The Structure of the Tetrahalogenocuprate Ions in Solution

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THE structures adopted by the tetrahalogenometallate ions of the first-row transition metals have aroused theoretical interest.[1,2] Recently there have been attempts[3,4] to separate the intrinsic from the lattice-induced distortion of the $CuCl_4^{2-}$ ion by examining the e.s.r. of this ion doped into various lattices.

Here it is demonstrated that the distortions apparent in solid compounds containing $CuCl_4^{2-}$ and $CuBr_4^{2-}$ ions persist in solution. Two independent methods have been used in this study.

An MX_4 species with T_d symmetry has four normal modes of vibration; two of these modes (F_2) are infrared-active, corresponding to predominantly M–X stretching (ν_3) and X–M–X bending (ν_4). Any distortion from T_d symmetry will remove the triple degeneracy of these modes. Studies[5,6] of solid compounds containing the MCl_4^{2-} ions (where M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}), show that ν_3 for these ions falls in the region 250—300 cm.$^{-1}$.

An infrared spectrum of $[Et_4N]_2[CuCl_4]$ dissolved in nitromethane containing a large excess of $[Et_4N]Cl$ (to prevent solvolysis[7]) in the region 200—400 cm.$^{-1}$ showed a strong band at 278 cm.$^{-1}$ and a band of medium intensity at 237 cm.$^{-1}$. A spectrum of $[Et_4N]_2[CoCl_4]$ run under the same conditions showed a single strong band at 296 cm.$^{-1}$ This indicates that the $CuCl_4^{2-}$ ion retains a distorted structure in solution.

Isotropic n.m.r. shifts in paramagnetic systems can arise *via* contact[8] or pseudo-contact[9] mechanisms. Pseudo-contact shifts are observed in systems with anisotropic *g*-tensors. A further condition for observation of pseudo-contact shifts in solution is that the nucleus in question must have a preferred position with respect to the paramagnetic metal. This position is usually adopted because of chemical bonding, but can arise in systems in which there is no chemical bonding (direct or indirect) between the resonating nucleus and the paramagnetic metal. Thus ^1H n.m.r.

spectra of $[Bu_4N]^+$ $[MI_3(Ph_3P)]^-$ ($M = Ni^{II}$ or Co^{II}) in $CDCl_3$ show isotropic shifts of the butyl proton resonances because of a preferred ion-pair geometry along the C_3 axis of the anions.[10,11]

The n.m.r. spectrum at 60 Mc./sec. and 37° of $[Bu_4N]_2[CuBr_4]$ (0·1 M) *in* $CDCl_3$ which is also 0·2 M with respect to $[Bu_4N]Br$ (to prevent solvolysis[7]) shows that the tetrabutylammonium resonances are shifted slightly downfield (*e.g.*, the CH_3 resonance is shifted about 20 c./sec. downfield from its diamagnetic position). Addition of more $[Bu_4N]Br$ moves the resonances closer to their diamagnetic position, showing that there is rapid exchange between ion-paired and non-ion-paired cations. These shifts must be attributed to the pseudocontact mechanism. Since a regularly tetrahedral $CuBr_4^{2-}$ ion would have an isotropic *g*-tensor, this result indicates that the $CuBr_4^{2-}$ ion is distorted in solution. The observation of a downfield pseudocontact shift for the ion pairs in $[Bu_4N]_2[CuBr_4]$ dissolved in $CDCl_3$ suggests that ion pairs are preferentially formed along the S_4 axis of the $CuBr_4^{2-}$ ion, if a D_{2d} structure is retained in solution.

The distortion evident from crystal-structure determinations on solids containing $CuCl_4^{2-}$ [12] and $CuBr_4^{2-}$ [13] is therefore due to an intrinsic property of the copper ion. Liehr[1] suggested that both the tetrahalogeno-cuprates and -nickelates ought to exhibit a regular structure because spin–orbit coupling should be sufficient to remove the orbital degeneracy ($^2T_2$ and $^3T_1$ for Cu^{II} and Ni^{II} respectively in T_d symmetry) of the ground states, which otherwise would be susceptible to a Jahn–Teller distortion. However, Lohr and Lipscomb[2] using a molecular-orbital one-electron LCAO method, calculated that a greater stabilisation energy would come about by a distortion of the $CuCl_4^{2-}$ ion to D_{2d} symmetry. Moreover, a distorted structure was calculated[2] to be energetically favoured for $NiCl_4^{2-}$. A recent and thorough crystal-structure determination[14] has shown that the $NiCl_4^{2-}$ ion in $[Ph_3MeAs]_2[NiCl_4]$ is regularly tetrahedral to within a small experimental error. A unifying theory for these systems is desirable.

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