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Paramagnetic Resonance Absorption Studies in the Autoxidation of Titanium(III) and Vanadium(III) Trisacetylacetonates[1]

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Single crystals of aluminum(III) trisacetylacetonate containing small amounts of titanium(III) trisacetylacetonate were oxidized in air and showed a free-radical electron paramagnetic resonance spectrum of four species. Three of these were analyzed and had nearly identical principal g values of 2.004, 2.010, and 2.024. Oxidized single crystals containing vanadium(III) trisacetylacetonate showed two species with the typical vanadyl hyperfine splitting of eight lines. The principal g values of both species were close to 1.937, 1.978, and 1.978, while the hyperfine constants were 171×10^{-4} and 65×10^{-4} cm^{-1}. These values were shown to be virtually identical with those obtained from a dilute single crystal of vanadyl(IV) bisacetylacetonate in aluminum(III) trisacetylacetonate. It is concluded that the titanium resonance is most likely due to the TiO_2^{3+} species while the vanadium resonance is due to VO^{2+}. End product studies showed that the titanium autoxidation formed dimer species with oxygen, while the vanadium autoxidation produced vanadyl(IV) bisacetylacetonate. The relation of the epr results to the observed end products is discussed in terms of the probable reaction mechanism.

Introduction

Although the oxidation of organic compounds by molecular oxygen has been well studied, that of organometallic chelates has received much less attention. The only extensive investigation of the destructive autoxidation of chelates was undertaken by Arnett and coworkers, who studied a large number of β-diketonates.[2] They were primarily concerned with kinetic studies and end product determinations.

A new approach for adducing detailed information about the autoxidation of the metal chelates appeared possible when it was observed that a free-radical type of paramagnetic resonance was seen in single crystals of aluminum(III) trisacetylacetonate containing small amounts of titanium(III) trisacetylacetonate.[3] These crystals slowly change color in air, and after about 1 week, a definite boundary is established between the original blue area characteristic of Ti(III) and a yellow area appearing along certain crystal edges (see Figure 1). With time the boundary moves perpendicularly to the 110 crystal face. Since Ti(III) compounds are known to decompose readily upon exposure to air, the paramagnetic resonance seen was considered to be due to an intermediate in the Ti(III) to Ti(IV) oxidation, caused by oxygen migrating into the crystal. For the concentrations employed (0.1–1%) the single crystals were observed to remain intact even after complete conversion. Other instances of paramagnetic resonances due to oxygen migrating into a crystal and attacking at some reactive site have been reported.[4,5]

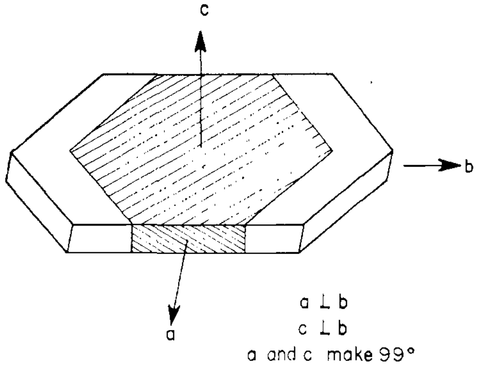

Figure 1.—Aluminum(III) trisacetylacetonate crystals containing titanium(III) trisacetylacetonate in a partially oxidized condition.

The dilute single crystal with the reactive molecule effectively isolated provides an excellent system for determining the initial consequences of an attack by oxygen. Furthermore, since many other metal acetylacetonates might be expected to produce paramagnetic species upon oxidation, electron spin resonance (esr) would be a valuable tool for investigating the structure and orientation of the reaction intermediates in the crystal.

The present research was undertaken to determine the nature of the paramagnetic resonances found in the titanium(III)-doped crystal and its implications for the mechanism of autoxidation of the pure acetylacetonate. It was also proposed to study possible paramagnetic products in a crystal similarly doped with vanadium(III) trisacetylacetonate.

Experimental Section

Chemical Preparations.—Aluminum(III) trisacetylacetonate,[6] vanadium(III) trisacetylacetonate,[7] and vanadyl(IV) bisacetylacetonate[8] were prepared according to standard methods. Titanium(III) trisacetylacetonate was synthesized by a method

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[1] Taken from the dissertation of E. L. Tepper to the faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy (chemistry). This work was carried out under Research Grants GP-753, GP-4215, and GP-7133 of the National Science Foundation.

[2] M. Mendelsohn, E. M. Arnett, and H. Freiser, *J. Phys. Chem.*, **64**, 660 (1960); E. M. Arnett, H. Freiser, and M. A. Mendelsohn, *J. Am. Chem. Soc.*, **84**, 2482 (1962); E. M. Arnett and M. Mendelsohn, *ibid.*, **84**, 3821, 3824 (1962).

[3] B. R. McGarvey, *J. Chem. Phys.*, **38**, 388 (1963).

[4] R. J. Lontz, *ibid.*, **45**, 1339 (1966).

[5] E. G. Janzen, F. J. Johnston, and C. L. Ayers, *J. Am. Chem. Soc.*, **89**, 1176 (1967).

[6] R. C. Young, *Inorg. Syn.*, **2**, 25 (1946).

[7] D. Grdenić and B. Korpar-Čolig, *Inorg. Chem.*, **3**, 1328 (1964).

[8] B. E. Bryant and W. C. Fernelius, *Inorg. Syn.*, **5**, 115 (1957).

analgous to the aluminum(III) trisacetylacetonate procedure.[8] Fresh Fisher 20% titanium trichloride solution was mixed with acetylacetone (2,4-pentanedione) dissolved in dilute ammonia, and the crude acetylacetonate was precipitated by adjusting the pH to 7 with 6 *M* ammonia. The product was purified by vacuum sublimation at 156° and stored in sealed tubes. Oxygen was excluded from contact with the final product by operating within a glove bag under an atmosphere of nitrogen purified through chromous chloride gas-scrubbing bottles.

Crystal Preparations.—Dilute crystals of vanadyl(IV) bisacetylacetonate in aluminum(III) trisacetylacetonate were grown by slow evaporation from methanol solutions saturated at room temperature. The titanium(III) and vanadium(III) dilute crystals were grown from solutions saturated with aluminum(III) trisacetylacetonate at 12° and stored in a refrigerator at 4°.[9] They were prepared with careful exclusion of oxygen from the solvent and the use of sealed flasks and nitrogen-filled glove bags. Depending upon uncontrollable crystallizing conditions crystals of dimensions less than 1 mm to those of 1 cm were obtained. The evaporation technique was more successful in consistently producing larger crystals.

Crystal Oxidation.—Although the titanium(III) crystals would oxidize at atmospheric pressure, the reaction was normally accelerated by oxidizing in a Parr No. 1102 double-valve oxygen bomb with an A102A5 head. The filling pressure of the oxygen (USP) was approximately 25 atm as measured by the low-pressure mechanical gauge attached to the cylinder head. While 2 days of oxidation was sufficient to give an appreciable signal for the titanium-doped crystal, the vanadium crystal required 1 week or more depending upon crystal size.

Esr Spectra Measurements.—All spectra were recorded at room temperature on a Varian Associates Model V-4500 esr spectrometer operating at 9.507 MHz with a modulating frequency of 100 kHz. The magnetic field was determined by an Alpha Scientific AL67 nuclear magnetic resonance gaussmeter calibrated by a 100-kHz crystal calibrator standardized against the 10-MHz signal of WWV (National Bureau of Standards radio station). N,N-Diphenylpicrylhydrazyl was used as a reference signal.

Esr Results

Titanium System.—Preliminary esr investigations of pure aluminum(III) trisacetylacetonate crystals and those that were subjected to oxygen under pressure for 1 week showed no resonance at room temperature using the maximum sensitivity of the spectrometer. Although the broad absorption due to Ti^{3+} was seen,[3] a freshly made mixed crystal containing $Ti(acac)_3$ and exposed to the atmosphere for under 1 hr showed no free-radical resonance. After 1 week in the air, an extremely weak new resonance appeared. The mixed crystal oxidized under pressure for 1 week showed a strong spectrum at room temperature composed of four main narrow (2-G half-width) pairs of lines of relative intensities in the derivative curve of 1:1.3:2:3 (Figure 2). These relative intensities did not vary markedly from crystal to crystal or even between crystals oxidized under different pressures of oxygen. These four resonance lines show no H^1 hyperfine splitting, but in many orientations additional weak lines are observed with intensities of 1–5% that of the main lines. Although the complete orientation dependence of these weak lines could not be determined, enough data were obtained to establish that many of them were due to independent radicals that were either different species than those giving rise to the main absorption lines or the same species differently oriented in the lattice. The latter is considered more likely since the weak lines showed similar variations in *g* to those of the main lines. Some weak lines appeared to be satellites of the main lines and suggested the possibility of C^{13} hyperfine lines. This was ruled out, however, by the observations that in most instances the intensity was much greater than the 0.5% expected for C^{13} lines and that these lines did not appear in many orientations in which their resolution should have been possible. There was, also, no evidence for Ti^{47} ($I = {}^5/_2$) or Ti^{49} ($I = {}^7/_2$) hyperfine splitting which would have shown up as satellites of about 1% of the intensity of the main line. The aluminum(III) trisacetylacetonate host lattice belongs to the monoclinic space group $P2_1/c$.[10] In this space group, two of the molecules in the unit cell are related to the other two by a glide plane in the *ac* plane. Provided that both a molecule and its mirror image are attacked with the same probability, the two species will be magnetically nonequivalent in orientations of the magnetic field out of the *ac* plane. This accounts for the occurrence of lines in pairs of equal intensities.

Since each resonance was composed of a single line with a *g* factor of about 2 which varied only slightly with orientation, the system for which $S = {}^1/_2$ follows the spin-Hamiltonian

$$\mathcal{H} = g_x\beta_e H_x S_x + g_y\beta_e H_y S_y + g_z\beta_e H_z S_z$$

It was further observed that the esr spectrum did not exhibit axial symmetry, and it was necessary to investigate three independent rotations to extract the three principal *g* factors and their orientation in the crystal. For this purpose rotations were made about the *b* axis, the *a* axis, and an axis perpendicular to *b* and 45° between the *a* and *c′* axes. To facilitate calculations, the laboratory axes chosen were the crystal *a* and *b* axes and a *c′* axis which completes an orthogonal-coordinate system in the right-handed sense with *a* and *b*. The experimental *g* values were measured in the three rotations and fitted by a least-squares procedure to the expected theoretical $\cos^2$ relationship. From the fitted parameters of these curves, the *g* values and orientations of the principal-coordinate system were calculated. The *g* values and principal axes are given in Table I for the three pairs of lines of relative intensities 1, 2, and 3. Extensive overlap with other lines in many orientations prevented the evaluation of the *g* tensor for the line of relative intensity 1.3. The assignment of *x*, *y*, and *z* was made such that g_z was the largest value and g_x was the smallest value. The initial observation to be made from these results is that the close similarity of each of the three *g* values for the three species measured is a good indication that one is dealing with identical species, differing only in orientation within

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[9] T. S. Piper and R. L. Carlin, *Inorg. Chem.*, **2**, 260 (1963).

[10] P.-K. Hon, *Dissertation Abstr.*, **26**, 1906 (1965). We wish to thank Professor C. E. Pfluger for making some of the X-ray results available before the conclusion of the thesis.

Table I

The Principal g Values and Their Orientations in the Crystal for the Free Radicals in an Autoxidized Crystal of Titanium(III) Trisacetylacetonate in Aluminum(III) Trisacetylacetonate[a]

Rel line intens	g	g value	Angle to b,[b] deg	Proj ac plane,[b] deg
3	g_x	2.0036	84	24
	g_y	2.0099	17	−84
	g_z	2.0236	74	116
3′	g_x	2.0036	85	24
	g_y	2.0095	19	−82
	g_z	2.0240	72	116
2	g_x	2.0041	28	−118
	g_y	2.0092	66	29
	g_z	2.0234	76	125
2′	g_x	2.0036	27	−110
	g_y	2.0091	69	29
	g_z	2.0240	73	125
1	g_x	2.0035	78	132
	g_y	2.0098	69	37
	g_z	2.0247	24	−110
1′	g_x	2.0035	78	131
	g_y	2.0096	69	36
	g_z	2.0249	25	−110

[a] Uncertainty in the g's is ±0.0010 and in the angles is ±4°. [b] There is an ambiguity in the orientation of the principal axes, in that the positive directions of x, y, and z are arbitrary. For ease of comparison, the coordinate axes are all reported as right-handed systems. Further, since the principal axes of the pair related by an ac glide plane differ only by a 180° rotation about the b axis, the coordinates for both components of the pair are reported as being in the same direction, the differences reflecting only experimental uncertainties. The projection is measured positively from the a axis toward the c axis.

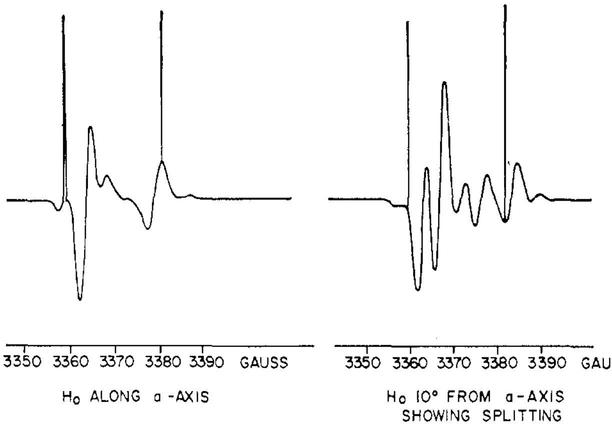

Figure 2.—Some representative spectra of the free-radical resonance in an oxidized titanium(III)-doped crystal. The marker pips are 23.49 G apart.

the crystal lattice.

Vanadium System.—After 1 week of oxidation under pressure, the dilute single crystals containing vanadium(III) trisacetylacetonate showed a strong spectrum of two pairs of resonances (4-G half-width) with relative intensities in the derivative curve of 1:1.3. Each species showed the eight hyperfine lines characteristic of V^{51} ($I = {}^7/_2$). In addition, no other resonances were detected such as those that might be due to free radicals. Preliminary results, showing almost the same minimum hyperfine splitting and maximum g factor for rotations about the b axis and perpendicular to the b axis, indicated an axially symmetric system. For $S = {}^1/_2$, the axial system follows the spin-Hamiltonian

$$\mathcal{H} = g_\perp\beta_e(H_xS_x + H_yS_y) + g_{||}\beta_eH_zS_z + A_\perp(I_xS_x + I_yS_y) + A_{||}I_zS_z$$

The two rotations necessary to solve for the principal components of the axial Hamiltonian were chosen to be about the b axis, and about an axis making angles of 30° with a and 60° with c'. For each individual orientation of H, the values of the g factor and K, the hyperfine splitting constant, were obtained from the spectrum using the second-order perturbation solution to the axial spin-Hamiltonian.[11] The experimental values for g and K were fitted by least-squares analysis to the appropriate $\cos^2$ relations from which the values for $g_{||}$, $g_\perp$, $A_{||}$, and $A_\perp$ given in Table II were obtained. β and α_P are the polar angles for the unique axis, with α_P being the angle between the a axis and the projection of the molecular axis into the ac plane. There was some evidence of noncoincidence of the g and A tensors amounting to less than 5° which was neglected in the calculations. Here again the immediate observation is that the two resonances are due to the same species differing slightly in orientation.

Table II

The Principal g and A Values for the Paramagnetic Resonances in an Autoxidized Crystal of Vanadium(III) Trisacetylacetonate in Aluminum(III) Trisacetylacetonate[a]

	Rel line intens	
Parameter	1.3	1
$g_{\|\|}$	1.9356	1.9383
$g_\perp$	1.9785	1.9780
$A_{\|\|}$,[b] cm^{-1}	171×10^{-4}	171×10^{-4}
$A_\perp$,[b] cm^{-1}	66×10^{-4}	65×10^{-4}
β, deg	74	80
α_P, deg	120	121

[a] The other line pair has the same principal values with $\beta = 180° - \beta$. Uncertainty in the g's is ±0.0010, in the A's is $\pm 2 \times 10^{-4}$, and in orientation is ±4°. [b] $A(\text{cm}^{-1}) = A(\text{G})g/2.14197 \times 10^4$.

Vanadyl System.—Because of the similarity of the oxidized vanadium(III) spectra with that which one would expect for the vanadyl ion, an attempt was made to grow a crystal of aluminum(III) trisacetylacetonate containing vanadyl(IV) bisacetylacetonate. Although the solubility of the vanadyl complex in the methanol was small, enough complex was included in the host crystal to give a strong resonance at room temperature. The spectrum showed three line pairs (4-G half-width) of intensity ratios in the derivative curve of 1.3:1:0.5. There was evidence for a fourth weak line which appeared only in very few orientations due to overlap and was not susceptible to calculation. The preliminary observations showed that this spectrum and

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(11) B. Bleaney, *Phil. Mag.*, **42**, 441 (1951).

the oxidized vanadium(III) spectrum were very similar. The calculations, carried out in a manner identical with that for the oxidized crystal, bore out these observations. The results are presented in Table III. As far as is known, this represents the first reported spectrum of vanadyl(IV) bisacetylacetonate in a single crystal.

TABLE III

THE PRINCIPAL g AND A VALUES OF A DILUTE SINGLE CRYSTAL OF VANADYL(IV) BISACETYLACETONATE IN ALUMINUM(III) TRISACETYLACETONATE

Parameter	Rel line intens		
	1.3	1	0.5
$g_{\parallel}$	1.9346	1.9361	1.9342
$g_{\perp}$	1.9787	1.9762	1.9778
$A_{\parallel}$,[a] cm^{-1}	173×10^{-4}	170×10^{-4}	174×10^{-4}
$A_{\perp}$,[a] cm^{-1}	65×10^{-4}	68×10^{-4}	71×10^{-4}
β, deg	72	75	73
α_P, deg	121	121	120

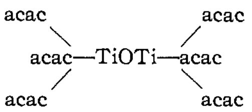
[a] See Footnote *b* to Table II.

End Product Investigations

Vanadium(III) trisacetylacetonate air oxidation was reported by Morgan and Moss in 1913 to give vanadyl(IV) bisacetylacetonate.[12] In the present investigation, this report was confirmed by subjecting the pure, finely pulverized vanadium(III) compound to 25 atm of oxygen in the bomb for 52 hr. The original brown V^{3+} compound was seen to have turned blue-green, characteristic of the vanadyl ion. In addition, a brown, tarlike liquid was formed. After drying the green product, its infrared spectrum was taken in a KBr pellet on a Perkin-Elmer 521 grating spectrophotometer. It was identical with the spectrum taken from vanadyl(IV) bisacetylacetonate synthesized by the standard method[8] and with that reported in the literature.[13] The brown liquid was not identified. Its infrared spectrum between NaCl plates showed peaks characteristic of carboxyl groups and especially carboxylic acids.

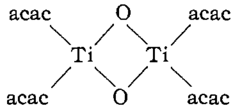
A further interesting observation was that upon continuing the vanadium(III) oxidation for 5 days the green vanadyl(IV) bisacetylacetonate disappeared, and a black, gummy product was produced which dissolved in water to form a green solution. The infrared spectrum of this product in a KBr pellet showed a typical inorganic pattern with no evidence of carboxyl groups at all.

The end product of titanium(III) trisacetylacetonate autoxidation was studied by Chakravarti.[14] To the dark orange end product of the oxidation in benzene solution, he assigned the structure



on the basis of cryoscopic molecular weight determinations in benzene and elemental analysis. The product had a molecular weight of 701 against the calculated theoretical value of 705.8.

Bridged titanium–oxygen compounds containing acetylacetonate rings have been reported in a few instances. Yamamoto and Kambara synthesized



by the hydrolysis of dibutoxytitanium(IV) bisacetylacetonate.[15] This formula was assigned on the basis of elemental analysis and molecular weight determination. The infrared spectrum of the compound was also reported. Another oxygen-bridged compound, $(TiCl(acac)_2\text{–O–}TiCl(acac)_2)\cdot CHCl_3$, was produced by the partial hydrolysis of $TiCl_2(acac)_2$ in chloroform solution, and its structure was confirmed by X-ray crystallography.[16]

Titanium(III) trisacetylacetonate autoxidation in the solid state was reported by Cox, Lewis, and Nyholm.[17] The product they found was a yellow solid which was recrystallized from benzene and was given the formula $TiO(acac)_2$ on the basis of molecular weights and elemental analysis. They also took the infrared spectrum of this product and found a band of medium intensity at 1087 cm^{-1}. This band which is not present in the spectrum of the dimer product of Yamamoto and Kambara was assigned to the Ti=O stretching vibration. Metal–oxygen vibrations are commonly found in the 1000-cm^{-1} region. This band occurs in the $VO(acac)_2$ spectrum at 997 cm^{-1}. It was further observed that the strong band appearing at 829 cm^{-1} in the dimer spectrum and assigned to a Ti–O–Ti vibration was absent in the monomer spectrum. Cox, *et al.*, verified the work of Yamamoto and Kambara but claimed that although the dimer structure for their hydrolysis product is correct in benzene solution, the compound apparently dissociates in nitrobenzene giving a molecular weight characteristic of the monomer.

To clarify the disparity between the reports of Chakravarti and Cox, *et al.*, some solid blue titanium(III) trisacetylacetonate was oxidized by exposure to air for several weeks and was seen to turn orange. The product was found to be a mixture of at least two substances. By extracting with benzene at room temperature, the color-producing component could be removed, leaving a yellow, water-soluble solid. The yellow product was considerably less soluble in benzene than the orange component. Although it was not possible to recrystallize the orange substance from benzene,

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(12) G. T. Morgan and H. W. Moss, *J. Chem. Soc.*, **103**, 78 (1913).

(13) K. E. Lawson, *Spectrochim. Acta.*, **17**, 248 (1961).

(14) (a) B. N. Chakravarti, *Naturwissenschaften*, **45**, 286 (1958); (b) B. N. Chakravarti, private communication, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Ontario, Canada. We wish to thank Dr. A. T. Prince of the Mines Branch for making this report available to us.

(15) A. Yamamoto and S. Kambara, *J. Am. Chem. Soc.*, **79**, 4344 (1957).

(16) K. Watenpaugh and C. N. Caughlan, *Inorg. Chem.*, **6**, 963 (1967).

(17) M. Cox, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2840 (1965).

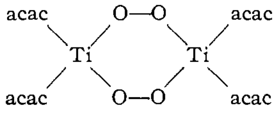
it was deposited upon evaporation of the solvent as a red-brown, waxy plate.

An analysis of the yellow product was performed. *Anal.* Calcd for $TiO(C_5H_7O_2)_2$: C, 45.82; H, 5.38; Ti, 18.27. Calcd for $TiO_2(C_5H_7O_2)_2$: C, 43.19; H, 5.07; Ti, 17.22. Found: C, 45.30; H, 7.59; Ti, 18.24. Cryoscopic measurements of the molecular weight were attempted, and the results, although not highly accurate, indicated a dimer of $[TiO(C_5H_7O_2)_2]_2$ or $[TiO_2(C_5H_7O_2)_2]_2$ rather than a monomer as the principal constituent. Analysis by mass spectrometry showed a band of peaks with an average molecular weight of 556 indicating a species consistent with the structure $[TiO_2(C_5H_7O_2)_2]_2$. A similar but weaker band of peaks was also observed 32 mass units lower. Since this lower band could be a fragmentation of the species at m/e 556 or could result from the presence of $[TiO(C_5H_7O_2)_2]_2$ in the sample, we can infer that a major if not primary constituent of the yellow product is $[TiO_2(C_5H_7O_2)_2]_2$.

The red-brown product was also analyzed. *Anal.* Found: C, 53.77; H, 7.48; Ti, 14.08; mol wt (by osmometry in benzene), 635.

The infrared spectra of these two substances (recorded in KBr pellets) are given in Figure 3 and show all of the bands commonly found for acetylacetonate rings. The spectrum of the yellow product showed a large absorption at 592 cm^{-1}, a medium band at 497 cm^{-1}, and a weak band at 818 cm^{-1}, which are not present in the metal acetylacetonates. It is significant that the band at 1087 cm^{-1} found by Cox, *et al.*, and attributed to Ti=O was not present in the spectrum. The weak absorption at 818 cm^{-1} is perhaps due to incomplete removal of the red-brown component. The infrared spectrum of the red-brown solid contained additional peaks at 1700, 1663, 818, and 1095 cm^{-1}, plus some weak peaks at 592 and 497 cm^{-1} which were probably due to some yellow product taken into the benzene layer upon extraction. While the 818-cm^{-1} peak is perhaps analogous to the strong absorption found by Yamamoto at 829 cm^{-1} for a Ti—O vibration not on an acetylacetone ring, it is doubtful that the 1095-cm^{-1} band represents the medium Ti=O absorption seen by Cox at 1087 cm^{-1} since its intensity is much too small.

The elemental analysis and molecular weight data for the yellow product indicate a major component to be $[TiO_2(C_5H_7O_2)_2]_2$ which could have one of two structures



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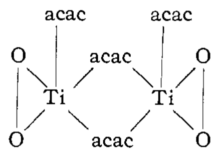

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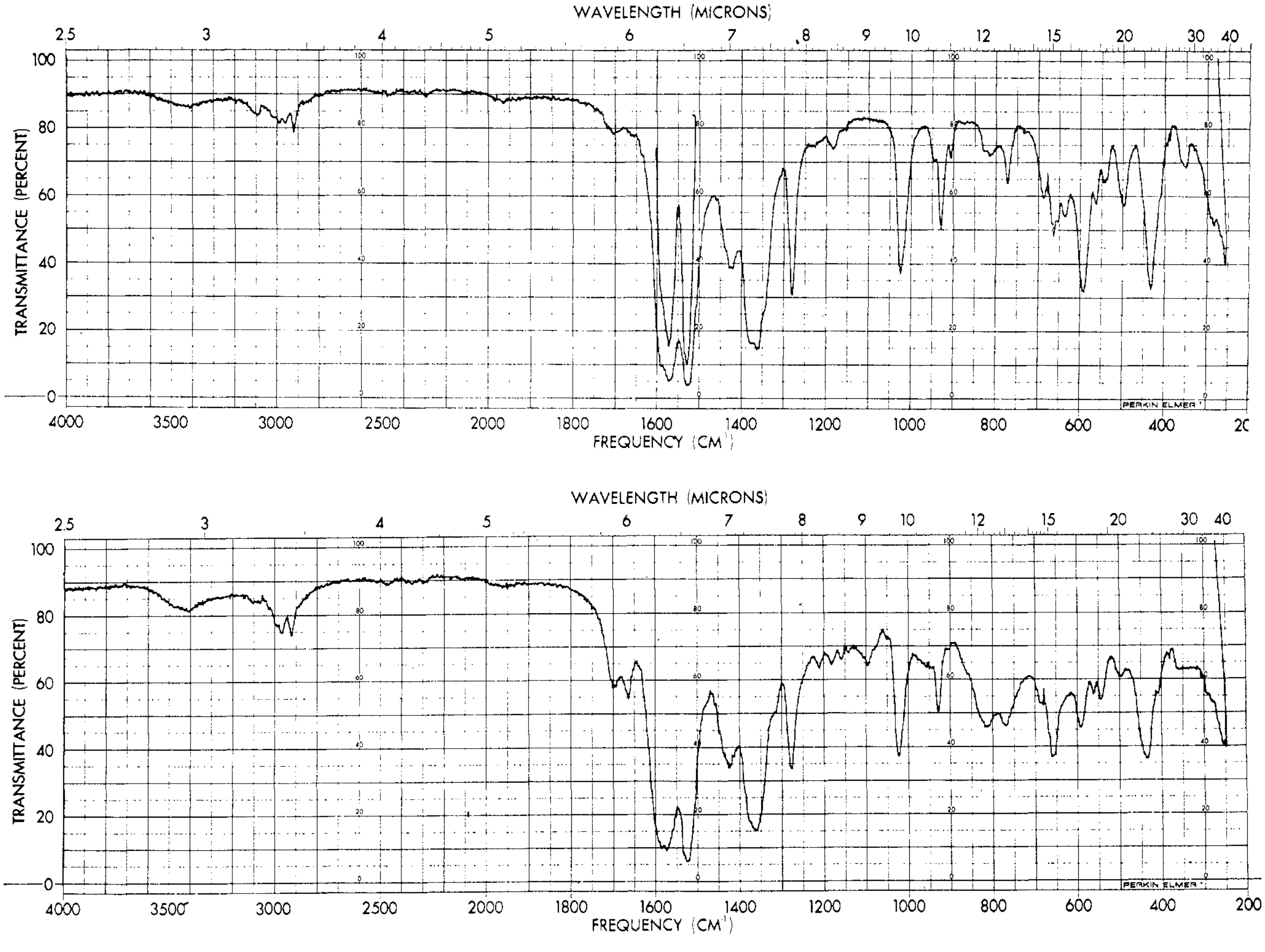
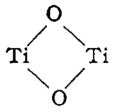
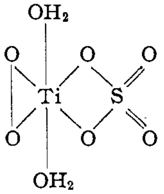


Figure 3.—Infrared spectra of the yellow (top) and red-brown (bottom) oxidation products of titanium(III) trisacetylacetonate.

The presence of large amounts of $[TiO(C_5H_7O_2)_2]_2$ is ruled unlikely by the absence in the ir spectrum of the 1087-cm^{-1} band for Ti=O and the 829-cm^{-1} band for



The bands at 592 and 497 cm^{-1} are similar to Ti—O stretching and bending modes at 500 and 448 cm^{-1} found by Jere and Patel[18] for peroxytitanium sulfate which has the structure



and at 545 and 400 cm^{-1} for barium titanate which is composed of Ti–O–Ti–O–Ti–O chains.[19]

Although the spectrum indicates the red-brown product to have some yellow product impurity, its molecular weight, color, and elemental analysis are similar to those reported by Chakravarti. For a species with three doubly coordinated acetylacetonate groups, it is difficult to postulate an additional oxygen coordinating at a seventh position. The appearance of the peaks at 1700 and 1663 cm^{-1} is indicative of uncoordinated carboxyl groups and it is possible that this product represents an intermediate stage between the tris and bis compounds with the third ring having only one of its oxygens coordinated, the other coordination position occupied by the attacking oxygen.

Discussion

An examination of Table II shows that the g, A, and α_P values of the two species produced in the oxidized vanadium(III) single crystal are nearly the same. The β's differ slightly. This indicates that one is dealing with two identical species differing slightly in orientation and in molecular structure. A further comparison of these results with those obtained from the vanadyl(IV) single crystal (Table III) provides convincing evidence that the oxidized species formed in the cage is vanadyl(IV) bisacetylacetonate with the third ring either trapped in the lattice or weakly bonding in the sixth coordinating position. The fact that in one case three resonances are seen and in the other only two are seen is undoubtedly due to the different ways that the species are introduced into the lattice and to the presence, in one case, of the acetylacetonate ring trapped in the lattice. These values conform with those found in the literature for the various vanadyl species tabulated in Table IV. Thus the vanadyl(IV) bisacetylacetonate appears to be formed immediately upon reaction with the oxygen. Since no radical resonances could be detected in these crystals, any free radicals resulting from the attack of O^+ which must be released in the formation of VO^{2+} must disappear rapidly at room temperature by secondary processes.

TABLE IV

g FACTORS FOR VANADYL(IV) SPECIES IN VARIOUS SYSTEMS

Species	$g_\parallel$	$g_\perp$	$10^4A_\parallel$, cm^{-1}	$10^4A_\perp$, cm^{-1}	Ref
$VO(C_5H_7O_2)_2$ in benzene	1.9582	1.9920	173.5	62.1	*a*
$VO(H_2O)_5^{2+}$ in zinc, Tutton's salt	1.9331	1.9807	182.8	72.0	*b*
$VOCl_5^{3-}$ in ammonium pentachloroindate	1.9450	1.9847	173.0	63.8	*c*
$VO(H_2O)_5^{2+}$ in					
$RbAl(SO_4)_2 \cdot 12H_2O$	1.932	1.975	182.4	66.6	*d*
$CsAl(SO_4)_2 \cdot 12H_2O$	1.932	1.979	183.4	65.7	

[a] F. A. Walker, R. L. Carlin, and P. H. Rieger, *J. Chem. Phys.*, **45**, 4181 (1966). [b] R. H. Borcherts and C. Kikuchi, *ibid.*, **40**, 2270 (1964). [c] DeArmond, B. B. Garrett, and H. S. Gutowsky, *ibid.*, **42**, 1019 (1965). [d] A. Manoogian and J. A. MacKinnon, *Bull. Am. Phys. Soc.*, **12**, 641 (1967).

The disappearance of the blue color of Ti(III) indicates that a conversion to Ti(IV) has taken place in the crystal. The presence of the new radical type of resonance in only the colorless portions of the oxidized crystal and its absence in crystals of pure aluminum acetylacetonate treated with oxygen tell us that this new paramagnetic species is a primary or secondary product of the oxidation of Ti(III) in the crystals.

The new species could be a free radical formed from the acetylacetonate ligand. The absence of hyperfine lines due to hydrogen and the average g value of 2.0124 indicate the radical is not of the form R· as these radicals have large hyperfine interactions and g's close to 2.0023. Alkoxy radicals RO· are also unlikely as these have g values less than 2.010.[20] The remaining possibility is a peroxy radical ROO·. These have been detected in a number of systems which are listed in Table V along with the observed g values. Comparison of these g values with those of the Ti^{3+} system suggests that the observed species could be a peroxy radical.

The superoxide ion O_2^- is another possibility since this ion could result from a direct one-electron transfer from Ti^{3+} to O_2. Reported values of g for the superoxide ion trapped in various lattices are given in Table VI. Although there is only a small variation in g_x and g_y, it is observed that g_z varies markedly from lattice to lattice. Theory of the g values[21,22] has established that the largest g is along the O–O direction of the ion and that deviations in this g from 2.0023 are proportional to λ/δ, where λ is the spin–orbit coupling constant and δ is the energy separation between the π_x and π_y antibonding orbitals of the ion. Therefore, the marked sensitivity of g_z to environment is due to the sensitivity of δ to the surroundings. Kasai[22] has noted that g_z becomes smaller as the charge of the nearby cation increases.

Iyengar, *et al.*,[23] have detected a resonance, which

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[19] J. T. Last, *Phys. Rev.*, **105**, 1740 (1957).

[20] M. Bersohn and J. R. Thomas, *J. Am. Chem. Soc.*, **86**, 959 (1964).

[21] J. H. Lunsford and J. P. Payne, *J. Chem. Phys.*, **44**, 1487 (1966).

[22] P. H. Kasai, *ibid.*, **43**, 3322 (1965).

[23] R. D. Iyengar, M. Codell, J. S. Karra, and J. Turkevich, *J. Am. Chem. Soc.*, **88**, 5055 (1966).

TABLE V

g FACTORS FOR PEROXY RADICALS

Radical	g_x	g_y	g_z	g_{av}	Ref
$(C_6H_5)_3COO\cdot$ by γ radiolysis of triphenylmethyl chloride in the air				2.0146	*a*
$(NO_2C_6H_4)_3COO\cdot$ by reaction of O_2 on $(NO_2C_6H_4)_3C\cdot$				2.006	*b*
$C_6H_5C(CH_3)_2COO\cdot$ by oxidation of $C_6H_5C(CH_3)_2H$				2.0144–2.0155	*c*
$ROO\cdot$ by electron irradiation of $RH + O_2$				2.0148–2.0155	*c*
$NH_2CO(CF_3)CFOO\cdot$ by γ irradiation of $CF_3CF_2CONH_2 + O_2$	2.0267	2.0193	2.0102	2.0187	*c*
$(CH_3)_3COO\cdot$ by uv on $(CH_3)_3COOH$ glass				2.0137	*c*
$C_{10}H_{11}OO\cdot$ by uv on $C_{10}H_{11}OOH$	2.0306	2.0085	2.0073	2.0155	*c*
$(CH_3)_3COO\cdot$ by photolysis of $(CH_3)_3COOH$ soln				2.0146	*d*
Cumylperoxyl radical by photolysis of liquid cumeno hydroperoxide				2.014	*c*

[a] See ref 5. [b] F. M. Schimmel and F. W. Heineken, *Physica*, **23,** 781 (1957). [c] K. U. Ingold and J. R. Morton, *J. Am. Chem. Soc.*, **86,** 3400 (1964). [d] J. R. Thomas, *ibid.*, **88,** 2064 (1966).

TABLE VI

g FACTORS OF SUPEROXIDE IONS

	g_x	g_y	g_z	Ref
O_2^- on uv-irrad MgO	2.0011	2.0073	2.077	*a*
O_2^- on ZnO	2.0020	2.0082	2.051	*a*
O_2^- in NaO_2	2.000	2.000	2.175	*a*
O_2^- in KCl	1.9512	1.9551	2.4359	*a*
O_2^- in Ba–Y, X-irrad zeolite	2.0046	2.0090	2.057	*b*
O_2^- in Na–Y, γ-irrad zeolite	2.0016	2.0066	2.113	*b*

[a] Reference 21. [b] Reference 22.

they attribute to the superoxide ion, on rutile surfaces that have been first subjected to high temperatures under vacuum and then exposed to oxygen. Their proposed mechanism suggests that at high temperatures there is a loss of oxygen from the surface. This produces a Ti^{4+} ion which dissociates to give Ti^{3+}

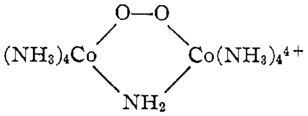
$$Ti^{4+} \longrightarrow Ti^{3+} + \text{hole}$$

The Ti^{3+} then combines with O_2 after release of the vacuum

$$Ti^{3+} + O_2 \longrightarrow Ti^{4+} + O_2^-$$

The principal *g* values are 2.002, 2.0106, and 2.0216 which are almost identical with those observed in the Ti(acac)$_3$ autoxidation.

A superoxide ion associated with Ti^{4+} would be expected to show a hyperfine interaction with Ti^{47} and Ti^{49} similar to that shown by the paramagnetic peroxy-bridged dimers of cobalt. These compounds have been pictured as primarily a superoxide ion connecting two cobalt ions. Weil and Kinnaird[24] reported a cobalt hyperfine interaction of 12.4 G in



If we assume a similar interaction for TiO_2^{3+}, the smaller magnetic moments for titanium would give a hyperfine interaction of only 3 G which would be difficult to see in our system since the line widths are of the same magnitude. Therefore, we cannot exclude TiO_2^{3+} just because no hyperfine interaction for Ti^{47} and Ti^{49} was observed.

An examination of the orientations of the principal axes given in Table I reveals some interesting regularities. All three species have nearly the same principal axes if we ignore the labels of *x*, *y*, and *z*. For example, species 3 and 2 have the same *z* axis but the *x* and *y* axes are interchanged. Further the *z* axis is similar to the VO axis found in the vanadium system. Species 1 has the same *y* axis as species 2 but the *z* and *x* axes are interchanged. The fourth species with intensity 1.3, which could not be completely characterized, appears to have the same *z* axis as species 1 with *x* and *y* axes interchanged. The directions of the principal axes are close to those of the Al–O bonds in the host crystal:[10] β: 72, 23, 75°; α_P: 125, −101, 30°. β is the angle to the *b* axis and α_P is the angle between *a* and the projection on the *ac* plane. The directions given are those which contain the molecular trigonal axis (at $\beta = 31°$, $\alpha_P = 74°$[3,25]) in the first octant. These observations can be readily explained if we assume that the peroxide radical or superoxide ion (theory requires that the *z* axis of both be the O–O bond direction) has the O–O direction parallel to a Ti–O bond. The pair of species labeled 3 and 2 would then be the product of the attack by O_2, along the same Ti–O axis, of the two optical isomers present in the crystal. The pair labeled 1 and 1.3 would be the two isomer products with the O–O axis lying along a second Ti–O bond direction.

Although peroxy radicals cannot be ruled out in the Ti^{3+} case, it is difficult to understand how they can be formed in the Ti^{3+} case but not in the V^{3+} system. It seems more consistent to propose that there is a direct transfer of one electron to O_2 by both V^{3+} and Ti^{3+}. The resulting superoxide ion is stable in the presence of Ti^{4+} but is not in the presence of V^{4+} which forms the very stable VO^{2+} instead. VO^{2+} is found to occur as a stable entity in many more systems than TiO^{2+}. In fact, it has been called the most stable binuclear ion known.[26] This mechanism has the advantage that it readily explains the production of dimers in the oxidation of Ti(acac)$_3$ since the intermediate $Ti\text{–}O\text{–}O^{3+}$ would attack a second Ti(acac)$_3$ forming dimers with oxygen bridges. Similar peroxymetal complexes play an important role in autoxidation of many hydrated ions such as Fe^{2+}, V^{2+}, and Cr^{3+}.[27]

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Conclusions

The esr investigations of the autoxidation of titanium(III) and vanadium(III) trisacetylacetonates in dilute single crystals of aluminum(III) trisacetylacetonate show that both of these complexes react by an attack of an oxygen molecule on the metal. The vanadium(III) is immediately converted to the vanadyl(IV) ion with the second oxygen atom presumably going off as O^+ to attack one of the rings. The titanium(III), however, appears to form a stable TiO_2^{3+} peroxy radical. This radical, in solution or pure solid, is then able to attack another chelate molecule forming a dimeric species containing titanium–oxygen bridges.

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Stoichiometry and Kinetics of the Acid Cleavage of Some Single-Bridged Binuclear Chromium(III) Complexes[1]

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The stoichiometry and kinetics of the cleavage of the rhodo ion, $(NH_3)_5Cr(OH)Cr(NH_3)_5^{5+}$, the aquoerythro ion, $(NH_3)_5Cr(OH)Cr(NH_3)_4OH_2^{5+}$, and the chloroerythro ion, $(NH_3)_5Cr(OH)Cr(NH_3)_4Cl^{4+}$, by aqueous $HClO_4$ have been studied. The products of the cleavage reactions are $(NH_3)_5CrOH_2^{3+}$ from the rhodo ion, $(NH_3)_5CrOH_2^{3+}$ and *cis*-$(NH_3)_4Cr(OH_2)_2^{3+}$ from the aquoerythro ion, and $(NH_3)_5CrOH_2^{3+}$ and *trans*-$(NH_3)_4Cr(OH)_2Cl^{2+}$ from the chloroerythro ion. The cleavage rates are independent of $[H^+]$ in 0.1–1.0 M $HClO_4$, the rate law being $-d[\text{dimer}]/dt = k[\text{dimer}]$, where $k = (7.6 \pm 0.1) \times 10^{-4}\ \text{sec}^{-1}$ at 55.0° and $E_a = 28.7 \pm 0.3$ kcal mol^{-1} for the rhodo ion; $k = (11.8 \pm 0.4) \times 10^{-4}\ \text{sec}^{-1}$ at 55.0° and $E_a = 28.1 \pm 0.3$ kcal mol^{-1} for the chloroerythro ion; $k = (4.0 \pm 0.3) \times 10^{-4}\ \text{sec}^{-1}$ at 65.0° and $E_a = 28.7 \pm 0.4$ kcal mol^{-1} for the aquoerythro ion, all at $\mu = 1.00$ M. The cleavage of the aquoerythro ion becomes more rapid in the presence of Cl^-, and *cis*-$(NH_3)_4Cr(OH_2)Cl^{2+}$ is found among the products. It is postulated that the aquoerythro ion reacts with Cl^- to give the *cis*-chloroerythro ion, which cleaves more rapidly than the aquoerythro ion.

Introduction

By now it is well established that the binuclear chromium(III) complexes of the rhodo–erythro series have as a common structural feature a single oxygen bridge.[2-4] The present paper is concerned with the solution chemistry of three of these ions, the rhodo ion, $(NH_3)_5Cr(OH)Cr(NH_3)_5^{5+}$, the aquoerythro ion, $(NH_3)_5Cr(OH)Cr(NH_3)_4OH_2^{5+}$, and the chloroerythro ion, $(NH_3)_5Cr(OH)Cr(NH_3)_4Cl^{4+}$. These ions are all known to undergo cleavage to monomeric species in acidic solutions,[2,3] the cleavage of the rhodo ion by hydrochloric acid being in fact the most convenient source of $[(NH_3)_5CrCl]Cl_2$.[5] However, no quantitative data on the rates of acid cleavage have been published, and even the immediate products of acid cleavage are in doubt, since the reported products could in some cases have arisen by anation of the immediate cleavage products.[2,3]

A more thorough investigation of the cleavage reactions of these ions seemed warranted for several reasons. These ions are among the few well-characterized binuclear complexes having a single hydroxo bridge, and they are probably similar to the intermediates involved in the acid cleavage of binuclear complexes with two hydroxo bridges.[6,7] Since the ions of the erythro series contain a tetraammine fragment, they are potential sources of tetraamminechromium(III) complexes, some of which have not been synthesized heretofore. Further, the acid cleavage of these complexes represents an unusual sort of substitution reaction in that the leaving group bears a net positive charge; *e.g.*, in the cleavage of the rhodo ion the leaving group is $(NH_3)_5CrOH^{2+}$.

The aquoerythro and chloroerythro ions are capable of existing in two isomeric forms, *i.e.*, forms having the aquo or chloro ligand either *cis* or *trans* to the hydroxo bridge. Schwarzenbach and Magyar[4,8] believed that the aquoerythro ion, formed by base hydrolysis of the

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[1] Based on the Ph.D. Dissertation of D. W. Hoppenjans, May 1968. Supported by National Science Foundation Grant GP-5425.

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