Tris- and Tetrakisethylenediamine Chelates of Tripositive Lanthanide Ions

Sir:

Classically, most of the complex species containing the lanthanide ions have been derived from anionic ligands with oxygen, or combinations of oxygen and nitrogen, donor sites.[1] The facts that strongly basic amines precipitate hydrous oxides or hydroxides when added to aqueous lanthanide salt solutions and that isolable species containing less basic amines have been described only rarely have led to the assumption that nitrogen-atom coordination to the lanthanide ions is weak. More recently species containing 2,2′-bipyridyl or 1,10-phenanthroline have been isolated from aqueous ethanol, usually as bis chelates with the anions or solvent molecules satisfying the remaining coordination positions.[2] Only when the anion present was perchlorate could a tetrakis complex be isolated.[3]

By carefully controlling the experimental conditions and maintaining completely anhydrous systems, we have used the direct reaction of ethylenediamine with a lanthanide(III) salt in acetonitrile to prepare solid compounds of compositions $Ln(en)_3X_3$ and $Ln(en)_4X_3$ ($X = NO_3^-$, ClO_4^-, Cl^-, Br^-). Compositions have been established by microanalyses. These compounds are hygroscopic, crystalline substances that are rapidly hydrolyzed in contact with the atmosphere of the laboratory.

The infrared spectra of the $Ln(en)_3(NO_3)_3$ compounds indicate clearly the presence of coordinated (C_{2v}) nitrate groups; those of the $Ln(en)_4(NO_3)_3$ compounds indicate the presence of ionic (D_{3h}) groups. Both the ability of ethylenediamine to replace nitrate ion in the coordination sphere and the presence of at least eight-coordinate Ln^{3+} are indicated.

Calorimetric evaluation of the stepwise enthalpies of formation has demonstrated the thermodynamic stabilities of the species $Ln(en)_n^{3+}$ (n = 1–4) in acetonitrile solution. Four distinct enthalpy changes are observable as the ligand is added to a solution of the lanthanide salt. From plots of enthalpy change *vs.* ligand to metal ion mole ratio, stabilities of the species in solution were calculated.[4] Typical values for enthalpies of formation (ΔH_n) and formation constants (K_n) are summarized for the neodymium perchlorate system in Table I.

Table I. Data for Formation of $Nd(en)_n^{3+}$ in Acetonitrile

Species	$-\Delta H_n$, kcal mole^{-1}	Log K_n
$Nd(en)^{3+}$	18.0	10.1
$Nd(en)_2^{3+}$	16.1	8.4
$Nd(en)_3^{3+}$	13.0	6.4
$Nd(en)_4^{3+}$	10.1	3.4

Both the equilibria relating to the formation of the ethylenediamine chelates and the structural characteristics of the isolated compounds are under continuing investigation. Parallel studies involving other pure nitrogen donors are also in progress.

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Chemical Generation of the Ammoniated Electron *via* Ytterbium(II)

Sir:

We have found that substantial concentrations of the solvated electron in liquid ammonia can be prepared by treating ytterbium(II) solutions with potassium amide.

When ytterbium metal was dissolved in liquid ammonia[1] and allowed to stand at room temperature until the blue color was discharged, the solid formed was found to be virtually insoluble in liquid ammonia and to contain paramagnetic Yb(III). The solid appeared to consist of white and rust-colored constituents, and to have an over-all N/Yb ratio of 2.8; we regard the solid as an ytterbium(III) imide–amide mixture.

In attempts to prepare pure $Yb(NH_2)_2$, a light yellow-orange solution of ytterbium(II) iodide (from Yb metal and NH_4I) was mixed at 25° in a pressurized glass system with pale yellow potassium amide solution. An intense blue solution resulted, regardless of whether the YbI_2 or KNH_2 was in excess. A white precipitate was also formed, which on analysis gave an N/Yb ratio of 3.5; we regard this as ammoniated $Yb(NH_2)_3$. Ytterbium(II) thiocyanate, substituted for the iodide, also gave the blue solution. The imide–amide mixture, from ytterbium metal and ammonia, was found to yield no blue coloration when treated with KNH_2 in liquid ammonia; this is in harmony with the presence of Yb(III) and the absence of Yb(II).

The evidence that the blue solutions genuinely were of the ammoniated electron is as follows: (1) when decanted into a separate bulb and evaporated, first the characteristic golden color of concentrated metal solutions appeared, followed by the silvery metal itself; (2) extraction of the blue solution with mercury yielded a potassium amalgam; (3) ytterbium in the tripositive state was a product; (4) we observed the absorption spectrum of the blue solution in the near infrared and found the asymmetric band peaking at 5400 cm^{-1} at 24°, which is characteristic of ammoniated electrons, as reported by Corset and Lepoutre;[2] and (5) the absorbance of the solutions decayed by zero-order kinetics as the e_{am}^- was converted to H_2 and NH_2^-, as demonstrated by Warshawsky.[3]

Europium behaved in a manner analogous to that of ytterbium. Samarium, when treated similarly, exhibited only a faint blue coloration, and we believe that this can be attributed to the presence of a europium impurity (1.5% spectrographically). The evidence is that when Sm is dissolved in NH_3 solutions of NH_4I, it is oxidized to the tripositive state.

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