Ion Exchange Determination of Complexation of Triphenylarsine and Triphenylstibine to Europium(III) Ion in Benzonitrile

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It has been shown for the first time that a lanthanide can be complexed by a stibine or a neutral arsine.

No complexes of lanthanides with monodentate stibines have been reported. Salts of $HAsPh_2$ and $HASBu^t{}_2$ containing a lanthanide–arsenic bond have been reported by Schumann and coworkers,[1,2] but complexes of the neutral trialkyls or triaryls have not been reported. Furthermore, the order of complexing ability[3] of arsines and stibines with higher oxidation states of transition metals (such as Ni^{III}) decreases in the order As > Sb. We have found the opposite order for Eu^{III}. Also, in general the lanthanides prefer oxygen and nitrogen donors to those of arsenic or antimony.[4] We have found that Eu^{3+} bonds more strongly to triphenylarsine and triphenylstibine than to the C≡N group of benzonitrile.

The objective of this work was to determine by the ion exchange method whether complexes of Eu^{3+} could be formed with neutral arsines or stibines. The approach was to form first an essentially uncharged complex ion of Eu^{3+} with ClO_4^- in benzonitrile and then to displace the bound ClO_4^- ions stepwise with triphenylarsine or triphenylstibine to give complexes of progressively higher (+) charges. Ion exchange was chosen to determine the nature of the complexes because of its applicability when even only a few atoms of the metallic element are available[5] (as in mendelevium and heavier).

The ion exchange equilibrium between a radioactive tracer ion, B^{b+}, that forms a complexed ion ($BL_n^{+b-\lambda n}$), and a bulk displaceable ion, A^{a+}, can be represented by equation (1), where (R) refers to the resin phase and L to the ligand of charge $-\lambda$. In this work B is Eu^{3+}, A is Ba^{2+}, and L is ClO_4^-. The ion exchanger was Amberlyst 15, a sulphonic acid type macroreticular resin produced by Rohm and Haas.[6]

$$(b-\lambda n)A^{a+}{}_{(R)} + a(BL_n^{+b-\lambda n}) = a(BL_n^{+b-\lambda n})_{(R)} + (b-\lambda n)A^{a+} \quad (1)$$

If the distribution coefficient is defined in the usual way as $D_B = [B]_{(R)}/[B]$, then a plot of log D_B *vs.* log $[A^{a+}]$ will have a slope of $-(b-\lambda n)/a$ if [B] is in trace concentrations relative to [A], if A is uncomplexed, if the applicable activity coefficient ratios are constant, and if the formula of the species in solution is the same as on the resin.[7,8]

Distribution coefficients were determined by counting methods after the solutions and resin were equilibrated in batch type ion exchange experiments by shaking vigorously for 16—22 h. All experiments were carried out at room temperature under argon with a moisture content of less than 10 p.p.m.

In all experiments the $Ba(ClO_4)_2$ concentration was varied between ~0.03 and ~0.06 M. The plot of the experimentally determined log *D* of europium tracer *vs.* $Ba(ClO_4)_2$ concentration (M) in pure benzonitrile gave a slope near zero (−0.2). This near zero slope showed that almost three ClO_4^- on the average ions were bound to each Eu^{3+} ion to give a nearly uncharged species in solution. (It is already known from spectroscopic results that Eu^{3+} forms complexes with ClO_4^- in acetonitrile.[9]) When triphenylarsine was added to the benzonitrile to a concentration of 0.003 M, the slope was changed to -0.55 ($-1/2$). The change on the Eu complex was thus changed to 1+ from nearly zero showing that almost one ClO_4^- ion on the average had been displaced. An increase of the triphenylarsine concentration to 0.07 M caused the slope to increase to -0.92 ($-2/2$) showing that one more ClO_4^- had been displaced by the triphenylarsine from the Eu^{3+} to give a complex of charge 2+. On the other hand, if triphenylstibine was added to the benzonitrile at a concentration of only 0.003 M, a slope of -1.53 ($-3/2$) was obtained. Thus the triphenylstibine was able to displace all of the ClO_4^- ions on the Eu^{3+} whereas the arsine could not.

Changes in activity coefficients cannot produce different slopes from one set of experimental conditions to another because the addition of the molecular reagents triphenylarsine and triphenylstibine to the benzonitrile does not significantly alter the ionic strength or the bulk dielectric constant of the system. Furthermore the set of ion exchange results based on the slopes of the log D_{Eu} *vs.* $\log[Ba(ClO_4)_2]$ plots give an internally consistent picture of stepwise displacement of ClO_4^- ions from the central Eu^{3+} ion by the triphenylarsine or triphenylstibine to yield predominantly a single complex ion of a given charge at each stage. This internal consistency suggests that activity coefficients do not (as might be expected) significantly affect the slopes and that the theoretical slope of $-(b-\lambda n)/a$ is obtained in each case. The ideality of behaviour exhibited in these experiments has also been found in exchange of Eu^{III} *vs.* $CsClO_4$ and $Ba(ClO_4)_2$ in Me_2SO, where slopes of -3 and $-3/2$ were obtained even though the change in ionic strength was quite different in the two cases.[10]

In the above interpretation of the slopes, we assume that the charge on the barium ion is 2+; that is, that the barium ion is not complexed by ClO_4^-. It is known that the alkali and alkaline earth metals do not complex with arsines and stibines,[9] so the state of the barium ion is the same throughout these experiments. The only reasonable combination of numbers that can give 3/2 (as obtained in the 0.003 M triphenylstibine case) is 3+ on the Eu and 2+ on the Ba since it would be fortuitous indeed to have both the Eu and the Ba ions complexed with ClO_4^- in just the right amounts to give the theoretical slope for the bare ions. Thus the Ba can be assumed to be 2+ in all of the experiments.

These experiments then show that complexes can be formed between Eu^{3+} and a stibine and a neutral arsine. The stibine forms a stronger complex than the arsine in contrast to the behaviour of the higher oxidation states of the d transition metals.[3] It is also shown that the arsine and stibine are better able to displace the ClO_4^- from the europium than the benzonitrile solvent although, in general, lanthanides show a strong preference for oxygen and nitrogen donors over those of arsenic and antimony.[4]

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