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

[2] J. Corset and G. Lepoutre, "Solutions Métal-Ammoniac," G. Lepoutre and M. S. Sienko, Ed., W. A. Benjamin, Inc., New York, N. Y., 1963, p 186 ff.

[3] I. Warshawsky, ref 2, p 167 ff.

Kirschke and Jolly[4] showed that the equilibrium constant for the reaction $0.5H_2 + NH_2^- = NH_3 + e_{am}^-$ is 2×10^{-5}. It is understandable, therefore, that Yb(II) and Eu(II), being stronger reducing agents than hydrogen, should produce the ammoniated electron by interaction with amide ion. The oxidation potentials are further enhanced by the exceedingly low solubility of the resulting rare earth triamides. The over-all reaction might be represented: $Yb_{am}^{2+} + 3NH_2^- = Yb(NH_2)_3 + e_{am}^-$. We do not yet have the equilibrium constants or potentials which apply.

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[4] E. S. Kirschke and W. S. Jolly, *Inorg. Chem.*, **6**, 855 (1967).

Book Reviews

Interpretation of Mass Spectra. An Introduction. By F. W. McLafferty, Purdue University. W. A. Benjamin, Inc., 1 Park Ave., New York, N. Y. 1966. xvii + 229 pp. 14.5 × 21.5 cm. $9.00.

Organic chemists are now able to obtain mass spectra routinely, either from their own instruments or from commercial or National Institutes of Health sponsored mass spectrometry centers. The enthusiasm with which the American Chemical Society's Short Courses on Mass Spectrometry have been received attests the fact that these chemists wish to interpret their own data, rather than to rely on the interpretations of specialists. Dr. McLafferty has responded to this wish by writing an introduction to the interpretation of the mass spectra of organic compounds, intended for individual study and for use as a supplemental textbook. He states that the incentive for writing "Interpretation of Mass Spectra" was his opinion that mass spectrometry is for scientists, not just for mass spectrometrists.

The main purpose of the book is to help the scientist relate the positive ions formed by electron bombardment to the molecular structure of the sample. To achieve this purpose, the author suggests that the readers, who he assumes have no prior knowledge of mass spectrometry, follow a "Standard Interpretation Procedure." The Procedure is applicable to the "average" mass spectrum and is the basis upon which the book is organized. The author's approach is illustrated by his discussion of the mass spectra of many common types of organic compounds. The Standard Interpretation Procedure is a useful structure upon which the novice can develop his skill. However, as this skill increases, he may find the Procedure too confining and, therefore, abandon it in favor of his own approach.

The book is devoted to interpretation of low-resolution mass spectra, *i.e.*, those for which data are available to the nearest mass-to-charge unit. High-resolution mass spectrometry is discussed in three pages and high-resolution data are given for only one or two of the examples. The usefulness of "metastable" peaks is emphasized, and data of this type are included in the illustrations. Perhaps too much emphasis is given to determination of elemental formulas from natural isotopic abundances. Such determinations are most successful for low molecular weight compounds and require accurate peak-intensity measurements, often not found in routinely determined mass spectra.

Approximately 100 unknowns, most of them simple organic compounds containing combinations of C, H, S, N, O, and/or halogen, are included in bar graph, as well as tabular, form. Consequently, Chapter 10, "Solutions to Unknowns," is especially valuable since it contains the author's interpretation of each mass spectrum in addition to the structure of the unknown. Except for five unknowns for each of which one infrared absorption band is given, they are to be identified from their mass spectra alone. Some are too difficult for complete identification, but the reader should proceed as far as possible before turning to the solution in Chapter 10. These unknowns and solutions are the core of the book.

The longest chapter is entitled "Mechanisms of Unimolecular Ion Decomposition Reactions." Dr. McLafferty occasionally seems to depart from presenting an introduction to interpretation of mass spectra and, instead, seems to be reviewing the use of the "localized charge" concept. A number of mechanisms are presented "because the author finds them useful to correlate a sizable body of data that has not been previously treated in a general fashion." Only in passing does he warn that the arrows, fishhooks, and localized charges are "merely a system of electron bookkeeping that some have found convenient."

In my opinion, Dr. McLafferty has written an excellent, well-timed book. He has been a pioneer in the application of mass spectrometry to organic chemistry, and one can sense this in the authoritative manner in which he presents the material. A prime objective of the book was to show the "fun" of mass spectrometry by comparing interpretation of mass spectra to fitting together jig-saw-puzzle pieces. The author has been successful in maintaining this spirit throughout the book.

Perhaps the most impressive commendation of "Interpretation of Mass Spectra" is the enthusiastic response it has received from participants in academic and industrial courses on mass spectrometry and in the American Chemical Society's Short Courses on Mass Spectrometry. I recommend it to anyone who wishes to, or needs to, become as proficient in interpretation of mass spectra as he is in the interpretation of data from other spectroscopic methods of identification.

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Theory of Elementary Gas Reaction Rates. By Don L. Bunker. Pergamon Press Inc., 44-01 21st St., Long Island City, N. Y. 1966. xii + 115 pp. 15.5 × 23.5 cm. $5.50.

This book deals with fundamental aspects of gas kinetics, a subject which according to the author has experienced a resurgent interest starting roughly in 1959. Studies of this type have commanded new attention since they are aimed at uncovering the basic dynamic aspects responsible for a chemical reaction.

The author considers not formal theoretical problems, nor elegantly detailed experimental approaches, but rather the intersection of theory and critical experiments and the way one sheds light onto the other. The large growth in practical theoretical techniques and sophisticated experimental apparatus capable of getting at elementary, interpretable steps of a chemical reaction has provided the basis on which it again has become practical to ask questions about the nature of a chemical transformation. The author focuses attention on a broad range of those useful aspects of theory and experiment which have led to cross fertilization between the two. Hence he covers not only molecular beam experiments, but many of the other sophisticated novel approaches.

The author gives a critical survey of this new resurgence through 1964. Thus, unfortunately three of the seven important last years are not covered. This seems to be part of the inevitable lag of hard-