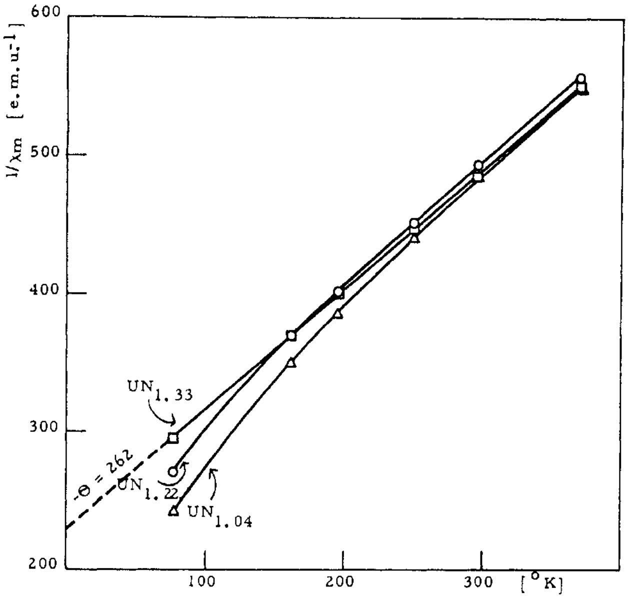

Fig. 1.—Plot of $1/\chi_m$ *vs.* *T* for uranium nitride samples of different composition.

tively; $UN_{1.04}$ results after 3 hr. *in vacuo* at 1950°. Above that temperature the material disappears rapidly. All these phases had a face-centered cubic lattice with $a_0 = 4.875 \pm 0.005$ Å.; their magnetic behavior was, however, markedly different. While $UN_{1.33}$ (U_3N_4) is clearly antiferromagnetic with a Weiss constant $\theta = -262$, the phases with lower nitrogen content behave in a manner characteristic of ferrimagnetic materials.[7] These values have been obtained reproducibly on several samples of the same composition, prepared in different ways. The Bohr magneton number $\mu_B = 3.04$ for U_3N_4, when compared with the literature values of 2.4 for $U(C_2O_4)_2$, 2.92 for UCl_4, 3.22 for UCl_3, and 3.12 for UO_2, does not allow an unambiguous assignment of an oxidation state to the uranium atoms. Neither is this possible on the basis of ionic radii, although if one assigns to the nitrogen a radius of 1.40 Å., which is characteristic of conductive rare earth nitrides, the resulting radius of 1.04 Å. for uranium agrees very well with Goldschmidt's value for U^{+4}.

Furthermore, the ferrimagnetic behavior of lower nitrides may be best explained by the presence of a sublattice of U^{+3} which would tend to form and grow as the nitrogen content is decreased. This assumption of mixed valency states is not inconsistent with the electrical properties of these compounds, which may be treated in a manner analogous to rare earth nitrides and sulfides.[1,8]

The monosulfide and the mononitride of thorium are electronic conductors with a low specific resistivity ($\sim 10^{-4}$ ohm-cm.) and a Seebeck coefficient of a few μvolts per degree at room temperature. The uranium compounds have been studied in more detail on sintered powders. Using previously described apparatus,[1] we have found that between room temperature and 1300°K. the resistivity increases very slightly: from 0.9 to 1.4×10^{-4} ohm-cm. for UN and from 3.6 to 4.3×10^{-4} ohm-cm. for US. Both materials are p-type conductors with a room temperature thermoelectric power of about +50 μv./deg., which reaches a peak value of 80 μv./deg. for US and 100 μv./deg. for UN around 700°K. and then decreases back to the room temperature value at 1300°K. No change in the temperature coefficient of resistivity has been found for US at the Curie point.

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[7] L. Neel, *Ann. Phys.*, **3**, 137 (1948).

[8] J. W. McClure, *J. Phys. Chem. Solids*, to be published.

Correspondence

Infrared Spectra of Ethylenediaminetetraacetic Acid (EDTA)

Sir:

A controversy still exists concerning the structure of EDTA (H_4Y).[1-5] We wish to report data which not only support structure I, recently proposed for solid H_4Y, but also allow a better understanding of the problems involved in the interpretation of infrared spectra of EDTA compounds.

In this laboratory we have prepared five different solid hydrochlorides of H_4Y, three of which are listed in Table I.

From Bellamy's correlations for carboxylic acids and α-amino acids,[6] it follows that the single band near

TABLE I

COMPOSITIONS OF SOLID PROTONATED EDTA COMPOUNDS

		C	H	Cl	N
$H_4Y \cdot 2HCl$	Calcd.	32.89	4.97	19.42	7.67
	Found	33.1	4.9	19.5	7.8
$H_4Y \cdot 2HCl \cdot 2H_2O$	Calcd.	29.94	5.53	17.67	6.98
	Found	29.8	5.9	17.3	6.7
$H_4Y \cdot HCl \cdot H_2O$	Calcd.	34.64	5.52	10.23	8.08
	Found	34.6	5.5	10.2	7.8
		34.7	5.6	10.5	8.2

TABLE II

CARBONYL FREQUENCIES OF SOLID PROTONATED EDTA COMPOUNDS[a]

Compound	Frequency, cm.$^{-1}$
H_4Y	1689 s
$H_4Y \cdot 2HCl$	1736 s
$H_4Y \cdot 2HCl \cdot 2H_2O$	1724 sh
	1712 sh
	1695 s
$H_4Y \cdot HCl \cdot H_2O$	1724 s

[a] s, sharp; sh, shoulder.

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[1] D. Chapman, *J. Chem. Soc.*, 1766 (1955).

[2] D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **75**, 4574 (1953).

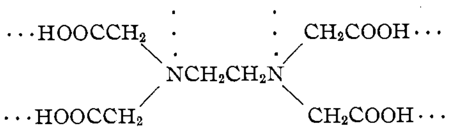
[3] R. E. Sievers and J. C. Bailar, Jr., *Inorg. Chem.*, **1**, 174 (1962).

[4] K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Am. Chem. Soc.*, **85**, 309 (1963).

[5] D. T. Sawyer and J. E. Tackett, *ibid.*, **85**, 314 (1963).

[6] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

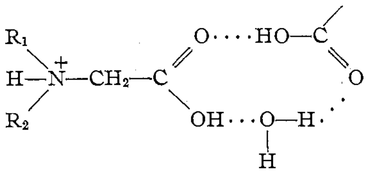
1700 cm.$^{-1}$ *observed* for *solid* H_4Y is due to dimeric –COOH groups attached to neutral nitrogen. This is in agreement with I, postulated by Nakamoto, *et al.*[4]



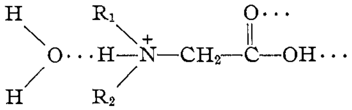
I

Bellamy[6] reports an average shift of 20 cm.$^{-1}$ due to the inductive effect of protonated nitrogen in α-amino acid while we observed a shift of 47 cm.$^{-1}$ for $H_4Y \cdot 2HCl$.

The importance of including hydrogen bonds at the –COOH group in *all* discussions of EDTA structures is demonstrated by the positions of the carbonyl bands of $H_4Y \cdot 2HCl \cdot 2H_2O$. The main band at 1695 cm.$^{-1}$ can only be explained by a system of maximal hydrogen bond strengths, involving two –COOH groups and one water molecule (a), or by the configuration shown in (b).



a



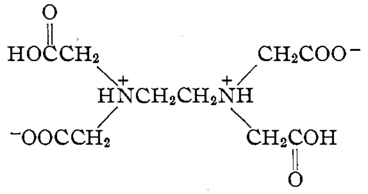
b

Bellamy and Pace[7] have recently published the structure of oxalic acid dihydrate, in which two water molecules are bonded as shown in (a) for one water molecule and which also produces a *lower* carbonyl frequency than the anhydrous compound. An example for (b) is not known.

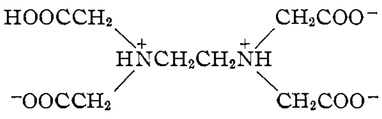
For $H_4Y \cdot HCl \cdot H_2O$ only a single carbonyl band at 1724 cm.$^{-1}$ is observed, which is good evidence for a symmetrical arrangement of the molecule.

These data show clearly that the environment of the –COOH groups, *i.e.*, dimerization and coordination of water, as well as the formal charge of both nitrogen atoms must be taken into consideration for discussions of their structures. This is even more important for the interpretation of infrared absorptions of EDTA *in solution*.

Sawyer, *et al.*,[5] suggest that aqueous EDTA has a double "zwitterion" structure (II) which would give carbonyl absorption bands at 1700 and 1620 cm.$^{-1}$. They have investigated EDTA in D_2O at various acidities and find "at conditions where D_3Y^{-3} (assumed to mean D_3Y^{-1}) is the major species, a small peak at 1700 cm.$^{-1}$ plus a peak three times as large at 1620 cm.$^{-1}$ would be expected if one COOH group plus three COO^- groups attached to the protonated nitrogen atoms is the proper structure (III)" and reproduced a spectrum which "indicates that such a structure is correct."



II

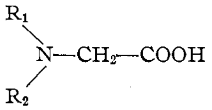


III

However, our data as well as those of Nakamoto, *et al.*,[4] for the solid state and those by Sawyer, *et al.*,[5] for aqueous solutions of EDTA do not support II or III in either state, for the following reasons:

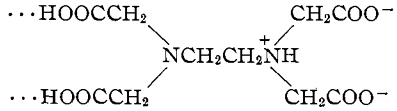
(1) Infrared data obtained with solid H_4Y are not necessarily identical with those of aqueous solutions.

(2) If, as it is apparently assumed by Sawyer, *et al.*,[5] the carbonyl frequency of an EDTA–carboxylic acid group



is 1700 cm.$^{-1}$ for both solid and solution, structures II and III *in solution* should have a band at 1620 cm.$^{-1}$ and another which is *higher than* 1700 cm.$^{-1}$, due to the inductive effect of protonated nitrogen on both –COO$^-$ and –COOH groups.

(3) The "small peak at 1700 cm.$^{-1}$" observed by Sawyer, *et al.*,[5] is actually a bulge between 1750 and 1680 cm.$^{-1}$, a range which would cover all four compounds listed in Table II. The peak area ratio of 1:3 cited in favor of III would actually indicate a 1:1 molar ratio of –COOH:–COO$^-$, based on the difference in extinction coefficients for both groups found by Nakamoto, *et al.*[4,8] Thus the spectrum recorded by Sawyer, *et al.*,[5] would in fact support IV, if pure H_3Y^- existed under their experimental conditions.



IV

In conclusion, the structures of H_4Y and H_3Y^- in aqueous solution remain uncertain since no definitive solution data are available and the use of solid state data is generally not justified to explain solution phenomena where structural changes might occur upon dissolving.

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EASTERN RESEARCH LABORATORY
FRAMINGHAM, MASSACHUSETTS

H. G. LANGER

RECEIVED MAY 1, 1963

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(7) L. J. Bellamy and R. J. Pace, *Spectrochim. Acta*, **19**, 435 (1963).

(8) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Am. Chem. Soc.*, **84**, 2081 (1962).

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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RECEIVED APRIL 25, 1963

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).