observation in keeping with the idea that the aluminum chloride functions mainly as an electrolyte. However, whereas a solution of aluminum chloride can be electrolyzed for several days without amperage decrease, the current rapidly drops and reaches zero in about 2 days when the titanate ester–aluminum chloride combination is used.[5]

Titanium must be reduced beyond the III state before appreciable amounts of nitrogen are reduced, as shown by a rough calculation of the amount of current having passed through the cell at the point where ammonia could first be detected. Also, in an experiment conducted in a divided cell, the solution in the cathode compartment rapidly turned blue during the electrolysis, suggesting the presence of Ti(III) in the solution. When approximately 1 mol equiv of electrons/mole of titanium had been passed through the cell, the solution started to turn black (indicating further reduction of titanium) and thereupon ammonia began to appear in bound form. When titanium trichloride was used in place of titanium tetraisopropoxide, ammonia was detected after hydrolysis at a point in time when considerably less (*ca.* 10%) electrons per mole of titanium had passed through the solution. The significance of this experiment is not clear, however, since only 1.5% ammonia was formed.

Despite the modest yields of ammonia but because of the practical import, the above preliminary findings are being communicated at this early stage. The nature of the titanium agent in this and related fixation–reduction experiments[1,3] is under active investigation and will, it is hoped, constitute the subject of a future publication.

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(5) Since the bound nitrogen in complexes like $Os{=}N^+{=}N^-$ probably has basic character, the aluminum chloride might be tied up in part as an acceptor of the $N_2$ ligand in a titanium coordination compound.

(6) On leave from Department of Organic Chemistry, Royal Institute of Technology, Stockholm, Sweden. Fellowship support was provided by the Swedish Council for Applied Research.

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## Synthesis and Structure of the Six-Coordinate Hexaisothiocyanatolanthanide(III) Complexes[1]

*Sir:*

Although there has been an increased interest in the coordination chemistry of the lanthanide ions during the past decade, most of this work has been concerned with complexes in which the coordination number of the lanthanide ion is greater than six.[2] It has become increasingly apparent that there are very few six-coordinate complexes of the trivalent lanthanide ions and that one must show extreme caution in formulating six-coordination. We wish to report the preparation and some properties of the tetra-*n*-butylammonium salts of the hexaisothiocyanato complexes of the trivalent lanthanides[3] and, moreover, the results of an X-ray structure determination of the erbium compound. To the best of our knowledge, this is the first structure determination on a discrete six-coordinate lanthanide complex.

The complexes of the heavier lanthanides are deposited in crystalline form from ethanol solutions containing the appropriate hydrated lanthanide chloride and tetra-*n*-butylammonium thiocyanate in the molar ratio of 1:10. The complexes of the lighter lanthanides crystallize slowly from a 1:1 ethyl alcohol–*t*-butyl alcohol solution of the lanthanide thiocyanate and tetra-*n*-butylammonium thiocyanate in a 1:3 molar ratio. The total analysis of the yttrium complex was as follows. *Anal.* Calcd for $\{(C_4H_9)_4N\}_3Y(NCS)_6$: C, 55.7; H, 9.4; S, 16.5; N, 10.8; Y, 7.7; $SCN^-$, 29.9. Found: C, 55.6; H, 9.3; S, 15.8; N, 10.8; Y, 7.7; $SCN^-$, 29.7. In addition satisfactory analyses for $Ln^{3+}$ and $SCN^-$ have been obtained for the praseodymium, neodymium, europium, samarium, holmium, erbium, thulium, and ytterbium compounds.

The complexes melt without apparent decomposition at temperatures less than 200° and are soluble in a number of organic solvents such as dichloromethane, nitromethane, nitrobenzene, acetonitrile, methanol, and ethanol. They are soluble in water upon heating and are subsequently decomposed. The molar conductances of solutions of three of the complexes in nitromethane and nitrobenzene are within the range expected for 3:1 electrolytes.[4] The conductances of the complexes of the lighter lanthanides are at the upper end of this range, probably indicating that additional dissociation is occurring. This is supported by the spectral measurements in the visible region.

The infrared spectra are suggestive of N-coordination[5] but are not conclusive since there is little shift in the bands due to the thiocyanate groups, an observation which is consistent with the weak polarizing properties of the lanthanide ions. The main absorption bands in KBr or Nujol are given below for a typical complex.

| | $\nu_{CN}$ | $\nu_{NCS}$ |
|---|---|---|
| $(C_4H_9)_4NCNS$ | 2060 | 465, 480 |
| $\{(C_4H_9)_4N\}_3Er(NCS)_6$ | 2090 sh, 2045 | 480 |

The colors of the compounds are characteristic of the particular lanthanide ion but are very pale. (It should be noted that those ions which should give colorless compounds yield complexes which are very faintly orange due to the presence of *ca.* 0.01% iron.) The absorption spectra have been measured on dichloromethane solutions and the diffuse reflectance spectra have been measured for powdered samples. The reflectance spec-

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(2) For recent reviews, see T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrús, G. R. Feistel, and W. J. Randall, *Chem. Rev.*, **65**, 1 (1965); T. Moeller, E. R. Birnbaum, J. H. Forsberg, and R. B. Gayhart, "Progress in the Science and Technology of the Rare Earths," Vol. III, L. Eyring, Ed., Pergamon Press, Oxford, England, in press.

(3) A. M. Golub, M. I. Olevinskii, and N. S. Zhiguline (*Zh. Neorgan. Khim.*, **11**, 1574 (1966)) have previously reported $(NH_4)_3Nd(NCS)_6 \cdot 4C_2H_5OH$ and $Na_3La(NCS)_6 \cdot 3C_2H_5OH$.

(4) The molar conductances of the complexes of Y, Er, and Nd were measured in nitromethane to be 241, 237, 284 ohm$^{-1}$, respectively; expected range for 3:1 electrolyte, 230–280 ohm$^{-1}$: N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959). The molar conductances of these complexes in nitrobenzene are 59, 62, 73 ohm$^{-1}$; expected range for 3:1 electrolyte (extrapolated), 60–90 ohm$^{-1}$: D. J. Phillips and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, 83, 1806 (1961).

(5) A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965).

tra are particularly weak and are comparable to the spectra of the $LnCl_6^{3-}$ ions.[6] The results are consistent with an essentially octahedral arrangement of ligands in $Ln(NCS)_6^{3-}$. The solution spectra of the complexes of the heavier lanthanides are also consistent with this hypothesis. The spectra of the complexes of the lighter lanthanides, however, indicate that the symmetry is less than octahedral in these solutions.

Crystals of the erbium(III) salt contain four $\{(C_4H_9)_4N\}_3Er(NCS)_6$ species in an A-centered triclinic cell of dimensions[7] $a = 22.63 \pm 0.03$ Å, $b = 16.73 \pm 0.02$ Å, $c = 18.82 \pm 0.02$ Å, $\alpha = 87.97 \pm 0.02°$, $\beta = 89.08 \pm 0.03°$, $\gamma = 92.47 \pm 0.03°$. The absence of any observable piezoelectric effect and the successful structure determination indicate the space group to be $A\bar{1}$, necessitating the placement of 70 atoms in the asymmetric unit. X-Ray intensity data were measured to a limit of $\theta_{Mo} < 20°$ *via* the moving-crystal–moving-counter technique on a Picker four-circle diffractometer. Placement of the erbium from a Patterson synthesis followed by solution of Fourier syntheses phased on the heavy atoms led to the crystalline arrangement. A least-squares refinement with isotropic thermal parameters was carried out in which only correlations between parameters of atoms within a given hexaisothiocyanatoerbium(III) or tetrabutylammonium ion were considered. The conventional discrepancy factor $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for the 3406 data thus far used in the refinement has been reduced from 0.48, for the erbium contribution only, to 0.12 at present. A difference map confirms the correctness of the structure.

The erbium(III) is N-bonded to six thiocyanates in an octahedral arrangement of essentially $O_h$-m3m symmetry. At the present stage of refinement we do not detect chemically significant deviations from this symmetry; we shall thus use average values for the bond lengths and angles in the following discussion and indicate the average value of an *individual* standard deviation in parentheses. The six Er–N bond lengths average to 2.34 (2) Å, somewhat shorter than that predicted by summing the atomic radii of erbium and nitrogen.[8] The Er–N–C–S groups are approximately linear with Er–N–C and N–C–S angles, 174 (2) and 176 (3)°, respectively. The nearness of the Er–N–C angle to 180° has been used as a criterion for the dominance of the $M{-}N^+{\equiv}C{-}S^-$ resonance structure in metal isothiocyanates.[9,10] Consistent with this hypothesis is the shortness of the N–C bond (1.10 (3) Å). The S–C bond length of 1.61 (3) Å is consistent with others reported[10] although shorter than that predicted by the resonance form above.[9]

Crystals of the tetra-*n*-butylammonium hexaisothiocyanatolanthanide(III) salts provide excellent examples of an ordered, magnetically dilute lanthanide ion of idealized $O_h$ local symmetry; owing to the presence of the bulky $(C_4H_9)_4N$ cations, the closest Er–Er interaction is 11.7 Å. Preliminary magnetic studies[11] show the magnetic moment of the erbium complex to be 9.48 BM, in good agreement with the predicted value for an octahedral complex.[12]

Examination of the nonbonded distances between the alkylammonium groups and the thiocyanates indicate only normal van der Waals interactions and very little penetration of the butyl groups into the sphere of influence defined by the sulfurs. We thus do not attribute the surprising stability of these hexacoordinated lanthanides to a stabilizing influence of the cations in the crystal structure.

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(6) J. L. Ryan and C. K. Jørgensen, *J. Phys. Chem.*, **70**, 2845 (1966).

(7) This corresponds to a primitive cell of dimensions: $a = 22.63$ Å, $b = 12.39$ Å, $c = 12.83$ Å, $\alpha = 96.52°$, $\beta = 91.13°$, $\gamma = 92.35°$.

(8) J. C. Slater, *J. Chem. Phys.*, **41**, 3199 (1964).

(9) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 273–274.

(10) For tabulations of data on metal isothiocyanates, see J. R. Knox and K. Eriks, *Inorg. Chem.*, **7**, 84 (1968); and A. C. Hazell, *J. Chem. Soc.*, 5745 (1963).

(11) R. L. Lintvedt, private communication. Temperature-dependent single-crystal magnetic studies are in progress on these compounds.

(12) W. G. Penney and R. Schlapp, *Phys. Rev.*, **41**, 194 (1932); J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932.

(13) National Science Foundation Undergraduate Research Participant, 1966–1968.

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## A Novel Route to α-Aminoalkylphosphonic Acids and Dialkyl α-Aminoalkylphosphonate Hydrochlorides

*Sir:*

It was recently reported that dialkyl aroylphosphonates could be converted to the corresponding oximes in high yield.[1] Reduction of the oximes by Al–Hg in ethanol–water proved highly successful for the synthesis of dialkyl α-aminoarylmethylphosphonates. Unfortunately, the method was inferior for the preparation of dialkyl α-aminoalkylphosphonate hydrochlorides or α-aminoalkylphosphonic acids, the phosphorus analogs of α-aminoalkylcarboxylic acids. Although a few methods[2] have been published for the synthesis of α-aminoalkylphosphonic acids, the present approach avoids the previous intrinsic limitations of low yields, long routes, and difficultly accessible starting materials. Diethyl acylphosphonates **1** are readily available[3] and are converted by methoxylamine hydrochloride to the O-methylated oximes **2** as shown in route A. Reduction of **2** in THF with diborane gave diethyl α-aminoalkylphosphonates which were dissolved in ether and converted by treatment with hydrogen chloride to the hydrochloride salts **3**.[4] Acid hydrolysis of **3**, after removal of the water at aspirator pressure, gives semisolids. Solution of the semisolids in a mini-

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(1) K. D. Berlin, R. T. Claunch, and E. T. Gaudy, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, No. P136.

(2) (a) J. R. Chambers and A. F. Isbell, *J. Org. Chem.*, **29**, 832 (1964); (b) M. I. Kabachnik and T. Ya. Medved, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 868 (1953); *Chem. Abstr.*, **49**, 840 (1955); (c) M. E. Chalmers and G. M. Kosolapoff, *J. Am. Chem. Soc.*, **75**, 5278 (1953); (d) M. I. Kabachnik and T. Ya. Medved, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 314 (1954); *Chem. Abstr.*, **48**, 10541 (1954); (e) M. I. Kabachnik and T. Ya. Medved, *Dokl. Akad. Nauk SSSR*, **83**, 689 (1952); (f) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **70**, 1283 (1948); (g) G. M. Kosolapoff, *ibid.*, **69**, 2112 (1947).

(3) K. D. Berlin, D. M. Hellwege, and M. Nagabhushanam, *J. Org. Chem.*, **30**, 1265 (1965); previous work is referenced in this paper.

(4) The technique used here was similar to that reported for reduction of O-methyl oximes of simple ketones; see H. Feuer, B. F. Vinvent, Jr., and R. S. Bartlett, *ibid.*, **30**, 2877 (1965). In our work, diborane was passed directly into a solution of **2** in THF.