

vessel was cooled in an ice bath. The reaction is highly exothermic. The clear solution was allowed to warm to room temperature. Approximately 2 moles of hydrogen chloride is evolved for every mole of I present. It was then refluxed for 3 hr. to remove the third mole of hydrogen chloride. The solvent was removed and the white crystalline residue was recrystallized from a dichloroethane-*n*-pentane solution. The compound is stable to hydrolysis. It will undergo only slight reaction when left in contact with cold water for several hours.

Preparation of $(C_6H_5)_4P_2N_3HB(C_6H_5)$ (IX).—A 2.0-g. (3.7 mmoles) sample of III was heated to 230° for 48 hr. at 0.5 mm. pressure. Hydrogen chloride gas and $C_6H_5BCl_2$ were evolved and compound IX was sublimed. The sublimate requires no further purification. This compound is very stable to hydrolysis. It is difficultly soluble in chloroform and dichloroethane.

Preparation of $(C_6H_5)_4P_2N_3HB$ Br (X).—This compound was prepared from a 1:1 reaction mixture by the same procedure described for the preparation of compound VIII. The reagents were refluxed for 6 hr. to get rid of the third mole of hydrogen bromide.

Elemental Analysis.—Elemental analyses were done by Galbraith Laboratories, Knoxville, Tenn.

Spectral Analysis.—A Beckman Model IR8 infrared spectrophotometer was used for taking infrared spectra. All sample spectra were of mulls in Nujol and hexachlorobutadiene. The ultraviolet spectra were taken on a Cary Model 15 spectrophotometer.

Acknowledgment.—The authors gratefully acknowledge the support of the National Science Foundation.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
AND RESEARCH LABORATORY OF ELECTRONICS,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
CAMBRIDGE, MASSACHUSETTS 02139

Electronic Spectra of Solutions of Europium and Ytterbium in Liquid Ammonia

By D. S. THOMPSON, D. W. SCHAEFER, AND J. S. WAUGH

Received September 21, 1965

It has been reported that both europium and ytterbium metals dissolve in liquid ammonia to give deep blue, paramagnetic solutions.¹ Paramagnetic resonance studies of these solutions give evidence that the metals dissolve to give divalent cations, perhaps ammoniated, and solvated electrons. In the case of europium solutions, a pair of hyperfine multiplets are observed² which can be shown to be due to paramagnetic, divalent europium.³ There is no direct evidence from paramagnetic resonance of the nature of the metal species in ytterbium solutions.

We have studied the electronic spectra of both europium and ytterbium solutions in liquid ammonia in order to characterize further the species present. The spectra of the two metals in ammonia solution are qualitatively similar as is shown in Figure 1. Both

(1) J. C. Warf and W. L. Korst, *J. Phys. Chem.*, **60**, 1590 (1956).

(2) R. Catterall and M. C. R. Symons, *J. Chem. Phys.*, **42**, 1466 (1965).

(3) D. S. Thompson, E. E. Hazen, Jr., and J. S. Waugh, to be published.

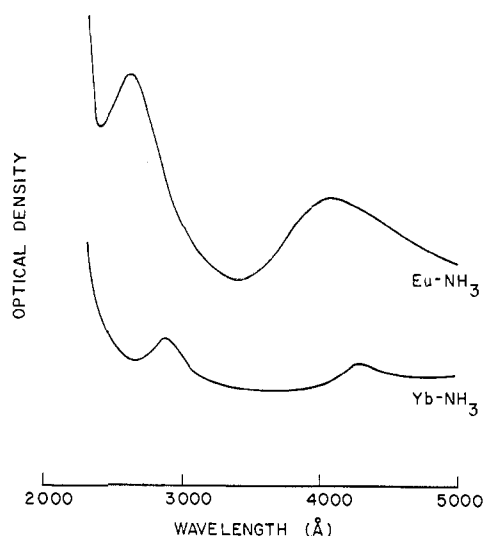


Figure 1.—Electronic spectra of solutions of europium and ytterbium in liquid ammonia at -45° . The approximate mole ratios are $Eu/NH_3 = 9 \times 10^{-5}$ and $Yb/NH_3 = 5 \times 10^{-5}$. The ordinate is optical density in arbitrary units.

show two broad bands in the visible and near-ultraviolet regions. These two bands are similar to the bands observed by Butement for aqueous solutions of divalent europium and ytterbium chlorides.⁴ The bands in ammonia solution are, however, appreciably shifted from those observed by Butement (see Table I).

TABLE I
ELECTRONIC ABSORPTION SPECTRA OF SOLUTIONS OF EUROPIUM AND YTTERBIUM IN LIQUID AMMONIA

Europium			
λ , Å. (Eu-NH ₃)	Strength	λ , Å. (EuCl ₂ aq.)	Oscillator strength ^a
2600	Strong	2480	31.2×10^{-3}
4050	Weak	3205	6.2×10^{-3}
Ytterbium			
λ , Å. (Yb-NH ₃)	Strength	λ , Å. (YbCl ₂ aq.)	Oscillator strength
2850	Strong	2460	27.5×10^{-3}
4250	Weak	3520	5.1×10^{-3}

^a The number of "classical oscillators" per rare earth ion.

Experimental Section

Solutions of ytterbium and europium were prepared by dissolving small, weighed pieces of metal in weighed amounts of purified ammonia. The ammonia was triply distilled from potassium before use. Manipulations were carried out under an argon atmosphere. It was necessary to clean all surfaces that were to come in contact with the solutions very carefully and to degas the preparation bulb and the optical cells thoroughly to prevent rapid decomposition of the europium solutions.

The extremely large extinction coefficient associated with the near-infrared absorption of the solvated electron necessitated the use of optical cells with path lengths of the order of 1 mm. or less. The optical cells were fabricated from fused quartz plates. The electronic spectra were run at temperatures from -60 to -20° on a Cary Model 14 recording spectrophotometer. The samples were thermostated by placing the optical cells in thermal contact with an aluminum block which had channels through which either cold methanol or cold nitrogen could be pumped. The temperature of the aluminum block thermostat was moni-

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

tored with a copper-constantan thermocouple. The sample compartment of the spectrometer was continuously swept with dry nitrogen to prevent condensation of moisture on the cell windows.

Since these solutions are not stable for long periods of time (*vide infra*), and their concentrations at any time are therefore not well known, it was not possible to obtain accurate values for the molar extinction coefficients.

Discussion of Results

The absorptions in divalent europium are ascribed to transitions between the $^8S_{7/2}$ ground state with its seven "optical" electrons in the 4f shell and excited states having one of these 4f electrons in a 5d, 6s, or 6p, etc., state. The lowest excited state in divalent europium is the $^6P_{7/2}$ state.⁵ The absorption at 4050 Å. is assigned to this transition.

If we use the energy separation between the $^6P_{7/2}$ state and the $^8S_{7/2}$ ground state thus obtained in conjunction with the g value of 1.990 ± 0.002 observed in the paramagnetic resonance experiments³ we can calculate the spin-orbit coupling constant for divalent europium. This calculation assumes that only the $^6P_{7/2}$ state mixes appreciably with the ground state.

$$f_{\text{exptl}} = (1 - \epsilon^2)g(^8S_{7/2}) + \epsilon^2g(^6P_{7/2})$$

where ϵ^2 is the fraction of $^6P_{7/2}$ character in the ground state and g is the theoretical Lande g factor corrected for relativistic and diamagnetic effects.⁶ The extent of the admixture in the case of divalent europium in liquid ammonia amounts to about $\epsilon^2 = 3.5\%$. Using this value for the per cent $^6P_{7/2}$ character of the ground state in conjunction with the theoretical relation

$$\epsilon^2 = \frac{14\zeta^2}{(E_p - E_s)^2}$$

where ζ is the spin-orbit coupling constant and $(E_p - E_s)$ the energy separation of the $^6P_{7/2}$ and the $^8S_{7/2}$ states, we obtain a value of $\zeta = 1230 \pm 20 \text{ cm.}^{-1}$ for the spin-orbit coupling constant of divalent europium in liquid ammonia. This value is in reasonably good agreement with that estimated for gaseous divalent europium, namely $1250 \pm 50 \text{ cm.}^{-1}$.⁶

The ground state of divalent ytterbium is 1S_0 ($4f^{14}$). The excited states have one of these electrons in a 5d, 6s, etc., shell as with divalent europium. These allowed excited states include $^1(P, D, F, G, H)$ and $^3(P, D, F, G, H)$. The transitions observed are probably between 1S_0 and 1P or 3P states.⁴

There is no evidence for an appreciable concentration of trivalent metal ions in either solution. The fact that we did not observe the sharp lines characteristic of the visible spectrum of trivalent europium and ytterbium is not, however, truly conclusive evidence that there are no trivalent ions in solution. The visible transitions of these trivalent ions are forbidden by the Laporte selection rule, and therefore their molar extinction coefficients are small.⁷ Since the total metal concentrations studied were quite small, it would be difficult to observe spectra from trivalent ions.

The two broad bands observed in the visible and near-ultraviolet are, we feel, characteristic of both divalent europium and ytterbium. We have not as yet explained the magnitudes of the shifts in the peaks with respect to those of the aqueous divalent chloride solutions observed by Butement. There is evidence, however, that at least the spectrum of divalent europium depends rather markedly on the nature of its environment in crystals—much more so than typical rare earths.⁸ Differences between the effective crystalline fields at the europium and ytterbium ions in ammonia solution and those in aqueous chloride solutions may be sufficient to account for the observed shifts of the visible and near-ultraviolet bands in ammonia with respect to the corresponding bands observed in aqueous chloride solutions.

The gradual disappearance of the blue color arising from the tail of the near-infrared absorption of the solvated electron species was monitored at -31° and 11,200 Å. In moderately dilute solutions, the optical density decreased linearly with time. The integrated intensities of the paramagnetic resonance signals of both the europium species and the solvated electron species show similar linear decays with time. The zero-order chemical kinetics of decomposition are in qualitative agreement with the zero-order kinetics observed by Warshawsky for the decomposition of alkali metal-ammonia solutions.⁹ A full discussion of the kinetics of decomposition of these solutions is forthcoming.³

Acknowledgment.—This work was supported in part by the Joint Services Electronics Program under Contract DA-36-039-AMC-03200(E) and in part by the National Science Foundation.

(7) P. K. Gallagher, *J. Chem. Phys.*, **41**, 3061 (1964).

(8) S. Freed and S. Katcoff, *Physica*, **14**, 17 (1948).

(9) I. Warshawsky in "Metal-Ammonia Solutions," W. A. Benjamin, Inc., New York, N. Y., 1964, p. 167.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA,
AND THE WASHINGTON RESEARCH CENTER,
W. R. GRACE AND COMPANY, CLARKSVILLE, MARYLAND

The Synthesis of Polymeric Dimethylphosphonitrile by Pyrolytic Condensation of Dimethyldiaminophosphonium Chloride

BY HARRY H. SISLER, STEPHEN E. FRAZIER, RIF G. RICE,
AND M. G. SANCHEZ

Received October 4, 1965

An intriguing feature of phosphonitrilic chemistry is the ability of certain cyclic derivatives to undergo decyclization and linear polymerization to form rubbery or elastomeric materials generally formulated as

(5) W. A. Runciman, *J. Chem. Phys.*, **30**, 1632 (1959).

(6) B. R. Judd and I. Lindgren, *Phys. Rev.*, **122**, 1802 (1961).