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An Unprecedented Coordination Mode of the Tris(pyrazolyl)methane Donor Set in $\{[Ph_2(O)POCH_2C(pz)_3Ag]_2(THF)_2\}(BF_4)_2$: κ^2–κ^1 Bimetallic, N_σ/N_π Chelating

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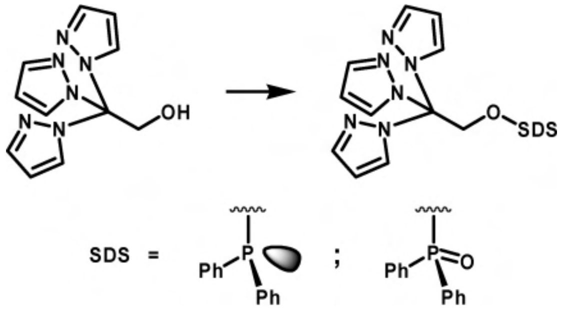
The structure of the compound $\{[Ph_2(O)POCH_2C(pz)_3Ag]_2(THF)_2\}(BF_4)_2$ (pz = pyrazolyl ring) revealed a new coordination mode for the tris(pyrazolyl)methane donor set: two pyrazolyl rings bridging the same two silvers atoms using normal σ-type orbitals on the nitrogen donor atoms while the third pyrazolyl ring coordinates side-on to one of the silver atoms with a nitrogen-based π-type orbital. The dimeric arrangement is also supported by a weak silver–silver interaction. This bonding description is supported by Fenske–Hall molecular orbital calculations.

We have recently described the chemistry of a variety of homomultimetallic complexes based on the $C_6H_{6-n}[CH_2OCH_2C(pz)_3]_n$ (n = 2, 3, 4, 6) family of ligands.[1] We desire to expand this chemistry to unsymmetrical ligands in order to develop new types of homo- and hetero-multimetallic systems. Our approach to the synthesis of such species is, among others, to replace the hydrogen atom from tris(pyrazolyl)ethanol[2] with a secondary donor set (SDS), as shown in Scheme 1, that has coordination properties very different from those of the tris(pyrazolyl)methane units also present in the polytopic ligand.

Scheme 1. Synthetic Strategy toward a Tris(pyrazolyl)methane Heteroditopic Ligand: Replacement of the Hydrogen Atom with a Secondary Donor Set (SDS)



In the course of our studies of such systems, we isolated the compound $\{[Ph_2(O)POCH_2C(pz)_3Ag]_2(THF)_2\}(BF_4)_2$ (**1**),[3] whose solid-state structure (cation depicted in Figure 1) consists of two $Ph_2(O)POCH_2C(pz)_3$ ligands coordinated to the same two silver(I) centers through the tris(pyrazolyl)methane units. In addition, two THF molecules, one for each silver atom, coordinate to the silver atoms. The distance

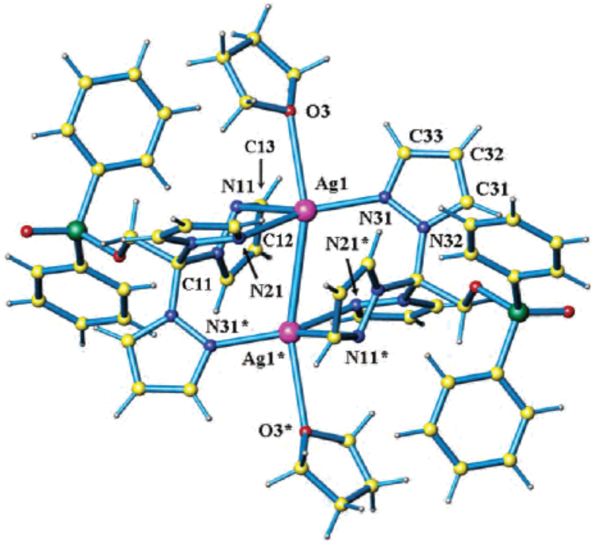


Figure 1. Solid-state structure of $\{[Ph_2(O)POCH_2C(pz)_3Ag]_2(THF)_2\}^{2+}$. Bond lengths and angles (Å and deg): Ag(1)−N(11) = 2.464(2), Ag(1)−N(21) = 2.257(2), Ag(1)−N(31) = 2.182(2), Ag(1)−O(3) = 2.795(3), Ag(1)−Ag(1*) = 3.3690(5), N(31)−Ag(1)−N(21) = 149.94(9), N(31)−Ag(1)−N(11) = 134.01(8), N(21)−Ag(1)−N(11) = 75.79(8). Color code: purple, silver; yellow, carbon; gray, hydrogen; blue, nitrogen; red, oxygen; green, phosphorus.

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(3) See Supporting Information for details.

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between the silver atoms is 3.36 Å, less than the sum of silver−silver van der Waals radii (3.44 Å),[4] which is indicative of a weak Ag−Ag interaction. Such interactions have been shown to influence the outcome of several supramolecular assemblies, and their importance has been crystallographically and theoretically documented.[5] Each silver is equatorially surrounded by three nitrogen atoms, two from one ligand and one from the second. The sum of the three N−Ag−N angles around the silver is 359.7°, thus placing it in a pseudo-trigonal-planar geometry, with a significant distortion caused by the restricted angle (75.79°) of the κ^2-bonded ligand. This type of distorted trigonal-planar geometry around a silver(I) atom was previously observed in other cases involving the tris(pyrazolyl)methane ligand.[1] If the THF molecules and the second silver atom are included, the geometry around each silver becomes pseudo-trigonal-bipyramidal.

A close examination of the structure reveals that the Ag−N(11) bond is almost perpendicular to the corresponding pyrazolyl ring plane, with Ag(1)−N(11) and Ag(1)−C(13) distances of 2.46 and 3.04 Å, respectively. For maximum overlap with the lone pair on the nitrogen donor atom, the metal would lie in the plane of each pyrazole ring. Any deviation where the metal lies out of this plane can be measured by the AgN(n1)−N(n2)C(n1) torsion angle, where *n* denotes the ring number. An ideal structural arrangement generated by the "normal" coordination of the nitrogen atom would generate torsion angles that would have a value of 180°. In the case of **1**, the torsion angles are as follows: Ag(1)N(31)−N(32)C(31) = 170.3°, Ag(1)N(21)−N(22)-C(21) = 150.4°, and Ag(1)N(11)−N(12)C(11) = 109.5°. Although deviations down to about 150° from the ideal geometry have been observed in several other cases,[1c,6] they were explained either by the size of the metallic center[6] or by the intra- and intermolecular noncovalent interactions involving the tris(pyrazolyl)methane−metal moiety.[1c] A deviation to 109° raised the question of whether the silver atom is coordinated by the normal nitrogen-based σ-type orbital or by a nitrogen-based π-type orbital.

To understand the nature of the bonding in **1** with regard to Ag−N and Ag−Ag interactions, we have performed Fenske−Hall molecular orbital calculations,[7] replacing the group bound to the methine carbon of the ligand with a hydrogen atom. Thus, the $\{[HC(pz)_3]Ag(THF)\}_2^{2+}$ dimer can be constructed from two Ag^+ units, two $[HC(pz)_3]$ units, and two THF units. This complex exhibits C_i symmetry, and the discussion of its bonding interactions herein is based on this point group. The key low-lying occupied orbitals for the $[Ag_2]^{2+}$ fragment, shown on the bottom right side of Figure 2, are the symmetric and antisymmetric combination of the metal d orbitals. The low-lying orbitals for the $[HC(pz)_3]_2$ fragment and the $[THF]_2$ fragment (shown on the left side of Figure 2) combine with the $[Ag_2]^{2+}$ fragment orbitals to generate bonding MOs for the dimeric complex as shown in the center of Figure 2.

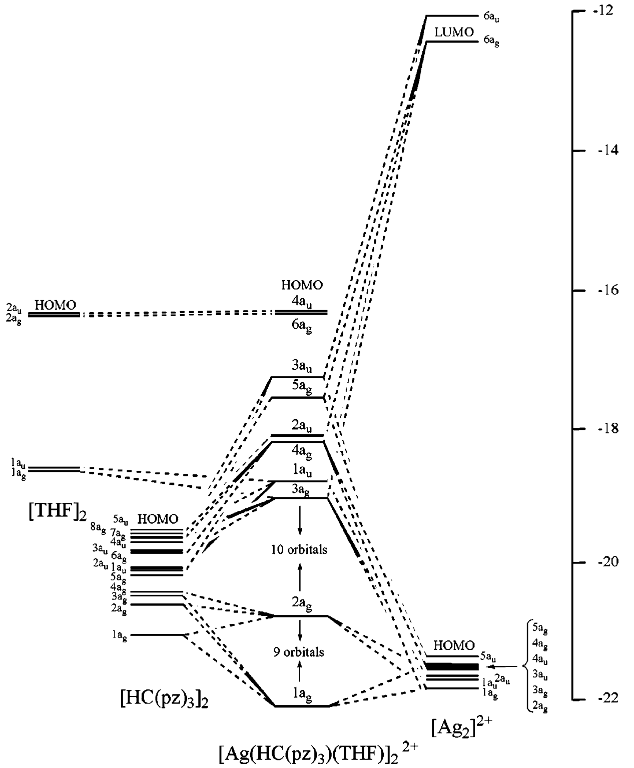

Figure 2. Fenske−Hall MO energy level diagram with orbital energy scale (eV) for compound **1**.

The $4a_g$, $2a_u$, $5a_g$, and $3a_u$ orbitals represent the main set of bonding orbitals of Ag with N(21) and N(31) (contour diagrams not shown) that form normal σ-type bonds. This bonding is supported by the crystallographic data, which show normal Ag−N distances of 2.182(2) and 2.257(2) Å. The best orbital overlap between Ag and N(11) is seen in the $2a_g$ orbital of **1**; see Figure 3. This orbital consists of the $[HC(pz)_3]_2$ $2a_g$ orbital, which has a major π-type component located on N(11), and the $[Ag_2]^{2+}$ $3a_g$ (d_{xy}) and $4a_g$ (d_{yz}) orbitals. The crystallographic data, which show a longer Ag−N distance of 2.464(2) Å, support this different bonding description from that with N(21) and N(31).

The Ag−Ag bonding interaction in the dimer is the $1a_g$ orbital of **1**, which consists mainly of the $1a_g$ (d_{z^2}) orbital of the $[Ag_2]^{2+}$ fragment; see Figure 4. This weak Ag−Ag bonding interaction can be attributed to the poor overlap between the two orbitals on each of the Ag atoms. The $[THF]_2$ fragment in this complex does not perturb either of the Ag−N(11) and Ag−Ag bonding interactions described above. This conclusion was confirmed by performing Fenske−Hall calculations on only the $\{[HC(pz)_3]Ag\}_2^{2+}$ frag-

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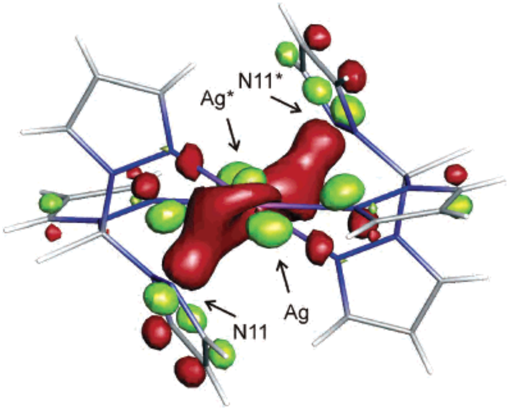


Figure 3. $2a_g$ orbital of **1**, showing interactions of the $2a_g$ orbital of the $[HC(pz)_3]_2$ fragment with the $3a_g$ and $4a_g$ orbitals of the $[Ag_2]^{2+}$ fragment. The $[THF]_2$ fragment has been omitted for clarity.

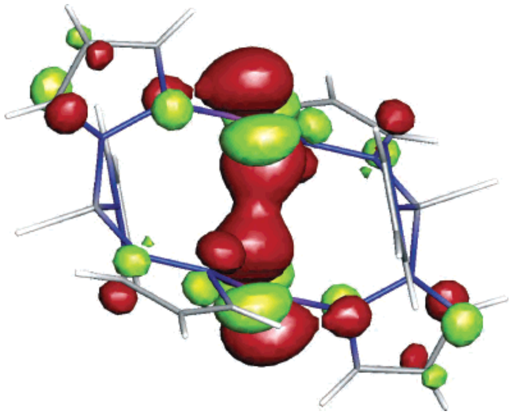
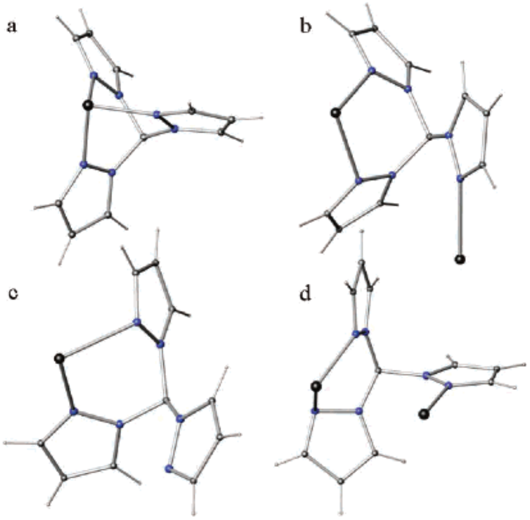


Figure 4. $1a_g$ orbital of **1** showing Ag−Ag interactions. The $[THF]_2$ fragment has been omitted for clarity.

ment, without the two THF molecules. This set of calculations shows the same Ag−N(11) and Ag−Ag interactions that were observed in orbitals $2a_g$ and $1a_g$ in **1**, respectively. The only significant interactions of the $[THF]_2$ fragment in the dimer is seen in the $1a_u$ and $3a_g$ orbitals of **1** (see Figure S1 in the Supporting Information). These two orbitals are the antisymmetric and symmetric combination formed by the $1a_u$ and $1a_g$ "p_z" orbital on the oxygen atom of the $[THF]_2$ fragment that interact with the $[Ag_2]^{2+}$ fragment.

It has been shown previously that the tris(pyrazolyl)methane unit (Chart 1) can act in different binding modes as (a) κ^3 tripodal; (b) $\kappa^2-\kappa^1$-bonded, bridging two metals; and (c) κ^2-bonded to a single metal with the third pyrazolyl not coordinated.[1,8] The unprecedented coordination mode present in **1** (Chart 1d) in which two pyrazolyl rings bridge two silver atoms using σ-type orbitals on the nitrogen donor atoms and the third pyrazolyl ring coordinates to one of the silver atoms with a π-type orbital on nitrogen represents the fourth coordination mode encountered so far for the tris(pyrazolyl)methane ligand.

Chart 1. Coordination Modes of Tris(pyrazolyl)methane Units: (a) κ^3 Tripodal; (b) $\kappa^2-\kappa^1$-Bonded, Bridging Two Metals; (c) κ^2, Chelating a Single Metal; and (d) $\kappa^2-\kappa^1$-Bonded, Bridging, N_σ /N_π Chelating



The bonding in compound **1** is also unique in that two tris(pyrazolyl)methane units bridge the *same* two metals. This type of bridging can be viewed either as a consequence of the Ag−Ag interaction or as forcing the bridged metals to be at close proximity. In all previous examples of type b, $\kappa^2-\kappa^1$ bonding, a single tris(pyrazolyl)methane ligand bridges the two metals, which are clearly out of bonding distance range. To the best of our knowledge, **1** represents the first example in the coordination chemistry of tris(pyrazolyl)methane ligands where such a coordination mode is found in a complex with a metal−metal interaction. There are a few known cases of two tris(pyrazolyl)borate ligands bonding $\kappa^2-\kappa^1$ to the same two metals,[9] but the use of a π orbital of one ring within this type of bonding appears to be unique to compound **1**.

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Supporting Information Available: Experimental procedures and the X-ray crystallographic file in CIF format for **1**. This information is available free of charge via the Internet at http://pubs.acs.org.

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