Crystal Structure of the First Mixed-Valence Silver(I,III) Cryptate

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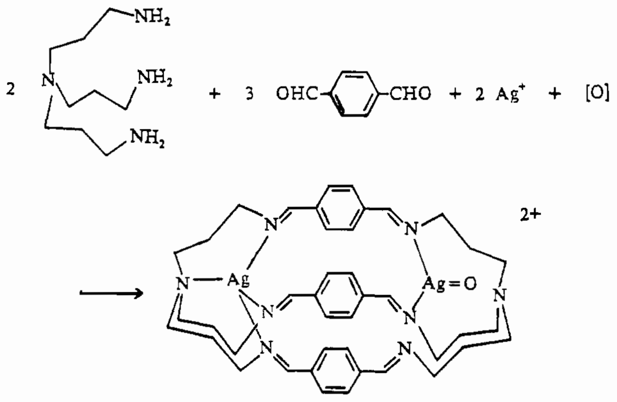
Transition metal complexes possess a capability of activating dioxygen and breaking the oxygen–oxygen bond to generate high-valence oxo–metal species.[1-3] This phenomenon is deeply involved with the catalysis and oxidation of substrate by monooxygenase.[4-6] Consequently, it has received considerable attention. Numerous high-valence oxo–metal complexes have been synthesized,[7-10] and their properties and structures have been studied. Here we report the crystal structure of a binuclear mixed-valence silver(I,III) cryptate with a Ag═O bond, which is obtained by condensation of tris(3-aminopropyl)amine and terephthalaldehyde in the presence of $AgNO_3$. To date, many siler(I) cryptates have been reported[11,12] but not a mixed-valence silver(I,III) cryptate. Moreover, the only mixed-valence silver compound previously reported is silver(I,III) oxide.[13]

The cryptate was synthesized by the following (2 + 3) Schiff-base condensation:



A solution of 0.376 g (2 mmol) of tris(3-aminopropyl)amine in 50 cm^3 of absolute methanol was added dropwise to a stirred solution of 0.402 g (3 mmol) of terephthaladehyde and 0.425 g (2.5 mmol) of $AgNO_3$ in 100 cm^3 of absolute methanol. After stirring for 1.5 h, the mixture was filtered and an excess of $NaClO_4$ was added to the filtrate. The product was precipitated as yellow microcrystals, yield 41%. Anal. Calc for $C_{42}H_{54}N_8O_9Cl_2Ag_2$: C, 45.75; H, 4.90; N, 10.17. Found: C, 45.64; H, 5.16; N, 10.03. Infrared spectra: 1640 s cm^{-1} ($\nu_{C=N}$). Electronic spectra (in DMF): λ 267 nm (ϵ = 30 300 $dm^3\ cm^{-1}\ mol^{-1}$). ^1H NMR (500 MHz, CD_3CN, TMS): δ 8.24 (6 H, s, CH═N), 7.00 (12 H, s, Ph–H), 3.72 (12 H, m, CH_2–N<), 2.55 (12 H, m, CH_2—N═), 1.87 (12 H, m, CH_2). Λ_M (CH_3CN): 307 S $cm^2\ mol^{-1}$. The cryptate is diamagnetic. Yellow crystals of the cryptate suitable for X-ray structure analysis[14] were grown from acetonitrile. It is air-stable at room temperature.

Safety Note. *Caution*! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with caution. The complex described in this report has, so far, been found to be safe when used in small quantities.

From the crystal structure diagram (Figure 1) of the complex cation $[AgAgO(C_{42}H_{54}N_8)]^{2+}$ ($C_{42}H_{54}N_8$ denotes the cryptand ligand), it can be seen that the coordination environments of the two silver atoms are apparently different. Ag(1) coordinates to one bridgehead nitrogen N(1) and three imino nitrogens N(2), N(6), and N(7). Ag(1) thus has a distorted tetrahedral environment. However, Ag(2) not only coordinates to two imino nitrogens but also bonds to one oxygen atom, in a trigonal-planar fashion. The bond length of Ag(1)–N(1) is 2.455(5) Å, being slightly longer than the corresponding distance of a silver cryptate derived from tris(2-aminoethyl)amine and terephthalaldehyde.[11] The other Ag(1)–N distances are in the range 2.29–2.30 Å, and Ag(1) deviates 0.1939 Å toward N(1) from the least-squares plane defined by N(2), N(6), and N(7). The bonds Ag(2)–N(5) and Ag(2)–N(6) are ca. 0.1 Å shorter than that around Ag(1). It is most interesting that the bond length of Ag(2)–O is 1.586(4) Å, which is consistent with the reported M═O bond lengths of transition metals (1.59–1.66 Å).[7] This shows that the silver atom has activated and cleaved an oxygen molecule, giving an Ag═O bond in the macrobicyclic compound. The distance Ag(1)···Ag(2) is about 7.409 Å, being longer than that of the silver complex of the cryptand analogue condensed by tris(2-aminoethyl)amine and terephthalaldehyde.[11] Owing to the coordination effect of metal ions, the three long flexible bridging chains twist recip-

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(14) Crystal data for $[AgAgO(C_{42}H_{54}N_8)](ClO_4)_2$: $C_{42}H_{54}N_8Cl_2O_9Ag_2$, triclinic, space group $P\bar{1}$, a = 9.536(4) Å, b = 15.632(2) Å, c = 16.928(6) Å, α = 106.16(2)°, β = 101.82(4)°, γ = 104.02(3)°, V = 2249(3) $Å^3$, Z = 2, D_c = 1.63 g cm^{-3}, $F(000)$ = 1124, μ(Mo Kα) = 10.43 cm^{-1}. Data for the yellow crystal having approximate dimensions of 0.52 mm × 0.25 mm × 0.11 mm were collected at 296 K on an Enraf-Nonius CAD-4 X-ray diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å), using the ω–2θ scan mode (scan width 0.6+0.35 tan θ, scan rate less than 5.50°/min in ω to $2\theta_{max}$ = 48°; h = 0 to 10, k = –17 to 17, l = –19 to 19). A total of 7511 unique reflections were measured, of which 5172 with $I \geq 4\sigma(I)$ were considered observed. The structure was solved by MITHRIL direct methods. An empirical absorption correction was applied, using the DIFABS procedure, which resulted in transmission factors ranging from 0.8982 to 1.1790. Hydrogen atoms were placed geometrically in calculated positions. The convergence of the last stage of full-matrix least-squares refinement reached R = 0.050, R_w = 0.067 ($w = 1/\sigma^2(F_o)$), and GOF = 1.94. The maximum and minimum peaks in the final difference electron density synthesis were +0.77 and –1.43 e/$Å^3$, respectively. All calculations were performed on a Micro-Vax 3100 computer using the TEXSAN package (Molecular Structure Corp., 1989).

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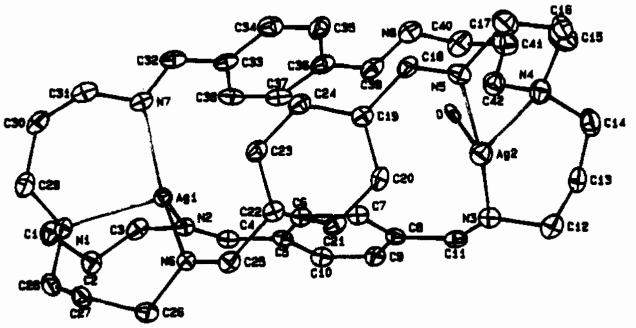

Figure 1. Structural representation of complex cation [AgAgO-($C_{42}H_{54}N_8$)]$^{2+}$ with hydrogen atoms omitted. Selected bond lengths (Å) and angles (deg): Ag(1)–N(7) = 2.286(6), Ag(1)–N(2) = 2.301(5), Ag(1)–N(6) = 2.308(5), Ag(1)–N(1) = 2.455(5), Ag(2)–O = 1.586(4), Ag(2)–N(3) = 2.181(6), Ag(2)–N(5) = 2.198(6); N(7)–Ag(1)–N(2) = 116.5(2), N(7)–Ag(1)–N(6) = 125.0(2), N(7)–Ag(1)–N(1) = 94.6(2), N(2)-Ag(1)–N(6) = 116.3(2), N(2)–Ag(1)–N(1) = 96.2(2), N(6)–Ag-(1)–N(1) = 93.8(2), O–Ag(2)–N(3) = 85.8(2), O–Ag(2)–N(5) = 82.4-(2), N(3)–Ag(2)–N(5) = 168.1(2).

rocally. In the unit cell, there are 2 complex cations and 4 ClO_4^- anions. This agrees with the molar conductivity, which indicates the cryptate is a 1:2 electrolyte. The oxidation state of Ag(2) is +3 since the cryptate is diamagnetic. From XPS spectra, the electron binding energy was obtained as 373.6 ($3d_{3/2}$) and 367.6 ($3d_{5/2}$) eV, implying no distinguishable Ag(III) chemical shift. The Au(I,III) complex[15] is a similar case. It is probably relevant to the formation of an Ag=O bond, in which the $O_{p\pi} \rightarrow Ag_{d\pi}$ interaction may reduce the electron binding energy of Ag(III). Further investigation is in progress.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, atom coordinates and thermal parameters, bond lengths, bond anlges, torsion angles, anisotropic thermal parameters, and hydrogen atom locations (15 pages). Ordering information is given on any current masthead page.

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