lato oxygen is involved at least once; the sodium to oxalato oxygen distances vary a good deal, but are definitely shorter on the average where uncomplexed oxygen is involved.

An oxygen atom, O_I, of a water molecule lying on a twofold axis has $2Na_I^+$ as closest neighbors at 2.41 Å.; O_I has also as near neighbors $2O_3$ at 3.02 Å., $2O_{II}$ at 3.07 Å., to give an electrostatically satisfactory array which nowhere provides the geometry required for strong localized hydrogen bonding. Eight other atoms, six oxygen and two carbon, are 3.25–3.45 Å. distant from O_I. An oxygen atom, O_{II}, of a water molecule in the general position has as near neighbors Na_1^+ at 2.44 Å., Na_3^+ at 2.53 Å., O_8 at 2.84 Å. (the one recognizable case of hydrogen bonding), O_I at 3.07 Å., O_6 at 3.11 Å., O_4 at 3.23 Å., and C_4 at 3.39 Å.

Water molecules occur as useful dielectric filler in a crystalline framework which is determined and stabilized primarily by direct interactions of sodium ions with oxalato oxygen. The pattern of these interactions is so complicated, their magnitude so large, that the observed deformation of the complex anion from $\bar{4}2m$ symmetry, limited as this is to the inner coördination group, is rather surprisingly modest.

It is asserted in HS[3] that the stereoisomeric type established for $Zr(C_2O_4)_4^{-4}$ enjoys particularly high *a priori* probability for tetrakisbidentate complexes because it is uniquely well suited to minimize the internal coulombic repulsions corresponding to any plausible distribution of the net charge. Taking $Zr(C_2O_4)_4^{-4}$ as a typical example we can see how this conclusion follows from a qualitative but convincing analysis. The resultant charge is taken to be evenly divided among the eight peripheral oxygen atoms, $4O_A^e$ and $4O_B^e$ in Fig. 2, as the most plausible assumption where the computed coulombic repulsive energy for the isolated anion necessarily runs to several hundred kcal./mole. (Interaction with sodium ions in the crystal might well modify this charge distribution, *e.g.*, to put some net charge on complexed oxygen atoms, but the following analysis would need only elaboration of detail.) We consider the coulombic repulsions in categories, those involving O_A^e–O_A^e, O_B^e–O_B^e, and O_A^e–O_B^e interactions, respectively. The tetrahedral shape (somewhat flattened along $\bar{4}$) of $Zr(C_2O_4)_4^{-4}$ immediately ensures near minimum values for O_A^e–O_A^e and O_B^e–O_B^e repulsions, at least as favorable as for any of the eight competing stereoisomeric types. It is, nevertheless, the O_A^e–O_B^e repulsions (twelve in number when only those between different oxalato groups are counted) which provide the really decisive margin in favor of the observed stereoisomeric type. The symmetry of $\bar{4}2m$ requires the O_A^e and O_B^e atoms to lie, respectively, in mutually perpendicular planes, a condition which automatically ensures uniformly large O_A^e–O_B^e separations. The antiprismatic "pinwheel" stereoisomer[3] *llll*, of D_4-422 symmetry, and the dodecahedral "bisphenoidal" stereoisomer,[3] *gggg*, of S_4-$\bar{4}$ symmetry, still in competition on the basis of just O_A^e–O_A^e and O_B^e–O_B^e interactions, fail badly by comparison with the observed stereoisomer in minimizing O_A^e–O_B^e repulsions.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
COLUMBIA UNIVERSITY, NEW YORK 27, NEW YORK

Solvent Effects on the Optical and Electron Spin Resonance Spectra of Vanadyl Acetylacetonate[1]

BY IVAN BERNAL[2] AND PHILIP H. RIEGER[3]

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The positions of certain bands in the optical absorption spectrum, as well as the vanadium nuclear hyperfine splitting constant in the electron spin resonance (e.s.r.) spectrum, of vanadyl acetylacetonate are found to be sensitive to changes in the solvent. The solvent effects on the optical spectrum are in good agreement with molecular orbital predictions of Ballhausen and Gray for the vanadyl ion. The optical data may be used to calculate *g*-values in good agreement with the e.s.r. results. A qualitative study of line widths in the e.s.r. spectra shows that the anisotropy of the nuclear hyperfine interaction tensor also varies with changes in solvent.

Introduction

The vanadyl ion, VO^{+2}, is the most common of the transition metal oxy-cations, and is of interest because of its relatively simple magnetic and spectral properties. It contains only one 3d electron and has a very strong and dominant axial field which is well characterized structurally.[4] As a result, it has been used to test crystal-field[5] and molecular-orbital (MO) theory[6] calculations. In addition, isotopic purity and high nuclear spin make the ion particularly attractive for testing theories of certain types of relaxation processes

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(1) Supported in part by the U. S. Air Force through the Office of Scientific Research.

(2) Socony Mobil Fellow, 1961–1962; David Sarnoff Fellow, 1959–1961.

(3) National Science Foundation Cooperative Fellow, 1959–1961.

(4) R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961).

(5) C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 73 (1957).

(6) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

in electron spin resonance (e.s.r.) spectroscopy.[7]

This paper reports an investigation of the effect of the solvent on the e.s.r. and optical spectra of vanadyl acetylacetonate, $VO(acac)_2$. This substance is stable and soluble in a large number of non-aqueous solvents without exchange of ligands, making it a convenient compound for our studies. The composition and structure are well established[4]: the two acetylacetone ligands lie flat in the equatorial plane and provide four oxygen ligands to the V^{+4} ion. The fifth ligand is the vanadyl oxygen, which is expected to dominate the electrostatic interactions between the central ion and the ligands by virtue of its close approach to the vanadium. The sixth position, *trans* to the vanadyl oxygen, is open and may be coördinated by solvent molecules. Thus, changes in the solvent may be expected to perturb the axially oriented molecular orbitals. The fashion in which these perturbations will manifest themselves in the optical and magnetic behavior of the complex can be predicted from the nature of the energy levels derived by Ballhausen and Gray[6] in their MO treatment of the vanadyl ion.

Experimental

Vanadyl acetylacetonate was prepared as described in the literature.[8] The solvents were of spectroscopic grade and were used without purification except in the case of pyridine and nitrobenzene, which were distilled immediately before use. The optical spectra were obtained using a Cary Model 14-M spectrophotometer. The e.s.r. measurements were made with an X-band spectrometer described elsewhere.[9] The solutions used for both the optical and e.s.r. measurements were 0.01 *M* in $VO(acac)_2$.

The optical absorption spectra of $VO(acac)_2$ in benzene and in pyridine, shown in Fig. 1, illustrate the effect of the solvent on the positions of the bands. The results of the other optical measurements are summarized in Table I. The optical absorption spectrum of $VO(acac)_2$ has been studied previously by Feltham[10] in methanol, pyridine, and chloroform, with results in good agreement with those reported here.

The e.s.r. spectra of $VO(acac)_2$ in benzene, acetone, methanol, and pyridine, shown in Fig. 2, display a marked effect of the solvent on the line widths. In addition, large shifts in the vanadium nuclear hyperfine splitting constant are observed on changing the solvent. The spectroscopic splitting factors (*g*-values) and nuclear hyperfine splitting constants obtained from the e.s.r. measurements are summarized in Table II. Figure 3 shows the variation of hyperfine component line width as a function of the nuclear spin quantum number, m_I, for $VO(acac)_2$ in methanol, acetonitrile, pyridine, and nitrobenzene. The line widths in acetone and benzene are qualitatively similar, respectively, to the widths in methanol and acetonitrile.

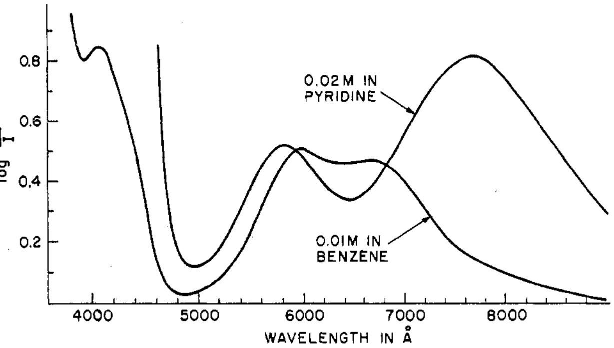

Fig. 1.—Optical absorption spectra of $VO(acac)_2$ in benzene and in pyridine. Note the shift in the $b_2 \rightarrow e\pi^*$ transition.

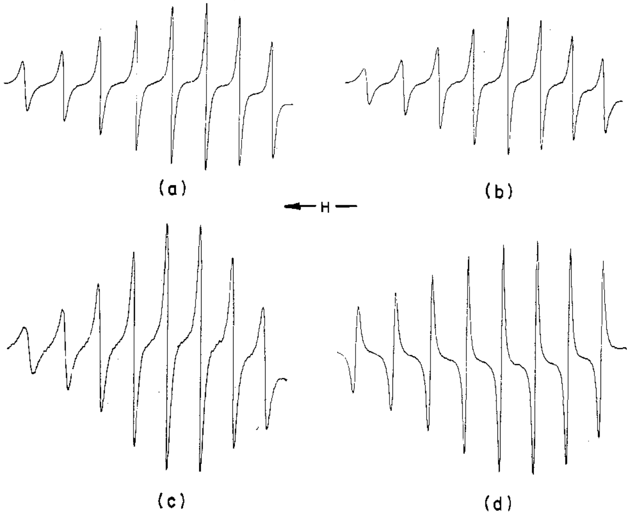

Fig. 2.—E.s.r. spectra of $VO(acac)_2$ in (a) benzene; (b) methanol; (c) pyridine; and (d) acetone.

TABLE I

SOLVENT EFFECT ON OPTICAL SPECTRUM OF $VO(acac)_2$

Solvent	Position of bands (extinction coefficient) $Cm.^{-1}$	$Cm.^{-1}$	$Cm.^{-1}$
Methanol	12,820 (40)	17,240 (16)	25,640 (91)
Pyridine	13,020 (41)	17,240 (27)	. . .
Acetone	14,280 (51)	16,660 (42)	25,570 (100)
Acetonitrile	14,280 (48)	16,660 (38)	25,570 (88)
Nitrobenzene	14,710 (48)	16,660 (45)	. . .
Benzene	15,150 (54)	16,780 (58)	25,320 (100)

TABLE II

E.S.R. DATA AND *g*-VALUES CALCULATED FROM OPTICAL MEASUREMENTS

Solvent	$<g>$ (measd.)[a]	$<A>$ (gauss)[b]	$g_{\parallel}$ (calcd.)[c]	$g_{\perp}$ (calcd.)[d]	$<g>$ (calcd.)[e]
Methanol	1.968	102.3	1.944	1.983	1.970
Pyridine	1.971	103.6[f]	1.944	1.983	1.970
Acetone	1.968	106.0	1.942	1.984	1.970
Acetonitrile	1.969	105.3	1.942	1.984	1.970
Nitrobenzene	1.972	104.6[f]	1.942	1.985	1.971
Benzene	1.970	108.0	1.942	1.985	1.971

[a] ±0.001. [b] ±0.1 unless otherwise noted. [c] Calculated from optical data in Table I using eq. 2. [d] Calculated from optical data in Table I using eq. 1. [e] Average *g*-value calculated using eq. 3. [f] ±0.6.

Discussion

Crystal field theory predictions[5] for the vanadyl ion have been found to give a suitable qualitative description of the energy level scheme found from optical data; however, the value of the parameter $10Dq$ predicted from the purely electrostatic model is too small, while the values of the parameters Ds and Dt are too large. (See reference 6 for a discussion of these aspects of the electrostatic approach.) The semi-empirical molecular orbital approach of Ballhausen and Gray[6] for the hydrated vanadyl ion produces an energy level scheme which reproduces the

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(7) R. N. Rogers and G. E. Pake, *J. Chem. Phys.*, **33**, 1107 (1960).

(8) R. A. Rowe and M. M. Jones, *Inorg. Syn.*, **5**, 115 (1957).

(9) J. M. Hirshon and G. K. Fraenkel, *Rev. Sci. Instr.*, **26**, 34 (1955).

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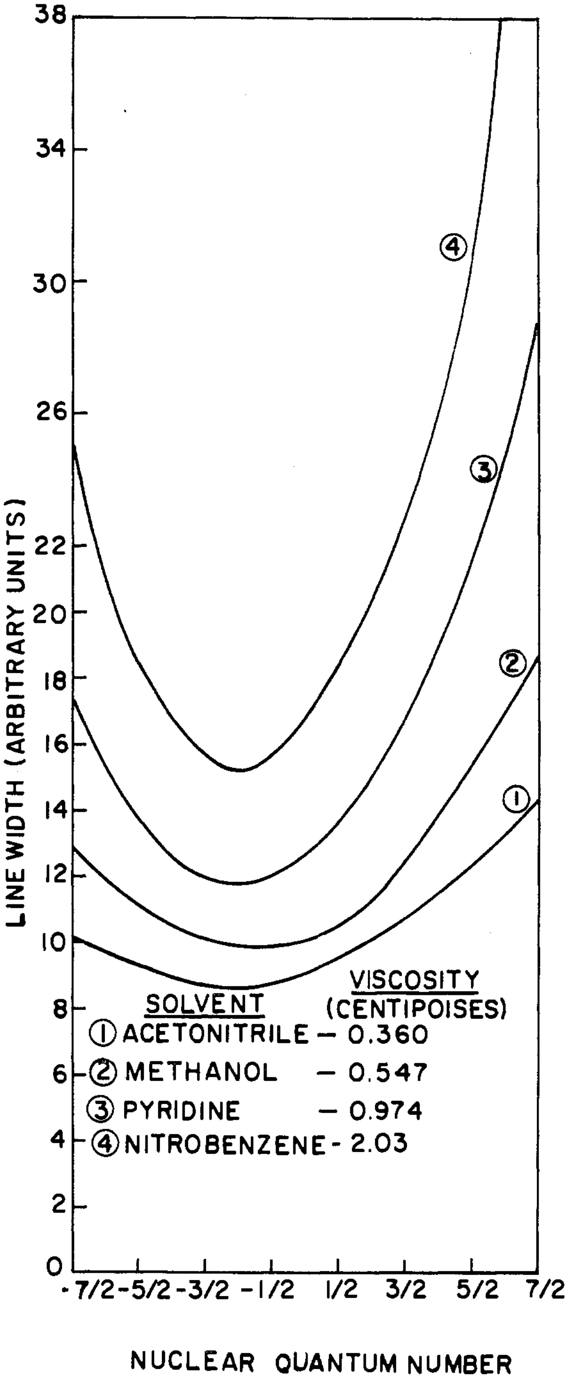

Fig. 3.—Variation of line width in VO(acac)$_2$ solutions. The viscosities (20°) were taken from the Handbook of Physics and Chemistry, 42nd Ed., p. 2197.

order of the levels predicted from crystal field considerations; in addition, it gives remarkably good agreement with a variety of experimental data. The present experiments should allow further tests of the MO approach since the two sets of data to be compared were obtained under the same conditions. The e.s.r. g-values should be calculable from the optical absorption data. In addition, shifts in the positions of the optical bands with changes in solvent provide qualitative tests of the assignment of the energy level scheme.

The energy level diagram of Ballhausen and Gray[6] for the hydrated vanadyl ion is given in Fig. 4. The ground state of the ion is $^2B_2$. We will assume that the bonding of the acetylacetonate oxygen ligands to the central vanadium ion is not significantly different from that of the four equatorial oxygens in the hydrated ion, and that the vanadium-oxygen multiple bond is effectively the same in both cases. Under these circumstances the properties of the molecule should depend critically on the nature of the solvent, because the sixth position of the vanadyl ion is sterically unhindered, and the ion can be perturbed strongly in this direction. In the MO treatment of the vanadyl problem,[6] it is postulated that the most important interaction of the V^{+4} ion is with the axial oxygen; therefore, any perturbation of the ion in the axial direction should have a marked effect on bands in the optical spectrum which involve transitions to or from orbitals with axial character. In addition, small changes in the g-value anisotropy might be expected.

The first transition in the optical spectrum, according to the MO level scheme shown in Fig. 4, is $^2B_2 \rightarrow {}^2E(I)$. The b_2 level is presumed to be an almost pure vanadium $3d_{xy}$ orbital, while the $e\pi^*$ orbital is made up of a linear combination of vanadium $3d_{xz}$ and $3d_{yz}$ orbitals with oxygen $2p_x$ and $2p_y$ orbitals. Thus the energy of the level should be sensitive to any perturbation that changes the axial compression in the VO bond. Indeed, a strong axial perturbation would be expected to reduce the V–O interaction, thus lowering the $e\pi^*$ level with respect to b_2. The optical data, summarized in Table I, show that the first band shifts approximately 2400 cm.$^{-1}$ to lower energies on changing the solvent from benzene to methanol.

The second transition is to the b_1^* level, which is made up of a linear combination of the $3d_{x^2-y^2}$ metal orbital and ligand orbitals concentrated in the equatorial plane. An axially directed solvent perturbation should, therefore, affect this transition only indirectly. The position of the second band is found to remain virtually unchanged except for a small shift to longer wave lengths on changing the solvent from methanol and pyridine to less polar media. This shift probably is due to a second-order effect associated with the large shifts caused by the axial perturbation.

The third band in the optical spectrum of VO(acac)$_2$ has a well defined maximum in most of the solvents, although it is at most 100 cm.$^{-1}$ from the very intense first charge transfer band, and is not seen at all in pyridine and nitrobenzene. The band probably arises from the transition $^2B_2 \rightarrow {}^2A_1$. Consequently, since, in the MO theory of Ballhausen and Gray,[6] the third vacant orbital represented by Ia_1^* involves an admixture of the metal $3d_{z^2}$ orbital with the metal 4s and ligand orbitals, one might expect to observe shifts in the band position with changes in the solvent. A small shift to higher energies on changing the solvent from benzene to methanol is observed experimentally, but, since this band is overlapped by the charge-transfer band, its position cannot be measured accurately. It is clear, however, that the shift is not as large as that observed for the first band. The reason for this behavior is not clear to us.

Spin-orbit admixture of the first two excited states with the ground state gives rise to g-value anisotropy, and Ballhausen and Gray[6] find that the components of the g-tensor are given by

$$g_{\perp} = 2\left[1 - \frac{(c_1^*)^2\xi}{E(^2B_2 \longrightarrow {}^2E(I))}\right] \quad (1)$$

$$g_{\parallel} = 2\left[1 - \frac{(c_1^*)^2 4\xi}{E(^2B_2 \longrightarrow {}^2B_1)}\right] \quad (2)$$

where the c_1^* are 0.907 and 0.946 for the first and second excited states, respectively; ξ is the spin-orbit coupling parameter, which is taken to be 135 cm.$^{-1}$; and the energies are obtained from the optical spectral data. The average g-value, computed from the parallel and perpendicular components, is given by

$$<g> = (^1/_3)(g_{\parallel} + 2g_{\perp}) \quad (3)$$

Included in Table II are values of $g_{\parallel}$, $g_{\perp}$, and $<g>$ computed from the optical data using the above formulas. The experimental g-values do not seem to show the small shift with solvent predicted from the optical data. This shift, however, is in the order of the experimental error of our e.s.r. measurements. The agreement between the g-value calculated from the optical data and the e.s.r. measurements is nonetheless gratifying, particularly when the approximations used in the calculation are taken into account.

The change in the hyperfine splitting constant, $<A>$, with changes in solvent is of considerable interest. In the theory of Ballhausen and Gray[6] the unpaired electron is assumed to be in an almost pure vanadium non-bonding $3d_{xy}$ orbital; the first two unoccupied levels, e_{π}^* and b_1, have no admixture of the vanadium 4s orbital, and so cannot contribute to the nuclear hyperfine interaction. The third excited state, Ia_1^*, has some 4s character, but is at too high an energy (approximately 25,000 cm.$^{-1}$ above the ground state) to contribute significantly to the observed hyperfine splitting. In addition, it appears to be fairly insensitive to the changes in the solvent. As a result, it is tempting to postulate that the vanadium hyperfine splitting can be accounted for by polarization of filled orbitals. In particular, the orbital represented by $IIIa_1^b$, which can have some 4s character, would be expected to be strongly affected by axial perturbations, and thus could be responsible for changes in the hyperfine interaction. Such a supposition, however, is unwarranted in the absence of even approximate estimates of the contribution of the appropriate structures to the ground state.

As seen in Fig. 2 and 3, there is a marked variation of the width of the vanadium nuclear hyperfine components with the nuclear spin quantum number, m_I. This effect has been studied theoretically by McConnell[11] and Kivelson[12,13] and experimentally by Rogers and Pake.[7] According to the somewhat simplified theory of McConnell, the hyperfine component width is proportional to $(\Delta gB - bM_I)^2$, where $\Delta g = g_{\parallel} - g_{\perp}$, $b = A_{\parallel} - A_{\perp}$, and B is the applied magnetic field. In nitrobenzene, pyridine, acetonitrile, and benzene, the narrowest hyperfine component of the spectrum corresponds to the $m_I = {}^3/_2$ component,[14] while in acetone and methanol, the $m_I = {}^1/_2$ component is the narrowest. Since, from the optical results, the g-value anisotropy is seen to change very little, these data suggest rather wide variations in the anisotropy of the nuclear hyperfine interaction. Further studies of this effect undoubtedly would be of interest in any attempt to determine the exact mechanism of the nuclear hyperfine interaction. The large differences in the average line widths in these solvents can, according to the theory, be accounted for by variations in the rate of tumbling of the molecules in solution. This rate is affected by such factors as the effective size of the complex and the viscosity of the medium. Although the effective size of the Vo(acac)$_2$ complex might be expected to vary somewhat between solvents, the major variation in the line widths seems to result from the large differences in viscosity, and, as seen in Fig. 3, the average line width in a spectrum is correlated qualitatively with the viscosity of the solvent.

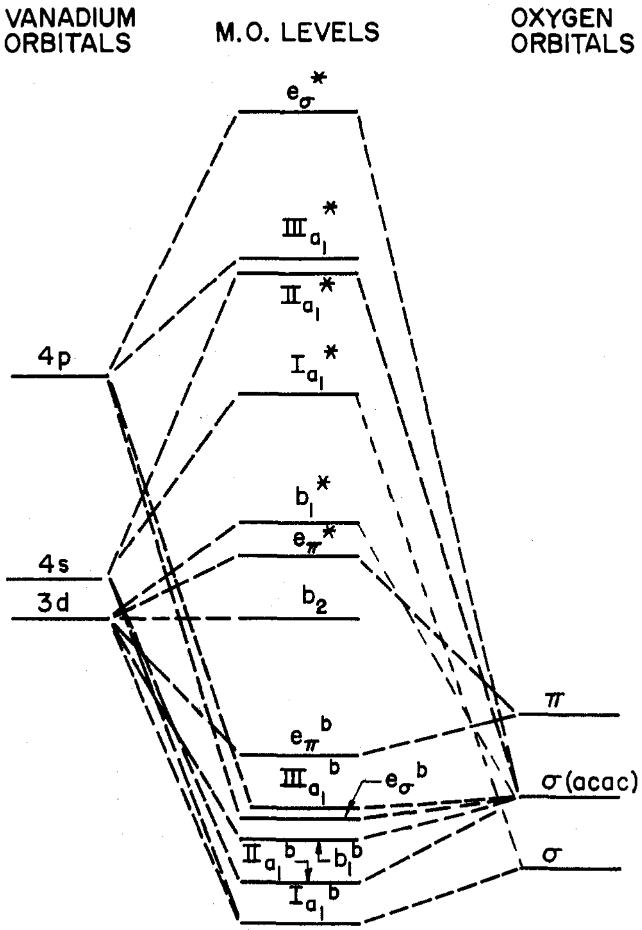

Fig. 4.—Energy level scheme derived by Ballhausen and Gray from semi-empirical molecular orbital calculations.

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[11] H. M. McConnell, *J. Chem. Phys.*, **25**, 709 (1956).
[12] D. Kivelson, *ibid.*, **27**, 1087 (1957).
[13] D. Kivelson, *ibid.*, **33**, 1094 (1960).
[14] For convenience in this discussion and in Fig. 3, we have assumed A to be positive; although it appears to be negative; see for instance, E. M. Roberts and W. S. Koski, *J. Am. Chem. Soc.*, **82**, 3006 (1960).

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.

CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORY OF CHEMISTRY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS, AND THE METCALF CHEMICAL LABORATORIES
OF BROWN UNIVERSITY, PROVIDENCE 12, RHODE ISLAND

Crystal Spectra of Some Trisacetylacetonates

BY T. S. PIPER AND RICHARD L. CARLIN

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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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