Ligand and Counterion Control of Ag(I) Architectures: Assembly of an {Ag_8} Ring Cluster Mediated by Hydrophobic and Ag…Ag Interactions

John Fielden,[a] De-liang Long,[a] Alexandra M. Z. Slawin,[b] Paul Kögerler[c] and Leroy Cronin.*[a]

[a]University of Glasgow, WestCHEM, Department of Chemistry, Joseph Black Building, University Avenue, Glasgow, G12 8QQ, United Kingdom. E-mail: L.Cronin@chem.gla.ac.uk

[b]University of St. Andrews, EastCHEM, School of Chemistry, North Haugh, St. Andrews, Fife, KY16 9ST, United Kingdom.

[c]Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, IA, 50011, USA.

Supplementary Data

Example high-mass ES^+-MS peak

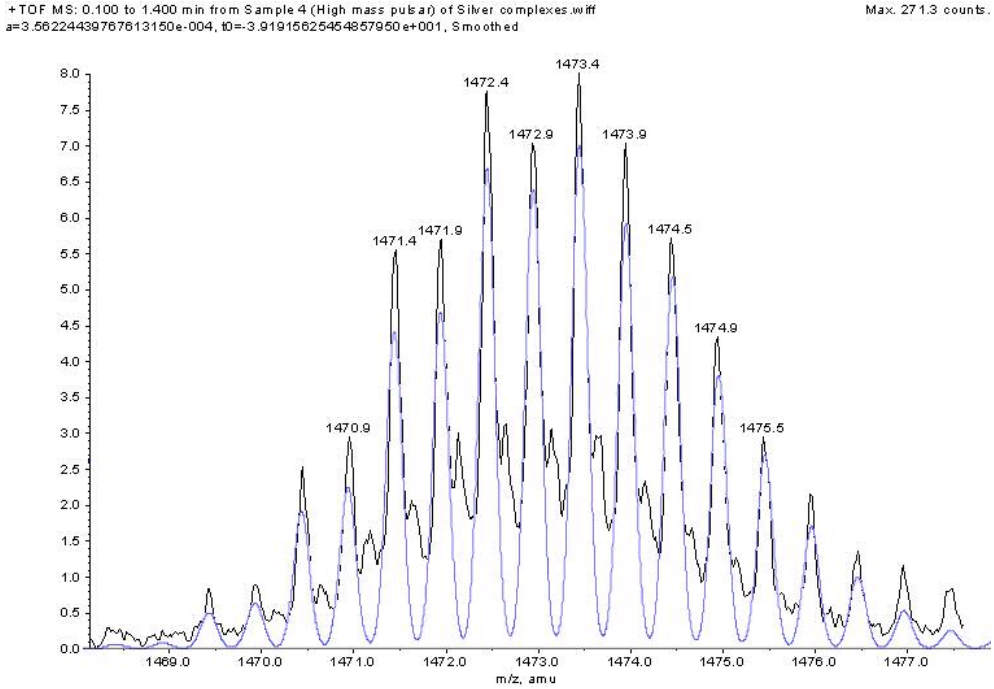

Figure 1. Measured (black) versus calculated[1] (pale blue) isotope pattern for $[Ag_8(DATC)_7(NO_3)_6]^{2+}$ observed in compound **4**. Spacing of 0.5 amu between isotopic peaks indicates 2^+ charge.

^{1}H-NMR measurement of diffusion rate (DOSY): DOSY is a 2D-NMR technique which plots chemical shift against the diffusion rate.[2] This technique was performed using a Bruker *DRX-400* NMR spectrometer controlled by Bruker *XWIN-NMR* Version 3.6 software. Data were processed with *XWIN-NMR* Version 3.1. Before acquisition of 2D data, the diffusion range was determined using the pulse program *ledbpgp2s1d*, with the diffusion time Δ (*D20*) being adjusted (in this case to 150 ms) such that a spectrum acquired with *gpz6* = 95 % had approximately 0.05 times the intensity of one acquired with *gpz6* = 2 %. 2D data was then collected using the pulse program *ledbpgp2s*, with 16 to 64 scans. Generally, adequate data could be obtained with 16 or 32 scans.

Interpretation of DOSY results and extraction of solution molecular weight: on the 2D DOSY plot, peaks from molecules with different diffusion rates appear in different positions on the *y*-axis (diffusion rate), and so can easily be assigned to each molecule. As this study does not require a highly accurate value for the molecular mass (the Ag_8 cation would have molecular mass of 2818.54 daltons, dissociation into the dimeric species would give a molecular mass of only 704.63 daltons), it is simply estimated using Graham's law of diffusion:

Diffusion rate, $r = K \,.\, (T/m)^{1/2}$

Where the constant K depends on geometric factors including the area over which the diffusion is occurring. By assuming constant temperature, and that K is the same for both species, the relative diffusion rate of two species A and B is given by:

$r_A/r_B = (m_B/m_A)^{1/2}$

Which also allows calculation of an unknown molecular mass, e.g.:

$m_B = m_A \,.\, (r_A/r_B)^2$

Therefore, diffusion rate data obtained by DOSY can be used to estimate a molecular mass by comparison with a known internal reference (the solvent), and also checked against external references (related molecules). There follow spectra and calculations for the silver macrocycle $[\{Ag_2(DATC)_2\}_4](NO_3)_8$ (**4**) and the free ligand DATC. It is important to note that, particularly at high intensity, the peaks broaden quite considerably along the diffusion rate (*y*) axis, so that accurate measurement is difficult. To obtain a reasonable estimate, the maxima of at least two peaks for each species were found using the cursor feature of *XWIN-NMR* and the diffusion rate taken as an average of the values at these points.

$[\{Ag_2(DATC)_2\}_4](NO_3)_8$ (4)

The DOSY spectrum of **4** in MeOD is shown in Figure 2, both at high and low intensity. Broadening of the peaks at high intensity means that the low intensity spectrum is clearer, even though only the silyl peaks of **4** are visible. Using the cursor in *XWIN-NMR*, maxima were found corresponding to log r = -9.71 for the solvent and log r = -10.20 for the complex. The ^{1}H signals in MeOD correspond to CD_2HOD or CD_3OH, with a molecular weight of 35.06.

Therefore: $m_{Ag8} = m_{MeOD} \times (r_{MeOD} / r_{Ag8})^2$

$m_{Ag8} = 35.06 \times (10^{-9.71} / 10^{-10.20})^2$

$m_{Ag8} = 334.80$

This value is far lower than the value of 2818.54 which would be expected for the $[\{Ag_2(DATC)_2\}_4]^{8+}$ cation, and is also significantly lower than the 704.63 which would correspond to the $[Ag_2DATC_2\}]^{2+}$ dimer. As such, it would appear to indicate that in a methanolic solution **2** dissociates into monomeric $[Ag(DATC)]^+$ cations (F_w = 352.32).

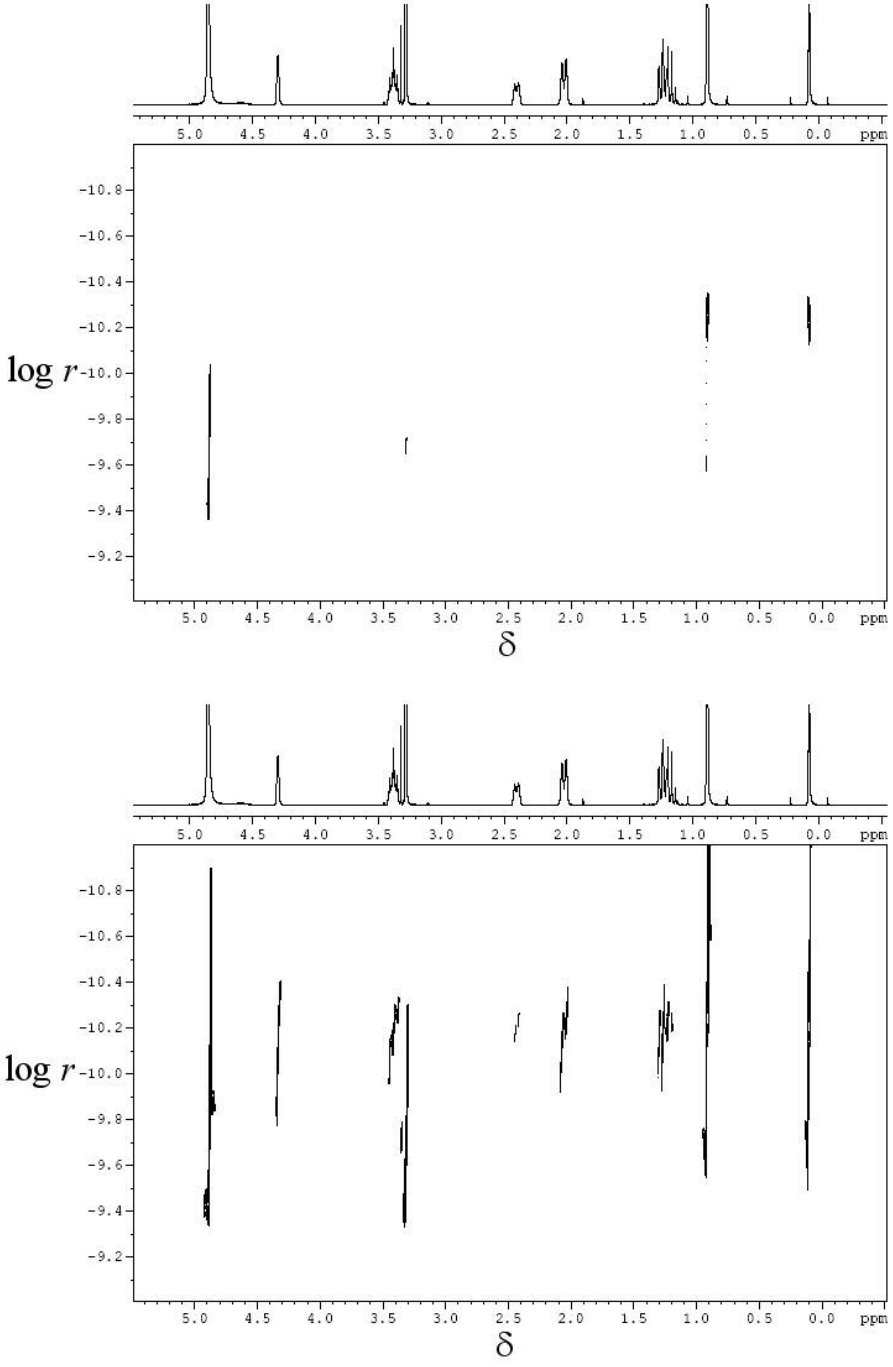

Figure 2. ^{1}H-DOSY NMR spectrum of [{$Ag_2(DATC)_2$}$_4$]$(NO_3)_8$, **4**. Top, low intensity; bottom, high intensity.

DATC

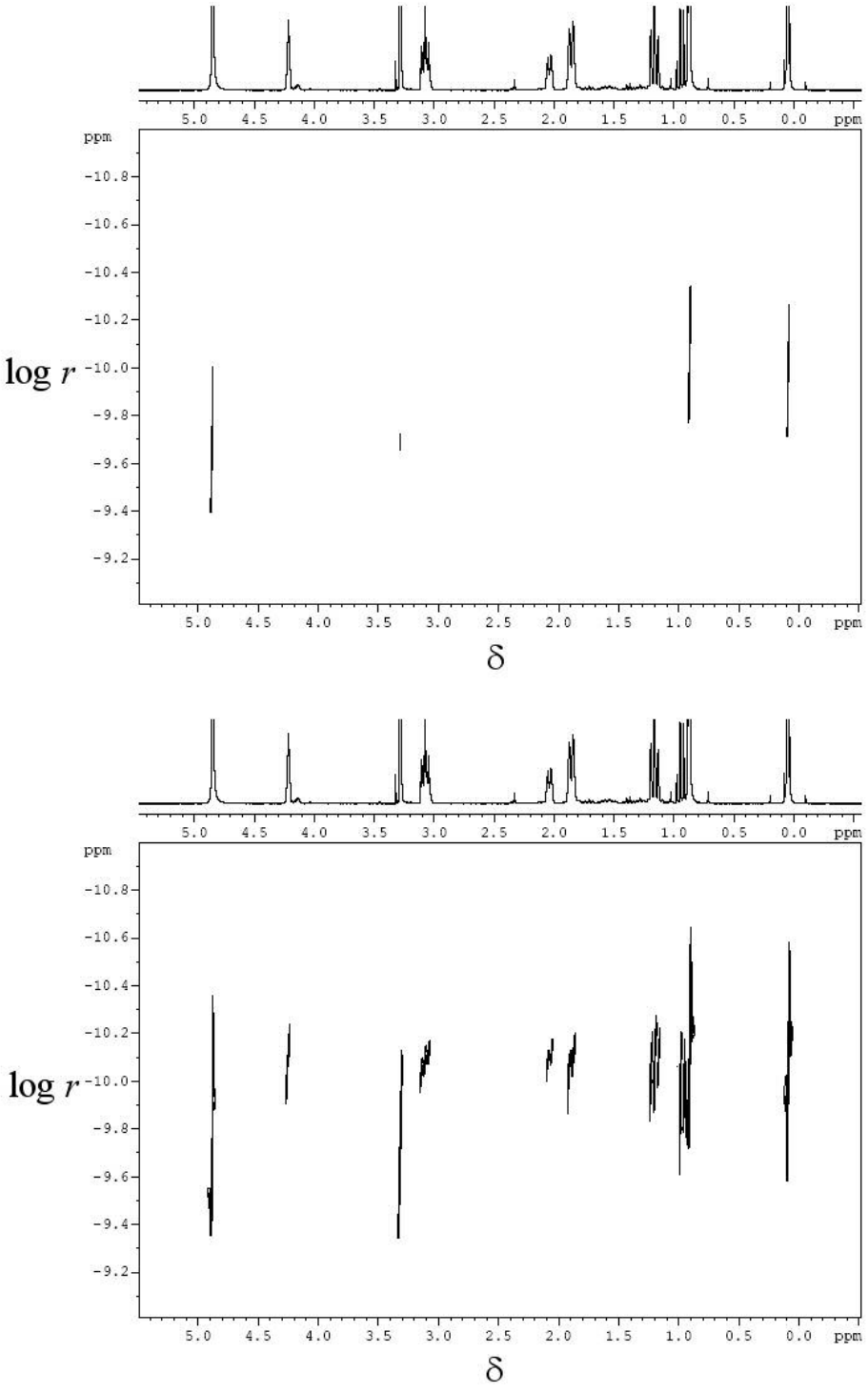

Figure 3. ^{1}H-DOSY NMR spectrum of the free ligand DATC. Top, low intensity; bottom, high intensity.

In the DATC sample (Figure 3), again log r_{MeOD} = -9.71, while log r_{DATC} was measured at -10.11. Repeating the calculation above:

$m_{DATC} = 35.06 \times (10^{-9.71} / 10^{-10.11})$

$m_{DATC} = 221.21$

The actual molecular mass of DATC is 244.45, around 10 % higher. This shows that suggesting that while this simple method does not measure molecular masses with perfect accuracy, it is certainly good enough to distinguish between the species of interest in this study.

References

1 Calculation performed using *Molecular Weight Calculator (Version 6.42)*, M. Monroe, **2006**.

2 C. S. Johnson Jr, *Prog. NMR Spectrosc.,* **1999**, *34*, 203.