suppose that, as for collagen, some kind of rearrangement or redistribution of hydrogen bonds during acetylation reduces peptide adsorption almost to zero, the observed fall in V_m to 1.93 mmoles/g. on acetylation can be made to fit into the general theory. The smaller magnitude of the polypeptide adsorption effect in fibroin appears consistent with the more compact physical structure of this protein.

If our interpretation of the data of Tables II and III is correct, it reopens the whole question of the relationship between V_m and the number of polar groups. Even when the hydrolytic products of the protein contain sufficient amino acids with polar side chains to account fully for V_m, it must still be established that, in the intact protein, these groups are available for ordinary chemical reactions before their number can be used to compute V_m.

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SINGAPORE, MALAYA

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

Studies on Coördination Compounds. IV. A Comparison of the Chelating Tendencies of β-Diketones toward Divalent Metals[1]

BY LEGRAND G. VAN UITERT, W. CONARD FERNELIUS AND BODIE E. DOUGLAS

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The formation constants for the chelate compounds formed by a series of divalent metal ions with a group of β-diketones have been determined and compared. The general order of increasing stability of these chelate compounds using nitrate salts and β-diketones with aromatic ring end-groups in 75 volume per cent. dioxane solution is: Ba, Sr, Ca, Mg, Cd, Mn, Pb, Zn, Co, Ni, Fe, (Cu, Be), Hg (log K_1). The stabilities of the chelate compounds increase with the electronegativities of the metal ions involved and hence are a function of the covalent character of the resulting bonds. The divalent metal ions Fe, Ni, Co, Zn, Mn and Mg form complex salts with acetylacetone (HCh) containing the stoichiometrical ratios of Na^+:M^{2+}:Ch^- = 1:1:3; nickel and zinc with acetylacetone form soluble chelate compounds containing the stoichiometric ratios $NiCh_2$, $ZnCh_2$, NiChCl, ZnChCl and Ni(OH)Ch and the *insoluble* chelate compounds having the stoichiometrical ratios of $NaNiCh_3 \cdot C_4H_8O_2$, $NaZnCh_3 \cdot C_4H_8O_2$, $Zn_2(OH)Ch_3$, and $Zn_5Ch_2(OH)_7Cl$.

Introduction

Information concerning the role of the metal ion in the process of chelation is of primary importance to the understanding of the nature of chemical bonding. In a previous publication[2] the chelating tendencies of β-diketones toward chlorides of a strongly chelating divalent metal ion, copper, one of intermediate behavior, nickel, and one having a relatively low chelating tendency, barium, were compared. Investigations on the formation constants of a series of divalent metal nitrates with a representative group of β-diketones are reported here.

The values of the "measured" chelation constants are dependent upon the salt anions present in solution and the solvent in which the measurements are made. The measurements reported here have been made in an approximately 75 volume per cent. dioxane–25 volume per cent. H_2O solution. Comparisons are based upon the coördinating behavior of the 0.01 *M* nitrate salt solutions. The equations

$$M(NO_3)_2(H_2O)_x + HCh \rightleftarrows M(NO_3)Ch(H_2O)_y + HNO_3 + (x - y)H_2O \quad (1)$$

and

$$M(NO_3)Ch(H_2O)_y + HCh \rightleftarrows MCh_2(H_2O)_z + HNO_3 + (y - z)H_2O \quad (2)$$

represent the equilibria that are involved in determining the first and second formation constants.

Experimental

The experimental procedure and calculations are the same as previously reported.[2] A nitrogen atmosphere was employed to avoid the oxidation of the unstable divalent metal ions. Specific exceptions are noted in the appropriate parts of the discussion. *Anal.* of the precipitate having the stoichiometry Na^+:Zn^{++}:$C_5H_7O_2^-$ = 1:1:3: Calcd. for $NaZn(C_5H_7O_2)_3 \cdot C_4H_3O_2$: C, 47.9; H, 6.15. Found: C, 48.0, 48.2; H, 5.41, 5.68.

Discussion

It has been shown[2] that the plotted points of the logarithms of the first, average or second formation constants (log K_{f_1}, log $K_{f_{av}}$ or log K_{f_2}) of a series of di-ring end-group β-diketones with a given metal salt *vs.* the negative logarithms of the dissociation constants (pK_D values) of the respective β-diketones fall on a common line. Dibenzoylmethane, 2-furoylbenzylmethane and 2-thenoyl-2-furoylmethane are representative of this series. Benzoylacetone and acetylacetone demonstrate the effect of substituting one and two methyl groups in place of aromatic ring end-groups on a β-diketone. The formation constants of these compounds with the nitrate salts of Cu, Be, Ni, Co, Zn, Pb, Mn, Cd, Mg, Ca, Sr and Ba are tabulated (Table I). The values for the perchlorate salts of Fe, Ni and Pb also are listed to allow certain approximations to be made.

The data given in Table I are plotted in Fig. 1. The values for copper that are given are based upon the measured value for $Cu(NO_3)_2$ with acetylacetone and an assumed proportional relationship to the data for $CuCl_2$[2] with the other chelating agents. Comparable values for iron(II), based upon a similar comparison of the chelate

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[1] A portion of a dissertation presented by L. G. Van Uitert in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1952.

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

Table I

Formation Constants of Divalent Metals with β-Diketones

(Nitrates Unless Otherwise Noted)

Chelating agent	pK_D n_2 = 0.380	log-K_f ( )	Be	Ni	Ni-$(ClO_4)_2$	Co	Zn	Pb	Pb-$(ClO_4)_2$	Fe-$(ClO_4)_2$	Mn	Cd	Mg	Cu	Ca	Sr	Ba
Acetylacetone	12.70	(1)	12.36	9.70	10.19	9.22	9.11	8.60	9.73	9.71	8.15	7.64	7.49	12.46	..	..	..
		(2)	10.94	8.15	8.21	7.86	8.09	6.77	7.10	8.48	6.87	6.42	6.09	11.20	..	..	..
Benzoylacetone	12.85	(1)	12.59	...	...	9.42	...	8.84	...	...	..	7.79	7.69	[a]	..	..	..
		(2)	11.42	...	...	8.41	...	7.51	...	...	..	6.75	6.40		..	..	..
Dibenzoylmethane	13.75	(1)	13.62	10.83	11.14	10.35	10.23	9.75	10.73	11.15	9.32	8.67	8.54	[a]	7.17	6.40	6.10
		(2)	12.41	9.89	9.91	9.70	9.42	9.04	9.46	10.35	8.47	7.96	7.67		6.38	5.70	5.40
2-Furoylbenzoyl-methane	12.95	(1)	13.10	...	...	10.03	...	..	...	...	..	8.46	8.37	[a]	..	..	..
		(2)	12.07	...	...	9.18	...	..	...	...	..	7.59	7.30		..	..	..
2-Furoyl-2-thenoyl-methane	12.30	(1)	12.73	10.20	10.59	9.79	9.60	9.10	...	10.40	8.81	8.23	8.10	[a]	6.72	5.95	[a]
		(2)	11.44	8.96	9.07	8.93	8.63	8.39	...	9.65	7.79	7.32	6.97		5.98	5.45	
2-Thenoylbenzoyl-methane	13.30	(1)	...	...	...	...	...	..	...	...	..	8.66	..	...	..	..	..
		(2)	...	...	...	...	...	..	...	...	..	7.82	..	...	..	..	..

[a] Insoluble compounds. For values for $CuCl_2$ see ref. 4.

compound formation tendencies of nickel and iron (II) perchlorates, are also indicated.

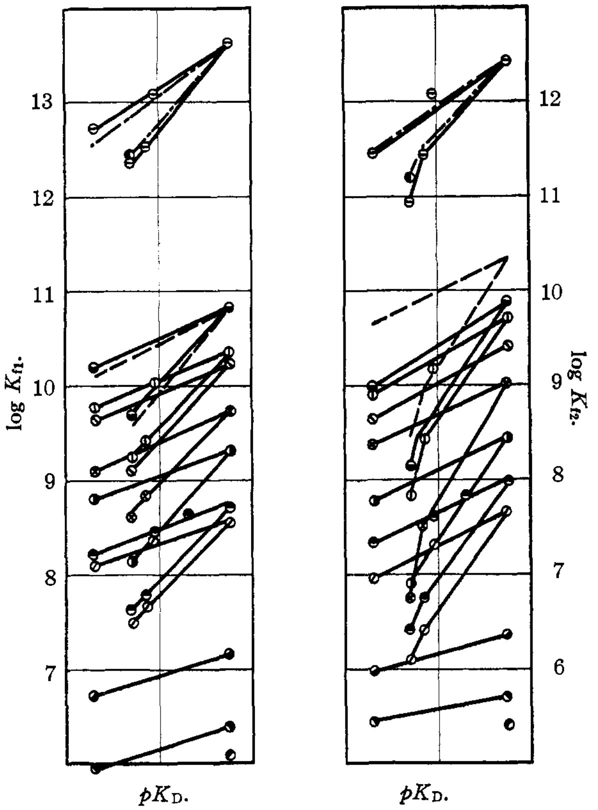

Fig. 1.—Plot of log K_{f1} and log K_{f2} *vs.* pK_D for β-diketones with nitrate salts at 30°: ◐, Cu; ⊖, Be; ◒, Ni; ⦶, Co; ⦸ Zn; ⊗, Pb; ◑, Mn; ◓, Cd; ⊘, Mg; ◔, Ca; ◕, Sr; ◍, Ba: — - —, Cu (calcd.); — — — —, Fe (calcd).

The following observations may be made from Fig. 1. (1) The order of increasing chelating ability of a β-diketone that has two aromatic ring end-groups with the metal nitrates is: Ba, Sr, Ca, Mg, Cd, Mn, Pb, Zn, Co, (Ni and Fe), (Cu and Be). The trend indicates that chelate compound stability increases with the electronegativities of the metal ions. Since the electronegativity of oxygen is 3.5 on Pauling's scale[3] while the values for the majority of the metal ions are much lower,[4] the covalent character of the bonds between the metal ions and the chelating agents which coördinate through oxygen also increase with the metal ion electronegativity.[5] The first formation constants for dibenzoylmethane with the series of metal ions are plotted against the metal ion electronegativities of Haïssinsky in Fig. 2.

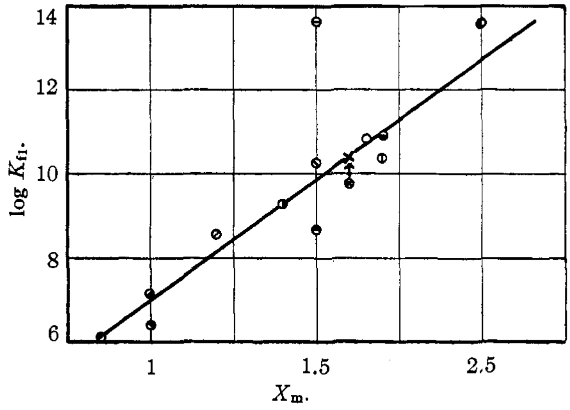

Fig. 2.—Log K_{f1} *versus* metal ion electronegativity for the chelate complexes employing dibenzoylmethane. See legend of Fig. 1.

(2) The β-diketones which have a methyl end-group do not appear to chelate as strongly as those with two aromatic rings that have comparable pK_D values. This difference is greater for the second chelation than for the first. It is especially large for the second chelation of lead. It is probable that the observed effect is due to the lesser shielding ability of a methyl group as compared to an aromatic ring.

It should be noted that the formation constants for the beryllium chelate compounds in particular. deviate from their expected values upon the basis of electronegativity (see Fig. 2). The log K_{f_1} values for the remaining metal ions largely fall on a common line within the accuracy with which their electronegativities are known. The value for lead, relative to nickel for the perchlorate salts *vs.* dibenzoylmethane, falls upon the indicated line (see Table I).

The formation constants for $Pb(NO_3)_2$ with HCh were obtained from measurements made upon a solution 0.20 *M* in chelating agent. A hydroxy

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[3] L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1948, p. 64.

[4] M. Haïssinsky, *J. Phys. Radium,* [8] **7**, 7 (1946).

[5] L. Pauling, ref. 3, p. 70.

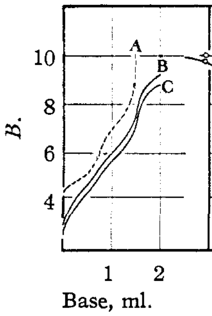
chelate compound is precipitated if a low concentration of chelating agent is employed. The titration B (*p*H meter reading) curve of a HCh = 0.40 *M* solution follows the curve of the 0.20 *M* solution 0.3 log unit below it, thus showing that these curves are not affected by the formation of hydroxides (Fig. 3). Both of these curves lie below the level at which the hydroxide compounds are formed (curve A of Fig. 3). To obtain this curve one millimole of $Pb(NO_3)_2$ was titrated with NaOH in the 75 volume per cent. dioxane solution. The following transformations were evident

$$Pb(NO_3)_2 + NaOH \longrightarrow NaNO_3 + Pb(OH)NO_3 \text{ a white ppt. and} \quad (4)$$

$$Pb(OH)NO_3 + NaOH \longrightarrow NaNO_3 + Pb(OH)_2 \text{ a yellow ppt.} \quad (5)$$

The change in the color of the precipitate corresponds to the stoichiometric rise at the mid-point of the titration.

The C curves ($p(Ch^-)$ *vs.* pK_D) for the $Pb(NO_3)_2$ chelation titrations are given in Fig. 4 to demonstrate relative substitution effect of the methyl end-group upon the first and second chelation.



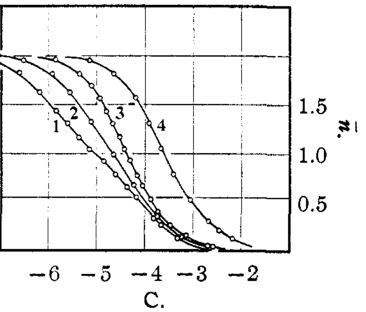


Fig. 3.—$Pb(NO_3)_2$ titration curves: A, $Pb(NO_3)_2$ alone; B, in 0.20 *M* acetylacetone; C, in 0.40 *M* acetylacetone.

Fig. 4.—$Pb(NO_3)_2$ C curves: 1, with acetylacetone; 2, with benzoylacetone; 3, with dibenzoylmethane; 4, with 2-thenoyl-2-furoylmethane.

Titrations similar to those for $Pb(NO_3)_2$ were carried out for $Hg(NO_3)_2$. The salt itself hydrolyzes to a starting *B* value (*p*H meter reading) of 2.0. The addition of chelating agent at this point results in a complete single chelation. A hydroxy chelate compound is the final product of the titration. Since a two-step curve showing a minimum difference of 3 log units between log K_{f_1} and log K_{f_2} is obtained by titrating $HgCl_2$ with acetylacetone in water, it can be inferred that the first chelation constant for Hg^{++} is greater than that for Cu^{++}. The relative position of the second constant was not determined.

The metal acetylacetonate complexes form an interesting series of compounds analogous to that previously described for nickel.[2] The stoichiometric ratios $M^{2+}:Na^+:Ch^- = 1:1:3$ occur in the cases of Fe, Ni, Co, Zn, Mn and Mg. As in the case of nickel, a molecule of dioxane is probably present in these compounds.

Metal ion	MCh_2	$NaMCh_3$
Iron	Yellow-brown	Orange-red
Nickel	Green	Pale blue
Cobalt	Ruby red	Pink
Zinc	White	White
Manganese	Yellow	Brown-gray
Magnesium	White	White

It is evident that more than one type of chelate compound can be present in a given solution. To investigate the nature of the hydroxy chelate compounds of zinc and nickel the following titrations with deficiency of chelating agent were carried out.

(a) In 100 ml. of 75 volume per cent. dioxane solution 1×10^{-3} mole of acetylacetone plus 1×10^{-3} mole of $NiCl_2$ were titrated with 1.302 *N* NaOH. The reaction $NiCl_2 + HCh + NaOH \rightarrow NiChCl + NaCl + H_2O$ occurred over the addition of the first stoichiometric equivalent of base. The soluble hydroxy chelate compound of nickel was formed over the addition of the second equivalent, $NiChCl + NaOH \rightarrow Ni(OH)Ch + NaCl$. At the stoichiometric second equivalence point the solution *B*-value rises to 12. Upon adding excess base the rearrangement

$$NaOH + 3Ni(OH)Ch + C_4H_8O_2 \rightleftarrows NaNiCh_3 \cdot C_4H_8O_2 + 2Ni(OH)_2 \quad (6)$$

takes place resulting in the dual precipitation of the complex nickel salt and nickel hydroxide. The *B*-values of the solution fall to below 9 over the next two-thirds equivalent of added base, at the end of which a final *B*-value rise is observed. The stoichiometry of the above titration suggests the equilibrium equation (6). After a period of digestion the precipitate resolves itself into a pale blue powder ($NaNiCH_3 \cdot C_4H_8O_2$) and a green jelly $[Ni(OH)_2]$ substantiating the observed stoichiometry.

(b) In 100 ml. of 75 volume per cent. dioxane solution and in 100 ml. of 50 volume per cent. dioxane solution 2×10^{-3} mole of acetylacetone plus 2×10^{-3} mole of $ZnCl_2$ were titrated. In each solution, precipitation occurred after adding approximately two equivalents of base. The stoichiometrical ratio of the minimum components of the precipitate in each case are in the ratio $Zn_5Ch_2(OH)_7Cl$ as shown by titrating the acidified filtrate after allowing the precipitate to digest and filtering at point of vertical rise after precipitation. This titration showed that about 0.75×10^{-3} mole of zinc and 1.5×10^{-3} mole of acetylacetone are in solution and therefore the materials removed from the solution are in the ratio $Zn_5Ch_2(OH)_7Cl$. The chloride ion is included to preserve electrical neutrality.

A second heavy precipitate was encountered farther along in the titration of the 75% dioxane solution. The stoichiometry at the vertical rise after precipitation was shown by titrating the acidified filtrate which indicated that the $ZnCh_2$ in solution had been hydrolyzed to $Zn_2Ch(OH)_3$ because 1×10^{-3} mole of acetylacetone and no zinc was present in the filtrate. All the forms of hydroxy chelate compounds are hydrolyzed to $Zn(OH)_2$ when six equivalents of base have been added. The over-all reactions in 75 volume per cent. dioxane, from consideration of the above, are

$$ZnCl_2 + HCh + NaOH \longrightarrow ZnChCl + NaCl + H_2O \quad (7)$$

$$8ZnChCl + 7NaOH \longrightarrow 3ZnCh_2 + Zn_5Ch_2(OH)_7Cl + 7NaCl \quad (8)$$

$$3ZnCh_2 + Zn_5Ch_2(OH)_7Cl + 5NaOH \longrightarrow 4Zn_2Ch(OH)_3 + 4NaCh + NaCl \quad (9)$$

$$Zn_2Ch(OH)_3 + NaOH \longrightarrow NaCh + 2Zn(OH)_2 \quad (10)$$

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State College, Penna.