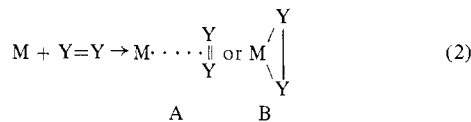


to define unambiguously the formal oxidation state of a complex in all cases and (ii) the recent discovery of new reactions of type 1 that are not oxidative in character.

For example, the addition of ethylene to a metal (eq 2,

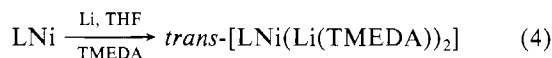


$Y = CH_2$) can be described as a ligand addition (eq 3) if the



structure of the adduct is considered as A or as an oxidative addition if the adduct is considered as B. For ethylene, structure A is often a better model, but for C_2F_4 ($Y = CF_2$) or the analogous oxygen adducts ($Y = O$), structure B is more appropriate.² The terms "oxidative addition" and "ligand addition" therefore merely express different ways of looking at the single process described by eq 2. The two terms, consequently, cannot be unambiguously defined and distinguished.

Jonas,³ in very elegant work, has observed additions of electropositive elements to various nickel complexes (eq 4).



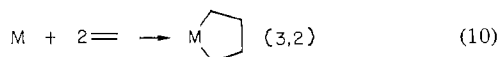
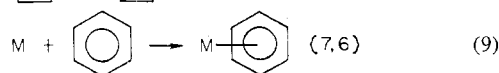
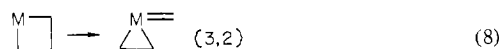
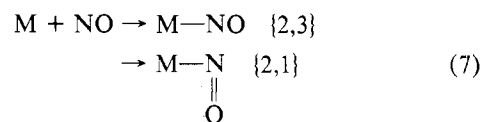
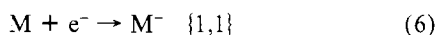
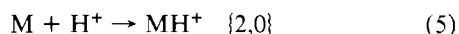
$L = 1,5,9\text{-cyclododecatriene}$; $\text{TMEDA} = \{\text{Me}_2\text{NCH}_2\}_2$

This author has called these processes "reductive additions", because they are analogous to eq 1 and since they cannot be oxidative in character.

Our own work in the addition of H_2 to certain cationic cyclooctadiene complexes of iridium leads us to believe that this addition, too, is reductive in character; the additions are favored by electron-acceptor ligands and inhibited by electron-donor ligands.⁴

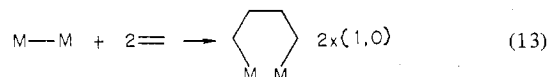
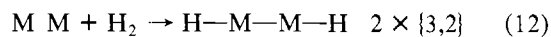
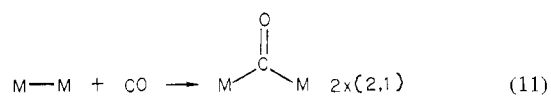
Clearly, the reductive or oxidative character of the addition depends on the electronegativity of the groups X in eq 1. Electronegative groups such as $X = Cl$ lead to an addition that is largely oxidative in character, less electronegative groups ($X = H$) lead to additions that are less oxidative and may even be reductive in character, and electropositive groups [$X = Li(TMEDA)$] lead to additions that can only be described as reductive in character.

The terms "oxidative addition" and "ligand addition" will no doubt continue to be used where no ambiguity arises. It may, however, be useful to develop new frameworks in which these examples can be discussed. We suggest that additions of type 1, 2, or 4 might be termed three-center, two-electron {3,2} additions. New bonds are formed by the metal to two X atoms (three-center), and the electron count of the metal rises by 2 units (two-electron) in each case. An addition of type 3 ($L = CO$), in contrast, would be a two-center, two-electron {2,2} addition. A large variety of processes could be described similarly, e.g.



This system describes only what happens to the metal. Equation 10 is globally a $2 + 2 + 2$ cycloaddition but a {3,2} process at the metal.

Multimetallic systems pose problems where a simple VB picture of the molecule cannot be used and electron counting becomes ambiguous. Some cases, however, are amenable to description:



This nomenclature describes the changes in the metal coordination number and electron count on reaction, both of which are relatively free from ambiguity. In contrast, the classical nomenclature relies on the often ambiguous concept of oxidation state and on assumptions, sometimes unjustified, as to the polarity of metal-ligand bonds.

Workers in the field are well aware of these shortcomings in our jargon, but perhaps by developing more logical terminology, we can make our ideas more accessible to fellow scientists in related disciplines.

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Received March 29, 1979

Application of the Edwards Equation to Formation of Adducts of Copper(II) Macrocyclic Tetraamine Complexes with Anions

Sir:

Edwards¹ has shown that equilibrium constants for various acid-base reactions can be quantitatively correlated by means of the equation

$$\log (K/K_0) = \alpha E_n + \beta H \quad (1)$$

In this equation, K is the equilibrium constant for the acid-base reaction, K_0 is the constant for a reference base (say, water) reacting with the same acid, H is a proton basicity factor defined by $H = 1.74 + pK_a$, and E_n is a redox factor defined by $E_n = E^\circ + 2.60$, where E° is the standard oxidation potential for the process, $2X^- \rightleftharpoons X_2 + 2e^-$. The parameters α and β are constants characteristic of the acid. The terms α , β , and α/β are of value and can be used as a measure of the

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(3) K. Jonas, *Angew. Chem., Int. Ed. Engl.*, **14**, 752 (1975). The structure of the Ni-Li complex was determined by X-ray crystallography.

(4) R. H. Crabtree, H. Felkin, T. Khan, and G. E. Morris, *J. Organomet. Chem.*, **168**, 183 (1979); R. H. Crabtree, *Acc. Chem. Res.*, **12**, 331 (1979). New ¹³C NMR evidence also supports the reductive character of the addition: an upfield shift, observed in the vinyl carbon resonances of $\text{Ir}(\text{cod})_2^+$ on addition of H_2 , suggests that the electron density at Ir increases (R. H. Crabtree and J. M. Quirk, unpublished results, 1979).

(1) Edwards, John O. *J. Am. Chem. Soc.* **1954**, *76*, 1540.

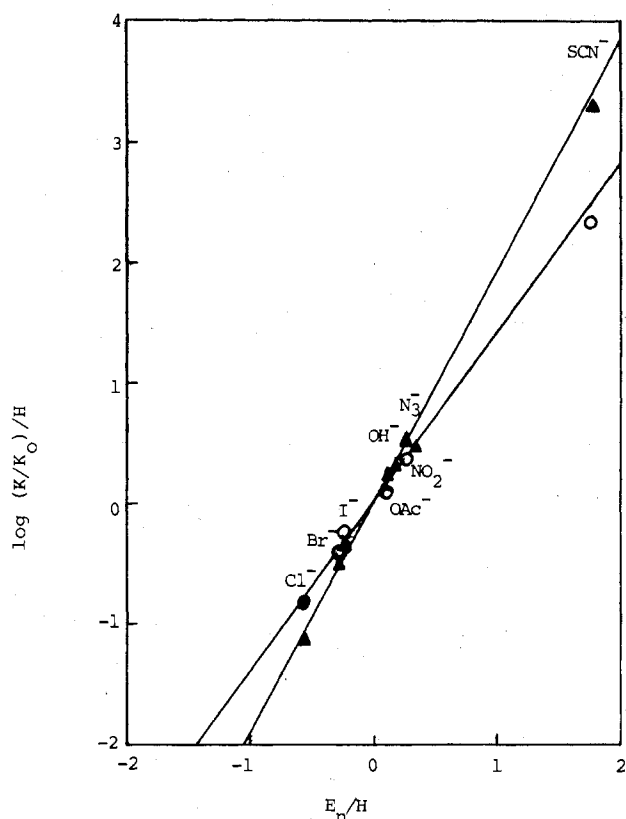
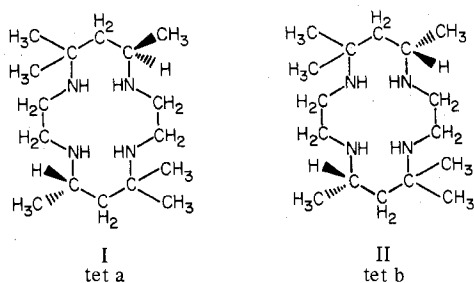


Figure 1. $(\log(K/K_0))/H$ vs. E_n/H plot in water at 25 °C: ▲, $[\text{Cu}(\text{tet a})(\text{blue})]^{2+}$; ○, $[\text{Cu}(\text{tet a})(\text{red})]^{2+}$.

sensitivity to nucleophilic ligand character or polarizability, a measure of the sensitivity to basicity of ligand toward proton, and a measure of the softness of the acid, respectively.²

In the case of the complex, the polarizability, acidity, and softness of the metal ion are not inherent properties of the particular atom at that site but can be influenced by the substituent atoms. In the current investigation, we have attempted to study the influences on these properties of copper(II) ion attributable to macrocyclic tetraamines.

The macrocyclic ligand 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane exists as two isomers, tet a (I) and tet b (II).³ Each of these isomers forms a blue and



a red complex with copper(II).⁴ The crystal structure determinations of these complexes have recently been completed.⁵⁻⁸ $[\text{Cu}(\text{tet a})(\text{red})](\text{ClO}_4)_2$ has the trans structure with

Table I. Equilibrium Constants (M^{-1})^{10,11} for the Reaction $\text{CuL}^{2+} + \text{X}^- \rightleftharpoons \text{CuLX}^+$, at 25 °C, $\mu = 0.1 \text{ M}$ ($\text{NaNO}_3 + \text{NaX}$)

| X^- | $[\text{Cu}(\text{tet b})(\text{blue})]^{2+}$ | $[\text{Cu}(\text{tet a})(\text{blue})]^{2+}$ | $[\text{Cu}(\text{tet b})(\text{red})]^{2+}$ | $[\text{Cu}(\text{tet a})(\text{red})]^{2+}$ |
|-----------------|---|---|--|--|
| Cl^- | 15.5 | 7.0 | 1.8 | 1.5 |
| Br^- | 18.1 | 9.5 | 3.2 | 2.3 |
| I^- | 22.2 | 11.3 | 6.5 | 3.0 |
| N_3^- | 84.5 | 45.3 | 8.6 | 4.0 |
| SCN^- | 147 | 48.1 | 9.3 | 4.6 |
| OH^- | 508 | 50.3 ^a | 0.96 ^a | 0.73 ^a |
| OAc^- | 1.8 ^a | 1.4 ^a | | |
| NO_2^- | 7.2 ^a | 4.0 ^a | | |
| CN^- | 2950 ^a | | | |
| SH^- | 300 ^a | | | |

^a This work.

Table II. Values of α and β for Copper(II) Complexes

| complex | α | β | α/β | hardness ^b |
|---|----------|---------|----------------|-----------------------|
| $[\text{Cu}(\text{tet b})(\text{blue})]^{2+}$ | 2.189 | 0.033 | 65.9 | S |
| $[\text{Cu}(\text{tet a})(\text{blue})]^{2+}$ | 1.913 | 0.031 | 62.5 | S |
| $[\text{Cu}(\text{tet b})(\text{red})]^{2+}$ | 1.512 | 0.026 | 57.4 | S |
| $[\text{Cu}(\text{tet a})(\text{red})]^{2+}$ | 1.395 | 0.025 | 55.8 | S |
| Cu^{2+} ^a | 2.259 | 0.233 | 9.7 | B |

^a See ref 2. ^b S = soft and B = borderline.

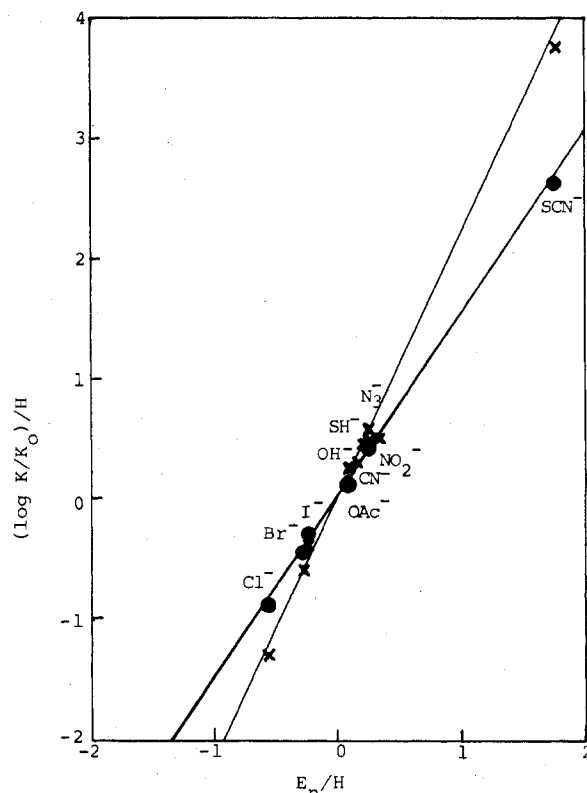


Figure 2. $(\log(K/K_0))/H$ vs. E_n/H plot in water at 25 °C: ×, $[\text{Cu}(\text{tet b})(\text{blue})]^{2+}$; ●, $[\text{Cu}(\text{tet b})(\text{red})]^{2+}$.

a square-planar arrangement of the four nitrogens of tet a.^{5,9} The copper of $[\text{Cu}(\text{tet b})(\text{red})](\text{ClO}_4)_2$ is four-coordinate with a very slightly distorted planar arrangement of the four nitrogens of tet b.⁷ Crystallographic studies of the blue species indicate that the ligand of $[\text{Cu}(\text{tet a})(\text{blue})]^{2+}$ is in a distorted planar configuration,^{6,9} while the ligand of $[\text{Cu}(\text{tet b})(\text{blue})]^{2+}$ is in a folded structure.⁸ Thus these complexes can provide the opportunity to elaborate the ways in which the different

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(3) Curtis, N. F. *J. Chem. Soc.* **1964**, 2644.

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(5) Bosnich, B.; Tobe, M. L.; Webb, G. A. *Inorg. Chem.* **1965**, *4*, 1102. Bosnich, B.; Mason, R.; Pauling, P.; Robertson, G. B.; Tobe, M. L. *Chem. Commun.*, **1965**, 97.

(6) Clay, R. M.; Murray-Rust, P.; Murray-Rust, J., unpublished work.

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Table III. Visible and Near-Infrared Absorption Bands

| complex | ν_{\max} , $\text{cm}^{-1} \times 10^3$ | ϵ_{\max} , $\text{M}^{-1} \text{cm}^{-1}$ |
|---|---|--|
| $[\text{Cu}(\text{tet a})(\text{red})]^{2+}$ | 19.6 | 135 |
| $[\text{Cu}(\text{tet b})(\text{red})]^{2+}$ | 19.1 | 174 |
| $[\text{Cu}(\text{tet a})(\text{blue})]^{2+}$ | 15.4 | 213 |
| $[\text{Cu}(\text{tet b})(\text{blue})]^{2+}$ | 12.0, 14.7 (sh) | 269, 172 |
| $\text{Cu}^{2+}(\text{aq})$ | 12.6 | 11 |

structures of the coordinated macrocyclic tetraamines convey properties on their metal complexes.

The present paper concerns the equilibria of the complexation reactions of these four copper(II) complexes with anionic ligands represented by the general formulation in eq 2. Here



L is the macrocyclic ligand, tet a or tet b. Equilibrium constants determined in this work and reported in earlier studies^{10,11} are summarized in Table I. These data were used along with the reported values of H and E_n ¹² to obtain α and β values of the Edwards equation (eq 1). A plot of $(\log K_x + 1.74)/H$ vs. E_n/H gives a straight line with slope α and intercept β for each of these copper(II) complexes as shown in Figures 1 and 2. The results obtained are given in Table II along with the parameters for Cu^{2+} reported by Yingst and McDaniel.²

As preliminary observations on the parameters in Table II, the following three trends are particularly noteworthy.

1. The value of α , which provides an indication of the sensitivity to nucleophilic ligand character, or polarizability, of the complex, varies in the order $[\text{Cu}(\text{tet a})(\text{red})]^{2+} < [\text{Cu}(\text{tet b})(\text{red})]^{2+} \leq [\text{Cu}(\text{tet a})(\text{blue})]^{2+} < [\text{Cu}(\text{tet b})(\text{blue})]^{2+} < \text{Cu}^{2+}(\text{aq})$.

2. The value of β , which provides an indication to the sensitivity to basicity of ligand toward proton, or acidic strength, of the complex, varies in the order $[\text{Cu}(\text{tet a})(\text{red})]^{2+} < [\text{Cu}(\text{tet b})(\text{red})]^{2+} < [\text{Cu}(\text{tet a})(\text{blue})]^{2+} < [\text{Cu}(\text{tet b})(\text{blue})]^{2+} \ll \text{Cu}^{2+}(\text{aq})$.

3. The value of α/β , which provides an indication of the softness of the complex, varies in the order $\text{Cu}^{2+}(\text{aq}) \ll [\text{Cu}(\text{tet a})(\text{red})]^{2+} < [\text{Cu}(\text{tet b})(\text{red})]^{2+} < [\text{Cu}(\text{tet a})(\text{blue})]^{2+} < [\text{Cu}(\text{tet b})(\text{blue})]^{2+}$.

The cis effect pointed out by Busch,¹³ that the ability of a metal ion to electrophilically distort a substrate or ligand could be enhanced by the presence of a weak ligand field, suggests there must be a relation between the values of α and the spectral properties of the complexes. The principal absorption bands of the complexes in aqueous solution are given in Table III.

$[\text{Cu}(\text{tet b})(\text{blue})]^{2+}$ is unique among these complexes. The ligand of $[\text{Cu}(\text{tet b})(\text{blue})]^{2+}$ is in a folded rather than a planar configuration. The spectrum of this complex in aqueous solution exhibits two d-d bands, while the spectra of the other macrocyclic copper(II) complexes in which the ligand is in a planar or distorted planar, rather than a folded configuration, exhibit a single λ_{\max} . For investigation of the effect of the strength of the ligand field of the copper(II) complexes upon the value of α , the wavenumber of the maximum of the d-d

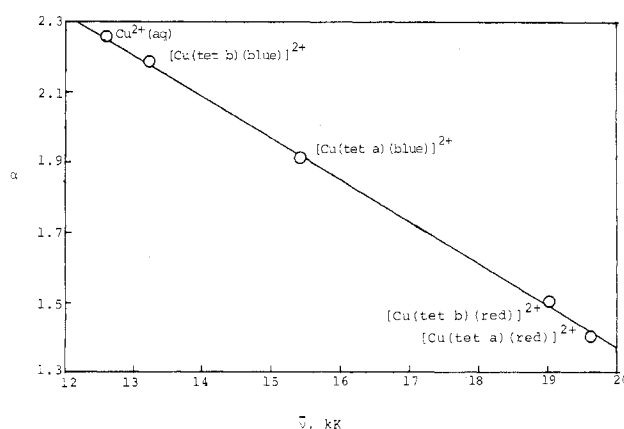


Figure 3. α parameter vs. $\bar{\nu}$ of the maximum of the electronic spectra of the copper(II) macrocyclic tetraamine complexes in aqueous solution at 25 °C.

band or the average of the wavenumbers of the two bands was considered as an approximate measure of the strength of the ligand field. Figure 3 shows that the correlation between α and $\bar{\nu}$ is quite good.

In order to account for the sequence of the sensitivity to the proton basicity factor, it is necessary to consider the basicity of the donor atoms and the structure of the complex. The results given in Table II provide interesting illustrations of the influences of these two factors. In view of the electronegativities of N and O, it is not surprising that the value of β for Cu^{2+} is much larger than that for the copper(II) macrocyclic tetraamine complex. The most striking result is the fact that β varies strongly with the structure of the macrocyclic ligand. On the basis of both crystal field stabilization energy and steric effect, we might expect that the copper(II) macrocyclic tetraamine complex which has a trans structure would be insensitive to the proton basicity factor of the ligand and that the value of β would increase as the degree of distortion of the macrocyclic ligand increases. The sequence for β , $[\text{Cu}(\text{tet a})(\text{red})]^{2+} < [\text{Cu}(\text{tet b})(\text{red})]^{2+} < [\text{Cu}(\text{tet a})(\text{blue})]^{2+} < [\text{Cu}(\text{tet b})(\text{blue})]^{2+}$, lends support to these views.

In aqueous solution, copper(II) ion is on the borderline between hard and soft. Addition of four basic amines softens the copper(II) and makes it a soft acid, in accord with the symbiosis pointed out by Jørgensen.^{14,15} The softness of the copper(II) tetraamine complex is mainly due to the low value of β , insensitivity to the proton basicity factor of the ligand.

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Registry No. $[\text{Cu}(\text{tet b})]^{2+}$, 53447-11-3; $[\text{Cu}(\text{tet a})]^{2+}$, 24830-76-0; Cl^{-} , 16887-00-6; Br^{-} , 24959-67-9; I^{-} , 20461-54-5; N_3^{-} , 14343-69-2; SCN^{-} , 302-04-5; OH^{-} , 14280-30-9; OAc^{-} , 71-50-1; NO_2^{-} , 14797-65-0; CN^{-} , 57-12-5; SH^{-} , 15035-72-0.

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