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.

Acknowledgment.—The support of this work by National Science Foundation Grant GU-3287 is gratefully acknowledged.

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

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Received June 2, 1970

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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TABLE I

MÖSSBAUER PARAMETERS FOR $(CH_3)_4N[Fe(C_2B_9H_{11})_2]$ AND RELATED COMPOUNDS

No.	Compd	Temp, °K	IS,[a] mm/sec	QS, mm/sec	Line width, mm/sec
1	$(CH_3)_4N[Fe(C_2B_9H_{11})_2]$[b]	295	0.41	0.60	0.61 0.63
		80	0.50	0.64	0.73 0.62
2	$[(CH_3)_4N]_2[Fe(C_2B_9H_{11})_2]$	295	0.48	2.75	0.24
		80	0.56	2.80	0.27
3	$(\pi\text{-}C_5H_5)Fe(C_2B_9H_{11})$[c]	140	0.608	0.529	
4	$(\pi\text{-}C_5H_5)_2Fe$	80	0.79	2.42	0.31
5	$[(\pi\text{-}C_5H_5)_2Fe][FeCl_4]$	80	0.58		0.35
			0.81		0.43
6	$[(\pi\text{-}C_5H_5)_2Fe]$pic	80	0.82		0.49
7	$[(\pi\text{-}C_5H_5)_2Fe][BF_4]$	80	0.84		0.61
8	$[(\pi\text{-}C_5H_5)_2Fe][PF_6]$	80	0.83		0.64
9	$[(\pi\text{-}C_5H_5)_2Fe]Cl$	80	0.80		0.70
10	$[(\pi\text{-}C_5H_5)_2Fe]B(C_6H_5)_4$	80	0.84		0.77

[a] Isomer shifts are relative to sodium nitroprusside at 295°K and are accurate to ±0.01 mm/sec. [b] The relative areas of the low-to-high velocity components of the quadrupole doublet are as follows: 295°K, 1:1.6; 80°K, 1:1.2. [c] Data taken from ref 2.

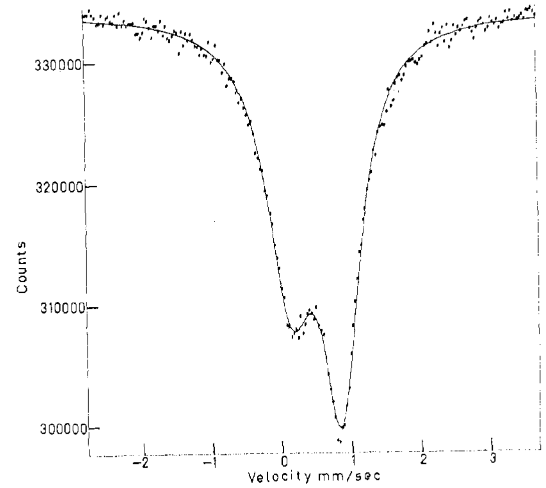

Figure 1.—Mössbauer spectrum of $(CH_3)_4N[Fe(C_2B_9H_{11})_2]$.

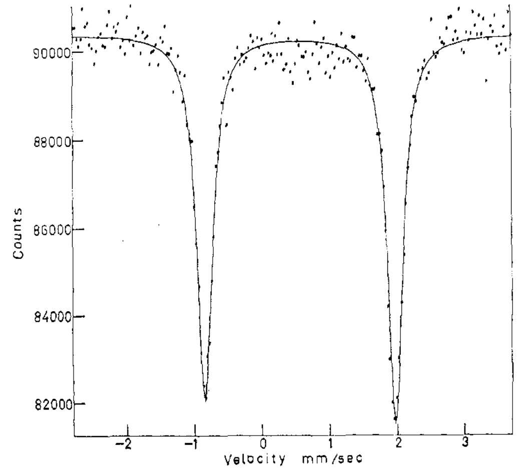

Figure 2.—Mössbauer spectrum of $[(CH_3)_4N]_2[Fe(C_2B_9H_{11})_2]$.

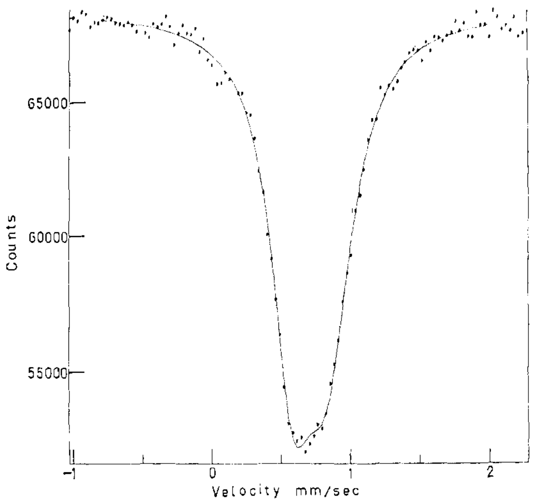

Figure 3.—Mössbauer spectrum of $[(\pi\text{-}C_5H_5)_2Fe]FeCl_4$.

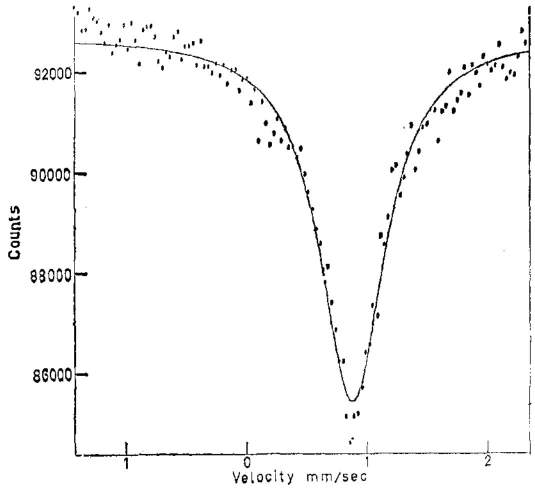

Figure 4.—Mössbauer spectrum of $[(\pi\text{-}C_5H_5)_2Fe]BF_4$.

Figures 1–4. Our data for the bis(carbollyl)iron **1** do not at first sight seem to agree with those reported previously.[2] The spectrum in Figure 1 clearly shows an asymmetric quadrupole-split absorption whereas Herber[2] fitted his spectrum to a single broad absorption. Close examination of the previously reported spectrum[2] reveals a discontinuity in the absorption envelope, indicating that this spectrum is in fact the same as that shown here, though less well resolved. Since the higher velocity component is the more intense, the reported isomer shift[2] is weighted toward this component and is therefore higher than the true value.

This asymmetry is of considerable interest and could arise for one or more of the following reasons. (i) The sample could be contaminated by an iron-containing impurity having a single-line resonance which overlaps with the higher velocity component of the quadrupole-split spectrum. (ii) If the compound packs in the holder in some preferred crystal orientation, then the two components of the quadrupole-split absorption would have different intensities depending upon the angle of the incident γ ray to the axis of the electric field gradient. (iii) There is anisotropy of the recoil-free fraction, commonly known as the Gol'danskii effect[7] but first described mathematically by Karyagin.[8] (iv) There is line asymmetry due to spin–lattice or spin–spin relaxation processes.

The red crystalline compound **1** gave a satisfactory

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analysis making the probability of impurities unlikely. Reduction of **1** gave the ferrocene analog (**2**) having the Mössbauer spectrum shown (Figure 2): no impurity peaks were detected. Furthermore oxidation of **2** back to **1** resulted in a Mössbauer spectrum identical with that shown in Figure 1. Sampling methods used by Gibb and coworkers[9] which were successful in removing the asymmetry in the case of $Fe_2(CO)_9$ produced no effect on our spectrum. Recording the spectrum at 45° to the incident γ ray also had no effect upon the asymmetry. Clearly neither impurities nor preferred crystal packing are causing the observed effect.

We note that the asymmetry increases with increasing temperature which would appear to favor possibility (iii). However if this is an example of a Gol'danskii effect, one might also have expected $(\pi\text{-}C_5H_5)Fe(C_2B_9H_{11})$ to show a similar asymmetry. This is not the case: the spectrum for this compound is observed as a relatively sharp equal intensity doublet. While a Gol'danskii effect is a possibility, the broad lines suggest that a spin-relaxation mechanism is also operating; the most likely possibility being *via* a spin–spin mechanism. A broadening of resonance lines has been observed for Fe^{3+} when it is in low concentration in a crystal lattice or when the Fe^{3+} is incorporated in large molecules such as $Fe^{III}(acac)_3$.[10] In the case of $Fe(C_2B_9H_{11})_2^-$, the Fe^{3+}'s being sandwiched between two large carborane fragments may not be able to interact with one another very effectively with the result that the spin–spin relaxation process is slowed down and the lines are broadened (Table I). Since the $\pm{}^3/_2 \rightarrow \pm{}^1/_2$ and $\pm{}^1/_2 \rightarrow \pm{}^1/_2$ transitions will not relax at the same rate, an asymmetry will be created. That the lines appear of normal width in the cyclopentadienylcarbollyl complex reported by Herber[2] lends some support to a relaxation process. Replacement of one carbollyl group by a cyclopentadienyl group would considerably reduce the size of the molecule, and furthermore no cation is required, thus allowing a closer interaction between Fe(III) spins and hence sharper resonance lines. The broad asymmetric doublet could therefore be the result of a spin–spin relaxation process with the possibility of a Gol'danskii effect also present.

The values obtained for the quadrupole splittings of the bis(1,2-carbollide) ions **1** and **2** are completely analogous to the corresponding bis-cyclopentadiene case. A large quadrupole splitting for **2** (2.8 mm/sec) collapses to a much smaller splitting for **1** (0.6 mm/sec), presumably for the same reasons as for the cyclopentadiene analogs.[11] The values for the bis-carbollyl compounds are larger than those obtained for the corresponding cyclopentadienide complexes (Table I), indicating that there is additional asymmetry. This presumably arises because the three borons of the C_2B_3 face of the carborane icosahedron do not make exactly the same contribution as carbon atoms. In line with this is the lower value (0.529 mm/sec) for the mixed cyclopentadienecarbollyl complex reported by Herber.[2] One notes also a marked trend in isomer shift to more positive values as the 1,2-carbollyl ligands are replaced by cyclopentadienide groups for both the formally iron(III) and iron(II) series. There is clearly a higher "s" electron density at the iron nucleus in the carborane complexes than in the ferrocenes probably indicating a more effective removal of metal d electrons *via* π bonding.

Mössbauer parameters for a number of ferricinium salts have been summarized by Fluck[1] where apparent changes in isomer shift and quadrupole splitting are noted as the anion varies. The results reported here indicate that the anion has little effect, the isomer shift values being virtually constant at ~0.82 mm/sec in agreement with the value for the picrate previously reported.[12]

Tracer experiments by Stukan[13] have established the structure of $(C_5H_5)_2Fe_2Cl_4$ as ferricinium tetrachloroferrate(III). This should yield two separate Mössbauer resonances; Figure 3 shows two lines, incompletely resolved, one due to $(C_5H_5)_2Fe^+$ with the characteristic shift of 0.81 mm/sec and another due to $FeCl_4^-$ at 0.58 mm/sec. This latter value agrees well with the reported shifts for other $FeCl_4^-$ salts.[14]

The results of Stukan[13] do not eliminate the possibility of interaction between cation and anion which might result in a distorted ferricinium ion as suggested by Maitlis.[15] Such a distortion would be expected to result in changes in both IS and QS. Neither Mössbauer parameter is detectably changed and we therefore conclude that interaction between cation and anion is very weak if present at all.

Various quadrupole splitting parameters are quoted for ferricinium salts,[1] varying from 0.1 up to 0.76 mm/sec for the tetrafluoroborate salt.[16] All our preparations of this latter compound produced a single-line Mössbauer spectrum with no evidence for any quadrupole splitting (Figure 4). It will be noted from Table I that the line widths at half-height are all quite large for the ferricinium salts, and it may well be a temptation to attribute this broadness to unresolved quadrupole splitting. However, we feel that a more reasonable explanation lies in the relaxation effect discussed above. In this regard it should be noted that the ferricinium salt with the narrowest lines contains a paramagnetic anion, *i.e.*, $FeCl_4^-$, and relaxation between spins might be expected to be more rapid and hence produce narrower lines. A slower relaxation, in addition to causing broadening, would also produce deviations from Lorentzian line shapes and account for the poor fit in Figure 4.

Acknowledgment.—Thanks are due to the National Research Council of Canada for financial assistance.

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