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Characterization of the $\{Ag(dmb)_2{}^+\}_n$ Oligomers (dmb = 1,8-Diisocyano-*p*-menthane) in Solution

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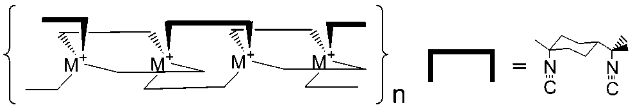
The crystallographically characterized polymers $\{[Ag(dmb)_2]Y\}_n$ (Y = $BF_4{}^-$, $NO_3{}^-$, $ClO_4{}^-$) extensively dissociate in solution, contrarily to the Cu analogue, and common molecular weight determination techniques such as light scattering, osmometric, and intrinsic viscosity measurements fail to provide data allowing full characterization. Using pulsed NMR experiments, notably ^{13}C NMR T_1 (spin lattice relaxation time) and NOE (nuclear Overhauser enhancement) measurements on various ionic $[\{Ag(dmb)_2]Y\}_n$ materials (Y = $BF_4{}^-$, $NO_3{}^-$, $ClO_4{}^-$) and their related mononuclear $[Ag(CN\text{-}t\text{-}Bu)_4]Y$ salts in acetonitrile-d_3 (as comparative standards), the dipole–dipole spin lattice relaxation times ($T_1{}^{DD}$) of a selected quaternary ^{13}C probe are measured. These data allow us to extract the correlation times (τ_c), which in turn permit us to estimate the volume of the tumbling species in solution. The comparison of the data between the $\{Ag(dmb)_2{}^+\}_n$ and $Ag(CN\text{-}t\text{-}Bu)_4{}^+$ species indicates the oligomeric nature of the former species, where the average number of $Ag(dmb)_2{}^+ \sim 8$ ($M_n \sim 4000$–5000).

Introduction

Since the discovery of the title polymer in 1992 (Scheme 1)[1] and its Cu analogue,[2] many new related polymers such as $\{Pt_4(dmb)_4(diphos)_2{}^+\}_n$ [3] (diphos = $Ph_2P(CH_2)_mPPh_2$ (m = 4−6), $\{Pd_4(dmb)_4(dmb)^{2+}\}_n$,[4] mixed-metal $\{Cu_xAg_{1-x}(dmb)_2{}^+\}_n$,[5] and mixed-ligand $\{M(dmb)(dppm)^+\}_n$ (M = Cu, Ag; dppm = $Ph_2PCH_2PPh_2$)[5] have been prepared and confidently characterized from X-ray crystallography or molecular weight determination. Applications in the area of semiconducting materials and photovoltaic cells have also been explored based upon the $M(dmb)_2{}^+$ polymers (M = Cu, Ag) in the solid state.[6] Recently, two new polymer isomers of the title materials were discovered[7] and were prepared from the latter's by simply changing the counterion and crystallization solvent conditions. The occurrence of these isomeric forms depends on a conformation change of the dmb bridging ligand (either U- or Z-shape), and this isomerization reaction can only proceed if dmb is labile in solution. This isomerization process is not observed for the $\{Cu(dmb)_2{}^+\}_n$ materials which indicates a lesser lability of dmb in this case. This observation is corroborated by the fact that M_W (160 000)[2] and M_n (133 000)[6] are obtained for this Cu polymer from light scattering and osmometric measurements, respectively, while no data could be acquired for the much "smaller" $\{Ag(dmb)_2{}^+\}_n$ species in solution.[8]

Scheme 1



$\{M(dmb)_2{}^+\}_n$; M = Cu, Ag

This work fits within a broader investigation of the optical and photophysical properties of these materials. Our earlier work indicated the presence of an important intrachain exciton phenomenon for both types of polymers (Cu, Ag) in solution, frozen matrixes, and the solid state.[2] Among the unusual features, the emission spectra exhibit a significantly red-shifted luminescence band (up to 35 nm) between the mononuclear model species $M(CN\text{-}t\text{-}Bu)_4{}^+$ and $\{M(dmb)_2{}^+\}_n$

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(1) Perreault, D.; Drouin, M.; Michel, H.; Harvey, P. D. *Inorg. Chem.* **1992**, *31*, 3688.
(2) Fortin, D.; Drouin, M.; Turcotte, M.; Harvey, P. D. *J. Am. Chem. Soc.* **1997**, *119*, 531.
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(4) Zhang, T.; Drouin, M.; Harvey, P. D. *Inorg. Chem.* **1999**, *38*, 1305.
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(8) Other techniques were employed in attempts to extract M_n but failed because of the lack of solubility in common solvents. Acetonitrile is still one of the better solvents for these polymers.

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polymers (M = Cu, Ag), and other photophysical behaviors are profoundly altered as well, such as the presence of nonexponential decay traces for the emission and depolarization of the luminescence light. While it is established that the $\{Cu(dmb)_2^+\}_n$ polymer exhibits ~300 repetitive units, the question arises to what extent the polymer length influences this intrachain exciton phenomenon. A better knowledge of the $\{Ag(dmb)_2^+\}_n$ polymer dimension in solution is now essential. We now wish to report a series of pulsed NMR data that will establish the oligomeric nature of the title materials in solution. Using the closely related $Ag(CN\text{-}t\text{-}Bu)_4^+$ mononuclear complex as a comparative standard, the average number of repetitive units is estimated (~8).

Experimental Section

Materials. The $\{[M(dmb)_2]Y\}_n$ polymers and $[Ag(CN\text{-}t\text{-}Bu)_4]Y$ mononuclear complexes (M = Cu, Ag; Y = BF_4^-, NO_3^-, ClO_4^-, $CH_3CO_2^-$) were prepared according to procedures outlined in refs 1 and 2. dmb was prepared by standard procedures.[9] The starting materials $AgNO_3$, $AgBF_4$, $AgClO_4$, $AgCH_3CO_2$, $Cu(BF_4)_2{\cdot}6H_2O$, and CN-*t*-Bu were from Aldrich and were used as received.

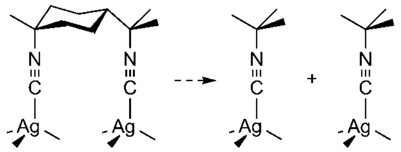
Spin–Lattice Relaxation Times (T_1's). The T_1's were measured by an inversion recovery pulse technique. The measurements were performed on a Bruker AC-F 300 NMR spectrometer operating at 75.47 MHz for ^{13}C. The temperature was 293 K, and the sampling was done over a 20 000 Hz sweep width using 8192 data points to describe the FID. The polymer solutions were saturated in all cases in order to improve the signal-to-noise ratio. The uncertainties are of ±0.2 s based upon multiple measurements (at least 3). The second instrument was a Varian 500 MHz instrument located at McGill University. The experimental procedure is the same as that described previously.

Mass FAB Analysis. The mass spectra were acquired using a Kratos MS-50 TCTA spectrometer using an Iontech Saddle Field Source Model FAB 11NF operating at 70 kV with 2 mA current. The samples were immersed either in nitro benzyl alcohol (most of the samples) or in thioglycerol matrixes unless stated otherwise. The data analyses were performed using a homemade program written in GW BASIC computing all mathematically possible solutions for each fragment mass. Only the chemically meaningful solutions were retained using a window of ±2 g. The MALDI-TOF data were obtained at the Université de Bourgogne (Dijon, France) using a PROFLEX III Bruker spectrometer. This instrument was set in linear mode and used a N_2 laser.

Results and Discussion

The fact that no data could be obtained for M_n and M_W for the $\{Ag(dmb)_2^+\}_n$ species from osmometric and intrinsic viscosity measurements and the results from the light scattering experiments indicate that these values must range approximately at or lower than the detection limit of the techniques (~10 000). On the other hand, mass FAB data for both types of polymers $\{M(dmb)_2^+\}_n$ (M = Cu, Ag) indicate the inadequateness of the technique where only fragments exhibiting 2–4 units are observed in the spectra (Supporting Information).[10] These results suggest that $\{Ag(dmb)_2^+\}_n$ is indeed oligomeric with an average number of units ranging from ~3 to ~20.

Scheme 2



NMR methods offer the possibility of long time data acquisition addressing solubility problems. M_n can be estimated from the knowledge of the volume (V) of the tumbling molecules in solution, which in turn can be evaluated from the correlation time (τ_c). The latter data are extracted from T_1^{DD} (dipole–dipole spin–lattice relaxation time). The analysis is complicated by the fact that the estimated volume is the hydrodynamic volume due to the dragging of solvent molecules and counterions during tumbling. This volume is unavoidably bound to be greater than the X-ray datum.

To minimize this problem, the mononuclear $[Ag(CN\text{-}t\text{-}Bu)_4]^+$ complex has been investigated as a comparative standard, hence making sure that electronic and steric environments are quasi-identical about the probed nuclei for both standards and polymers (Scheme 2). This probe nucleus is the sp^3-hybridized quaternary carbon, more particularly ^{13}C located in the dmb-cyclohexyl ring. This nucleus is selected for the following reasons. The rigidity of the $M{-}C{\equiv}N{-}^{13}C$ unit allows one to measure a T_1 process that is less influenced by intramolecular motions such as spin-rotation relaxation known for methyl groups, for instance, and motion of alkyl chains. In addition, a quaternary ^{13}C relaxes more slowly than others, because of the absence of close $^1H\cdots{}^{13}C$ dipole–dipole interactions which are known to induce efficient relaxation of the ^{13}C nuclei. As a result, the larger time scale provides an opportunity to gain accuracy. A typical ^{13}C NMR spectrum for $\{Ag(dmb)_2^+\}$ is presented in Figure 1 (complete analysis can be found in the Supporting Information), and C#2 is selected as probe (note that data for C#8 give similar results).

The T_1^{DD} data (300 MHz ^1H) are extracted from experimental T_1 and NOE measurements, according to eq 1[11]

$$\frac{1}{T_1^{\ DD}} = \frac{\eta}{\eta_{max}}\cdot\frac{1}{T_1} \qquad (1)$$

where η is the fractional NOE constant and η_{max} is the maximum η value of 1.988 in the extreme narrowing limit.[12] η is found to be salt independent within the experimental error, $\eta = 1.31 \pm 0.03$ as anticipated, and the overall data are presented in Table 1. This table summarizes the experimentally measured T_1, the calculated T_1^{DD}, and the τ_c data for 3 different $[Ag(CN\text{-}t\text{-}Bu)_4]Y$ salts (Y = NO_3^-, BF_4^-,

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(9) Weber, W. P.; Gokel, G. W.; Ugi, I. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 530.

(10) MALDI-TOF measurements were also performed on the $\{[Ag(dmb)_2]BF_4\}_n$ polymer, but despite the milder conditions of excitation, fragment peaks of similar masses of those observed in the mass FAB spectra are seen (Supporting Information). This technique was not used further in this work.

(11) Wehrli, F. W.; Wirthlin, T. *Interpretation of Carbon-13 NMR Spectra*; Heyden: London, 1980.

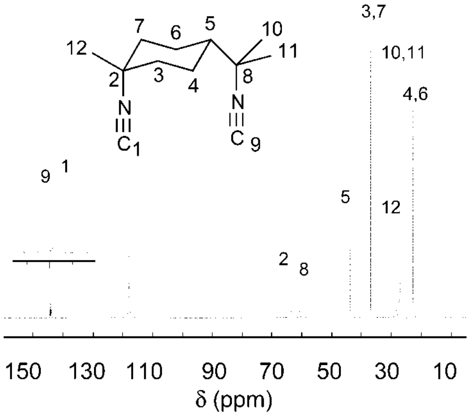


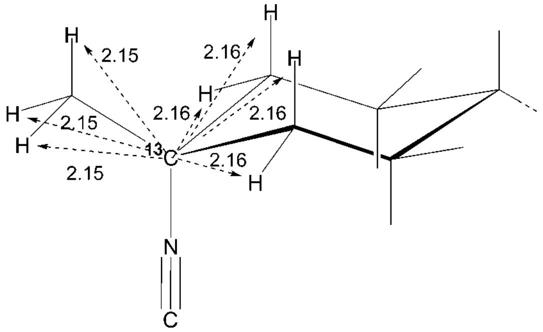
Figure 1. Typical ^{13}C NMR spectrum of $\{[Ag(dmb)_2]BF_4\}_n$ in acetonitrile-d^3 at 293 K. The full assignments are provided in the Supporting Information. The probe peak is C#2.

Table 1. Selected Data for the $[Ag(CN\text{-}t\text{-}Bu)_4]Y$ Complexes[a]

Y:	NO_3^-	BF_4^-	ClO_4^-
T_1 (±0.2 s)	36.0	37.5	37.1
T_1^{DD} (±1.5 s)	54.6	57.0	65.3
τ_c ($\times 10^{-10}$ s ± 3%)	2.20	2.11	2.14
V (±75 Å)	2470	2370	2400

[a] T_1 and η are measured for the peak located at 58.1 ppm in the ^{13}C spectra (i.e., $C{\equiv}N{-}^{13}C(CH_3)_3$) using acetonitrile-$d_3$ at 293 K.

Scheme 3



ClO_4^-). These parameters are found not to vary much from one salt to another, as anticipated. The τ_c is extracted from eq 2 also for the extreme narrowing limit:[11]

$$\frac{1}{T_1^{DD}} = \sum_{i=1}^{n} \frac{\hbar_2 \gamma_C^2 \gamma_H^2}{r_{CH}^6} \cdot \tau_c \qquad (2)$$

with $\hbar$ the Plank constant ($\hbar = h/2\pi$), γ the magnetogyric ratio for ^{13}C and ^1H, and r the distance between the probe ^{13}C nuclei and the nearest ^1H (here 2.155 Å on the basis of X-ray data for the $Ag(dmb)_2{}^+$ polymers[1−7] (Scheme 3)). On the basis of the Stokes−Einstein−Debye equation for spherical molecules ($\tau_c = V\eta_{visc}/kT$; η_{visc} = solvent viscosity; k = Boltzmann constant; T = temperature), the hydrodynamic volume (V) of the tumbling species is determined for the 3 standards.

Table 2. Selected Data for the $\{[Ag(dmb)_2]Y\}_n$ Polymers[a]

Y:[b]	NO_3^-	BF_4^-	ClO_4^-
T_1 (±0.20 s)	6.90	7.53	7.93
T_1^{DD} (± 0.20 s)	7.84	8.55	9.77
τ_c ($\times 10^{-9}$ s ± 3%)	1.97	1.81	1.58
V (Å^3)	22 000	20 300	17 700
av no. of units[c]	∼9	∼8	∼7

[a] T_1 and η are measured for the peak located at 63.3 ppm in the ^{13}C spectra (i.e., ^{13}C #2, see Figure 1) using acetonitrile-d_3 at 293 K. Here, η is 1.75 ± 0.03. [b] T_1 for Y = $MeCO_2^-$ is 8.07 ± 0.02 s. [c] The number of units is obtained by dividing $V(Ag(dmb)_2{}^+)_n$ by $V(Ag(CN\text{-}t\text{-}Bu)_4{}^+)$ from Table 1 for each individual salt. It is assumed that $V(Ag(dmb)_2{}^+) \sim V(Ag(CN\text{-}t\text{-}Bu)_4{}^+)$, as explained in ref 13. The uncertainty on each individual datum is ±1.

The same measurements and calculated data for the corresponding $\{[Ag(dmb)_2]Y\}_n$ oligomers have been summarized in Table 2. Again, the data do not drastically vary from one salt to another, indicating again the rather weak dependence of the counteranion on the NMR parameters. By assuming that $V(Ag(CN\text{-}t\text{-}Bu)_4{}^+) \sim V(Ag(dmb)_2{}^+)$ (∼ 614.8 Å^3 Scheme 2),[13] the approximate average number of units in the $\{Ag(dmb)_2{}^+\}_n$ polymers in solution can be determined by dividing the extracted V from the Stokes−Einstein−Debye equation of the oligomers, by V of the estimated $\{Ag(dmb)_2{}^+\}_n$ unit.[13] The data for the 3 salts are very similar and indicate that the average number of units ranges between 7 and 9 with an estimated uncertainty of ±1, giving M_n of 4000−5000 (taking into account the counterion masses).[15] These findings are consistent with the fact we could not obtain light scattering data for these materials, while M_w for the $\{Cu(dmb)_2{}^+\}_n$ polymers has been evaluated by this technique. These small oligomers appear as short rigid rods (Figure 2) of about 43−50 Å length by

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(12) T_1 decreases with the field (H_0), indicating the extreme narrowing limit. T_1^{DD} can also be extracted from the intercept in the plot $1/T_1$ vs H_0 but requires the use of many spectrometers at various fields for accuracy. Only two spectrometers are available to us. Nonetheless, this extracted T_1^{DD} was similar to that found using the NOE method, but this latter method was favored for convenience and accuracy. Addition of the free isocyanide ligand did not shift the ^{13}C peaks, indicating absence of important chemical exchange. Finally, the full-width-at-half-maximun (fwhm) is not strongly temperature dependent between 20 and 40 °C.

(13) (a) According to the Cambridge Data Bank, no X-ray data for tetrahedral $M(CN\text{-}t\text{-}Bu)_4$ species appear to be reported, but the complex $Fe(CN\text{-}t\text{-}Bu)_5$ has been characterized.[13b] These X-ray data allow us to estimate the volume of a $M(CN\text{-}t\text{-}Bu)_4$ species according to $V(Fe(CN\text{-}t\text{-}Bu)_5) \times {}^4/_5 \sim V(Fe(CN\text{-}t\text{-}Bu)_4) \sim 600$ Å^3. The $V(Ag(dmb)_2{}^+)$ datum is obtained according to $V(Ag(dmb)_2{}^+) = V(Ag(dmb)_2TCNQ{\cdot}CH_2Cl_2)^7 - V(TCNQ)^{13c} - V(CH_2Cl_2)^{13d} = 978.5$ Å^3 − 106.0 Å^3 ∼ 614.8 Å^3. Thus, assuming that $V\{Ag(CN\text{-}t\text{-}Bu)_4\}^+ \sim V\{Ag(dmb)_2{}^+\}$ appears reasonable. (b) Basset, J.-M.; Berry, D. E.; Barker, G. E.; Green, M.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1979**, 1003. (c) Shield, L. *J. Chem. Soc., Faraday Trans. 2* **1985**, 81. (d) Calculated from the density for CH_2Cl_2 is 1.33 g/mL.

(14) The Stokes−Einstein−Debye equation is inappropriate for nonspherical molecules, and a small error is induced in the analysis of the $\{Ag(dmb)_2{}^+\}_n$ oligomers. For the much larger $\{Cu(dmb)_2{}^+\}_n$ polymers, such an equation is far too inadequate to be applied, and for this reason, no investigation was undertaken for these materials at this time. Data for the analogous $Cu(CN\text{-}t\text{-}Bu)_4{}^+$ and $\{Cu(dmb)_2{}^+\}_n$ species are available in ref 5. Numerous authors have addressed the problem of correlating τ_c with the molecular shape of the tumbling molecules, but such analysis is far too complex and probably irrelevant to be useful for the accurate determination of M_n for nonspherical polymers.

(15) Attempts to evaluate M_n from end group analysis by IR spectroscopy were unsuccessful because of reactivity of the polymers with the NaCl, KBr, and CsI windows giving the corresponding $Ag_2(dmb)_2X_2$ dimers (X = Cl, Br, I),[18] according to $\{Ag(dmb)_2{}^+\}_n + nX^- = {}^n/_2Ag_2(dmb)_2X_2 + n$dmb. This behavior further demonstrates evidence for lability of the dmb ligand in the Ag species. A typical example is provided in the Supporting Information where the peak associated with free $-N{\equiv}C$ (∼2135 cm^{-1}) is already present within the first minutes of contact with the solution.

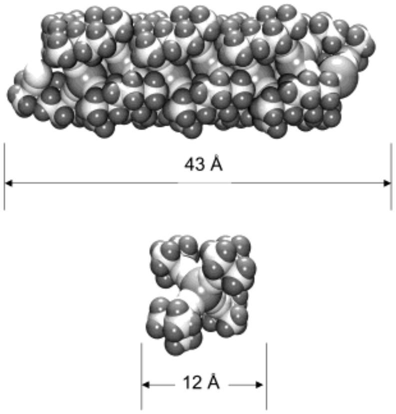

Figure 2. Comparison of space filling model for the $\{Ag(dmb)_2{}^+\}_7$ oligomer as an example with Ag(CN-*t*-Bu)$_4{}^+$. These models are based on X-ray data.

about 12 Å diameter on the basis of space-filling models. The comparison of light scattering data between the longer $\{Cu(dmb)_2{}^+\}_n$ and shorter $\{Ag(dmb)_2{}^+\}_n$ polymers (when available) describing the shape of the molecules in solution should prove very interesting.

A point of details is the nature of the end-of-chain for these oligomers. Dissociation of these polymers in solution generates unsaturated Ag centers, which in turn can interact with the acetonitrile solvent molecules and the counteranions. Solid state data clearly demonstrate that unsaturated Ag ions interact strongly with counterions such as $NO_3{}^-$ and $CH_3CO_2{}^-$ and more weakly with $TCNQ^-$ (7,7,8,8-tetracyano-quinodimethane).[16] However, these ions can be extremely labile in solution, as well as the acetonitrile molecules, as supported by the evidence provided for the dmb ligand itself in this work and in ref 7. The best description for the end-of-chains is an unsaturated Ag center exchanging with solvent and isocyanide groups and counterions. To clarify this situation, an exhaustive NMR study similar to this one with the parameters temperature, solvent, and concentration of added anions is necessary. Such a study should also prove useful to determine whether oligomer sizes can be altered.

Relevant to the exciton work, since similar profound perturbation of the photophysical behavior for both $\{M(dmb)_2{}^+\}_n$ materials in solution (M = Ag, Cu) is seen,[2] these new results indicate that the number of units does not need to be extensive to be effective, nor is the exciton delocalization felt only over a very large number of units. At first glance, this observation appears surprising but not inconsistent with the fact that weak “communications” or “interactions” have been demonstrated between two metals separated by distances well exceeding the sum of the van der Waals radii.[17−19] In the meantime, this work has allowed us to determine $\sim M_n$ for these small oligomers in solution and may be applied to other systems. The two conditions for this method to be reliable are, first, the materials should not be shaped far off from a sphere, and, second, one must employ a closely related standard as an adequate model for the tumbling of the oligomers in solution.

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Supporting Information Available: Mass FAB data for $\{[M(dmb)_2]Y\}_n$ (M = Cu, Ag; Y = ClO_4, NO_3, BF_4); ^{13}C NMR data for $\{[Ag(dmb)_2]Y\}_n$ and free dmb; evolution of the FTIR spectra of $\{[Ag(dmb)_2]BF_4\}_n$ in CH_2Cl_2 in contact with NaCl vs time; MALDI-TOF spectrum and analysis for $\{[Ag(dmb)_2]BF_4\}_n$. This material is available free of charge via the Internet at http://pubs.acs.org.

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