

electrons to a nickel atom⁷ and probably is to be preferred.

This structure also permits a simple explanation of the bonding for which it is convenient to regard the compound as a complex of Ni(0) with the triphenylcyclopropenyl cation. Each nickel is approximately tetrahedrally surrounded by electron pairs, two from bromide anions, one from the carbon monoxide group, and one from the cyclopropenyl group. The latter is assumed to be parallel to the (111) face of the corresponding cube. There will then be effective overlap between the cyclopropenyl $E(\pi)''$ (D_{3h}) and the d_{z^2} and $d_{x^2-y^2}$ $E(Td)$ orbitals.

Although the triphenylcyclopropenyl radical should show Jahn-Teller instability, it is probably complexed as an equilateral triangle. In tetraphenylcyclobutadiene-iron tricarbonyl the cyclobutadiene is square-planar⁸ although this configuration is probably an order of magnitude less favored than is the equilateral triangle one for triphenylcyclopropenyl.⁹

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(7) This resembles the suggestion first made by J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953), to explain the bonding of ethylene to transition metals.

(8) R. P. Dodge and V. Schomaker, *Nature*, **186**, 798 (1960).

(9) L. C. Snyder, *J. Phys. Chem.*, **66**, 2299 (1962).

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The Polarized Crystal Spectra of Malonate Complexes

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For the interpretation of the polarized spectra of a crystalline compound the relative orientations in the unit cell of the chromophoric ions must be known. If these ions occupy equivalent crystallographic positions, the interpretation of the spectra is straightforward,¹ but if they do not, the task is more difficult. It follows that in ideal cases information about the relative positions of ions in a crystal can be obtained from polarized spectra by comparison with results obtained from known systems. Here the polarized spectra of ammonium tris(malonato)ferrate(III) are presented and compared with those of $\text{NaMg}[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 9\text{H}_2\text{O}$. The spectra of the tris(malonato)chromate(III) ion obtained from a single crystal of $(\text{NH}_4)_3[(\text{Fe}, \text{Cr})(\text{C}_3\text{H}_2\text{O}_4)_3]$ are presented and discussed.

(1) T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, **35**, 1809 (1961).

Experimental

Large light green crystals of ammonium tris(malonato)ferrate(III) were grown from aqueous solution as described by Jaeger and Mees.² A face exhibiting maximum dichroism was chosen by examination under the microscope; of the other two planes perpendicular to this face one exhibited similar dichroism and the other very little. The absorption spectra were recorded with a Cary Model 14 spectrophotometer, using a Nicol prism in some cases and a Polaroid lens in other cases. The spectra are presented in Fig. 1. The thickness of the crystal was measured with the microscope and found to be 1.95 mm. In order to minimize errors in the calculation of ϵ due to imperfections, the density of single crystals of $(\text{NH}_4)_3[\text{Fe}(\text{C}_3\text{H}_2\text{O}_4)_3]$ was determined by the volume displacement method and was found to be 1.47 g./cm.³. The extinction coefficients of the spectral bands were calculated from the peak heights of several unpolarized spectra using the formula $I = I_0 10^{-\epsilon cl}$ where the concentration is in moles per liter of crystal and the path length, l , is in cm. These data, which are not too precise because of experimental difficulties, are presented in Table I.

TABLE I
SPECTRAL DATA FOR THE TRIS(MALONATO)METALLATE IONS

Ion	Band max., cm. ⁻¹	Transition	$\Delta\nu$, cm. ⁻¹	ϵ
$\text{Fe}(\text{C}_3\text{H}_2\text{O}_4)_3^{3-}$	25,800	${}^6A_1 \rightarrow {}^4T_2({}^4D)$
	22,880	${}^6A_1 \rightarrow {}^4A_1, {}^4E$	800	2.4
	22,660			
	15,720	${}^6A_1 \rightarrow {}^4T_2$	2700	0.9
$\text{Cr}(\text{C}_3\text{H}_2\text{O}_4)_3^{3-}$	11,090	${}^6A_1 \rightarrow {}^4T_1$	3400	0.7
	17,060	${}^4A_2 \rightarrow {}^4E$...	^a
	17,240	${}^4A_2 \rightarrow {}^4A_1$...	

^a $\epsilon_\pi/\epsilon_\sigma = 1.4$.

Results and Discussion

The Spectra of $(\text{NH}_4)_3[\text{Fe}(\text{C}_3\text{H}_2\text{O}_4)_3]$.—The bands in the spectrum which are listed in Table I can be assigned with a great deal of certainty by reference to the Sugano-Tanabe diagram. The experimentally obtained energies, which are in good agreement with those obtained by Jørgensen,³ were fitted to the parameters Dq , B , and C assuming an octahedral field. Values for these parameters of 1419, 609, and 3135 cm.⁻¹, respectively, were obtained. Piper and Carlin¹ have reported values of 1522, 609, and 3283 cm.⁻¹ for the corresponding oxalate complex. The energy of the ${}^6A_1 \rightarrow {}^4T_2({}^4D)$ transition, which could only be observed at liquid nitrogen temperature because of the tailing of an ultraviolet band, agrees well with the energy predicted using the experimental parameters.

By analogy with the spectra of $\text{NaMg}[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 9\text{H}_2\text{O}$, the intensities of the ${}^6A_1 \rightarrow {}^4T_1({}^4G)$ and ${}^6A_1 \rightarrow {}^4T_2({}^4G)$ bands in the two polarizations indicate that the face chosen for this study was parallel to the trigonal axis of the tris(malonato)iron(III) ion and furthermore indicate that these ions are packed in the crystal with their trigonal axes parallel or nearly parallel to one another. The splitting of the ${}^4A_1, {}^4E$ level which is degenerate in an octahedral field is a result of the lower symmetry associated with the tris(malonato)ferrate(III) ion. It is interesting to note that the splitting

(2) F. M. Jaeger and R. T. A. Mees, *Proc. Acad. Sci. Amsterdam*, **20**, 283 (1918).

(3) C. K. Jørgensen, *Discussions Faraday Soc.*, **26**, 110 (1958).

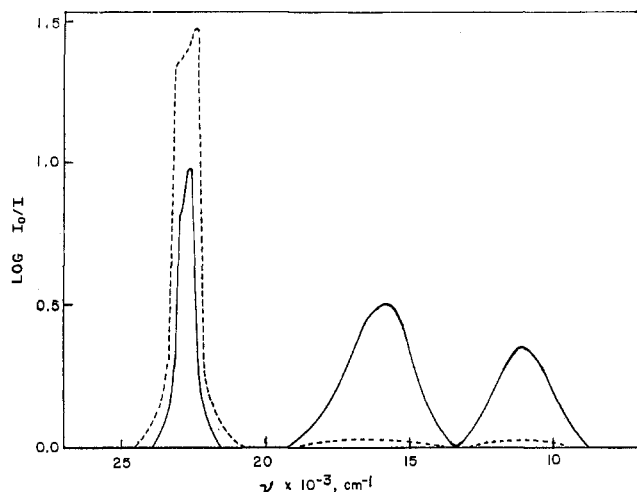


Fig. 1.—Polarized spectra of $(\text{NH}_4)_3\text{Fe}(\text{C}_3\text{H}_2\text{O}_4)_3$. The solid line is the σ polarization and the dashed line is the π polarization.

is less than half as large as that observed for the oxalato complex,¹ for which a greater trigonal distortion would not be unexpected. This observation is further supported by the spectra of $\text{Cr}(\text{C}_3\text{H}_2\text{O}_4)_3^{3-}$ (see below).

The Spectra of the Trismalonatochromate(III) Ion.—This research was initiated to study the differences that might be expected to exist in the spectral properties of malonato and oxalato complexes. A concerted effort was made to find a proper colorless host malonato complex for trivalent first transition series metal ions. This goal has not yet been achieved, but trismalonatochromate(III) ions have been introduced as impurities in the ammonium trismalonatoferrate(III) crystals and the polarized spectra recorded. After subtracting the spectrum for the iron complex, the results which are listed in Table I can be compared with those for the oxalato complex. Although the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ transition could not be observed because of intense bands in the iron compound, the close agreement of $\epsilon_\pi/\epsilon_\sigma$ of the low-energy band with that of the oxalato complex indicates that the $\text{Cr}(\text{C}_3\text{H}_2\text{O}_4)_3^{3-}$ ions occupy positions which are identical with those of the $\text{Fe}(\text{C}_3\text{H}_2\text{O}_4)_3^{3-}$ ions.

The trigonal splitting parameter, K , was estimated from the splitting of the ${}^4\text{T}_2$ level into ${}^4\text{A}_1$ and ${}^4\text{E}$ in the trigonal field and was found to be -120 cm^{-1} . Although the magnitude of K so determined may not be very reliable, the sign of K is.^{3,4} There are two possible contributions to an error in K . These are the uncertainty in the spectrum of $\text{Fe}(\text{C}_3\text{H}_2\text{O}_4)_3^{3-}$ which was subtracted from the spectrum of $\text{Cr}(\text{C}_3\text{H}_2\text{O}_4)_3^{3-}$ in the σ polarization and misalignment of the C_3 molecular axes in the crystal. Both of these would tend to decrease the absolute value of K . Piper and Carlin⁵ have shown that the sign of K depends on the polar angle and thereby on the O–M–O angle within the chelate ring if the radial parameters are unchanged. Since there is little change in $10Dq$ in going from $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ to $\text{Cr}(\text{C}_3\text{H}_2\text{O}_4)_3^{3-}$, there is evidently little

(4) T. S. Piper, *J. Chem. Phys.*, **35**, 1240 (1961).

(5) T. S. Piper and R. L. Carlin, *ibid.*, **36**, 3330 (1962).

change in the radial parameters. The change in sign of K from 270 cm^{-1} for $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$, which has an O–Cr–O angle of $83\text{--}85^\circ$, to -120 cm^{-1} for $\text{Cr}(\text{C}_3\text{H}_2\text{O}_4)_3^{3-}$ indicates that the O–Cr–O angle in the malonate chelate ring is slightly greater than 90° .

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The Formation of Some Volatile Hydrides from Lower Oxides

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As part of a study of the chemistry of some lower oxides, samples of solid silicon monoxide were made by quenching the vapor over heated mixtures of silicon and silica. According to Erasmus and Personn² and Grube and Speidel,³ quenched silicon monoxide, in contrast to material made by slower cooling from the vapor, is completely soluble in hydrofluoric acid. When the silicon monoxide made in this work was treated with 10% HF it dissolved completely with evolution of hydrogen and volatile silanes. This is thought to be the first report of this reaction of silicon monoxide.

The silicon monoxide was made by heating equimolar mixtures of finely divided 99.8% pure silicon and 99.7% pure silica under vacuum in an alumina tube furnace to $1350\text{--}1400^\circ$. The vapor was condensed on a water-cooled copper cold finger in the hot zone of the furnace. The monoxide was obtained as a brown-black solid, commonly in the form of needles oriented perpendicular to the cold finger surface. On exposure to air the solid frequently caught fire, and if allowed to oxidize more slowly it became a light brown color. No evidence of crystalline character could be obtained by X-ray diffraction studies on the solid.

Samples of 100–500 mg. of the solid were dissolved in 10% HF and the evolved silanes were trapped and separated gas chromatographically. Mono-, di-, tri-, iso- and *n*-tetra-, iso- and *n*-penta-, and iso- and *n*-hexasilane were identified from the mixture by their gas chromatographic retention times and in some cases by physical measurements. The same hydrides are formed by acid hydrolysis of magnesium silicide,⁴ but the proportions of the different silanes are not exactly the same from the two sources. Table I shows

(1) Address communications to this author at Department of Chemistry Rice University, Houston, Texas.

(2) H. deW. Erasmus and J. A. Personn, *J. Electrochem. Soc.*, **95**, 316 (1949).

(3) G. Grube and H. Speidel, *Z. Elektrochem.*, **53**, 339 (1949).

(4) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933; K. Borer and C. S. G. Phillips, *Proc. Chem. Soc.*, 189 (1959).