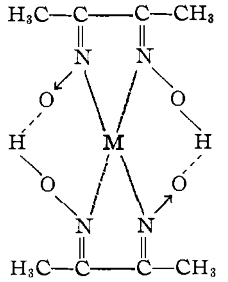

It is the hydrogen bonding of the oxygens in this structure which is responsible for the increased stability of these complexes.[9]

Copper dimethylglyoxime remains in solution as the deep red complex. The nickel compound precipitates after the first few additions of base. The measurements for nickel were made in the supersaturation region for the complex since the complex precipitates without the addition of base if a sufficient period of time is allowed.

The titration curves for 1-nitroso-2-naphthol follow the pattern of Fig. 1b and those for ethyl benzoylacetate, ethyl benzoylpyruvate and salicylaldehyde follow the pattern for Fig. 1a. The formation constants reported for salicylic acid are for the complex formed when only the carboxyl group proton has been lost.

STATE COLLEGE, PENNA.

[9] H. Freiser, University of Pittsburgh, Report of Jan. 31, 1951, on Contract AT(30-1)-860.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Studies on Coordination Compounds. X. Correlation of the Solution Stabilities of the Chelate Compounds of Ligands Coördinating through Nitrogen and Oxygen[1]

BY LEGRAND G. VAN UITERT[2] AND W. CONARD FERNELIUS

RECEIVED JUNE 18, 1953

The correlation of the stability constants of ligands coördinating through oxygen and nitrogen in aqueous solution serve to demonstrate the general factors involved in coördination chemistry. This correlation can be effected through consideration of the electronegativities and the hybrid bond states of the partners, the inductive influences involved, and the number of coördinating positions on the ligand.

The factors governing the solution stabilities of chelate compounds are quite complex. Although it is not possible at present to calculate the stability constant of a given compound from strictly theoretical considerations, it can be shown that the relationships involved are consistent and to a degree predictable.

The approach to the problem that has been employed is based upon the consideration of factors influencing bond stability as presented by Walsh.[3]

Experimental

The compounds referred to by number in Figs. 1, 3 and 4 are the following: 1, ammonia; 2, ethylenediamine; 3, glycine; 4, 2-nitroso-1-naphthol; 5, 1-nitroso-2-naphthol; 6, 8-hydroxyquinoline[4]; 7, 1-(2-hydroxy-5-methylbenzeneazo)-2-benzoic acid; 8, 1-(2-hydroxynaphthylazo)-2-naphthol-4-sulfonic acid; 9, 1-(2-hydroxy-5-nitrobenzeneazo)-2-naphthol; 10, 1-(2-hydroxy-5-chlorobenzeneazo)-2-naphthol; 11, 1-(2-hydroxybenzeneazo)-2-naphthol; 12, 1-phenyl-3-methyl-4-(2-hydroxy-4-sulfonic acid-naphthylazo)-5-pyrazolone; 13, 1-phenyl-3-methyl-4-(2-hydroxybenzene)-5-pyrazolone; 14, 1-phenyl-3-methyl-4-(4-nitrobenzeneazo)-5-pyrazolone; 15, 1-phenyl-3-methyl-4-(4-chlorobenzeneazo)-5-pyrazolone; 16, 1-phenyl-3-methyl-4-(benzeneazo)-5-pyrazolone; 17, 1-phenyl-3-methyl-4-(4-methylbenzeneazo)-5-pyrazolone[5]; 18, salicylaldehyde; 19, 2-acetyl-1-naphthol; 20, ethyl benzoylpyruvate[4]; 21, tropolone[6]; 22, *d*-tartaric acid (2 protons lost); 23, ethyl benzoylacetate[4]; 24, 2,4-pentanedione; 25, 2,2-dimethyl-3,5-hexanedione[7]; 26, *d*-tartaric acid (3 protons); 27, benzoylpyruvic acid; 28, salicylic acid.[4] All values for the above are for 75 volume % dioxane solution, and are expressed as activity constants.

Discussion

Factors Influencing Bond Strength.—It would appear that in the gaseous state the main factors involved in determining bond strength are: (1) the electronegativities of the partners involved, (2) the dipole character of the bond, and (3) the effects of nuclear repulsion in the cases of the highly electronegative atoms. From spectroscopic measurements it has been determined that: (a) the energy of the bond between two partners can be represented as a function of the product of their respective electronegativities, (b) bond strength is weakened by the development of dipole character in a bond, and (c) influences that affect the electronegativity of highly electronegative atoms may result in effects opposite to what would be expected in accordance with a.

Nitrogen and oxygen hold onto their electrons so tightly that appreciable nuclear repulsion is often developed between bonding partners in which one of them is involved. In these cases, a small reduction in the electronegativity of nitrogen or oxygen is more than compensated for by the resulting increase in wave function overlap.

Walsh further indicates that bond stability can be viewed as a function of the total charge interchange between partners. Pauling[8] has calculated the relative hybrid bond stability ratios for the

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[1] For IX in this series see L. G. Van Uitert and W. C. Fernelius, THIS JOURNAL, **76**, 375 (1954).

[2] Union Carbide and Carbon Corporation Fellow, 1951–1952.

[3] A. D. Walsh, *J. Chem. Soc.*, 398 (1948).

[4] L. G. Van Uitert and W. C. Fernelius, THIS JOURNAL, **76**, 375 (1954).

[5] F. A. Snavely, Dissertation, The Pennsylvania State College, 1952.

[6] B. E. Bryant, W. C.Fernelius and B. E. Douglas, THIS JOURNAL, **75**, 3784 (1953).

[7] L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, *ibid.*, **75**, 457 (1953).

[8] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, pp. 81, 82, 92, 96.

strengths of the bonds that may result from the combination of a given atom in different bond hybrid states with a second atom that bonds in a fixed manner. The relative charge interchanges involved in the bonds between different atoms with a common third atom while in comparable hybrid bond states must also be taken into consideration. In accordance with 1 above this latter quantity may be taken to be a function of the product of the electronegativities of the partners involved.

Relative Measures of Bond Energy.—The electronegativities of the atoms or ions involved in forming a bond can be considered to vary with the hybrid bond state; hence, bond strength will be considered to be a function of the product of the specific hybrid bond state electronegativities. In those cases where the partners involved are both highly electronegative, the above picture is modified by 3, the effect of nuclear repulsions.

In reference to Coulsen's work[9] Walsh demonstrates that the bonding electronegativities of the carbon atom increase with the s character of the σ-bonds.

Bond	σ-Hybrid	
C—H (radical)	p	increase in bond
H_3C—H	sp^3	energy and carbon
$H_2C{\equiv}CH$—H	sp^2	↓ electronegativity
HC≡C—H	sp	

This is a consequence of the fact that the s orbital lies closer (energetically) to the nucleus than do the p-orbitals.

It may be expected that a similar increase in the multiple bond character of isoelectronic nitrogen and oxygen will result in an increased bond hybrid electronegativity for these atoms. The characteristic electronegativities for these atoms should increase in the orders

$$-N<,\ \geqslant N,\ -N{=}N-,\ \equiv N \text{ and } -O^-,\ \overset{\diagdown\ \diagup}{O},\ {=}O$$

Then, in accordance with 3 above, as the less electronegative states of these atoms exert the smaller nuclear repulsion forces toward the highly electronegative metal ions, the above orders will also represent decreasing coördinating ability toward such ions; this is to say that the "effective" electronegativities (in connection with the highly electronegative metal ions), which are derived to conform with 1 above, decrease in the above order.

General Considerations.—The ability of the concept of electronegativity to correlate phenomena presumes a uniform behavior in the attractive forces between particles such that the ratio of the tendencies for solvent particles "S" and added particles "X" to associate with "M" is a function of the ratio of the "effective" electronegativities of S and X. Upon going into the dissolved state, the particles S compete for M with the particles X of the added compound in the association process. In a polar medium the orientation of dipoles about the particles in solution and the increased dielectric constant of the medium both tend to decrease the effective stability of the added compound. The association of M with X is limited by a function of the "effective" electronegativities of X and S and their relative concentrations in solution.

The proton affinity of the above nitrogen and oxygen states in the condensed state may serve as a measure of their "effective" electronegativities. Single bonded nitrogen is strongly basic (amines), double bonded ring nitrogen is weakly basic (pyridine), diazo nitrogen is neutral (azobenzene), and triple bonded nitrogen is acidic in character as evidenced by its ability to influence the dissociation of the proton in HCN. The enolate ion is basic, water is neutral, and double-bonded oxygen has sufficient influence on an enol carbon to form an acidic group (COOH). Gordy and Stanford[10] found that the spectroscopic perturbations which are produced as a consequence of hydrogen bonding indicate that the proton attracting power of 42 liquids increased in the order: nitro compounds < esters < aldehydes and ketones < ethers < amines. This series is also in agreement with the above relative "effective" electronegativities.

Chelate Compound Bond Stability. The Contribution of the Metal Ion.—In terms of functional notation bond energy (E) might be formulated as

$$E = f(X_aX_b,\ X_a - X_b,\ \psi_0)$$

where the first term represents the product of the electronegativities of the partners involved in accordance with 1 above. The second term represents the dipole character of the bond due to the difference in the electronegativities of the partners in accordance with 2. The third term represents the influences of nuclear repulsion on wave function overlap in the cases of nitrogen and oxygen. If ΔS is small, $RT \ln K_f$ (K_f = formation constant) may be used as a measure of bond strength.[11]

Hence in the above equation, $E \propto F \propto \ln K_f$ at constant temperature, where F is the free energy of formation and K_f is the equilibrium constant involved. Hence

$$\ln K_f = f(X'_mX_c,\ X'_m - X_c,\ \psi_0)$$

where X'_m is the metal ion hybrid bond electronegativity and X_c is the "effective" chelating agent hybrid bond electronegativity. When the stability constants for a series of metal ions are determined with a common chelating agent the relationship would be expected to become

$$\Delta \log K_f = fX'_m$$

since ψ_0 is principally associated with X_c and the latter quantity is held constant. This hybrid bond metal-ion electronegativity may be written as f $X_m \cdot V_m$ where X_m is the characteristic electronegativity of the metal ion and V_m is a parameter principally controlled by and proportional to the valence state of the metal ion. It has been shown[12] that the log K_{f_1} values for the metal ions that exist as such in solution follow the equation

$$\log K_{f_1} = cX_m \cdot V_m + b$$

describing an essentially straight line relationship. This relationship has been found to hold in general

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(9) C. A. Coulsen, V. Henri Memorial Volume, Desoer, Liege, 1948, p. 314.

(10) W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **8**, 170 (1940).

(11) A. R. Burkin, *Ouart. Rev.*, **5**, 5 (1951).

(12) L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, submitted for publication.

for a given chelating agent with a series of metal ions.[5,6]

The Contribution of the Chelating Agent.—Since values for X_c are not known, a direct analysis of the problem as above is not possible. However, it can be shown that X_c values for different chelating agents vary in a predictable manner.

To get a relative evaluation of X_c-values for different chelating agents, their $\log K_{f_1}$ values are plotted as a function of $\log K_{f_1}$ for NH_3 (in water) in Fig. 1. The results give a smoother plot than when X_m is employed for the abscissa. Figure 1 indicates that the relationship between X_c values is complex. One may consider X_c to be a function of the number of coördinating atoms in the chelating agent N and the "effective" electronegativities of these atoms. The latter value may be separated into a characteristic value (X_α) the average of the values for the hybrid bond state of the atom and (X_I) the average effect of inductive influences on these atoms. The reference state for nuclear repulsions would be involved in X_α and variations of this state involved in X_I.

On this basis

$$\log K_f = f(X'_m, N, X_\alpha, X_I)$$

By limiting the number of factors that vary in any series of comparisons it is possible to obtain relative evaluations of the varied factors. In Fig. 2 the $\log K_{f_1}$ values for ammonia,[13] ethylenediamine,[13,14] diethylenetriamine and triethylenetetramine[15] in water are plotted as a function of $\log K_{f_1}$ for ammonia. Changes in X'_m are held constant since the same series of metal ions are used, and the values of X_α and X_I are essentially constant. Hence the slopes of the lines should stand in the order of the values of N for the different ligands since N is variable on the ordinate and constant ($N = 1$) on the abscissa. The ratios of the slopes are approximately 1:2:3:4 corresponding to the number of amine nitrogens in the ligands. It should be noted that such convergent series meet at a point representative of the minimum stability of the complexes formed by members of the group. The point is close to zero on the log scale.

In Fig. 3, the chelating agents have the same chelating nucleus hence the N and X_α values are the same on each axis as well as the X'_m increments traversed. The variable along the ordinate therefore is X_I and the slopes stand in the order of this effect. Increasing the hybrid bond electronegativities of the members of the chelating nucleus by substituting increasingly electronegative groups into the indicated position (X = H, Cl, NO_2) decreases the stability of the resulting chelate complexes as predicted. Such a series varying in X_I alone would be expected to converge approximately in the same manner as the series varying in N. A series that varied in N and X_I alone then would be expected to approximate a convergence at a common point near zero on the log scale. The value of $\log K_{f_1}$ along the ordinate of such a plot is directly related to the slopes of the lines at a fixed value of $\log K_f$ on the abscissa. Hence when the slopes of the lines of Fig. 1 are plotted as a function

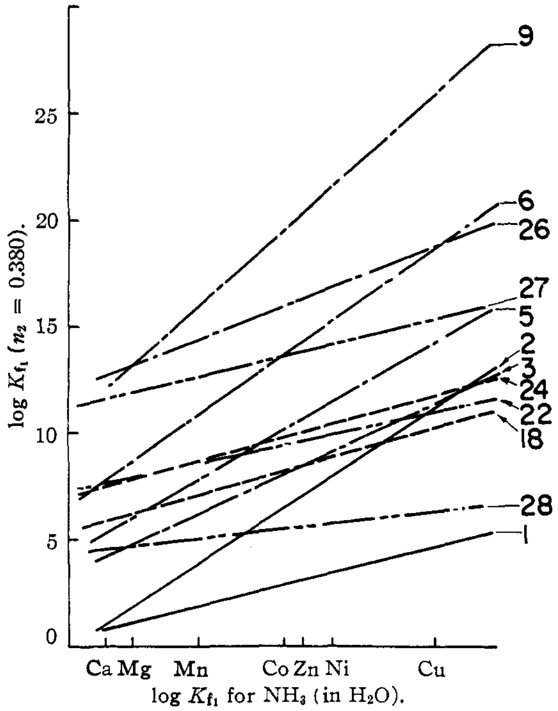

Fig. 1.—Variation of $\log K_{f_1}$ with the electronegativity of the metal for various chelating agents.

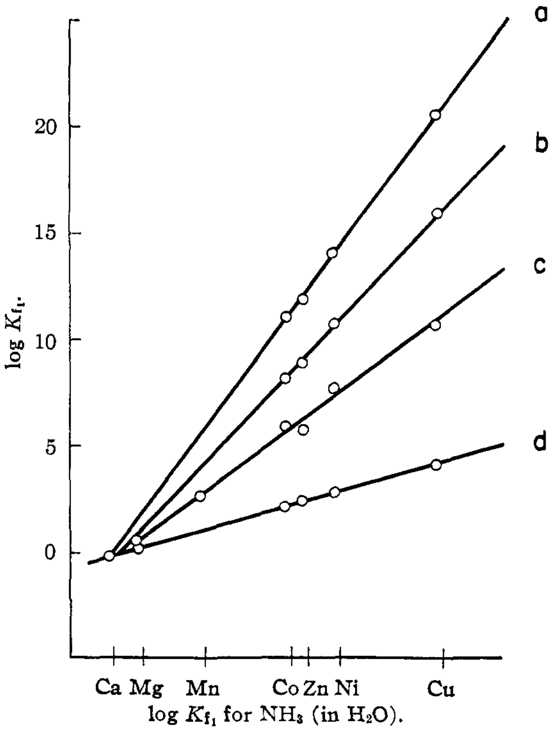

Fig. 2.—Effect of N when X_I is small and X_a is constant. The curves are for the following amines in water: a, triethylenetetramine; b, diethylenetriamine; c, ethylenediamine; d, ammonia.

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(13) J. Bjerrum, "Metal Ammine Formation in Aqueous Solutions," P. Haase and Son, Copenhagen, 1941.

(14) G. Carlson, J. P. McReynolds and F. H. Verhoek, THIS JOURNAL, **67**, 1334 (1945).

(15) G. Schwarzenbach, "Report No. DRL/146" Dept. of Inorganic Chem., Imperial Chemical Industries, Ltd., Butterwick Research Labs. (1950).

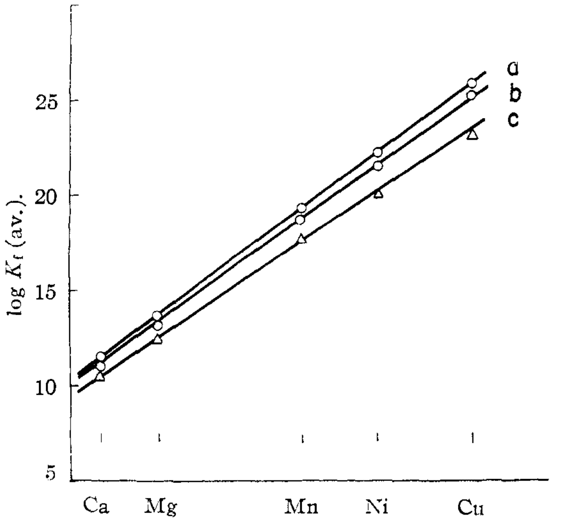
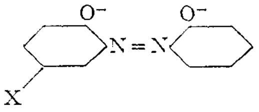


Fig. 3.—Effect of X_I when N and X_a are constant. The curves are for azo compounds of the type



where X = H (a), Cl (b), and NO_2 (c).

of log K_{f_1} for nickel (see Fig. 4) the points for all such lines that converge to a common point at zero on the log scale in Fig. 1 should lie on a straight line passing through zero in Fig. 4. Each such line in Fig. 4 should then represent a series of compounds for which N and X_I are the variables. As an approximation of the slopes of the lines in Fig. 1 the value of (log K_{f_1} for Ni^{++}) minus (log K_{f_1} for Mg^{++}) is employed.

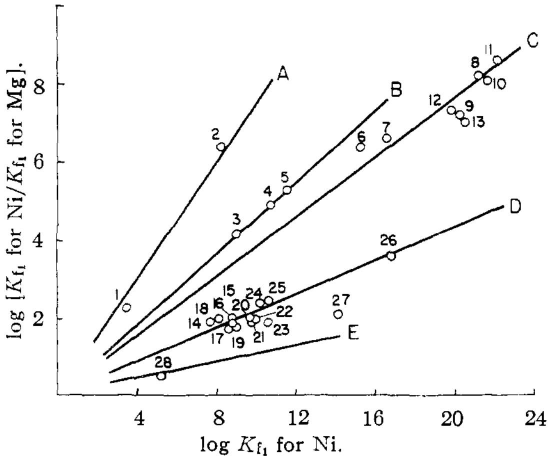
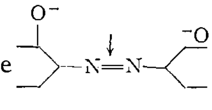
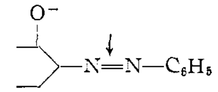


Fig. 4.—A relative evaluation of X_a (reference numbers given in text). The curves represent coördination through various kinds of reactive groups: A, —N<; B, ⩾N, -O⁻; C, —N═N—, 2 -O⁻; D, -O⁻, —N═N— and -O⁻, ═O; E, -COO⁻, -O⁻.

In Fig. 4, then, the ordinate is a function of N and X_I while the abscissa is a function of X_α, N and X_I (X'_m is held constant). Hence the resulting slopes in Fig. 4 indicate the relative X_α values for the chelating agents falling near the different lines. The slopes of the lines decrease with an increase of the characteristic hybrid bond electronegativities of the coördinating atoms involved.

The lines of Fig. 4 have been drawn to indicate the directions in which common X_α properties are expected to be found. The spread of these lines may be expected to vary with the properties of the solvent in which the measurements are made. This is particularly true when one considers that there are several charge types present. If this work could have been carried out in a medium having a very high dielectric constant, the most suitable coördination power comparison basis would have been obtained for comparing ligands of different charge types. However, Fig. 4 is in agreement with the predicted trends and is consistent with data which have been measured in water.

It will be observed that compounds whose functional groups are a mixture of those for which a given line is drawn lie between those lines. For example glycine (3) lies between the lines for $-NH_3$ and -COOH and benzoylpyruvic acid (27) lies between the lines for -COOH and -O⁻, ═O. There appears to be a difference in the behavior of the —N═N— group in the monoprotic and diprotic compounds employed. In the diprotic compounds (see Fig. 3) the chelated metal ion is probably centralized on the  double bond, while in the monoprotic compounds  there is an increased probability that the chelated metal ion is coördinated by only one of the nitrogen atoms. Centering the chelated metal ion on the double bond seems to have an advantage over coördinating through one nitrogen alone.

The above indicates that a relationship following the pattern shown in Fig. 5 exists, where the convergence points for series which have common X_α values occur at lower values of X'_m as the relative characteristic hybrid bond electronegativities for the different groups increase.

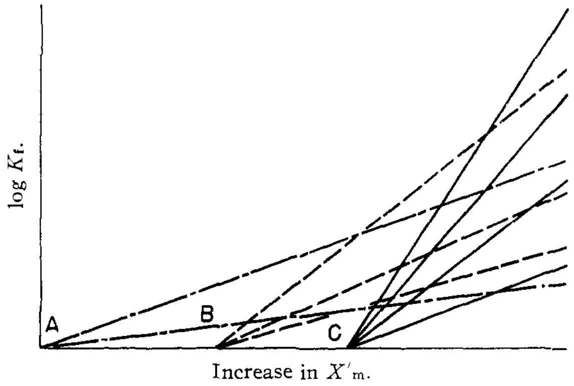


Fig. 5.—Generalized relationship among chelate complexes. The convergence points A, B and C represent series with common X_a values. The group characteristic hybrid bond electronegativities decrease A → B → C.

The development of wave function overlap by minimizing nuclear repulsion effects is a crucial factor in establishing bond strengths between metal ions and the hybrid states of nitrogen and oxygen. The highly electronegative metals coördinate more strongly with the *low* bonding electronegativity states of nitrogen and oxygen ($-N<$ and $-O^-$) since these forms exert the lowest nuclear repulsions. The metal ions of low electronegativity, on the other hand, since the system tends to distribute charge between the metal ion and the ligands to where they both have the same electronegativity, can donate enough charge to the bond to minimize nuclear repulsion effects. Therefore, they tend to form more stable bonds with the high bond electronegativity states of nitrogen and oxygen since the electronegativity product term is larger in these cases. Restating the above—when the metal ion involved is one of low enough electronegativity, nuclear repulsion forces are minimized and bond strength increases as a function of the product of the electronegativities of the partners; while in the case of the highly electronegative metal ions, nuclear repulsion forces between the partners are effective since both try to pull the electrons between them close to their respective nuclei. Variations in the two effects with X'_m are continuous as indicated in Fig. 5.

The effect of nuclear repulsion may also be used to explain the changing ratios of log K_f to pK_D, the acid dissociation constant of the chelating agent for a series of related chelate compounds. Figure 6 shows a plot of the log K_f (average) values for a series of β-diketones with $CuCl_2$, $NiCl_2$ and $BaCl_2$ in the 75 vol. % dioxane solution.[7]

Inductive effects pulling charge away from the oxygen atoms increase the degree of dissociation of the β-diketone by increasing the bond-weakening effect of nuclear repulsion between the enol oxygen atom and the proton more rapidly than the increase in bond strength attributable to an increase in the electronegativity product of the partners. The observed nuclear repulsion effects are much smaller for the less electronegative metal ions since they can donate charge to the bond while the proton cannot. Hence the enolate ions increasingly prefer to associate with metal ions rather than protons as pK_D decreases. For this reason the acidic trifluoro-β-diketones are effective chelating agents for many metal ions in acidic solution. It should be noted that the ratio of log K_f to pK_D increases going from barium the least electronegative metal ion shown to copper the most electronegative metal ion.

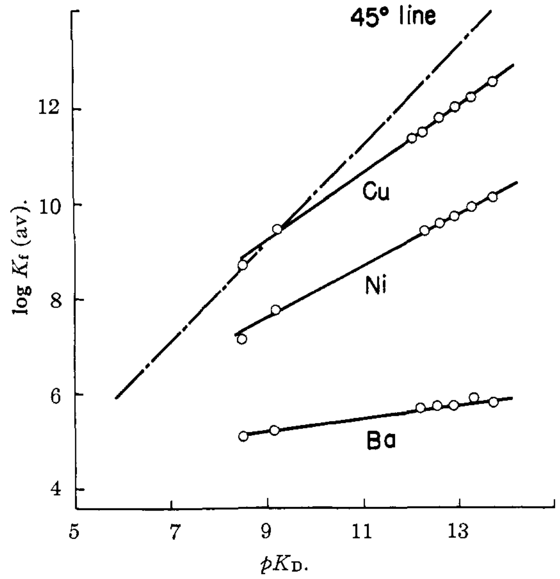


Fig. 6.—The effect of nuclear repulsion on the ratio of log K_f to pK_D.

STATE COLLEGE, PENNA.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND ORGANIC CHEMISTRY OF THE UNIVERSITY OF SYDNEY]

Sexadentate Chelate Compounds. VII

BY FRANCIS P. DWYER, NAIDA S. GILL,[1] ELEONORA C. GYARFAS AND FRANCIS LIONS

RECEIVED JULY 2, 1953

The bis-salicylidene derivatives of 3,4-bis-(γ-amino-α-thiapropyl)-toluene, 3,4-bis-(δ-amino-α-thiabutyl)-toluene, 1,4-bis-(o-aminophenyl)-1,4-dithiabutane, and the 5-bromosalicylidene derivative of 1-amino-6-(o-aminophenyl)-3,6-dithiahexane have been prepared. The formation of the usual cationic complexes with cobalt demonstrates that replacement of the polymethylene bridges between the coördinating atoms by one side of a benzene ring does not destroy the sexadentate character of the chelate compounds.

In an endeavor to obtain more experimental evidence bearing on the structure of the complex ions derived from cobalt(III) and the various azomethine bases which have been shown capable of functioning as sexadentate chelate compounds[2] it was considered that it would be of value to prepare a series of diamines based on the structure I but in which one or more of the polymethylene bridges between hetero atoms had been replaced by one side of a benzene ring. Atoms attached to a benzene ring are constrained to lie in the plane of that ring. Thus, for example, in the complex ions derived from cobalt(III) and the bis-salicylidine derivative of 1,4-bis-(o-aminophenyl)-1,4-dithiabutane (BEB base,[3] II) each benzene ring

$$NH_2—(CH_2)_x—S—(CH_2)_y—S—(CH_2)_z—NH_2$$

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[1] Commonwealth Research Assistant, University of Sydney.

[2] *Cf.* F. P. Dwyer and F. Lions, THIS JOURNAL, **72**, 1545 (1950); F. P. Dwyer, N. S. Gill, E. C. Gyarfas and F. Lions, *ibid.*, **74**, 4178 (1952); **74**, 3134 (1952); **75**, 1526 (1953); **75**, 2443 (1953).

[3] The nomenclature suggested is, for brevity, similar to that introduced in Part III and designates an o-phenylene group as B. It was found convenient in preparing compounds with such an o-phenylene group replacing the $-(CH_2)_y-$ bridge of I to use the available 3,4-dithioltoluene. The substituent methyl group does not increase the possibilities of isomerism in the final Co(III) complex ions as can be shown by a model. The base 3,4-bis-(γ-amino-α-thiapropyl)-toluene is designated in this paper as EBE base.