of this type have been isolated and characterized. Robinson and Shaw[26] have prepared a stable hydrido-diolefin complex of iridium [IrHCl$_2$(cycloocta-1,5-diene)]$_2$, and very recently reaction intermediates in which a platinum atom is bonded simultaneously to hydride ion, an olefin, and trichlorostannate anion have been reported.[27] It is also worth mentioning that one of the products of the reaction of tetrafluoroethylene and *trans*-PtHCl(PEt$_3$)$_2$, which was originally[28] formulated as a π-bonded tetrafluoroethylene complex, PtHCl(PEt$_3$)$_2$ (π-C$_2$F$_4$), has been shown[29] to be a carbonyl complex, *trans*-[PtClCO)(PEt$_3$)$_2$]BF$_4$.

Concerning the mechanisms depicted in Figures 2 and 3, we favor the reductive elimination scheme of Figure 2. Either mechanism is compatible with the kinetic results relating to isotope effect, solvent effect, and relative reactivity of the chloro and bromo complexes. However, we believe that an argument can be made for the reductive elimination mechanism of Figure 2 on the basis of the fact that the compound isolated from the reaction of PtHCN(PEt$_3$)$_2$ and TCNE was the hydridoolefinic complex, PtHCN(PEt$_3$)$_2$TCNE, whereas, in the reaction of PtHX(PEt$_3$)$_2$ (X = Cl, Br) with TCNE, an intermediate hydridoolefinic complex, PtHX(PEt$_3$)$_2$TCNE, was not isolated. If the reaction path of Figure 3 was operative in reactions of PtHX-(PEt$_3$)$_2$ with TCNE, isolation of the σ-cyanoethyl complex B (or the conjugate base C) should instead be more likely if step C → D is rate determining. On the other hand, if step A → B is rate determining in the mechanism of Figure 3, there is no reason for believing that PtHCN(PEt$_3$)$_2$TCNE should be more stable than PtHX(PEt$_3$)$_2$TCNE (X = Cl, Br). To the contrary, it would seem that PtHX(PEt$_3$)$_2$ (X = Cl, Br) would behave as stronger π bases toward the π acid TCNE than PtHCN(PEt$_3$)$_2$ since the cyanide group is a much stronger π-acceptor ligand than is chloride or bromide.

In conclusion, we surmise that the contrasting behavior of ethylene and tetracyanoethylene toward hydridoplatinum(II) complexes as mentioned in the introductory section is primarily a manifestation of the greater strength of the platinum–TCNE bond relative to the platinum–ethylene bond.[30] Thus, when either TCNE or C$_2$H$_4$ reacts with PtHX(PR$_3$)$_2$, a 1:1 adduct, PtHX(PR$_3$)$_2$(olefin), is formed initially as an intermediate, but for TCNE elimination of HX is more favorable energetically than "insertion" whereas the reverse is true for ethylene. The fact that we were able to isolate PtHCN(PEt$_3$)$_2$TCNE, but not PtHX(PEt$_3$)$_2$-TCNE (X = Cl, Br), is reasonable in terms of the greater strength of the Pt–CN bond as compared to the Pt–Cl and Pt–Br bonds.

(26) S. D. Robinson and B. L. Shaw, *Tetrahedron Letters*, 1301 (1964).
(27) H. A. Tayim and J. C. Bailar, *J. Am. Chem. Soc.*, **89**, 4330 (1967).
(28) H. C. Clark and W. S. Tsang, *Chem. Commun.*, 123 (1966); H. C. Clark and W. S. Tsang, *J. Am. Chem. Soc.*, **89**, 529 (1967).
(29) H. C. Clark, P. W. R. Corfield, K. R. Dixon, and J. A. Ibers, *ibid.*, **89**, 3360 (1967).

(30) The complex Pt(Ph$_3$P)$_2$(ethylene) decomposes at 122–125° (C. D. Cook and G. S. Jauhal, *Inorg. Nucl. Chem. Letters*, **3**, 31 (1967)), whereas the complex Pt(Ph$_3$P)$_2$(tetracyanoethylene) decomposes at 268–270°.

# Direct Characterization of the Mixed Complexes of Aluminum(III) with N,N-Dimethylformamide and 2,4-Pentanedione. Proton Magnetic Resonance Study of First-Coordination-Sphere Stoichiometry and Kinetics of Ligand Exchange

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**Abstract:** Proton magnetic resonance (pmr) spectra of N,N-dimethylformamide (DMF) solutions of Al(DMF)$_6$-(ClO$_4$)$_3$ and tris(2,4-pentanedionate)aluminum(III) (Al(acac)$_3$) have been used to characterize directly the complexes Al(acac)(DMF)$_4$$^{2+}$ and *cis*- and *trans*-Al(acac)$_2$(DMF)$_2$$^+$. Thermodynamic parameters were obtained from the temperature dependence of the equilibria among these species and Al(DMF)$_6$$^{3+}$ and Al(acac)$_3$. Below 5° pmr signals of DMF in the first coordination sphere of complexes containing acac$^-$ can be distinguished, and, from a complete line-shape analysis of these signals, the rate of exchange of DMF from the acac complexes was estimated. Also below 5°, separate pmr signals are discernible for the *cis* and *trans* isomers of Al(acac)$_2$(DMF)$_2$$^+$. The kinetic parameters obtained from the latter are consistent with a rate-determining step for *cis–trans* isomerization which proceeds by dissociation of DMF. Data from these studies are compared with those obtained for analogous Be(II) complexes.

Little is known about the solution chemistry of the colorless, diamagnetic, labile complexes of cations having d$^0$ and d$^{10}$ electronic configurations, primarily because the properties of the cations preclude their study with the experimental techniques conventionally used in transition metal chemistry. Recently it has
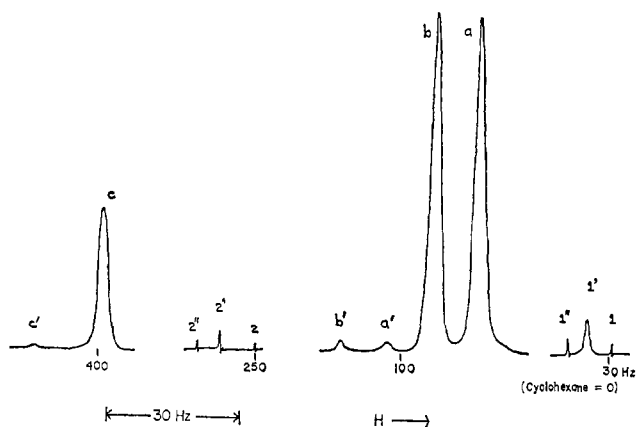
Figure 1. 60-MHz pmr spectrum of Al(III)–acac–DMF complexes in DMF at 37°. Formal solution composition: Al(acac)$_3$ = 0.135 $m$ and Al(DMF)$_6{}^{3+}$ = 0.130 $m$.



Figure 2. DMF and acac protons corresponding to the assignments in Table I and Figure 1.

been shown that nuclear magnetic resonance (nmr) techniques are particularly well suited to the study of these ions,[1-13] and the initial results indicate that their coordination chemistry will be as rich and diverse as that for transition metals. Complexes which have been characterized by nmr spectroscopy include, for example, Al(OH$_2$)$_6{}^{3+}$,[1,4,11] Ga(OH$_2$)$_6{}^{3+}$,[1,8,9,11] Be(OH$_2$)$_4{}^{2+}$,[1,4] Mg(OH$_2$)$_6{}^{2+}$,[12] Mg(CH$_3$OH)$_6{}^{2+}$,[12,13] Mg(CH$_3$OH)$_{6-n}$(OH$_2$)$_n{}^{2+}$,[3] Al(DMSO)$_6{}^{3+}$,[6] Al(DMF)$_6{}^{3+}$,[7] Be(DMF)$_4{}^{2+}$,[10] and Be(acac)(DMF)$_2{}^{+}$.[10] (DMSO represents dimethyl sulfoxide; DMF represents N,N-dimethylformamide; acac$^-$ represents the 2,4-pentanedionate anion.)

We have been particularly interested in kinetic and thermodynamic ligand–ligand interactions in mixed complexes of nontransition metal ions. In a recent study[10] it was shown that, although ligand–ligand interactions are small or compensating as reflected in the thermodynamic parameters for the formation of Be(acac)(DMF)$_2{}^{+}$ from Be(DMF)$_4{}^{2+}$ and Be(acac)$_2$ in DMF, such interactions must have a pronounced effect on the kinetic parameters for DMF chemical exchange from Be(DMF)$_4{}^{2+}$ and Be(acac)(DMF)$_2{}^{+}$. As an extension of that study, we wish to report the direct characterization of the kinetic and thermodynamic properties of the complexes Al(acac)(DMF)$_4{}^{2+}$ and cis- and trans-Al(acac)$_2$(DMF)$_2{}^{+}$, using proton nmr spectroscopy.

## Experimental Section

**Reagents.** Eastman White Label DMF was purified,[14] and the complexes Al(DMF)$_6$(ClO$_4$)$_3$ were prepared[7] as described previously.

(1) J. A. Jackson, J. F. Lemons, and H. Taube, *J. Chem. Phys.*, **32**, 553 (1960).
(2) H. Taube, *Progr. Stereochem.*, **3**, 95 (1962).
(3) J. H. Swinehart and H. Taube, *J. Chem. Phys.*, **37**, 1579 (1962).
(4) R. E. Connick and D. N. Fiat, *ibid.*, **39**, 1349 (1963).
(5) T. J. Swift and W. G. Sayre, *ibid.*, **44**, 3567 (1966).
(6) S. Thomas and W. G. Reynolds, *ibid.*, **44**, 3148 (1966).
(7) W. G. Movius and N. A. Maywiyoff, *Inorg. Chem.*, **6**, 847 (1967).
(8) T. J. Swift, O. G. Fritz, Jr., and T. A. Stephenson, *J. Chem. Phys.*, **46**, 406 (1967).
(9) D. N. Fiat and R. E. Connick, *J. Am. Chem. Soc.*, **88**, 4754 (1966).
(10) N. A. Matwiyoff and W. G. Movius, *ibid.*, **89**, 6077 (1967).
(11) D. Fiat and R. E. Connick, *ibid.*, **90**, 608 (1968).
(12) N. A. Matwiyoff and H. Taube, *ibid.*, **90**, 2796 (1968).
(13) S. Nakamura and S. Meiboom, *ibid.*, **89**, 1765 (1967).
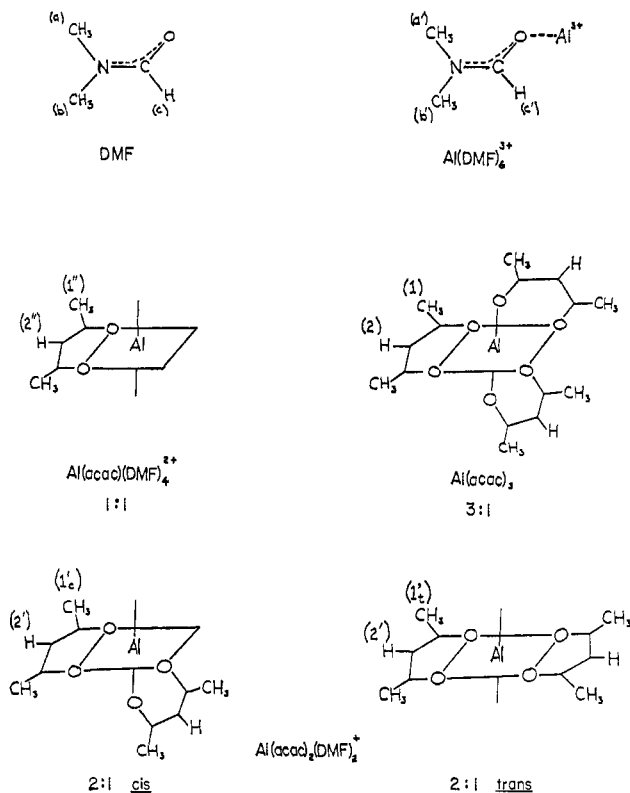(14) N. A. Matwiyoff, *Inorg. Chem.*, **5**, 788 (1966).

**Measurements.** Proton nmr spectra were obtained at 60 and 100 MHz using the Varian A-60A and HA-100 spectrometers. The spectrometers were equipped with variable-temperature probes and the Varian variable-temperature control system, V-6057. The systems were calibrated and the measurements were obtained in the manner described previously.[6,14] Relative signal areas were obtained by manual integration. The pmr data for the Al–acac–DMF complexes were obtained using ten independent solutions in which the composition was varied over the limits 0.05 $m$ ≤ Al(DMF)$_6{}^{3+}$ ≤ 0.2 $m$ and 0.05 $m$ ≤ Al(acac)$_3$ ≤ 0.2 $m$.

Electronic absorption spectra were obtained using a Carey Model 15 spectrometer and matched 1-cm cells equipped with standard taper stoppers.

Computer programs were run on the IBMOS 360/67.

## Results

**Nuclear Magnetic Resonance Measurements.** The solvation of Al(III) by DMF and the kinetics of exchange of DMF between the complex Al(DMF)$_6{}^{3+}$ and the bulk of the solvent have been discussed in a previous paper.[7] In Figure 1 is reproduced a proton nmr spectrum typical of those for DMF solutions containing Al(DMF)$_6$(ClO$_4$)$_2$ and Al(acac)$_3$ at 37°. The signals are assigned to the proton sites defined in Figure 2 and in the discussion below. Chemical shifts corresponding to the assignments are tabulated in Table I.

Of the six signals due to DMF, three may be assigned to DMF in the first coordination sphere of Al(III) (a', b', c') and three to DMF in the bulk of the solvent (a, b, c).[7] The signals of DMF in each environment consist of a low-field formyl peak (c or c') and two high-field N-methyl peaks (a, b or a', b'), the magnetic nonequivalence of which arises from hindered rotation about the C–N bond. The higher field N-methyl resonance for DMF in each environment is assigned to

Table I. Proton Chemical Shifts of Al(III) Complexes in DMF at 60 MHz and 37°[a]

| Solute in DMF (concn, m) | DMF protons | | | | | | acac protons | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | a | b | c | a' | b' | c' | 1 | 1' | 1'' | 2 | 2' | 2'' |
| Al(DMF)$_6$(ClO$_4$)$_2$ (0.2) | 83 | 93 | 398 | 103 | 114 | 415 | .. | .. | .. | ... | ... | ... |
| Al(acac)$_3$ (0.2) | 83 | 93 | 398 | ... | ... | ... | 29 | .. | .. | 250 | ... | ... |
| Al(DMF)$_6$(ClO$_4$)$_2$ (0.1) + Al(acac)$_3$ (0.1) | 83 | 93 | 398 | 103 | 114 | 415 | 29 | 35 | 39 | 250 | 258 | 263 |

[a] Shifts are in Hz downfield relative to internal cyclohexane; assignments are based on the proton sites defined in Figure 2.

the methyl group *cis* to the oxygen atom.[14–16] Retention of N-methyl nonequivalence upon coordination of DMF to Al(III) indicates that coordination of DMF occurs *via* the oxygen atom.[14]

Also exhibited in the spectrum are several resonances due to the acac⁻ ligand. Those upfield from the DMF methyl signals are assigned to methyl groups of the acac⁻ (1, 1', 1''), those downfield are assigned to the ring or vinylic proton of acac⁻ (2, 2', 2''). Employing the considerations discussed at length for the Be(II)–acac⁻–DMF system,[10] we can readily assign these signals as follows: 1 and 2 to acac⁻ in the complex Al(acac)$_3$, 1' and 2' to acac in both the *cis* and *trans* complexes Al(acac)$_2$(DMF)$_2$⁺, and 1'' and 2'' to acac in the complex Al(acac)(DMF)$_4$²⁺ (see Figure 2).
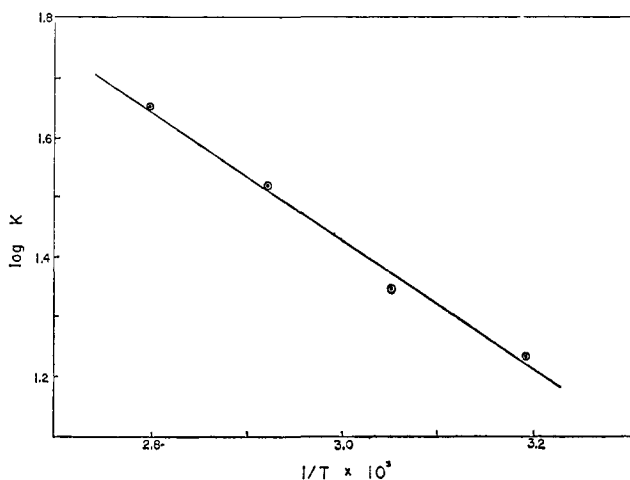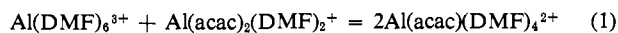


Figure 3. Plot of log $K$ vs. 10³/$T$ for reaction 2. The $K$ values were derived from the relative areas of the acac⁻ methyl pmr signals.

From the known solution composition, relative signal areas, and their temperature dependence over the temperature range 32–100°, thermodynamic parameters for reactions 1 and 2 were calculated and are given below. A typical plot of log $K$ vs. 1/$T$, derived from the tem-

$$Al(DMF)_6{}^{3+} + Al(acac)_2(DMF)_2{}^+ = 2Al(acac)(DMF)_4{}^{2+} \quad (1)$$

$$K_1 = 0.65 \pm 0.10 \ (25°)$$

$$\Delta H_1 = 7.7 \pm 1.0 \ \text{kcal/mole}$$

$$\Delta S_1 = 25 \pm 2 \ \text{eu}$$

$$Al(acac)(DMF)_4{}^{2+} + Al(acac)_3 = 2Al(acac)_2(DMF)_2{}^+ \quad (2)$$
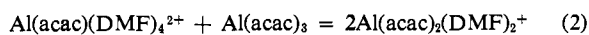
$$K_2 = 3.6 \pm 0.5 \ (25°)$$

$$\Delta H_2 = 4.2 \pm 0.5 \ \text{kcal/mole}$$

$$\Delta S_2 = 19 \pm 2 \ \text{eu}$$

perature dependence of the relative areas of the acac⁻ methyl pmr signals, is shown in Figure 3. A comparison between the relative signal areas observed and those calculated from $K_1$ and $K_2$ at 32° is provided in Table II for a representative DMF solution containing Al-

Table II. Comparison of Calculated and Experimental Signal Areas for Al(III)–acac⁻ Complexes in DMF[a]

| Signal[b] | Exptl area | Calcd area |
|---|---|---|
| 1 | 0.10 ± 0.02 | 0.13 ± 0.02 |
| 1' | 0.75 ± 0.01 | 0.68 ± 0.12 |
| 1'' | 0.15 ± 0.02 | 0.19 ± 0.04 |

[a] $T = 32°$, $K_1 = 0.87 \pm 0.18$, $K_2 = 14 \pm 3$, Al(DMF)$_6$(ClO$_4$)$_3$ = 0.130 m, Al(acac)$_3$ = 0.135 m. [b] For assignments see Figure 2.

(DMF)$_6$³⁺ and Al(acac)$_3$. It should be noted that the equilibrium constants given above are merely the ratios of the first and second or second and third equilibrium quotients for the formation of Al(acac)$_n$(DMF)$_{6-2n}{}^{+3-n}$ from Al(DMF)$_6$³⁺ and acac⁻.

Separate signals for the *cis* and *trans* isomers of Al(acac)$_2$(DMF)$_2$⁺ cannot be distinguished in the acac⁻ regions of the pmr spectra at temperatures above 5°. However, below 5°, the methyl signal due to acac⁻ in this complex (1') broadens and splits into two peaks as shown in Figure 4. The high-field peak (1) is due to the complex Al(acac)$_3$, and the others are assigned to the *cis* (1'$_c$) and *trans* (1'$_t$) isomers of the 2:1 complex. This assignment is based upon the expectation that the acac⁻ methyl environment in the 3:1 complex will resemble the environment of the *cis* 2:1 complex more closely than that of the *trans*.[17] The vinylic region of the spectra does not exhibit such behavior. Only three narrow peaks are distinguished throughout the temperature range, and for each complex the ratio of signal areas, methyl:vinyl, is 3:1. Although the onset of pronounced viscosity broadening of the acac⁻ pmr signals below −20° precluded an accurate evaluation of all the thermodynamic and kinetic parameters for *cis–trans* isomerization of the 2:1 complex, a reliable estimate of the ratio of peak areas, *trans:cis*, could be made from spectra obtained at −17°. That ratio and the equilibrium constant for the *cis* to *trans* conversion is 1.2 ± 0.05. Between 0 and −60°, the equilibrium constant for *cis–trans* isomerization is 1.2 ± 0.1 and exhibits no apparent trend with temperature.[18] A first-

(17) (a) We thus ascribe the chemical shift differences to neighboring acac rings which are magnetically anisotropic. (b) The acac methyl groups of the *cis* complex are stereochemically distinct, two being *cis* and two *trans* to DMF. However, even at −60°, no structure could be distinguished for either the 1'$_c$ or 1'$_t$ signals, although at all temperatures the 1'$_c$ signal is broader than that of 1'$_t$. The broadness of the former may be due to the overlap of two signals of nearly equal chemical shift.

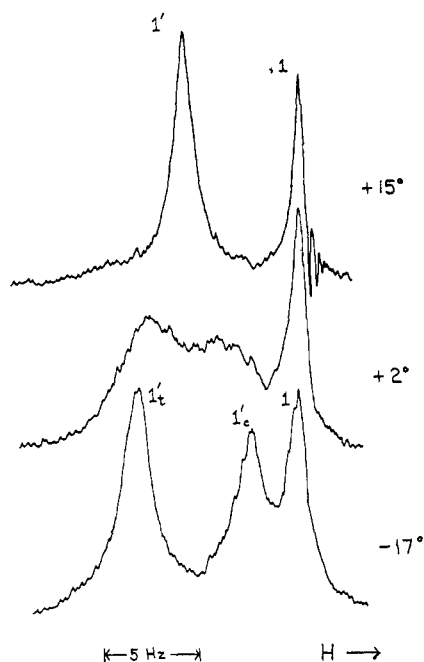(18) In the calculation of the thermodynamic parameters for reac-

(15) J. V. Hatton and R. E. Richards, *Mol. Phys.*, **3**, 253 (1960).
(16) B. B. Wayland, R. S. Drago, and H. F. Henneike, *J. Am. Chem. Soc.*, **88**, 2455 (1966).

Figure 4. Temperature dependence of the 60-MHz pmr spectrum of a DMF solution of Al(acac)$_3$ and Al(acac)$_2$(DMF)$_2^+$ in the acac$^-$ methyl region. The formal composition of the solution is Al(acac)$_3$ = 0.165 m and Al(DMF)$_6^{3+}$ = 0.078 m.

order rate constant for *cis–trans* isomerization of 18 sec$^{-1}$ at the coalescence temperature, 5°, was estimated from the difference in the chemical shifts between the acac$^-$ methyl signals at −20°.[19]

Above 15° the only detectable pmr signals due to DMF in the primary coordination sphere at Al(III) (a', b', c') in these solutions can be assigned to the complex Al(DMF)$_6^{3+}$ by comparison of peak areas and chemical shifts. However, below 15°, new peaks in the DMF methyl region can be distinguished within 2 Hz of those for Al(DMF)$_6^{3+}$ as shown in Figure 5 and can be assigned to complexes containing acac$^-$. By comparing the relative signal areas and the complex concentrations calculated from the acac$^-$ signals, the following assignments can be made: b''' to DMF in *cis-* and *trans*-Al(acac)$_2$(DMF)$_2^+$; b$_1$'', b$_2$'', and a$_1$'' to DMF in Al(acac)(DMF)$_4^{2+}$, one set designated by subscript 1 or 2, due to DMF *trans* to an acac$^-$ oxygen atom, and one set due to DMF *cis*. Two of the coordinated DMF signals, a''' and a$_2$'', are shifted under the bulk DMF signal (b). Because of the low intensity of the formyl peaks, separate formyl resonances could not be distinguished for the 1:1 and 2:1 complexes. Accurate values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the exchange of DMF from these complexes were not attainable because of the many overlapping peaks. However, the DMF exchange rates at the coalescence temperature (of the signals b and b$_1$'', b and b''', etc.) were estimated using a computer program for a complete line-shape analysis described elsewhere.[20] From the known populations and the chemical shift between the ex-

tions 1 and 2, it was assumed that only one 2:1 complex is formed. Because $\Delta H \cong 0$ ($K$ is independent of temperature) and $K = 1$ for *cis–trans* isomerization, those parameters are unaffected, within the error limits, if the distribution of the 2:1 complex into *cis* and *trans* isomers is incorporated in the calculation.

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

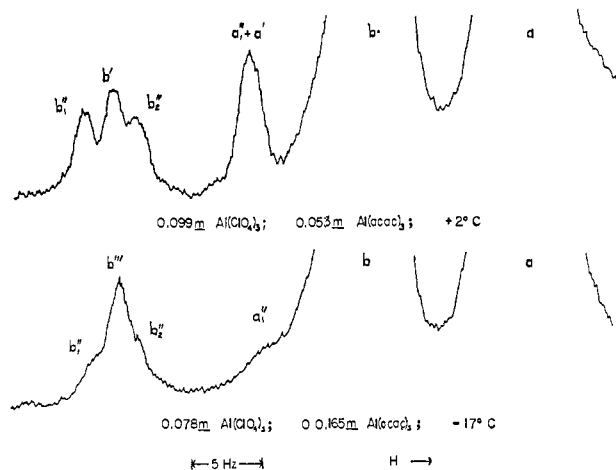(20) P. E. Darley and N. A. Matwiyoff, *J. Am. Chem. Soc.*, in press.



Figure 5. 60-MHz pmr spectra of the Al(acac)(DMF)$_4^{2+}$ and Al(acac)$_2$(DMF)$_2^+$ in the DMF N-methyl region.

changing sites, the rate constant for exchange at DMF from these complexes can be estimated to be 30 sec$^{-1}$ at coalescence, here defined as the temperature at which no minimum occurs between the two absorption signals. The coalescence temperature is 5° for the complex Al(acac)$_2$(DMF)$_2^+$ and 15° for Al(acac)(DMF)$_4^{2+}$.

**Electronic Absorption Spectra.** The ligand acac$^-$ and its metal complexes exhibit an intense $\pi$–$\pi^*$ transition in the uv region.[21] The spectral parameters for this electronic transition of Al(acac)$_3$ dissolved in chloroform have been reported to be $\lambda_{max}$ 288 m$\mu$ and $\epsilon_{max}$ 42,800. From the ultraviolet spectra of various mixed solutions of Al(acac)$_3$ and Al(DMF)$_6$(ClO$_4$)$_3$ in DMF we obtain the parameters $\lambda_{max}$ 288 m$\mu$ and $\epsilon_{max}$ 13,500 for all complexes (including Al(acac)$_3$), where $\epsilon_{max}$ was calculated using the total formal concentration of acac$^-$.

### Discussion

It is of interest to compare the data obtained for this Al(III) system to that for the corresponding Be(II) system, for, although Be(II) is four-coordinate and Al(III) is six-coordinate, the two metal ions have similar chemistries due mainly to similar charge-to-radius ratios: Al(III) 6.0, Be(II) 6.5. In Table III are summarized data for the Al(III)–acac$^-$–DMF[7] and the Be(II)–acac$^-$–DMF systems,[10] along with that for the corresponding water systems.[11,22,23] The first set of kinetic parameters refers to solvent exchange from complexes containing only DMF or H$_2$O; the second set refers to DMF exchange from complexes containing acac$^-$. The thermodynamic parameters refer to reaction of the type depicted in eq 1 and 2. The $\Delta S_{cor}$ values listed in Table III were obtained by subtracting the conformational contribution to the entropy change from $\Delta S_1$ and $\Delta S_2$. From the "site" symmetries of Al(DMF)$_6^{3+}$ (O$_h$), Al(acac)(DMF)$_4^{2+}$ (C$_{2v}$), *cis*-Al(acac)$_2$(DMF)$_2^+$ (C$_2$), *trans*-Al(acac)$_2$(DMF)$_2$ (D$_{2h}$), and Al(acac)$_3$ (D$_3$) and also taking into consideration the optical activities of the 3:1 and *cis* 2:1 complexes, conformational contributions to the entropy change of 8

(21) R. H. Holm and F. A. Cotton, *ibid.*, **80**, 5658 (1958).

(22) G. Czerlinski, H. Diebler, and M. Eigen, *Z. Physik. Chem.* (Frankfurt), **19**, 246 (1959).

(23) (a) R. M. Izatt, W. C. Fernelius, C. G. Haas, Jr., and B. P. Block, *J. Phys. Chem.*, **59**, 170 (1955); (b) R. M. Izatt, W. C. Fernelius, and B. P. Block, *ibid.*, **59**, 235 (1955).

**Table III.** Kinetic and Thermodynamic Parameters for Al(III)-
and Be(II)-acac⁻ Complexes[a]

| | Al(III) | | Be(II) | |
|---|---|---|---|---|
| | DMF[b] | H₂O[c] | DMF[d] | H₂O[e] |
| Kinetic Parameters | | | | |
| $k$, sec$^{-1}$ | 4 | 6 | 310 | 100 |
| $\Delta H^{\ddagger}$, kcal | 17.7 | 27 | 14.6 | ... |
| $\Delta S^{\ddagger}$, eu | 4.7 | 28 | 2.6 | ... |
| $k$, sec$^{-1}$ | 30 (15°)[f] | ... | 22[h] | ... |
| | 30 (15°)[g] | | | |
| $\Delta H^{\ddagger}$, kcal | ... | ... | 13.9 | ... |
| $\Delta S^{\ddagger}$, eu | ... | ... | -6 | ... |
| Thermodynamic Parameters | | | | |
| $K_1$ | 0.65 | 5 (30°) | 10 | 13 (20°) |
| $K_2$ | 3.6 | 130 (30°) | | |
| $\Delta H_1$, kcal | 7.7 | ... | 0 | -4.9 |
| $\Delta H_2$, kcal | 4.9 | ... | | |
| $\Delta S$, eu | 25 | ... | 5 | 21 |
| $\Delta S_2$, eu | 19 | ... | | |
| $\Delta S_{1,cor}$, eu | 17 | ... | 0 | 16 |
| $\Delta S_{2,cor}$, eu | 18 | | | |

[a] The temperature is 25° unless stated otherwise. [b] This work
and ref 7. [c] References 11 and 23. [d] Reference 10. [e] References
22 and 23. [f] Al(acac)(DMF)₄²⁺. [g] Al(acac)₂(DMF)₂⁺. [h] Be-
(acac)(DMF)₂⁺.

and 1 eu are calculated for reactions 1 and 2, respec-
tively.[24] The conformational contributions to $\Delta S$ for
the Be(II) system have been discussed previously.[10]

Differences between the Al(III) and Be(II) systems are
pronounced. The rate of exchange of DMF from com-
plexes containing only DMF is much larger for Be(II)
than for Al(III). Even more marked is that the rate of
exchange of DMF increases upon addition of acac⁻
to the first coordination sphere of Al(III) whereas it
decreases for Be(II). The sequence of relative labilities,
Al(DMF)₆³⁺ < Be(acac)(DMF)₂⁺ < Al(acac)-
(DMF)₄²⁺ < Be(DMF)₄²⁺, Al(acac)₂(DMF)₂⁺,[25] cannot
be rationalized using electrostatic arguments alone if
the SN1 mechanism for DMF exchange is accepted.[10]
Steric arguments are also inadequate, for by using
scaled molecular models it can be shown that the Al(III)
and Be(II) complexes are about equally sterically

(24) S. W. Benson, *J. Am. Chem. Soc.*, **80**, 5151 (1958).
(25) The rate constants for DMF exchange from the 1:1 and 2:1
Al(III) complexes were evaluated only at 15 and 5°, respectively. How-
ever, an assessment of the gross temperature dependence of the DMF
line widths reveals that, 10 kcal $\leq \Delta H^{\ddagger} \leq$ 15 kcal. Using this range
of $\Delta H^{\ddagger}$ values, we can fix the gross order of labilities of the complexes.

hindered, and that upon addition of acac⁻ ligands to the
first coordination sphere trends are toward less hin-
drance for both metal ions. Data for the Be(II) system
suggest that the sequence of labilities is due primarily
to an entropy effect which may be associated with sol-
vent molecules beyond the first coordination sphere.[10]
Because all the kinetic parameters could not be obtained
for the Al(III) system, a more detailed comparison of
the data is not possible.

As discussed previously,[10] the distribution of species
at equilibrium for the reaction Be(acac)₂ + Be-
(DMF)₄²⁺ = 2Be(acac)(DMF)₂⁺ is the statistically ex-
pected one. For the corresponding reactions of the
Al(III)-acac-DMF complexes the distribution is not
statistical and, unlike the Be(II) system, is a consequence
of large values of $\Delta H$ and $\Delta S_{cor}$. We have not been
able to devise a simple electrostatic or steric model for
the bonding in the first coordination spheres of these
complexes which can account consistently for the data
obtained in *both* systems. A comparison of the thermo-
dynamic parameters in Table III for the water and
DMF complexes suggests that solvation effects in the
second coordination spheres may be important in deter-
mining the distribution of species resulting from acac
exchange. It is particularly interesting to note that
the distribution of species in the Be(II)-acac-H₂O sys-
tem is *not* statistical and that associated with the forma-
tion of Be(acac)(H₂O)₂⁺ are large values of $\Delta H$ and
$\Delta S_{cor}$.

The rate of exchange of DMF from the complexes
*cis*- and *trans*-Al(acac)₂(DMF)₂⁺ is somewhat less than
twice that for *cis-trans* isomerization. This ratio of
rates is of the magnitude expected if the rate-determin-
ing step for *cis-trans* isomerization is dissociation of
DMF.[26] In view of the much slower rates of isomeriza-
tion exhibited by unsymmetrical Al(III) tris-β-dike-
tonates,[27] an intramolecular mechanism for the rate-
determining step of isomerization of Al(acac)₂(DMF)₂⁺
is unlikely. The complex Co(ethylenediamine)₂(H₂O)₂⁺
resembles Al(acac)₂(DMF)₂⁺ at least superficially and,
for the former, Kruse and Taube[28] found that the water
exchange rates exceed the rates of isomerization by at
least a factor of 2.

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