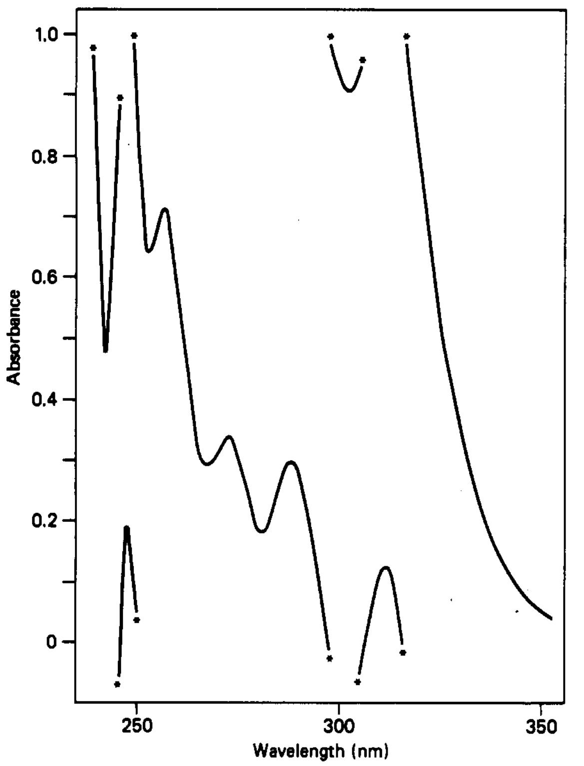

Figure 3. Spectrum of 1 × 10^{-2} M ytterbium(II) in AHF. An asterisk indicates a change of scale.

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.

0020-1669/91/1330-0343$02.50/0 © 1991 American Chemical Society

for these solvated cations. A particular advantage of preparing lanthanide(II) solutions in AHF is that lanthanide trifluorides are insoluble so that solutions for spectroscopic investigation or for preparation of solid derivatives of lanthanides in oxidation state II are not contaminated by lanthanides in oxidation state III. In a study of the effect of different Lewis acids on the solutions we found that the weak Lewis acid GeF_4 was particularly effective in precipitating the dipositive lanthanide cations from AHF, as it has also proved to be with many dipositive d-transition-metal cations.

On addition of GeF_4, the yellow AHF solution containing Sm^{2+} yielded a stable, stoichiometric yellow solid $SmGeF_6$, which was characterized by chemical determination of the oxidation state as well as by infrared and Raman spectroscopy, by powder X-ray diffraction techniques, and by determination of the magnetic moment. Although, for characterization studies, this compound was handled in a nitrogen-filled glove box, it remained bright yellow in the open atmosphere for a period of over 1 h, gradually taking on the brown color of Sm(III) through hydrolytic oxidation. This simple observation indicates a very low solubility of the compound in polar solvents.

Experimental Procedures

Our earlier report[4] described the reagents used, purification of HF, and manipulation of volatile reagents in vacuum systems and of involatile products in a nitrogen-filled glovebox, as well as removal of surface oxide from metallic Sm and the preparation of a solution of Sm^{2+} and F^- in AHF.

Instrumental Methods. Infrared spectra were obtained (Perkin-Elmer 457) from Nujol mulls between CsI windows.

A Spex-Ramalog instrument was used for recording Raman spectra, 514.5-, 647.1-, and 676.4-nm excitation wavelengths being employed.

X-ray powder photographs were exposed on a Philips Debye-Scherrer camera (PW 1024/10), diameter 114.5 mm, using Cu Kα radiation. Magnetic data were determined by the Gouy method with $HgCo(NCS)_4$ as calibrant.

Isolation of $SmGeF_6$. A solution containing Sm^{2+} and F^- ions was prepared and frozen at −196 °C. An excess of GeF_4 was admitted to the tube, and the contents were allowed to warm to room temperature. Rapid precipitation of $SmGeF_6$ occurred, and the colorless supernatant solution was discarded. The precipitate was washed with fresh AHF (5 mL), which was decanted away, and the solid was dried by being maintained under vacuum for several hours at room temperature. $EuGeF_6$ and $YbGeF_6$ can be recovered in similar fashion from the solutions described in our earlier paper.[4]

Results and Discussion

The oxidation state of the lanthanide was determined by oxidation of solid $SmGeF_6$ with excess acidified MnO_4^- and back-titration with standardized Fe^{2+}. The experimentally determined value was 1.95 (theoretical 2.0), equivalent to a samarium content of 47.1% (calcd, 44.6%).

IR spectra showed bands at 630 (sh), 608 (s), 450 (w), 360 (m), and 330 (m) cm^{-1} in excellent agreement in position, relative intensity, and profile with the spectrum published for $BaGeF_6$.[5] X-ray powder photography indicated that the compound was isomorphous with $BaGeF_6$.[6]

In a Raman experiment conducted at ambient temperature, excitation at 514.5 nm caused thermolysis of the solid sample, but the problem was eliminated when the 647.1- and 676.4-nm lines were used. Intense laser-induced fluorescence occurred. Two lines at 1058 and 904 cm^{-1} together with several weaker features were evident when excitation at 647.1 nm (15454 cm^{-1}) was employed. When the 676.4-nm (14784-cm^{-1}) line was used, the lines were shifted to 384 and 233 cm^{-1}, respectively. The shifts effectively mirror the differences in the excitation frequencies used. On converting the energies to wavelengths, we are therefore observing emission from the Sm^{2+} at 694.6 and 687.5 nm, values in excellent agreement with emission near 690 nm reported for Sm^{2+} in host lattices.[7,8]

Emission from the cation so dominated the spectra that scattering from the anion could not be positively identified even when the experiments were conducted at low temperatures.

The compound has a magnetic moment, $\mu_{eff} = 3.13\ \mu_B$, at 293 K. Surprisingly little magnetic data has been reported for Sm^{2+}. The ion is isoelectronic with Eu^{3+} for which moments in the range 3.4–3.5 are usually found.[2b] In contrast, moments for Sm^{3+} are usually near 1.6 μ_B.[2c]

We believe that the data confirm the formulation of the samarium compound as $SmGeF_6$, and together with the solids isolated by adding GeF_4 to the solutions previously reported as containing Eu^{2+} and Yb^{2+},[4] we have prepared a new series of compounds that are easily synthesized at or below room temperature that contain divalent lanthanide ions: $LnGeF_6$ (Ln = Sm, Eu, Yb).

---

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

(2) Moeller, T. *The Chemistry of the Lanthanides*; Pergamon Press: Oxford, England, 1973; (a) p 76, (b) p 13, (c) p 11.

(3) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2698.

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

(5) Griffiths, J. E.; Irish, D. E. *Inorg. Chem.* **1964**, *3*, 1134.

(6) Hoard, J.; Vincent, W. B. *J. Am. Chem. Soc.* **1940**, *62*, 3126.

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

(8) Dieke, G. H.; Sarup, R. *J. Chem. Phys.* **1962**, *36*, 371.

Contribution from the Laboratoire de Chimie
de Coordination du CNRS, UPR 8241 liée
par conventions à l'Université Paul Sabatier
et à l'Institut National Polytechnique,
205 route de Narbonne, 31077 Toulouse Cedex, France,
and Laboratoire de Chimie des Agroressources,
Institut National Polytechnique de Toulouse,
Ecole Nationale Supérieure de Chimie de Toulouse,
118 route de Narbonne, 31077 Toulouse Cedex, France

Reactivity of Polyaza Diphosphorus Macrocycles

Jean-Pierre Majoral,*,† Meryam Badri,† Anne-Marie Caminade,† Michel Delmas,‡ and Antoine Gaset‡

Received May 3, 1990

Introduction

We recently described an easy synthesis of polyaza diphosphorus macrocycles[1] by reacting phosphodihydrazides with 1,2, 1,3, 1,4, 1,6, or 1,11 dicarboxaldehydes.[2] These reactions do not require high dilution or drastic conditions since these derivatives are obtained in nearly quantitative yield when both reactants are stirred in methanol for 3 h at room temperature. Another significant advantage of this type of reaction is the formation of *free* macrocycles. This was not the case for the other known reactions leading to phosphorus Schiff base large-membered rings: all the reported experiments involved template reactions and therefore led to macrocycle complexes.[3]

The possibility to form easily these first free P–N–N-containing macrocycles prompted us to investigate both their reactivity and their complexation properties.

We herein report some examples of the reactivity of these macrocycles involving either imino functions or phosphoryl and thiophosphoryl groups. We also demonstrate that these molecules possess tailored internal cavities and allow one to prepare selectively macrocyclic hydrazino phosphonium salts. To our knowledge, no examples of cyclic or even linear (alkylhydrazino)phosphonium salts have been reported so far.

---

† Laboratoire de Chimie de Coordination du CNRS.
‡ Ecole Nationale Supérieure de Chimie de Toulouse.

0020-1669/91/1330-0344$02.50/0