the d_{z^2}, d_{xz}, d_{yz}, and d_{xy} orbitals, with a square-planar configuration.

Gold trifluoride belongs to the space group $P6_1$ or $P6_12$. Accordingly, the gold atoms must all be equivalent in the crystal and also must be related by the 6_1-screw axis. The structure probably consists of either monomeric AuF_3 (which we believe unlikely) or infinite spiral chains parallel to the *c* axis. The space group rules out the possibility of dimers.

The spiral model would include two distinct kinds of fluorine atom, one in a special position of sixfold symmetry and the other in a general position. The former could be in a position (a) of $P6_12$ and would be "bridging fluorines," linking AuF_2 groups in infinite spirals about the sixfold screw axis. Four fluorines would be bonded to each gold atom, and the configuration of these four fluorines about the gold atoms could be approximately planar and square. The intensities of reflections in the Weissenberg photographs suggest that the gold atoms might lie in special positions (b) of space group $P6_12$. An estimate of the single-position parameter of the gold atom could be made from (h00) intensities. A preliminary calculation of relative powder pattern line intensities was made with Au only, $x_{(\mathrm{Au})} = 0.24$. Satisfactory agreement between most observed and calculated intensities was obtained, and, though these Au parameters give no direct indication of F positions, a spiral chain model could be developed from the Au skeleton in the symmetry framework of $P6_12$. However, a more complete and accurate set of single-crystal data is needed for further calculations.

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A π-Cyclopropenyl Derivative of Nickel Carbonyl

BY E. W. GOWLING AND S. F. A. KETTLE

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There are two reports in the literature[1,2] of unsuccessful attempts to stabilize the triphenylcyclopropenyl radical by forming a π-complex with a transition metal atom.[3] We now report that triphenylcyclopropenyl bromide or chloride[4] reacts with nickel carbonyl forming a complex which gives strong evidence for the presence of this radical.

Nickel carbonyl added to a methanolic solution of triphenylcyclopropenyl bromide at room temperature under nitrogen gave a two-phase system of which the upper layer, essentially methanolic triphenylcyclopropenyl bromide, soon became red. Carbon monoxide was evolved. After several minutes brick-red crystals formed at the interface.[5] The reaction was complete within 1 hr. at room temperature or within a few minutes if the reaction mixture was gently warmed. The product was triphenylcyclopropenyl nickel carbonyl bromide. *Anal.* Calcd. for $NiCOBr(C_6H_5)_3C_3$: C, 60.9; H, 3.5; Ni, 13.5; CO, 6.5; Br, 18.4. Found: C, 59.2; H, 3.5; Ni, 12.1; CO, 6.6; Br, 19.2. The chloride was similarly prepared. *Anal.* Calcd. for $NiCOCl(C_6H_5)_3C_3$: C, 67.8; H, 3.9; Cl, 9.1. Found: C, 67.9; H, 4.3; Cl, 9.2.

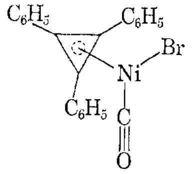
Triphenylcyclopropenyl nickel carbonyl bromide is sparingly soluble in both tetrahydrofuran and methanol to give pale red solutions instantly oxidized on exposure to air. The solid, in contrast, is fairly air stable, only decomposing completely after several weeks exposure. Under vacuum the solid appears stable indefinitely.

Attempts to purify the reaction product failed because of its low solubility and oxygen sensitivity in solution. It decomposes at *ca.* 120° under vacuum without subliming.

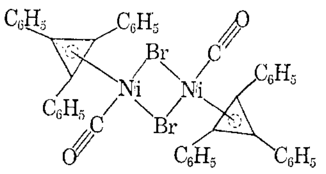
The infrared spectrum in the carbonyl region shows a sharp peak at 2039 cm.$^{-1}$ but no strong absorption at either 1710 or 1400 cm.$^{-1}$, eliminating structures analogous to those found by Coffey[1] or Chatt and Guy,[2] although the analysis is consistent with the former if only the terminal carbonyl is liberated during the analysis for CO. *Anal.* Calcd. for $C_{23}H_{15}BrNiO_2$: C, 59.8; H, 3.3; Ni, 12.7; CO, 6.1; Br, 17.3.

The solid is weakly paramagnetic (about 0.2 unpaired electron) at room temperature, but this may be due to an impurity.

The simplest formulation of the compound is as I but a more plausible structure is II. The infrared spectrum suggests that the latter has a center of symmetry.



I



II

Higher polymers are also possible formulations but the sharpness of the 2039 cm.$^{-1}$ infrared peak and its failure to split in either a mull or potassium bromide disk make these unlikely. Structure II, which is similar to that found for tetramethylcyclobutadiene nickel dichloride,[6] satisfies the "inert gas rule" if the $A_2''(\pi)$ of each cyclopropenyl radical donates two

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(1) C. E. Coffey, *J. Am. Chem. Soc.*, **84**, 118 (1962).

(2) J. Chatt and R. G. Guy, *Chem. Ind.* (London), 212 (1963).

(3) R. B. King, *Inorg. Chem.*, **2**, 642 (1963), reports that the reaction between triirondodecacarbonyl and 1,3,3-trimethylcyclopropene does not yield a complex with the triangular moiety π-bonded to the transition metal.

(4) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 2367 (1961).

(5) This method resembles one recommended for the preparation of crystals for X-ray measurements (see C. W. Bunn, "Chemical Crystallography," Oxford, 1946, p. 23).

(6) J. D. Dunitz, H. C. Mez, O. S. Mills, and H. M. M. Shearer, *Angew. Chem.*, **72**, 755 (1962); *Helv. Chim. Acta*, **45**, 647 (1962).

electrons to a nickel atom[7] 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-planar[8] although this configuration is probably an order of magnitude less favored than is the equilateral triangle one for triphenylcyclopropenyl.[9]

Acknowledgment.—We are indebted to the International Nickel Company (Mond) Limited for a gift of nickel carbonyl and to the Department of Industrial and Scientific Research for a maintenance grant (E. W. G.).

[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 trismalonatoferrate(III) are presented and compared with those of $NaMg[Fe(C_2O_4)_3]\cdot 9H_2O$. The spectra of the trismalonatochromate(III) ion obtained from a single crystal of $(NH_4)_3[(Fe,Cr)(C_3H_2O_4)_3]$ are presented and discussed.

Experimental

Large light green crystals of ammonium trismalonatoferrate(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 $(NH_4)_3[Fe(C_3H_2O_4)_3]$ 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 TRISMALONATOMETALLATE IONS

Ion	Band max., cm.$^{-1}$	Transition	$\Delta\nu$, cm.$^{-1}$	ϵ
$Fe(C_3H_2O_4)_3^{3-}$	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
	11,090	$^6A_1 \rightarrow {}^4T_1$	3400	0.7
$Cr(C_3H_2O_4)_3^{3-}$	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 $(NH_4)_3[Fe(C_3H_2O_4)_3]$.—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 Carlin[1] 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 $NaMg[Fe(C_2O_4)_3]\cdot 9H_2O$, 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 trismalonatoiron(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 trismalonatoferrate(III) ion. It is interesting to note that the splitting

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

[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).