Bipyridine Complexes

Sir:

We have been determining[1] and collecting stability constants of metal complexes with pyridine and its derivatives for many years. The paper of Atkinson and Bauman[2] on the thermodynamics of transition metal complexes with 2,2′-bipyridine therefore received our special attention. We note that even the second decimal for the logarithm of each stability constant is given in this paper. However, there is little agreement between these constants and the values found by other authors[3] or obtained in our own laboratory.[4] The discrepancies are in some cases higher than one log K unit, which make it obvious that they could not be due to differences in ionic strength. An inspection of the dissertation[5] from which the data of ref. 2 have been extracted made it clear that the authors have underestimated the large errors which arise if a pH method is used in strongly acid solutions. The classical Bjerrum method for determining stability constants is unsuitable for very weakly basic ligands which form metal complexes of considerable stability, such as bipyridine. The findings of Bauman and Atkinson that the degree of complex formation with Mn^{2+} and Zn^{2+} rises up to $\bar{n} = 5.87$ and 6.09, respectively, should have made the authors suspicious of the usefulness of their experimental method. A collection of the more trustworthy stability constants of the bipyridine–transition metal complexes has recently been given by Irving and Mellor.[6]

(1) G. Anderegg, *Helv. Chim. Acta*, **43**, 414, 1530 (1960); **45**, 1643 (1962).
(2) G. Atkinson and J. E. Bauman, Jr., *Inorg. Chem.*, **1**, 900 (1962).
(3) H. Irving, private communication. Cited in ref. 2 and Proc. of 1959 Intern. Conf. on Coordination Compounds, London.
(4) Unpublished results. For instance: Mn^{2+}, log $K_1 = 2.5$; Cu^{2+}, log $K_1 = 8.0$ at 20° and $\mu = 0.1$.
(5) J. E. Bauman, Thesis, University of Michigan, 1962.
(6) H. Irving and D. H. Mellor, *J. Chem. Soc.*, 5222 (1962).

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RECEIVED MARCH 27, 1963

Bipyridine Complexes

Sir:

Our recent papers[1,2] presented a consistent set of ΔF and ΔH values for pyridine and bipyridine complexes of Mn^{+2}, Ni^{+2}, Cu^{+2}, and Zn^{+2}. We did not feel then nor do we feel now that this work represents the final word on the thermodynamics of these systems. Nor do we feel that the classical Bjerrum method is totally free of error in log K_i determinations in these systems. We do feel that the thermodynamic data show an internal consistency that is encouraging and that no other method yet proposed is superior to the Bjerrum technique for these systems.

The letter of Anderegg[3] refers to unpublished data from his laboratory. Since we have not been so priviliged as to see this data nor been informed as to how it was obtained, we must reserve comment on it.

The Irving–Mellor data referred to by Anderegg have been examined[4] and there are some doubts about the validity of the distribution method used by the authors and apparently proposed as a standard by which all other methods and data are to be judged. The method used involved the extraction of free ligand from an aqueous solution containing ligand and metal, buffered with sodium acetate and HCl and containing KCl to bring it to what is supposed to be an ionic strength of 0.1. First of all, the authors make no mention of the fact that acetate complexes and chloride complexes of divalent transition metals are well known and, in quite a few cases, their stability constants have been measured.[5] They also ignore the strong possibility of mixed ligand complexes as well as passing over the real problem of knowing or calculating the ionic strength in such a mixture. Examination of the log k_n/k_{n+1} values obtained shows curious inconsistencies not related to obvious problems such as Fe^{+2} spin-pairing and Cu^{+2} coordination changes.

To propose this technique as an interesting and useful approach is certainly valid. To propose it as a standard by which to judge all others is not justified by their work as presented. Their "recommended values" seem to be only their own data rounded off to two significant figures.

(1) G. Atkinson and J. Bauman, *Inorg. Chem.*, **1**, 900 (1962).
(2) G. Atkinson and J. Bauman, *ibid.*, **2**, 64 (1963).
(3) G. Anderegg, *ibid.*, **2**, 1082 (1963).
(4) H. Irving and D. H. Mellor, *J. Chem. Soc.*, 5222 (1962).
(5) "Stability Constants," The Chemical Society, London, 1957.

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The Electronic Spectra of α-Silyl Ketones

Sir:

In 1957 Brook synthesized the first α-silyl ketone, triphenylsilyl phenyl ketone, and established that this compound was yellow in color.[1] This striking observation was followed by an investigation of the electronic spectra of a number of silyl ketones, which showed that in every case the long wave length carbonyl transition was shifted to the visible region.[2] Brook attributed the large spectral shift to interaction between lone-pair electrons on the carbonyl *oxygen* and 3d orbitals of the

(1) A. G. Brook, *J. Am. Chem. Soc.*, **79**, 4373 (1957).
(2) A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, *ibid.*, **82**, 5102 (1960).