[Contribution from the Department of Chemistry, Massachusetts Institute of Technology]

Spectral Investigations of Metal Complexes of β-Diketones. I. Nuclear Magnetic Resonance and Ultraviolet Spectra of Acetylacetonates[1]

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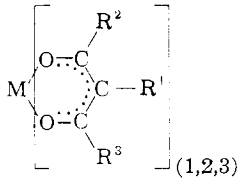
This paper reports proton resonance and ultraviolet spectra of a broad range of metal ion complexes of acetylacetone. The n.m.r. spectra of diamagnetic complexes provide no support for the postulate of benzenoid resonance in the chelate rings, as had been suggested by Calvin nor are any great differences in electron density at the unique carbon atom in the ring indicated. Definitive ultraviolet spectra of thirty acetylacetone complexes are reported. All of these data in general and particularly in certain comparisons indicate that the electrostatic model of Belford, *et al.*, cannot account for the variation in energy of the presumed π–π^* transition. The energy of this transition cannot be correlated with any simple parameter of the complexed metal ion, and it is believed that it is determined by several such parameters, among which is the ability of the metal ion to participate in dπ–pπ overlap with the π system of the chelate ring.

Introduction

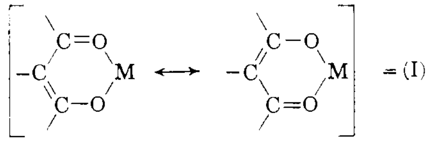
Complexes of metal ions with acetylacetone have been the subject of a wide variety of physical studies for many years. Despite this activity, there is still relatively little concerning their electronic structures which may be stated with certainty. Several years ago a broad program of spectroscopic investigations of complexes of the general type I was begun in this Laboratory. The various phases of this program include: (1) nuclear resonance studies of diamagnetic acetylacetone complexes; (2) study of the ultraviolet spectra, with particular emphasis on obtaining complete and definitive data, of a wide variety of acetylacetone complexes; (3) correlated study of the magnetic properties and ligand field spectra of transition metal acetylacetonates; (4) detailed analysis of the infrared spectra of metal complexes of variously deuterated acetylacetones; (5) study of the effect of variation of the groups R^1, R^2 and R^3 (in I) on the ultraviolet spectra of complexes in order to substantiate the assignment of various bands as n-π^*, π-π^*, charge transfer, etc.; and (6) study of the solvent dependence of the ultraviolet spectra of various acetylacetone and substituted acetylacetone complexes in order to substantiate band assignments In this paper the results of parts (1) and (2) are reported.



(I)

For purposes of the discussion to follow in this and succeeding papers, certain structural features and bonding possibilities may be mentioned explicitly at the outset. Several structural studies of acetylacetone complexes have established the existence of certain critical symmetry elements in the chelate rings. A study of tris-(acetylacetonato)-iron(III) by Roof,[3] in which interatomic distances were established to within ± 0.02 Å., is particularly important. Roof's results lead to the following important conclusions: (a) the six-membered chelate ring is planar; (b) the individual rings have C_{2v} symmetry, the pairs of M–O, O–C and C–C distances being of equal length to within experimental error; (c) the ring C–C distances are 1.39 Å., intermediate between single and double bond distances (and also equal to the C–C distance in benzene), and the C–O distances are 1.28 Å., also intermediate between single and double bond distances. Bis-(acetylacetonato)-Cu(II) has been studied by several investigators.[4–6] The X-ray studies[4,5] of the cupric compound are not as completely refined as they might be, and apparent discrepancies in the ring C–C distances have been reported (1.38, 1.44 Å.). However, Shugam himself comments that the values converge as refinement proceeds, and there is little reason to doubt that complete refinement of the calculations would show symmetrical chelate rings. The only other acetylacetonate studied[7] is bis-(acetylacetonato)-Ni(II)[8] but this study is incomplete and, moreover, it shows that there is some degree of trimerization in the crystals.

The structural data cited above force one to conclude that there is some kind of resonance in the chelate rings which results in equalization of the pairs of C–C, C–O and M–O distances. The type of resonance implied in I and set out explicitly in II is sufficient to account for the three salient structural features of the chelate ring which are demonstrated in the work of Roof.



(II)

Calvin and Wilson,[9] in measuring the formation constants of Cu(II) complexes with organic chelating ligands, observed that any group appended to acetylacetone in place of $-CH_3$ and capable of partic-

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[1] Supported by the U. S. Atomic Energy Commission under Contract No. AT(30-1)-1965.

[2] Du Pont Predoctoral Teaching Fellow, 1957–1958.

[3] R. B. Roof, Jr., *Acta Cryst.*, **9**, 781 (1956).

[4] E. A. Shugam, *Doklady Akad. Nauk, S.S.S.R.*, **81**, 853 (1951); *C.A.*, **46**, 3894d (1952).

[5] H. Kogama, Y. Saito and H. Kuroya, *J. Inst. Polytech., Osaka City Univ.*, **C4**, 43 (1953); *C.A.*, **48**, 3097a (1954).

[6] S. Shibata and K. Sone, *Bull. Chem. Soc. Japan*, **29**, 852 (1956).

[7] J. M. Robertson (*J. Chem. Soc.*, 1222 (1951)) has reported inequalities in the pairs of Cu–O and C–O distances in the ditropolonate of Cu(II), where one might expect equalization through resonance as in the acetylacetonates. It would not seem too presumptuous to question the correctness of the reported structure for this compound.

[8] G. J. Bullen, *Nature*, **177**, 537 (1956).

[9] M. Calvin and K. W. Wilson, This Journal, **67**, 2003 (1945).

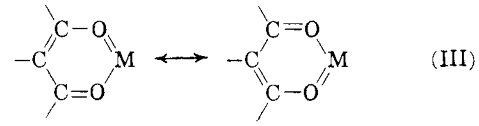
TABLE I

π-BONDING POSSIBILITIES IN METAL ACETYLACETONATES

Type of complex	Point group symmetry	Assumed σ hybridization[a]	Metal orbitals available for π-bonding With π_z ligand orbitals[b]	Metal orbitals available for π-bonding With π_x ligand orbitals[c]
MA_2, planar	D_{2h}	$d_{x^2-y^2}$, s, p_x, p_y	d_{xz}, d_{yz}, p_z	d_{xy}
MA_2, tetrahedral	D_{2d}	s, p_x, p_y, p_z, s; d_{xy}, d_{xz}, d_{yz}	$d_{x^2-y^2}$, d_{xz}, d_{yz}, $d_{x^2-y^2}$, p_x, p_y	d_{z^2}, d_{xy}, d_{xz}, d_{yz}; d_{z^2}, p_x, p_y, p_z
MA_3, octahedral	D_3	$d_{x^2-y^2}$, d_{z^2}, s, p_x, p_y, p_z	d_{xz}, d_{yz}, d_{xy}	d_{xz}, d_{yz}, d_{xy}

[a] Not uniquely determined in any case. Reasonable assumptions have been made. [b] Orbitals forming part of ligand π system. [c] Orbitals containing non-bonding electrons on oxygen.

ipating in the ring resonance, *e.g.*, $-OC_2H_5$ by virtue of unshared pairs on oxygen, caused a lowering of the stability constant, β_n. ($\beta_n = [MA_n]/[M^{+n}][A]^n$; A = organic ligand.) They also found that, when another resonating π system (*e.g.*, a benzene or naphthalene system) was fused to the chelate ring, a lowering of stability resulted. In order to explain these facts and also to account for the high stability of acetylacetone chelates in general, Calvin and Wilson suggested that there might be some degree of "benzenoid" resonance as shown in III in addition to the enolate type resonance shown in II.



(III)

It may be noted that the structural data now available are consistent with III but cannot be said to require it, for this can be explained assuming only the resonance shown in II. However, the plausibility of "benzenoid" resonance in these compounds may be questioned from the point of view of charge separations resulting in the molecule.

Double bonds between metals and donor systems may be of the dπ-pπ or dπ-dπ types, the first being exemplified by M–CN bonds and the second by $M-PX_3$ bonds, for example. The dπ-pπ and dπ-dπ bonding in such cases is useful and perhaps enhanced because it operates to relieve the charge separation resulting from the formation of donor σ bonds. In other words, the bonding involved may be crudely symbolized as $\mathrm{M} \underset{\smile}{\overset{\frown}{\leftarrow}} \mathrm{X}$. Now if metal-oxygen π-bonding is to occur in metal acetylacetonates, it is not too difficult to see that it would also have to be dative, but in the opposite sense, *i.e.*, symbolized as $\mathrm{M} \underset{\smile}{\overset{\frown}{\leftarrow}} \mathrm{O}$. This is because in no case are there any bonding orbitals of π-symmetry on the acetylacetonate anion which are vacant, but for certain metal ions there are vacant dπ and pπ orbitals. Of course, in some cases, *e.g.*, Co^{+3}, the metal does not have any vacant (3)dπ orbitals and unless the use of (4)d orbitals is to be considered no metal-oxygen π-bonding appears possible. Thus, when considered in this light there is really no parallel between the π-bonding which might occur in metal acetylacetonates and that believed to occur in cyanides, carbonyls, phosphine complexes, etc., and the factor principally responsible for the difference, *viz.*, increasing rather than decreasing the negative charge on the metal, is such that π-bonding is much less likely to occur in metal acetylacetonates.

Although extensive O$p\pi$ → M$p\pi$(or dπ) bonding does not appear to be likely, some mixing of O$p\pi$ and metal pπ and/or dπ orbitals will doubtless occur where permitted by symmetry and is likely to have some effect on the electronic structure and spectrum as the following experimental results suggest. In this connection it appeared worthwhile to tabulate the π-bonding possibilities as determined by the methods of group theory. The ligand has two distinguishable kinds of pπ orbitals which are designated as π_z and π_x. The former occur on the oxygens and all of the ring carbon atoms; their nodal plane is the plane of the chelate ring. The latter exist only on the oxygen atoms and lie perpendicular to the p_z orbitals, and, we shall presume, perpendicular to the M–O bonds. The results of the analysis are presented for ready reference in Table I.

Experimental

Preparations.—Nearly all compounds were prepared according to methods already described in the literature.[10] Some specific details concerning individual preparations will be reported in a forthcoming article on visible spectra and magnetic properties. Analyses were performed when there was any reason to question the identity or the purity of the compound.

N.M.R. Measurements.—Proton resonance spectra were observed at room temperature (26 ± 3°) on a Varian Associates Model V-4300B high resolution spectrometer at a frequency of 40 Mc. Chemical shifts were measured with reference to a Pyrex capillary containing water, using the difference between benzene and water for a scale calibration. The capillary was placed within the Pyrex tube containing the sample solution; the sample tubes were spun with the usual air turbinic device. All measurements were made in CCl_4 solutions. The tris-(acetylacetonate) of Y used in these measurements was prepared from the highest purity Y_2O_3 obtainable from the Ames, Iowa, Laboratory of the Atomic Energy Commission. Ordinary Y salts were found to be too highly contaminated with paramagnetic impurities to produce good spectra. LaA_3 was found to be too insoluble in CCl_4 to be measured. No attempt was made to observe resonance at more than one concentration because in nearly all cases a saturated or near saturated solution was required to observe resonance. With the more soluble Be compound, the effect of dilution on δ was studied and found to be negligible.

Ultraviolet Measurements.—All spectra were measured at 25° on a Cary recording spectrophotometer using 1-cm. quartz cells. The solutions measured were all $\sim 10^{-5}$ *M*; they were first made up to $\sim 10^{-4}$ *M* by weight using a microbalance, then diluted to the desired concentrations. The solvents employed were freshly opened Fisher reagent grade chloroform, U. S. Industrial Chemicals Company absolute pure reagent ethanol and distilled water. Extinction coefficients were calculated from $\epsilon = (\log I_0/I)$/molarity. The reproducibility of the ϵ values was found in general to be <5%. Wave lengths given are reliable to ±1 mμ. Great care was taken in the measurements of ϵ and λ since for several compounds previously reported data differed by considerably more than could be attributed to minimal experimental error. We believe the present measurements to be definitive to within the stated errors.

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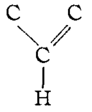
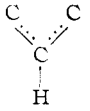
(10) For details and further references see, for example, W. C. Fernelius and B. E. Bryant, "Inorg. Syntheses," Vol. V, p. 105; R. West and R. Riley, *J. Inorg. Nucl. Chem.*, **5**, 295 (1958).

Discussion

N.m.r. Spectra.—In an attempt to detect differences in electronic distribution in the chelate ring as a function of the metal ion completing the ring, nuclear resonances of the hydrogen bonded to the middle carbon of the chelate ring and of the similar hydrogen in the enol form of acetylacetone were observed in CCl_4 solutions. Table II lists values of the chemical shifts δ[11]; the complexes listed represent nearly all of the diamagnetic complexes of this type sufficiently soluble in CCl_4 to allow observation of resonance. The mean shift is $+0.59 \pm 0.05$ p.p.m. and only the complexes of Be, Sc and Co(III) lie outside this range of δ values. The magnitude of the shifts is close to that observed for olefinic protons observed under the same conditions.[12] The shifts are equally consistent with the situations





and allow no real distinction to be made between them. No large positive shift of the order of the +2.50 p.p.m. shift observed for benzene protons[12] was found, but this does not preclude the possibility of benzenoid resonance, for little is known concerning proton shifts in aromatic rings containing more than one hetero atom. It is interesting to note that the shifts appear to be nearly independent of the nature of the metal ion completing the chelate ring with regard to charge, size and ability to π-bond with the ligand system; however, these effects may be largely attenuated before reaching the immediate environment of the ring proton.

TABLE II

N.M.R. DATA FOR METAL ACETYLACETONES IN CCl_4

Compound	$\delta \pm 0.05$ p.p.m.
H[a]	+0.63
Be	+ .70
Zn	+ .60
Al	+ .56
Ga	+ .54
In	+ .54
Sc	+ .70
Y	+ .58
Co(III)	+ .52
Zr(IV)	+ .56
Th(IV)	+ .57
mean	$+0.59 \pm 0.05$

[a] Extrapolated to infinite dilution.

Ultraviolet Spectra.—Thirty-one metal acetylacetonates and acetylacetone were examined in $CHCl_3$ and/or absolute ethanol in the 240–400 mμ region. The spectra are comparable to others previously reported[13–20] in $CHCl_3$ and other solvents with regard to wave lengths of maxima, but sizable disagreements in intensities were noted in some cases.[14,15,20] The spectra can be roughly grouped into three classes. Class I is exemplified by the spectra of acetylacetone in $CHCl_3$ and of Li, Na and K acetylacetonates in absolute ethanol and in water. A single nearly symmetric peak is observed. Class II is typical of all other complexes examined except those of Cu(II), Fe(III), Co(III) and Cr(III). In this case again only one strong band is seen, but there is a shoulder always appear-

TABLE III

ULTRAVIOLET DATA FOR METAL ACETYLACETONATES

	Compound	Solvent	λmax		ε (l. mole^{-1} cm.$^{-1}$)
			mμ	cm.$^{-1}$	
Class I	H	$CHCl_3$	274	36,500	10,600
	Li	H_2O	292	34,200	11,400[a]
		EtOH	290	34,500	13,000[a]
	Na	H_2O	292	34,200	10,800[a]
		EtOH	288	34,700	10,400[a]
	K	H_2O	292	34,200	11,300[a]
		EtOH	286	35,000	9,500[a]
Class II	Be	$CHCl_3$	294	34,000	33,300
		EtOH	292	34,200	33,200
	Mg	$CHCl_3$	284	35,200	21,200
		EtOH	284	35,200	27,600
	Ca	EtOH	290	34,500	25,800
	Sr	EtOH	282	35,500	~20,000
	Ba	EtOH	288	34,700	19,000
	Al	$CHCl_3$	288	34,700	42,800
	Ga	$CHCl_3$	285	35,100	37,600
	In	$CHCl_3$	281	35,600	31,800
	Zr	$CHCl_3$	275	36,400	34,700
	Th	$CHCl_3$	274	36,500	40,900
	Zn	$CHCl_3$	275	36,400	20,200
		EtOH	284	36,500	28,900
	Cd	EtOH	289	34,600	19,800
	Sc	$CHCl_3$	297	33,700	28,800
	Y	$CHCl_3$	282	35,500	25,900
	$La \cdot 2H_2O$	$CHCl_3$	275	36,400	24,900
	V(III)	$CHCl_3$	280	35,700	19,600
	$VO(IV) \cdot H_2O$	$CHCl_3$	301	33,200	20,000
	Mn(II)	$CHCl_3$	276	36,200	20,500
	$Mn(II) \cdot 2H_2O$	$CHCl_3$	275	36,400	19,600
	Mn(III)	$CHCl_3$	274	36,500	24,000
	Co(II)	$CHCl_3$	292	34,200	16,200
	Ni(II)	EtOH	294	34,000	23,700
		$CHCl_3$	265	37,700	15,200
		$CHCl_3$	296	33,800	12,400
Class III	Fe(III)	$CHCl_3$	274	36,500	29,600
		EtOH	237	42,200	16,600
		EtOH	273	36,600	27,000
	Co(III)	$CHCl_3$	258	38,800	~34,000
		EtOH	228	43,900	~34,000
		EtOH	257	38,900	32,900
	Cu(II)	$CHCl_3$	245	40,800	20,100
		$CHCl_3$	296	33,800	24,600
		EtOH	242	41,300	15,000
		EtOH	294	34,000	24,500
	Cr(III)	$CHCl_3$	336	29,800	15,800

[a] ε calculated on the basis of the formula $MC_5H_7O_2$, M = Li^+, Na^+, K^+.

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(11) $\delta = (H_{ref} - H_{sample})/H_{ref}$; reference compound, pure H_2O.

(12) J. S. Waugh and R. W. Fessenden, THIS JOURNAL, **79**, 846 (1957).

(13) H. E. Acly and H. S. French, *ibid.*, **49**, 847 (1927).

(14) L. F. Hatch and G. Sutherland, *J. Org. Chem.*, **13**, 249 (1948).

(15) K. Sone, I. Miyake, H. Kuroya and K. Yamasaki, *J. Chem. Soc., Japan, Pure Chem. Sect.*, **69**, 70 (1948).

(16) K. Yamasaki and K. Sone, *Nature*, **166**, 998 (1950).

(17) E. M. Larsen, G. Terry and J. Leddy, THIS JOURNAL, **75**, 5107 (1953).

(18) R. L. Belford, A. E. Martell and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).

(19) I. Lifschitz, *Rec. trav. chim.*, **69**, 1495 (1950).

(20) K. Sone, THIS JOURNAL, **75**, 5207 (1953).

ing on the log wave length side. This classification is most useful for diamagnetic complexes. Some paramagnetic complexes placed in this class do not show as pronounced shoulders as do most of the diamagnetic complexes examined. Class III spectra, which include those of the Cu(II), Fe(III) and Co(III) acetylacetonates, are identical with those of Class II except for a band at higher energy which is observed only in the three compounds mentioned. These classifications are made with regard to the most intense bands appearing in the spectra. Table III lists spectral data for the strong bands of the complexes according to classes. Many weaker bands are observed in the 240–400 mμ region and are thought to be either ligand field or charge transfer bands and will be discussed in subsequent publications. Class III spectra are shown in Fig. 1. The spectrum of CrA_3 is rather unique in its complexity and cannot be included in any of the three classes; it is shown in Fig. 2.

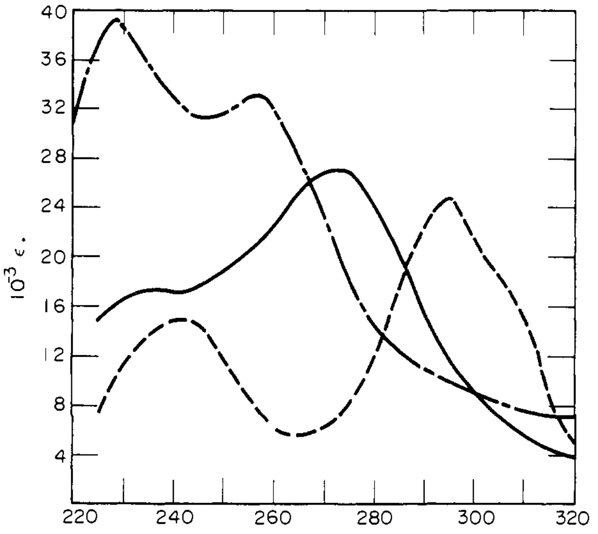

Fig. 1.—Class III spectra: ———, FeA_3 in absolute ethanol; —·—, CoA_3 in absolute ethanol; -·-·-----, CuA_2 in absolute ethanol.

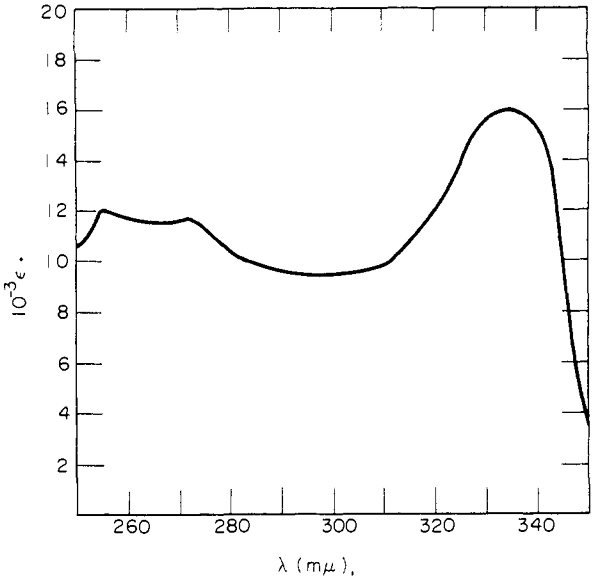

Fig. 2.—Anomalous CrA_3 spectrum in $CHCl_3$.

The predominant feature of each of the three classes of spectra is the very strong absorption band occurring usually from about 270–300 mμ with an ϵ_{max} generally > 20,000, although CoA_3 has its strongest band at 258 mμ. These strong bands are thought to be due to the same kind of transition in each case, probably a π-π* type.[21] λ_{max} for these bands is not a simple function of parameters such as size and charge of the ion completing the chelate ring. It is especially evident that there is no simple correlation between λ_{max} and ionic charge of the metal ion. Belford, *et al.*,[18] made a crude MO calculation which predicted that as the charge on the cation completing the chelate ring was increased, a red shift should be observed for the strong band under discussion. In the model used for this calculation it was assumed that this band is due to a π-π* transition, and the MOs involved were derived from linear combinations of the ligand pπ orbitals only. No mixing of the metal orbitals of π symmetry with ligand π orbitals was considered, so that the model considered was a purely electrostatic one. A red shift was observed by them upon replacing H^+ by Cu^{++}, but examination of the data in Table III shows that this correlation between the calculated and observed shifts of λ_{max} is purely fortuitous for the case considered and is most certainly not true in general.

TABLE IV

COMPARISON OF λ_{max} FOR ALKALI AND ALKALINE EARTH ACETYLACETONATES

Ions (radii[a] in parentheses)	Δ[b]
$Li^+(0.60) - Mg^{++}(0.65)$	− 700
$Na^+(.95) - Ca^{++}(0.99)$	+ 200
$Na^+(.95) - Sr^{++}(1.13)$	− 800
$K^+(1.33) - Ba^{++}(1.35)$	+ 300
Calcd. by electrostatic theory	+2800

[a] A. F. Wells, "Structural Inorganic Chemistry," Oxford, 1950, p. 70. [b] λ_{max} for alkali metal compound − λ_{max} for alkaline with compound, in $cm.^{-1}$.

To pursue this point a little further, if the predictions of an electrostatic model are to be tested, it would seem appropriate to choose a group of the most electrostatic compounds in which, to a good approximation, only the charge on the metal ion varies, π-bonding possibilities, ion size, etc., being essentially constant. The group of compounds most nearly meeting these requirements would appear to be those of the alkali and alkaline earth metals. Table IV gives the results of such a comparison, and it may be seen that the prediction of the purely electrostatic model is quite poor. Further, the facts that the octahedral tris-(acetylacetonates) of Co(III) and Sc(III) show the largest observed shifts but in opposite directions, does not suggest that the electrostatic approach is even pragmatically useful.

Although certain relationships between formation constants for acetylacetonate complexes and properties of the metal ions therein have been pointed out, there seem to be no such simple cor-

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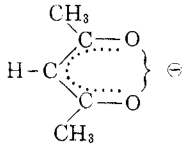
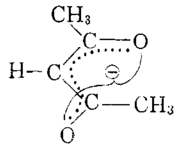
[21] Evidence supporting this assignment will be presented in a later publication.

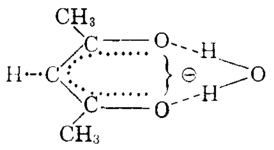
relations between λ_{max} for the strongest absorption and various characteristic parameters of the metal ions. Izatt, *et al.*,[22,23] have shown that a nearly linear correlation exists between log β_2 of the complex and the second ionization potential for divalent cations. For divalent and trivalent cations, they have shown an apparent linearity between log β_1 and the electronegativity and the second or third ionization potential. λ_{max} values reported here do not vary linearly with any of these parameters, although some trends are evident from examination of Table III. Yamasaki and Sone,[16] taking the red shift of λ_{max} from that in acetylacetone as a measure of stability, concluded that the order of stability in divalent acetylacetonates is Cu > Ni > Co > Zn > Fe, Mn, the trend being borne out by experimentally determined β_2 values.[22,24] There is no correlation between β_3[23] for certain tris-(acetylacetonates) and λ_{max}.

We believe that λ_{max} of the main absorption band is a sensitive function of a number of parameters, the most important being probably cation charge, cation size and its distortion effect on the ring π-system and the π-bonding ability of the metal ion. In most cases these effects are inseparable and lead to a near random placement of λ_{max} as can be seen from the data in Table III.

The alkali metal acetylacetonates (and BeA_2) represent the only cases where the electrostatic effect is to a very considerable extent separable from other factors, particularly the π-bonding question. In aqueous solutions a Class I band is observed, the Li, Na and K salts all giving a peak at 292 mμ, indicative of a single π-π^* transition in the free anion. Only one peak is evident, although two isomeric anionic forms are possible, roughly similar to butadiene where different electronic energies exist for the *cis* and *trans* forms.[25] Hydrogen bonding of the type below may tend to maintain the anion in the *cis* form and decrease hydrolysis. The spectra in absolute ethanol show the same nearly symmetric envelope with λ_{max} shifting to shorter wave lengths. In this medium of lower dielectric constant it is most likely that the anion and cation are intimately associated in tight ion pairs demanding the *cis* form of the anion.







By comparison of KA and CaA_2 with complexes of the first transition series, the possibility of M–O π-bonding is emphasized. No such bonding is possible with the alkali compounds and is quite unlikely with the alkaline earths, but becomes possible with the transition metals. An abrupt red shift is noted with ScA_3, λ_{max} 297 mμ, an effect probably not entirely electrostatic in origin and interpretable on the assumption of some Sc–O dπ-pπ overlap, if one chooses to adopt a free electron model for the π electrons in the chelate ring. In a conjugated system it has been amply shown that as the number of atomic centers over which electrons are delocalized increases (*i.e.*, length or circumference of "box"), λ_{max} shifts to longer wave lengths. With the complexes of the transition metals, dπ-pπ bonding increases the length of the π-electron system.

In moving across the first transition series, there is observed a decrease in λ_{max} relative to ScA_3. There are two important changes in the nature of the metal dπ orbitals through this series of ions, *viz.*, a fairly regular drop in energy and a steady filling with metal d electrons. It would seem that the former trend would tend to increase their overlap with the oxygen pπ orbitals, while the latter would decrease their ability to accept electrons. The latter trend culminates abruptly in no possibility for accepting ligand pπ electrons when Co(III) is reached. However, the variation of λ_{max} in the series Sc(III), V(III), Mn(III), Fe(III), Co(III) is not regular. We cannot suggest any simple explanation for the irregularities except possibly that in going from Fe(III) to Co(III) the dπ orbitals become completely filled, thus possibly abruptly lessening the delocalization energy.

Proceeding down in the groups Sc–Y–La, Al–Ga–In and Be–Mg–Ca–Sr–Ba one notes a steady decrease in λ_{max} in the first two cases, but an irregular change in the last case. The first case might be explainable on the basis of decreased delocalization due to the more diffuse character (and, hence, poorer overlapping ability) of 4dπ and 5dπ metal orbitals; the second case probably involves less π-bonding so that the change may be due partly to steric effects on the rings which may indirectly alter the energies of the π-orbitals. The irregularity in the last case is not readily explainable in terms of the foregoing arguments.

No mention has yet been made of the shoulder on the long wave length side of the principal band in the Class II spectra. Two possibilities immediately present themselves: (1) n-π^* transition, (2) singlet-triplet ($^1\pi$-$^3\pi^*$) transition. The n-π^* transition would involve *n* (non-bonding) electrons on the ring oxygens moving to anti-bonding MO's of the π-system. As has been pointed out by Matsen,[26] such bands have been observed in some cyclic conjugated systems as, for example, in pyridine. When a CH group in benzene is replaced by N, an additional band appears on the long wave length side of the 260 mμ band found in both compounds. Kasha[27] has attributed this absorption to an n-π^*

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transition involving the unshared pair of electrons on the nitrogen. Bands of this type are expected to be solvent dependent; solvent effects on the spectra of pyridine and diazines have been found,[28] lending support to Kasha's assignment. The shoulders observed here were most evident in the diamagnetic acetylacetonates and in CuA_2, and in these cases lay in the 300–320 mμ region. These shoulders show little or no solvent dependence either in intensity or position. However, the shoulder in the CuA_2 spectrum completely disappears when the compound is measured in a solution of 40% CH_3NH_2 in H_2O, an effect similar to that observed in the spectra of certain carbonyl compounds in aqueous solution[29] where the intensities of the $n \rightarrow \pi^*$ transitions diminish, presumably due to solvent interactions with the non-bonding electrons. In any event, solvent effects may be diminished in the acetylacetonates by partial shielding of the ring oxygens by neighboring $-CH_3$ groups so that failure to observe them does not constitute firm evidence against the n-π^* assignment.

We have no direct evidence concerning the possibility of singlet-triplet transitions of the π-electrons in the chelate ring system. Evans[30] and others have identified singlet-triplet absorption bands in benzene and other aromatic hydrocarbons by perturbing the triplet state with the inhomogeneous field of the paramagnetic oxygen molecule. In the acetylacetonates, the paramagnetic metal ion, intimately associated with the π-system, might have been expected to accomplish a similar enhancement of the intensity. In the paramagnetic complexes, except for those of Cu(II) and VO(IV), no very pronounced shoulder is present on the long wave length side of the main absorption band and a number of smaller bands are present at longer wave lengths. However, we have been unable to distinguish these bands as either $n \rightarrow \pi^*$, singlet-triplet, or, in some cases, ligand field absorptions.

Finally, we have investigated three complexes of the lower transition series, Rh(III), Pd(II), Pt(II). These spectra fit into none of the above classes and are indeed a great deal richer. The three spectra are somewhat similar, all showing their most intense band at 240–250 mμ and a less intense band at ~300 mμ. In addition other less intense bands are observed in the region 260–290 mμ.

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Chelates of Violuric Acid

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An investigation of the coördinating properties of violuric acid has indicated that the reagent forms chelates with Fe(II), Fe(III), Cu(II) and Co. From the evidence presented Co is probably trivalent. The coördinating species was indicated to be a univalent violurate ion. Chelate species of 1,3-dimethylvioluric acid were found to be identical in their visible spectra over the pH range 3–7 with those of violuric acid. The stabilities of the violurate chelates are discussed and structures are proposed for them. A colorimetric method for copper utilizing violuric acid was developed.

Introduction

Violuric acid, the 5-oxime of alloxan, is known to exist as a mixture of keto–enol tautomers (Fig. 1).[1] Morton and Tipping[2] cite its pK as 4.7 and we have substantiated this value. Welcher[3] mentions the possibility of violuric acid as an analytical reagent for chromatographic separation of cations, but does not discuss its coördinating properties. Kuster[4] discusses the reaction of ferrous iron with violuric acid and, we believe, formulates the resultant species incorrectly. Hantzsch[5] reports violurate salts but does not refer to any violurate complexes. Aside from Kuster's work, no structural formulations have been attempted regarding the metal ion–violurate products. Coördination presumably occurs through the oxime functions (either the oxime or nitroso form) since the metal ion reactions of violuric acid are quite different from those of alloxan.

Since no thorough study was indicated, the authors decided to investigate violuric acid as a coördinating reagent. Spectrophotometric and polarographic studies were employed to determine formulas, stabilities, oxidation states (in case of cobalt) and, by deduction, structures of the metal chelates.

Experimental

Materials and Apparatus. Chemicals—Violuric acid, supplied by Eastman Kodak Co. and du Pont Co., was used as furnished, as was the dimethylurea and ethyl malonate used in the synthesis of 1,3-dimethylvioluric acid. Solutions of the metal ions, all sulfates, were prepared from recrystallized salts. Iron and copper solutions were standardized titrimetrically by the dichromate and thiosulfate methods, respectively. Cobalt solutions were standardized by the perborate method, with subsequent titration with thiosulfate.[6] All other chemicals were J. T. Baker analyzed reagents.

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