Mn(bipy)Br <sub>2</sub>	5.93
Mn(phen)Br <sub>2</sub>	5.83
Fe(bipy)Br <sub>2</sub>	5.86
Fe(phen)Br <sub>2</sub>	5.08
Co(bipy)Br <sub>2</sub> (grayish blue)	5.17
Co(bipy)Br <sub>2</sub> (deep blue)	4.83
Co(phen)Cl <sub>2</sub> (greenish blue)	4.88
$Co(phen)Cl_2$ (pale blue)	5.14
Co(phen)Br <sub>2</sub>	5.10

Table 3. Magnetic moments (B.M.)

X-ray powder patterns and magnetic susceptibility studies

Complete tables of d values and relative intensities of the X-ray powder patterns are available from the authors upon request. Comparisons of these powder patterns show that the complexes are isostructural. The powder patterns of the deep blue  $Co(bipy)Br_2$  and greenish blue  $Co(phen)Cl_2$ differ significantly from the others. It is believed that the  $Co(bipy)Br_2$  compounds are polymorphous, both being octahedral.

The magnetic moments of those complexes whose magnetic moments have not been previously reported are listed in Table 3. These moments support the assigned stereochemistries [17], except for  $Fe(phen)Br_2$  whose moment is lower than normally observed [18, 19] for octahedral Fe(II) complexes.

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## Localised interactions of silver ions with hydrocarbons

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RECENTLY, we have demonstrated [1, 2] that in many of the silver ion complexes with heterocyclics and hydrocarbons, silver ions prefer to interact at localised sites, i.e. either at a part of the molecule with a large double bond character or with just a single atom. In order to understand in more detail about the localised interaction of the silver ions with hydrocarbons, we have extended these studies to a series of hydrocarbons. Our primary aim was to determine and compare the relative importance of the role played by isolated double bond and delocalised double bond in the formation of silver ion complexes.

In our previous communication [1] we have studied indene and styrene which provided systems

- 1. K. K. Deb, T. C. Cole and J. E. Bloor, Org. Magnet. Res. 2, 491 (1970).
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Notes

containing a benzene ring with conjugated vinyl group. The hydrocarbons, stilbene, cyclohexene, toluene and benzene are chosen as examples of electron donors which could be studied in a systematic way with the acceptor silver ion. Stilbene provides a double bond attributed to the delocalised systems so that there could be extensive delocalisations of the  $\pi$ -electrons of the double bond. Cyclohexene provides a completely localised N-system and toluene provided a benzene ring which is not further conjugated.

## **EXPERIMENTAL**

All donors were commercially available materials and no further purification was carried out. The physical method chosen here for studying weak complexes requires a large excess of the acceptor compared with the donor. This requires a solvent which will dissolve a large amount of the acceptor as well as a smaller amount of the organic donor. Acetonitrile was chosen as the suitable solvent because it would form at least 10.0 m solution of silver nitrates.

Samples of varying concentrations of the acceptor silver ions were prepared as described previously [1]. The solutions were made by weight measurements with the silver ion concentrations being expressed in molal units. The silver nitrate concentrations were varied from 2.0 to 10.0 M in the preparation of samples.

The PMR spectra of about 10-12 samples were recorded at a fixed radio frequency of 100 MHz on a Varian HA-100 instrument with the use of a time averaging computer and the probe of the instrument was thermostatted at  $30 \cdot 0^\circ \pm 0.5^\circ$ C during each measurement. The instrument was internally locked on the MeCN peak and the chemical shifts of the donor protons were measured relatively to the locked signal with the help of an electronic counter. Suitable corrections were made for the movement of the acetonitrile peak with the different concentrations of the silver ions. The chemical shifts of the various protons of the donors were the average values of about 3-4 measurements. The chemical shifts were measured to an estimated accuracy of  $\pm 0.5$  Hz.

## **RESULTS AND DISCUSSIONS**

We have demonstrated [1, 2] that the assumed equilibrium reactions between silver ions and organic donors in the solvent MeCN include the replacement of one solvent molecule on silver ion by the organic donor in order to form 1:1 silver ion-organic complex. The equilibrium expression for such competition equilibria then becomes,

$$AS_2 + D \rightleftharpoons DAS + S \tag{1}$$

where  $S_2$  represent two solvent molecules (S). Equation (1) assumed that D is not specifically solvated. If Eq. (1) is combined with the NMR equation relating to the chemical shifts in rapid equilibrium

[3], we obtain the following equation for the acceptor concentration in molal unit,

$$\frac{1}{\Delta_o} = \frac{m_s}{K\Delta_c} \cdot \frac{1}{m_A} + \frac{1}{\Delta_c} \left( 1 - \frac{2}{K} \right)$$
(2)

where  $m_s =$  moles of solvent per Kg of solvent.

 $\Delta_o$  = observed shift of the donor proton (s) in the uncomplexed state and

 $\Delta_c$  = shift of the donor proton (s) in the pure complex.

Thus, the plots of  $1/\Delta_0$  vs  $1/m_A$  should be linear for the 1:1 complex and K and  $\Delta_c$  may be directly obtained from the gradient and intercept of the line with the ordinate. We obtained good linear plots with positive intercepts using Eqn (2) from the data on all silver ion-organic complexes reported in this investigation.

The chemical shifts and equilibrium constants for silver nitrate-hydrocarbon complexes studied are given in Tables 1 and 2. The data were derived from molality units for the silver nitrate concentrations. The common feature of all silver nitrate complexes with organic donors is the downfield shift of the donor proton resonance when the complex is formed. It can be seen from Tables 1 and 2 that all of the silver ion-hydrocarbon complexes have relatively low formation constant. Cyclohexene with

## 3. H. S. Gutowsky and A. Saika, J. chem. Phys. 21, 1688 (1953).

Donors	Ref.	H <sub>1</sub>	H₂	H <sub>3</sub>	H4	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>
	*	66-2	66-2					
CH <sub>3</sub>	*	†	10·2‡					
4	[1]	16.2	22-2	40·8	14.0			
5 6 7 $CH_2$	[1]	14.8	37.6	44·2	15.2	13-4	13.0	14-8
	*	7-8§	13.1	13.1	7·8§			

Table 1.  $\Delta_c$  Values for silver ion complexes with hydrocarbons (in Hz)

\*Present investigation.

†Resonance signal under MeCN resonance.

<sup>‡</sup>Downfield peak of aromatic multiplet.

§Center of unresolved multiplet due to the phenyl rings.

its isolated double bond seems to form the strongest complex. The cyclohexene olefinic protons also have the largest shift change of all the hydrocarbon protons. The toluene complex with a completely delocalised system has a very low formation constant and the smallest proton shift change of all the hydrocarbons. The observed chemical shift change for the benzene-silver ion complex was too small for accurate measurements. This is probably due to two factors; (i) the formation constant is so small that only a very small amount of benzene is complexed even at high silver ion concentration and (ii) the interaction of the silver ion with benzene produces only a slight perturbation of the benzene proton resonance.

Indene vinyl protons shift change[1] are relatively high though not as high as the shift changes for cyclohexene. The indene aromatic proton shifts change[1] upon complex formation is about the same amount as the toluene aromatic protons. These changes are agreeable with the assumption that the silver ions interact more strongly with the isolated double bonds than with delocalised systems. The equilibrium constant of about 2.0 for the indene[1] is considerably below the value obtained for the isolated double bond of cyclohexene. Extensive delocalisation of the  $\pi$ -electrons of the double bond with the aromatic ring may be the cause of the weakened complex.

Styrene-silver ion complex[1] has an equilibrium constant near that expected based on the values for cyclohexene and toluene. The chemical shift change for the protons of the exocyclic double bond of styrene are lower than the vinyl protons of indene. Probably the ring structure of indene forces the vinyl double bond to be planar with the aromatic ring. This may allow the double bond of indene to react more strongly with the aromatic ring than the double bond of styrene.

The stilbene-silver ion complex also has a formation constant between that of cyclohexene and toluene. Again the chemical shift changes are abnormally low. The aromatic protons did not change enough for accurate measurements to be made. The vinyl protons show a shift change of only -15 Hz. The arguments used for explaining the styrene vinyl shift [1] can be invoked in order to explain the small shift change of the vinyl protons of stilbene. The downfield shift of the vinyl proton resonance

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Donors	Ref.	H1	H <sub>2</sub>	H <sub>3</sub>	H₄	H₅	H <sub>6</sub>	H <sub>7</sub>
	*	3.8	3.8					
CH <sub>3</sub>	*	†	2·2‡					
4	[1]	2.4	2.0	2.0	2.5			
5 6 7 $CH_2$ $CH_2$	[1]	1.8	1.5	1.4	1.6	1-8	1.7	1.5
	*	4·9§	4.3	4.3	4·9§			

Table 2. Equilibrium quotients (K) for silver ion complexes with hydrocarbons

\*Present investigation.

†Resonance signal under MeCN resonance.

‡Downfield peak of aromatic multiplet.

§Center of unresolved multiplet due to the phenyl rings.

produced by the  $\beta$ -phenyl groups of the uncomplexed stilbene is partially reduced by rotation of the  $\beta$ -phenyl group when complexation occurs.

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