that overtone arguments should be disregarded, only that overtones can presumably best be used when they are sufficiently well separated that accidental degeneracies do not restrict their value and the limitations are fully appreciated.

Experimental Section

Preparation of Compounds.—The carbonyls $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were obtained from Alfa Inorganics but were recrystallized from toluene and sublimed prior to use. The hydrides $HMn(CO)_5$ and $HRe(CO)_5$ were prepared by the acidification of the corresponding sodium pentacarbonylmetalate, which had first been heated at 60° *in vacuo* (0.01 mm) for 72 hr. They were carefully dried by repeated bulb-to-bulb distillations onto P_4O_{10}. Several further distillations were carried out to remove traces of P_4O_{10} which distils slowly under high vacuum. No traces of any impurities could be found in the pure samples of the colorless hydrides in the microwave, mass, or nmr spectra.[7] The $BrMn(CO)_5$ was made by the procedure of Abel and Wilkinson.[10]

Physical Measurements.—The spectra were obtained on a Perkin Elmer LR-1 equipped with a helium–neon laser and a Cary Model 81 with Hg 4358 A excitation. The accuracy of the Raman lines is believed to be ± 3 cm^{-1}. The polarizations were obtained on the LR-1, since the laser presents an inherently more convenient and accurate arrangement. The use of the red line laser excitation is particularly valuable with $Mn_2(CO)_{10}$ and $BrMn(CO)_5$ because of their color. The use of the Toronto arc with $HMn(CO)_5$ was particularly inconvenient due to free-radical decomposition induced by the radiation.[11] The carbonyl hydrides were run as neat liquids, the others as solids. The assignments of the principal lines in the carbonyl hydride spectra are listed in Table I. No corrections were made for instrument polarization. However, the depolarization ratios are relatively accurate for $HMn(CO)_5$ (on this instrument the value of 0.007 for the A_1 mode of CCl_4 is very close to that predicted). A 0.25-ml microcell was used for the $HRe(CO)_5$ measurements; hence, reflections tend to give high values of ρ (this presumably accounts for the observation that ρ_1 is greater than 0.75). The values for the B_1 and E modes are probably within the experimental error; however, a portion of their polarization is very likely due to the A_1 mode beneath them. Presumably the $A_1^{(1)}$ mode is weak and buried under the B_1 and E modes; a shoulder is observed at 2031 cm^{-1} in $HRe(CO)_5$ which may be due to this vibration.[13] The relative intensities of the lines in the other spectra are given in Figure 2. The numerical values for the Raman lines (in cm^{-1}) are: $BrMn(CO)_5$, 1984, 2072, 2086, 2137; $Mn_2(CO)_{10}$, 1973, 1984, 2007, 2017, 2112; $Re_2(CO)_{10}$, 1977, 1985, 2015, 2024, 2126.

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(7) The microwave spectra were determined using both a conventional Stark modulated spectrometer and a Hewlett-Packard phase-stabilized Model 8400 X-band spectrometer capable of sensitivities of 5×10^{-10}/cm. THF has an intense microwave spectrum and preliminary drying of the sodium carbonylmetalates must be carried out for 72 hr or more to avoid contamination with THF. The absence of the THF lines in the microwave spectrum of the samples indicates essentially complete removal of this impurity. It was hoped that further information regarding the structure of hydrides would be forthcoming from their microwave spectra. The absence of any detectable spectra, even in the extremely sensitive Hewlett-Packard instrument, indicates that the dipole moment of 0.75 D. calculated by conventional methods[8] is an upper limit. Comparison with the intensity of the spectrum[9] of $C_5H_5Mn(CO)_3$ suggests that the dipole moment is probably less than 0.5 D. (assuming of course that the C_{4v} structure is retained in the gas phase and that some tunneling mechanism is not reducing the effective moment). The mass spectrum gave no indication of THF or P_4O_{10} impurities; however, it does attest to the stability of the manganese–hydrogen bond, for the fragmentation pattern showed consecutive loss of carbon monoxide moieties with a large percentage of the metal-containing fragments retaining the hydrogen.

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(13) The line of $HMn(CO)_5$ at 1993 cm^{-1} is not assigned as the A_1 mode on the basis of polarization; however, the depolarization ratio is not necessarily small in any but cubic point group molecules. Therefore, it might well be that the shoulder at 2031 cm^{-1} in $HRe(CO)_5$ is the E mode and that the 1994 cm^{-1} line in $HRe(CO)_5$ and the 1993 cm^{-1} line in $HMn(CO)_5$ are A_1 modes.

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Proton and Aluminum-27 Nuclear Magnetic Resonance Studies of Aluminum(III) Perchlorate in N,N-Dimethylformamide

BY W. G. MOVIUS AND N. A. MATWIYOFF

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Proton Resonance.—In recent proton nmr studies of N,N-dimethylformamide (DMF) solutions of anhydrous perchlorate salts of transition metal ions, it has been shown that the primary solvation spheres of the cations Ni^{2+},[1] Co^{2+},[1] Cu^{2+},[2] Fe^{3+},[2] and Cr^{3+} [2] are kinetically well defined. Although the solvent molecules in the primary solvation spheres of most diamagnetic cations are apparently too labile to detect by ordinary techniques, isotope dilution[3] and oxygen-17 nmr studies[4,5] of the aqueous solutions of $Al(ClO_4)_3$ have been used to distinguish water in the primary solvation sphere of Al^{3+} from that in the bulk of the solution. A recent report[6] of the determination by proton nmr of the primary solvation number (six) of Al^{3+} in the solvent dimethyl sulfoxide has prompted this communication of our study of the kinetics and stoichiometry of the solvation of the Al^{3+} ion in anhydrous DMF.

At temperatures below 95°, the 100-Mc proton nmr spectra of solutions of $Al(DMF)_6(ClO_4)_3$ in DMF consist of six signals, three of which can be assigned to DMF in the primary coordination sphere of the Al^{3+} ion and three to DMF in the bulk of the solution. The three signals of DMF in each environment consist of a low-field signal due to the formyl proton and two high-field signals due to the nonequivalent N-

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methyl groups (see Figure 1). The higher field N-methyl resonance is assigned to the methyl group *cis* to the oxygen atom.[1,7] The site of coordination is assumed to be the oxygen rather than the nitrogen atom because the C–O stretching frequency of DMF in $Al(DMF)_6(ClO_4)_3$ is 11 cm^{-1} lower than that of DMF itself.[8,9] The nonequivalence observed for the N-methyl protons in the coordination sphere of Al^{3+} also suggests[1] that coordination is through the oxygen.

In Table I are summarized the chemical shifts and relative areas of the signals observed for a 0.20 *m* solution of $Al(DMF)_6(ClO_4)_3$ in anhydrous DMF at 36°. The primary solvation number, 6.0 ± 0.3, which was calculated using the relative areas and the known concentration of the Al^{3+} ion, did not exhibit any apparent trend as a function of temperature in the range 0–80°. Similar results were obtained using solutions containing 0.10 and 0.15 *m* $Al(ClO_4)_3$.

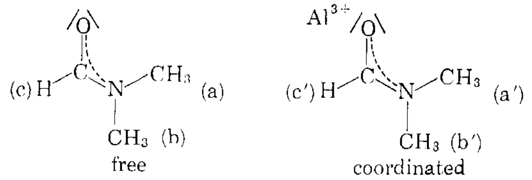

Figure 1. DMF protons corresponding to the assignments in Table I.

TABLE I

CHEMICAL SHIFTS AND RELATIVE AREAS OF THE PROTON NMR SIGNALS OBSERVED AT 100 MC FOR A 0.20 *m* SOLUTION OF $Al(ClO_4)_3$ IN DMF AT 36°

Proton[a]	Chem shift ± 0.1 cps[b]	Rel area[c]
a	. . .	3.00 ± 0.015
b	−16.1	3.00 ± 0.015
c	−523.9	1.00
a′	−33.6	0.29 ± 0.015
b′	−44.7	0.29 ± 0.015
c′	−554.2	0.095 ± 0.015

[a] Assignment as in Figure 1. [b] Chemical shift with respect to proton a. [c] Ratio of the area of a given peak to that for peak c. For method used to obtain areas, see ref 1.

The temperature dependence of the width ($\Delta\nu$) of the nmr signal b′ for the complex, Al $(DMF)_6^{3+}$, in the three solutions is summarized in Table II. Within the temperature range included in Table II, the chemical shifts of the DMF protons in the free and coordinated sites are temperature independent. Consequently the line widths of the complex should conform to the equation[10,11]

$$\pi\Delta\nu = \frac{1}{\tau} + \frac{1}{T_2^0} = \frac{k_1}{6} + \pi\Delta\nu^0$$

where $1/\tau$ represents the mean lifetime of DMF in the primary coordination sphere of $Al(DMF)_6^{3+}$, k_1 represents the pseudo-first-order rate constant for the exchange of DMF between free solvent and coordinated sites, and $1/T_2^0$ and $\Delta\nu^0$ are, respectively, the transverse relaxation rate and the line width of a proton of DMF in $Al(DMF)_6^{3+}$ when the rate of the solvent exchange reaction is negligible. Since it was observed that the widths of the free and coordinated DMF are equal within the temperature range 0–40°, the quantity $\Delta\nu^0$ was taken to be the width of the appropriate signal of the pure solvent DMF at a given temperature.

TABLE II

TEMPERATURE DEPENDENCE OF THE LINE WIDTHS OF PROTON b′ OF THE COMPLEX $Al(DMF)_6^{3+}$ AND THE RATE CONSTANT FOR THE EXCHANGE OF DMF WITH THE BULK SOLVENT

Solution concn	Temp, °C	$\Delta\nu$, cps	$\Delta\nu - \Delta\nu^0$	k_1, sec^{-1}
0.20 *m* $Al(ClO_4)_3$	80.0	9.6	7.8	150
	75.0	6.4	4.6	87
	70.0	5.3	3.5	66
	65.0	4.4	2.6	49
	60.0	3.4	1.6	30
	55.0	2.6	0.8	15
	50.0	2.4	0.6	11
	45.0	2.2	0.4	8
	40.0	1.8	. . .	. . .
0.15 *m* $Al(ClO_4)_3$	80.0	9.7	7.9	150
	70.0	5.3	3.5	66
	60.0	3.4	1.6	30
	50.0	2.3	0.5	9
	40.0	1.8	. . .	. . .
0.10 *m* $Al(ClO_4)_3$	75.0	6.5	4.7	88
	65.0	4.4	2.6	49
	55.0	2.7	0.9	17
	50.0	2.1	0.3	6
	45.0	1.8	. . .	. . .

The values of k_1 listed in Table II are equal, within experimental error, to those obtained from the widths of the signals c′ and a′. The activation enthalpy, $\Delta H^{\ddagger}$, and entropy, $\Delta S^{\ddagger}$, for the rate of exchange of DMF between $Al(DMF)_6^{3+}$ and the free solvent, calculated from the rate constants in Table II, are 17.7 kcal $mole^{-1}$ and 1.2 ± 0.2 cal deg^{-1} $mole^{-1}$, respectively. These values are both slightly less than those obtained for the dimethyl sulfoxide complex.[6]

Aluminum-27 Resonance.—Very few studies of ^{27}Al nmr have been reported,[12–14] especially with respect to Al^{3+} ions in coordinating solvents.[15,16] Much of the work which has been reported has utilized the fact that ^{27}Al has a quadrupole moment, so that deviations of the electric field about the aluminum nucleus from spherical symmetry result in a broadening of the resonance line. In Table III are summarized the data for the ^{27}Al resonance at 37°. Values for aqueous solutions are in accord with those previously obtained.[16] The difference in the line widths of $Al(ClO_4)_3$ in aqueous and DMF solutions is probably a viscosity effect. The narrowness of the ^{27}Al signal in $Al(DMF)_6^{3+}$ is indicative of a nearly spherical field about the Al^{3+} ion, which is in agreement with the presumed octahedral coordination of DMF. The width of the ^{27}Al signal in solu-

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Table III

^{27}Al Chemical Shifts and Line Widths for Solutions of Aluminum Compounds at 12.0 Mc

Compound	Solvent	Chemical shift ± 5 cps	Line width, cps
$Al(ClO_4)_3$ (0.20 *m*)	DMF	+990	39 ± 2
$Al(ClO_4)_3$ (satd)	H_2O	+970	55 ± 2
$Al(acac)_3$ (1.0 *m*)	Benzene	+940	120 ± 2
$KAl(OH)_4$ (0.20 *m*)	Aqueous KOH	...	200 ± 5

tions of $Al(acac)_3$, which has a D_3 perturbation upon its grossly octahedral geometry, and $Al(OH)_4^-$, which is tetrahedral, demonstrate how marked the broadening is with the lowering of symmetry.

These studies are now being extended to mixed complexes of the type $Al(DMF)_{6-n}X_n^{3-n}$, utilizing both the proton and ^{27}Al resonances.

Experimental Section

Acetylacetone (2,4-pentanedione) was obtained from Matheson Coleman and Bell and distilled before use. Eastman White Label N,N-dimethylformamide (DMF) was purified in the manner previously described.[1] Aluminum trisacetylacetonate was prepared by dissolving stoichiometric amounts of $Al(ClO_4)_3$ and acetylacetone in water and neutralizing the resulting solution with aqueous ammonia. The precipitate which formed was separated by filtration and recrystallized from a benzene-petroleum ether (bp 67–92°) solution. The complex $Al(DMF)_6(ClO_4)_3$ was prepared from $Al(ClO_4)_3 \cdot 9H_2O$ (G. F. Smith Chemical Co.) using the method of Drago, *et al.*[17] *Anal.* Calcd for $Al(DMF)_6(ClO_4)_3$: Al, 3.52; ClO_4, 39.1. Found: Al, 3.4; ClO_4, 39.2.

The proton nmr spectra were obtained at 100 Mc using a Varian HA-100 spectrometer operated in the HR mode. The spectrometer was equipped with a variable-temperature probe and the Varian variable-temperature control system, V-6057. The system was calibrated and the measurements were obtained in the manner described previously.[1] The line widths were reproducible to within ±0.2 cps.

The ^{27}Al nmr spectra were obtained at 12 Mc using a Varian HR-40 spectrometer equipped with a 12-Mc probe and radiofrequency unit. The magnetic field was calibrated with an audio oscillator monitored by a frequency counter. Each of the line widths and chemical shifts reported is the average obtained from four spectra. The chemical shifts were obtained using an aqueous solution of potassium tetrahydroxoaluminate(III) as the external standard.

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Contribution from the Central Research Division,
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Bis(cyclopentadienyl)titanium(IV) Compounds with Sulfur-Containing Groups[1]

By S. A. Giddings

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Transition metals to the left of the periodic table are considered to be type A using the Chatt[2] designation or to be "hard" acids in the Pearson[3] designation. Titanium(IV) would have to be considered typical of the above as it has no d electrons and thus should not be able to enter into $d\pi$–$d\pi$ back bonding with donors such as sulfur- and phosphorus-containing ligands which have empty d orbitals. It would be expected to form compounds more readily with oxygen and nitrogen donors (hard bases). Obvious attempts to form bis(cyclopentadienyl)titanium diethoxide were unsuccessful[4,5] using a variety of approaches. Efforts to prepare the diphenoxide by the author also proved unsuccessful and will be reported elsewhere. This paper reports the synthesis of the dimercaptide derivatives of bis(cyclopentadienyl)titanium and an investigation of the dithiocyanate derivative.

Experimental Section

All glass apparatus was thoroughly dried and rections were carried out under dry argon unless noted. Solvents were dried by standard procedures.

a. **Preparation of Bis(cyclopentadienyl)titanium Dimethylmercaptide.**—A 2-ml amount (excess) of methanethiol (Eastman) was added to 0.3 g of sodium (0.013 g-atom) in 50 ml of dry ether. A Dry Ice condenser was used along with a trap containing pellets of KOH to prevent escape of traces of the malodorous thiol. The mixture was stirred at room temperature for 3 days and then 50 ml of toluene was added, followed by bis(cyclopentadienyl)titanium dichloride (1.25 g, 0.005 mole). Stirring was continued for 3 hr and the red solution turned burgundy in color. The mixture was heated to the reflux temperature of toluene and was then filtered while still hot. On cooling overnight, at 0° deep burgundy crystals (0.82 g, yield 60%) were obtained, mp 193–197°. *Anal.* Calcd for $C_{12}H_{16}S_2Ti$: C, 52.76; H, 5.91; S, 23.55. Found: C, 53.43; H, 5.54; S, 23.20.

b. **Preparation of Bis(cyclopentadienyl)titanium Didodecylmercaptide.**—Dodecanethiol (Eastman 3.03 g, 0.015 mole) was mixed with 25 ml of dry benzene and 5 ml triethylamine. Bis(cyclopentadienyl)titanium dichloride (1.87 g, 0.0075 mole) was added to the above mixture which was then brought to reflux and maintained for 1 hr. The reaction mixture was filtered while hot and the filtrate was evaporated to dryness. The solid obtained was treated with hot hexane and filtered, and the filtrate was reduced in volume. A solid product appeared when the solution was cooled to 0°; it could not be filtered at room temperature as it tended to melt. Filtration at 0° gave 4.50 g of a deep burgundy material which melted on warming to room temperature. Purification of this material was not possible but infrared spectra showed no unusual bands.

c. **Preparation of Bis(cyclopentadienyl)titanium Diphenylmercaptide.**—Bis(cyclopentadienyl)titanium dichloride (2.49 g, 0.01 mole) was dissolved in a solution of 90 ml of toluene and 10 ml of triethylamine. Thiophenol (2.204 g, 0.02 mole) was added; the mixture was stirred for 2 hr at room temperature and then heated at reflux temperature for 30 min. The reaction mixture was filtered while still hot and the solvent was then stripped from the filtrate. The solid obtained was then recrystallized from toluene; yield, 3.40 g (86%) of very deep burgundy crystals, mp 199–201°. *Anal.* Calcd for $C_{22}H_{20}TiS_2$: C, 66.57; H, 5.10; S, 16.17; mol wt, 396.4. Found: C, 66.52; H, 5.25; S, 16.26; mol wt, 395 (in benzene).

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