negativities of the halogens[25] present give linear relationships.

In Fig. 1 is shown a typical correlation diagram for the CO and NC bands in the series of compounds $Fe(CO)_{4-n}(CNC_7H_7)_nCl_2$.

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CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

The Preparation and Properties of Some Complexes of the Type β-Diketonatobis(ethylenediamine)cobalt(III) Iodide and Bis(β-diketonato)tetrakis(ethylenediamine)dicobalt(III) Iodide

BY L. J. BOUCHER AND JOHN C. BAILAR, JR.

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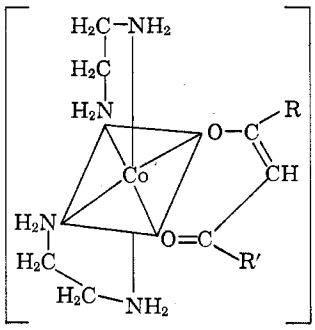
Seven mononuclear complexes of the general type β-diketonatobis(ethylenediamine)cobalt(III) iodide and four dinuclear complexes of the general type bis(β-diketonato)tetrakis(ethylenediamine)dicobalt(III) iodide have been prepared. The infrared spectra and ultraviolet and visible electronic spectra of these complexes have been measured and are found to support the structures proposed. The unique structure of one of the dinuclear complexes is briefly noted.

Introduction

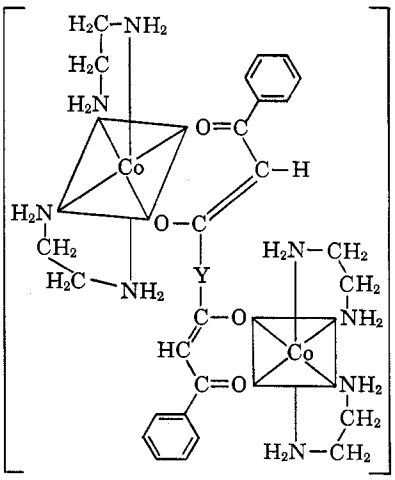
Werner[1] prepared and characterized a large number of dinuclear cobalt complexes which, in addition to stereochemical considerations, have many interesting properties, *i.e.*, intense color and large molecular rotations. These complexes have not been investigated extensively, mainly because they are extremely difficult to prepare. However, current work in coordination polymers has revived interest in the formation of polynuclear complexes. Coordination polymers are generally intractable, and very little information, other than composition and thermal stability, has been derived from them. A logical approach to the study of the preparation and properties of polymeric complexes consists in the preparation of monomeric, dimeric, and higher units and a comparison of their properties. An investigation of this kind perhaps would provide a greater insight into the formation and properties of the dinuclear complexes reported by Werner.

One method of preparing polymeric complexes involves the use of bisdifunctional ligands. Since the preparation and chelating properties of bis-β-diketones are well known, they were chosen as ligands in the study reported here. An additional advantage is that the corresponding β-diketones can be used to prepare the mononuclear complexes.

Werner reported the preparation of the β-diketonatobis(ethylenediamine)cobalt (III) cation in which the β-diketone was acetylacetone or propionylacetone.[2] The procedure which he outlined is not general for other β-diketones or bis-β-diketones, but by simple modifications we have prepared the complexes I–VII.[3] Similar procedures were used to prepare the dinuclear complexes VIII–XI.



I, R = R′ = CH_3
II, R = CH_3; R′ = C_2H_5
III, R = CH_3; R′ = CF_3
IV, R = CH_3; R′ = OC_2H_5
V, R = C_6H_5; R′ = OC_2H_5
VI, R = CH_3; R′ = C_6H_5
VII, R = R′ = C_6H_5



VIII, Y = nothing (chelate rings directly connected)
IX, Y = $-(CH_2)_{-2}$
X, Y = $-(CH_2)_{-8}$
XI, Y = p-C_6H_4-

Experimental

Ligands.—The following ligands were obtained commercially and used without further purification: 2,4-pentanedione (acetylacetone); 1-phenyl-1,3-butanedione (benzoylacetone); 1,3-diphenyl-1,3-propanedione (dibenzoylmethane); 1,1,1-trifluoro-2,4-pentanedione (trifluoroacetylacetone); 1-ethoxy-1,3-butanedione (ethyl acetoacetate); 1-ethoxy-3-phenyl-1,3-propanedione (ethyl benzoylacetate).

(1) A. Werner, *Ann.*, **375**, 1 (1910).

(2) A. Werner, J. E. Schwyzer, and W. Karrer, *Helv. Chim. Acta*, **4**, 113 (1921).

(3) Recently the complex with R = R′ = CF_3 has been reported: D. A. Buckingham and J. P. Collman, Abstracts, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962, p. 36N.

2,4-Hexanedione (propionylacetone) was prepared by the condensation of methyl ethyl ketone and ethyl acetate; copper chelate m.p. 198°; lit.[4] 197–198°.

1,6-Diphenyl-1,3,4,5-hexanetetraone (oxalyldiacetophenone) was prepared by the condensation of acetophenone and diethyl oxalate; m.p. 180–181°, lit.[5] 179–180°.

1,8-Diphenyl-1,3,6,8-octanetetraone (succinyldiacetophenone) was prepared by the Claisen condensation of acetophenone and diethyl succinate; m.p. 92–95°, lit.[6] 92–93°.

1,14-Diphenyl-1,3,12,14-tetradecanetetraone (sebacoyldiacetophenone) was prepared by the condensation of acetophenone and dimethyl sebacate; m.p. 108–110°, lit.[7] 110°.

1,1′-Phenylenebis[3-phenyl-1,3-propanedione] (terephthaloyldiacetophenone) was prepared by the condensation of acetophenone and dimethylterephthalate; m.p. 175–178°, lit.[8] 176–177°.

Complexes.—*cis*-Chloroaquobis(ethylenediamine)cobalt(III) bromide was prepared by the method of Werner.[9] The other complexes were prepared from it, using three different methods.

Method 1.—2,4-Pentanedionatobis(ethylenediamine)cobalt(III) iodide (I), 2,4-hexanedionatobis(ethylenediamine)cobalt(III) iodide (II), and 1,1,1-trifluoro-2,4-pentanedionatobis(ethylenediamine)cobalt(III) iodide (III) were prepared by this method. A solution of 1.50 g. of *cis*-$[Co(en)_2H_2OCl]Br_2 \cdot H_2O$ (3.64 mmoles) in 3 ml. of 10% aqueous potassium hydroxide was treated with 1 ml. of the appropriate ligand (acetylacetone, propionylacetone, or trifluoroacetylacetone) in 2 ml. of ethanol. After the resulting solution was heated to 40° on a steam bath, 2.0 g. of powdered potassium iodide was added, whereupon the iodide precipitated. The desired product, which was contaminated with *cis*-$[Co(en)_2H_2OOH]I_2$ (insoluble in methanol) was collected on a filter and dissolved in hot methanol. The alcoholic solution was filtered and then evaporated to dryness in an air stream. The red-orange solid was dissolved in water, reprecipitated with potassium iodide, collected on a filter, washed with small amounts of acetone and ether, and air dried.

Method 2.—1-Ethoxy-2,4-butanedionatobis(ethylenediamine)cobalt(III) iodide (IV) and 1-ethoxy-3-phenyl-1,3-propanedionatobis(ethylenediamine)cobalt(III) iodide (V) were prepared by this method. A solution of 1.50 g. of *cis*-$[Co(en)_2H_2OCl]Br_2 \cdot H_2O$ in 3 ml. of 10% aqueous potassium hydroxide was treated with 1 ml. of either ethyl acetoacetate or ethyl benzoylacetate in a mixture of 15 ml. of methanol and 10 ml. of water. The solution was stirred for 4 hr. at room temperature. The reaction mixture was filtered and the filtrate evaporated to dryness in an air stream. The red-orange solid was taken up in water and the iodide precipitated by adding powdered potassium iodide. The pure product was collected on a filter, washed with acetone and ether, and air dried.

Method 3.—1-Phenyl-2,4-butanedionatobis(ethylenediamine)cobalt(III) iodide (VI) and 1,3-diphenyl-1,3-propanedionatobis(ethylenediamine)cobalt(III) iodide (VII) were prepared by method 3A: A solution of 1.50 g. of *cis*-$[Co(en)_2H_2OCl]Br_2 \cdot H_2O$ in 3 ml. of 10% aqueous potassium hydroxide was mixed with a solution of either 0.56 g. (3.64 mmoles) of benzoylacetone or 0.82 g. of dibenzoylmethane in 50 ml. of methanol, and the resulting mixture was stirred for 12 hr. at room temperature. The reaction mixture was filtered. The impure product was isolated from the filtrate by the chromatographic separation described below. The bromide residue from the chromatographic separation was dissolved in 50 ml. of water and the filtered solution was treated with 5.0 g. of powdered potassium iodide. The red-orange iodide was collected on a filter and reprecipitated from water with potassium iodide. The pure product was collected, washed with a small amount of acetone and ether, and air dried.

1,6-Diphenyl-1,3,4,6-hexanetetraonatotetrakis(ethylenediamine)dicobalt(III) iodide (VIII), 1,8-diphenyl-1,3,6,8-octanetetraonatotetrakis(ethylenediamine)dicobalt(III) iodide (IX), 1,14-diphenyl-1,3,12,14-tetradecanetetraonatotetrakis(ethylenediamine)dicobalt(III) iodide (X), and 1,1′-phenylenebis(3-phenyl-1,3-propanedionato)tetrakis(ethylenediamine)dicobalt(III) iodide (XI) were prepared by method 3B: A solution of 3.00 g. of *cis*-$[Co(en)_2H_2OCl]Br_2 \cdot H_2O$ (7.28 mmoles) in 6 ml. of 10% aqueous potassium hydroxide was mixed with either 1.06 g. (3.64 mmoles) of oxalyldiacetophenone, 1.20 g. of succinyldiacetophenone, 1.50 g. of sebacoyldiacetophenone, or 1.16 g. of terephthaloyldiacetophenone in 100 ml. of methanol, and the resulting mixture was stirred for 18 hr. at room temperature. The reaction mixture was filtered and the filtrate volume reduced to less than 50 ml. The impure product was isolated by the chromatographic separation described below. The residue was dissolved in 100 ml. of water and the filtered solution was treated with 10.0 g. of powdered potassium iodide. The red-orange solid was collected on a filter and reprecipitated from water with potassium iodide. The pure product was collected and washed with acetone, then ether, and air dried.

Chromatographic Separation.—A glass tube (10 cm. i.d., 60 cm. in length), fitted with a stopcock at the lower end, was used as a column. A plug of glass wool was inserted just above the stopcock and finely divided sand was added in a slurry to a height of 2 cm. Whatman cellulose powder (standard grade) was added in a slurry and allowed to settle to a height of 40 cm. The cellulose was washed with distilled water until the effluent was clear. In general, the solution of the reaction mixture (25–50 ml.) was adsorbed on the column and eluted successively with 2 l. of acetone, 3 l. of 20% water–80% acetone, and, finally, with enough water to wash all the color off the column. Upon addition of the water–acetone mixture, an orange band separated; this contained the desired product. The orange cut was collected and evaporated to dryness in an air stream.

Deuterium Exchange.—Exchange of the labile hydrogens in the complexes with deuterium was effected by dissolving the appropriate complex in a minimum amount of deuterium oxide (>99.7%), heating on a steam bath for a few minutes, and evaporating the resulting solution to dryness in an air stream.

Infrared Spectra.—Spectra were obtained with a Perkin-Elmer Model 21 double beam recording spectrophotometer with sodium chloride optics, using Nujol mulls between rock salt plates.

Visible–Ultraviolet Spectra.—Spectra were taken with a Cary Model 14M recording spectrophotometer using aqueous solutions in 1-cm. cells. The extinction coefficients for the mononuclear complexes were calculated in the usual manner while those of the dinuclear complexes were calculated using an equivalent weight, per metal atom, rather than a molecular weight.

Discussion and Results

Preparation of Complexes.—The synthetic route by which these complexes are prepared can be described by the equations

$$cis\text{-}[Co(en)_2ClH_2O]^{2+} + OH^- \longrightarrow cis\text{-}[Co(en)_2OHH_2O]^{2+} \quad (1)$$

$$cis\text{-}[Co(en)_2OHH_2O]^{2+} + Hdik \longrightarrow [Co(en)_2dik]^{2+} \quad (2)$$

where Hdik is a β-diketone. The preparation of the dinuclear complexes is accomplished in an analogous manner. While reaction 1 is very rapid, the speed of reaction 2 is dependent on the particular β-diketone used. The β-diketone ligands can be divided into three groups based on the ease of reaction 2. With acetylacetone, trifluoroacetylacetone, and propionylacetone the reactions are essentially complete in a few

(4) G. T. Morgan and H. G. Reeves, *J. Chem. Soc.*, **123**, 444 (1923).
(5) E. Brömme and L. Claisen, *Ber.*, **21**, 1131 (1888).
(6) G. H. Daub and W. S. Johnson, *J. Am. Chem. Soc.*, **72**, 501 (1950).
(7) E. H. Holst, Ph.D. Dissertation, The Pennsylvania State University, 1955.
(8) D. F. Martin, M. Shamma, and W. C. Fernelius, *J. Am. Chem. Soc.*, **80**, 4891 (1958).
(9) A. Werner, *Ann.*, **386**, 122 (1912).

TABLE I

ELEMENTAL ANALYSIS OF COMPLEXES[a]

No.	Empirical formula	Calculated, % C	H	N	Found, % C	H	N
I	$C_9H_{23}N_4O_2I_2Co$	20.11	4.32	10.43	20.12	4.38	10.28
II	$C_{10}H_{25}N_4O_2I_2Co \cdot H_2O$	21.28	4.82	9.93	21.18	5.12	10.14
III	$C_9H_{20}N_4O_2F_3I_2Co$	18.53	3.46	9.60	18.81	3.58	10.09
IV	$C_9H_{25}N_4O_3I_2Co$	21.15	4.46	9.92	21.11	4.36	9.68
V	$C_{15}H_{27}N_4O_3I_2Co \cdot H_2O$	28.04	4.55	8.66	27.89	4.33	8.89
VI	$C_{14}H_{25}N_4O_2I_2Co \cdot H_2O$	27.26	4.41	9.09	26.95	4.27	9.02
VII	$C_{19}H_{27}N_4O_2I_2Co \cdot 1.5H_2O$	33.38	4.42	8.19	33.29	4.28	7.59
VIII	$C_{26}H_{44}N_8O_4I_4Co_2 \cdot H_2O$	26.53	3.94	9.52	26.52	3.97	9.25
IX	$C_{28}H_{48}N_8O_4I_4Co_2 \cdot H_2O$	27.90	4.18	9.30	27.76	4.20	8.78
X	$C_{34}H_{60}N_8O_4I_4Co_2 \cdot H_2O$	31.48	4.21	8.64	31.34	4.62	7.92
XI	$C_{32}H_{48}N_8O_4I_4Co_2 \cdot 2H_2O$	30.18	4.13	8.80	30.06	4.24	8.96

[a] Microanalyses by J. Nemeth, University of Illinois.

minutes and the product is formed in good yield (60–70%). With ethyl acetoacetate and ethyl benzoylacetate the reaction time is somewhat lengthened (4 hr.) and the yields are lowered (~50%). With benzoylacetone, dibenzoylmethane, and bis(β-diketones), the reaction time is long (12–18 hr.) and the yield is low (~20%). The formation of the dinuclear species would necessarily require a stepwise reaction with the formation of a second chelate ring probably being slow.

The relatively low yields obtained in the reactions with the third group of ligands, in spite of the simplicity of the reactions involved, may be partly explained by mechanical losses in separation and repeated recrystallizations required to obtain pure products. A more important factor is the apparent instability of the various ligands in the presence of the cobalt substrate even under the mild conditions used. The long reaction times may lead to decomposition of the desired product, but the complexes seem to be stable to decomposition when in the pure form. A brown, water-insoluble residue containing cobalt and an acetone-soluble organic moiety can be isolated from the reaction mixture. Very little unreacted ligand is ever recovered while the cobalt-containing ions isolated include *cis*-$[Co(en)_2OH_2O]^{2+}$ and $[Co(en)_3]^{3+}$. There are apparently complex oxidation–reduction processes taking place in solution in addition to the formation of the chelate compounds.

These complexes are stable in water at room temperature for periods of several months and are not noticeably attacked by 0.1 *N* acid or base at room temperature. The mononuclear complexes are appreciably soluble in water and methanol but less soluble in ethanol and acetone. Their solubilities in acetone increase with the size of the organic group on the chelate ring. The dinuclear complexes are appreciably soluble in methanol but less soluble in water, ethanol, and acetone. The preparation of several other mononuclear and dinuclear complexes has been attempted without success. The following methylene (γ) carbon-substituted β-diketones do not form complexes with the cobalt substrate under the conditions used in this work: 2-methyl-1,3-diphenyl-1,3-propanedione, 3-phenyl-2,4-pentanedione, and 1,4-bis-(2,2-diacetylethyl)benzene. The nonchelating ability of these ligands may be accounted for by steric and solvation effects.[10]

Infrared Spectra.—The β-diketone–cobalt chelate ring exhibits characteristically intense absorption in the 1500–1600 cm.$^{-1}$ region. The bands are assigned to the C=C and C=O group vibrations[11,12] and their presence in the spectra of β-diketone complexes is excellent proof of chelate formation. Table II summarizes the pertinent data obtained from the infrared spectra of the complexes reported here.

In general, the spectra of the mononuclear and dinuclear complexes are quite similar, indicating noninteraction of the two metal–chelate rings in the latter. The infrared spectra have a single intense band in the region 1508–1523 cm.$^{-1}$ (B band) and one or two less intense bands in the 1545–1605 cm.$^{-1}$ region (A band). An exception to this is furnished by the dinuclear complex VIII, the spectrum of which has two bands in the lower frequency region at 1503 and 1535 cm.$^{-1}$. This may be explained by the possibility of resonance between the diketone chelate rings.

Upon substitution of the methyl group of acetylacetone by phenyl, ethoxy, or trifluoromethyl, the expected upward shift in the higher frequency A band occurs.[13,14] The frequency of vibration of the B band varies only slightly in these complexes and does not seem to depend strongly on substitution of bulky electron-withdrawing or electron-donating groups at the carbonyl carbon atom. In every case in which R is electronically different from R′ or Y there are two bands in the higher frequency region but when R and R′ (or Y) are equivalent, there is only one. It would be tempting to assign these two bands to the vibrations of nonequivalent carbonyl groups. This has not been observed in the tris-β-diketonatocobalt(III) complexes containing unsymmetrical β-diketones. However, the copper(II) complexes of ethyl acetoacetate,[15] 2-furoyl-

(10) D. F. Martin and B. B. Martin, *Inorg. Chem.*, **1**, 404 (1962).
(11) J. Lecompte, *Discussions Faraday Soc.*, **9**, 125 (1950).
(12) J. Lecompte, C. Duval, and R. Freymann, *Bull. Soc. Chim. France*, **19**, 106 (1952).
(13) R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).
(14) H. F. Holtzclaw, Jr., and J. P. Collman, *J. Am. Chem. Soc.*, **79**, 3318 (1957).
(15) R. P. Dryden and A. Winston, *J. Phys. Chem.*, **62**, 635 (1958).

Table II

Characteristic Infrared Bands of Complexes[a]

No.	R	R′	Y	A band, cm.$^{-1}$		B band, cm.$^{-1}$	
I	CH_3	CH_3	...		1565 (ms)		1523 (ms)
II	CH_3	C_2H_5	...		1565 (ms)		1518 (ms)
III	CH_3	CF_3	...	1605 (s)	1563 (ms)		1523 (ms)
IV	CH_3	OC_2H_5	...	1598 (s)	1568 (s)		1510 (ms)
V	C_6H_5	OC_2H_5	...	1600 (s)	1575 (s)		1513 (ms)
VI	C_6H_5	CH_3	...	1583 (ms)	1548 (ms)		1515 (ms)
VII	C_6H_5	C_6H_5	...	1583 (m)			1520 (ms)
VIII	C_6H_5	...	Nothing	1583 (m)	1560 (m)	1535 (s)	1503 (s)
IX	C_6H_5	...	$-(CH_2)-_2$	1583 (ms)	1545 (ms)		1510 (s)
X	C_6H_5	...	$-(CH_2)-_3$	1583 (ms)	1545 (ms)		1508 (s)
XI	C_6H_5	...	p-C_6H_4–	1585 (ms)			1513 (s)

[a] m, medium; ms, medium strong; s, strong.

trifluoroacetone, and 2-furoylperfluorobutylmethane,[14] as well as the bis(ethylacetoacetato)diisopropoxytitanium(IV) complex,[15] show two bands in the high-frequency region which have been assigned to nonequivalent carbonyl vibrations.

There is a possibility of ambiguity in the assignment of the carbonyl and C=C frequencies in these complexes, since the NH_2 deformation is expected to be in the same region.[16] The infrared spectra of the deuterated complexes, $[Co(en)_2dik]I_2$, where dik represents acetylacetone or benzoylacetone, show new bands at 2280 and 935 cm.$^{-1}$ and a shoulder at 2380–2320 cm.$^{-1}$. The former may be assigned to a stretching vibration and an in-plane deformation of a deuterium on the central (γ) carbon atom in the β-diketone,[17] while the latter is probably due to an N–D stretching vibration.[18] The A and B band frequencies are almost identical with those in the spectra of the nondeuterated complexes. The noninterference of the NH_2 deformation also is evidenced by the fact that the A and B band frequencies in $[Co(acac)_3]$[19] are almost identical with those in $[Co(en)_2acac]I_2$.

The A band and B band have been assigned to the C=C and C=O group vibrations, respectively, based on a normal coordinate analysis of the tris(acetylacetonato)cobalt(III) complex.[20] However, the report that substitution at the central carbon atom of a β-diketone shifts the B band downward while the A band is unaltered[15] indicates, quite empirically, that the A and B bands can be assigned to the C=O and C=C group vibrations, respectively. It must be emphasized that the vibrations in the β-diketone chelate ring may not be those of simple groups but may involve the whole chelate ring. The unique environment in which the β-diketone chelate ring exists in the complexes reported here, *i.e.*, carbonyl *trans* to amine nitrogen and low molecular symmetry, may lead to the appearance of new bands in the infrared spectrum. In any case, the data presented here are not sufficient to make an explicit assignment of bands.

(16) D. B. Powell and N. Sheppard, *Spectrochim. Acta*, **17**, 68 (1961).
(17) C. Djordjevic and U. Katovic, *J. Inorg. Nucl. Chem.*, **25**, 1099 (1963).
(18) Deuterated $[Co(en)_3]Cl_3$ shows bands at 2370 and 2330 cm.$^{-1}$.
(19) J. P. Dismukes, L. H. Jones, and J. C. Bailar, Jr., *J. Phys. Chem.*, **65**, 796 (1961).
(20) K. Nakamoto, H. J. McCarthy, A. Ruby, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1066 (1961).

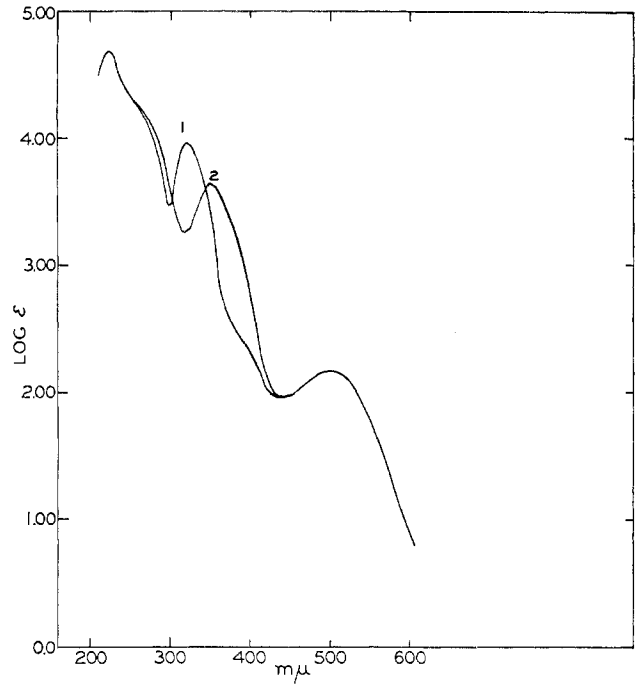


Fig. 1.—Spectra of $[Co(en)_2dik]I_2$ in water: 1, dik is acetylacetone (I); 2, dik is benzoylacetone (VI).

Electronic Spectra.—The electronic spectrum of the tris(acetylacetonato)cobalt(III) complex has been studied and the bands assigned on the basis of a molecular orbital treatment.[21,22] The spectrum of the β-diketone–cobalt chelate is expected to show, in addition to the simple d–d transitions of the cobalt atom, $\pi \rightarrow \pi^*$ transitions in the ligand and charge-transfer bands. The spectra of the compounds reported here are very complex and contain from three to five well-defined bands as well as a number of shoulders (Fig. 1 shows typical spectra). The spectra of all the complexes show a band at 224 mμ (log ϵ_{max} 4.65) which is associated with the iodide ion.

The bands can be divided into three types; d–d transitions, $\pi \rightarrow \pi^*$ transitions, and charge-transfer transitions. The positions of the absorption bands of the first type are listed in Table III. These bands are assigned to the simple d–d transitions on the basis of their positions and intensities; they compare favorably

(21) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961).
(22) D. W. Barnum, *ibid.*, **22**, 183 (1961).

TABLE III

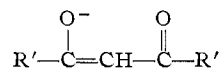
POSITION OF THE ABSORPTION BANDS

				$^1A_{1g} \rightarrow {}^1T_{1g}$		$^1A_{1g} \rightarrow {}^1T_{2g}$		$\pi \rightarrow \pi^*$				$d\epsilon \rightarrow \pi^*$	
No.	R	R′	Y	λ_{max}, mμ	log ϵ_{max}	λ_{max}, mμ	log ϵ_{max}	λ_{max}, mμ	log ϵ_{max}	λ_{max}, mμ	log ϵ_{max}	λ_{max}, mμ	log ϵ_{max}
I	CH_3	CH_3	...	496	2.15	376	2.50	obs.		260 (sh)	4.2	324	3.7
II	CH_3	C_2H_5	...	496	2.15	380 (sh)[a]	2.40	obs.		260 (sh)	3.9	324	3.6
III	CH_3	CF_3	...	492	2.10	378	2.60	235 (sh)	4.4	265	3.8	330	3.6
IV	CH_3	OC_2H_5	...	492	2.13	375 (sh)	2.30	obs.		255 (sh)	3.9	290	3.9
V	C_6H_5	OC_2H_5	...	500	2.18	380 (sh)	2.50	obs.		260 (sh)	4.2	320	4.0
VI	C_6H_5	CH_3	...	500	2.18	obs.[b]		250 (sh)	4.3	280 (sh)	4.1	360	3.9
VII	C_6H_5	C_6H_5	...	490	2.25	obs.		262	4.4	300	4.2	372	4.1
VIII	C_6H_5	...	Nothing	500 (sh)	2.35	obs.		258	4.2	324	3.9	425	4.0
IX	C_6H_5	...	$-(CH_2)-_2$	496	2.30	obs.		255	4.3	280 (sh)	4.1	355	3.9
X	C_6H_5	...	$-(CH_2)-_8$	496	2.25	obs.		250 (sh)	4.3	280 (sh)	4.1	352	3.9
XI	C_6H_5	...	p-C_6H_4–	500 (sh)	2.35	obs.		268	4.2	315	4.0	406	4.0

[a] sh = shoulder. [b] obs. = obscured.

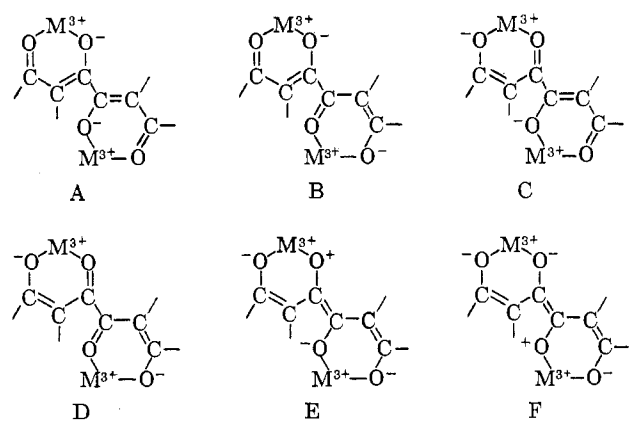
with those of the analogous type of complex $[Co(en)_2ox]^+$ (λ_{max} 496, 354 mμ; log ϵ_{max} 2.0, 2.3). The positions of these bands vary very little through the series of compounds, thus indicating that the ligand field about the cobalt atom remains almost constant. This is to be expected since the arrangement of the two diamines and the β-diketone molecules around the cobalt is the same in each case. The positions of the absorption bands of the second type are listed in Table III. These bands are assigned to ligand $\pi \rightarrow \pi^*$ type transitions because of their high energy and intensity. It is interesting to note that the electronic spectrum of $[Co(acac)_3]$ shows two bands of similar intensity at 228 and 256 mμ which are assigned to $\pi \rightarrow \pi^*$ type transitions.[23] The positions of the absorption bands of the third type are listed in Table III. This band, in $[Co(acac)_3]$, has been assigned to a $d\epsilon \rightarrow \pi^*$ metal–ligand charge-transfer transition. The data presented here are consistent with this assignment.

Both the $\pi \rightarrow \pi^*$ and $d\epsilon \rightarrow \pi^*$ bands steadily decrease in energy as the length of the conjugated π-system increases, *i.e.*, λ_{max} varies in the order VIII > XI > VII > VI ~ IX ~ X > I ~ II ~ III. This can be explained in the following way: the energy levels of the ligand π-system move closer together while moving to lower energies with increasing delocalization of the π-electrons (by analogy with the particle in a box), thus decreasing the energy separation between the stationary metal $d\epsilon$ level and the ligand π^* level as well as between the π and π^* levels.[24] Conversely, the mesomeric effect of the lone pairs on the oxygen in the OC_2H_5 group shortens the conjugated path by making the carbonyl groups grossly nonequivalent. This gives an increase in the energy of the transitions. The above assignments are only tentative and subject to change when studies are made with other metals. An energy level scheme of enolate anions



would greatly aid in the interpretation of the spectra of these compounds.

Conclusion.—One very interesting compound that emerges from this work is compound VIII, in which the two chelate rings are directly attached through the carbonyl carbons. A number of resonance structures can be drawn. Undoubtedly A, B, C, and D contribute



very largely to the actual structure. Invocation of structures E and F allows the assignment of a partial double bond character to the C–C bond that connects the two chelate rings. This is in agreement with the interpretation of the infrared and electronic spectra. This seems to be the only example of this in metal chelate chemistry, and for this reason the compound merits further study.

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(23) R. H. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 5658 (1958).

(24) The position of compound VIII instead of XI as the first member of the series can be rationalized by considering molecular models which show that while the two chelates in VIII can be coplanar, the *p*-phenyl group in XI cannot be in the plane of the two chelate rings; this gives rise to a smaller degree of delocalization and consequently a lower λ_{max}. The rest of the series, as expected, follows the number of phenyl groups present, *i.e.*, λ_{max} varies in the order VII (two phenyl rings) > VI (one phenyl ring) > I (no phenyl ring).