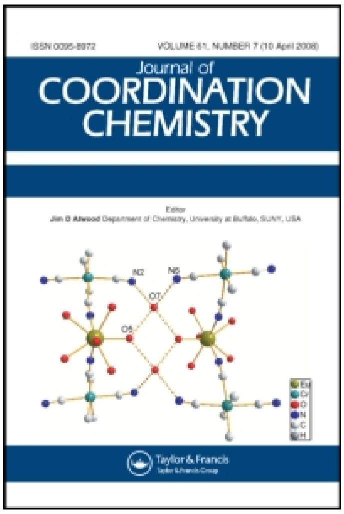

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Lim, Yau Yan(1978) 'Proton Magnetic Resonance Studies of $[NMeR_3]_2[CoBr_4]$ where R = n-C_4H_9 and n-C_8H_{17} in Non-aqueous Solvents', Journal of Coordination Chemistry, 8: 2, 105 — 107
To link to this Article: DOI: 10.1080/00958977808073079
URL: http://dx.doi.org/10.1080/00958977808073079

J. Coord Chem.
1978, Vol. 8, pp. 105–107

SHORT COMMUNICATION
Proton Magnetic Resonance Studies of $[NMeR_3]_2[CoBr_4]$ where $R = n—C_4H_9$ and $n—C_8H_{17}$ in Non-aqueous Solvents

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(Received June 8, 1977; in final form September 16, 1977)

The proton isotropic shifts of the N-methyl and N-methylene protons in $[NMeR_3]_2[CoBr_4]$ where $R = n\text{-}C_4H_9$ and $n\text{-}C_8H_{17}$ were determined in a number of non-aqueous solvents. Almost equal isotropic shifts were observed for both sets of protons. This is interpreted as unrestricted cation motion within the ion pair structure, in marked contrast to the $[NMeR_3][CoBr_3(PPh_3)]$ case reported before.[1,2]

INTRODUCTION

The isotropic n.m.r. shift of cationic protons in the presence of paramagnetic anions serves as a powerful tool for investigating ion pairing in solutions.[3] The shift arises from the following two terms: the Fermi contact shift and the dipolar or "pseudo-contact" shift. Although there is the problem of estimating the relative contribution of the contact and dipolar shift to the total isotropic shift, certain useful information concerning the ion pair geometries and concentration association constants can still be obtained from isotropic shift measurements.[1, 2, 4]

In our earlier n.m.r studies[1, 2] of the ion association of some unsymmetrically substituted tetra-alkyl-ammonium tribromo(triphenylphosphine) cobaltate(II) complexes in various solvents, it was found that there is a preferred orientation of the N-methyl group towards the anion and that there is a linear dependence of the difference in observed proton isotropic shifts of the N-methyl and N-methylene protons on the dielectric constant (ϵ) of the solvents for $\epsilon \leqslant 10$ but not at higher values of ϵ. As the system studied is a 1:1 electrolyte it is of fundamental interest to examine whether similar behaviour is found in a 2:1 electrolyte. With this in mind, we have prepared $[NMeR_3]_2[CoBr_4]$ where R = n-Butyl and n-Octyl and their n.m.r. properties studied. This article is to report the results of such work.

EXPERIMENTAL

Preparation of Complexes

The salt $[NMeBu^n_3]_2[CoBr_4]$ was prepared according to a method reported before.[5] The blue compound was recrystallized from a 3:1 ethyl acetate/n-butanol mixture (m.p. 148–150°C). Its zinc analog was prepared in the same manner (m.p. 138–139°C).

In the preparation of $[NMe(n\text{-}C_8H_{17})_3]_2[MBr_4]$ where M = Co(II) and Zn(II), one of the starting materials, $[NMe(n\text{-}C_8H_{17})_3]Br$, was prepared by treating $(n\text{-}C_8H_{17})_3N$ with CH_3Br in acetone and purified by column chromatography using activated alumina (neutral) as adsorbent and CH_2Cl_2 as solvent. After mixing stoichiometric amount of $[NMe(n\text{-}C_8H_{17})_3]Br$ and anhydrous MBr_2 in acetone the solvent was evaporated off using rotary evaporator and the resultant thick and viscous liquid mass was washed several times with anhydrous ether. A continuous stream of dry nitrogen gas was then passed over the viscous mass for 1–2 hours with occassional stirring of the viscous mass until it solidified. The cobalt(II) product has m.p. 96–98°C while the zinc analog has m.p. 110–118°C. Various attempts to recrystallize the products failed but the purity was confirmed by elemental microanalysis.

Anal. Calcd. for $C_{50}H_{108}Br_4N_2Co$: C, 53.82%; H = 9.70%; N = 2.51%;

Co = 5.28%
Found: C, 53.00%; H = 9.69%;
N = 2.42%; Co = 5.3%
Calcd. for $C_{50}H_{108}Br_4N_2Zn$:
C = 53.50%; H = 9.69%;
Br = 28.47%
Found: C = 53.72%; H = 9.46%;
Br = 28.1%

Analyses were performed by the Australian Microanalytical Service, Division of Applied Organic Chemistry, CSIRO.

Physical Measurements

The n.m.r. spectra were obtained on a Hitachi Perkin–Elmer R-20B Spectrometer at 34°C. TMS was used as the internal reference. The visible spectra were obtained with a Beckmann DB-G spectrophotometer at room temperature.

All solvents used in this work were purified according to methods described before.[1,2]

RESULTS AND DISCUSSION

Visible Spectral Studies

This work was carried out in order to determine whether the complex anion, $CoBr_4^{2-}$ remains intact in a non-aqueous solvent. The electronic spectrum of $CoBr_4^{2-}$ had been reported before[6] and in this work, we are focusing our attention on the ν_3 transition ($^4A_2 \rightarrow {}^4T_1(P)$) which occurs in the visible region of the spectrum. The ν_3 transition consists of four subbands which have ϵ_{max} at 15620, 15030, 14340 and 13870 cm^{-1} with the relative molar extinction coefficient increasing in that order. Any marked deviation from this characteristic spectrum is taken to mean that the complex anion decomposes in that solvent. Using this approach, it was found that solvents such as dimethylsulphoxide, acetonitrile and alcohols would decompose the anion and therefore not suitable for n.m.r. studies.

N.m.r. Studies

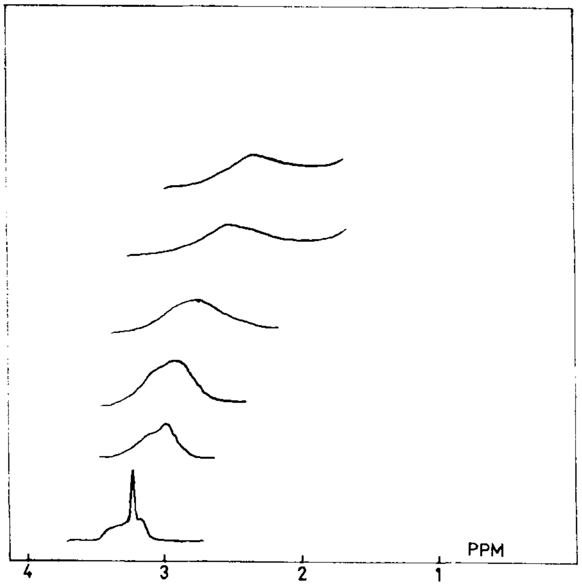

FIGURE The appearance of N-methyl and N-methylene peaks with increasing amount of cobaltate species while keeping the overall cation concentration at 0.04M in CH_2Cl_2. From bottom to up, cobaltate concentration increases in the order: 0%; 10%; 15%; 25%; 40%; 50%. Note that the other aliphatic hydrogen peaks are not shown. TMS is the internal reference.

In low dielectric constant solvents with concentration in the range 0.04–0.1 mol dm^{-3}, the N-methyl and N-methylene peaks are either hidden under the other aliphatic hydrocarbon peaks of the n-octyl/n-butyl chain which are situated at about 0.7–1.7 p.p.m. downfield from TMS or occur as shoulders. Their positions were determined indirectly by a mole-ratio method,[5] i.e. by extrapolating a plot of the observed isotropic shift against the mole fraction of the paramagnetic complex in solutions containing various amounts of the paramagnetic and diamagnetic species and where the overall cation concentration was kept constant at 0.04 mol dm^{-3}. The reliability of this method had been fully tested before. It is to be noted that more solvents can be used for study for the bulkier complex system because of its favourable solubility. It was found that for both the complexes, the N-methyl and N-methylene peaks overlap in all solvents as the amount of Co(II) increases (See figure). This means that the observed isotropic shifts for both sets of protons are equal within limits of experimental error. (See Table for summary of results).

The origin of the cationic proton shift in the presence of $[CoBr_4]^{2-}$ has been the subject of interest recently.[7] The bulk of evidence favours the axial dipolar interaction as the dominant shift mechanism where

$$\Delta\nu_{ax} = F(\chi_{\parallel}, \chi_{\perp})\, |G.F.|$$

and

$$|G.F.| = \frac{(3\cos^2\theta - 1)}{r^3}$$

TABLE
N.m.r. data[a] for 0.04 mol dm^{-3} solution of
$[NMe(n\text{-}C_8H_{17})_3]_2\ [CoBr_4]$

Solvent	ϵ^b	$\Delta\nu^\circ(N{-}CH_2)^c$	$\Delta\nu^\circ(N{-}CH_3)^c$
Benzene	2.26	194	206
Chloroform	4.56	132	131
Chlorobenzene	5.47	150	154
Methylene chloride	8.57	120	116
Nitrobenzene	33.2	57	52

[a] At 60 MHz and 34°C

[b] Dielectric constant data from Ref. 2.

[c] Observed isotropic shifts for N-methylene and N-methyl protons. The error is estimated to be ±4 Hz.

Here, θ is the angle between the metal-proton vector and the principal magnetic axis on the anion, r is the length of this vector and F is a function of the magnetic susceptibilities of the complex. Thus, the almost equal shifts for the N-methyl and N-methylene protons would mean that on the n.m.r. time scale, the two sets of protons are equivalent with respect to the principal axis of the anion. This would imply unrestricted cation motion within the ion-pair structure, in marked contrast to the $[CoBr_3(PPh_3)]^-$ case where there is preferred orientation of the N-methyl group with respect to the anion and the preference decreases with increasing dielectric constant.[1, 2] The $[CoBr_3(PPh_3)]^-$ case was explained by noting that in low dielectric constant solvents, the interionic distance is so short that it hinders free movement of the cation with respect to the anion in the ion pair but as the dielectric constant increases, the interionic distance increases and the movement of the cation is less restricted. The preferred orientation of the N-methyl group due to restriction to the free movement of the cation has been termed "trapping" of the cationic site.[7] In view of this, our observation in $CoBr_4^{2-}$ system would seem to indicate that the interionic distance even in the low dielectric constant solvents, is large enough for unrestricted cation motion within the ion pair structure.

Earlier work in Drago's laboratory[8] and our laboratory[2] have shown that a linear relationship exists between $\Delta\nu^\circ(N{-}CH_3)$ and ϵ in $[NMe(n{-}C_8H_{17})_3]_3\ [Fe(CN)_6]$ system but not between them in $[NMe(n\text{-}C_8H_{17})_3]\ [CoBr_3(PPh_3)]$ system. In $[NMe(n\text{-}C_8H_{17})_3]_2\ [CoBr_4]$ case, as can be seen from the Table, no relationship exists between them. As has been discussed before, our result would suggest that for this kind of 2:1 electrolyte, the clusters of bulky cations are not able to protect the anion from specific interactions with the solvents. This is particularly true in chloroform where preliminary work shows that there is a hydrogen-bonding interaction between chloroform and $[CoBr_4]^{2-}$ resulting in low observed isotropic shift values for both N-methyl and N-methylene groups.

ACKNOWLEDGEMENT

The author thanks Miss P. Y. Low and Miss K. E. Lim for some of the experimental works mentioned in this paper. Financial support from the Vote F Committee of the University of Malaya is also gratefully acknowledged.

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