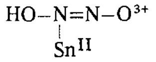
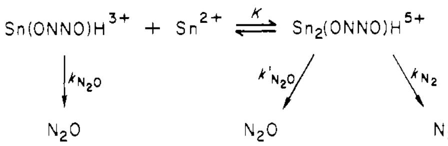


$$\mathrm{HO{-}\underset{\displaystyle Sn^{II}}{\underset{|}{N}}{=}N{-}O^{3+}}$$

by analogy with nitrosohydroxylamine-*N*-sulfonate, which also decomposes to yield N_2O and the two-electron oxidized form of the substituent.[10]

If it is assumed that this species is stable enough to be present in traces, to which a second stannous ion can add reversibly, the production of N_2 is accounted for. The observed form of the stoichiometric law is recovered if it is assumed that either the one-Sn(II) or two-Sn(II) species can yield N_2O, but only the two-Sn(II) species can yield N_2:



The stoichiometry predicted by this scheme is

$$\frac{\text{yield of } N_2}{\text{yield of } N_2O} = (Kk_{N_2}/k_{N_2O})\frac{[Sn^{2+}]}{1 + (Kk'_{N_2O}/k_{N_2O})[Sn^{2+}]}$$

and the experimental data indicate that $k_{N_2}/k'_{N_2O} = 0.36$.

Registry No. NO, 10102-43-9; Sn, 7440-31-5.

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(10) T. L. Nunes and R. E. Powell, *Inorg. Chem.*, **9**, 1916 (1970).

Contribution from the Department of Chemistry,
Florida State University, Tallahassee, Florida 32306

Determination of the Stability Constant for MHL Formation by a Tracer Method

S. M. Shanbhag and G. R. Choppin*

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Many polybasic acid ligands form protonated metal complexes in solutions of appropriate acid pH values. Since the deprotonated complex is usually formed also, evaluation of the stability constants from the usual potentiometric titration technique is relatively complicated. In this note we describe a tracer method that allows direct measurement of β_{101} (for the formation of ML) and of β_{111} (for that of MHL) when both ML and MHL form. In principle, the method can be extended to obtain the constants for any pair of complexes ML_i and MHL_i. Although this technique is an extension of the standard method for measuring stability constants by solvent extraction, it provides a convenient and straightforward means to study relatively complicated equilibrium systems.

For a solvent extraction system we define a distribution coefficient as

$$D = \Sigma[M]_o/\Sigma[M]_a \qquad (1)$$

With the assumption of a constant organic-phase composition—e.g., MS_n where S is the extracting agent—and the presence of various species in the aqueous phase, eq 1 can be expanded

$$D = [MS_n]_o/([M]_a + [ML]_a + [MHL]_a + [ML_2]_a + [MHL_2]_a + ...) \qquad (2)$$

where L is a complexing anion. This equation can be rewritten with the conventional symbols for stability constants[1] as

$$D = [MS_n]_o/([M]_a(1 + [\beta_{101} + \beta_{111}[H]_a] \times [L]_a + [\beta_{102} + \beta_{112}[H]_a][L]_a^2 + ...)) \qquad (3)$$

At constant pH

$$\beta_1 \equiv \beta_{101} + \beta_{111}[H] \qquad \beta_2 \equiv \beta_{102} + \beta_{112}[H]$$

and

$$D = \frac{[MS_n]_o}{[M]_a(1 + \beta_1[L]_a + \beta_2[L]_a^2 + ...)}$$

In the absence of the complexing ligand

$$D_o = [MS_n]_o/[M]_a$$

and

$$D = \frac{D_o}{1 + \beta_1[L]_a + \beta_2[L]_a^2 + ...}$$

This is the usual equation for determination of stability constants by solvent extraction.

If the extraction experiments are conducted over limited ranges of [L], to minimize formation of ML_2 and MHL_2, β_1 can be determined at various values of [H]. Then a plot of β_1 vs. [H] gives an intercept equal to β_{101} and a slope of β_{111}.

To show the validity of this approach, we studied the Eu(III)–malonic acid system. The relatively few values of β_{111} reported in the literature for lanthanide complexes have been obtained by computer analysis of systems containing LnL, LnHL, LnL_2, etc., and hence, no reliable "standard" values are available for comparison. The malonate system is possibly the one most studied.

Experimental Section

Bis(2-ethylhexyl)phosphoric acid, HDEHP, was obtained from Pfaltz and Bauer Inc. and purified by a modification[3] of a method of Peppard et al.[4] Analytical grade malonic acid and sodium perchlorate were used without further purification. ^{152}Eu, ^{154}Eu tracer in HCl solution was obtained from Oak Ridge National Laboratory. A portion was evaporated to dryness and redissolved in 1 M $HClO_4$ prior to use.

A 10-mL quantity of an aqueous solution of constant pH and total ionic strength of 0.1 M ($NaClO_4$) with varying total concentrations of malonic acid up to 10^{-3} M and europium tracer were equilibrated with an equal volume of toluene solution of HDEHP of concentration 1×10^{-3} to 6×10^{-3} appropriate for the pH. After overnight equilibration at 25.0 °C in a water bath, the phases were separated and aliquots counted in a NaI(Tl) well type scintillation counter.

Results and Discussion

These distribution studies were conducted at pH 2.50, 2.80, 3.02 and 3.20. The values of β_1 from these experiments are shown in Figure 1 as a function of the $[H]_a$. From this figure, we calculate

$$\beta_{101} = (1.92 \pm 0.06) \times 10^4$$

$$\beta_{111} = (9.22 \pm 0.26) \times 10^6$$

The errors in β_{101} and β_{111} are calculated according to Student's *t* test, 95% significance level.

Ke et al.[5] have reported $\beta_{111} = 1.5 \times 10^7$ at $\mu = 0.15$ M ($NaClO_4$) but Dellien and Grenthe[6] questioned this value. At $\mu = 1.0$ M ($NaClO_4$) these authors reported $\beta_{101} = 5.25 \times$

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(1) L. G. Sillen and A. E. Martell, *Spec. Publ.—Chem. Soc.*, No. **17** (1964).

(2) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants", McGraw-Hill, New York, 1961.

(3) P. M. Shanbhag, Ph.D. Dissertation, Florida State University, 1979.

(4) D. P. Peppard, G. W. Mason, J. L. Vaier and W. F. Driscoll, *J. Inorg. Nucl. Chem.*, **4**, 334 (1957).

(5) C. H. Ke, P. C. Kong, H. S. Cheng, and N. C. Li, *J. Inorg. Nucl. Chem.*, **30**, 961 (1968).

(6) I. Dellien and I. Grenthe, *Acta Chem. Scand.*, **25**, 1387 (1971).

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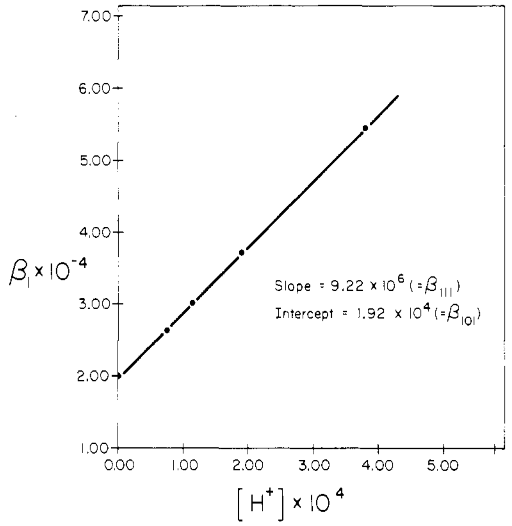

Figure 1. Variation of β_1 with $[H^+]$ for the Eu-malonate system at $\mu = 0.10$ M ($NaClO_4$) at 25.0 °C.

10^3 and $\beta_{111} = 3.0 \times 10^6$. Paramonova et al.[7] measured the complexation in 0.5 M $NaNO_3$ medium and calculated $\beta_{101} = 4.0 \times 10^3$ and $\beta_{111} = 3.3 \times 10^6$ while an earlier study from our laboratory[8] used potentiometry to obtain $\beta_{101} = 4.17 \times 10^4$ at $\mu = 0.10$ M ($NaClO_4$) and pH 3.5–3.7. No analysis was made for β_{111}. Powell et al.[9] measured β_{101} at pH >4.8 where formation of [EuHL] is negligible and reported a value of 2.03×10^4 in 0.1 M KNO_3. This would correspond to $\beta_{101} = 2.9 \times 10^4$ at $\mu = 0.10$ ($NaClO_4$). The agreement between these values (with allowance for differences in ionic strength, etc.) is not completely satisfactory and probably reflects differences (and difficulties) in calculational procedures for obtaining β_{101} and β_{111} from potentiometric techniques. The method we have described reduces that problem considerably.

Acknowledgment. This research was supported by a contract with the USDOE.

Registry No. Eu, 7440-53-1; malonic acid, 141-82-2.

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[7] V. I. Paramonova, A. S. Kereichuk, and A. V. Chizhov, *Radiokhimiya*, **5**, 63 (1963).

[8] G. Degischer and G. R. Choppin, *J. Inorg. Nucl. Chem.*, **34**, 2823 (1972).

[9] J. E. Powell, J. L. Farrell, W. F. S. Neillie, and R. Russel, *J. Inorg. Nucl. Chem.*, **30**, 2223 (1968).

Correspondence

The Question of a Synergystic Metal-Metal Interaction Leading to π-Back-Bond Stabilization in Dirhodium Tetrabutyrate Adducts

Sir:

We have recently[1] claimed that the large radial projection in the d orbitals in rhodium(II) leading to a metal–metal interaction in Rh_2^{4+} systems gives rise to a π-antibonding orbital that projects toward the axial donors in such a way as to make π*-back-bonding system (see Figure 1). Apparently our position was not made clear because this conclusion was challenged[2] recently with a very distorted view of the basis for our conclusion about π stabilization. It is the purpose of this paper to rectify these problems and, in so doing, demonstrate the very strong case that can be made for π stabilization. The observations involved are (1) thermodynamic data, (2) redox potentials for 1:1 adducts, and (3) electronic transitions. It is stated[2] that (1) and (2) above "do not provide positive evidence for π bonding, and the correctness of Drago's conclusion depends critically on the spectral data and his interpretation thereof, namely, that the lowest energy, strong, electron transition in all the bis adducts is the $\pi^* \rightarrow \sigma^*$ transition...." Drago, Tanner, Richman, and Long[1] in no way wish to imply that they support such an indefensible position and regret that our publication could have been interpreted in this way. The argument for π-back-bond stabilization receives its strongest support from our thermodynamic analysis, and it was our intent to show[1] that the electonic absorption spectra and redox potentials show *general trends* that are consistent with this assessment. The least convincing and most difficult observation to interpret of those mentioned above is the electonic absorption spectrum. The problems involved in interpreting this data, even when the assigment is obvious, have been clearly stated.[3] We would never base a bonding argument primarily on an observation as complex as an electronic transition even for the 1:1 adducts where the assignment is clear. Thus, the fact that the 2:1 adducts may undergo a different electron transition is irrelevant to the essential conclusion.

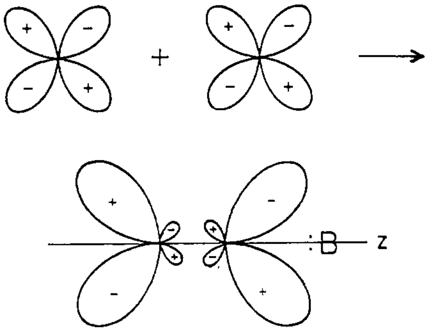

Figure 1. Metal–metal π interactions leading to π*.

The thermodynamic analysis provides by far the best data to utilize to infer relative coordinating tendencies and to understand how bonding considerations influence these tendencies. In terms of sensitivity and the direct bearing this data has on the bond strength contribution to chemical reactivity, no other information is as valuable. Confusion may have arisen in our report[1] as a result of our presentation of these data in terms of the *E* and *C* model. The *E* and *C* parameters are 3.21 and 1.32, respectively, for $Rh_2(But)_4$ (But = butyrate), and, for example, those for BF_3 are 9.9 and 1.6. This means that it is impossible to have a normal σ-donor interaction that will lead to stronger binding to $Rh_2(But)_4$ than to BF_3 since both *E* and *C* are greater for the latter. It is to be emphasized that the empirical nature of the *E* and *C* parameters means that all known thermodynamic data support this point. There

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[1] Drago, R. S.; Tanner, S. P.; Richman, R. M.; Long, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 2897. Drago, R. S.; Long, J. R.; Cosmano, R. *Inorg. Chem.* **1981**, *20*, 2920.

[2] Bursten, B. E.; Cotton, F. A. *Inorg. Chem.* **1981**, *20*, 3042.

[3] See, for example: Drago, R. S. "Physical Methods in Chemistry"; W. B. Saunders: Philadelphia, PA, 1977; p 105.

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