

spectrum of the  $[\text{Ni}(\text{NC}_2\text{H}_5)_6]^{++}$  ion. The 33,500  $\text{cm}^{-1}$  absorption band observed in the methanol solution spectrum of  $[\text{Ni}(\text{NC}_2\text{H}_5)_6]^{++}$  apparently is to be correlated with the "spin-forbidden" transition  $\Gamma_5 \rightarrow \Gamma_j$  ( $j = 3, 5$ ), which has a calculated energy of 35,000  $\text{cm}^{-1}$ . Although we are unable to resolve accurately the 10,500  $\text{cm}^{-1}$  band from a weak, "spin-forbidden" transition  $\Gamma_5 \rightarrow \Gamma_3$  expected at 12,400  $\text{cm}^{-1}$ , the slightly non-Gaussian shape on the high-energy side of the 10,500  $\text{cm}^{-1}$  band suggests that this  $\Gamma_5 \rightarrow \Gamma_3$  transition is present in the experimental spectrum.

In the absorption spectra of octahedral  $[\text{Co}(\text{NC}_2\text{H}_5)_6]^{++}$  ion only two absorption bands, with the centers of the bands located at 8900 and 19,800  $\text{cm}^{-1}$ , were observed. These absorption bands, like those of Ni(II), are rather broad. This may be seen from Fig. 2. Using the Orgel energy level diagram<sup>4</sup> for cobalt(II), a consistent assignment of the experimental spectrum is possible taking  $10Dq = 10,300 \text{ cm}^{-1}$ . The observed absorptions are correlated with the energy level transitions: (i)  ${}^4T_{1g} \rightarrow {}^4T_{2g}$ , 8,900  $\text{cm}^{-1}$ ; (ii)  ${}^4T_{1g} \rightarrow {}^4A_{2g}$ , 19,200  $\text{cm}^{-1}$ ; (iii)  ${}^4T_{1g} \rightarrow {}^4T_{1g}(\text{P})$ , 22,400  $\text{cm}^{-1}$ . From Fig. 2, transitions (ii) and (iii) apparently appear as a single peak. Al-

though we are unable to resolve accurately the 19,800  $\text{cm}^{-1}$  band, the slightly non-Gaussian shape on the high-energy side of this peak suggests that the  ${}^4T_{1g} \rightarrow {}^4T_{1g}(\text{P})$  transition is present in the experimental spectrum. A complete resolution of this peak occurring at 19,800  $\text{cm}^{-1}$  was quite difficult. However, we estimate the higher-energy transition to occur at approximately 21,000  $\text{cm}^{-1}$ .

The electrostatic theory calculations presented in Table II, with the crystal field stabilization energy taken into account, give the calculated bond energies for the two complexes we have considered. Although the "experimental" bond energies were not calculated for the two complexes, the calculated bond energies of the ethylenimine complexes of nickel(II) and cobalt(II) appear to agree with calculated bond energies of comparable<sup>15</sup> complexes (*e.g.*,  $\text{M}(\text{OH}_2)_6^{++}$ ,  $\text{M}(\text{NH}_3)_6^{++}$ , and  $\text{M}(\text{en})_3^{++}$ ).

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(15) Reference 14, p. 65.

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## A Consideration of Steric Effects in the Chelating Tendencies of Some Methylene-Substituted $\beta$ -Diketones

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Three series of compounds were prepared and chelating tendencies determined: I,  $\text{CH}_3\text{COCH}(\text{R})\text{COCH}_3$ ; II,  $\text{CH}_3\text{OCH}_2\text{COCH}(\text{R})\text{COCH}_3$ ; III,  $\text{C}_6\text{H}_5\text{COCH}(\text{R})\text{COC}_6\text{H}_5$ . A linear  $pK_D$ - $\log K$  relationship was observed for uranyl chelates of series II and III and for beryllium chelates of series II, but such a relationship was not observed for copper and other divalent metal chelates of series I, II, and III. Several possible steric effects are considered, and rationalizations of these are presented. An alternate interpretation, *viz.*, that of solvation effects, is favored.

### Introduction

The effect of a methylene-substituent,  $\text{R}'$ , upon the chelating tendency of a  $\beta$ -diketone,  $\text{RCOCHR}'\text{COR}''$ , has been examined by previous workers<sup>1,2</sup>: An alkyl substituent lowers the acidity, as would be expected, and, generally, the stability of the copper chelates is less than that

expected on the basis of a  $pK_D$ - $\log K$  relationship. This effect has been attributed to steric interaction ( $\text{R}$  and  $\text{R}''$  with  $\text{R}'$ ) and concomitant deformation of the planar ring structure which seems to be necessary for maximum stability.<sup>1</sup> However, it has been suggested<sup>3</sup> that steric *or* solvation factors may be involved in anomalous

(1) M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, **67**, 2008 (1945).

(2) B. B. Martin and W. C. Fernelius, *ibid.*, **81**, 2342 (1959).

(3) R. N. Keller and R. W. Parry in J. C. Bailar, Jr., "The Chemistry of the Coordination Compounds," Reinhold Publishing Corp., New York, N. Y., 1956, p. 183.

TABLE I  
 PHYSICAL PROPERTIES OF  $\beta$ -DIKETONES,  $\text{RCOCH(R'')COR'}$ 

Compound	Yield, %	B.p., °C.	Mm.	$n_D^{20}$	$t$	Carbon, %		Hydrogen, %		Enol <sup>a</sup> test
						Calcd.	Found	Calcd.	Found	
3-Methyl-2,4-pentanedione	33	80 <sup>b</sup>	33	1.4440	22	63.13	63.10	8.83	8.97	Purple
3-Phenyl-2,4-pentanedione	20	54-55 <sup>c</sup>				74.98	75.00	6.86	6.82	Purple
3-Methyl-1-methoxy-2,4-pentanedione	32	95-96	12	1.4372	26.8	58.30	58.38	8.40	8.78	Red
3-Ethyl-1-methoxy-2,4-pentanedione	48	107-108	15	1.4389	26.8	60.73	60.51	8.92	9.05	Red
3- <i>n</i> -Propyl-1-methoxy-2,4-pentanedione	50	68-70	1	1.4408	26.5	62.76	62.72	9.36	9.56	Red
3- <i>n</i> -Butyl-1-methoxy-2,4-pentanedione	41	90-91	1	1.4442	20.5	64.50	64.36	9.75	9.69	Purple
2-Methyl-1,3-diphenyl-1,3-propanedione	96 <sup>d</sup>	87-88 <sup>e</sup>				80.65	80.71	5.92	5.97	...
2-Ethyl-1,3-diphenyl-1,3-propanedione	62	90.5-91 <sup>f</sup>				80.92	81.09	6.39	6.38	...

<sup>a</sup> Saturated methanolic  $\text{FeCl}_3$ . <sup>b</sup> Reported b.p. 77-79° (30 mm.) [J. T. Adams, Jr., and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 345 (1944)]. <sup>c</sup> M.p. (petroleum ether, b.p. 90-110°); reported<sup>g</sup> m.p. 58.5-59°. <sup>d</sup> Crude yield. <sup>e</sup> M.p. (95% ethanol); reported m.p. 82.5-84° [R. D. Abel, *J. Chem. Soc.*, 928 (1901)]. <sup>f</sup> M.p. (95% ethanol); reported m.p. 87-88° [C. H. Sluiter, *Rec. trav. chim.*, **24**, 370 (1905)].

stabilities of copper chelates of substituted malonates.

That the anomalous chelating tendencies of methylene-substituted  $\beta$ -diketones are due to steric factors is indeed plausible. However, the effect of steric factors cannot be considered in detail, nor can the possibility of solvation effects, because of lack of data. Thus, the purpose of the present study was threefold: To vary the size of the methylene substituent and the terminal groups and study the effect on the chelating tendency; to extend the study to other metal ions, notably beryllium and uranyl; and to study compounds of the type  $\text{CH}_3\text{COCH(R')COCH}_2\text{OCH}_3$ , for presumably these would form soluble metal chelate compounds. The present communication reports the results of this study.

#### Experimental<sup>4</sup>

**Synthesis of  $\beta$ -Diketones (Table I).**—The procedure used to prepare the substituted  $\beta$ -diketones is a modification of a previously described procedure.<sup>2</sup> The preparation of 3-*n*-butyl-1-methoxy-2,4-pentanedione represents a typical synthesis. The alkylation of dibenzoylmethane was effected using a 1:1 molar ratio of ketone:alkyl halide. All compounds were colorless liquids or white solids.

**3-*n*-Butyl-1-methoxy-2,4-pentanedione.**—To a stirred solution of potassium (7.8 g., 0.2 g.-atom) in *t*-butanol (200 ml.) was added dropwise methoxyacetylacetone (27.3 g., 0.21 mole) and, 10 min. after the addition was complete, *n*-butyl iodide (36.8 g., 0.2 mole). The mixture was stirred at reflux temperature for 24 hr., and three-fourths of the solvent was evaporated under reduced pressure. The residue was washed with water and the mixture extracted with ether. The combined ether extracts were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and distilled. Upon distillation under reduced pressure the residue yielded 15.9 g. of clear, colorless liquid.

**Methoxyacetylacetone.**—A commercial product, was

(4) Microanalyses were performed under the direction of Mr. Josef Nemeth of the University of Illinois.

redistilled, b.p. 74° at 13 mm.,  $n_D^{20}$  1.4570; reported<sup>5</sup> b.p. 68° at 12 mm.,  $n_D^{20}$  1.459.

**3-Methyl-2,4-pentanedione** was prepared by Mr. R. J. Hine, under the direction of Prof. N. J. Leonard, using a previously described procedure.<sup>6</sup>

**Potentiometric Titrations.**—The titrations were performed as described previously,<sup>7</sup> using dioxane which was purified by distillation from sodium and which was redistilled from sodium immediately before use. Formation constants were calculated using the method of Block and McIntyre.<sup>8</sup> Formation constants could not be obtained for manganese(II) chelates because precipitates formed before appreciable coordination had occurred.

#### Discussion

**Acid Dissociation Constants.**—The  $pK_D$  values of the methylene-substituted  $\beta$ -diketones were determined as a function of mole fraction of dioxane ( $N_2$ ) at 30°, and mathematical expressions for the linear  $pK_D$  relationships are listed in Table II. As is characteristic of  $\beta$ -diketones,<sup>9</sup> the  $pK_D$

TABLE II

$pK_D$  EQUATIONS ( $pK_D = aN_2 + b$ )<sup>a</sup> OF SOME  $\beta$ -DIKETONES,  $\text{RCOCHR'COR''}$

R	R'	R''	a	b	$N_2$ Range
$\text{CH}_3$	$\text{CH}_3$	$\text{CH}_3$	10.78	10.22	0.137-0.380
$\text{CH}_3$	$\text{C}_6\text{H}_5$	$\text{CH}_3$	12.80	8.89	.137- .380
$\text{CH}_3\text{OCH}_2$	H	$\text{CH}_3$	11.80	7.47	.077- .380
$\text{CH}_3\text{OCH}_2$	$\text{CH}_3$	$\text{CH}_3$	11.08	9.55	.137- .380
$\text{CH}_3\text{OCH}_2$	$\text{C}_2\text{H}_5$	$\text{CH}_3$	11.03	9.94	.137- .380
$\text{CH}_3\text{OCH}_2$	<i>n</i> - $\text{C}_3\text{H}_7$	$\text{CH}_3$	10.97	9.93	.137- .380
$\text{CH}_3\text{OCH}_2$	<i>n</i> - $\text{C}_4\text{H}_9$	$\text{CH}_3$	10.93	9.95	.137- .380
$\text{C}_6\text{H}_5$	$\text{CH}_3$	$\text{C}_6\text{H}_5$	12.67	9.94	.137- .310
$\text{C}_6\text{H}_5$	$\text{C}_2\text{H}_5$	$\text{C}_6\text{H}_5$	13.95	10.09	.137- .241

<sup>a</sup> Reliable within  $\pm 0.05$ .

(5) W. Renard and A. Maquinay, *Bull. soc. chim. Belges*, **55**, 98 (1946).

(6) C. R. Hauser and R. M. Manyik, *J. Org. Chem.*, **18**, 577 (1953).

(7) L. G. Van Uitert, *et al.*, *J. Am. Chem. Soc.*, **75**, 457 (1953); **76**, 5887 (1954).

(8) B. P. Block and C. H. McIntyre, Jr., *ibid.*, **75**, 5687 (1953).

(9) L. G. Van Uitert, G. G. Haas, W. C. Fernelius, and B. E. Douglas, *ibid.*, **75**, 455 (1953).

TABLE III

FORMATION CONSTANTS ( $\log K_n$ )<sup>a</sup> OF BIVALENT METAL CHELATES OF SOME METHYLENE-SUBSTITUTED  $\beta$ -DIKETONES, RCOCHR'COR'' (HCh) (in 75 vol.-% dioxane ( $N_2 = 0.380$ ) at 30°)

R	R'	R''	$pK_D$	$n$	UO <sub>2</sub> <sup>b</sup>	Be <sup>b</sup>	Cu <sup>b</sup>	Ni	Co	Zn
CH <sub>3</sub>	H	CH <sub>3</sub>	12.70 <sup>d</sup>	1	11.46 <sup>c</sup>	12.36 <sup>d</sup>	12.78 <sup>d</sup>	10.19 <sup>d</sup>	9.68 <sup>d</sup>	9.52 <sup>d</sup>
				2	9.87	10.94	11.24	8.21	7.92	8.05
CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	14.32	1	12.94 ± 0.01 <sup>e</sup>	11.36 ± 0.03	13.28 ± 0.01	9.60	9.35	10.16
				2	10.96 ± 0.04	10.15 ± 0.01	10.35 ± 0.04	Ppt.	Ppt.	Ppt.
CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	13.76	1	12.95 ± 0.02	Ppt.	...	10.09 ± 0.02	9.63 ± 0.01	9.68
				2	10.92 ± 0.03	11.24	8.14 ± 0.02	8.06 ± 0.01	Ppt.	
CH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	14.79 <sup>f</sup>	1	...	13.50	Ppt.	Ppt.	Ppt.	
				2	11.18	...	10.30 ± 0.03	9.65	9.47 ± 0.01	
CH <sub>3</sub> OCH <sub>2</sub>	H	CH <sub>3</sub>	11.96	1	11.70 ± 0.02	11.20	...	8.09 ± 0.01	9.65	9.47 ± 0.01
				2	10.27 ± 0.01	Ppt.	10.78	8.09 ± 0.01	Ppt.	7.69 ± 0.01
CH <sub>3</sub> OCH <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	13.76	1	12.23 ± 0.02	11.65 ± 0.02	12.77 ± 0.02	9.18	8.93	9.45
				2	10.35 ± 0.02	10.23 ± 0.03	12.21 ± 0.02	...	Ppt.	Ppt.
CH <sub>3</sub> OCH <sub>2</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	14.12	1	12.40 ± 0.01	11.89 ± 0.03	12.27	8.95	Ppt.	Ppt.
				2	10.89 ± 0.02	10.65 ± 0.03	Ppt.	Ppt.	Ppt.	
CH <sub>3</sub> OCH <sub>2</sub>	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	14.10	1	12.37 ± 0.02	11.88 ± 0.03	11.32	8.95	Ppt.	Ppt.
				2	10.92 ± 0.03	10.76 ± 0.03	Ppt.	Ppt.	Ppt.	
CH <sub>3</sub> OCH <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	14.11	1	12.29 ± 0.01	11.83 ± 0.02	Ppt.	9.00	Ppt.	Ppt.
				2	10.86 ± 0.02	10.64 ± 0.02	Ppt.	Ppt.	Ppt.	
C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	13.75 <sup>d</sup>	1	12.32 <sup>e</sup>	13.62 <sup>d</sup>	...	11.14 <sup>d</sup>	10.74 <sup>d</sup>	10.59 <sup>d</sup>
				2	11.86	12.41	...	9.91	9.79	9.41
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	14.76	1	12.83 ± 0.02	12.36	Ppt.	Ppt.	Ppt.	Ppt.
				2	11.77 ± 0.02	Ppt.	Ppt.	Ppt.	Ppt.	
C <sub>6</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	15.42	1	13.47 ± 0.02	Ppt.	Ppt.	Ppt.	Ppt.	Ppt.
				2	12.44 ± 0.01	Ppt.	Ppt.	Ppt.	Ppt.	

<sup>a</sup>  $\log K_1$  and  $\log K_2$  for the equilibria  $M^{++} + Ch^- \rightleftharpoons MCh^+$  and  $MCh^+ + Ch^- \rightleftharpoons MCh_2$ , respectively. <sup>b</sup> These values were obtained in this study using nitrate rather than perchlorate salts. <sup>c</sup> D. M. Ericson and W. C. Fernelius, AEC Document NYO-7711, May, 1956. <sup>d</sup> L. G. Van Uitert, W. C. Fernelius, and B. E. Douglas, *J. Am. Chem. Soc.*, **78**, 2736, 2739 (1956). <sup>e</sup> 95% confidence limits. <sup>f</sup> Reference 2.

values deviate slightly at lower values of  $N_2$  (below 0.14).

The  $pK_D$  values (for  $N_2 = 0.380$ ) of the  $\beta$ -diketones show the expected inductive effects; substitution of a methylene hydrogen by a methyl group is accompanied by a marked increase in the  $pK_D$  value; a further increase is noted for the ethyl analog, but the *n*-propyl and *n*-butyl derivatives of methoxyacetylacetone are acids of equal strength. Moreover, methoxyacetylacetone is more acidic than acetylacetone, and the variation of  $pK_D$  with substitution appears to be parallel for the two series of  $\beta$ -diketones.<sup>10</sup> By way of contrast, bis-( $\beta$ -diketones) of the type [(RCO)(R'CO)CH]<sub>2</sub>CHR'' derived from acetylacetone have  $pK_D$  values which are anomalous, being lower than those for the methoxyacetylacetone series.<sup>11</sup>

**Formation Constants (Table III).**—For the series of alkyl methoxyacetylacetones, the copper chelates are much less stable than would be expected on the basis of a  $pK_D$ - $\log K_1$  relationship<sup>9</sup> as is the situation with the nickel and possibly the cobalt(II) and zinc chelates. However, the stabilities of the uranyl and beryllium chelates

vary regularly with ligand  $pK_D$  (Fig. 1).

Few data are available for the alkylated dibenzoylmethanes because of the insolubility of the metal chelates. The uranyl chelates show a regular  $pK_D$ - $\log K_1$  relationship, but the beryllium derivative of C<sub>6</sub>H<sub>5</sub>COCH(CH<sub>3</sub>)COC<sub>6</sub>H<sub>5</sub> apparently is much less stable than is the derivative of dibenzoylmethane.

Also, because of solubility problems, few data are available for the 3-substituted-2,4-pentanediones, but the  $\log K_2$  values for the copper chelates are independent of ligand acidity. Surprisingly, the beryllium chelate of 3-methyl-2,4-pentanedione is less stable than beryllium acetylacetonate, and at least one of the uranyl chelates does not follow the expected order of stability.

In attempting to rationalize these results it would be logical first to consider steric effects.

First of all, the interaction of the terminal groups and methylene substituent could result in the deformation of the planar chelate ring. Such an effect could be the cause of the reduced stability of the copper and other metal chelate compounds. However, such an effect also should be prominent in the uranyl and beryllium chelates, but these, generally, have the expected degree of stability.<sup>12</sup>

(10) The  $pK_D$  value of 3-*n*-butyl-2,4-pentanedione is 14.79 at  $N_2 = 0.380$ .

(11) D. F. Martin and W. C. Fernelius, *J. Am. Chem. Soc.*, **81**, 1509 (1959).

(12) While it might be argued that the stability of beryllium chelates is unaffected by "resonance," such an argument would not be valid for the uranyl chelates because, though beryllium lacks the requisite d-orbitals, uranium does not.

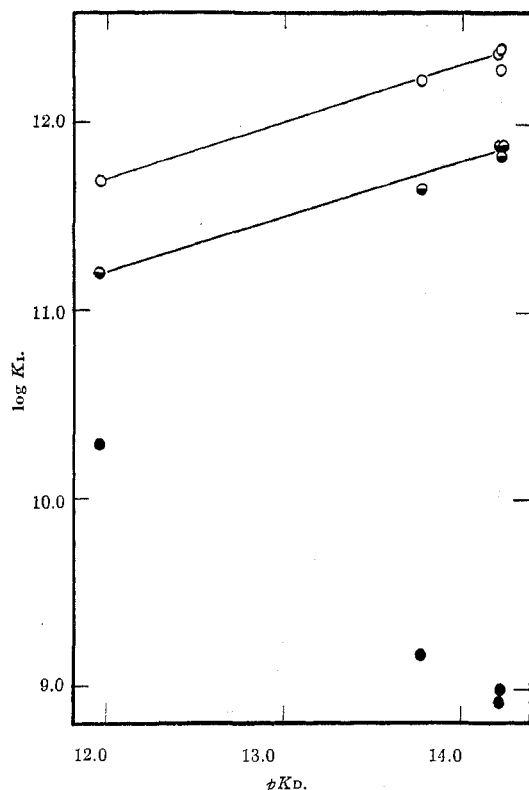


Fig. 1.—Variation of  $\log K_1$  of divalent metal chelates as a function of  $pK_D$  for methoxyacetylacetones: O,  $UO_2$ ; ●, Ni.

Secondly, the interaction of the terminal groups and the methylene substituent could force the oxygen atoms closer together. The O—O distance might decrease sufficiently to permit the ready accommodation of small ions, e.g., beryllium and lithium, while representing an unfavorable situation for larger ions. An effect of this type appears to be involved in the exceptional stability of lithium dipivaloylmethane.<sup>13</sup> It is not possible to attribute the stability of the uranyl chelates to a decrease in the O—O distance in view of the large (ca. 1.07 Å.)<sup>14</sup> radius of uranium in the equatorial plane of the uranyl ion. Furthermore, the beryllium, but not the uranyl, chelate of  $C_6H_5COCH(CH_3)COC_6H_5$  is much less stable than expected; the lithium chelate is much less stable.<sup>15</sup>

A third steric effect to be considered is F-

strain,<sup>17</sup> which may make it troublesome for a ligand to approach a monochelated species,  $MCh^+$ . If such an effect is operative, it would be indicated by an anomalously great separation factor,  $K_1/K_2$ . The requisite data are available for the uranyl chelates, and it is interesting that anomalous separation factors are observed for the methyl chelates,  $RCOCH(CH_3)COR'$ , and for  $(CH_3CO)_2CHC_6H_5$ . Oddly enough, an increase in the chain length of the alkyl group substituent is not accompanied by an increase in the magnitude of the separation factor. The factors for the series  $CH_3OCH_2COCHRCOCH_3$  reach a maximum of 1.88 ( $CH_3$ ) and remain constant (1.51–1.43) for the ethyl-, *n*-propyl-, and *n*-butyl-derivatives. Fewer data are available for beryllium, but no exceptionally large deviations are observed.

Guter and Hammond<sup>18</sup> have suggested a fourth steric factor, *viz.*, that terminal groups can shield the region around the metal–oxygen bond from solvation. This factor would be indicated by anomalously low separation factors. Possibly, this effect may be involved in determining the stability of the uranyl chelates because the separation factors of the alkyl-dibenzoylmethanes are less than those of the corresponding alkyl methoxyacetylacetones. However, this type of shielding effect could not be invoked to explain anomalies in  $K_1$  values.

It would appear from the foregoing that there are indications that steric effects may be involved in the chelating tendencies of the methylene-substituted  $\beta$ -diketones. However, the effects are not as definite and as generally applicable as might be expected.

In view of this it seems wise to consider an alternate possibility: Steric effects indeed may be involved but in a manner less important than solvent effects. A reasonable interpretation is that the observed steric effects are really a manifestation of the increase in hydrophobic character of the ligand due to the substitution of a methylene hydrogen by an alkyl group. The increase in hydrophobic character of the chelate anion is a consequence of the distribution of the same charge over a greater surface and one that is less polar because of the presence of an additional hydrocarbon moiety. An increase in the hydrophobic character of the chelate anion would be accom-

(13) G. A. Guter and G. S. Hammond, *J. Am. Chem. Soc.*, **78**, 6166 (1956).

(14) Cf. W. H. Zachariassen and H. A. Plettinger, *Acta Cryst.*, **15**, 526 (1959).

(15) Compare the  $pK_D$  values of dibenzoylmethane and  $C_6H_5COCH(CH_3)COC_6H_5$  (13.75 vs. 14.76) with the  $\log K$  values for the lithium chelates (5.95<sup>16a</sup> vs. 3.70,<sup>16b</sup> in 75% dioxane–water).

(16) (a) L. G. Van Uitert and W. C. Fernelius, *Acta Chem. Scand.*, **8**, 1726 (1954); (b) D. F. Martin and B. B. Martin, unpublished results.

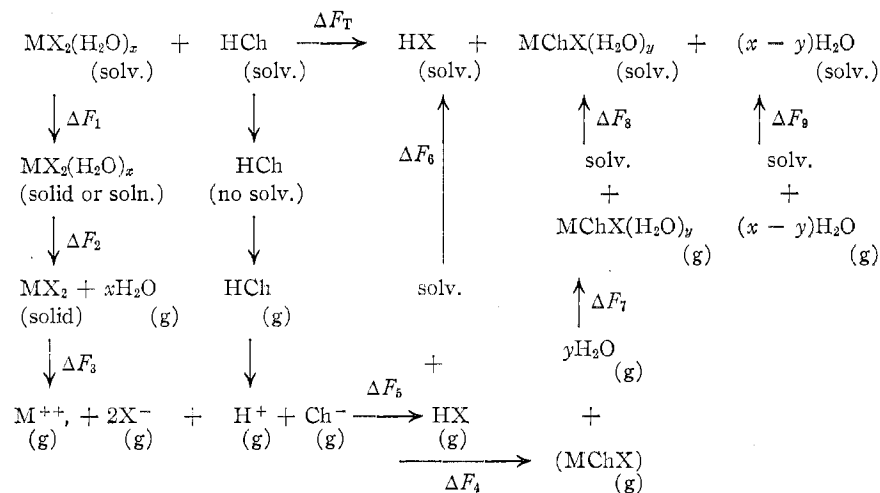
(17) H. C. Brown, H. Bartholomay, and M. D. Taylor, *J. Am. Chem. Soc.*, **66**, 435 (1944).

(18) G. A. Guter and G. S. Hammond, *ibid.*, **81**, 4686 (1959).

panied by a decreased tendency to displace water molecules from about the metal ion. This effect would be most prominent for the strongly hydrated metal ions such as lithium and those of the first transition series. Because of its size and shape, uranyl ion should be less strongly hydrated, and the hydrophobic character of the chelate anion should not be an important factor.

While the concept of the hydrophobic character of the ligand can be used successfully to rationalize the anomalous stabilities of lithium and the transition metal ions, it can be used only with partial success as an aid to understanding the behavior of the beryllium chelates. Beryllium, which probably is the most strongly hydrated of all dipositive ions in solution, does not show anomalous chelating tendencies with methoxyacetylacetonone, although the beryllium chelates of  $(\text{CH}_3\text{CO})_2\text{CHCH}_3$  and  $(\text{C}_6\text{H}_5\text{CO})_2\text{CHCH}_3$ , which probably are more hydrophobic than  $\text{CH}_3\text{OCH}_2\text{COCH}(\text{CH}_3)\text{COCH}_3$ , are less stable than expected.

In view of the difficulties in understanding the behavior of the beryllium chelates, it seems wise to examine the situation in more detail. A useful approach<sup>19</sup> is to examine the chelation process in terms of a thermodynamic cycle involving the free energy function



where  $F_T = \Delta F_1 + \Delta F_2 + \Delta F_3 + \Delta F_4 + \Delta F_5 + \Delta F_6 + \Delta F_7 + \Delta F_8 + \Delta F_9$ .

(19) We wish to express our appreciation to Professor R. W. Parry for useful discussions regarding this approach.

The effect of salt anions X (nitrate and perchlorate) upon the "observed" formation constants has been studied.<sup>20</sup> In 75 volume-% dioxane, divalent metal salts are associated beyond the extent expected for strong electrolyte behavior, but such association does not appear to be the case for the nitrate or perchlorate salts of monochelated divalent cations.

The terms  $\Delta F_1$ ,  $\Delta F_8$ , and  $\Delta F_9$  would be designated as "solvent effects" by Parry and Keller.<sup>21</sup> Although  $\Delta F_8$  is regarded as the major solvent effect, some variation in the value of  $\Delta F_8$  can be attributed to the incursion of the fourth steric factor, *i.e.*, the shielding effect.

The hydrophobic character of the chelate anion would be significant primarily in determining the value of  $\Delta F_9$ , which is a function of the magnitude of the term  $x - y$ . However, the values of  $\Delta F_7$  and  $\Delta F_8$  would be influenced by methylene substitution inasmuch as the value of both terms is a function of the size of the ion.

In summary, it may be said that the effect of methylene substitution upon the chelating tendency of  $\beta$ -diketone anions is complicated. None of the steric effects that have been suggested previously can be used to explain all of the observed facts. The concept of the hydrophobic

character of the ligand can be used to explain many but not all of the present results.

(20) L. G. Van Uitert, W. C. Fernelius, and B. E. Douglas, *J. Am. Chem. Soc.*, **75**, 2739 (1953).

(21) R. W. Parry, private communication.