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Structural and Catalytic Properties of Bis(guanidine)copper(I) Halides

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The neutral, bicyclic guanidine 1,3,4,6,7,8-hexahydro-2*H*-pyrimido-[1,2-*a*]pyrimidine (hppH) coordinates to Cu(I) halides via the imine nitrogen, and the complexes are stabilized by intramolecular NH···X interactions (X = Cl, Br) or are partially dissociated (X = I) in the solid state; in all cases, fluxional behavior is observed in solution. Selected complexes have been tested as catalysts for the polymerization of methyl methacrylate.

The use of neutral amidines as ligands in copper chemistry was first described in 1956, when the reaction between $Cu(OAc)_2$ and the formamidine [HC{=NAr}{NHAr}] (Ar = Ph, *p*-tolyl) was reported to give an unstable bis-ligand adduct, the precise structure of which was not determined.[1] In contrast, 4 equiv of 1,1,2,2-tetramethylguanidine was accommodated around a copper center in the tetrahedral compound $[Cu(HN{=}C\{NMe_2\}_2)_4][ClO_4]_2$ which, on the basis of IR spectroscopy, was believed to coordinate the ligand via the imine nitrogen.[2] As part of a study of the application of the bicyclic guanidine, 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hppH) as a neutral ligand in Cu(I) chemistry,[3] we wish to report the solid-state structure and solution-state behavior of the series $[(hppH)_2Cu{-}X]$ (X = Cl, Br, I). Preliminary results in the application of such complexes in polymerization of methyl methacrylate (MMA) are also discussed.

Previous work by ourselves[4] and others[5] has demonstrated the use of hppH as a source of the anionic guanidinate ligand, $[hpp]^-$, which is able to chelate to main group and transition metal elements in an N,N′-coordination mode. Another common bonding motif encountered with this anion is as a bridging group across two metal centers,[6] chiefly exploited by Cotton and co-workers in the stabilization of metal−metal bonded systems.[7] This latter situation is observed in the copper(I) compound $Cu_2(hpp)_2$, synthesized from CuCl and hppLi. Rather than displacing the halide from the metal center, we were interested in forming simple coordination complexes of the type $[(hppH)_nCu\text{-}X]$, for possible applications in atom transfer radical polymerization (ATRP) reactions.

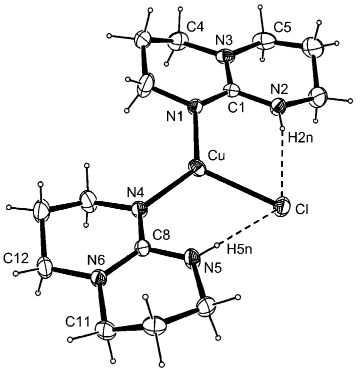

Figure 1. Molecular structure of **1**. H-atoms on N(2) and N(5) were freely refined, isotropic. Selected bond lengths (Å) and angles (deg): C(1)−N(1) 1.316(3), C(1)−N(2) 1.345(3), C(1)−N(3) 1.356(3), H(2n)−Cl 2.452, C(8)−N(4) 1.311(3), C(8)−N(5) 1.354(3), C(8)−N(6) 1.369(3), H(5n)−Cl 2.472; N(1)−Cu−N(4) 130.37(9), N(1)−Cu−Cl 115.43(6), N(4)−Cu−Cl 113.86(7).

The combination of hppH (2 equiv) and copper(I) halide in THF afforded the soluble bis-ligand complexes $[(hppH)_2Cu{-}X]$ (**1**, X = Cl; **2**, X = Br; **3**, X = I). The IR data (Nujol mull) of the isolated, colorless crystals showed a low energy shift of the $\nu(C{=}N)$ absorption (**1**, 1597 cm^{-1}; **2**, 1592 cm^{-1}; **3**, 1587 cm^{-1}) relative to the value for noncoordinated hppH (1641 cm^{-1}) indicative of coordination through the imine nitrogen atom.[2,8] It should be noted, however, that a recent X-ray structure of the neutral ligand revealed a hydrogen-bonded dimer in the solid state with disorder of the NH position and considerable delocalization across the C−N bonds.[9] This is also predicted to reduce the value of

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(9) Oakley, S. H.; Coles, M. P.; Hitchcock, P. B. Manuscript in preparation.

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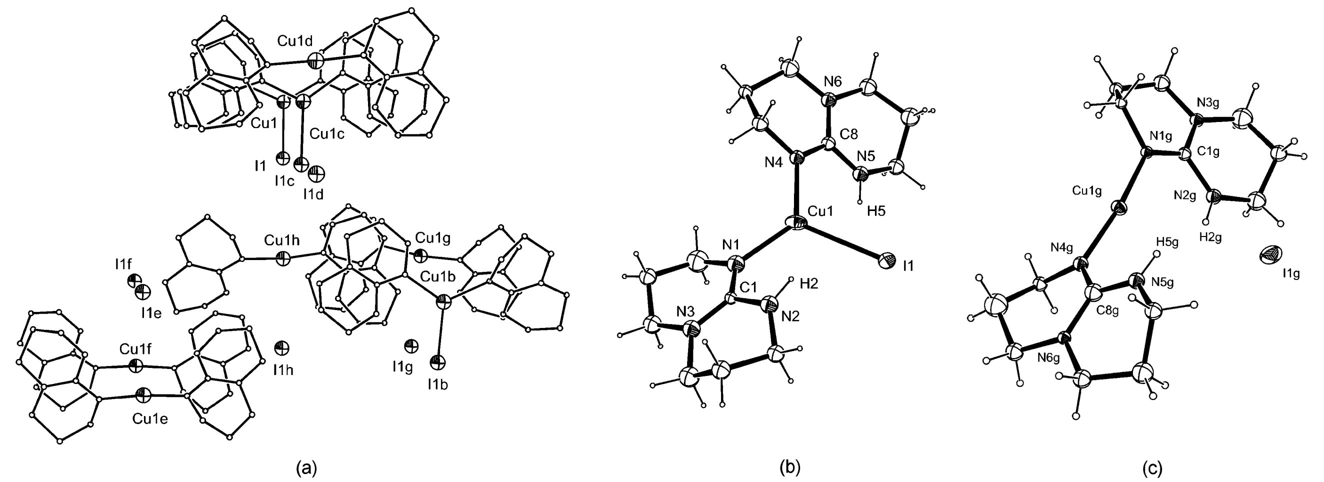

Figure 2. Molecular structure of **3**. (a) Unit cell showing eight independent molecules. (b) $(hppH)_2CuI$ molecule. (c) Example of $[(hppH)_2Cu]^+[I]^-$ ion pair.

ν(C=N) relative to accepted values for typical imine stretching frequencies and hence should be taken into account when comparing these values. The IR and ^{1}H NMR spectra of **1**−**3** also indicated the presence of an NH group, consistent with coordination of a neutral guanidine.

The molecular structures of compounds **1**−**3** were determined using X-ray crystallography. Compounds **1** and **2**[10] are isostructural (data for **1** described), consisting of a monomeric complex with two imine-bound hppH molecules at a trigonal planar [Σ_{angles} 359.66°] copper center (Figure 1). Although formally consisting of localized C−N and C=N bonds within the neutral ligand, inspection of the distances reveals relatively low Δ_{CN} values,[11] [0.029 and 0.043 Å] suggesting partial delocalization of π-electron density as observed in the noncoordinated neutral ligand structure.[9] In addition, the C(1)−N(3) and C(8)−N(6) distances [1.356(3) and 1.369(3) Å] are considerably shorter than expected for a C(sp^2)−N single bond [1.47 Å],[12] a consequence of delocalization of the N(3)/N(6) lone pair into the core of the ligand arising from the enforced coplanar arrangement of the C(1/8)−N(1/4)−N(2/5) and C(4/11)−N(3/6)−C(5/12) moieties (torsion angle 6.96° and 10.28°, respectively). The stability of **1** is further enhanced by two intramolecular NH···Cl hydrogen bonds of distance 2.452 and 2.472 Å.

In contrast to the structures of **1** and **2**, the iodide **3**[13] consists of eight independent molecules in the unit cell (Figure 2a), three of which possess copper−iodine bonds (Figure 2b), while the remaining five are $[(hppH)_2Cu]^+[I]^-$ ion pairs (Figure 2c). Unfortunately, six of the molecules have an alternative lower occupancy Cu site corresponding to the other bonding mode, resulting in unresolved disorder of the hppH ligands,[14] and restricting the validity of any comparisons between bond lengths and angles. The gross structural differences between the two types of molecules can be clearly seen, however, presumably reflecting the relative weakness of the Cu−X bond (CuCl, 360.7 kJ mol^{-1}; CuBr, 330.1 kJ mol^{-1}; CuI, ~142 kJ mol^{-1}).[15] Another contributing factor to the partial dissociation is the more pronounced twist of the ligand out of the approximate "N$_2$-CuI" plane. This is most likely due to the size of the iodide, which prevents formation of any stabilizing NH···I interactions.

The ^{1}H NMR spectra expected assuming the solid-state structures of **1**−**3** are maintained in solution consist of six resonances for each unique methylene unit in the ligand backbone, and a low field resonance for the NH proton. However, at room temperature only three signals corresponding to the CH$_2$ units are observed, indicating a fluxional process that most likely involves decoordination of the hppH ligand from the "Cu−X" fragment.[16] Upon cooling, the peaks were resolved into six distinct resonances consistent with a fixed coordination geometry (Figure 3). The average $\Delta G^\ddagger$ value[17] for **3** (44.9 ± 0.4 kJ mol^{-1}) is lower than that for **1**

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(10) Data for **1** follow: $C_{14}H_{26}N_6ClCu$, $M = 377.40$, $T = 173(2)$ K, monoclinic, space group $P2_1/c$ (No. 14), $a = 7.3071(3)$ Å, $b = 14.3936(7)$ Å, $c = 16.0124(5)$ Å, $\beta = 96.679(3)°$, $U = 1672.7(1)$ Å^3, $Z = 4$, $D_c = 1.50$ Mg m^{-3}, μ(Mo Kα) = 1.47 mm^{-1}, independent reflections = 3968 [$R_{\text{int}} = 0.051$], R1 [for 3008 reflections with $I > 2\sigma(I)$] = 0.042, wR2 (all data) = 0.106. For **2**: $C_{14}H_{26}N_6BrCu$, $M = 421.86$, $T = 173(2)$ K, monoclinic, space group $P2_1/c$ (No. 14), $a = 7.2583(3)$ Å, $b = 14.5542(6)$ Å, $c = 16.1243(6)$ Å, $\beta = 97.144(2)°$, $U = 1690.13(12)$ Å^3, $Z = 4$, $D_c = 1.66$ Mg m^{-3}, μ(Mo Kα) = 3.66 mm^{-1}, independent reflections = 2960 [$R_{\text{int}} = 0.041$], R1 [for 2620 reflections with $I > 2\sigma(I)$] = 0.033, wR2 (all data) = 0.076.

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(12) Sutton, L. E. *Interatomic Distances and Configuration in Molecules and Ions*; Special Publications 18; The Chemical Society: London, 1965.

(13) Data for **3** follow: $C_{14}H_{26}N_6CuI$, $M = 468.85$, $T = 173(2)$ K, orthorhombic, space group $Pna2_1$ (No. 33), $a = 16.4312(3)$ Å, $b = 33.6903(9)$ Å, $c = 25.8835(7)$ Å, $U = 14328.4(6)$ Å^3, $Z = 32$, $D_c = 1.74$ Mg m^{-3}, μ(Mo Kα) = 2.95 mm^{-1}, independent reflections = 17517 [$R_{\text{int}} = 0.062$], R1 [for 11409 reflections with $I > 2\sigma(I)$] = 0.053, wR2 (all data) = 0.121.

(14) All of the hppH ligands were refined with isotropic thermal parameters and with 1,2 and 1,3 distances constrained to be equal in all ligands (using the SAME instruction in SHELXL).

(15) Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*, 3rd ed.; Harper Collins: New York, 1983.

(16) The ^{1}H NMR of the noncoordinated ligand also shows only 3 resonances for the methylene groups. Low temperature (196 K) spectra did not resolve the groups into the six resonances expected in a localized structure, suggesting a rapid process by which the H-atom of the NH group is rapidly moving between the two nitrogen atoms (in agreement with the solid-state structure) or is present in a delocalized (symmetric) situation.

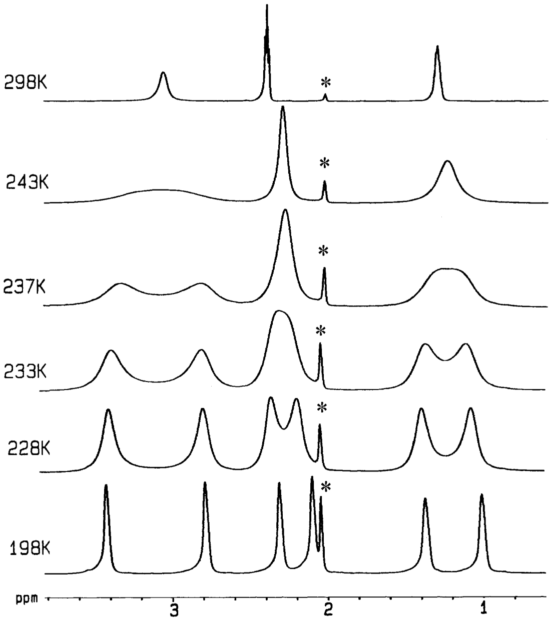

Figure 3. Variable temperature ^1H NMR spectra of **1** (* = toluene).

Table 1. Polymerization Data for Attempted ATRP of MMA with **1**[a]

time (min)	conversion	M_n	M_w	PDI
30	0.415	9750	20 300	2.08
60	0.543	11 700	25 300	2.16
90	0.570	12 800	28 000	2.19
120	0.669	12 900	28 700	2.22
240	0.779	15 800	31 700	2.01

[a] Conditions: solvent = toluene (20 cm^3); temperature = 90 °C; initiator = ethyl-2-bromoisobutyrate. Molar ratio: **1**/initiator/MMA = 1/1/100.

(45.8 ± 0.2 kJ mol^{-1}) reflecting a less strongly bound ligand with no stabilization by H-bonding. However, the NMR data for the bromide **2** indicate a slightly higher energy process ($\Delta G^\ddagger = 47.2 \pm 0.4$ kJ mol^{-1}) and a stronger interaction with the metal center. In all cases, lower values were recorded in comparison with a recent study of Cu(I) bipy ($\Delta G^\ddagger \sim 65-67.4$ kJ mol^{-1}) and pyridine imine ($\Delta G^\ddagger \sim 58.2$ kJ mol^{-1}) complexes,[18] a likely consequence of these two ligand types interacting with the copper via two N−Cu bonds to form a more stable five-membered metallacycle.

It has been established that chelating N,N′-based ligands at copper provide the correct environment for the generation of active species in the ATRP of methacrylates, while monodentate N-ligands are inferior for this purpose.[19] While not chelating to the metal per se, the hppH ligand is bidentate to the metal halide fragment and may therefore be considered as an intermediate type interaction between mono- and bidentate coordination. As such, a preliminary study into the possible application of **1** as a catalyst in the ATRP of MMA was conducted.[20] Compound **1** was active under the conditions investigated, showing high conversions to poly(methyl methacrylate) (pMMA), Table 1. Examination of the GPC data, however, indicated PDI values greater than predicted from a living polymerization. In addition, the observed M_n values rapidly exceed the theoretical value of ~10 000 implying that partial conversion to a highly active catalytic species is occurring. Running the experiment for longer periods of time did not result in a significant increase in the conversion, suggesting that this active species is not stable under the conditions of the polymerization experiment. It was also noted that, as polymerization reactions progressed, an insoluble green oil formed around the walls of the reaction vessel. Synthetic investigations into the stability of the $CuCl_2$ analogue of **1** have thus far only resulted in isolation of a green oil, and a plausible explanation for the observed polymerization behavior is that formation of the Cu^{II} species during the course of the reaction results in gradual deposition from solution, preventing the establishment of a rapid reversible deactivation pathway required for living ATRP. As a consequence, the concentration of propagating chains increases, leading to radical combinations that result in the observed high molecular weights and short lifetime of the polymerization. Current effort is underway to modify the ligand such that (i) a greater barrier to decoordination is present and (ii) increased solubility of the Cu^{II} species is observed.

In summary, we have isolated the series of compounds $[(hppH)_2Cu-X]$ for X = Cl, Br, I and have investigated their solid- and solution-state properties. Preliminary attempts at the polymerization of MMA under ATRP conditions suggest the Cu^{II} species formed during the reaction is insoluble resulting in nonideal behavior.

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Supporting Information Available: Experimental procedures for the synthesis of **1**−**3**, details of polymerization procedures employed, X-ray structural data for **1**−**3** in CIF format, and ORTEP representation of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The relationship $\Delta G^\ddagger = RT_c[22.96 + \ln(T_c/\Delta \upsilon)]$ was used to calculate activation energies. The average value for the three different methylene coalescence temperatures is quoted for comparative purposes.

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