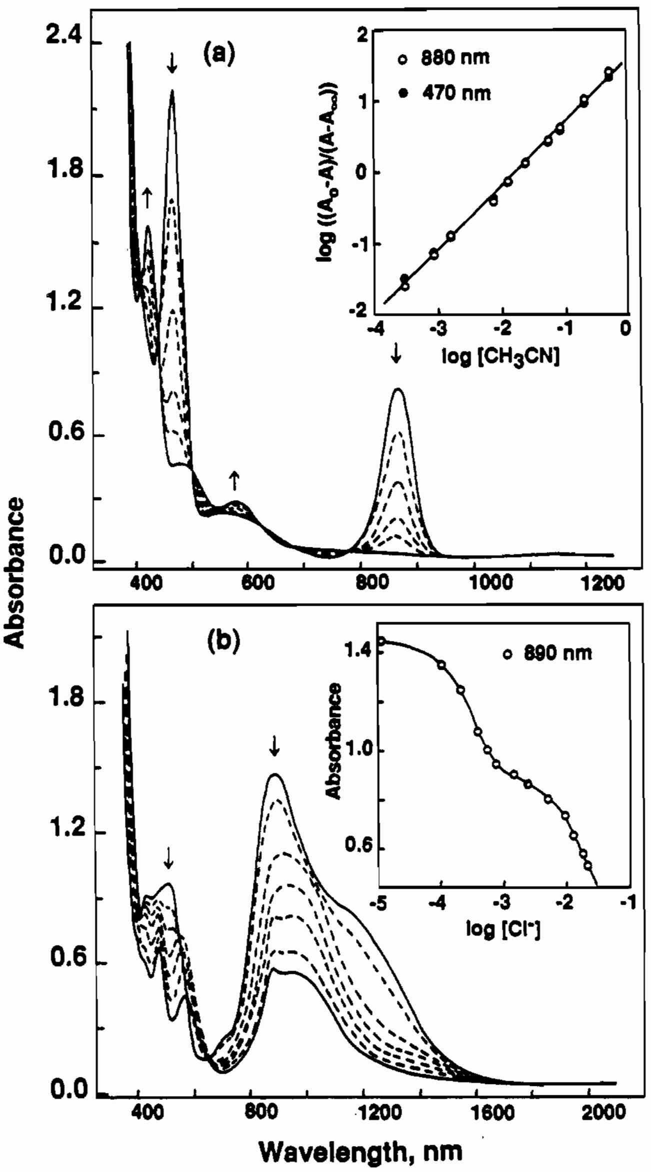

Figure 4. (a) Changes in the electronic absorption spectra of $Rh_2(dpf)_4$ in CH_2Cl_2 during titration with CH_3CN. The insert shows analysis of spectral data at 470 (•) and 880 (○) nm. (b) Changes in the electronic absorption spectra of $[Rh_2(dpf)_4]^+$ during titration with (TBA)Cl. The insert is a plot of absorption at 890 nm vs log [Cl^-].

obtained, even up to the addition of 100 equiv of Cl^-.

Figure 2b shows cyclic voltammograms of **1** in CH_2Cl_2 containing different concentrations of (TBA)CN. The binding of CN^- to $Rh_2(dpf)_4$ and $[Rh_2(dpf)_4]^+$ is accompanied by a decrease in currents for the processes at 0.34, 1.15, and −1.21 V, as two new waves appear at $E_{1/2}$ = −0.20 and 0.86 V. The second oxidation (process 3) completely disappears when 1 equiv of CN^- is added to solution, but an irreversible wave at 0.34 V (process 2) still exists under these conditions. This suggests an incomplete formation of $[Rh_2(dpf)_4(CN)]^-$, but there is a quantitative conversion to $Rh_2(dpf)_4(CN)$ after the first oxidation. The first oxidation and the first reduction of **1** both completely disappear upon addition of about 1.3 equiv of CN^- to solution.

The binding of CN^- to $Rh_2(dpf)_4$ strongly destabilizes both the LUMO and the HOMO of the complex. The relative magnitude of K_1 vs K_1' (K and K' are the formation constants for $[Rh^{II}_2(dpf)_4(CN)]^-$ and $[Rh^{II}Rh^{III}(dpf)_4(CN)]$) is given by $E_{1/2}' = E_{1/2} + (RT/nF) \log (K_1/K_1')$ where $E_{1/2}$ and $E_{1/2}'$ are half-wave potentials for the $[Rh^{II}_2(dpf)_4]/[Rh^{II}Rh^{III}(dpf)_4]^+$ and $[Rh^{II}_2(dpf)_4(CN)]^-/[Rh^{II}Rh^{III}(dpf)_4(CN)]$ couples, respectively. The cathodic potential shift of 0.54 V for the first oxidation is associated with a K_1/K_1' ratio of 7.0×10^{-10}, and the cathodic shift of 0.29 V for the second oxidation is related to a K_1'/K_1'' ratio of 1.2×10^{-5} (K'' is the formation constant for $[Rh_2(dpf)_4(CN)]^+$). The value of K_1 for the conversion of $Rh_2(dpf)_4$ to $[Rh_2(dpf)_4(CN)]^-$ was calculated as 7.0×10^4 from the UV–vis data, and this value was then used to obtain K_1' and K_1'', which were calculated as 1.0×10^{14} and 8.3×10^{18}, respectively.

A titration of **1** with (TBA)Cl was also carried out in CH_2Cl_2, 0.1 M TBAP. A cathodic shift of the second oxidation occurs as Cl^- is added to solution and is due to the formation of $Rh_2(dpf)_4Cl$. However, the first oxidation was always irreversible in the presence of Cl^-. The resulting voltammogram has an anodic peak at 0.31 V and a cathodic peak at −0.09 V, thus suggesting coordination of Cl^- by $\mathbf{1}^+$ but not by **1**. Binding constants for $Rh_2(dpf)_4(Cl)$ and $[Rh_2(dpf)_4(Cl)]^+$ were calculated as 8.2×10^3 and 3.2×10^8, while constants of 1.4×10^4 and 1.4×10^4 were calculated for the formation of $[Rh_2(dpf)_4(CH_3CN)]^+$ and $[Rh_2(dpf)_4(CH_3CN)]^{2+}$ from $[Rh_2(dpf)_4]^+$.

Summary. The structures of **1**, **1L**, and $\mathbf{1L}^+$ show that the Rh–Rh bond length is relatively insensitive to either axial ligation or change in formal oxidation state of the complex but that the Rh–N bond lengths and the N–Rh–Rh–N torsion angle are both sensitive to these perturbations. Complexation with CN^-, Cl^-, or CH_3CN stabilizes the higher oxidation states of the dirhodium species according to the order $CN^- > Cl^- > CH_3CN$. In contrast, a complexation with CO stabilizes Rh^{II}_2 but strongly destabilizes Rh^IRh^{II}. An axial polarization of the SOMO is reflected in the ESR spectra of $Rh^{II}Rh^{III}(dpf)_4(L)$ and the strong tendency for **1** to form only monoadducts. The reduction of $Rh_2(dpf)_4$ to $[Rh_2(dpf)_4]^-$ is metal centered, and the resulting product is structurally stable. $[Rh_2(dpf)_4]^-$ axially binds to CH_3CN, and the ESR spectrum of $[Rh_2(dpf)_4(CH_3CN)]^-$ is consistent with a $\sigma^*_{Rh-Rh}\sigma^*_{Rh-L}$ SOMO assignment where the odd electron is delocalized over the two rhodium centers and the nitrogen of the axially bound CH_3CN ligand.

Acknowledgment. This work was supported by the Robert A. Welch Foundation (J.L.B., Grant No. E-918; K.M.K., Grant No. E-680).

Supplementary Material Available: Tables SI–SIII, listing the UV–visible data, half-wave potentials, and ESR data for the various $Rh_2(dpf)_4$ adducts, and Tables SIV–SVII, listing data collection and processing parameters, atomic coordinates, hydrogen atomic coordinates, and anisotropic thermal parameters for **1**, **1L**, and $\mathbf{1L}^+$ (13 pages); Tables SVIII–SX, listing observed and calculated structure factors (57 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Inorganic Chemistry
and Physical Chemistry, University of Melbourne,
Parkville, Victoria 3052, Australia

Electronic Spectra of the Cations of Europium(II), Samarium(II), and Ytterbium(II) in Anhydrous Hydrogen Fluoride

Colin G. Barraclough, Russell W. Cockman,
and Thomas A. O'Donnell*

Received May 1, 1990

Anhydrous hydrogen fluoride (AHF), the acidity of which has been deliberately enhanced by the addition of Lewis acids, has been shown to be an excellent solvent for solvated transition-metal cations in both "normal", e.g. Co^{2+} and Pr^{3+},[1] and unusually high oxidation states, e.g. Ag^{2+}.[2] Much of our work has further extended the known and expected resistance of AHF toward powerful oxidants such as Ag^{2+}. It would require a very powerful oxidant to produce F_2 from HF. However, we have also dem-

---

* To whom correspondence should be addressed at the Department of Inorganic Chemistry.

onstrated an unexpected resistance to attack by powerful reductants, enabling the preparation and study of spectra of stable solutions of U^{3+}[3] and of Ti^{2+}, V^{2+}, and Cr^{2+}[4] to be carried out with comparative ease.

Earlier in this program of recording spectra of cations of d and f transition metals a general procedure was employed for solution preparation in which metals or fluorides in suspension in AHF were reacted with an excess of a Lewis acid such as SbF_5, AsF_5, or BF_3, and the resulting solutions were then investigated by UV–visible spectroscopy and other suitable spectroscopic methods.

We have extended our studies of solvated cations in AHF to include a comprehensive investigation of the lanthanides and have recorded spectra in AHF for virtually all of the lanthanides in oxidation state III.[2] As expected, the spectra in AHF, arising from f–f transitions, are very similar to those in water.

Our earlier preparation of stable solutions of U^{3+} and Ti^{2+} led us to study the possible generation in AHF of dipositive lanthanide cations. Values of $E°$ for the Ln^{3+}/Ln^{2+} couple in aqueous solution are −0.35, −1.05, and −1.55 V for the Eu, Yb, and Sm systems, respectively.[5] Solid compounds of Eu(II) are easily prepared, and Eu^{2+} is stable in acidic aqueous solution. Yb(II) and Sm(II) solid compounds can be prepared, particularly as iodides, but Yb^{2+} and Sm^{2+} reduce H_2O.[6a]

We have shown in this work that Eu^{2+}, Yb^{2+}, and Sm^{2+} cations are stable, even in *basic* HF, whereas dispositive d-transition-metal cations give insoluble fluorides in neutral AHF. Metallic Eu, Sm, and Yb react with *neat* AHF and dissolve with evolution of H_2, producing colorless (Eu, Yb) or yellow-orange (Sm) solutions that are remarkably stable and that contain HF-solvated divalent cations and solvated fluoride anions, the latter causing the solutions to be basic:

$$\mathrm{Ln} + 2\mathrm{HF} \xrightarrow{\mathrm{HF}} \mathrm{Ln}^{2+}(\mathrm{solv}) + 2\mathrm{F}^{-}(\mathrm{solv}) + \mathrm{H}_2$$

$$\mathrm{Ln} = \mathrm{Sm}, \mathrm{Eu}, \mathrm{Yb}$$

The cations have been observed previously as solutions of varying stability in a variety of media such as aqueous solution,[7,8] acetonitrile,[9] a calcium fluoride matrix,[10] liquid ammonia,[11] hexamethylphosphortriamide,[12] molten LiCl–KCl,[8] and room-temperature melts.[13–14]

In AHF the cations were characterized by their UV–visible spectra, which in general showed superior resolution to those obtained in other media. Reactions with some Lewis acids in HF solution were studied. Of particular interest was the reaction with GeF_4, which yielded insoluble precipitates that were identified as $LnGeF_6$. The yellow samarium compound was extensively studied by IR and Raman spectroscopies, X-ray powder photography, measurement of magnetic moment, and oxidation state determination by chemical means. Its properties are reported separately.[15]

Well-established chemistry of the lanthanides shows that the elements close to La, Gd, and Lu can be used to generate compounds in oxidation states other than III, the oxidation state typical of the series.[6b] Thus, Ce(IV) is stable in aqueous solution and in solids, but oxidation state IV becomes progressively more difficult to stabilize through Pr to Nd. The elements Tb and Dy, following Gd, show a similar trend. Eu, preceding Gd, is easily reduced to Eu(II) and Sm much less so. Unfortunately, Pm is not available to investigate any extension of this trend. On this basis, unsuccessful attempts were made to generate Tm^{2+} in AHF. La is among the least likely of the lanthanides to give high or low oxidation states. Metallic Tm and La reacted with AHF, but there was no evidence for divalent cations in solution.

Experimental Procedures

All volatile fluorides were manipulated in passivated Kel-F or stainless-steel vacuum systems as described previously.[1]

Commercial HF was routinely purified by four trap-to-trap distillations discarding "heads and tails". The purity was checked by measurement of conductance, and the product proved to be entirely satisfactory for all subsequent purposes.

All solid air-sensitive materials were manipulated in a N_2-filled glovebox.

UV-visible spectra were recorded (Cary 14) in Kel-F cells with synthetic sapphire windows previously described.[1]

Gaseous Lewis Acids. GeF_4, SiF_4, PF_5, and AsF_5 (Ozark-Mahoning) were used as supplied.

Lanthanides. The metals were obtained commercially (Koch-Light) as "massive" crystalline material in order to minimize oxide contamination. Surface oxide coatings were removed chemically for the reasons given, and by the methods described, below.

Preparation of Solutions. Any oxide present in a metallic sample would be protonated ultimately to H_3O^+ in AHF. It has been shown previously that the presence of protonated water in AHF markedly reduces the lifetime of strongly reducing solutes.[4] It was imperative therefore in this work that the oxide surfaces of the solid lanthanide metals be removed prior to attempted preparation of the Ln^{2+} solutions.

In a typical experiment ca. 100 mg of metal was weighed into a Kel-F tube. After evacuation, ca. 1 cm^3 of AHF was distilled onto the metal, which reacted readily (Sm, Eu) or sluggishly (Yb). After a few seconds each solution was decanted away in vacuo and a fresh quantity of AHF was added. Three or four washings were normally deemed to be sufficient to effectively remove oxide from the system, since additional treatments did not further extend the ultimate lifetimes of the solutions. Finally, AHF (5 cm^3) was distilled onto the cleaned metals and reaction was allowed to proceed at room temperature until the metals had dissolved. The solutions were then frozen at 196 °C, and the liberated H_2 was pumped away.

Other experimental procedures, such as the addition of Lewis acids and filling of cells, were carried out as described earlier.[1]

Results and Discussion

Lanthanide metals are highly electropositive and, in contrast to d transition metals, react easily with neutral AHF even without the addition of Lewis acids to give solutions that contain high concentrations of solvated divalent cations with solvated fluoride as anion in each case. The europium and ytterbium solutions are colorless, samarium(II) being yellow-orange.

Ready solubility of the lanthanide difluorides in the absence of added Lewis acid is not surprising, since the ionic radii of the Ln^{2+} ions[6c] are comparable with the radii of Ca^{2+} and Sr^{2+} and the difluorides of these alkaline-earth elements are appreciably soluble in *neat* AHF,[16] i.e. HF made slightly basic as a result of a small addition of the base F^- through dissolution of the solid difluorides. Quantitative measurements gave saturation in AHF at about 0.5 M for SmF_2 and 0.15 M for YbF_2 at room tem-

---

(1) Barraclough, C. G.; Cockman, R. W.; O'Donnell, T. A. *Inorg. Chem.* **1977**, *16*, 673.

(2) Cockman, R. W. Ph.D. Thesis, University of Melbourne, 1983.

(3) Baluka, M.; Edelstein, N.; O'Donnell, T. A. *Inorg. Chem.* **1981**, *20*, 3279.

(4) Barraclough, C. G.; Cockman, R. W.; O'Donnell, T. A.; Schofield, W. S. J. *Inorg. Chem.* **1982**, *21*, 2519.

(5) Morss, L. R. In *Standard Potentials in Aqueous Solution*; Bard, A. J., Parsons, R., Jordan, J., Eds.; IUPAC publication, Marcel Dekker: New York, 1985.

(6) Moeller, T. *The Chemistry of the Lanthanides*; Pergamon Press: Oxford, England, 1973; (a) pp 75–76, (b) pp 4–6, (c) p 21.

(7) Butement, F. D. S. *Trans. Faraday Soc.* **1948**, *44*, 617.

(8) Johnson, K. E.; McKenzie, J. R.; Sandoe, J. N. *J. Chem. Soc. A* **1968**, 2644.

(9) Dyke, J. M.; Hush, N. S. *J. Electroanal. Chem. Interfacial Electrochem.* **1972**, *36*, 337.

(10) McClure, D. S.; Kiss, Z. *J. Chem. Phys.* **1963**, *39*, 3251.

(11) Peer, W. J.; Lagowski, J. J. *J. Phys. Chem.* **1980**, *84*, 1110.

(12) Kamenskaya, A. N.; Bukietynska, K.; Mikeev, N. B.; Spitsin, V. I.; Jezowska-Trzebiatowska, B. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1979**, *24*, 633.

(13) Schoebrechts, J. P.; Gilbert, B. P.; Duyckaerts, G. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *145*, 127.

(14) Schoebrechts, J. P.; Gilbert, B. P.; Duyckaerts, G. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *145*, 139.

(15) Barraclough, C. G.; Cockman, R. W.; O'Donnell, T. A. *Inorg. Chem.*, following note in this issue.

(16) Jache, A. W.; Cady, G. *J. Phys. Chem.* **1952**, *56*, 1106.

(17) Johnson, K. E.; Sandoe, J. N. *J. Chem. Soc. A* **1969**, 1694.

(18) Spedding, D. H.; Pikal, M.; Ayers, B. O. *J. Phys. Chem.* **1966**, *70*, 2440. Habenschuss, A.; Spedding, F. H. *J. Chem. Phys.* **1979**, *70*, 2797. Habenschuss, A.; Spedding, F. H. *Ibid.* **1979**, *70*, 375. Habenschuss, A.; Spedding, F. H. *Ibid.* **1980**, *73*, 442.

Table I. Peak Positions for Europium(II) in HF and H_2O

	intense bands: 4f–5d		sharp bands: f–f
	λ, nm	ε, $m^2\ mol^{-1}$	λ, nm
HF	235	140	319 (sh), 317, 316, 314
H_2O^a	320.5	50	
	248	210	323, 320.5, 318, 315.5

[a] Reference 7.

Table II. Peak Positions for Samarium(II) in HF and H_2O

broad bands: 4f–5d				narrow bands: f–f	
HF		H_2O^a		HF	H_2O^a
λ, nm	E, cm^{-1}	λ, nm	E, cm^{-1}	λ, nm	λ, nm
~550	18 500	559	17 900	460	459
426	23 500	474	21 100	446	449
379	26 400	427	23 400	380 (sh)	442
364	27 500	331	30 200	378	378
		307	32 600	375	
314	31 800	260	38 500	355	
293	34 100	239	41 900	350	
278 (sh)				338 (sh)	
				327 (sh)	
208	48 100			266 (sh)	
201	49 800				

[a] Reference 7.

perature, values that compare favorably with 0.3 M for SrF_2 and 0.15 M for CaF_2 at 0 °C.[16]

The solutions as prepared showed remarkable stability, a solution 1×10^{-2} M in Sm^{2+} exhibiting the spectral characteristics of the ion even after 5 days at room temperature whereas Eu^{2+} was stable indefinitely. In contrast, the lifetime of Sm^{2+} in oxygen-free acidified aqueous solution is of the order of minutes. On very long standing, solutions of Sm^{2+} in HF were oxidized by the solvent. The expected quantity of H_2 was measured by PVT relationships, and SmF_3 was precipitated:

$$Sm^{2+}(solv) + 2F^-(solv) + HF \rightarrow SmF_3 + \tfrac{1}{2}H_2$$

UV–visible spectra gave no evidence for the respective trivalent ions, which is not surprising since the trifluorides are essentially insoluble in basic AHF. AHF is therefore a very convenient solvent, providing easy preparation from the metal of stable solutions of Ln^{2+} together with the effective exclusion of trivalent impurities, thus allowing study of very "clean" lanthanide(II) spectra.

For the purposes of discussion, the spectra of Eu^{2+} and Sm^{2+}, which contain bands due to f–f and 4f–5d transitions, will be examined together, whereas the spectrum of Yb^{2+} ($4f^{14}$), which exhibits only 4f–5d transitions, will be discussed separately.

Europium(II) and Samarium(II) Spectra. The spectra of Eu^{2+} and Sm^{2+} are shown in Figures 1a,b and 2. Peak positions are given in Tables I and II, respectively. The spectra contain both f–f and 4f–5d absorptions and are useful for comparison of the relative intensities and line shapes of the two types of absorptions. The forbidden f–f transistions occur deep within the electronic manifold of the ions and well away from the perturbations of ligand electric fields and are therefore sharp whereas the 5d levels are very sensitive to ligand fields and the allowed 4f–5d transitions are considerably broader and more intense. In the process of reducing the size of the Sm^{2+} spectrum for publication as Figure 2, a feature of the original spectrum as experimentally recorded on the chart has been lost. There was evidence for a band centered around 550 nm and believed to be responsible for the long-wavelength tail extending from about 500 to 800 nm.

We have shown previously that for Pr^{3+} and Nd^{3+},[1] and indeed for all the Ln^{3+} ions that have observable f–f transitions,[2] the f–f absorptions are shifted to higher energy by a small amount (typically ca. 200 cm^{-1}) in AHF solution when compared with those of spectra in other coordinating media such as H_2O or F^-. However, the energies of the 4f–5d transitions are very sensitive to the ligand field and are found to be shifted to higher energies by about 5000 cm^{-1} in the case of Ce^{3+} and Tb^{3+} in AHF when compared with other environments.[2]

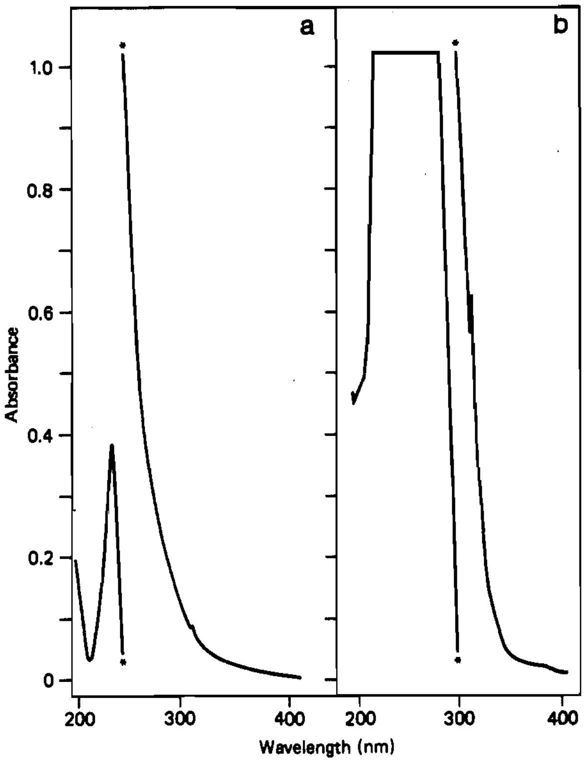

Figure 1. Spectra of europium(II) in AHF: (a) in dilute solution 1.5×10^{-2} M, showing 4f–5d band; (b) in more concentrated solution 1.2×10^{-1} M, showing f–f bands. An asterisk indicates a change of scale.

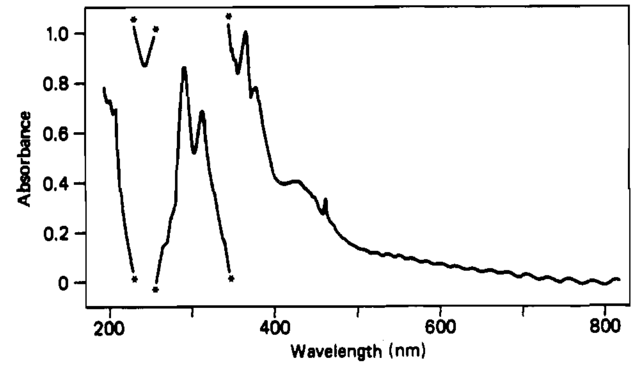

Figure 2. Spectrum of 6×10^{-2} M samarium(II) in AHF. An asterisk indicates a change of scale.

These generalizations are very much in evidence when the spectra of Eu^{2+} and Sm^{2+} in AHF are compared with those in H_2O. For Eu^{2+} in AHF only one 4f–5d transition is visible at wavelengths longer than 200 nm whereas two are present in the aqueous spectrum.[7] The AHF solvent absorbs strongly below 200 nm. So, while it is possible there may be a high-energy transition below 200 nm, we have not been able to see it. The absolute intensities are comparable in both solvents. Four f–f transitions are observed in each medium and these lie at somewhat higher energies in AHF, in agreement with our previous results.[1] For samarium a more complex spectrum is observed, as would be expected; but, by comparison with the aqueous spectrum,[7] most of the bands are better resolved.

Ytterbium(II) Spectra. Spectra of Yb^{2+} ($4f^{14}$) contain only 4f–5d transitions that mostly occur in the ultraviolet region. The spectrum recorded in AHF is shown in Figure 3. The peak positions, as well as those of two shoulders not shown in Figure 3, are given in Table III. The aqueous spectrum of Yb^{2+} shows only two bands.[7] It is probable that in both solutions there are absorption bands below 200 nm that are hidden by the strong solvent absorption. The solid-state spectrum of Yb^{2+} in CaF_2

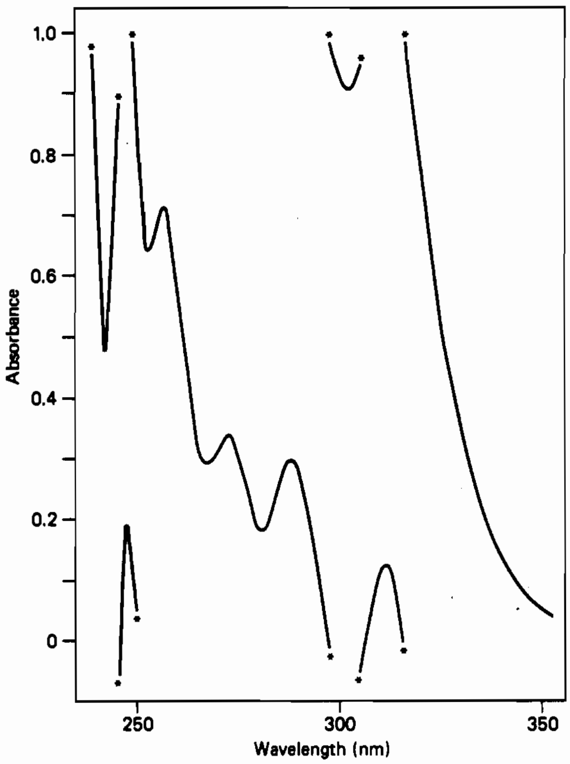

Figure 3. Spectrum of 1 × 10^{-2} M ytterbium(II) in AHF. An asterisk indicates a change of scale.

Table III. Peak Positions of Ytterbium(II) in HF and H_2O

HF		H_2O[a]	
λ, nm	*E*, cm^{-1}	λ, nm	*E*, cm^{-1}
310	32 260	352	28 400
287	34 840		
272	36 760		
256	39 060		
246	40 650	246	40 650
232 (sh)	43 100		
220 (sh)	45 450		

[a] Reference 7.

reported by Loh[19] shows a strong absorption around 56 000 cm^{-1}, and this has been confirmed by McClure.[20]

Some assignments have been made for Ln^{2+} spectra in alkaline-earth-metal fluorides, where it is certain that the ions are in a cubic environment.[10,21] However, in AHF solution the nature of the environment is much less certain. Other studies in aqueous solution[19] suggest that a coordination number of 9 is likely for the lighter Ln^{3+} ions, reducing to 8-coordination for the heavier and hence smaller ions. In much earlier work[1,2,4] we have used electronic spectra to show that coordination by solvent molecules of transition-metal cations is the same in aqueous and in HF solutions. In terms of ionic radius considerations the inherently larger divalent ions should have a coordination number of at least 9. Because of uncertainty about the environments of the solvated cations, we have not thought it useful to attempt any detailed assignment of the observed spectra.

Reactions of Lanthanide(II) Solutions with Lewis Acids. Studies, centering mainly on Sm^{2+}, were undertaken with the purpose of isolating solids containing the divalent ions. With an excess of AsF_5 ready oxidation occurred, as indicated by the rapid decoloration of the solution, without evolution of H_2.

$$2Sm^{2+} + 7AsF_5 + 4F^- \rightarrow 2Sm^{3+} + 6AsF_6^- + AsF_3$$

Addition of excess PF_5 or SiF_4 gave no decolorization or precipitation. However, when an excess of the nonoxidizing Lewis acid GeF_4 was added to each solution of Ln^{2+}, instantaneous precipitation occurred and the solution became noticeably warm. Reaction occurred without evolution of H_2, indicating that the solids contained Ln^{2+} and not Ln^{3+}. The yellow samarium compound, which is somewhat air-sensitive but indefinitely stable in an inert atmosphere, was investigated by a variety of techniques, confirming the formulation as $SmGeF_6$:

$$Sm^{2+}(solv) + 2F^-(solv) + GeF_4 \xrightarrow{HF} SmGeF_6$$

Characterization of this compound is the subject of a separate report.[15]

Reactions of Thulium and Lanthanum with Anhydrous Hydrogen Fluoride. For the reasons given in the introduction, reactions of AHF with these elements were also investigated. Thulium, in particular, has a well-defined divalent state, which has been observed in room-temperature melts[14] and which was believed might be stabilized in solution in AHF. Both metals showed slow reaction with AHF, but we could find no evidence for divalent ions in solution. If the divalent ions do form, they must be very unstable, as the respective trifluorides and hydrogen are the only products observed in these reactions.

Acknowledgment. We wish to acknowledge continued and substantial financial support from the Australian Research Grants Scheme.

---

(19) Loh, E. *Phys. Rev.* **1968**, *175*, 533.
(20) McClure, D. S. Private communication.
(21) Piper, T. S.; Brown, J. P.; McClure, D. S. *J. Chem. Phys.* **1967**, *46*, 1353.

Contribution from the Departments of Inorganic Chemistry
and Physical Chemistry, University of Melbourne,
Parkville, Victoria 3052 Australia

Preparation and Characterization of Samarium(II) Hexafluorogermanate

Colin G. Barraclough, Russell W. Cockman,
and Thomas A. O'Donnell*

Received May 1, 1990

On the basis of the reported redox potentials for lanthanide(III/II) couples in aqueous solutions, only three members of the lanthanide series might be expected to yield solid binary compounds containing dipositive lanthanide cations. These would be Eu with *E*° for Eu^{3+}/Eu^{2+} given as −0.35 V and, with less ease, Yb and Sm, for which the corresponding *E*° values are −1.05 and −1.55 V, respectively.[1] Compounds with stoichiometry LnI_2 have been reported for most of the lanthanide elements; but, for elements other than Eu, Yb, and Sm, these are believed to be best described as $[Ln(I^-)_2e]$.[2a] Formal lanthanide(II) hydrides, sulfides, and carbides can be described in similar terms. Kagan and colleagues prepared SmI_2 and YbI_2 *in solution* in tetrahydrofuran for use as reducing agents in organic syntheses by reacting the metals with 1:2 diiodoethane in THF.[3]

Solids containing Eu^{2+} are easily prepared. Thus, $EuSO_4$ can be precipitated from aqueous solution; but preparation of simple compounds of Yb^{2+} and Sm^{2+} has usually involved high-temperature reduction reactions, e.g. of the trihalide by the appropriate lanthanide metal. The reported colors of the resulting solids suggest in many cases that they may contain some higher oxidation state material.

In a separate report[4] we have described the relatively simple preparation of stable solutions of Eu^{2+}, Yb^{2+}, and Sm^{2+} by dissolution of the oxide-free lanthanide metal in anhydrous hydrogen fluoride (AHF) and the subsequent recording of electronic spectra

---

* To whom correspondence should be addresed at the Department of Inorganic Chemistry.