

Structures of Silver Pyrazolates in Hydrocarbon Solutions via Vapor-Pressure Osmometry

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Molecular weights of $\{[3,5-(\text{CF}_3)_2\text{Pz}]\text{Ag}\}_3$, $\{[3-(\text{C}_3\text{F}_7)-5-(t\text{-Bu})\text{Pz}]\text{Ag}\}_3$, and $\{[3,5-(i\text{-Pr})_2\text{Pz}]\text{Ag}\}_3$ at various solution concentrations have been investigated using vapor-pressure osmometry. Depending on the concentration, the trinuclear $\{[3,5-(\text{CF}_3)_2\text{Pz}]\text{Ag}\}_3$ either dissociates into mono- and dinuclear moieties or remains trinuclear or aggregates to hexanuclear species in toluene. In contrast, $\{[3-(\text{C}_3\text{F}_7)-5-(t\text{-Bu})\text{Pz}]\text{Ag}\}_3$, which has a bulky and relatively electron-rich pyrazolate, retains the trinuclear form even at low concentrations in toluene. Both $\{[3,5-(\text{CF}_3)_2\text{Pz}]\text{Ag}\}_3$ and $\{[3,5-(i\text{-Pr})_2\text{Pz}]\text{Ag}\}_3$ adopt trinuclear structures in heptane at low concentrations. At higher concentrations, $\{[3,5-(i\text{-Pr})_2\text{Pz}]\text{Ag}\}_3$ forms hexanuclear species. The aggregation–segregation points are rather sharp and are reminiscent of the all-or-none character of phase transitions. Remarkably, at higher concentrations, the aggregation states of these silver pyrazolates are similar to those expected based on solid-state data.

Homoleptic pyrazolates of silver are of significant current interest^{1–8} because of their structural diversity, fascinating luminescent properties, π -acid/ π -base chemistry, propensity to form supramolecular aggregates with argentophilic interactions, and use as porous materials and as precursors for the chemical vapor deposition of silver metal. Among the different structural types, the trimeric forms like $\{[3,5-(\text{CF}_3)_2\text{Pz}]\text{Ag}\}_3$ (Figure 1) are more common and have received the most attention. In the solid state, they feature planar or distorted nine-membered Ag_3N_6 metallacycles and often show various types and degrees of intertrimer $\text{Ag}\cdots\text{Ag}$ contacts, leading to supramolecular assemblies with chair, prismatic, and star-shaped dimers of trimers or chain structures. For example, trimeric $\{[3,5-(\text{CF}_3)_2\text{Pz}]\text{Ag}\}_3$ crystallizes from CH_2Cl_2 as dimers of trimer units [with the shortest intertrimer $\text{Ag}\cdots\text{Ag}$ distance = 3.2037(4) Å] that

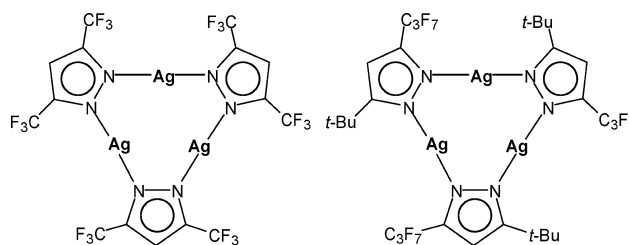


Figure 1. Structures of $\{[3,5-(\text{CF}_3)_2\text{Pz}]\text{Ag}\}_3$ ($[\text{Ag}_3]$) and $\{[3-(\text{C}_3\text{F}_7)-5-(t\text{-Bu})\text{Pz}]\text{Ag}\}_3$ ($[\text{Ag}_3']$).

are loosely connected via additional $\text{Ag}\cdots\text{Ag}$ contacts, generating zigzag chains.⁶ Crystals obtained from hexane show weakly linked columns of $\{[3,5-(\text{CF}_3)_2\text{Pz}]\text{Ag}\}_3$ consisting of alternating dimers of trimers [shortest intertrimer

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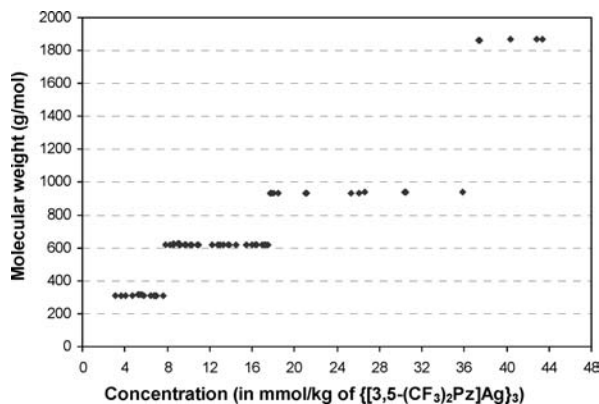


Figure 2. Osmogram showing the change in the MW of solution species as the concentration of {[3,5-(CF₃)₂Pz]Ag}₃ changes in toluene.

Ag···Ag distance = 3.3073(13) Å] and trimers.⁷ The {[3,5-(*i*-Pr)₂Pz]Ag}₃ containing an electron-rich pyrazolate forms dimer of trimer units⁵ with two close intertrimer Ag···Ag contacts at 2.9870(4) Å, whereas the trinuclear {[3-(C₃F₇),5-(*t*-Bu)Pz]Ag}₃ (Figure 1) containing two bulky substituents on the pyrazolyl rings do not form extended structures with intertrimer Ag···Ag contacts.⁴

{[3,5-(CF₃)₂Pz]Ag}₃ ([Ag₃]) and {[3-(C₃F₇),5-(*t*-Bu)Pz]Ag}₃ ([Ag₃']) are also excellent π acids.^{3,4} For example, they crystallize from toluene (a π base), forming extended columnar structures of the type {[Ag₃]·toluene}_∞ and {[Ag₃']·toluene}_∞, respectively, in which toluene interleaves and makes face-to-face contacts with dimers of {[3,5-(CF₃)₂Pz]Ag}₃ [with the shortest intertrimer Ag···Ag distance of 3.0911(4) Å] or {[3-(C₃F₇),5-(*t*-Bu)Pz]Ag}₃.⁴ Despite the rich diversity of and extensive data on solid-state structures of silver pyrazolates, apart from routine NMR spectroscopic analysis, their *solution structures* have received scant attention. Here we demonstrate the use of vapor-pressure osmometry (VPO) to probe the molecular weights (MWs) of the species present in solutions of {[3,5-(CF₃)₂Pz]Ag}₃, {[3-(C₃F₇),5-(*t*-Bu)Pz]Ag}₃, and {[3,5-(*i*-Pr)₂Pz]Ag}₃. We also describe the effect of the concentration, solvents, and pyrazolyl ring substituent on the degree of aggregation in solutions of silver pyrazolates.

Investigation of the MW of the silver adduct in solution using different concentrations of {[3,5-(CF₃)₂Pz]Ag}₃ in two different solvents (toluene and heptane) gave very interesting results. Data from toluene solutions were particularly fascinating (Figure 2) and revealed that at low concentrations (2–8 mmol/kg of {[3,5-(CF₃)₂Pz]Ag}₃) the experimentally determined MW of the silver adduct in solution is about 310–320 g/mol. However, upon an increase in the molality above ~8 mmol/kg, the MW of the solution species increased abruptly to 615–625 g/mol and remained steady until the molality was increased beyond ~17 mmol/kg. At this point, the second jump in the MW to 930–935 g/mol was observed. Then, at the molality of about 37 mmol/kg, the MW of the solution species changed abruptly again to about 1860–1866 g/mol and remained constant to the high concentration limit (due to solubility limitations) of 43 mmol/kg. These results point to the presence silver pyrazolate moieties [3,5-(CF₃)₂Pz]Ag (MW = 310.9 g/mol), {[3,5-(CF₃)₂Pz]Ag}₂

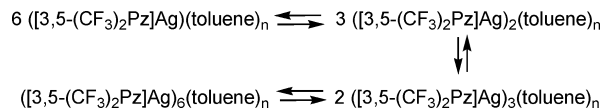


Figure 3. Major species present (most likely as toluene coordinated or solvated) in toluene solution at different concentrations of {[3,5-(CF₃)₂Pz]Ag}₃ (3–43 mmol/kg).

(MW = 621.9 g/mol), {[3,5-(CF₃)₂Pz]Ag}₃ (MW = 932.8 g/mol), and {[3,5-(CF₃)₂Pz]Ag}₆ (MW = 1865.6 g/mol) at different concentration ranges described above. They represent the monomer, dimer, trimer, and dimer of trimer (hexanuclear species) of the silver pyrazolate [3,5-(CF₃)₂Pz]Ag, respectively (Figure 3). Although we do not have direct evidence, solid-state data from related molecules suggest that these mono- and dinuclear species very likely exist as toluene-coordinated adducts while tri- and hexanuclear units perhaps exist as toluene-sandwiched species through π -acid/ π -base interactions. For example, isolable molecules containing the dinuclear moiety {[3,5-(CF₃)₂Pz]Ag}₂ stabilized by donors like pyridines are known.⁹ Arene complexes of silver(I) are common especially when weakly coordinating anions are involved.¹⁰ Several types of arene-sandwiched adducts of [Ag₃] have been reported, which include benzene·[Ag₃]·benzene and benzene·[Ag₃]₂·benzene.³ It is also noteworthy that at higher concentrations [3,5-(CF₃)₂Pz]Ag aggregates to a hexanuclear unit. This is consistent with the X-ray crystal structural data because {[3,5-(CF₃)₂Pz]Ag}₃ is known to crystallize as {[Ag₃]₂·toluene}_∞ (dimer of trimer sandwiched between toluene molecules) from toluene.⁴

Interestingly, this *aggregation process is reversible*, and the hexanuclear species reverts back to the trimer, dimer, and monomer upon dilution with toluene in the above-mentioned concentration ranges. The sharp, reversible aggregation–segregation steps exhibited by this four-state system at threshold concentrations are reminiscent of the all-or-none character of phase transitions and self-assembly of surfactant molecules at critical micelle concentrations. Careful studies at monomer to dimer, dimer to trimer, and trimer to dimer of trimer transition points indicate that these changes occur at {[3,5-(CF₃)₂Pz]Ag}₃ concentrations of ~7.6, ~17.4, and ~37 mmol/kg, respectively. Interestingly, these aggregations occur when the concentrations are roughly at twice the lower critical concentration. However, despite repeated attempts, such changes were not observed in solutions of {[3,5-(CF₃)₂Pz]Ag}₃ in nonpolar hydrocarbon solvents like heptane. For example, the experimentally determined MW in *n*-heptane was 932 g/mol even at low concentrations (2–12 mmol/kg), which shows that, unlike in toluene, trimer does not dissociate to monomer or dimer in heptane. It exists as discreet trinuclear units. This is not surprising because nonpolar heptane is not a good donor like toluene, which can easily stabilize smaller fragments like monomers and dimers (e.g., via Ag^I–arene bonds). The relatively low

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solubility of $\{[3,5-(\text{CF}_3)_2\text{Pz}]\text{Ag}\}_3$ in heptane prevented us from probing at higher concentration regions to detect the dimer (or chains) of trimer formation point.

We have also investigated the effect of steric–electronic properties of the pyrazolyl ring substituents on the solution structure of silver pyrazolates using $\{[3-(\text{C}_3\text{F}_7),5-(t\text{-Bu})\text{Pz}]\text{Ag}\}_3$ and $\{[3,5-(i\text{-Pr})_2\text{Pz}]\text{Ag}\}_3$. Unlike $\{[3,5-(\text{CF}_3)_2\text{Pz}]\text{Ag}\}_3$, $\{[3-(\text{C}_3\text{F}_7),5-(t\text{-Bu})\text{Pz}]\text{Ag}\}_3$ does not dissociate into mono- or dinuclear systems at very low concentrations even in toluene. It has a relatively electron-rich pyrazolate (compared to $[3,5-(\text{CF}_3)_2\text{Pz}]^-$) with sterically demanding substituents. The average MW remains at 1198 g/mol (1195–1200 g/mol range; compared to the calculated value of 1197.2 g/mol for $\{[3-(\text{C}_3\text{F}_7),5-(t\text{-Bu})\text{Pz}]\text{Ag}\}_3$) in the 1–25 mmol/kg concentration range, pointing to the existence of a trinuclear species. Although we cannot detect the π -acid/ π -base chemistry between $\{[3-(\text{C}_3\text{F}_7),5-(t\text{-Bu})\text{Pz}]\text{Ag}\}_3$ and toluene in solution (because toluene is the solvent), such interactions most likely exist in solution, stabilizing the trinuclear species. Solubility limitations prevented us from exploring the higher concentration regime for trimer aggregations. We note, however, that $\{[3-(\text{C}_3\text{F}_7),5-(t\text{-Bu})\text{Pz}]\text{Ag}\}_3$ does not form $\text{Ag}\cdots\text{Ag}$ bonded dimer or trimers even in the crystalline state. This is perhaps a result of the steric effects of bulky pyrazolyl ring substituents. It affords $\{[\text{Ag}_3]^\cdot\text{toluene}\}_\infty$ -type solids upon crystallization from toluene.⁴

$\{[3,5-(i\text{-Pr})_2\text{Pz}]\text{Ag}\}_3$ has the most electron-rich pyrazolate among the three systems studied and exists as a dimer of trimer in the solid state.⁵ In fact, at higher concentrations (above the ~ 30 mmol/kg molality region in heptane), it retains the hexanuclear nature (experimentally observed MW = 1560 g/mol). There is one brief note on the use of VPO

in silver pyrazolate chemistry. Meyer et al. have obtained the MW of $\{[3,5-(i\text{-Pr})\text{SCH}_2)_2\text{Pz}]\text{Ag}\}_3$ and found it to be hexanuclear (as in the solid state) in toluene.⁸ More importantly, we also observed the trimeric form in *n*-heptane at the 2–30 mmol/kg concentration range (MW of 777 g/mol from VPO data compared to the calculated MW value of 777.3 g/mol for $\{[3,5-(i\text{-Pr})_2\text{Pz}]\text{Ag}\}_3$). This shows that dimer of trimers with even fairly short, unsupported $\text{Ag}\cdots\text{Ag}$ contacts may be separated in solution.

Overall, we obtained solution structural information on silver(I) pyrazolates using VPO and show, for the first time, the presence of mono-, di-, tri-, and hexanuclear species in solution in the Ag^{I} adduct of $[3,5-(\text{CF}_3)_2\text{Pz}]^-$ and critical concentrations for aggregation–dissociation. The effects of solvent and pyrazolyl ring substituents on solution species were also investigated. Remarkably, at higher concentrations, these silver pyrazolates adopt solution structures similar to those expected based on solid-state data (see the Supporting Information). We plan to augment this study with further data using different spectroscopic probes. We are also extending this work to other coinage metal azolates and different solvent systems.

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Supporting Information Available: Experimental details and figures showing proposed structures and related structurally characterized molecules. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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