Acknowledgments.—We wish to thank Professors Carl Ballhausen and Harry Gray for a preprint of their paper and for permission to reproduce their energy level diagram. In addition, we are grateful to Professor Gray, and to Professors George Fraenkel and Richard Carlin, for many helpful discussions.

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Crystal Spectra of Some Trisacetylacetonates

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Polarized visible spectra of single crystals of aluminum acetylacetonate with part of the Al isomorphously replaced by the trivalent ions of Ti, V, Mn, and Fe are reported. The electronic energy levels are assigned, and interpretations of the spectral intensities and estimates of octahedral and trigonal field strengths are presented. The trigonal field parameter K varies between $+600$ and -900 cm.$^{-1}$, with an anomalous value for the vanadium compound. The question of π-bonding in these molecules is discussed briefly.

The spectra of the readily available trivalent iron series ions in the trigonal crystal $NaMgAl(C_2O_4)_3 \cdot 9H_2O$ have been reported.[1] Polarized spectra of these materials allowed us to assign the observed electronic transitions as well as to estimate the trigonal field parameter, K. Continuation of this work led to our recent reports on the crystal spectra of cobalt[2] and chromium[3] trisacetylacetonates in the diluent crystal, aluminum acetylacetonate. In this paper we report the crystal spectra of the remaining trisacetylacetonates of the first-row elements. We shall find it useful to refer to Barnum,[4] who has measured the solution spectra of the first-row transition metal acetylacetonates and has presented a molecular orbital treatment of the metal–ligand π-orbitals.

Experimental

Preparations.—The metal(III) acetylacetonates [to be abbreviated $M(acac)_3$] were prepared by standard methods.[5] The concentration of iron in reagent grade chemicals was found to be high enough to cause a distinct coloration of the aluminum compound. Therefore, ferric iron was removed from all metal salts before preparation of the corresponding acetylacetonate. This was accomplished by adjusting a solution of the salt to pH 1, and then extracting with a 1:1 solution of acetylacetone–chloroform several times.[6] Pure products were more readily obtained if freshly distilled acetylacetone was used. No precautions were taken in the synthesis of the air-sensitive titanium compound. A commercially available 20% aqueous solution of titanium trichloride was added to a solution of acetylacetone, previously neutralized with aqueous ammonia. The insoluble blue material was filtered in air, washed, and sublimed *in vacuo* at 150° for purification. Brown vanadium(III) acetylacetonate is best separated from the blue-green vanadyl compound by extraction with ether. It was noted that some of the acetylacetonates, particularly those of iron and manganese, slowly decompose in air; the decomposition is presumably photochemical.

Growth of Large Single Crystals.—Crystals of the acetylacetonates were easily obtained by evaporation of an acetone solution in an open dish. Pure crystals as well as dilute crystals, where the desired metal acetylacetonate isomorphously replaced part of the colorless aluminum acetylacetonate, were obtained in this manner. Although the ferric acetylacetonate belongs to a crystal system different from that of the aluminum compound, it readily enters the host lattice in small concentrations. Crystals of titanium and vanadium acetylacetonates, each of which is unstable to air, were grown from a supersaturated methanol solution. The desired solution was made up at room temperature in a nitrogen atmosphere, and then was placed in a 4° cold room to allow crystallization. The dilute titanium crystals slowly decompose in air. Decomposition of the blue crystals to a yellow product is noticeable after several weeks. It is interesting that the decomposition proceeds more rapidly along the b-axis of the crystal than perpendicular to it; the boundary between the blue Ti(III) and oxidized product moved perpendicular to the 110 faces. The dilute vanadium crystals are stable in air in the dark indefinitely, unlike the pure crystals.

Spectra.—All crystal spectra were obtained with a Cary Model 14 spectrophotometer. A standard double-walled silvered glass dewar served for obtaining the spectra at liquid nitrogen temperature (77°K). A Nicol prism was used to polarize the light. Solution spectra of titanium acetylacetonate were obtained by subliming a sample into an evacuated cell attached to a vacuum line; solvent then was distilled into the cell.

Analysis of the Spectra.—For the most part the spectra were taken with light incident on the (001) face and polarized with respect to the monoclinic b-axis.[7] This face is the prominent one of the pseudo-hexagonal plates. The b-axis is readily identified by the triangular etch-pits pointing normal to it, and the C_{2h} symmetry of the crystal. Since the molecular pseudo-trigonal axes are inclined by ±31° to the b-axis, the crystal spectra had to be analyzed to obtain spectra presumed characteristic of the oriented gaseous molecule. We have already considered this problem.[2] However, to avoid confusion, since the equations previously presented are not strictly correct except for small absorbance, we provide the equations used in this paper, which are

$$a_\pi = +1.368a_\parallel - 0.368a_\perp$$
$$a_\sigma = -0.020a_\parallel + 1.020a_\perp$$

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[1] T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, **35**, 1809 (1961).
[2] T. S. Piper, *ibid.*, **35**, 1240 (1961).
[3] T. S. Piper and R. L. Carlin, *ibid.*, **36**, 3330 (1961).
[4] D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 183, 221 (1961).
[5] W. C. Fernelius and B. E. Bryant, *Inorg. Syn.*, **5**, 105 (1957).
[6] J. P. McKaveny and H. Freiser, *Anal. Chem.*, **29**, 290 (1952).
[7] W. T. Astbury, *Proc. Roy. Soc.* (London), **A112**, 448 (1926)

In these equations a is the absorbance, $\log I_0/I$, $\|$ and $\perp$ refer to the polarizations with respect to the b-axis, while π ($\|$) and σ ($\perp$) refer to the polarizations with respect to the molecular axis. It may be seen that the σ and $\perp$ spectra are the same to a very good approximation. For analysis of the (100) spectrum see the earlier paper.[2] The decadic extinction coefficients ϵ are in units of l./mole-cm.

Results and Discussion

Since these trisacetylacetonates are comprised of six-membered chelate rings, it might be expected that distortions from an octahedral field about the metal ion would be small. There is, however, no reliable information which supports this hypothesis. The work of Singer[8a] and Jarrett[8b] suggested that there are indeed axial fields present in these compounds, and the visible spectra we report here confirm these results.

We shall discuss the spectrum of each of the compounds in turn. The assignments are generally less certain than those we have made for the oxalato complexes. This is because we have been able to observe only a few spin-forbidden transitions, and no higher energy d–d bands which tend to overlap with the charge transfer and the π–π^* bands.

Titanium.—The spectrum in ethanol solution[4] shows a band at 16,900 cm.$^{-1}$ (ϵ = 1520). Our solution spectra in CCl_4 show distinct shoulders at about 15,400 and 18,200 cm.$^{-1}$. The near-infrared was investigated to 5000 cm.$^{-1}$ without finding any further d–d transitions. In the crystal further resolution was detected; see Fig. 1. The maxima and shoulders at 15,400, 16,700, 18,200, 20,000, and 22,000 cm.$^{-1}$ suggest a vibrational progression with spacings of about 1500 cm.$^{-1}$. Upon analysis into the σ and π components it is found that less than 10% of the band intensity is in the π component.

The ground octahedral state[9] of Ti(III) is $^2T_2$; in a trigonal field this will be split into $^2A_1$ and ^2E_a components. Jarrett,[8b] on the basis of powder electron spin resonance spectra, suggested a $^2A_1$ ground state and a trigonal splitting of 13,000 cm.$^{-1}$. Recently, McGarvey[10] studied the e.s.r. spectra of our dilute single crystals; he confirmed the ground state assignment but also showed that a ground state splitting of 2000 to 4000 cm.$^{-1}$ could account for the g-values.

Our crystal spectra are consistent with McGarvey's findings, in that the $^2E_b \leftarrow {}^2A_1$ transition should be σ-polarized. Taking into account the ground state splitting, Dq is then about 1300–1400 cm.$^{-1}$. The further splittings of the excited state must be vibronic in origin, at least in part, since Jahn–Teller splittings can give at best only two levels. The spacing of 1500 cm.$^{-1}$ suggests that the carbon–oxygen stretch may be excited. The weak lines at 25,010, 25,640, and 26,320 cm.$^{-1}$ are π-polarized. The corresponding shoulder in the solution spectrum has been assigned to a $\pi_4 \leftarrow t_2$ transition, where π_4 is an excited level of the metal–ligand π-system.[4] The π_4 level gives rise to A_1 and E components. Transitions to A_1 are forbidden in the trigonal field and those to E should be σ-polarized. Thus the observed polarization rules out this assignment. At present the most likely assignment appears to be a $\pi_4 \leftarrow \pi_3$ or $\pi_4 \leftarrow$ n transition which would be spin-forbidden in the free ligand but is allowed in the complex by interaction with the metal states.

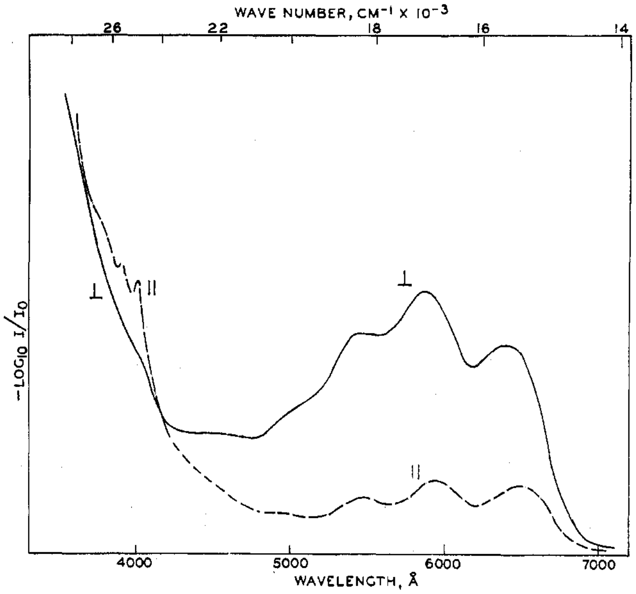

Fig. 1.—Crystal spectrum of (Al,Ti)(acac)$_3$ at 77°K. with light incident on the (001) face.

Vanadium.—The octahedral ground state $^3T_1$ will be split in a trigonal field into $^3A_2$ and ^3E components. The solution spectrum[4] shows no maxima but rather shoulders at 18,200 and 21,700 cm.$^{-1}$, of which the lowest energy transition most probably is assigned to the excited state, $^3T_2$. The crystal spectra are rather similar and provide little improvement in the resolution of these bands. The polarization of the ultraviolet tail is similar to that of the trisoxalate[1] since it is considerably stronger in the σ-polarization. At 77°K. the low energy shoulders appear at 17,500 ($\|$) and 18,800 cm.$^{-1}$ ($\perp$). This again is similar to the oxalate and consistent with a trigonal splitting constant K of negative sign. Thus the ground state is probably $^3A_2$. These data require a Dq of about 1800 cm.$^{-1}$. A search in the near-infrared on a concentrated crystal failed to reveal the singlet levels expected in the 10,000 cm.$^{-1}$ region. The magnetic susceptibility[11] is also consistent only with a $^3A_2$ ground state.

Manganese.—The visible spectrum of Mn(acac)$_3$ in solution[4] shows a shoulder at 18,200 cm.$^{-1}$ on a general absorption which increases in intensity with increasing energy. The transition responsible for the shoulder is undoubtedly $^5T_2 \leftarrow {}^5E$. The transition $^3T_1 \leftarrow {}^5E$ occurs as a broad band[4] at 8900 cm.$^{-1}$. We estimate that the oscillator strength is about 1.2×10^{-3}, a surprisingly large value for a spin-forbidden transition.

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[8] (a) L. S. Singer, *J. Chem. Phys.*, **23**, 379 (1955); (b) H. S. Jarrett, *ibid.*, **27**, 1298 (1957).

[9] The room temperature magnetic moment of Ti(acac)$_3$ is 1.68 B.M. We thank Dr. J. G. Verkade for this measurement.

[10] B. R. McGarvey, to be published. We thank Dr. McGarvey for letting us see his results before publication.

[11] B. N. Figgis, J. Lewis, and F. Mabbs, *J. Chem. Soc.*, 2480 (1960).

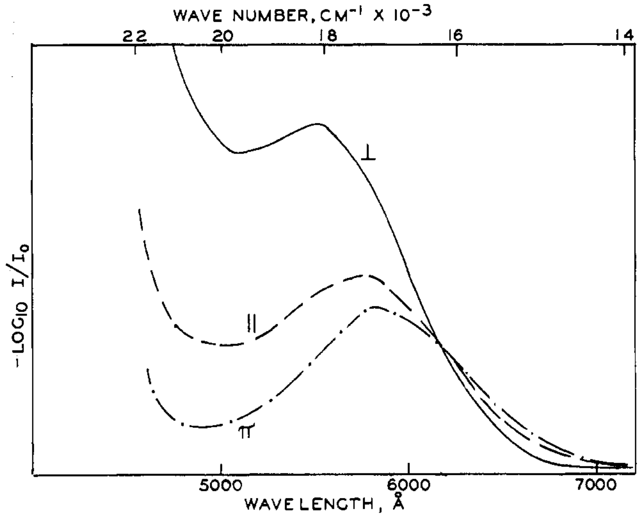

Fig. 2.—Crystal spectrum of (Al,Mn)(acac)$_3$ at 77°K. with light incident on the (001) face. The ϵ_{max} of the parallel component is about 120.

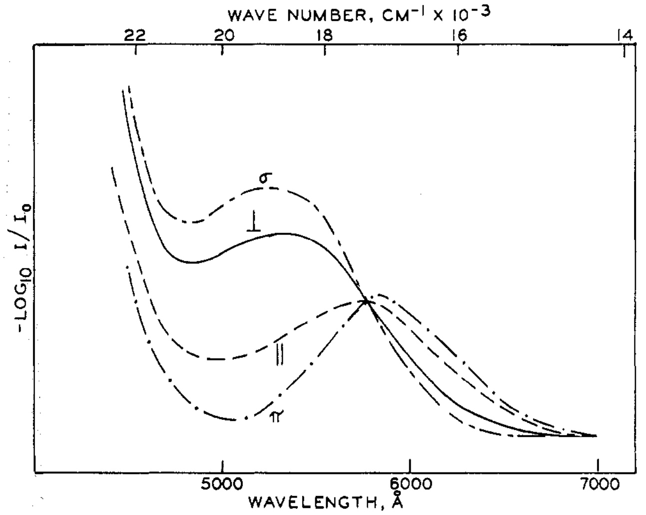

Fig. 3.—Crystal spectrum of (Al,Mn)(acac)$_3$ at 77°K. with light incident on the (100) face.

In the crystal at 77°K. the spin-allowed band sharpens up considerably; see Fig. 2 and 3. Unlike the case of Co(acac)$_3$ the σ-spectra calculated from the (001) and (100) spectra are not in complete agreement. The π-spectra agree; both have maxima at 17,200 cm.$^{-1}$. However the σ-components have quite different band shapes and the maxima occur at 19,000 cm.$^{-1}$ in the (100) spectrum and 18,200 cm.$^{-1}$ in the (001) spectrum. We cannot ascribe the large discrepancy to rhombic fields of the monoclinic crystal, since if these fields were large the cobalt spectrum also would be expected to be affected. The likely explanation is a distortion of the molecule from trigonal symmetry as required by the Jahn–Teller theorem. Such distortions of E ground states are known to be very substantial. Despite the large rhombic fields it seems safe to say that the trigonal field constant K is positive and of the order of magnitude of 300–600 cm.$^{-1}$.

The enormous intensity of the spin-forbidden transition (about 10^5 times greater than most such bands) and the general absorption (brown color) indicate to us an almost complete mixing of all the triplet and quintet levels in this region by spin-orbit coupling, rhombic fields, and molecular orbital formation.

Iron.—The solution spectrum of Fe(acac)$_3$ shows four bands in the visible and near-infrared regions which can be classified into two groups on the basis of intensities. A 1.12 M acetone solution of Fe(acac)$_3$ with a 5-cm. path was required in order to measure the transitions in the infrared. The first broad band, at 9760 cm.$^{-1}$, has an extinction coefficient of 0.45 and $f = 5.2 \times 10^{-6}$. The next band, at 13,160 cm.$^{-1}$ (after subtracting out the tail of the visible band), has $\epsilon = 0.70$ and $f = 6.4 \times 10^{-6}$. These bands, caused by transitions from a sextet ground state to the first excited quartet states, are spin-forbidden and have the expected small intensities.

The infrared bands are strongly polarized in the crystal. The pure orthorhombic crystal at 77°K. displays absorption at 9300 and 12,940 cm.$^{-1}$ (these are, respectively, the transitions to $^4T_1$ and $^4T_2$). In the mixed monoclinic (Al,Fe)(acac)$_3$, the π-spectrum shows negligible absorption at 77°K. in this region, while σ-polarization yields broad bands at 10,000 ($\Delta\nu$ = 1700 cm.$^{-1}$) and 12,820 ($\Delta\nu$ = 1300 cm.$^{-1}$) cm.$^{-1}$. These polarizations are like those in the oxalate system and therefore confirm that the field is trigonal to a good approximation.

Turning to the more intense bands, an acetone solution has absorption bands at 23,120 and 28,410 cm.$^{-1}$ with extinction coefficients of 3250 and 3420, respectively. Barnum assigns the higher energy band to a $\pi_4 \leftarrow$ d transition. In the crystal at 77°K. the lower energy band is found at 22,000 (σ) and 22,700 cm.$^{-1}$ (π) with a half-width of 6700 cm.$^{-1}$; it is about four times as intense in the σ-polarization as in the π-polarization. This band occurs at a wave number appropriate for a transition to the $^4A_1$ and ^4E levels. However, these transitions of, for example, hydrated manganous ion and Fe(C$_2$O$_4$)$_3^{3-}$ are sharp peaks of small intensity. Perhaps these levels are strongly mixed with nearby ligand π-levels. Most probably, however, the d–d transitions are obscured by strong transitions involving the ligand π-orbitals. Taking the band maxima of the solution spectrum and assuming that the transitions to $^4A_1$ and ^4E are near to if not exactly at the first intense band we calculate that $Dq = 1640$, $B = 530$, and $C = 3570$ cm.$^{-1}$. The Racah parameters B and C are lowered from the free-ion values by, respectively, 50 and 25%. This indicates a large delocalization of the metal electron density.

Conclusions

The investigation of the crystal spectra of the acetylacetonates has not been nearly as fruitful as our work on the trisoxalates.[1] The very intense ultraviolet transitions have made it impossible to study the high energy d–d transitions. Furthermore, it is clear that there is considerable mixing of the metal and ligand orbitals, presumably *via* these low lying ligand π-levels. This is indicated by the anomalous intensities of "spin-forbidden" transitions, the rather general absorption noted for some of the metals, and finally the rather large trigonal splittings. Evidence from spin-forbidden transitions of $Cr(acac)_3$ for considerably increased d_π–ligand π-interaction in the acetylacetonates over the oxalates already has been presented.[3]

In Table I we present a comparison of the crystal field parameters found in this work with earlier results. There are the usual trends of Dq with one striking exception—the rather low value of $Ti(acac)_3$. We can find no sensible explanation for this. The signs of the K values are all positive with the exception of vanadium, which shows here the same anomalous behavior as in the oxalate. Perhaps the source of this anomaly lies in the fact that we have used the approximation of neglecting off-diagonal trigonal field matrix elements. Alteration of the sign of the trigonal field parameter was not observed for metal ions in corundum.[12]

TABLE I

CRYSTAL FIELD PARAMETERS, CM.$^{-1}$

		Dq		K	
	$M(H_2O)_6^{3+}$	$M(C_2O_4)_3^{3-}$	$M(acac)_3$	$M(C_2O_4)_3^{3-}$	$M(acac)_3$
Ti	2030	<2400	1300–1400	>0	$+700$–1500
V	1800	1700	1800	-230	~ -900
Cr	1760	1770	1810	$+270$	$+500$
Mn	2100	1700	~ 1700	$+500$	$\sim +500$
Fe	1400	1500	~ 1640	...	...
Co	1910	~ 2000	~ 2100	-100	$+600$

Acknowledgment.—We wish to thank Mr. Mark L. Miller (University of Illinois) for remeasuring the crystal spectra of the titanium and manganese acetylacetonates. This work was supported at the University of Illinois by a grant and a coöperative fellowship (R. L. C.) from the National Science Foundation and at Brown University by a grant from the National Science Foundation and by the Materials Science Center.

[12] D. S. McClure, *J. Chem. Phys.*, **36**, 2757 (1962).

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Reaction of Metal Carbonyls with β-Diketones to Produce β-Ketoenol Complexes[1a]

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It is reported that some β-ketoenol complexes of transition metals can be prepared by refluxing the metal carbonyl in the neat β-diketone. Examples reported here are $Mo(C_5H_7O_2)_3$, $Mo(C_5H_4F_3O_2)_3$, $Cr(C_5H_7O_2)_3$, $Cr(C_5H_4F_3O_2)_3$, and $Fe(C_5H_7O_2)_3$. The molybdenum compounds are the first reported β-ketoenol complexes of Mo(III) and are described in some detail. Tris-(trifluoroacetylacetonato)-chromium(III) is also a new compound and is described adequately.

Introduction

It already has been shown in several instances that metal carbonyls can be used in synthesis as, effectively, sources of reactive, zero-valent metals. Thus, to choose two examples which happen to be familiar to the authors, metal carbonyls react with the weak acid cyclopentadiene to give π-cyclopentadienyl compounds[2] and $Mo(CO)_6$ reacts with carboxylic acids to give Mo^{II} carboxylates.[3] This paper reports a study of the feasibility of the reaction of metal carbonyls with β-diketones as a preparative method for metal β-ketoenolates. The genesis of this study was the observation by Dr. F. Calderazzo, in this Laboratory, that $Mo(CO)_6$ reacts with refluxing 2,4-pentanedione to give a brown, air-sensitive, crystalline substance which shows no infrared absorption in the range (2200–1700 cm.$^{-1}$) characteristic of the Mo–CO group. The present authors have shown that Calderazzo's compound is Mo^{III} acetylacetonate, a hitherto unknown substance, and subsequently have investigated the reactions of other metal carbonyls with acetylacetone and other β-diketones. This work has resulted in the preparation and characterization of several new compounds as well as the discovery of new methods for preparing some previously known compounds. In this paper we describe several reactions which are quite straightforward. Further studies of the scope and mechanism of the reaction have been made and are continuing; these will be the subject of a later report. We also describe here the characterization of two Mo(III) tris-β-ketoenol complexes which are the first such compounds of Mo(III) to be characterized and a new β-diketone complex of Cr(III).

Results and Discussion

In this paper we report the preparation of the five compounds: $Mo(C_5H_7O_2)_3$, $Mo(C_5H_4F_3O_2)_3$, $Cr(C_5H_7O_2)_3$, $Cr(C_5H_4F_3O_2)_3$, and $Fe(C_5H_7O_2)_3$, where $C_5H_7O_2^-$ is the enol anion of pentane-2,4-dione and $C_5H_4F_3O_2^-$ is the enol anion of 1,1,1-trifluoropentane-2,4-dione. All of these compounds can be prepared rather easily and in good yield by refluxing a mixture of the appropriate mononuclear

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[1] (a) Supported by the National Science Foundation; (b) Fellow of the Alfred P. Sloan Foundation.

[2] G. Wilkinson, *J. Am. Chem. Soc.*, **76**, 209 (1954).

[3] E. Bannister and G. Wilkinson, *Chem. Ind.* (London), 319 (1962).