Nuclear Magnetic Resonance Study of the Solvation Behaviour of Cobalt-(II) Halides in Non-aqueous Solvents †

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The variable-temperature ^{1}H n.m.r. behaviour of cobalt(II) halides has been studied in solvents of different basicities. The solvents were acetone, acetonitrile, acrylonitrile, and dimethyl sulphoxide. Coupling constants have been derived for each solvated species and comparison is made, where possible, with previous work. The behaviour of some systems was simulated using solvolytic equilibria.

THE solvated species present in non-aqueous solutions of cobalt(II) halides depend on the nature of the solvent.[1] ^{1}H N.m.r. is a valuable means of studying the co-ordination behaviour of proton-containing solvents since unpaired spin density may be delocalised from the metal ion to yield contact shifted peaks in the spectrum of the solution. The magnitude of the shift, relative to pure solvent, is dependent on the bonding and symmetry in the complex. For a complex having an isotropic ground state the contact shift $\Delta w/w$ at a temperature T is given by [2] equation (1)

$$\Delta w/w = (A/h)S(S+1)\gamma_e h/3kT\gamma_N \qquad (1)$$

where γ_e and γ_N are the magnetogyric ratios of the electron and proton respectively, S is the total electron spin quantum number, w is the operating frequency of the spectrometer, and (A/h) is a coupling constant which is either positive or negative for respectively positive or negative spin densities at the ligand protons; h, k, and T have their usual significance. For an anisotropic ground state there is also an anisotropic or pseudo-contact contribution in addition to the pure contact interaction given by equation (1). This may be allowed for if the geometry of the complex is known accurately.[3] In the limit of slow exchange both bulk and co-ordinated contact shifted peaks have been observed.[4]

In the fast exchange limit, the averaged signal $(\Delta w/w)$, is given by equation (2) where n_i is the

$$\Delta\bar{w}/w = \sum_i n_i N_i(\Delta w_i/w) \qquad (2)$$

co-ordination number of the i th complex of mole fraction N_i and contact shift, $\Delta w_i/w$. The temperature dependence of $\Delta\bar{w}/w$ is determined by the equilibria involving the co-ordinated species and by the temperature dependence of Δw_i. The latter is given by equation (1).

The object of these studies was to calculate, from variable-temperature n.m.r. measurements, the equilibrium constants and heats of reaction which describe the concentrations of each solvated species which have coupling constants given by equation (1).

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† Presented, in part, at the Annual Meeting of the Chemical Society, York, 1971.

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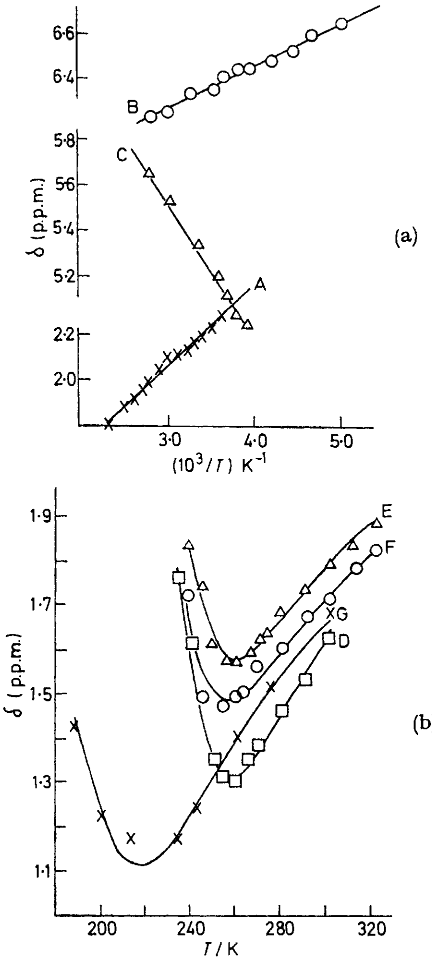
RESULTS AND DISCUSSION

For each system studied, we recorded the ^{1}H n.m.r. spectra over a range up to ± 300 p.p.m. from the pure solvent peak.* In no case were separate bulk and co-ordinated resonances observed as would be required in the slow-exchange limit.



Variation with temperature of the chemical shift, δ, in p.p.m. Solid lines are computed values and symbols (×, ○, △, □) represent experimental points: (a) A, $CoCl_2$–DMSO, [Co] = 0·50M; B, $CoCl_2$–ACRN, =CH_2 protons, and C, $CoCl_2$–ACRN, –CH= proton, [Co] = 0·65M. (b) D, $CoCl_2$–An, [Co] = 0·43M; E, $CoBr_2$–AN, [Co] = 0·30M; F, CoI_2–AN, [Co] = 0·27M; G, $CoCl_2$–AC, [Co] = 0·62M. Internal references (δ = 0 p.p.m.) were 2-methylpropan-2-ol for A and tetramethylsilane for B—G

Dimethyl sulphoxide (*DMSO*) *and Acrylonitrile* (*ACRN*).—Figure (a) summarises the behaviour of the $CoCl_2$–DMSO and $CoCl_2$–ACRN systems.

The chemical shift, δ, depended linearly on $1/T$, as required by (1) and (2) for a single solvated species. The results may be expressed numerically for solutions in which the mole fraction of cobalt is X_M and that of solvent is X_S: (a) *$CoCl_2$–DMSO.* $\delta = (1{\cdot}102X_S + 8359.\ X_M/T) \pm 0{\cdot}015$ p.p.m. Internal reference, δ = 0, was 2-methylpropan-2-ol. (b) *$CoCl_2$–ACRN.* Pure ACRN has a complex ABC n.m.r. spectrum[5] but, with added $CoCl_2$, the spectrum simplified into a low field (=CH_2) and a high field (–CH=) peak denoted by δ_1 and δ_2 respectively: $\delta_1 = (7{\cdot}56X_S - 17575\ .\ X_M/T) \pm 0{\cdot}09$ p.p.m.; $\delta_2 = (5{\cdot}87X_S + 3317\ .\ X_M/T) \pm 0{\cdot}12$ p.p.m. Internal reference, δ = 0, was tetramethylsilane. Uncertainties are given as twice the standard deviation of the mean. The dominant species in the $CoCl_2$–DMSO system has been shown to be[6,7] $[Co(DMSO)_6][CoCl_4]$. From our results, the coupling constant (A/h) calculated from equation (1) for this species was found to be $+0{\cdot}86 \times 10^5$ Hz. This is very similar to the result obtained for $[Co(DMSO)_6][ClO_4]_2$ by Thomas and Reynolds[8] and therefore indicates that ion-pairing effects may be unimportant in this solvent, in view of the possible additional contact shifts which may be caused by anions.[9]

Octahedral cobalt(II) complexes have orbitally degenerate ground states ($^4T_{1g}$) which give rise[10] to anisotropy in the electronic g values. This is expected[11] to give a small negative contribution to A/h by a pseudo-contact interaction. Pure contact interactions can give rise to larger contributions to A/h by σ- or π-electron delocalisation mechanisms.[12] For either mechanism, the ease of oxidation of cobalt(II) suggests that delocalisation will occur from the metal to the surrounding ligands. For those systems in which the π-mechanism is dominant,[12] A/h is often an order of magnitude greater than that found for DMSO. It therefore appears likely that delocalisation of positive spin density, from the $Co^{II}e_g$ orbitals to DMSO, occurs with rapid attenuation[13] through the σ-skeleton of the ligand.

The intense blue colour of the $CoCl_2$–ACRN solution suggests that a complex of the stoicheiometry $CoCl_2(ACRN)_2$ is the species present, by analogy with many similar nitrile complexes.[14] In contrast with DMSO, solvolysis does not, therefore, occur to any extent in ACRN. This may be due to the low donor strength of ACRN.[15] From the gradients of $\Delta\bar{\omega}/w$ for cobalt(II) chloride in ACRN we have calculated A/h to be $-24{\cdot}1 \times 10^5$ Hz and $+0{\cdot}16 \times 10^5$ Hz for the –CH= and =CH_2 protons respectively. The orbitally isotropic ground

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* Tables of experimental results are in Supplementary Publication No. SUP 20323 (4 pp., 1 microfiche). For details of Supplementary Publications see Notice to Authors No. 7, *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

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state of Co^{II} in C_{2v} microsymmetry is not expected to give rise to appreciable pseudo-contact contributions. Thus, the values of A/h imply a large negative spin density at the $-CH=$ position and a small positive spin density at the $=CH_2$ protons. The d_{z^2} and the $d_{x^2-y^2}$ orbitals transform as A_1 in the C_{2v} point-group and these may mix with the totally symmetric combinations of the ligand π- and σ-orbitals. Delocalisation of negative spin density from Co^{II} preserves the maximum exchange stabilisation in the metal d orbitals and this could give rise to the negative $-CH=$ coupling constant. The rapid attenuation of this effect may be cancelled at the $=CH_2$ position by the negative π-spin density which gives rise to a positive proton coupling constant.[16]

Mean values of coupling constants of cobalt complexes and thermodynamic parameters computed for equilibria 7(a) and 7(b)

System	Temp. range (K)	ΔH_a (kJ mol^{-1})	K_a	ΔH_b (kJ mol^{-1})	K_b	$10^{-4} \times A/h$ (Hz) (A)	(B)	(C)	U_J (Hz^2)
$CoCl_2$–AN	235—302	61	312	61	0·38	0·65	−14·7	−1·43	9·4
$CoBr_2$–AN	239—322	76	662	47	0·34	−0·57	−15·4	+1·54	8·3
CoI_2–AN	240—323	75	925	32	0·39	0·07	−24·2	+1·54	22·3
$CoCl_2$–AC	189—303	35	550	16	0·17	−0·16	−13·2	+3·8	20·2

Acetone (*AC*) *and Acetonitrile* (*AN*).—The ^1H n.m.r. behaviour which we have determined for cobalt(II) halide solutions is shown in Figure (b). We propose the following solvation model to account for our results:

$$CoAN_4X_2 \rightleftharpoons CoAN_2X_2 + 2AN \qquad (7a)$$

$$2AN + 2Co(AN)_2X_2 \rightleftharpoons CoAN_6^{2+} + CoX_4^{2-} \qquad (7b)$$

Other workers[17-20] have suggested equilibria similar to (7b) to be present at ambient temperatures. We consider that (7a) may be more important at lower temperatures by comparison with other cobalt(II) chloride–solvent systems.[21-23] Further evidence of 7(b) being the more important reaction at higher temperatures was obtained by adding tetraphenylphosphonium chloride (a source of ionic chloride) to an acetonitrile solution of cobalt(II) chloride. The resonance position was slightly, but consistently, to high field of that of an identical solution containing no added chloride above 265 K. Ionic chloride favours the production[20] of anionic chloro-complexes, as in equation 7(b), but should have less effect on 7(a).

An index of the quality of the fit to the observed data is given by the magnitude of the minimum value of U in equation (8).

$$U = \sum_k [\Delta\bar{\omega}_k - F_k(\mathbf{A}, \mathbf{K}, \Delta\mathbf{H})]^2 \qquad (8)$$

$\Delta\bar{\omega}_k$ and $F_k(\mathbf{A}, \mathbf{K}, \Delta\mathbf{H})$ are respectively the observed and calculated values of $\Delta\bar{\omega}$ for data point k, corresponding to temperature T_k, $\mathbf{A}$, $\mathbf{K}$, and $\Delta\mathbf{H}$ refer to the sets of coupling constants, equilibrium constants at 298 K and enthalpy changes (assumed independent of temperature). The minimisation of U was achieved by refining the unknown parameters in equation (8) by means of a direct grid search method using an ICL 1903A digital computer. The refined parameters for each of these systems, based on model (7) are shown in the Table. The species A, B, and C are CoL_4X_2, CoL_2X_2, and CoL_6^{2+} respectively (where L = AN or AC and X = Cl, Br, or I). The equilibrium constants, K_a and K_b, which refer to equations (7a) and (7b) respectively, are defined in terms of the mole fractions N_A, N_B, N_C, and N_S of the species A, B, C and solvent (AN or AC) respectively, at a temperature of 298 K.

$$K_a = \frac{N_B N_S^2}{N_A}; \quad K_b = \frac{N_C^2}{N_B^2 N_S^2}$$

No allowance for variation in activity coefficients in K_a and K_b was made. Over the concentration range used, N_S is near unity so that the equilibrium constants are almost identical to those defined in terms of concentrations. The enthalpy changes ΔH_a and ΔH_b correspond to average values over the temperature range studied and refer to equations (7a) and (7b) respectively. We have computed the species distribution on the basis of the above equilibrium constants and enthalpy changes and the predominant species present at ambient temperatures is CoL_2X_2. The species CoL_4X_2 only becomes important at the lowest temperature studied. The enthalpy change for reaction 7(b) was found to be in the sequence Cl > Br > I and this suggests that decreasing metal–ligand bond energies may be the most important factor relating to the ease of solvolysis which requires metal–ligand bond cleavage as a preliminary step. This sequence was also reported recently by Beech *et al.*[24] for the analogous decomposition reactions of the solid complexes and probably has a similar origin. The coupling constants, A/h, were small (positive or negative) for species A and C but large and negative for species B.

Matwiyoff and Hooker[11] in explaining the negative spin densities found on the protons of $[CoAN_6][ClO_4]$ in solutions of acetonitrile, postulated a mechanism

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involving a positive spin density on the nitrogen σ-orbitals which spin polarises the π-system, giving rise to negative spin densities at the protons.

The negative spin densities can also be explained in terms of a mechanism which is similar to that discussed above for acrylonitrile with additional mixing of negative spin density from the d_{z^2} and $d_{x^2-y^2}$ orbitals with the proton *s* orbitals by hyperconjugation.

EXPERIMENTAL

Materials.—Anhydrous cobalt(II) halides were prepared from the hydrated halides (B.D.H., AnalaR or Reagent grade) by dehydration with thionyl chloride.[25] The products were, finally, heated *in vacuo* for several hours.

The solvents were distilled from a dehydrating agent. Calcium hydride was used for DMSO, AC, and ACRN and phosphorus pentoxide for AN. The solvents were then stored over activated molecular sieves.

Spectroscopy.—Solutions (0·2—0·4M) of the metal halides in each solvent were prepared. The cobalt(II) iodide solutions were unstable and were used immediately. Halogen was determined by titration with silver nitrate.

A JEOL C60-HL 60 MHz spectrometer was used for the p.m.r. studies. The probe temperature was determined by a separate calibration using the methyl and hydroxyl peaks of methanol[26] (Hopkin and Williams Spectrosol). The peak positions were determined relative to an internal standard: tetramethylsilane for ACRN and AN and benzene or t-butyl alcohol for DMSO and AC.

We thank Mr. J. Cope for preparing the tetraphenylphosphonium chloride used in this work. We also thank Dr. G. Marr and Dr. B. W. Rockett for helpful discussions.

[1/1722 *Received, 20th September*, 1971]

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