Complexes of Amides with Cations of Low Charge Density: ^{1}H Nuclear Magnetic Resonance Study of the Ag$^+$–Dimethylacetamide Complex

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AMIDES are known to be able to give complexes with a variety of inorganic salts.[1–3] The complexes of N-methylformamide and NN-dimethylformamide with such salts as $AlCl_3$, $BeCl_2$, $GaCl_3$, $SbCl_5$, and $TiCl_4$ have recently been studied by means of ^{1}H n.m.r. technique.[2,3] In these compounds all of the observed spectral features can be interpreted in terms of the high values of the charge densities of the cations. However, this can not be the case for the complexes formed by NN-dimethylacetamide (D.M.A.)[1] in the solid state, with, among others, Li$^+$ or Ag$^+$.

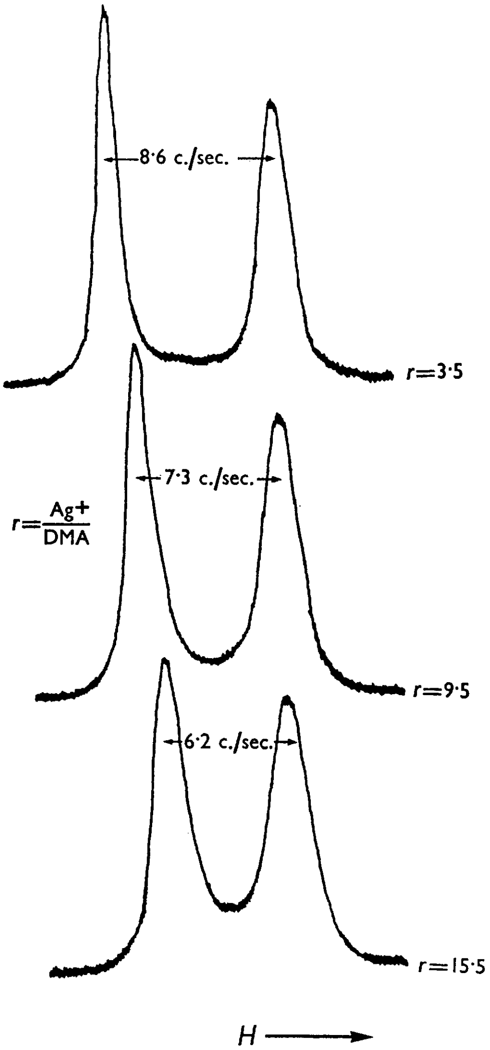

FIGURE. *Spectra of the* N–CH_3 *doublet of aqueous solutions of D.M.A. and* $AgNO_3$. *The r's are the molar ratios* $n_{Ag^+}/n_{D.M.A.}$.

The ^{1}H n.m.r. study reported here proves an Ag$^+$–D.M.A. complex to exist both in solution of D.M.A. itself and in aqueous solution. There is also indication that the nature of the Ag$^+$–D.M.A. interaction is more similar to that between H$^+$ and D.M.A.[4] than to that present in the systems studied by Fratiello and his co-workers.[2,3] Addition of Ag$^+$ ions to D.M.A. or aqueous D.M.A. reduces the relative chemical shifts of the N–CH_3 protons and destroys the fine structure of the higher-field N–CH_3 peak (Figure). The observed spectral changes† are consistent with the presence of varying amounts (for increasing r values) of two types of D.M.A. molecules, bulk and complexed, in rapid equilibrium, characterized by different N–CH_3 doublet separations. The broadening of both N–CH_3 peaks can be due either to a not too high value of the exchange rate between bulk and complexed molecules or to the presence of a small amount of another Ag$^+$–D.M.A. complex in which the two N–CH_3 groups are equivalent.

The spectra of an aqueous solution, with $r = 3{\cdot}5$, run at different temperatures (in the range 300—360° K) seem to favour this latter hypothesis. A marked decrease in the coalescence temperature was observed (with respect to that of the uncomplexed amide) corresponding, roughly, to a decrease in the free energy of activation of 5 kcal./mole. This Ag$^+$ induced lowering of the activation barrier of the chemical exchange of the two N–CH_3 groups, closely resembles that due to H$^+$ catalysis.[4] Accordingly this may indicate the existence, in solution, of two different complexes, one (with Ag$^+$ linked to the oxygen atom of the amide) which is responsible of the decrease for the doublet

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† Spectra of D.M.A. solutions in water at pH's equal to those of the samples containing $AgNO_3$ were also measured in order to exclude H$^+$ catalysis being the main cause of the spectral changes.

separation at increasing *r* values, the other one (with Ag^+ linked to the nitrogen) responsible for the lowering of the activation barrier. The spectra were measured on an A60-A spectrometer.

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