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# Synthesis and Structure of Dimeric Silver Azooximates. Hydrogen Bonding and Nonbonded Ag···Ag Interaction

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## Introduction

Nonbonded distances between neighboring closed-shell heavy atoms can fall below the sum of van der Waals radii due to relativistic effects.[1] Gold(I) ($5d^{10}$) compounds provide model examples.[2] The status of silver(I) ($4d^{10}$) is less well defined and is under active experimental scrutiny.[3,4] The excellent affinity[5,6] of azooximes for copper(I) ($3d^{10}$) has prompted us to search for the silver(I) complexes. Herein, we report the synthesis and structures of two such compounds, both hydrogen bonded and dimeric but with a large variation in coordination geometry. In one of these the metal−metal contact is significantly shorter than the van der Waals sum.

## Results and Discussion

**A. Ligands and Complexes.** The concerned species are listed in Chart 1. Two azooxime ligands, HRL (R = Me, Ph), **1**, where H refers to the dissociable oxime proton, have been used. The reaction of ammoniacal silver hydroxide (Tollen's reagent) with HMeL has afforded the brown-colored dimer **2**. The same complex is deposited irrespective of the $Ag^{+}$:HMeL ratio. Upon replacement of HMeL by HPhL, the product was again a brown dimer but of composition **3**.

Even though the difference between HMeL and HPhL is only in the substituent R, the effect of the latter on the composition and structure (vide infra) of the complexes formed is indeed remarkable. This highlights the flexibility that silver can exhibit with respect to coordination number and geometry. We also note that very few authentic silver complexes of oxime ligands have been isolated and structural characterization is rare.[7]

**B. Structures.** The structures of both **2** and **3** have been determined. The former is centrosymmetric, the asymmetric unit consisting of the monomer, a view of which is shown in Figure 1. A line drawing of the dimer is depicted in Figure 2, and selected bond parameters are listed in Table 1.

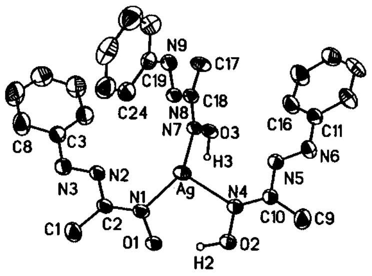


**Figure 1.** Perspective view and atom-labeling scheme of the Ag(MeL)(HMeL)$_2$ monomer in **2**. All atoms are represented by their 30% thermal probability ellipsoid.

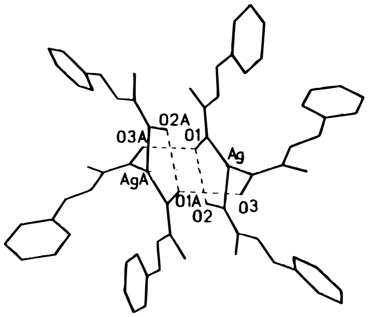
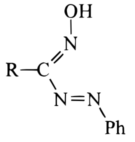


**Figure 2.** The [Ag(MeL)(HMeL)$_2$]$_2$ dimer.

**Chart 1**

1. 

HRL (R = Me, Ph)

2. [Ag(MeL)(HMeL)$_2$]$_2$
3. [Ag(PhL)(HPhL)]$_2$
4. [Cu(MeL)(HMeL)]$_2$

**Table 1.** Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for [Ag(MeL)(HMeL)$_2$]$_2$

| | | | |
|---|---|---|---|
| | Distances | | |
| Ag−N1 | 2.252(3) | N1−O1 | 1.349(3) |
| Ag−N7 | 2.233(3) | N4−O2 | 1.371(4) |
| Ag−N4 | 2.423(3) | N7−O3 | 1.369(4) |
| N2−N3 | 1.257(4) | O1···O2 | 2.566(6) |
| N5−N6 | 1.253(4) | O1···O3A | 2.546(6) |
| N8−N9 | 1.258(4) | Ag···Ag | 3.517(1) |
| | Angles | | |
| N1−Ag−N7 | 152.1(1) | N4−Ag−N7 | 118.4(1) |
| N1−Ag−N4 | 89.6(1) | | |

In **3** the whole dimer constitutes the asymmetric unit, the two monomers (molecules 1 and 2) being metrically similar. A view of molecule 1 and a line drawing of the dimer are shown in Figures3 and 4, respectively. Selected bond lengths and angles are listed in Table 2. Corresponding atoms of molecules 1 and 2 are numbered $n$ and $n + 50$ such as Ag1 and Ag51.

**a. Coordination Geometry.** Coordinated oxime and azo nitrogen atoms will be generally designated as $N^{o}$ and $N^{a}$, respectively. In **2** each ligand is bonded to the metal solely at the $N^{o}$ atom, the azooxime function having a transoid disposition. The nearly perfectly planar (mean deviation 0.01 Å) $AgN^{o}_{3}$

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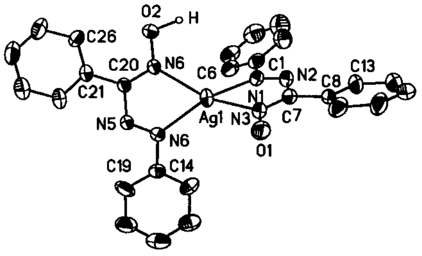

**Figure 3.** Perspective view and atom labeling scheme of the Ag(PhL)(HPhL) monomer (molecule 1) in **3**. All atoms are represented by their 30% thermal probability ellipsoid.

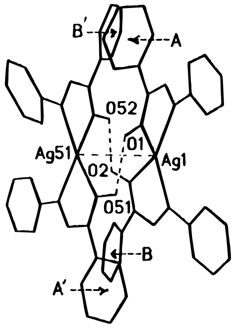

**Figure 4.** The [Ag(PhL)(HPhL)]$_2$ dimer; A, A$^{/}$, B, B$^{/}$ are the centroids of the concerned phenyl rings.

**Table 2.** Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for [Ag(PhL)(HPhL)]$_2$

| | | | |
|---|---|---|---|
| | Distances | | |
| Ag1−N6 | 2.319(4) | Ag51−N56 | 2.311(4) |
| Ag1−N4 | 2.320(4) | Ag51−N54 | 2.338(4) |
| Ag1−N1 | 2.319(4) | Ag51−N51 | 2.338(4) |
| Ag1−N3 | 2.325(5) | Ag51−N53 | 2.306(4) |
| N1−N2 | 1.259(5) | N51−N52 | 1.262(5) |
| O1−N3 | 1.322(5) | O51−N53 | 1.342(5) |
| O2−N6 | 1.346(5) | O52−N56 | 1.329(5) |
| N4−N5 | 1.263(5) | N54−N55 | 1.257(5) |
| O1···O51 | 2.414(5) | O2···O52 | 2.426(5) |
| Ag···Ag | 3.395(1) | | |
| | Angles | | |
| N6−Ag1−N4 | 68.3(2) | N56−Ag51−N54 | 67.8(2) |
| N6−Ag1−N1 | 127.8(2) | N56−Ag51−N51 | 125.0(2) |
| N4−Ag1−N1 | 145.4(2) | N54−Ag51−N51 | 143.7(2) |
| N6−Ag1−N3 | 135.9(2) | N56−Ag51−N53 | 141.3(2) |
| N4−Ag1−N3 | 125.6(2) | N54−Ag51−N53 | 126.9(2) |
| N1−Ag1−N3 | 67.8(2) | N51−Ag51−N53 | 67.3(2) |

coordination sphere has a distorted-T shape. The Ag−N4 bond is ~0.2 Å longer than the Ag−N7 and Ag−N1 bonds, the N1−Ag−N7 angle being 152.1(1)°.

In **3**, the azooxime function has cisoid disposition and each ligand is chelated to the metal via N$^{o}$ and N$^{a}$ atoms, affording satisfactorily planar (mean deviation 0.02−0.05 Å) five-membered chelate rings. The AgN$^{o}_{2}$N$^{a}_{2}$ coordination spheres are strongly squashed tetrahedra, vide infra. The Ag−N distances lie within the range 2.31−2.34 Å.

**b. Hydrogen Bonding.** In **2** both the intramonomer O1···O2 and intermonomer O1···O3A distances lie near 2.55 Å, indicating the presence of strong oxime−oximato hydrogen bonds.[8−10] The hydrogen atoms attached to O2 and O3 (Figure 1) were directly observed in the difference Fourier maps, and the relevant bond parameters are O2−H2, 0.97 Å; O1···H2, 1.61 Å; O2−H2···O1, 165.3°; and O3−H3, 1.03 Å; O1A···H3, 1.57 Å; and O3−H3···O1A, 155.6°. The bonding is unsymmetrical[8] and is bifurcated at the deprotonated O1 site.

In **3** the intramonomer O···O distance is ~5.72 Å. The intermonomer O1···O51 and O2···O52 lengths are ~2.40 Å. This is about the lowest possible limit of the hydrogen-bonded O···O distance below which oxygen−oxygen repulsion becomes dominant.[8] The hydrogen atom H2 was located in difference Fourier maps at distances of 1.13 and 1.27 Å from O2 and O52, respectively, the O2−H2···O52 angle being 175°. Here the hydrogen bonding is more symmetrical than that in **2**, consistent with the shorter O···O distance.[8]

**c. Silver−Silver Affinity.** The HMeL ligand affords **2** with silver(I), but with copper(I) it yields the bis complex [Cu(MeL)(HMeL)]$_2$, **4**.[5] We do not have a good explanation for this difference, but fortunately the structures of **3** and **4**[6] are grossly similar, thus providing an opportunity for silver−copper comparison. The MN$_4$ coordination sphere is far more squashed in **3** than in **4**: the average N$^{a}$−M−N$^{a}$ angle is 145° in **3** and 126° in **4**, while the average N$^{o}$−M−N$^{a}$ angle is 139° in **3** and 123° in **4**. The effect of this is that the Ag···Ag distance in **3** (3.395(1) Å) is ~1 Å *shorter* than the Cu···Cu distance in **4** (4.377(2) Å) even though the silver(I) atom is significantly bigger[11] than the copper(I) atom. Indeed the Ag···Ag distance in **3** has fallen below the sum of van der Waals radii, 3.44 Å, due to relativistic contraction.

The metrical difference between **3** and **4** is not due to the difference in substituents (C−Ph in **3** and C−Me in **4**). There is no significant Ph···Ph stacking in **3**. The distances between the centroids (A, A′, B, B′) of the C−Ph rings which appear to lie relatively close to each other in Figure 4 are A···B′ = 5.92 Å, dihedral angle 25.2°, and A′···B = 5.50 Å, dihedral angle 25.6°.

The interdimer O···O separation is ~2.4 Å in both **3** and **4**.[6] Indeed, if not for the rigidity imposed by the very short hydrogen bond, the Ag···Ag distance in **3** could have been even shorter. In **2** the Ag···Ag separation, 3.517(1) Å, is slightly longer than the van der Waals sum. Significantly, strong hydrogen bonds controlling structural rigidity are more in number in **2** (four) than in **3** (two). In these structures the strong hydrogen bonding supports the dimeric forms, thus providing the opportunity for pairs of silver atoms to come near each other in the first place. The geometries assumed by the silver atoms (planar in **2** and highly squashed tetrahedral in **3**) are also conducive to close approach. But the rigidity of the hydrogen-bonding system stiffly restrains this closeness beyond a level. There is thus a compromise, and in effect, relativistic contraction finds only a mild expression in the present species.

## Concluding Remarks

The main findings of this work will now be summarized. The reaction of ammoniacal silver hydroxide with **1** has afforded dimeric **2** and **3**, thus providing an opportunity to scrutinize the status of intradimer silver−silver contacts. The transoid ligand in **2** binds via N$^{o}$ only, the geometry of AgN$^{o}_{3}$ being distorted-T. In **3**, the cisoid ligand is chelated and the AgN$^{o}_{2}$N$^{a}_{2}$

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tetrahedron is highly squashed. A total of four and two strong O···O hydrogen bonds characterize **2** and **3**, respectively.

The squashing that makes the Ag···Ag separation in **3** less than the sum of van der Waals radii is believed to be the result of relativistic contraction. The observed effect is relatively mild because of the structural rigidity imposed by hydrogen bonds. In **2**, the molecular environment is more rigid and the Ag···Ag contact is also longer.

The complexes **2** and **3** are useful starting materials for synthesis of azooxime chelates that are otherwise not accessible. The chemistry based on this feature will be presented elsewhere.

## Experimental Section

**Physical Measurements.** A Hitachi 330 spectrophotometer was used to record UV−vis spectra, a Perkin-Elmer 2400 Series(II) elemental analyzer was used to collect microanalytical data (CHN), and IR spectra were recorded by Perkin-Elmer 783 spectrometer.

**Synthesis of Ligands and Complexes.** The ligands were synthesized as previously described,[12] and the complexes were prepared as described below.

**[(Phenylazo)acetaldoximato][bis(phenylazo)acetodoxime]silver(I), $[Ag(MeL)(HMeL)_2]_2$.** A 0.05 g (0.29 mmol) portion of silver nitrate was dissolved in 10 mL of water, and a dilute solution of sodium hydroxide was added to it dropwise till complete precipitation of silver hydroxide. The precipitate was dissolved by adding a minimum volume of dilute ammonia, and the colorless solution so formed (Tollen's reagent) was added to a methanolic solution (20 mL) of HMeL (0.144 g, 0.88 mmol). The mass was allowed to stir for 2 h. The brown precipitate that separated out was filtered, washed with 1:1 aqueous methanol, and dried in vacuo over fused $CaCl_2$. Yield: 0.158 g (90%). Anal. Calcd for **2**, $C_{48}H_{52}N_{18}O_6Ag_2$: C, 48.33; H, 4.39; N, 21.14. Found: C, 48.28; H, 4.38; N, 21.18. UV−vis ($CH_2Cl_2$, $\lambda_{max}$, nm ($\epsilon$, $M^{-1}$ $cm^{-1}$)): 350(12 090); 310 (14 340). IR (KBr, $cm^{-1}$): $\nu_{OH}$ 2850 (br).

**[(Phenylazo)benzaldoximato][(phenylazo)benzaldoxime]silver(I), $[Ag(PhL)(HPhL)]_2$.** This complex was prepared by the same procedure as above starting from 0.05 g (0.29 mmol) of silver nitrate and 0.133 g (0.59 mmol) of HPhL. Yield: 0.160 g (88%). Anal. Calcd for **3**, $C_{52}H_{42}N_{12}O_4Ag_2$: C, 56.13; H, 3.62; N, 15.11. Found: C, 56.08; H, 3.60; N, 15.09. UV−vis ($CH_2Cl_2$, $\lambda_{max}$, nm $\epsilon$, $M^{-1}$ $cm^{-1}$)): 415 (6196); 390 (6270). IR (KBr, $cm^{-1}$): $\nu_{OH}$ 2800 (br).

**X-ray Structure Determination.** Crystals of $[Ag(MeL)(HMeL)_2]_2$ (0.3 × 0.4 × 0.3 mm) and $[Ag(PhL)(HPhL)]_2$ (0.3 × 0.3 × 0.4 mm) were grown by slow diffusion of hexane into benzene solutions. For both the complexes cell parameters were determined by the least-squares fit of 30 machine-centered reflections ($2\theta = 15-30°$). Data were collected by the $\omega$-scan technique in the $2\theta$ range 3−50° on a Siemens R3m/V four-circle diffractometer with graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.710\ 73$ Å). Two check reflections measured after every 98 reflections showed no intensity reduction. Data were corrected for Lorentz-polarization effects, and an empirical absorption correction was performed on both sets of data on the basis of azimuthal scans[13] of six reflections. For $[Ag(MeL)(HMeL)_2]_2$ 6537 reflections were collected, 6229 were unique, and 3599 satisfying $I > 2\sigma(I)$ were used for structure solution. In the case of $[Ag(PhL)(HPhL)]_2$ the corresponding numbers are 9305, 8675, and 4522, respectively.

**Table 3.** Crystallographic Data for $[Ag(MeL)(HMeL)_2]_2$ and $[Ag(PhL)(HPhL)]_2$

| | $[Ag(MeL)(HMeL)_2]_2$ | $[Ag(PhL)(HPhL)]_2$ |
|---|---|---|
| empirical formula | $C_{48}H_{52}N_{18}O_6Ag_2$ | $C_{52}H_{42}N_{12}O_4Ag_2$ |
| fw | 1192.82 | 1114.72 |
| space group | $P2_1/c$ | $P\bar{1}$ |
| $a$, Å | 12.038(3) | 8.761(4) |
| $b$, Å | 10.331(3) | 14.433(4) |
| $c$, Å | 22.003(7) | 20.570(9) |
| $\alpha$, deg | | 80.35(4) |
| $\beta$, deg | 92.88(2) | 77.61(4) |
| $\gamma$, deg | | 74.79(3) |
| $V$, Å$^3$ | 2732.8(13) | 2434(2) |
| $Z$ | 2 | 2 |
| $T$, K | 293(2) | 293(2) |
| $\lambda$, Å | 0.710 73 | 0.710 73 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.450 | 1.521 |
| $\mu$, cm$^{-1}$ | 7.80 | 8.63 |
| R1$^a$ [$I > 2\sigma(I)$], % | 5.00 | 5.12 |
| wR2$^b$ [$I > 2\sigma(I)$], % | 10.28 | 7.84 |

$^a$ $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^b$ $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

All calculations for data reduction, structure solution and refinement were done using programs of SHELXTL, Ver. 5.03.[14] Both the structures were solved by direct methods and were refined by full-matrix least-squares on $F^2$. All non-hydrogen atoms in both the structures were refined anisotropically. A few hydrogen atoms were located in difference Fourier maps, and the rest were included in calculated positions. Significant crystal data are listed in Table 3.

The Cu···Cu distance in $[Cu(MeL)(HMeL)]_2$ was calculated using the available atomic coordinates.[6]

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**Supporting Information Available:** X-ray crystallographic files, in CIF format, for $[Ag(MeL)(HMeL)_2]_2$ and $[Ag(PhL)(HPhL)]_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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