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Thiophosphoryl Complexes of Trivalent Lanthanide Cations: Importance of Counterions and Stoichiometry for Binding Energies. A Theoretical Study

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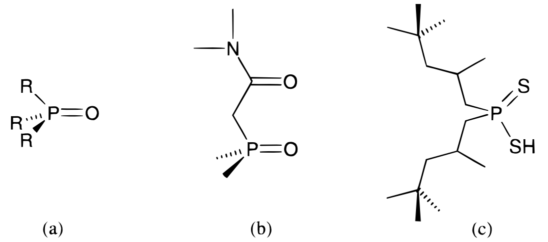
The intrinsic interaction energies ΔE between trivalent lanthanide cations ($M^{3+} = La^{3+}$, Eu^{3+}, and Yb^{3+}) and thiophosphoryl $R_3P{=}S$ (R = H, Me, Et, and Ph) ligands **L** are investigated by quantum mechanical calculations on charged $\mathbf{L}M^{3+}$ or neutral $\mathbf{L}MCl_3$ and $\mathbf{L_2}MCl_3$ complexes. Counterions are found to markedly modulate the binding properties. First, in 1:1 complexes, the order of the alkyl and phenyl substituent effects is inversed in R_3PM^{3+} (where ΔE increases in the order R = Me ≪ Et ≪ Ph) compared to R_3PMCl_3 (where ΔE increases in the order R = Ph < Me < Et). Second, the coordination mode of the thiophosphoryl bond evolves from a linear coordination in $\mathbf{L}M^{3+}$ (related to polarization of **L** induced by the "hard" M^{3+} cation) to a bent coordination in $\mathbf{L}MCl_3$ (related to the “soft” metal sulfur interaction), as in the protonated forms R_3PSH^+. In addition, the stoichiometry of the complexes is found to determine the selectivity in the cation series. In all charged or neutral 1:1 complexes, ΔE increases with the cation hardness ($La^{3+} < Eu^{3+} < Yb^{3+}$) for a given **L**. However, in the 1:2 $(Me_3PS)_2MCl_3$ complexes, ΔE follows the order $Yb^{3+} < Eu^{3+} < La^{3+}$, due to the interplay between the ligands, the anions, and their interactions with the M^{3+} cation. These results are important for our understanding of the factors which determine the arrangements of ligands around M^{3+} cations in condensed phases where the first coordination sphere is saturated and generally involves neutralizing counterions. They also have bearing on the discrimination between hard vs less hard cations (like trivalent lanthanides vs actinides) by extractant molecules involving soft binding sites.

1. Introduction

Neutral organophophorus-based ligands are widely used in the field of liquid−liquid extraction of lanthanide and actinide ions from aqueous solutions.[1−5] Examples involve small molecules of monodentate (e.g., TPPO and TBP) or bidentate types like CMPO (Scheme 1), or more complex systems like cavitands[6,7] or recently developed calixarenes incorporating phosphoryl binding groups anchored to a lipophilic platform.[8,9] As analyzed in host−guest complexes,[10,11] the selectivity and binding strength of such ligands depend for a large part on the basic metal−ligand interactions which compete with solvent and other environment effects.[12,13] Qualitative trends in selected series may be obtained from structure−activity relationships between the “acids” (metals) and “bases” (ligands).[14−16] A more precise assessment of the individual metal−ligand interaction energies may be obtained from gas phase data on small systems,[17−19] but such data are presently not available for highly charged lanthanide or actinide cations. Quantum-mechanical (QM) calculations represent an important alternative to gather insights into the intrinsic energetic and structural features of these interactions, in the absence of a competing environment.[20] However, QM studies covering this subject are rather scarce. The uranyl cation and its salts were examined[21,22] and some QM studies dealt with the hydrates[22−24] or the trihalide salts[25−30] of the trivalent lanthanide cations. To our knowledge, no QM studies on these cations interacting with model or real extractant molecules have been reported prior our efforts. We recently reported QM investigations on the interactions between model ligands of the phosphoryl $R_3P{=}O$ type and trivalent lanthanide[31] or uranyl cations[32] which demonstrated the importance of electronic effects (charge transfer to the cation and polarization of the ligand) in the stabilization of R_3POM^{3+} complexes and the role of counterions and stoichiometry on the structural and energy features of complexation. Recently, the interaction between Gd^{3+} and polyaminocarboxyalate ligands has been studied by QM.[33]

SCHEME 1: Organophosphorus Compounds for Liquid−Liquid Extraction of Lanthanide and Actinide Cations: (a) TPPO (R = Ph), TOPO (R = *n*-octyl), TBP (R = *t*but-O); (b) CMPO; (c) CYANEX-301



(a) (b) (c)

We now want to proceed with a study of thiophosphoryl ligands. Thiophosphoryl and dithiophosphinate ($R_2PS_2^-$) substructures may play an important role in the development of selective ligands for the lanthanide−actinide separation. For instance, a high Am^{3+}/Eu^{3+} separation factor was obtained with CYANEX-301 (bis(2,4,4-trimethylpentyl)thiophosphinic acid; see Scheme 1) combined with 10% of TBP.[34−36] In such synergistic systems, the phosphoryl containing TBP ligands likely act as “hard” binding sites and provide the necessary binding strength, while the sulfur-based ligands act as “softer” sites which provide the selectivity for Am^{3+}, considered to be softer than Eu^{3+}. Recently developed neutral thiophosphoryl ligands also display remarkable extraction properties for trivalent

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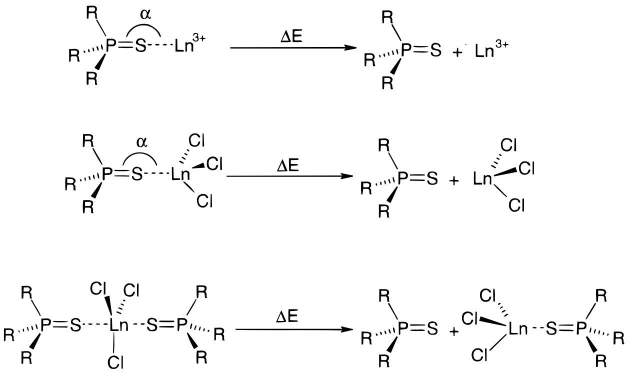
SCHEME 2: Calculated Compounds and Dissociation Energies ΔE's



lanthanide or actinide cations.[37] It is thus important to assess the intrinsic binding properties of phosphoryl *vs.* thiophosphoryl ligands. As a first approach, we compare three lanthanide cations La^{3+}, Eu^{3+}, and Yb^{3+} of increasing hardness, interacting with phosphoryl/thiophosphoryl ligands. Cation discrimination by these ligands should indeed give insights into the cation discrimination by "soft" vs "hard" phosphoryl derivatives. Compared to the $R_3P{=}O\cdots M^{3+}$ interactions, the $R_3P{=}S\cdots M^{3+}$ ones should lead to reduced charge⋯dipole contributions, but to enhanced polarization and charge transfer effects. We notice that the structure−activity relationships according to which the sulfur atom is "less basic" than the oxygen atom are generally obtained by analysis of weak interactions (hydrogen bonded complexes or enthalpies of complexation with Lewis acid in a polar solution).[38,39] It it not clear whether trends would be the same with hard M^{3+} cations.

More specifically, we report Hartree−Fock calculations on complexes of neutral thiophosphoryl ligands R_3PS with R being hydrogen, methyl, ethyl, and phenyl, respectively. Scheme 2 shows the compounds and reactions covered. The variation of R will allow us to assess the dependency of the metal−ligand binding strength on the type of substituent R. The comparison of the methyl and ethyl substituents will show the influence of the alkyl chain length, while the results with the phenyl substituent will reveal whether aryl-groups connected to P enhance or decrease the metal−sulfur bond strength. Enhanced extraction capabilities are known for bidentate diphosphine dioxide ligands with arylic instead of alkylic substituents on P, while generally arylic substituents are assumed to have a negative effect caused by their larger electronegativity.[2,8]

The first part of our study will deal with 1:1 complexes of the general formula $[R_3PSM]^{3+}$. The results allow us to assess the intrinsic features of the sulfur−metal coordination in the absence of perturbations from competing coordinated species like counterions, other ligands, or solvent molecules. Furthermore, calculated proton affinities have been suggested as a way to predict trends in extraction capabilities of different ligands.[2] The data obtained here should be more relevant. The selectivity of the different ligands is studied by a comparison of lanthanides with decreasing sizes, namely, La^{3+}, Eu^{3+}, and Yb^{3+}. It has to be noted, though, that the ability of the substituents to compensate for the increased charge transfer to the cations is amplified in the $[R_3PSM]^{3+}$ complexes, compared to the situation found when the first coordination sphere is saturated and smaller charge deficiencies on the cation are to be expected.

The second part of this study deals with complexes of the type R_3PSMCl_3. Like the complexes presumably formed in the organic phase in liquid−liquid extraction experiments, they are neutral and therefore better suited to obtain information about the extraction and selection capabilities of the studied ligands. In these neutral 1:1 complexes, the properties of the sulfur−metal bonds are perturbed by the steric and electronic influences of the counterions. Therefore a comparison of the results with those obtained for the $[R_3PSM]^{3+}$ complexes will be crucial for the interpretation.

The final group of complexes considered in this work will be of the general formula $(Me_3PS)_2MCl_3$, where two ligands are coordinated to the cation. Because of computer time limitations we only consider Me_3PS as a ligand for these 2:1 complexes. These complexes, compared to the Me_3PSMCl_3 ones, will provide insights into the effect of the coordination number of the cation on the metal−ligand binding features and on the cation discrimination by a given type of ligand. In the discussion section of the paper, we discuss structural features of cation coordination to the thiophosphoryl ligands and compare the latter with the phosphoryl ones.

2. Methods

The R_3PS ligands were fully optimized at the Hartree−Fock level of theory. On sulfur, phosphorous, and carbon the Dunning−Huzinaga double-ζ plus polarization basis sets[40] were used. A basis set of the same type without polarization function was used on hydrogen.

For the complexes two different approaches were chosen. In the case of the ionic $[R_3PSM]^{3+}$ compounds a quasirelativistic effective core potential (ECP) of the Stuttgart group[41,42] was used on the lanthanides, together with the affiliated (5/4/3) valence basis, to which one f-function with an exponent optimized by Frenking et al.[43] was added. The optimized geometries of the ligands were retained in the optimizations of the $[R_3PSM]^{3+}$ complexes; only the S−P distance was optimized together with the S−M distance and the P−S−M angle. The suitability of this approach has been proven in our investigation of the phosphoryl complexes.

The Gaussian94 program,[44] which was used throughout this study, cannot calculate energy derivatives when f-functions are used together with ECPs. Therefore, with the basis described above, we were restricted to using the Fletcher−Powell geometry optimization algorithm, which does not use energy derivatives. However, the optimization of the neutral R_3PSMCl_3 and $(Me_3PS)_2MCl_3$ complexes with this algorithm proved to be difficult. Thus we decided to leave out the f-functions on the lanthanide in these complexes and the MCl_3 compounds and fully optimized their geometry with the standard Berny algorithm.[45] In one case we added the f-function after this procedure and reoptimized the parameters that involve the lanthanide atom, in order to prove the suitability of this approach (see Tables 1 and 2).

To obtain an estimation of the influence of correlation effects, some of the calculations were repeated using density functional theory with gradient corrected exchange and correlation functionals as derived by Becke[46] and Perdew,[47] respectively. A BSSE correction[48] was also applied in a few cases. However, the small size of the corrections and the fact that they are constant within 0.5 kcal/mol (see also ref 31) diminish their importance for this work.

3. Results

3.1. The $[R_3PSM]^{3+}$ Complexes. The total energies of the complexes can be found in Table S1 (Supporting Information), while the dissociation energies ΔE of the lanthanide−sulfur bond (see Scheme 2), together with the relative values, are in Table 1. As expected from the electron deficiency of the M^{3+}

TABLE 1: Calculated Metal−Ligand Dissociation Energies ΔE (kcal/mol) from HF Calculations (see Scheme 1 for Definitions)

complex	HF results ΔE	 $\Delta\Delta E_L$[a]	 $\Delta\Delta E_M$[b]
$[H_3PSLa]^{3+}$	+135.8	0.0	−40.7
$[H_3PSEu]^{3+}$	+151.9	+16.1	−43.2
$[H_3PSYb]^{3+}$	+166.8	+31.0	−45.8
$[Me_3PSLa]^{3+}$	+176.5	0.0	0.0
$[Me_3PSEu]^{3+}$	+195.2	+18.7	0.0
$[Me_3PSYb]^{3+}$	+212.6	+36.1	0.0
$[Me_3PSH]^{+}$	+223.4	+46.9	0.0
$[Et_3PSLa]^{3+}$	+188.9	0.0	+12.4
$[Et_3PSEu]^{3+}$	+208.5	+19.6	+13.4
$[Et_3PSYb]^{3+}$	+226.5	+37.6	+13.9
$[Et_3PSH]^{+}$	+228.6	+39.7	+5.2
$[Ph_3PSLa]^{3+}$	+205.6	0.0	+29.1
$[Ph_3PSEu]^{3+}$	+226.6	+21.0	+31.5
$[Ph_3PSYb]^{3+}$	+245.7	+40.1	+33.1
$[Ph_3PSH]^{+}$	+233.6	+28.0	+10.2
$Me_3PSLaCl_3$	+35.9	0.0	0.0
$Me_3PSEuCl_3$	+37.5	+1.6	0.0
$Me_3PSYbCl_3$	+38.6	+2.7	0.0
$Me_3PSEuCl_3$[c]	+36.7		
$Et_3PSLaCl_3$	+36.9	0.0	+1.0
$Et_3PSEuCl_3$	+38.6	+1.7	+1.1
$Et_3PSYbCl_3$	+39.8	+2.9	+1.2
$Ph_3PSLaCl_3$	+34.9	0.0	−1.0
$Ph_3PSEuCl_3$	+36.2	+1.3	−1.3
$Ph_3PSYbCl_3$	+36.9	+2.0	−1.7
$Me_3PSEuCl_3$[d]	+33.6		0.0
$Ph_3PSEuCl_3$[d]	+32.3		−1.3
$(Me_3PS)_2LaCl_3$	+23.1	0.0	
$(Me_3PS)_2EuCl_3$	+22.7	−1.4	
$(Me_3PS)_2YbCl_3$	+21.5	−1.6	
$(Me_3PS)_2LaCl_3$[e]	+26.6	0.0	
$(Me_3PS)_2EuCl_3$[e]	+27.2	+0.6	
$(Me_3PS)_2YbCl_3$[e]	+27.5	+0.9	

[a] Difference in ΔE's for a given ligand, relative to the lanthanum complex. [b] Difference in ΔE's for a given metal, relative to the Me_3PS complex. [c] With f-orbitals on M. [d] BSSE corrected values. [e] Relative to constrained fragments.

ion, the M−S dissociation energies in these complexes are very high (from 135.8 to 245.7 kcal/mol).

The binding energy is very much dependent on the substituent R on the ligand R_3PS. For example, in the case of europium the ligand with the lowest binding energy, H_3PS, has a ΔE smaller by 74.7 kcal/mol than the ligand with the highest binding energy, Ph_3PS (see $\Delta\Delta E_M$ in Table 1). However, the larger part of this difference, 43.2 kcal/mol, is also observed by going from H_3PS to Me_3PS, which proves that H_3P is a poor model for $(alkyl)_3P$ ligands. Compared to Me_3PS, Ph_3PS still binds stronger to Eu^{3+} by 31.5 kcal/mol, thereby showing a strong aryl effect. Lengthening of the alkyl chain from Me_3PS to Et_3PS on the other hand leads to a strengthening of the Eu−S bond of just 13.4 kcal/mol. As further lengthening of the alkyl chain should have less and less influence, it is likely that in the $[R_3PSM]^{3+}$ complexes aryl ligands bind generally stronger than alkyl ones.

In this context it is interesting to compare the protonation energies of the studied ligands (see Table 1). They range from 223.4 kcal/mol for Me_3PS to 233.6 kcal/mol for Ph_3PS, and hence, are of the same order of magnitude as the binding energies to the M^{3+} cations. They also follow the same order ($Me_3PS < Et_3PS < Ph_3PS$), which is the order of polarizabilities of R. However, while for example the range covered by the binding energies to Yb^{3+} for these ligands is 33.1 kcal/mol, it is only 10.2 kcal/mol for the protonation energies. This means that the influence of the substituent R gets smaller, probably due to the decreasing importance of the ligand polarization when forming a covalent $R_3PS{-}H^+$ bond.

TABLE 2: Selected Optimized Distances (r, Å) and Angles (α; degrees) from HF Calculations

compound	HF results r(S−M)[a]	 r(P−S)	 r(M−Cl)[b]	 α(P−S−M)	 α(S−M−Cl)[c]
$LaCl_3$			2.676		
$EuCl_3$			2.572		
$YbCl_3$			2.478		
H_3PS		1.958			
Me_3PS		1.973			
Et_3PS		1.980			
Ph_3PS		1.979			
$[H_3PSLa]^{3+}$	2.585	2.077		180.0	
$[H_3PSEu]^{3+}$	2.472	2.083		179.9	
$[H_3PSYb]^{3+}$	2.376	2.088		180.0	
$[Me_3PSLa]^{3+}$	2.534	2.133		180.0	
$[Me_3PSEu]^{3+}$	2.425	2.144		179.9	
$[Me_3PSYb]^{3+}$	2.336	2.152		180.0	
$[Me_3PSH]^{+}$	1.334	2.090		96.2	
$[Et_3PSLa]^{3+}$	2.513	2.147		179.1	
$[Et_3PSEu]^{3+}$	2.410	2.157		179.0	
$[Et_3PSYb]^{3+}$	2.323	2.164		179.8	
$[Et_3PSH]^{+}$	1.334	2.096		96.1	
$[Ph_3PSLa]^{3+}$	2.486	2.179		178.2	
$[Ph_3PSEu]^{3+}$	2.386	2.197		180.0	
$[Ph_3PSYb]^{3+}$	2.302	2.214		178.8	
$[Ph_3PSH]^{+}$	1.333	2.106		96.1	
$Me_3PSLaCl_3$	3.040	2.030	2.738	112.9	93.1
$Me_3PSEuCl_3$	2.918	2.032	2.633	112.2	95.9
$Me_3PSEuCl_3$[d]	2.911	2.032	2.615	112.3	96.0
$Me_3PSYbCl_3$	2.811	2.034	2.539	111.6	98.5
$Et_3PSLaCl_3$	3.028	2.037	2.736	113.8	94.6
$Et_3PSEuCl_3$	2.907	2.039	2.631	113.1	97.4
$Et_3PSYbCl_3$	2.801	2.041	2.538	112.5	99.9
$Ph_3PSLaCl_3$	3.039	2.038	2.727	112.4	100.6
$Ph_3PSEuCl_3$	2.916	2.041	2.622	113.1	102.3
$Ph_3PSYbCl_3$	2.807	2.044	2.528	113.5	103.7
$(Me_3PS)_2LaCl_3$	3.107	2.021	2.769	110.0	89.2
$(Me_3PS)_2EuCl_3$	2.987	2.023	2.666	109.8	88.7
$(Me_3PS)_2YbCl_3$	2.884	2.024	2.575	109.8	90.1

[a] M = H in the protonated species. [b] In case of different M−Cl bond lengths, the longest one is given. [c] The angle belonging to the given M−Cl bond length. [d] Values obtained with f-orbitals on Eu.

Regarding the cation selectivity of a given ligand, it comes out that the ligand with the highest binding energy, Ph_3PS, also displays the largest selectivity. The difference in ΔE between La^{3+} and Yb^{3+} for this ligand is 40.1 kcal/mol, compared to 37.6 kcal/mol for Et_3PS and 36.1 kcal/mol for Me_3PS. Therefore, the cation size and hardness have a large influence on binding energies. However, the changes in cation selectivity as a function of R are relatively small, and rather represent a scaling of the total dissociation energies observed, than any intrinsic difference in the ligand−metal bonds.

The phosphoryl (R_3PO) complexes studied in ref 31 generally show larger binding energies than their thiophosphoryl (R_3PS) analogues, the range of calculated dissociation energies for the same complexes as considered here going from 181 to 300 kcal/mol. This means that the cation−ligand bonds in the thiophosphoryl complexes have about 80% of the energy of the same bonds in the phosphoryl complexes. The effects of the substituent R and the metal size appear to be amplified accordingly. For example, the difference between $[Me_3POEu]^{3+}$ and $[Ph_3POEu]^{3+}$ amounts to 49.2 kcal/mol instead of the 31.5 kcal/mol found for $[Me_3PSEu]^{3+}$ and $[Ph_3PSEu]^{3+}$.

Like the phosphoryl ligands, all thiophosphoryl ligands considered here bind linearly to the M^{3+} cations (see Table 2). This contrasts with the protonated ligands where P−S−H bond angles are about 96°, indicating that the $S{-}H^+$ bond is more covalent than the $S{-}M^{3+}$ bond.

The M−S distances (see Table 2) depend on the metal, the La−S ones being about 0.1 Å longer than the Eu−S ones, which in turn are about 0.1 Å longer than the Yb−S bonds.

TABLE 3: Mulliken Charges q_i

	HF results			
compound	q(M)	q(P)	q(S)	q(Cl)[a]
$LaCl_3$	+1.64			−0.55
$EuCl_3$	+1.50			−0.50
$YbCl_3$	+1.40			0.47
H_3PS		+0.13	−0.41	
Me_3PS		+0.54	−0.46	
Et_3PS		+0.45	−0.48	
Ph_3PS		+0.37	−0.43	
$[H_3PSLa]^{3+}$	+2.51	+0.23	−0.61	
$[H_3PSEu]^{3+}$	+2.43	+0.24	−0.55	
$[H_3PSYb]^{3+}$	+2.36	+0.24	−0.50	
$[Me_3PSLa]^{3+}$	+2.39	+0.60	−0.63	
$[Me_3PSEu]^{3+}$	+2.30	+0.59	−0.56	
$[Me_3PSYb]^{3+}$	+2.22	+0.58	−0.50	
$[Et_3PSLa]^{3+}$	+2.34	+0.51	−0.61	
$[Et_3PSEu]^{3+}$	+2.25	+0.51	−0.55	
$[Et_3PSYb]^{3+}$	+2.17	+0.50	−0.48	
$[Ph_3PSLa]^{3+}$	+2.26	+0.42	−0.61	
$[Ph_3PSEu]^{3+}$	+2.17	+0.41	−0.54	
$[Ph_3PSYb]^{3+}$	+2.08	+0.41	−0.48	
$Me_3PSLaCl_3$	+1.50	+0.56	−0.49	−0.60
$Me_3PSEuCl_3$	+1.37	+0.56	−0.47	−0.56
$Me_3PSYbCl_3$	+1.29	+0.56	−0.46	−0.54
$Et_3PSLaCl_3$	+1.49	+0.46	−0.50	−0.59
$Et_3PSEuCl_3$	+1.36	+0.46	−0.48	−0.56
$Et_3PSYbCl_3$	+1.28	+0.45	−0.47	−0.54
$Ph_3PSLaCl_3$	+1.52	+0.36	−0.47	−0.58
$Ph_3PSEuCl_3$	+1.39	+0.36	−0.46	−0.54
$Ph_3PSYbCl_3$	+1.31	+0.36	−0.45	−0.52
$(Me_3PS)_2LaCl_3$	+1.40	+0.57	−0.47	−0.60
$(Me_3PS)_2EuCl_3$	+1.29	+0.56	−0.45	−0.57
$(Me_3PS)_2YbCl_3$	+1.23	+0.56	−0.44	−0.55

[a] The charge belonging to the M−Cl bond length given in Table 2.

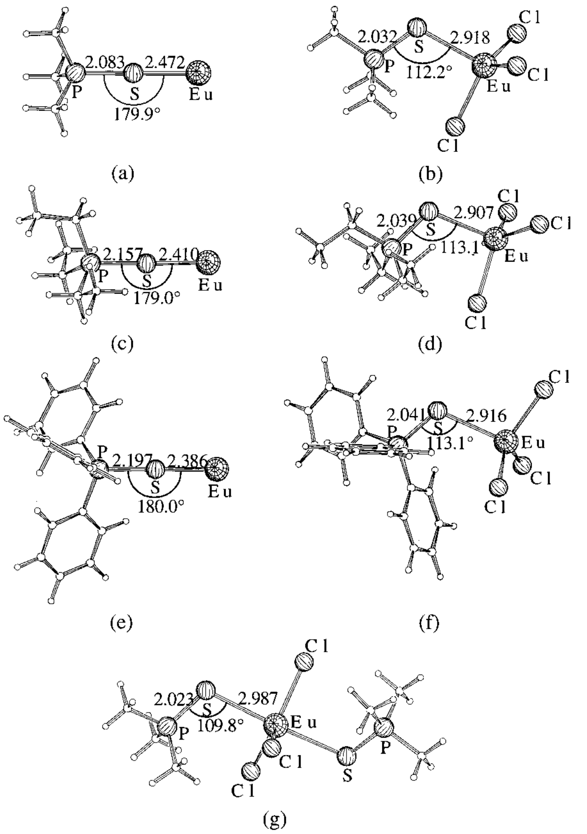


Figure 1. Structures of the calculated europium complexes.

Furthermore, for a given cation, the M−S distances depend on the substituent R of the ligand. They follow the general observation that stronger bonds tend to be shorter than weaker ones. For example, the Eu−S distance reduces from 2.425 Å in $[Me_3PSEu]^{3+}$ ($\Delta E = +195.2$ kcal/mol) to 2.410 Å in $[Et_3PSEu]^{3+}$ ($\Delta E = +208.5$ kcal/mol) and to 2.386Å in $[Ph_3PSEu]^{3+}$ ($\Delta E = 226.6$ kcal/mol).

The Mulliken charges on the metal M follow the expected trends, getting less positive with decreasing metal ion size and increasing donor strength of the ligand **L**, the effect of the latter being much smaller (see Table 3). The lowest metal ion charge is therefore found in $[Ph_3PSYb]^{3+}$ (+2.08) where the largest part of the total positive charge still remains on the metal. This shows the prevalent ionic character of the S−M bond, which gets most of its strength from the charge−dipole interactions between the cation and the ligand. In the $[R_3PSM]^{3+}$ complexes, the sulfur atomic charge is more negative, and the phosphorus charge is somewhat more positive than in the corresponding R_3PS ligand (Table 3), due to the polarization induced in the P═S bond upon complexation.

3.2. The R_3PSMCl_3 Complexes. The most striking difference of the R_3PSMCl_3 complexes compared to the $[R_3PSM]^{3+}$ ones is their S−M dissociation energy, which is much weaker (Table 1). This is to be expected, because the ligand binds to a formally neutral MCl_3 moiety instead of a highly charged M^{3+} cation. This leads both to a decrease of the electrostatic attraction and a weakening of the donor-acceptor interaction due to the higher charge density in the valence space of the metal ion.

The total range of calculated dissociation energies for the R_3PSMCl_3 complexes goes from 34.9 kcal/mol to 39.8 kcal/mol (Table 1). The binding energy differences in the neutral 1:1 complexes are thus smaller by more than one order than in the ionic ones. One reason for this is that all influences are scaled down due to the generally weaker ligand−metal interaction in the neutral complexes. However, it has to be noted that in addition to this scaling effect, *differences* in the neutral complexes are still smaller than the results for the ionic complexes would suggest.

Regarding the influence of the substituents R on the ligand **L** the effect of a lengthening of the alkylic chain remains the same as in the charged complexes: it leads to an increased dissociation energy. The effect is small, however, in the case of $Me_3PSYbCl_3$ and $Et_3PSYbCl_3$ the difference is only 1.2 kcal/mol. For the other metals it is even less. Contrary to the observations with the ionic complexes, *exchanging alkylic substituents for arylic ones* leads to *a weakening of the sulfur−metal bond in the neutral compounds*. For $Et_3PSYbCl_3$ and $Ph_3PSYbCl_3$, the difference is 2.9 kcal/mol in favor of the former. Possible explanations for this vanishing of the aryl effect are repulsion between the chloride atoms and the phenyl rings and the increased covalent character of the ligand−metal bond in the neutral complexes, which benefits less from the polarizability of the phenyl substituents.

The order of binding energies for the different metals in the R_3PSMCl_3 complexes is the same as in the $[R_3PSM]^{3+}$ complexes, i.e., the harder the metal ion, the larger the sulfur−metal dissociation energy. The differences are much smaller, though. For $Et_3PSLaCl_3$ compared to $Et_3PSYbCl_3$ it is only 2.9 kcal/mol, for the other ligands it is even less. The same diminishing of metal ion selectivity was also observed for the R_3POMCl_3 complexes.[31]

The structures of the R_3PSMCl_3 complexes show two notable features (Table 1 and Figure 1). *The P−S−M bond is bent and the S−M bond length is much larger than in the ionic compounds*. The latter is consistent with the lower sulphur-metal binding energies and the decreased positive charge on the cation. The effect is quite large, the biggest difference being about 0.7 Å by which the S−La bond in $Ph_3PSLaCl_3$ is longer than the one in $[Ph_3PSLa]^{3+}$. The bending about the sulphur atom shows that *there is a fundamental difference between the sulfur−metal bonds in the charged and neutral species*, as the bonding changes from an ionic bond in the former to a partially covalent directed bond in the latter. The preference for the actual structures is quite strong for both compound types. Bending of the P−S−Eu bond in $[Me_3PsEu]^{3+}$ from $\alpha = 180°$ to $\alpha = 130°$ (see Scheme 2) increases its energy by nearly 70 kcal/mol. This contrasts with the $Me_3PSEuCl_3$ system, where the optimized linear structure is about 15 kcal/mol above the optimized bent form ($\alpha = 112°$), energetically.

3.3. The $(Me_3PS)_2MCl_3$ Complexes. The dissociation energy of the second thiophosphoryl ligand bound to the lanthanide atom is about two third of that of the first one (Table 1). The decrease relates to reduced cationic charge and orbital availability in Me_3PSMCl_3, compared to MCl_3. The most interesting fact about the dissociation energy decrease is that it gets larger for the smaller lanthanide cations. This leads to *a change of order regarding the cation selectivity*, i.e., the second ligand binds stronger to the larger cations. Between $(Me_3PS)_2LaCl_3$ and $(Me_3PS)_2YbCl_3$ the difference is 1.6 kcal/mol in favor of the former. If one just looks at the average per ligand dissociation energies of both Me_3PS ligands, the cation size selectivity almost vanishes (the values are 29.5, 30.1, and 30.1 kcal/mol for La, Eu, and Yb, respectively).

The reason for this order change becomes clear when one looks at the neutral 1:1 complexes, in which the MCl_3 moiety is distorted towards a tetrahedral shape. This effect gets stronger from La to Yb, with increasing ligand−metal binding strength. Accordingly, it also increases from Me_3PS to Et_3PS and Ph_3PS ligands (Table 1). When the second Me_3PS ligand is attached to Me_2PSMCl_3, this distortion is reversed again to an approximately planar shape of the MCl_3 substructure. This costs the more energy the stronger the distortion is, which means it needs the most energy in the case of Yb and causes the observed change of order of selectivity. To prove this assumption we have calculated the Me_3PSMCl_3 complexes under the constraint of a planar MCl_3 substructure. If one calculates the dissociation energies of the second ligands relative to these constrained complexes, the original order of selectivity is reestablished (see Table 1). It is thus clear that *the selectivity of the thiophosphoryl ligands cannot be derived solely from the intrinsic properties of the sulfur−metal interactions in 1:1 ionic complexes*, but is the result of the effects of all ligands involved.

Concerning geometrical features (Table 2), the main distinctions between the 1:1 and the 2:1 neutral complexes are the longer S−M bonds, in line with the corresponding lower dissociation energies. The M−Cl bonds are also longer, due to increased repulsions with the ligands, and/or reduced attractions by the cation. The P−S−M angles are a few degrees smaller than in the 1:1 complexes, which suggests that there is no significant crowding in the coordination sphere of the metal atom. This is also indicative of the softer binding character of the sulfur−lanthanide bond, when the coordination number of the metal is increased.

4. Discussion

4.1. Comparison of Calculated Structures to Related X-Ray Data. We now will try to assess the reliability of the calculated structures. This is difficult because we know no experimental structures of thiophosphoryl complexes of lanthanides. We therefore have to compare our results with experimental data obtained for dithiophosphinate complexes, where the ligands formally have a charge of −1. Most of them bear O-alkyl, instead of alkyl substituents (Table 4). The structures calculated by us are collected in Table 2, while selected experimental parameters can be found in Table 4.

TABLE 4: Experimental Structures

compound	formula	$(Ln-S)_{long}$	$(Ln-S)_{short}$	ref
CAXYIJ[a]	$((iPrO)_2PS_2)_3(AcNMe_2)_2La$	3.045	2.988	*i*
DOJKUI[b]	$((EtO)_2PS_2)_3((PhCH_2)_2SO)_2La$	3.091	2.992	*j*
DUWSET[c]	$((iPrO)_2PS_2)_3(DMSO)_2La$	3.015	2.984	*k*
ETPLAP10[d]	$((EtO)_2PS_2)_3(Ph_3PO)_2La$	3.092	2.981	*l*
ASTPSA[e]	$[((EtO)_2PS_2)_4La]^-$	3.013	2.958	*m*
FEMJEM[f]	$[(Et_2PS_2)_4La]^-$	3.013	2.926	*n*
DUWSIX[g]	$[((iPrO)_2PS_2)_2(DMSO)_3Eu]^+$	2.891	2.872	*k*
DUWSIX[h]	$[((iPrO)_2PS_2)_4Eu]^-$	2.912	2.872	*k*

[a] bis(*N*,*N*-Dimethylacetamide)-tris(O,O′-di-isopropyl-dithiophosphato)-lanthanium(III). [b] bis(dibenzylsulfoxide)-tris(O,O′-diethyldithiophosphato-S,S′)-lanthanum(III). [c] tris(O,O′-Di-isopropyl dithiophosphato-S,S′)-bis-(dimethylsulfoxide-O)-lanthanum(III). [d] tris(O,O′-Diethyl-phosphorodithioato)-bis(triphenylphosphine oxide) lanthanum(III). [e] tetrakis(O,O′-diethyldithiophosphato)-lanthanum(III) (1^-). [f] tetrakis(diethyldithiophosphinate-S,S′)-lanthanum(III) (1^-). [g] bis(O,O′-Di-isopropyl dithiophosphato-S,S′)-tris(dimethylsulfoxide-O)-europium(III). [h] tetrakis(O,O′-di-isopropyl dithiophosphato-S,S′)-europium(III) (1^-). [i] Nagai, K.; Sato, Y.; Kondo, S.; Ouchi, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2605. [j] Imai, T.; Shimoi, M.; Ouchi, A. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 669. [k] Imai, T.; Nakamura, M.; Nagai, K.; Ohki, Y.; Suzuki, Y.; Shimoi, M.; Ouchi, A. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2115. [l] Pinkerton, A. A.; Schwarzenbach, D. *J. Chem. Soc., Dalton Trans.* **1976**, 2466. [m] Pinkerton, A. A.; Schwarzenbach, D. *J. Chem. Soc., Dalton Trans.* **1981**, 1470. [n] Pinkerton, A. A.; Schwarzenbach, D.; Spiliadis, S. *Inorg. Chim. Acta* **1987**, *128*, 283.

Experimental La−S bond lengths (rows 1−6 in Table 4) range from 2.926 to 3.092Å. For the $[R_3PSLa]^{3+}$ complexes, we obtained bond lengths from 2.486 to 2.585 Å, which are much shorter. However, in these complexes the electron deficiency on the lanthanum is certainly very high, which causes very strong interactions and therefore explains the short La−S bond. In the neutral $R_3PSLaCl_3$ and $(Me_3PS)_2LaCl_3$ complexes we obtain bond lengths from 3.028 to 3.107 Å. These values are within the experimentally observed range. However, we want to point out that the La−S bonds in the experimental set of compounds should be somewhat longer than those in the computed set, due to increased ligand−ligand repulsion.

We know only one X-ray structure of a dithiophosphinate complex of europium. In this complex the Eu−S distances (lines 7 and 8 in Table 4) range from 2.872 to 2.912 Å. As in the case of the lanthanum complexes, and for the same reason, the calculated $[Eu_3PSM]^{3+}$ type complexes show much shorter Eu−S bond lengths, from 2.386 to 2.472 Å. In the neutral $R_3PSEuCl_3$ and $(Me_3PS)_2EuCl_3$ complexes the calculated Eu−S distances range from 2.907 to 2.987Å, which is about 0.05 Å more than in the experimental structure. However, as our main concern is the comparison of energy trends and, furthermore, the structures obtained do not deviate qualitatively from experiment, we conclude that the accuracy of the reported structures is fully sufficient.

Concerning the binding mode of the cation, we notice that in the X-ray structures of dithiophosphinate complexes, the metal displays a bridging coordination to the PS_2- moiety, implying therefore a bent P−S−M angle. This feature can however hardly be compared to our systems.

4.2. Discussion of Possible Improvements to the Used Methods. In order to keep this work consistent with previous efforts,[31] and also to save computer time, we have concentrated on the HF method, thereby denying the effects of electron correlation. As shown in refs 31 and 52, correlation effects calculated on the DFT level have a significant impact on the

TABLE 5: Calculated Metal−Ligand Dissociation Energies ΔE (kcal/mol) from DFT Calculations (see Table 1 for Definitions)

	DFT results		
complex	ΔE	$\Delta\Delta E_L$	$\Delta\Delta E_M$
$[H_3PSLa]^{3+}$	+171.7	0.0	
$[H_3PSEu]^{3+}$	+191.3	+19.6	−45.9
$[Me_3PSEu]^{3+}$	+237.2		0.0
$(Me_3PS)_2LaCl_3$	+20.4	0.0	
$(Me_3PS)_2EuCl_3$	+20.5	+0.1	
$(Me_3PS)_2YbCl_3$	+20.2	−0.2	

TABLE 6: Selected Optimized Distances (r; angströms) and angles (α, degrees) from DFT Calculations (see Table 2 for Definitions)

	DFT results				
compound	r(S−M)	r(P−S)	r(M−Cl)	α(P−S−M)	α(S−M−Cl)
H_3PS		1.968			
Me_3PS		1.983			
H_3PSEu^{3+}	2.439	2.165		179.5	
Me_3PSEu^{3+}	2.410	2.205		179.6	
$Me_3PSLaCl_3$	2.983	2.045	2.702	108.7	96.0
$Me_3PSEuCl_3$	2.862	2.047	2.598	108.1	98.8
$Me_3PSYbCl_3$	2.757	2.049	2.506	107.8	101.0
$(Me_3PS)_2LaCl_3$	3.040	2.035	2.729	105.7	89.3
$(Me_3PS)_2EuCl_3$	2.917	2.037	2.629	106.3	90.7
$(Me_3PS)_2YbCl_3$	2.815	2.039	2.541	106.7	91.8

dissociation energies and geometries obtained for some phosphoryl complexes. We now want to expand this discussion to some of the thiophosphoryl complexes covered here.

Tables 5 and 6 show the dissociation energies and geometries obtained using the BP86 functional with the same basis set as in the HF calculations. For the charged complexes the dissociation energies calculated on the DFT level are higher by about 40 kcal/mol, compared to their HF counterparts. However, the energy trends and, within a few kcal/mol, also the *differences* in ΔE's are the same on the HF and the DFT level. For the dissociation energies of the neutral 2:1 complexes the values obtained with DFT are smaller by a few kcal/mol than those obtained on the HF level. The differences in ΔE's caused by the change of the lanthanide cations get very close to zero, leaving no significant trend in the series. However, generally the agreement of energy trends between HF and DFT is satisfying.

For the structures obtained on the DFT level the most important change from the HF geometries is the shortening of the lanthanide−sulfur bond. This effect is stronger in the neutral compounds, where it amounts to about 0.07 Å, compared to only about 0.03 Å in the charged ones. As can be seen from section 4.1, the DFT results for the Ln−S bond lengths are therefore in better agreement with "experiment" than the HF values. The second important trend when going from HF to DFT is the elongation of the sulfur−phosphorous bond. Unlike the Ln−S bond shortening, this effect is stronger in the charged complexes. Metal−ligand bond elongation upon changing from the HF to the DFT level is not uncommon. An example related to this work has been reported for dithiophosphinate complexes of zinc.[49]

As stated in section 2, we did not use a set of f-orbitals in the valence basis set of the lanthanide cations, as they are implicitly included in the ECP. The justification for this approach can be seen from the test calculation we did on $Me_3PSEuCl_3$. Both the dissociation energy (Table 1) and the geometry (Table 2) do not change significantly upon the introduction of f-orbitals and the effects are considerably smaller than those of electron correlation discussed above.

4.3. Comparison of Phosphoryl and Thiophosphoryl Ligands. While phosphoryl and thiophosphoryl ligands **L** are isoelectronic and therefore basically have the same binding capabilities, R_3PO is considered to be a hard base while R_3PS is considered to be a soft base.[50] One should expect that this leads to lower binding energies for the thiophosphoryl complexes due to the hardness of the lanthanide cations. On the other hand it is conceivable that the thiophosphoryl ligands show more selectivity for the differently sized metals. However, only the first assumption holds. In the cationic **L**M^{3+} series the dissociation energies of the thiophosphoryl complexes are about 80% of those of the phosphoryl complexes. In the neutral **L**MCl_3 series they are less than 60%. The cation selectivity of the thiophosphoryl ligands is somewhat smaller than that of the phosphoryl ligands as well. For example, the difference between the binding energy of Ph_3PO to La^{3+} vs Yb^{3+} is 42.9 kcal/mol or 14.3% of the total binding energy of $[Ph_3POYb]^{3+}$. The same values for the corresponding complexes of Ph_3PS are 40.1 kcal/mol or 16.3%. The dissociation energy difference of $Et_3POLaCl_3$ and $Et_3POYbCl_3$ is 7.4 kcal/mol or 10.0% of the total value for the latter. The same difference for $Et_3PSLaCl_3$ and $Et_3PSYbCl_3$ is 2.9 kcal/mol or 7.3%. Whether similar trends would hold when actinides are compared to lanthanides remains to be investigated.

While the dissociation energies of the thiophosphoryl complexes are smaller than those of the phosphoryl complexes, we notice that the trends are the same for both types of compounds. The influence of exchanging the substituent R or binding to a different metal cation is basically equivalent. The same is true for the structures of the cationic species. Of course the bond lengths to the oxygen atoms are shorter than those to the sulphur atoms but nevertheless all trends are the same. For the neutral R_3POMCl_3 phosphoryl complexes a linear P−O−M arrangement was assumed in ref 31 but more recent geometry optimizations lead to a slightly bent coordination.[51] The calculations reported here show that the thiophosphoryl compounds are also bent, when counterions are taken into account.

4.4. Binding Strength and Selectivity of Thiophosphoryl Ligands. Whether compounds containing thiophosphoryl groups are worth being investigated as ligands for lanthanide/actinide separation cannot be clarified based solely on the results obtained here. However, some points should be kept in mind when looking at this option. The calculations show that the thiophosphoryl−lanthanide interactions are intrinsically weaker and less selective than the phosphoryl−lanthanide interactions. However, these energies are still high, and comparable to those obtained with neutral amide or pyridine ligands.[52] The situation should markedly improve with the dithiophosphinate ligands, which are negatively charged and can achieve a bidentate binding mode. The small preference of the thiophosphoryl ligand for the different metals in the neutral cases make its *selective properties dependent on the other ligands present in the coordination sphere of the metal*, and on solvent effects, though. This is illustrated by the change of the metal preference order when going from the neutral 1:1 to the 2:1 complexes. It has to be concluded that when one searches for efficient extracting ligands, the basic properties, indices like proton affinity or even intrinsic "gas phase" interaction energies in 1:1 **L**M^{n+} complexes may only be very rough guidelines.

5. Conclusions

The calculations reported here give insight in the intrinsic gas phase properties of the sulfur−metal bond in thiophosphoryl complexes of lanthanides. They show that the thiophosphoryl group is a very effective ligand for trivalent lanthanide cations but less strong and less selective than phosphoryl containing ligands.

The substituents R on the ligand play an important role for the dissociation energies of the cationic 1:1 complexes, but their influence decreases considerably when counterions are present. For the ionic $\mathbf{L}M^{3+}$ complexes a strong preference for arylic substituents was found, while the neutral $\mathbf{L}MCl_3$ complexes slightly prefer alkylic substituents. However, as the differences in the neutral complexes are small, no general rule for which choice of R is preferable can be given, as the nature of the counterions and the question of monodentate vs. bidentate binding of dithiophosphinate ligands likely modulate the alkyl/aryl substituent effects as well.

In the positively charged and neutral 1:1 complexes the dissociation energies get higher when the metal gets smaller. This ordering is turned around in the 2:1 complexes. In all the neutral complexes the effect of the metal size is small, which means that *the selective properties of the thiophosphoryl ligands are heavily depending on the coordination sphere of the metal*.

Regarding the structures it was found that the sulfur atom prefers the bent arrangement, also known from experimental structures, in the presence of counterions. In the absence of counterions a linear arrangement is preferred. It is interesting to note that the ligand−metal interactions “under experimental conditions” in condensed phases, i.e., with counterions present, are in fact closer related to ligand−proton than to ligand−M^{3+} interactions. The ligand−proton bond shows a partially covalent character and is bent about the sulfur such as it is also found experimentally and with MCl_3, whereas the ligand−M^{3+} bond is almost purely ionic and linear.

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Supporting Information Available: Calculated total energies in hartrees. Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

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