TABLE III

$AgClO_4$ COMPLEXES IN CD_3COCD_3

Concn × 10, M Ag^+	Concn × 10, M Olefin	$\Delta\delta_{obsd}$, Hz	$\Delta\delta_{max}$, Hz	K	Av K
		Cyclohexene			
1.9	3.8	18	51	8.7	8.1
3.7	3.7	29		8.2	
3.7	1.5	34		7.4	
4.9	3.9	33		7.4	
7.6	3.6	41		8.8	
		1-Methylcyclohexene			
1.6	3.2	4	49	0.80	0.72
3.1	6.2	6		0.64	

Discussion

The results which we have obtained clearly show that a variety of silver(I)–olefin complexes do dissociate in organic solvents to give a mixture of free and complexed olefin and free $Ag(I)^+$. Within the limits of experimental technique and some assumptions in the calculations, nmr appears to be the most efficient tool available for determining the equilibrium constants in a wide variety of organic media.

The accuracy of the determination of the equilibrium constants is greatly dependent on the accuracy of the measurement of $\Delta\delta_{max}$ and on the correctness of the assumption that equilibrium 2 can be ignored.[12] The ideal situation for the determination of $\Delta\delta_{max}$ would be one involving a slow enough equilibrium so that separate resonances for the free and for the complexed olefin could be seen. This is not the case for any of the systems which we have studied and an attempt at resolving this question with cooling methods offered no hope of success down to −55° with $AgBF_4 \cdot C_6H_{10}$ in CD_3COCD_3 although a slight increase in $\Delta\delta_{obsd}$ was noted.

Although the method which we were forced to use to determine $\Delta\delta_{max}$ is not ideal, we feel that it is sound nonetheless. In all cases we added sufficient excess silver salt so that some solid remained undissolved in the bottom of the nmr tube. This allowed for the removal of free olefin from solution as the solid complex. While we must admit to having no exact knowledge of the position of the equilibrium for this latter process, we must assume that it is far enough to the side of removal of olefin from solution so that nmr measurements on the saturated solutions recorded spectra of complexed olefin only. To the extent that this latter assumption is incorrect, $\Delta\delta_{max}$ as recorded is too small and K, as presently calculated, is too large. This possibility, which is greatest when K is smallest, does define an area of uncertainty and indicates that the range of K in this series of solvents may be greater than we have calculated.[13]

We have ignored the possibility of the participation of equilibrium 2 and assumed that it is not significant. The validity of this assumption is shown by the fact that, in most cases, K does not vary considerably with concentration. Deviations at higher concentrations and large K values indicate that some $[Ag \cdot 2(\text{olefin})]^+$ formation may be occurring.

One important question raised by the current work is why earlier workers in this field did not detect the equilibria which we have found. We believe that the answer lies in the methods of detection employed. Quinn's group searched for equilibria by the conventional technique of lowering the probe temperature while keeping the species concentration constant.[2b] This technique has been applied with great success in the past, but it is limited, perforce, to those situations in which the equilibria are temperature dependent. Clearly, the Ag(I)–olefin equilibria are only very slightly temperature dependent and their detection is possible only by use of the more time-consuming method of making measurements at different concentrations.

If the original intention of using nmr in these studies (to obtain information concerning the nature of the silver–olefin bond) is to be fulfilled, then perhaps the really significant relationship which should be considered is that between the equilibrium constants of a series of complexes in one solvent and the strength of the coordinate bond.

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[12] If the energy level of $[Ag \cdot 2(\text{olefin})]^+$ is less than that of $[Ag \cdot \text{olefin}]^+$, then K_2 can become an important factor, especially for large K_1. The necessity for ignoring equilibrium 2 is dictated by the fact there is no way of measuring $\Delta\delta_{max}$ for $[Ag \cdot 2(\text{olefin})]^+$, and any attempt to include a term for K_2 thus renders the algebraic equations insoluble.

[13] The K values (Table I) for CH_3NO_2 do vary considerably with concentration and may indicate participation of equilibrium 2. In this case we would suspect that K_1 as measured is much smaller than the real K_1 and that the energy level of $[Ag \cdot 2(\text{olefin})]^+$ is much less than that of $[Ag \cdot \text{olefin}]^+$ in this solvent.

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d-Orbital Orderings of Tetragonal Chromium(III) Complexes

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The considerable interest in low-symmetry complexes of the first transition series has generated a large number of publications, both experimental and theoretical.[1–5] Since the work of Wentworth and Piper on Co(III) complexes,[2] the analysis of low-symmetry complexes has been extended to Ni(II),[1] Fe(II),[3] and Cr(III).[4] The analysis of Ni(II)[1] and Fe(II)[3] complexes has been adequately stated elsewhere and valuable insights into the electronic structure of the complexes were obtained. The case of Cr(III) has presented a variety of problems resulting from qualitative interpretation of the experimental data. These problems are differing

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[1] (a) D. A. Rowley and R. S. Drago, *Inorg. Chem.*, **7**, 795 (1968); (b) D. A. Rowley and R. S. Drago, *ibid.*, **6**, 1092 (1967).

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TABLE I

ABSORPTION SPECTRA AND SPLITTING PARAMETERS FOR CHROMIUM COMPLEXES WITH D_{4h} SYMMETRY

Complex	Band max, kK				Ref	Splitting parameters					
						B	*Dq*	*Ds*	*Dt*	$\delta\pi$	$\delta\sigma$
$Cr(en)_2Br_2^{+}$ [a]	16.78	21.79	24.81	26.95	4	730	2179	420	534	705	−1421
$Cr(en)_2(H_2O)_2^{3+}$ [a]	19.68	22.47	27.47	29.67	4	745	2247	−382	319	1370	−100
$Cr(en)_2(OH)_2^{+}$ [a]	18.25	19.92	25.19	30.30	4	1055	1992	1097	150	−1270	−1927
$Cr(en)_2(H_2O)(OH)^{2+}$ [a]	18.02	20.20	25.16	29.41	4	958	2020	871	214	−772	−1708
$[Cr(en)_2F_2]ClO_4$ [d]	18.5	21.7	25.3	29.3	5	692	2170	−741	362	2017	+433
$Cr(NH_3)_4F_2^{+}$ [a]	18.1	20.9	24.7	28.2	6	667	2090	−640	317	1752	+341
$Cr(en)_2Cl_2^{+}$ [a]	17.54	21.88	25.38	27.70	4	750	2188	453	461	473	−1317
$[Cr(en)_2Cl_2]Cl$ [b]	17.3	22.1	25.3	26.5	8	665	2210	254	519	917	−1354
$[Cr(en)_2Cl_2]Cl$ [c]	17.71	22.73	25.08	27.78	*e*	673	2273	509	528	557	−1753

[a] Solution spectrum. [b] Polarized single-crystal spectrum (300°K). [c] Mull spectrum (80°K). [d] Polarized single-crystal spectrum (4°K). [e] This work.

assignments of electronic transitions and differing d-orbital orderings. We therefore have undertaken a systematic investigation of tetragonal Cr(III) complexes in order to resolve these problems. Our initial study centered on an evaluation of the literature data for complexes of the form $Cr(en)_2X_2^{n+}$ where X = F^-, Cl^-, Br^-, H_2O, or OH^-.[4-6] We report here the results of this study.

Collected in Table I are the experimental data currently available for complexes with D_{4h} symmetry. Assignments of the observed transition energies are made on the basis of the best available evidence. The calculations fitting theory to experiment were performed as described in a previous paper.[1] It should be noted that, with four transitions observed and four parameters (*B*, *Dq*, *Ds*, *Dt*) needed to describe the transition energies of the system, necessarily there is no independent check on the parameters obtained. Thus the derived parameters are only as good as the experimental data.

The derived parameters calculated in this study differ significantly from those already published in the literature.[4,7] This is due to the fact that the method used reproduces the experimental data exactly. No approximations are made concerning the relationship between *Ds* and *Dt* or the values of *Dq* and *B*. These results convey more accurately the effect of the low-symmetry field on the electronic structure of the chromium(III) complexes.

We have made assignments based on the results of published polarized single-crystal studies[5,8] and then by analogy to the similar compounds. The order of the transition energies is $^4B_{1g} \rightarrow {}^4E_g$, $^4B_{2g}$, ^4E_g, $^4A_{2g}$ for the *trans*-difluoro compounds and $^4B_{1g} \rightarrow {}^4E_g$, $^4B_{2g}$, $^4A_{2g}$, ^4E_g for all the other complexes discussed. These results verified by polarized single-crystal spectra are in contrast to those previously reported in the literature.[4,7]

The results obtained from the analysis of the spectra allow us to order the one-electron energy levels of chromium(III). Three different orderings result and they are given below.

(1) $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz}, d_{yz}$. This is the result predicted on the basis of simple crystal field theory, when the ligand along the *z* axis has a smaller *Dq* than those ligands in the *xy* plane. The complexes are $Cr(en)_2(OH)_2^+$ and $Cr(en)_2(OH)(H_2O)^{2+}$.

(2) $d_{x^2-y^2} > d_{z^2} > d_{xz}, d_{yz} > d_{xy}$. The complexes exhibiting this order are $Cr(en)_2X_2^{n+}$ (X = Cl^-, Br^-, H_2O).

(3) $d_{z^2} > d_{x^2-y^2} > d_{yz}, d_{xz} > d_{xy}$. The complexes with this energy level ordering are $[Cr(en)_2F_2]ClO_4$ and $Cr(NH_3)_4F_2^+$.

The striking result observed is that there are 3d orbital orderings for the same type of chromium(III) complex (the *Dq* of the ligands in the *xy* plane is stronger than that of the ligands along the *z* axis). The first d-orbital ordering is that expected on the basis of simple crystal field theory and is similar to the results obtained for nickel(II) complexes.[1] The second ordering in which the d_{xz} and d_{yz} orbitals are located at a higher energy than the d_{xz} orbital is similar to the results obtained for tetragonal cobalt(III) complexes. These axial ligands have the ability to π bond to the metal, which would make the degenerate pair more antibonding than the d_{xy} orbital, since ethylenediamine cannot π bond to the metal.

The most disturbing ordering obtained is no. 3; note that the d_{z^2} orbital lies highest in energy even though the calculated *Dq* for fluoride is less than that of ethylenediamine or ammonia. This implies that the notion that *Dq* is a measure of the interaction of the ligands with the metal d orbital is not valid for these complexes. At this point, there is no consistent interpretation of the varied orderings based on a crystal field approach; thus another method of interpretation must be found.

Such an approach has been advanced by McClure.[9] He defined two parameters, $\delta\pi$ and $\delta\sigma$, where $\delta\pi$ (or $\delta\sigma$) is a measure of the difference between the π (or σ) antibonding ability of the axial and in-plane ligands. The orderings of $\delta\pi$ and $\delta\sigma$ are as follows: for $\delta\pi$, $F^- \gg H_2O > Br^- \gg Cl^- \gg OH^-$; for $\delta\sigma$, $F^- > H_2O \gg Br^- > Cl^- > OH^-$. For comparison, the *Dq* ordering of the axial ligands is $OH^- > H_2O > F^- >$

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[6] J. Glerup and C. E. Schaeffer in "Progress in Coordination Chemistry," M. Cais, Ed., Elsevier Amsterdam, 1960, p 500.

[7] (a) J. R. Perumareddi, *J. Phys. Chem.*, **71**, 3144 (1967); (b) J. R. Perumareddi, *ibid.*, **71**, 3155 (1967).

[8] S. Yamada, *Coord. Chem. Rev.*, **2**, 83 (1967).

[9] D. S. McClure in "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, p 498.

TABLE II

ABSORPTION SPECTRA AND SPLITTING PARAMETERS FOR CHROMIUM COMPLEXES WITH C_{4v} SYMMETRY[a]

Complex	Band max, kK				B	Dq	Ds	Dt	$\delta\pi$	$\delta\sigma$
$Cr(NH_3)_5F^{2+}$ [b]	19.60	21.00	26.20	28.20	713	2100	377	148	−195	−843
$Cr(NH_3)_5Cl^{2+}$ [c]	19.42	21.50	26.60	27.05	639	2150	109	231	414	−597
$Cr(NH_3)_5Br^{2+}$ [c]	18.99	21.50	26.46	26.77	645	2150	88	279	565	−655

[a] Data taken from ref 10. [b] Polarized liquid nitrogen temperature spectrum. [c] Polarized room-temperature spectrum.

$Cl^- > Br^-$. As can be seen, there is no correlation between the σ-antibonding ability of the ligand and the Dq^z of the ligand. This is in direct contrast to the results obtained previously for similar nickel(II) complexes!

It then became of interest to determine if the same d-orbital orderings prevailed in the $Cr(NH_3)_5X^{2+}$ series, where $X^- = Br^-$, Cl^-, or F^-. The same energy level orderings and transition assignments are expected for these complexes as were observed for the analogous trans-disubstituted complexes. The only difference that should be observed is Ds and Dt for the $Cr(NH_3)_5X^{2+}$ should be half those of *trans*-$Cr(NH_3)_4X_2^+$. The available data[10] for the $Cr(NH_3)_5X^{2+}$ are presented in Table II along with the results of the calculations. Assignments based on polarized single-crystal studies indicate the order of the electronic transitions to be ${}^4B_{1g} \rightarrow {}^4E_g$, ${}^4B_{2g}$, ${}^4A_{2g}$, ${}^4E_g$ for all compounds listed. As can be seen for the data presented in Tables I and II Dt for the C_{4v} complexes is almost exactly half the Dt of the corresponding D_{4h} complex.

When the ordering of d orbitals is considered, order no. 2 above is found for the $Cr(NH_3)_5Cl^{2+}$ and $Cr(NH_3)_5Br^{2+}$ complexes and order no. 1 is observed for the $Cr(NH_3)_5F^{2+}$ complex. At present there is no consistent interpretation that can be advanced for both the C_{4v} and D_{4h} complexes.

It should be pointed out that we are trying to compare data that are taken both from solution and from the solid state; this can be somewhat hazardous.[1] Thus a comparison was made with *trans*-$Cr(en)_2Cl_2^+$ in both the solid and liquid states. As can be seen from the data in Table I, the numbers change somewhat, but the general features, such as d-orbital ordering and transition assignments, remain the same.

In conclusion, the results of this study have indicated that crystal field theory breaks down for the *trans*-difluoro complexes of chromium(III) and the results obtained for the D_{4h} complexes can be best explained in terms of the MO approach of McClure. The results for the C_{4v} complexes are not consistent with those of the D_{4h} complexes, and no consistent explanation can be given at this time. Furthermore, the results of the computer fitting of theory to experiment do not allow for approximation and the results obtained are more valuable than those done in any other manner.

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[10] J. A. Stanko, Ph.D. Thesis, University of Illinois, 1967.

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Mössbauer Spectroscopy of Bis(carbollyl)iron Anions and Related Molecules

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A number of ferricinium salts have been examined by means of Mössbauer spectroscopy and the data summarized by Fluck.[1] More recently Herber has reported spectra for related carbollyliron complexes.[2] We have had occasion to reexamine the spectrum of the bis(carbollyl)iron(III) complex and, unlike Herber, obtain an asymmetric quadrupole-split doublet. The origin of this asymmetry is discussed. Data on related ferricinium salts are also reported and the broadness of the single-line absorptions obtained is interpreted as being the result of spin-relaxation processes rather than unresolved quadrupole splitting.

Experimental Section

$(CH_3)_4N[Fe(C_2B_9H_{11})_2]$ generously supplied by Dr. F. P. Olsen of this department was used as received. Its analysis was carried out by A. B. Gygli, Toronto. *Anal.* Calcd for $(CH_3)_4N[Fe(C_2B_9H_{11})_2]$: C, 24.35; H, 8.73; N, 3.55. Found: C, 24.61; H, 8.67; N, 3.65. Reduction of this compound by standard procedures[3] afforded $[(CH_3)_4N]_2[Fe(C_2B_9H_{11})_2]$. The ferricinium salts were prepared according to standard procedures[4,5] or modifications thereof. The tetraphenylborate salt was obtained from an aqueous solution of ferricinium tetrachloroferrate(III) by addition of a saturated aqueous solution of sodium tetraphenylborate.

Mössbauer spectra were recorded on apparatus already described in the literature.[6] Spectra were analyzed by a least-squares-fit program; the solid lines in the figures are the computed Lorentzian line shapes.

Results and Discussion

The Mössbauer data are summarized in Table I and

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