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Multiple Bonding Involving Late Transition Metals. The Case of a Silver−Oxo Complex

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Calculations at a variety of theoretical levels were carried out on putative silver−oxo species, models of an experimentally proposed complex. Additionally, statistical analysis of metal−oxo bond lengths involving the early and middle transition series metals was carried out. This work casts doubt on the formulation of a reported complex as a diamagnetic, Ag(III)−oxo species. Two major points of contention are found. First, a cationic Ag(III)−oxo species is predicted to have a triplet ground state, with the singlet lying much higher in energy. Even the triplet would be an unstable species, due to its very low predicted bond energy. Second, the experimentally determined "silver−oxo" bond length of 1.59 Å is very short in comparison to values obtained from calculation and estimated from the crystal structures of other metal−oxo species.

Introduction

There has been a growing interest in the chemistry of multiply bonded complexes of the late transition metals. The synthesis and structural characterization of an iridium−oxo species, $OIrMes_3$ (Mes = 2,4,6-trimethylphenyl), by Wilkinson and co-workers in 1993 is a significant achievement.[1] Recently, through the use of resonance-stabilized carbenes of the type developed by the Arduengo laboratory, there has been an increase in research on late transition metal carbenes.[2] For late transition metal carbenes, and indeed for almost any late transition metal−main group element multiply bonded complex, there is room for speculation as to whether the metal−ligand linkage can be properly described as a double bond or whether a lower bond order is more appropriate.[3] Indeed, the lability of late transition metal−element multiple bonds, in contrast to that of the very strong metal−element multiple bonds formed by metals from the early to middle transition series,[4] may be used to synthetic advantage. Such species have been envisaged as intermediates in group transfer reactions such as aziridination and cyclopropanation.[5]

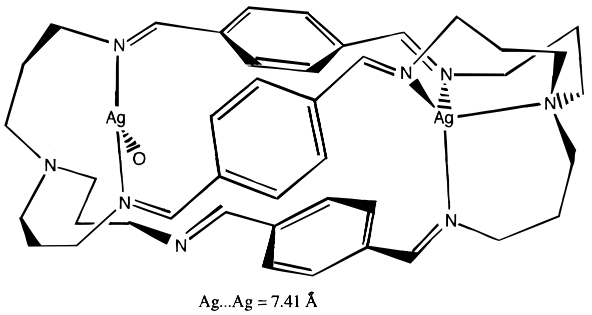

Figure 1. The $[(AgO)(Ag)(cryptand)]^{2+}$ complex reported by Yu et al. Hydrogen atoms are omitted for clarity.[6] An interactive, three-dimensional visualization of this complex, obtained from data deposited in the Cambridge Structural Database[7] is available on the World Wide Web at http://www.people.memphis.edu/~tcundari/hecwuh.pdb and is viewable with the Chime plug-in.

Recently, Yu and co-workers reported an intriguing species that they have formulated as $[(AgO)^+(Ag^+)(cryptand)](ClO_4)_2$, a diamagnetic complex, Figure 1. The cryptand is formed from the condensation of 3 equiv of p-$C_6H_4(C(O)H)_2$ and 2 equiv of $N(CH_2CH_2CH_2NH_2)_3$ in the presence of a slight excess of silver nitrate.[6] The reaction mixture is then worked up with sodium perchlorate to yield the bis(perchlorate) salt. In this bis(silver) cryptand, the first silver is in a typical +1 oxidation state with four nitrogen ligands forming a pseudotetrahedral coordination geometry. It is the other silver that is of interest, having has two imine ligands (AgN = 2.18 and 2.20 Å) plus a third amine nitrogen in close contact (AgN = 2.56 Å). The third ligand on this formally Ag(III) center is a terminal oxygen (oxo) at a distance of 1.59 Å. There are other structural features of interest, Chart 1; there are close contacts between the oxo oxygens and N(4) (2.14 Å), C(43) (1.91 Å), H(47) (2.05 Å), and H(48) (1.46 Å). The closest Ag contact with a perchlorate oxygen (O(4) in Chart 1) is 2.78 Å. These distances are very short given the van der Waals radii of these atoms ($r_{vdW}(C) \sim 1.4$ Å; r_{vdW}(H)

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(1) Hay-Motherwell, R. S.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *Polyhedron* **1993**, *12*, 2009.

(2) (a) Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *Organometallics* **1993**, *12*, 3405. (b) Arduengo, A. J., III; Harlow, R. L.; Marshall, W. J.; Prakasha, T. K. *Heteroatom* **1996**, *7*, 421. (c) Arduengo, A. J., III; Gamper, S. F.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1994**, *116*, 4391. (d) Arduengo, A. J., III; Dias, H. V. R.; Davidson, F.; Harlow, R. L. *J. Organomet. Chem.* **1993**, *462*, 13. (e) Arduengo, A. J., III; Tamm, M.; McLain, S. J.; Calabrese, J. C.; Davidson, F.; Marshall, W. J. *J. Am. Chem. Soc.* **1994**, *116*, 7927. (f) Herrmann, W. A.; Kocher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162.

(3) Mayer, J. M. *Comments Inorg. Chem.* **1988**, *4*, 125.

(4) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

(5) (a)*Transition Metal Carbene Complexes*; Dötz, K. H., Ed.; VCH: Weinheim, Germany, 1983. (b) Doyle, M. P. in *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Abel, E., Stone, F. G. A., Eds.; Pergamon: New York, 1995; pp 387, 449. (c) Li, H.; Dai, L. X.; Aggarwal, V. K. *Chem. Rev.* **1997**, *97*, 2341 and references therein.

(6) Yu, S.-Y.; Luo, Q.-H.; Shen, M.-C.; Huang, X.-Y. *Inorg. Chem.* **1994**, *33*, 1251.

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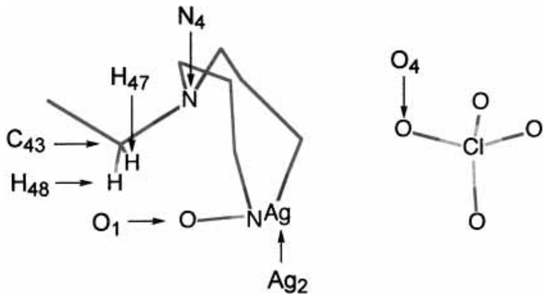
Chart 1



$\sim$ 1.2 Å; r_{vdW}(O) $\sim$ 1.3 Å) and an estimated van der Waals radius of 2.0 Å for silver.[7]

A silver−oxo complex is a very interesting entity if indeed it is formed. Adsorbed oxygen on silver surfaces is well-known in epoxidation catalysis.[8] One could, for example, easily envision a silver−oxo complex as a potent epoxidation system. Hence, it is of interest to explore the bonding and structure of such species using computational chemistry. Additionally, reported structural features are compared to those for analogous compounds.

Computational Methods

All ab initio calculations were carried out with explicit inclusion of electron correlation, using MP2, DFT, and CCSD(T) methods. Computations at the Møller−Plesset second-order perturbation level of theory (MP2) employed the GAMESS program,[9] while the density functional theory (DFT) calculations used the B3LYP hybrid density functional and were performed with Gaussian 98.[10] The coupled-cluster calculations were performed using the MOLPRO 98 program.[11] Searches and statistical analyses of the Cambridge Structural Database were performed with the QUEST and VISTA programs, respectively.[7]

All quantum calculations employed effective core potentials on the silver atom, either those of Stevens et al. (SBK),[12] those of Hay and Wadt,[13] or those of the Stuttgart group.[14] In all cases, the silver effective core potential was relativistically derived and the outermost core 4s and 4p electrons and orbitals were explicitly calculated in addition to the normal valence 4d, 5s, and 5p. This resulted in a 28-electron core for silver.

A variety of basis sets were employed, with the largest being used for relatively small model complexes such as $[\mathrm{AgO\{N({=}CH_2)(CH_3)\}_2}]^+$. Smaller basis sets were employed for larger models. For MP2 optimizations the following basis sets were employed: silver, SBK valence basis set + the f function ($\zeta_f = 1.611$) of Frenking et al.;[15] oxygen, 6-311G plus Dykstra's[16] ELP basis; N, 6-311G(d); carbon and hydrogen, STO-3G. This basis will be referred to as BS I. For the DFT geometry optimizations of the smaller model compounds, the same basis sets were used, except that, for N and O, the 6-31+G(d) basis was used (BS II). For the largest models of section 4 under Results and Discussion, the LANL2DZ core potentials and valence basis sets were used for all atoms (BS III). For the coupled-cluster calculations, the silver atom was described by the relativistic ECP of ref 14, with its associated triple-ζ basis set, which was augmented by a single f function ($\zeta_f = 1.3$), while the oxygen atom was described by the correlation consistent cc-pVTZ basis set[17] (BS IV). For the correlated MP2 and CCSD(T) calculations, only the valence electrons, i.e., for H the 1s, for C, N, and O the 2s and 2p, and for Ag the 4d electrons, were included in the correlation treatment.

Results and Discussion

1. The Silver−Oxo Cation. Calculations were first done on the diatomic ion $\mathrm{AgO^+}$. This species has been the object of an experimental beam study[18] involving collision of $\mathrm{Ag^+}$ ions with $\mathrm{O_2}$. This led to a tentative assignment of the bond dissociation energy (BDE) as 28 ± 1 kcal mol^{-1}, although experimental difficulties led the authors to stress the speculative nature of this prediction. The paper also discussed bonding mechanisms in this ion, with respect to the lowest atomic asymptotes deriving from $\mathrm{Ag^+}$ ($4d^{10}\ {}^1S$) ($4d^9 5s^1\ {}^3D$) and O (${}^3P$ or ${}^1D$). A ${}^3\Sigma^-$ ground state (r(Ag−O) $\sim$ 2.3−2.4 Å depending on the level of theory, Table 1) derived from the lowest atomic asymptote was suggested. This state was indeed found to be the lowest lying using both DFT and CCSD(T) methods; it has however a much lower BDE than the experimental suggestion, as shown in Table 1. The bonding can be considered to result merely from the charge-induced dipole interaction between $\mathrm{Ag^+}$ and O (${}^3P$). While it is possible that the theoretical methods used here are not entirely converged with respect to bond energies, we consider it likely that the experimental prediction is, in this case, in need of revision. Singlet states of $\mathrm{AgO^+}$ must derive from excited O atoms or $\mathrm{Ag^+}$ ions, and since both of the corresponding excitation energies are high,[18] they can be expected to lie higher in energy. This was indeed what was found, at both levels of theory, Table 1. The bond lengths (r(Ag−O) $\sim$ 1.9 Å, Table 1) were somewhat shorter than those in the triplet species but still much longer than those in the proposed silver−oxo complex, and the BDEs were small with respect to the lowest singlet asymptote.[19] Since the triplet surface is much more stable, the singlet species would likely undergo spin inversion and dissociate rapidly.

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(7) Allen, F. H.; Kennard, O. *Chem. Design Autom. News* **1993**, *8*, 31.

(8) Computational papers discussing the catalytic epoxidation of ethylene by silver surfaces include: (a) Van den Hoek, P. J.; Baerends, E. J.; van Santen, R. A. *J. Phys. Chem.* **1989**, *93*, 6469. (b) Goddard, W. A.; Carter, E. A. *Surf. Sci.* **1989**, *209*, 243. Experimental papers on this topic include: (c) Epling, W. S.; Hoflund, G. B.; Minahan, D. M. *J. Catal.* **1997**, *171*, 490. (d) Minahan, D. M.; Hoflund, G. B.; Epling, W. S.; Epling, S.; Schoenfeld, D. W. *J. Catal.* **1997**, *168*, 393. (e) Minahan, D. M.; Hoflund, G. B. *J. Catal.* **1996**, *162*, 48. (f) Minahan, D. M.; Hoflund, G. B. *J. Catal.* **1996**, *158*, 109. (g) Serafin, J. G.; Liu, A. C.; Seyedmonir, S. R. *J. Mol. Catal. A* **1998**, *131*, 157.

(9) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su S. J.; Windus T. L.; Dupuis, M.; Montogomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A. Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(11) MOLPRO 98 is a package of ab initio programs written by H.-J. Werner, and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, S. T. Elbert, C. Hampel, R. Lindh, A. W. Lloyd, W. Meyer, A. Nicklass, K. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, M. E. Mura, P. Pulay, M. Schütz, H. Stoll, and T. Thorsteinsson.

(12) Stevens, W. J.; Krauss, M.; Basch, P.; Jasien, P. G. *Can. J. Chem.* **1992**, *11*, 55.

(13) Hay; P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270, 284, 299.

(14) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.

(15) Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 111.

(16) Dykstra, C. E.; Liu, S.-Y.; Malik, D. J. *Adv. Chem. Phys.* **1989**, *55*, 37.

(17) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

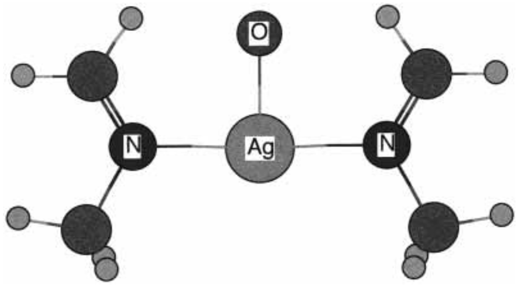
(18) Chen, Y.-M.; Armentrout, P. B. *J. Chem. Phys.* **1995**, *103*, 618.

Table 1. Summary of Computational Data on Ag−O Species[a]

species	level	tot. energy	*r*(Ag−O)	BDE to O(^{1}D)	BDE to O(^{3}P)
AgO^+ ($^1\Sigma^+$)	B3LYP/BS II	−220.981 73	1.89	13.20	−50.31
	CCSD(T)/BS IV	−220.956 03	1.88	−2.15	−52.99
AgO+ ($^3\Sigma^-$)	B3LYP/BS II	−221.084 76	2.26	77.85	14.34
	CCSD(T)/BS IV	-221.057 47	2.39	61.51	10.67
$^1[AgO\{N({=}CH_2)(CH_3)\}_2]^+$	B3LYP/BS II	−487.238 79	1.92	55.08	−8.43
	MP2/BS I	−485.430 02	1.83	64.13	−3.49
$^3[AgO\{N({=}CH_2)(CH_3)\}_2]^+$	B3LYP/BS II	−487.269 42	2.15	74.30	10.79

[a] Total energies of optimized species, in atomic units, are included for reference; bond lengths are in Å; bond dissociation energies (BDEs) are in kcal mol^{-1}; negative bond energies indicate a species unstable toward dissociation.

Chart 2



The qualitative conclusions of the present calculations were thus at odds with the X-ray diffraction experiment, in that bare AgO^+ was predicted to have a triplet ground state, with a long equilibrium bond length, and that the singlet was predicted to be highly unstable.

2. The Bis(*N*-methylmethyleneimine)silver−Oxo Cation. Because of the inconsistency of the above calculations with the experimental formulation of a diamagnetic $[(AgO)^+(Ag^+)(cryptand)](ClO_4)_2$ complex, further calculations were pursued to examine whether ligand coordination changes the bonding factors in favor of a singlet silver−oxo complex. Calculations were carried out on a silver−oxo bis(imine), $[AgO\{N({=}CH_2)(CH_3)\}_2]^+$, Chart 2, to model the inner coordination sphere of the putative silver−oxo complex. The calculations were performed at the MP2 and B3LYP levels of theory, the latter in particular having been shown to yield results in good agreement with the reliable CCSD(T) method.

It was found, upon MP2 optimization, that the silver−oxo bis(imine) complex adopted a structure in which the oxygen is in the molecular plane formed by the silver, nitrogen, and carbon atoms, Chart 2. This was despite the fact that the MP2 optimization was started from the X-ray experimental geometry (after slight geometric perturbation to impose C_s symmetry), in which the oxygen−silver bond lies perpendicular to the plane defined by the other heavy atoms. There was slight evidence of a weak H-bonding interaction with the vinylic C−H bonds (for example, O- - -H = 2.06 Å, O- - -C = 2.74 Å, and O- - -H- - -C = 117° at the MP2 level of theory).

The B3LYP geometry optimization on the same singlet state led to a very similar structure, apart from the silver−ligand bond lengths and angles, which differed by up to 4%: Ag−O = 1.92 Å, Ag−N = 2.11 Å, O−Ag−N = 90°, N−Ag−N = 180°, Ag−N═C = 121°, Ag−N−C = 117° for B3LYP; Ag−O = 1.83 Å, Ag−N = 2.03 Å, O−Ag−N = 89°, N−Ag−N = 178°, Ag−N═C = 120°, Ag−N−C = 118° for MP2. A B3LYP geometry optimization with the more compact BS III was performed in preparation for calculation on an even larger model complex (vide infra) and again led to similar results: Ag−O = 1.97 Å, Ag−N = 2.11 Å, O−Ag−N = 90°, N−Ag−N = 179°, Ag−N═C = 121°, Ag−N−C = 117°.

Given the results that showed AgO^+ has a triplet ground state, B3LYP/BS II geometry optimization was also performed on triplet $[AgO\{N({=}CH_2)(CH_3)\}_2]^+$. The geometry was found to change little (Ag−O = 2.15 Å, Ag−N = 2.15 Å, O−Ag−N = 93°, N−Ag−N = 175°, Ag−N═C = 122°, Ag−N−C = 118°), except for the silver−oxygen bond length. At 2.15 Å, the AgO bond for triplet $[AgO\{N({=}CH_2)(CH_3)\}_2]^+$ is 0.23 Å longer than this same bond in the corresponding singlet at this level of theory. The lengthening of AgO upon going from a singlet to triplet spin state is in line with the results for the bare AgO^+. The geometry of singlet $[Ag\{N({=}CH_2)(CH_3)\}_2]^+$ was also optimized, allowing Ag−O BDEs to be computed. These are qualitatively similar to those for the bare ion, as shown in Table 1. Thus, the triplet complex was lowest in energy, and having a weak BDE (∼11 kcal mol^{-1}) with respect to $^1[Ag\{N({=}CH_2)(CH_3)\}_2]^+$ and O (^{3}P), it was thus again best viewed as a charge-induced dipole association. While singlet $[AgO\{N({=}CH_2)(CH_3)\}_2]^+$ had a much stronger AgO bond with respect to O (^{1}D) than in the bare ion, it is still considerably less stable than the triplet. In fact, at both the MP2/BS I and the B3LYP/BS II levels, the triplet was lower in energy than the singlet even at the optimized singlet geometry!

As with the calculations on the diatomic ion, the calculations on the bis(*N*-methylmethyleneimine)silver−oxo cation thus yield two points that contradict experiment. First, a triplet, not a singlet, ground state was indicated. Second, the calculated silver−oxygen bond lengths were considerably longer than those determined from the X-ray crystallographic experiment.

3. Database Analyses. To put a potential silver−oxo species into an appropriate structural context, database searches were done to compare the AgO bond of the complex of Yu et al.[6] with other silver−oxygen bonds (all of those contained in the Cambridge Structural Database (CSD)[7] as well as subsets of AgO bonds) and other transition metal−oxo bonds involving metals for which numerous examples of bona fide oxo ligands have been structurally characterized.

i. Silver−Oxygen Bond Lengths. A search was performed of the CSD for all silver−oxygen bonds regardless of bond type and coordination number of either the oxygen or the silver. The histogram resulting from this search is shown in Figure 2. Statistical analysis of the silver−oxygen bond lengths (for complexes with $R \leq 10\%$) yielded a range from 1.59 Å (the complex of Yu et al. with the CSD reference code HECWUH) to 3.05 Å with an average of 2.47 ± 0.17 Å for 886 examples. The next shortest AgO bond length in the CSD was 2.03 Å, more than 28% longer. Even with a large standard deviation

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(19) The CCSD(T) bond energy with respect to Ag^+ (^{1}S) and O (^{1}D) is negative. This is due to problems in describing the excited oxygen atom in a single reference ansatz such as RCCSD(T) or RB3LYP, as is done here, and multireference methods should be used instead. However, since our aim here is mainly to understand bonding in the putative silver−oxo complex, which should be well described with the methods employed, we have not pursued the use of multireference methods.

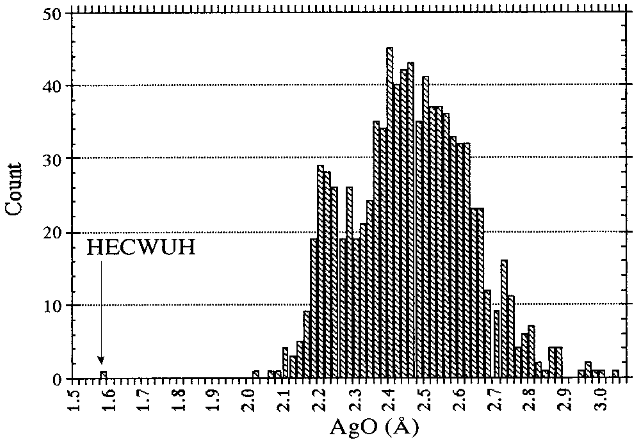


Figure 2. Histogram of X-ray bond lengths for all silver−oxygen bonds (regardless of silver or oxygen coordination number and without specification of a silver−oxygen bond order) in the CSD,[7] subject only to constraint that the experimental *R* value is less than or equal to 10%.

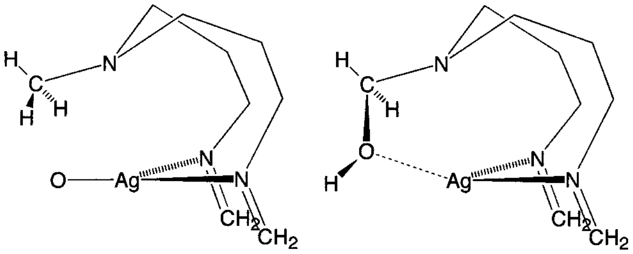
for silver−oxygen bond lengths, HECWUH was more than five standard deviations away from the average.

A second search (as before, $R \leq 10\%$) was done for silver complexes with oxygen ligands; no restriction was placed on the silver coordination number, but the ligated oxygen was fixed to a coordination number of 2 (as for a carboxylate O, alkoxide O, nitrate O, etc.). The distances were only slightly shorter than those for the entire set of AgO bond lengths: range = 2.09−3.00 Å, average = 2.44 ± 0.17 Å for 507 examples. One popular motif that should have a particularly strong, and thus presumably short, AgO bond is silver−O(carboxylate). For the 28 examples in the CSD, the range of AgO distances was 2.10−2.69 Å with an average of 2.30 ± 0.16 Å. Even for this subset of silver−oxygen bonds, the AgO bond length in HECWUH was more than four standard deviations below the average. Similar results were seen for Ag−O(nitrate) complexes: range = 2.14−2.86 Å, average = 2.51 ± 0.13 Å for 200 examples. Hence, the experimental bond length of 1.59 Å was very short compared to those of other structurally characterized examples with AgO bonds. Calculated bond lengths for $[\mathrm{AgO}\{\mathrm{N}(=\mathrm{CH_2})(\mathrm{CH_3})\}_2]^+$ were thus closer to a single-bond value than a double-bond value.

ii. Comparison with Other Transition Metal−Oxygen Multiple Bonds. In general, a roughly linear correlation between metal−oxo bond length and the covalent radius of the metal was expected. A search of the CSD ($R \leq 10\%$) was performed for monooxo complexes of the second-row metal niobium, which, like silver, has a covalent radius of 1.34 Å. After removal of statistical outliers, the average niobium−oxo bond length and standard deviation of this bond were determined. The statistical analysis of niobium monooxo complexes yielded $r(\mathrm{Nb{=}O})_{\mathrm{av}}$ = 1.72 ± 0.03 Å and range = 1.67−1.78 Å for 31 examples. Another transition metal with a covalent radius similar to that of silver is titanium ($r_{\mathrm{cov}}(\mathrm{Ti})$ = 1.32 Å). A search for titanium−oxo complexes in the same manner as was done for niobium yielded the following data: $r(\mathrm{Ti{=}O})_{\mathrm{av}}$ = 1.64 ± 0.02 Å, range = 1.61−1.68 Å for 13 examples. However, titanium is substantially more electropositive ($\chi_{\mathrm{Pauling}} = 1.54$) than silver ($\chi_{\mathrm{Pauling}} = 1.93$).

Perhaps the transition metals closest to silver in terms of covalent radius and electronegativity and with the possibility of forming sufficient metal−oxo bonds to obtain a statistical sampling are technetium ($r_{\mathrm{cov}}(\mathrm{Tc})$ = 1.27 Å; $\chi_{\mathrm{Pauling}}(\mathrm{Tc}) = 1.9$) and rhenium (($r_{\mathrm{cov}}(\mathrm{Re})$ = 1.28 Å; $\chi_{\mathrm{Pauling}}(\mathrm{Re}) = 1.9$). A CSD search for monooxo complexes of these metals yielded $r(\mathrm{M{=}O})_{\mathrm{av}}$ = 1.68 ± 0.03 Å and range = 1.61−1.77 Å for 431 examples (M = Tc, Re). As most technetium and rhenium complexes possess either d^0 or d^2 configurations, these metals can form strong metal−oxygen π bonds. This is not expected to be the case for a formally d^8 Ag(III) complex. For Tc and Re, a metal−oxo bond length of 1.59 Å would be roughly three standard deviations short of the average, which suggested that an AgO bond length of this value was quite short in relation to the covalent radius of silver.

Chart 3



4. Large Models. As mentioned above, in addition to the formulation of a silver−oxo bond, the experimental structure of Yu et al.[6] shows some interesting close contacts between the oxo oxygen and the atoms of a noncoordinated amine functionality. It occurred to us that these close contact interactions might play some role in stabilizing the proposed silver−oxo linkage.

Semiempirical calculations (ZINDO/1 using the HyperChem program[20]) were carried out using the crystal coordinates by starting from the complete +2 complex. Zerner's INDO/1 parametrization has been repeatedly shown to be reliable for describing the electronic structure of transition metal complexes.[20] Element−hydrogen bond lengths were put at standard values using an MM2 optimization with a frozen heavy atom skeleton. The full model was then selectively "pruned" by removing groups distant from the silver−oxo site. Analysis of the ZINDO/1 electronic properties (e.g., atomic charges) during the pruning process yielded the complex in Chart 3(left-hand side) as the smallest model that preserved important interactions between noncoordinated functionalities and the silver−oxo−bis(imine) center. There is little effect on the AgO core by appending further parts of the full cryptand complex. However, "pruning" the model beyond this point results in the loss of crucial interactions (most notably the Me group α to the noncoordinated nitrogen, Chart 3). Hence, this complex was used as the starting point for a LANL2DZ/B3LYP geometry optimization (singlet spin state).

Geometry optimization of the model in Chart 3 at the LANL2DZ/B3LYP level of theory results in a complex in which the oxygen is transferred from the silver. Hence, there results a two-coordinate Ag(I) complex with amine and alcohol functionalities in close contact (right-hand side of Chart 3). Such a species would be diamagnetic and represents another possible

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(20) *HyperChem (version 5.1) User's Manual*; Hypercube, Inc.: Gainesville, Florida, 1996. For recent applications of Zerner's INDO/1 parametrization to the electronic structure and spectroscopy of transition metal complexes see: (a) Estiu, G. L.; Zerner, M. C. *J. Am. Chem. Soc.* **1999**, *121*, 1893. (b) Pearl, G. M.; Zerner, M. C. *J. Am. Chem. Soc.* **1999**, *121*, 399. (c) Stavrev, K. K.; Zerner, M. C.; Meyer, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 8684. (d) Dos Santos, H. F.; De Almeida, W. B.; Zerner, M. C. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2519. Derivation and application of the ZINDO/1 parametrization to second-row transition metals is discussed in the following publications: (e) Anderson, W. P.; Cundari, T. R.; Zerner, M. C. *Int. J. Quantum Chem.* **1991**, *39*, 31. (f) Anderson, W. P.; Cundari, T. R.; Drago, R. S.; Zerner, M. C. *Inorg. Chem.* **1990**, *29*, 1.

formulation of the complex of Yu et al.[6] Another plausible formulation is a coordinated *N*-oxide, which may arise from the sodium perchlorate used in the oxidation of the Schiff base condensation products. An LANL2DZ/B3LYP geometry optimization of an *N*-oxide isomer of the complexes in Chart 3 shows it to be ≥30 kcal mol^{-1} higher in energy than the N−CH_2OH complex.

Summary

Calculations at a variety of theoretical levels were carried out on putative silver−oxo species, models of an experimentally proposed complex. Statistical analysis of metal−oxo bond lengths involving the more prevalent early and middle transition series metals was also carried out. This work casts doubt on the formulation of the complex of Yu et al.[6] as a diamagnetic, Ag(III)−oxo species. Two major points of contention were found. First, a cationic Ag(III)−oxo species was predicted to have a triplet ground state, with a very low bond energy. Second, the experimentally determined “silver−oxo” bond length of 1.59 Å was very short in comparison to values obtained from calculation and other metal−oxo species. Reinvestigation of this species would be of interest as would further experimental research to isolate bona fide examples of late transition metal−oxo complexes.

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