Although the metal–sulphur bonds are stable in the vapour and solid states and in solution, ligand replacement takes place in the presence of other strong ligands. Most of the complexes are not very soluble in water, but they may be titrated with edta in aqueous acetone or aqueous ethanol solution. In this way we were able to displace the dithiophosphinate ligands, and obtain accurate reproducible analyses for the metal content of the complexes.

Another example of ligand-replacement reactions is given by the reaction of the tetrakis anionic complexes (R = OEt) with triphenylphosphine oxide in hot ethanolic solution. Cousins and Hart [14] showed that crystalline derivatives of the lanthanoids may be obtained with $PPh_3O$ and a number of anionic ligands. We find that the phosphine oxide will replace one or two dithiophosphinate ligands as in (3) and (4). In contrast

$$[Ln(S_2PR_2)_4]^- + 2PPh_3O \longrightarrow [Ln(S_2PR_2)_3(PPh_3O)_2] \quad (R = OEt,\ Ln = La\text{—}Pr) \quad (3)$$

$$[Ln(S_2PR_2)_4]^- + 3PPh_3O \longrightarrow [Ln(S_2PR_2)_2(PPh_3O)_3]^+ \quad (R = OEt,\ Ln = Nd\text{—}Lu \text{ and } Y) \quad (4)$$

to the work of Cousins and Hart, who found that the product depended largely on the stoicheiometry of the reaction,[14] we again find that the most important factor is the radius of the lanthanoid ion. The large light members crystallise as eight-co-ordinate species, the smaller heavy ions crystallise as seven-co-ordinate cationic complexes. Although analytical data gave the stoicheiometry of the products, we were not able to confirm by vibrational spectroscopy that there was a decrease in co-ordination number, as was done for a similar species $[Ln(NO_3)_2(PPh_3O)_4][NO_3]$.[14] It is evident, however, that there are two different types of complex, the heavier members suggesting two non-equivalent ligand environments from the increase in the number of ν(P–S) bands. By n.m.r. spectroscopy we were able to show that in $CDCl_3$ solution the complex $[La\{S_2P(OEt)_2\}_3(PPh_3O)_2]$ contains only one type of dithiophosphinate ligand [$\delta(CH_2)$ 3.60, $\delta(CH_3)$ 0.87 p.p.m.] whereas the complex $[Sm\{S_2P(OEt)_2\}_2(PPh_3O)_3][S_2P(OEt)_2]$ contains two different ligands [$\delta(CH_2)$ 2.80 and 3.88, $\delta(CH_3)$ 0.53 and 1.08 p.p.m.]. This was interpreted in terms of the above ionic formulation rather than as due to two chemically different bonding sites in the complex because of the stereochemical non-rigidity of high co-ordination numbers.[15] The above hypothesis was recently confirmed in the solid state by the *X*-ray crystal-structure determinations for the two complexes.[9] The La is co-ordinated to six sulphur atoms and two oxygen atoms in a distorted square-antiprismatic arrangement. The Sm is co-ordinated to four sulphur atoms and three oxygen atoms forming a pentagonal bipyramid, and the structure contains free $[S_2P(OEt)_2]^-$ ions.

An interesting additional observation was made while treating $[NH_4][S_2P(OPh)_2]$ with lanthanoid ions in ethanolic solution. The expected product was a tris complex, as was obtained with R = cyclohexyl, due to the bulky phenoxy-groups. In fact the only product obtained was the result of the transesterification reaction (5). The known ethoxy-substituted complexes have

$$\text{‘}[Ln\{S_2P(OPh)_2\}_4]^-\text{’} + 8EtOH \longrightarrow [Ln\{S_2P(OEt)_2\}_4]^- + 8PhOH \quad (5)$$

been crystallised as the ammonium or tetraphenylarsonium salts and characterised by elemental analysis

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and i.r. spectra. This shows a drastic change in the reactivity of the ligand on complex formation because the salt $[AsPh_4][S_2P(OPh)_2]$ may be heated under reflux in ethanol and crystallised unchanged.

*Infrared Spectra.*—All the isolated complexes were characterised by their i.r. spectra (Table 2). As expected, the spectra change very little on going from La to Lu for any one series of complexes. We assign bands in the 200—300 $cm^{-1}$ region to ν(M–S) as has previously been proposed for analogous transition-metal complexes.[16] Lanthanoid–sulphur bonding has been previously proposed on the basis of bands in the 300 $cm^{-1}$ region in the spectra of complexes of monothiodiketonates.[17] It is noteworthy that the oxygen donor $PPh_3O$ must be a better donor of electrons than sulphur towards lanthanoid ions because ν(M–S) decreases when one dithiophosphinate ligand is replaced by two molecules of $PPh_3O$. Similarly, the weakening of the M–S bond on increasing the co-ordination number is manifested in the lowering of ν(M–S) for similar complexes, *e.g.* tris- and tetrakis-(dicyclohexyldithiophosphinato)-complexes, or the seven- and eight-co-ordinate species containing $PPh_3O$. The above behaviour, and the values obtained for ν(M–S), suggest that there is little difference in the M–S bond character between the lanthanoids and the transition metals. A similar conclusion was reached with regard to M–S bond lengths and SPS angles when comparing values for lanthanoid dithiophosphinato-complexes with those for their transition-metal analogues.

For the $PS_2$ unit we expect two vibrations, $\nu_{sym}$ and $\nu_{asym}$.[18,19] We assign bands in the 500—600 $cm^{-1}$ region to $\nu_{sym}$ and in the 600—700 $cm^{-1}$ region to $\nu_{asym}$. The assignments are based on a comparison with transition-metal analogues, the band shifts between the free ligand and the complex, and the small changes observed within the same series of complexes. They also show an increase in wavenumber due to the increase in electron density on the metal ion produced by the formation of the $PPh_3O$ adducts. This increase in energy is expected from the inductive effect which strengthens the P–S σ bond.[19]

The bands at 1 151 and 1 136—1 141 $cm^{-1}$ in the two types of phosphine oxide complex may be assigned to ν(P=O). The lower-wavenumber band is associated with a lower co-ordination number and a more positive charge on the metal ion. Cousins and Hart[14] reported that there was a systematic increase in the energy of ν(P=O) with increasing atomic number in lanthanoid complexes due to a coupling of ν(P=O) with ν(M–O). In the present case the changes are very small, 5 $cm^{-1}$ from the complex of Nd to that of Lu.

TABLE 2

Infrared spectra ($cm^{-1}$) for dithiophosphinato-complexes of the lanthanoids[a]

| | | | | $[Ln\{S_2P(C_6H_{11})_2\}_3]$ | | | |
|---|---|---|---|---|---|---|---|
| $[Ln\{S_2P(OEt)_2\}_4]^-$ | $[Ln\{S_2P(OEt)_2\}_3(PPh_3O)_2]$ | $[Ln\{S_2P(OEt)_2\}_2(PPh_3O)_3][S_2P(OEt)_2]$ | $[Ln\{S_2P(C_6H_{11})_2\}_4]^-$ [b] | [c] | [d] | $[Ln(S_2PMe_2)_4]^-$ | |
| | 1 151s | 1 136—1 141m | | | | | ν(P=O) |
| 659—667m | 678m | 680 (sh)—688m<br>678m<br>657—663w | 635—640s<br>618—625s | 613s<br>605m (sh) | 614—620s<br>605—610m | 610—616s | $\nu_{asym}$(P–S) |
| 540—545s | 581w | 581w<br>540s | 568m<br>556—559s | 552s | 553—558s | 505—510s | $\nu_{sym}$(P–S) |
| 255m | 250w | 255w | 230s<br>227s | 271s<br>245s<br>236m | 272—276m<br>243—245m<br>215—220w | 291m<br>271—266m<br>240s | ν(M–S) |

[a] Ranges are quoted in the order La—Lu. [b] Ln = La—Nd. [c] Ln = Pr or Nd. [d] Ln = Sm—Lu.

*Electronic-absorption Spectra.*—The electronic-absorption spectra present a number of interesting features. The dithiophosphinates are strongly reducing ligands, hence we would expect to observe broad charge-transfer (c.t.) bands in or near the visible region for those lanthanoid ions which are easily reduced to the bivalent state.[2] Indeed, the complexes of Eu and Yb are red and yellow respectively due to the presence of such transitions, and similar bands are observed in the u.v. for the analogues of Sm and Tm. The energy of the first c.t. band, most likely from the occupied non-bonding π orbital of the ligand to a metal *f* orbital, should be related to the redox potential of the ion.[20] It has been shown that the variation of the redox potential of the lanthanoids, $E^{\ominus}(Ln^{II}–Ln^{III})$, and the energy of the c.t. bands, $\sigma_{c.t.}$, are a linear function of the number of *f* electrons, *q*, if corrected for the spin-pairing energy;[2,20] $\sigma_{c.t.}$ is also a linear function of $E^{\ominus}(Ln^{II}–Ln^{III})$ if corrected for the differences in the effective nuclear charge and the interelectronic repulsion parameters, $\Delta(E - A')$, between the complex and the aqua-ion[20] (Figure 1).

As an alternative description of the above phenomenon we may ascribe an optical electronegativity, $\chi_L$, of 2.64—2.73 ($C_6H_{11}$ < Me ~ OEt) to the dithiophosphinate ligands from the relation $\sigma = 30[\chi_L - \chi_M]$ where σ is the observed energy in $10^3$ $cm^{-1}$ of the first c.t. band and $\chi_M$ is the electronegativity of the metal ion uncorrected for spin pairing, as reported by Jørgensen. This is in agreement with values of $\chi_L$ obtained from similar transition-metal analogues.[2,21]

A general feature in the spectra of lanthanoid ions is a shift of the absorption bands towards lower energy on

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complex formation, *i.e.* the nephelauxetic effect. This is due to a lowering of the interelectronic-repulsion parameters in the complex.[21] As the energies of the free-ion terms are not well known for all the lanthanoids, and due to the large number of bands observed, an exact treatment of this phenomenon is not in general possible. A qualitative measure of the effect may be obtained however, from relation (6) where $\nu_i^{\text{comp.}}$ and $\nu_i^{\text{aq.}}$ are the

$$\beta = \frac{1}{n} \sum_{i=1}^{n} \frac{\nu_i^{\text{comp.}}}{\nu_i^{\text{aq.}}} \qquad (6)$$

observed baricentres in cm$^{-1}$ of the *i*th *f*–*f* transition in the complex and aqua-ion respectively.[22] A number of observations may be made with regard to the magnitude of the parameter β (Table 3). First, the change in the nephelauxetic effect on changing the substituent at phosphorus is small. Decreasing the co-ordination number, however, leads to greater spectral shifts, *i.e.* β decreases. This is presumably due to a shorter metal–ligand distance.[8,10] Although the magnitude of β is similar to that obtained for analogous dithiocarbamato-complexes,[5,6] it is perhaps instructive to compare the nephelauxetic effect of sulphur-donor ligands with other known systems (Table 4). It is evident that, although we are looking at a very small effect, sulphur donors are among the stronger ligands in a nephelauxetic sense.

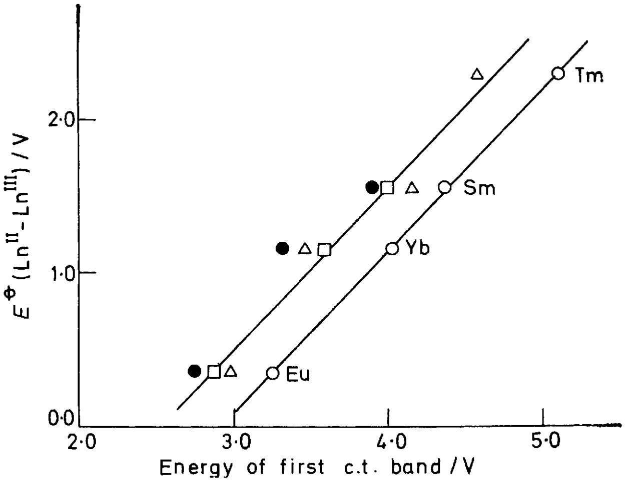

FIGURE 1 Energy of the first charge-transfer band of dithiophosphinato-complexes of the lanthanoids plotted against the redox potential of the metal ion. R = OEt, (△) observed, (○) corrected by $q\Delta(E - A')$, $\Delta(E - A')$ = 0.044 V; R = $C_6H_{11}$, (●) observed, (□) corrected by $q\Delta(E - A')$, $\Delta(E - A')$ = 0.020 V

TABLE 3

Nephelauxetic parameters,* β, for $[\text{Ln}(S_2PR_2)_n]^{(n-3)-}$

| Ln | R = Me, $n$ = 4 | R = OEt, $n$ = 4 | R = $C_6H_{11}$, $n$ = 4 | R = $C_6H_{11}$, $n$ = 3 |
|---|---|---|---|---|
| Pr | 0.975 | 0.978 | 0.977 | 0.972 |
| Nd | 0.981 | 0.983 | 0.984 | 0.973 |
| Sm | 0.973 | 0.984 | | 0.968 |
| Dy | 0.994 | 0.990 | | 0.990 |
| Ho | 0.994 | 0.992 | | 0.987 |
| Er | 0.996 | 0.994 | | 0.991 |
| Tm | | 0.989 | | 0.980 |

* Spectra for the tetrakis complexes were recorded in $C_2H_4Cl_2$ solution, those for the tris complexes were obtained from the solid by reflectance.

TABLE 4

Nephelauxetic parameters, β, for complexes of Nd$^{\text{III}}$

| β | Ligand [a] |
|---|---|
| 0.996 | $NdCl_3$ in tributyl phosphate [b] |
| 0.994 | $NdCl_3$ in MeOH [b] |
| 0.991 | oxalate (2) [b] |
| 0.991 | ethyl acetoacetate (2) [c] |
| 0.989 | benzoylmethanide (3) [b] |
| 0.989 | phthalate (2) [b] |
| 0.987 | naphthalenate (2) [b] |
| 0.985 | $S_2P(OEt)_2$ (4) [d] |
| 0.984 | anhydrous $NdCl_3$ [b] |
| 0.984 | $S_2P(C_6H_{11})_2$ (4) [d] |
| 0.983 | $S_2CNEt_2$ (4) [e] |
| 0.982 | 2,2′:6′,2″-terpyridyl (1) [b] |
| 0.982 | $S_2CNBu^i{}_2$ (4) [f] |
| 0.981 | 2,2′-bipyridyl (2) [b] |
| 0.981 | $S_2PMe_2$ (4) [d] |
| 0.974 | $Nd_2O_2$ [b] |
| 0.973 | $S_2P(C_6H_{11})_2$ (3) [d] |

[a] The number of ligands in the complex is given in parentheses. [b] S. P. Sinha, *Spectrochim. Acta*, 1966, **22**, 57. [c] N. K. Dutt and S. Rahut, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2905. [d] This work. [e] Ref. 6. [f] Ref. 5.

Another point of interest in these spectra is the intensity of the *f*–*f* transitions. Although certain transitions are known to be hypersensitive, the intensities of the others do not normally change very much on complex formation.[23] However, the oscillator strengths of the normal *f*–*f* transitions of the dithiophosphinato-complexes were found to be up to three times greater than those of the aqua-ions, whereas the hypersensitive bands are up to nine times more intense than the corresponding bands in the aqua-ions. Similar results were also obtained for the dithiocarbamato-complexes.[6] It has been suggested [24] that there may be a borrowing of intensity from c.t. bands to account for the intensity of the hypersensitive transitions. This mixing of states should become more important with c.t. bands of low energy, such as those observed in the present case due to the reducing nature of the ligands. Thus, the spectra of the dithiophosphinato- and dithiocarbamato-complexes lend some support to the above mechanism.

*N.M.R. Spectra.*—The most important effect observed in the $^1H$ n.m.r. spectra of complexes of the lanthanoids is the large chemical shifts produced by the presence of the paramagnetic ions. There are two possible contributions to this effect: (*i*) the contact hyperfine interaction; (*ii*) the pseudo-contact interaction due to the anisotropy of the magnetic moment of the lanthanoid ion.[25] Bleaney [26] has shown that the shift produced by the pseudo-contact mechanism is as in (7) in the case of

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TABLE 5

Paramagnetic shifts[a] in the $^1$H n.m.r. spectra of $[Ln\{S_2P(OEt)_2\}_4]^-$

| Ln | $\Delta[\delta(CH_3)]$ | $\Delta[\delta(CH_2)]$ | $\Delta[\delta(CH_2)]/\Delta[\delta(CH_3)]$ | $g^2J(J+1)(2J-1)(2J+3)\langle J\|\alpha\|J\rangle$[b] |
|---|---|---|---|---|
| Ce | −0.49 | −1.50 | 3.1 | −11.8 |
| Pr | −1.30 | −3.63 | 2.8 | −20.7 |
| Nd | −0.59 | −1.83 | 3.1 | −8.08 |
| Sm | −0.10 | −0.32 | 3.2 | 4.28 |
| Eu | 0.63 | 1.85 | 2.9 | |
| Tb | −12.67 | −33.68 | 2.7 | −157.5 |
| Dy | −14.59 | −39.10 | 2.7 | −181 |
| Ho | −5.50 | −15.52 | 2.8 | −71.2 |
| Er | 4.53 | 11.93 | 2.6 | 58.8 |
| Tm | 5.92 | 16.07 | 2.7 | 95.3 |
| Yb | 2.05 | 6.00 | 3.0 | 39.2 |

[a] Shifts are in p.p.m. relative to the diamagnetic lanthanum complex [$\delta(CH_3)$ 1.22, $\delta(CH_2)$ 4.15 p.p.m. relative to $SiMe_4$]. [b] Ref. 26.

axial symmetry. In an isomorphous series of complexes we may make the approximation that the geometrical

$$\frac{\Delta\nu}{\nu_0} = -\frac{g^2\beta^2J(J+1)(2J-1)(2J+3)}{60(\boldsymbol{k}T)^2r^3}\cdot \langle r^2\rangle\langle J||\alpha||J\rangle\,(2A^0{}_2)(3\cos^2\theta-1) \quad (7)$$

factors, $(3\cos^2\theta - 1)r^{-3}$, are constant and that the crystal-field coefficients, $A^0{}_2\,\langle r^2\rangle$ vary in a regular manner.

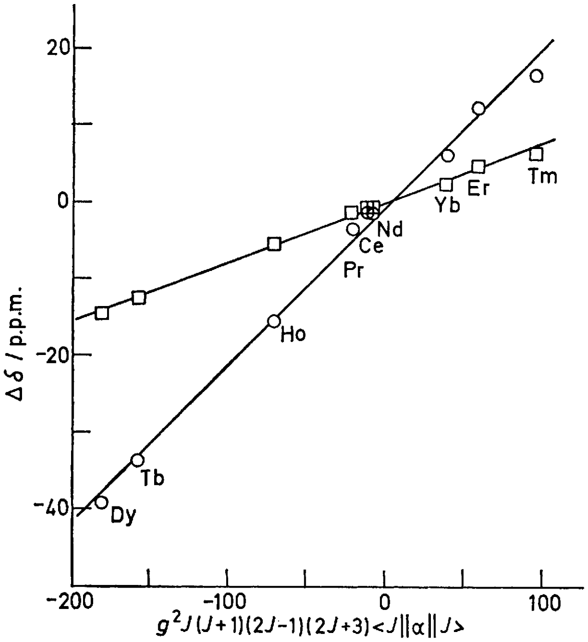

FIGURE 2 Paramagnetic shifts in the $^1$H n.m.r. spectra of $[Ln\{S_2P(OEt)_2\}_4]^-$. The shifts are in p.p.m. relative to the diamagnetic lanthanum complex, and the term on the abscissa is taken from ref. 26: (□), $CH_3$; (○), $CH_2$

If measurements are carried out at constant temperature we can make two observations. First, the ratio of the shifts produced for two different protons should remain constant on changing the lanthanoid ion. This is seen to be the case for the methyl and methylene protons in the bis(*OO'*-diethyl dithiophosphate) series of complexes (Table 5). Secondly, the shift should be proportional to $g^2J(J+1)(2J-1)(2J+3)\,\langle J||\alpha||J\rangle$, the values for which have been tabulated by Bleaney.[26] In Figure 2 the observed shifts are plotted against this function and give two straight lines for the ethoxy-protons. We thus conclude that, under the conditions of slow intermolecular and fast intramolecular exchange, there is no contact contribution to the shifts and that they are dipolar in origin.

*Conclusion.*—The results presented above demonstrate that the formation of lanthanoid complexes with sulphur-donor ligands may no longer be considered unusual. There remain, however, many questions concerning the nature of the metal–sulphur bond and the spectral properties of these complexes. We are at present carrying out a more detailed study of the absorption and n.m.r. spectra which we hope will further characterise this class of complex, as well as improve our understanding of the chemistry of the lanthanoids in general.

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