Abstract of Paper Presented at the Symposium on Metal Chelate Chemistry at Brooklyn Polytechnic Institute on April 26, 1952

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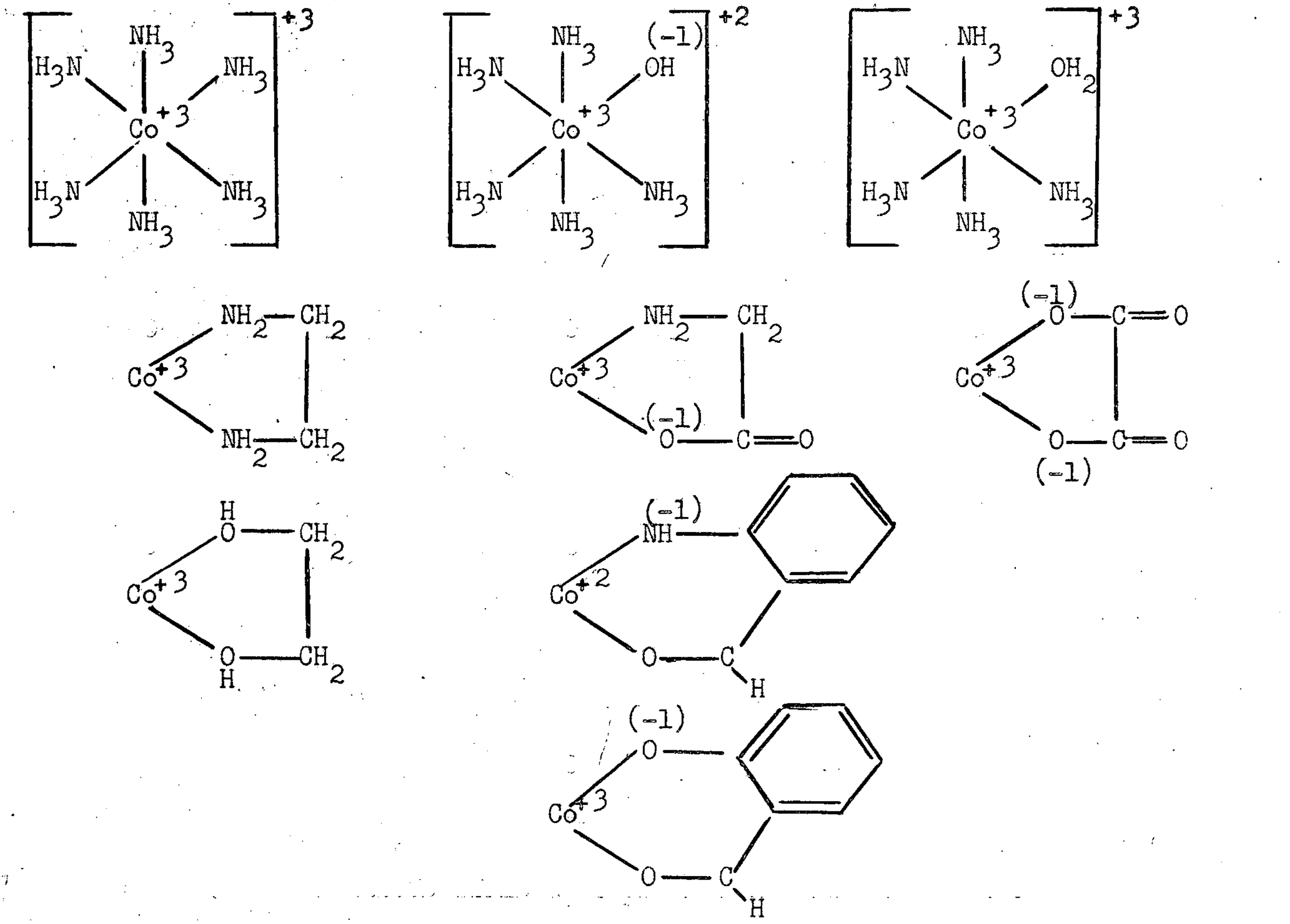
ABSTRACT OF PAPER PRESENTED AT THE SYMPOSIUM ON METAL CHELATE CHEMISTRY AT BROOKLYN POLYTECHNIC INSTITUTE ON APRIL 26, 1952

BY MELVIN CALVIN

The essential structural element which differentiates metal chelate compounds from metal coordination compounds, or metal complexes in general, is the existence of some linkage between two or more of the donor atoms in the first coordination sphere of the metal. It is the purpose of the present discussion to examine the influences that this structural factor may have upon the physical and chemical properties of chelate compounds. Examples of well known, simple coordination compounds involving a variety of donor atoms (Oxygen, Nitrogen), as well as a variety of electrostatic situations, are shown in the following formula. Below each one are listed a few corresponding chelate structures.



Various types of complex ions and chelate compounds

Perhaps one of the simplest and most easily definable properties of such compounds is the stability of the complex. This stability can be most readily defined in terms of association, or formation, constants, as follows:

$$Me^{+n} + Ke^{-m} \rightleftharpoons MeKe^{+n-m} \qquad k_1 = \frac{[MeKe^{+n-m}]}{[Me^{+n}]\;[Ke^{-m}]}$$

$$MeKe^{+n-m} + Ke^{-m} \rightleftharpoons [MeKe_2]^{+n-2m} \qquad k_2 = \frac{[MeKe_2^{+n-2m}]}{[MeKe^{+n-m}]\;[Ke^{-m}]}$$

$$\vdots \qquad \vdots \qquad\qquad\qquad\qquad\qquad \vdots$$

$$k_3$$

For the case $n = 2$, $m = 1$

$$K = k_1k_2 = (K_{av})^2$$

Stability defined in terms of association constants

The determination of such stability constants, for a wide variety of structures, has recently become a popular area of research activity. The reason for this is to be found in the important part played by chelate compounds in a wide variety of biological phenomena, particularly in enzymatic and co-enzymatic functions, as well as their increasing importance in industrial processes involving organic syntheses, the separation of difficultly separable elements such as rare earths, and various catalytic phenomena. All of this, of course, is to be added to the much older application in analytical chemistry, and their new application in textile chemistry and dyeing, especially of synthetic fibers.

The methods which have been used to determine stability constants are varied, and have been discussed in some detail by other members of the Symposium. They may be listed briefly as follows:

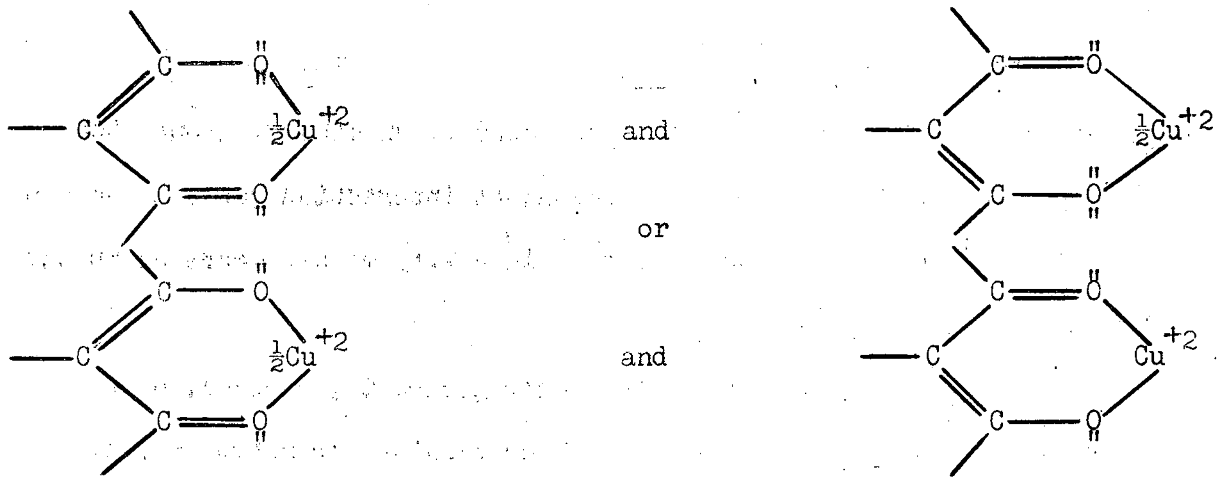
1. Direct measurement by titration (pH or Redox).
2. Direct determination of the concentration of species from absorption spectra.
3. Relative and absolute determination by polarigraphic reduction.
4. Relative and absolute determination from exchange rates, using isotopic metal ions.
5. Competition between two chelating agents for the same metal.
    a. In one phase
    b. In two liquid phases (extraction equilibrium).
    c. In one liquid and one solid phase (ion exchange equilibrium).

As a result of a general survey of the stability of complex compounds, it is possible to set down the number of factors which influence the stability of all complex compounds, irrespective of whether they be chelates or not. They may be divided into properties of the central metal atom, such as charge-radium ratios and available orbitals, and properties of the complex group, such as polarizability, size and basicity. In addition to these, however, there are a number of characteristics found uniquely in chelate compounds. These are:

1. Steric effects involving the size and shape of the chelate ring.
2. Entropy effects arising from differences in the number of particles on either side of the chelation equilibrium (or expressed otherwise, in terms of the necessity for simultaneous making or breaking of two or more ligends).

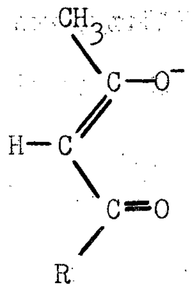
3. Resonance effects arising from the possibility of electronic interaction through the ring between the two or more donor atoms.

It is these latter factors, characteristic of chelating compounds, which constitute the subject of the present discussion. When an attempt was made to evaluate these factors in a more quantitative way, it became apparent that it would be necessary to find first some basis of comparison which would have recognized and accounted for these factors which are not characteristic of chelation, but rather of any change in the donor group. The most pronounced such effect lies in the variation of the basic property of the donor group, that is, the ability of these donor groups to bind protons. This was first illustrated in 1945 [1] by the approximate linear plots obtained when the logarithm of the stability constant for the binding of the cupric ion was plotted against the logarithm of the acidity constant (the binding of the proton) in a series of substituted salicylaldehydes. This type of relationship has since been greatly expanded for a wide variety of complexing groups [2]. When the stability constants for two different chelating groups having the same basic properties were found to differ very markedly, it became necessary to seen an understanding of this discrepancy in terms of structure of the chelate ring itself. This has led to the recognition of a resonance contribution to the structure of metal chelates in which the two donor groups are connected by conjugated systems. It may be illustrated by the β-diketone type of chelating agent, as follows:

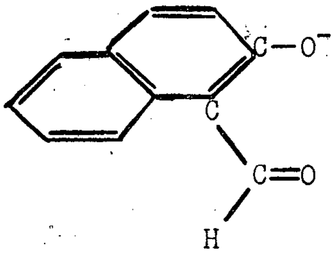


Thus the degree to which the two oxygen donors may interact electronically will be directly reflected in the stability of the chelate compound formed with such an ion as cupric ion. Any factor in the structure of the molecule which would tend to insulate the two donor atoms from each other electronically, that is, reduce the degree of conjugation between them, should reduce the stability constant for such an ion as cupric ion, even when corrected to the same basic strength (ability to bind protons). This is indeed the case as shown in the series 2,3-naphtholaldehyde, salicylaldehyde, 2,1-naphtholaldehyde and acetylacetone [1]. The relationships in these structures are shown in the following diagram:

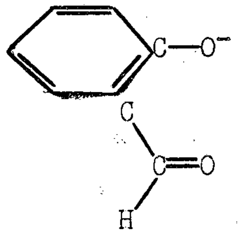
The Resonance Effect



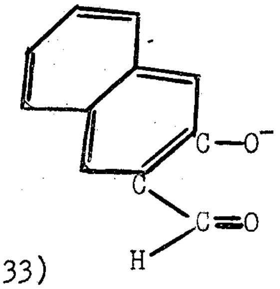
A (2)



B (1.67)



C (1.5)



D (1.33)

As the R Group in the diketone shown above is replaced by an ethoxyl group, there will be a considerable interference with the resonance interaction between the two chelating oxygen atoms and this will be reflected in a very marked decrease in the stability of chelates formed by β-keto acids.

The effect of the binding together of two donor groups is, perhaps, best illustrated by comparing the heat and entropy of the binding per nitrogen atom in the coordination compounds of nickel amines. Thus, when two amino-nitrogens are tied together by a carbon chain, as in ethylenediamine, the heat of formation of the nickel-nitrogen bond changes just a little, whereas the entropy of this reaction is markedly affected, as shown in the following sequence of reactions:

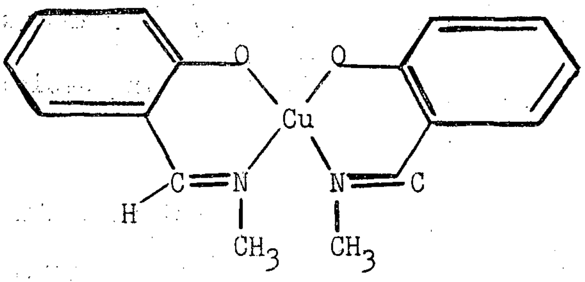
The Entropy Effect

$$\mathrm{Ni^{++}(H_2O)_x + 6NH_3(aq) \rightleftharpoons Ni(NH_3)_6^{++} + xH_2O} \qquad \Delta H \simeq 19;\ \Delta S \simeq .22$$

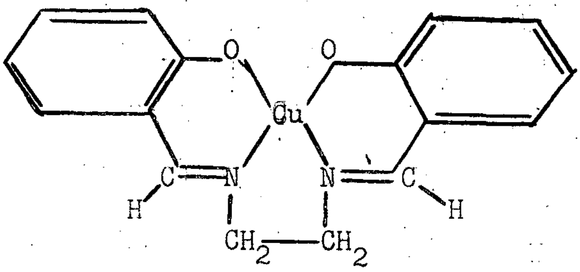
$$\mathrm{Ni^{++}(H_2O)_x + 3\ en(aq) \rightleftharpoons Ni(en)_3^{++} + xH_2O} \qquad \Delta H \simeq 25;\ \Delta S \simeq +2$$

$$\mathrm{Ni(NH_3)_6^{++} + 3\ en(aq) \rightleftharpoons Ni(en)_3^{++} + 6NH_3)_{aq}} \qquad \Delta H \simeq 6;\ \Delta S \simeq +24$$

A similar stabilizing effect of binding two or more donor groups together has been observed in a wide variety of cases [2,3]. This increased stability, resulting from the mere tying together of donor groups in the creation of a chelate structure, is reflected in a variety of other related properties as well [4,5].

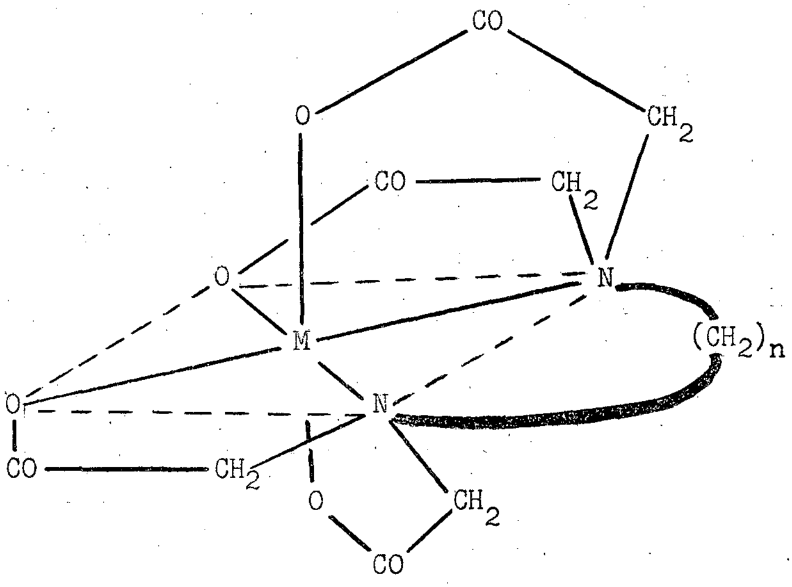


$E_{\frac{1}{2}}^{(1)} = +0.02$ $t_{\frac{1}{2}} < 15$ sec.



$E_{\frac{1}{2}}^{(1)} = -0.75$ $t_{\frac{1}{2}}$ 2.1 hrs.

One very interesting study in which the effect of the sizes of the chelate ring have been examined, is that of Schwarzenbach [3], who investigated the stability constants of homologs of ethylenediaminetetraacetic acids.



The relationships between the stability constants and acidity constants for a number of earth metals are given in the following table:

STABILITY CONSTANTS OF ALKALINE EARTH COMPLEXES WITH HOMOLOGS OF ETHYLENEDIAMINETETRAACETIC ACID

					Log K			
n	pK_1	pK_2	pK_3	pK_4	Mg^{+2}	Ca^{+2}	Sr^{+2}	Ba^{+2}
2	2.0	2.7	6.16	10.26	8.7	10.5	8.6	7.
3	2.0	2.7	7.91	10.27	6.0	7.1	5.2	4.
4	1.9	2.7	9.07	10.45		5.0		
5	2.2	2.7	9.50	10.58		4.6		

Undoubtedly as the quality and quantity of the measurements of stability constants increase, a final system will be developed regarding the relation between the structure of the chelating agent and the properties of the resulting chelate.

REFERENCES:

1. M. Calvin & K. W. Wilson, J. Am. Chem. Soc. 67, 2003 (1945)
2. Schwarzenbach, Ackerman & Ruckstuhl, Helv. Chim. Acta, 32, 1775 (1949)
3. Schwarzenbach & Ackerman, Helv. Chim. Acta, 31, 1029, (1949)
4. R. B. Duffield & M. Calvin, J. Am. Chem. Soc., 68, 557 (1946)
5. M. Calvin & R. H. Bailes, J. Am. Chem. Soc., 68, 949 (1946)