CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MICHIGAN STATE UNIVERSITY, EAST LANSING, MICHIGAN 48823

Nuclear Magnetic Resonance Studies of Ligand-Exchange Processes. II. Kinetics of Configurational Rearrangement for Some Mixed β-Diketonate Complexes of Gallium(III)[1]

BY THOMAS J. PINNAVAIA, JOHN M. SEBESON, II, AND DAVID A. CASE

Received September 9, 1968

Nmr studies of $Ga(acac)_2(hfac)$ in dichloromethane and of $Ga(acac)_2(bzbz)$ in benzene, where acac = acetylacetonate, hfac = hexafluoroacetylacetonate, and bzbz = dibenzoylmethanate, have shown that the molecules undergo intramolecular configurational rearrangement processes which result in exchange of nonequivalent terminal methyl groups on the acac ligands. First-order rate constants for the rearrangement processes have been determined by line-broadening techniques. The rate of methyl group exchange at 25° for $Ga(acac)_2(hfac)$ is *ca.* 10^4 times larger than the rate for $Ga(acac)_2(bzbz)$. Activation energies and activation entropies were found to be, respectively: 14.5 ± 1.1 kcal/mol and 1.7 ± 4.4 eu for $Ga(acac)_2(hfac)$; 20.6 ± 2.7 kcal/mol and 3.5 ± 8.0 eu for $Ga(acac)_2(bzbz)$. The activation energies are discussed briefly and are compared with available parameters for terminal group exchange in other group IIIb metal β-diketonates.

Introduction

Gallium(III) acetylacetonate, $Ga(acac)_3$, undergoes ligand-exchange reactions with gallium(III) hexafluoroacetylacetonate, $Ga(hfac)_3$, or gallium(III) dibenzoylmethanate, $Ga(bzbz)_3$, in organic solvents to give both of the possible mixed-ligand complexes.[2] The products $Ga(acac)_2(hfac)$ and $Ga(acac)_2(bzbz)$ have idealized C_2 symmetry and should give rise to two equally intense methyl proton nmr lines. It is possible, however, to observe time-averaged methyl resonances for both compounds, because of rapid configurational rearrangement processes which exchange methyl groups between the two nonequivalent environments. Using nmr line-broadening techniques, we describe here the kinetics of the rearrangement processes.

Experimental Section

$Ga(acac)_2(hfac)$ and $Ga(acac)_2(bzbz)$ were prepared by equilibrating mixtures of the corresponding parent complexes at room temperature. No attempt was made to isolate the products from the equilibrium mixtures, because the equilibria would be readily reestablished on dissolution of the complexes under ordinary conditions. The molar fraction of total ligand present as acetylacetonate was 0.667 for both equilibrium mixtures. At this value of ligand composition, the molar fraction of $Ga(acac)_2(hfac)$ or $Ga(acac)_2(bzbz)$ is a maximum.[2] Also, the total solute molarity was 0.20 *M* for both equilibrium mixtures.

Benzene and dichloromethane were dried by refluxing over calcium hydride for at least 24 hr and were subsequently handled under a dry-nitrogen atmosphere.

Methyl Proton Resonance Spectra.—Methyl proton magnetic resonance spectra were obtained as described previously.[2]

Nmr Line-Shape Parameters for $Ga(acac)_2(hfac)$.—In the determination of lifetimes for terminal methyl groups in $Ga(acac)_2(hfac)$, four line-shape parameters were used for comparing the observed nmr spectra with computer-calculated spectra. Below the coalescence temperature the spectra were compared with regard to $\delta\nu_e$, the frequency separation between the two resonance components, and r, the ratio of the maximum amplitude to the amplitude at $(\nu_A + \nu_B)/2$. Above coalescence the line widths at three-fourths and half maximum amplitude were compared. At each temperature three copies of the spectrum were recorded and the shape parameters were averaged. The calculated spectra consisted of 300 coordinate pairs spaced at intervals of 0.1 radian/sec about the mean frequency of the spectrum. The reliability of the shape-parameter method was checked by comparison of 24 coordinate pairs for spectra obtained at two temperatures below coalescence (−27.7, −31.3°) and one temperature above coalescence (−24.7°). This method of comparing observed and calculated spectra has been used previously in similar kinetic studies of metal β-diketonates.[3,4]

Results and Discussion

The exchange of nonequivalent methyl groups in $Ga(acac)_2(hfac)$ is sufficiently slow in dichloromethane solution below *ca.* −26.5° to observe two equally intense methyl proton resonance lines. The temperature dependence of the methyl resonances for the compound in an equilibrium mixture of $Ga(acac)_3$ and $Ga(hfac)_3$ is shown in Figure 1. At 16° the compound exhibits a single, rather broad line, which is positioned between two weak methyl lines due to equilibrium concentrations of $Ga(acac)(hfac)_2$ and $Ga(acac)_3$. As the temperature is decreased, the line broadens further and then splits into two lines of equal intensity below the coalescence temperature of *ca.* −26.5°. At −46° two well-resolved resonance components are observed.

The temperature dependence of the methyl proton resonance for $Ga(acac)_2(bzbz)$ in benzene solution is illustrated in Figure 2. Above *ca.* 60° the two methyl lines broaden and then merge into a single, very broad line at the coalescence temperature of *ca.* 81°. The line sharpens above the coalescence temperature and

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[1] Presented in part before the Division of Inorganic Chemistry, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

[2] T. J. Pinnavaia and S. O. Nweke, *Inorg. Chem.*, **8**, 639 (1969).

[3] A. C. Adams and E. M. Larsen, *ibid.*, **5**, 814 (1966).

[4] R. C. Fay and R. N. Lowry, *ibid.*, **6**, 1512 (1967).

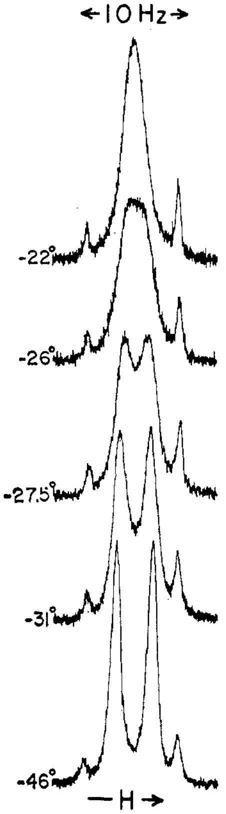

Figure 1.—Methyl proton resonance for Ga(acac)$_2$(hfac) in an equilibrium mixture of Ga(acac)$_3$–Ga(hfac)$_3$ in dichloromethane. Lines at lowest and highest fields, respectively, are due to the presence of Ga(acac)(hfac)$_2$ and Ga(acac)$_3$.

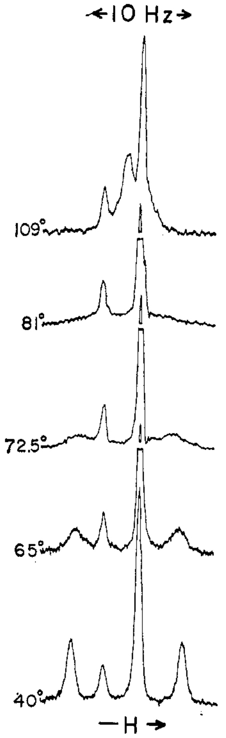

Figure 2.—Methyl proton resonance for Ga(acac)$_2$(bzbz) in an equilibrium mixture of Ga(acac)$_3$–Ga(bzbz) in benzene. The lines which appear at lowest and highest field in the spectrum at 109° are due to presence of Ga(acac)(bzbz)$_2$ and Ga(acac)$_3$, respectively.

appears between the methyl proton resonances of Ga(acac)(bzbz)$_2$ and Ga(acac)$_3$.

The exchange of nonequivalent terminal methyl groups in Ga(acac)$_2$(hfac) and Ga(acac)$_2$(bzbz) must occur *via* an intramolecular mechanism. In the case of Ga(acac)$_2$(hfac), for example, no broadening of Ga(acac)(hfac)$_2$ or Ga(acac)$_3$ methyl lines is observed under conditions where the rearrangement process is fast. Also, the same coalescence temperature was observed on diluting the solution by a factor of 2, which indicates that the residence time for the methyl groups is independent of Ga(acac)$_2$(hfac) concentration. Analogous results were obtained for Ga(acac)$_2$(bzbz).

For processes in which nuclei are exchanged between two nonequivalent sites, Gutowsky and Holm[5] have derived the dependence of the nmr line shape on (1) $\delta\nu$, the frequency separation between the resonance components assuming no exchange and no overlap of the components, (2) T_2, the transverse relaxation time, and (3) the quantity τ, which is given by $\tau_A\tau_B/(\tau_A + \tau_B)$, where τ_A and τ_B are the mean lifetimes of protons at each site. Since the two sites are equally populated, $\tau_A = \tau_B = 2\tau$. For Ga(acac)$_2$(hfac) in an equilibrium mixture of Ga(acac)$_3$ and Ga(hfac)$_3$ in dichloromethane, the methyl resonance lines due to Ga(acac)$_3$ and Ga(acac)(hfac)$_2$ are sufficiently weak to permit an accurate line-shape analysis for obtaining values of τ (*cf.* Figure 1). A similar analysis was not possible for Ga(acac)$_2$(bzbz), because of the unfavorable overlapping of the Ga(acac)$_2$(bzbz) lines with lines due to Ga(acac)$_3$ and Ga(acac)(bzbz)$_2$ (*cf.* Figure 2). In this latter case, however, values of τ could be determined using the simplified Gutowsky–Holm equation

$$\tau = \frac{\sqrt{2}}{2\pi}(\delta\nu^2 - \delta\nu_e^2)^{-1/2} \qquad (1)$$

where $\delta\nu$ and $\delta\nu_e$, the experimentally observed frequency separation, are expressed in hertz. Among the solvents investigated, which included chlorobenzene, chloroform, and 1,2-dichloroethane, benzene was best suited for kinetic studies of Ga(acac)$_2$(bzbz), because it gave the largest chemical shift separations.

In the determination of τ values for methyl groups in Ga(acac)$_2$(hfac), the value of $\delta\nu$ was taken to be equal to the frequency separation observed in the region of slow exchange, 3.35 Hz. Since the ratio of the line width at half-maximum amplitude to the frequency separation was less than 0.3, no correction due to the slight overlap of the two resonance components was necessary.[5] Within experimental error, $\delta\nu$ was independent of temperature over the entire region of slow exchange (−45 to −65°). Also, the resonance components in the region of slow exchange have equal widths, which indicates that $T_{2A} = T_{2B} = T_2$. Values of T_2 calculated from the line width in the very slow exchange limit (−60°) and the very fast exchange limit (36°) differ by a factor of 3. Therefore,

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(5) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

the temperature dependence of T_2 is appreciable. In order to estimate the values of T_2 appropriate to temperatures in the coalescence region, it was assumed that the line width observed for Ga(acac)$_3$ in dichloromethane is equal to the line width that Ga(acac)$_2$(hfac) would have at the same temperature in absence of methyl group exchange. The temperature dependence of the line width of Ga(acac)$_3$ is shown in Figure 3; values of the line width for Ga(acac)$_2$(hfac) at −60 and 36° are included for comparison. A similar procedure has been used to estimate T_2 values for *cis*-Ti(acac)$_2$X$_2$ complexes.[4] With $\delta\nu$ and the appropriate values of T_2, values of τ at several temperatures in the coalescence region were determined by comparing the observed nmr line-shape parameters with shape parameters calculated for various trial values of τ (see Experimental Section). Experimental line-shape parameters are presented in Table I. The scatter among the independent kinetic runs is attributed to differences in magnetic field homogeneity and to an uncertainty of *ca.* ±0.5° in the temperatures.

Table I

Line-Shape Parameters for the Methyl Proton Resonance of Ga(acac)$_2$(hfac)[a]

	Av values[b]		
Temp, °C	Line width,[c] Hz	$\delta\nu_e$,[d] Hz	r[e]
−15.6	1.50	...	...
−16.8	1.50	...	...
−22.1	2.43	...	...
−24.7	3.53	...	...
−24.8	3.38	...	...
−25.8	3.80	...	...
−25.9	3.64	...	...
−27.5	...	2.16	1.26
−27.6	...	1.78	1.07
−27.7	...	2.06	1.17
−30.9	...	2.85	2.05
−31.3	...	2.80	1.79
−33.5	...	3.00	2.39
−35.1	...	3.10	3.01
−35.7	...	2.95	2.75
−39.1	...	3.20	4.18

[a] In dichloromethane. [b] Average shape parameters obtained from three spectral measurements. [c] Width at half-maximum amplitude. [d] Frequency separation between the two resonance components. [e] Ratio of the maximum amplitude to the amplitude at $(\nu_A + \nu_B)/2$.

Unlike Ga(acac)$_2$(hfac), Ga(acac)$_2$(bzbz) did not exhibit a limiting value of $\delta\nu_e$. The temperature dependence of $\delta\nu_e$ for Ga(acac)$_2$(bzbz) in benzene is shown in Figure 4. The observed dependence over the entire temperature range from 15 to 80°, however, cannot be attributed to exchange effects. Within experimental error, the ratio of the line width of Ga(acac)$_2$(bzbz) to the line width of Ga(acac)$_3$ in the equilibrium mixture remains constant in the region 15–50°; above 50° the ratio increases rapidly as the rate of methyl group exchange increases. Therefore, the exchange is slow in the region 15–50°, and the observed temperature dependence of $\delta\nu_e$ must be due mainly to temperature-dependent solvation effects which cause the chemical shift difference between the two resonance components to decrease with increasing temperature. Similar effects have been observed previously for fluorine chemical shifts in aluminum(III) trifluoroacetylacetonate, Al(tfac)$_3$,[6,7] and Ga(tfac)$_3$[7] in chloroform solution. In order to obtain appropriate values of $\delta\nu$, the dependence of $\delta\nu_e$ in the region of slow exchange was extrapolated to the region of fast exchange, as is shown by the dashed line in Figure 4. This line was then assumed to represent the temperature dependence of the frequency separation that would be observed in the absence of exchange. Thus for each observed value of $\delta\nu_e$ in the region of exchange, the corresponding value of $\delta\nu$ needed to calculate τ from eq 1 was read off the extrapolated line. Values of the frequency separations are summarized in Table II.

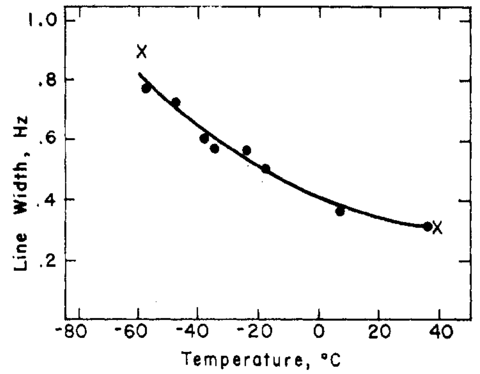

Figure 3.—Temperature dependence of methyl line width of Ga(acac)$_3$ in dichloromethane. Points marked X are the line widths for Ga(acac)$_2$(hfac) observed in the region of very slow (−60°) and very fast (36°) exchange.

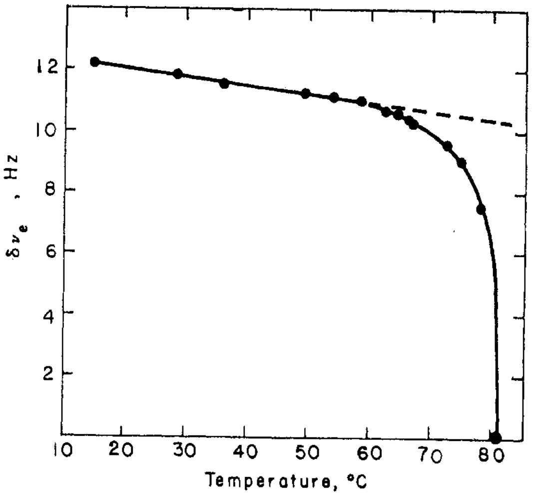

Figure 4.—Temperature dependence of the frequency separation between the methyl proton resonance components of Ga(acac)$_2$(bzbz) in benzene.

It should be noted that the simplified Gutowsky–Holm equation is based on the assumption that $T_2\delta\nu$

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(6) R. A. Palmer, R. C. Fay, and T. S. Piper, *Inorg. Chem.*, **3**, 875 (1964).
(7) R. C. Fay and T. S. Piper, *ibid.*, **3**, 348 (1964).

TABLE II

FREQUENCY SEPARATIONS FOR THE METHYL PROTON RESONANCE COMPONENTS OF $Ga(acac)_2(bzbz)$[a]

Temp, °C	$\delta\nu_e$,[b] Hz	$\delta\nu$,[c] Hz
78.0	7.50	10.45
75.0	8.96	10.50
72.5	9.53	10.60
67.0	10.28	10.75
66.2	10.47	10.75
62.5	10.70	10.85

[a] In benzene. [b] Observed frequency separation; the value reported at each temperature is the average value obtained from at least five spectral measurements. [c] Frequency separation in absence of exchange (obtained from the extrapolated line in Figure 4).

is large. In order to estimate the error introduced in using the simplified equation to calculate values of τ for $Ga(acac)_2(bzbz)$, T_2 was assumed to be equal to the relaxation time observed for $Ga(acac)_3$ in benzene at 68°, *viz.*, 0.71 sec. Spectra for the frequency separations at 78° were then calculated using the full Gutowsky–Holm equation. The value of τ for the spectrum that gave the observed value of $\delta\nu_e$ was only 2.5% larger than the τ value obtained from eq 1. The equation should provide even better estimates of τ at temperatures below 78°, because the error is expected to decrease as $\delta\nu_e/\delta\nu$ increases.[5]

TABLE III

KINETIC DATA FOR METHYL GROUP EXCHANGE

$Ga(acac)_2(hfac)$[a]				$Ga(acac)_2(bzbz)$[b]	
Temp, °C	$10^2\tau$, sec	Temp, °C	$10^2\tau$, sec	Temp, °C	$10^2\tau$, sec
−15.6	2.68	−27.6	8.94	78.0	3.09
−16.8	2.66	−27.7	10.1	75.0	4.11
−22.1	4.51	−30.9	17.8	72.0	4.85
−24.7	6.63	−31.3	15.7	67.0	7.16
−24.8	6.31	−33.5	20.8	66.2	9.23
−25.8	7.28	−35.1	26.1	64.6	9.74
−25.9	6.84	−35.7	23.9	62.5	12.5
−27.5	11.0	−39.1	38.6		
E_a, kcal/mol		14.5 ± 1.1[c]		20.6 ± 2.7	
log A		13.60 ± 0.96		14.00 ± 1.75	
ΔS^*, eu		1.7 ± 4.4		3.5 ± 8.0	
k_{25}, sec^{-1}		9.8×10^2		8.8×10^{-2}	

[a] In dichloromethane. [b] In benzene. [c] All errors are estimated at the 95% confidence level.

Values of τ for $Ga(acac)_2(hfac)$ and $Ga(acac)_2(bzbz)$, along with activation parameters for the exchange processes, are presented in Table III. The Arrhenius activation energies, E_a, and frequency factors, A, were obtained in the usual way from the least-squares line of log k *vs.* $1/T$ plots (see Figure 5), where $k = (2\tau)^{-1}$ is the first-order rate constant for exchange. Activation entropies, ΔS^*, were calculated at 25° from the equation

$$\Delta S^* = R \ln A - R\left[1 + \ln \frac{kT}{h}\right]$$

Extrapolated values of the first-order rate constants show that the rate of methyl group exchange at 25° for $Ga(acac)_2(hfac)$ is *ca.* 10^4 times larger than the rate for $Ga(acac)_2(bzbz)$. Although the 95% confidence level estimates of error indicate that no significance can be given the observed difference in activation entropies, the activation energy is smaller for $Ga(acac)_2(hfac)$ by at least 2.3 kcal/mol.

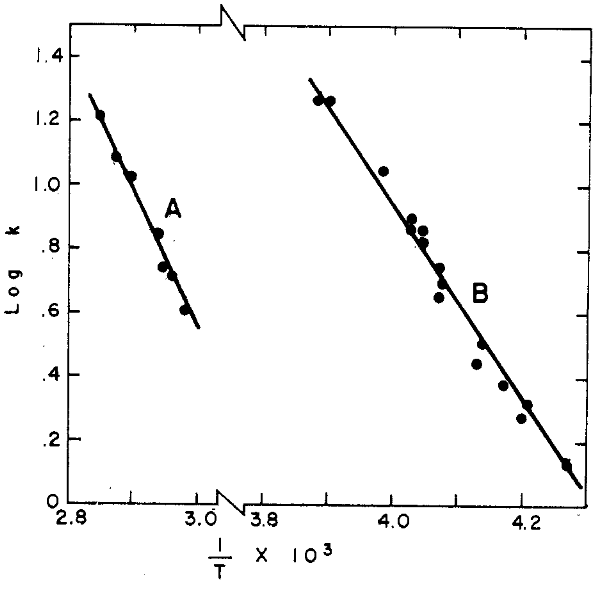

Figure 5.—Log k *vs.* $1/T$ plots for $Ga(acac)_2(bzbz)$ in benzene (A) and $Ga(acac)_2(hfac)$ in dichloromethane (B).

Fay and Piper[7] have cited evidence which favors bond rupture and formation of a five-coordinate intermediate for terminal group exchange in $Al(tfac)_3$, $Ga(tfac)_3$, and other trivalent metal trifluoroacetylacetonates. The same type of mechanism probably operates in the gallium complexes reported here. The trigonal-bipyramidal and square-pyramidal intermediates that can lead to terminal group exchange in octahedral complexes containing two different types of symmetric diketonate ligands have been illustrated by Fortman and Sievers.[8] In view of the probable mechanism, it is not unexpected that $Ga(acac)_2(hfac)$ exhibits the lower activation energy. Formation constants for copper(II) β-diketonates[9] indicate that hfac is a very much weaker chelating agent than acac or bzbz, which have approximately equal chelating strengths. Therefore, the mean gallium–oxygen bond energy is expected to be smaller for $Ga(acac)_2(hfac)$. Although the higher dielectric constant of the solvent used in the $Ga(acac)_2(hfac)$ exchange study is expected to lower the energy required for achieving charge separation in the transition state, the reported[7] dependence of the free energy of activation on solvent polarity for terminal group exchange in $Al(tfac)_3$ suggests that the difference in polarity between dichloromethane and benzene cannot account for the observed difference in activation energies.

The activation parameters in Table III are to be

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(8) J. J. Fortman and R. E. Sievers, *Inorg. Chem.*, **6**, 2022 (1967).

(9) L. G. Van Uitert, W. C. Fernelius, and B. E. Douglas, *J. Am. Chem. Soc.*, **75**, 457 (1953).

compared with available parameters for terminal group exchange in other group IIIb metal β-diketonates. Based on the frequency factor observed for isomerization of *cis*-Co(tfac)$_3$, Fay and Piper[7] estimated the activation energy for exchange of trifluoromethyl groups in Ga(tfac)$_3$ in deuteriochloroform solution to be 20.8 ± 1.6 kcal/mol; the activation energy was estimated to be somewhat higher for Al(tfac)$_3$, 23.5 ± 1.8 kcal/mol, and appreciably lower for In(tfac)$_3$, <13.5 ± 1.1 kcal/mol. Fortman and Sievers[8] used the simplified Gutowsky–Holm equation to obtain first-order rate constants for terminal group exchange in Al(acac)$_2$(hfac), Al(thd)$_2$(acac), and Al(thd)$_2$(hfac), where thd = dipivaloylmethanate, in chlorobenzene solution. The reported activation energies and the activation entropies which we calculate from the reported values of log A are, respectively: 2.7 kcal/mol and −46 eu for Al(acac)$_2$(hfac); 6.4 kcal/mol and −39 eu for Al(thd)$_2$(acac); 7.0 kcal/mol and −30 eu for Al(thd)$_2$(hfac). Despite the different nature of the metal ion and solvent, the latter activation parameters, especially those for Al(acac)$_2$(hfac), are in serious disagreement with the parameters reported here. The disagreement is attributed to temperature-dependent solvation effects which were not considered in obtaining values of $\delta\nu$ for the aluminum(III) complexes. If we take the largest observed frequency separation for Ga(acac)$_2$(bzbz) in benzene, 12.15 Hz at 15°, to be equal to $\delta\nu$ and attribute the temperature dependence of $\delta\nu_e$ above 15° to exchange effects (*cf.* Figure 4), which would be equivalent to the procedure used by Fortman and Sievers, then we also obtain a low activation energy, 4.6 ± 0.8 kcal/mol, and an unreasonably large, negative activation entropy, −42 ± 2 eu.

Based on the reported frequency separations for Al(thd)$_2$(acac), values of $\delta\nu_e$ and corrected values of $\delta\nu$ at four temperatures in the region of exchange give $E_a \simeq 19$ kcal/mol and $\Delta S^* \simeq -6$ eu. Insufficient data are reported for Al(acac)$_2$(hfac) and Al(thd)$_2$(hfac) in the region of exchange, but the frequency separations for Al(acac)$_2$(hfac) clearly indicate an appreciable temperature dependence for $\delta\nu$. Thus the desirability of correcting $\delta\nu$ for temperature-dependent solvation effects is to be emphasized.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. J. M. S. and D. A. C. wish to thank the National Science Foundation for undergraduate summer participantships.

CONTRIBUTION FROM THE INSTITUTE OF PHYSICAL AND CHEMICAL RESEARCH,
YAMATO-MACHI, SAITAMA, JAPAN, AND THE INSTITUTE FOR SOLID STATE PHYSICS,
THE UNIVERSITY OF TOKYO, ROPPONGI, MINATO-KU, TOKYO, JAPAN

The Electronic Structure of the Tris(α,α′-dipyridyl)iron(II) Ion

BY ICHIRO HANAZAKI AND SABURO NAGAKURA

Received September 30, 1968

The π-electron structure of the tris(α,α′-dipyridyl)iron(II) ion was theoretically studied by the method of composite system, with the results successful in explaining the observed peak positions and intensities of the electronic absorption spectrum. According to the results, the bands at ~20,000 and 33,600 cm^{-1} were assigned, respectively, to the charge-transfer transition from the metal to the lowest vacant MO of the ligand and to the π–π* transition within the ligand π-electron system. The other two bands at ~29,000 and ~40,000 cm^{-1} with several shoulders were assigned to the charge-transfer transition to the second lowest vacant MO and to the third charge-transfer transition mixing with the second π–π* transition in the ligand, respectively. The ground state was calculated to be stabilized by 0.86 eV by the charge-transfer interaction of π electrons between the metal ion and the ligand. This can explain the remarkable stability of the complex ion. The nature of the excited states was also discussed in detail, with the result that the transferred electron is delocalized on the whole ligand π-electron system, in contrast with the current view that the character of the charge-transfer transition is predominantly determined by the α-diimine skeleton.

Introduction

In previous papers,[1] we developed a theoretical method to treat the π-electron structures of metal complexes containing organic unsaturated molecules as ligands. The method was shown to be successfully applied to the tris-acetylacetonato complexes of the iron-series transition metal ions.

In the present paper, the theory is applied to a well-known complex ion, tris(α,α′-dipyridyl)iron(II).[2] This complex ion has long been an interesting research subject in view of its great stability, of the extremely strong charge-transfer absorption band appearing in the visible region, and also of the application to analytical chemistry. Several authors have extensively

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[1] I. Hanazaki, F. Hanazaki, and S. Nagakura, *J. Chem. Phys.*, in press.

[2] Hereafter abbreviated to Fe(dipy)$_3^{2+}$.