$[Ag(CO)_2][B(OTeF_5)_4]$: The First Structurally Characterized $M(CO)_2$ Complex[†]

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The recent isolation and structural characterization of a Ag(I) carbonyl complex, $[Ag(CO)][B(OTeF_5)_4]$,[1,2] was made possible by use of the very large, weakly coordinating $B(OTeF_5)_4^-$ anion.[3] The short C–O bond (1.077(16) Å), long Ag–C bond (2.10(1) Å), and very high value of $\nu(CO)$ (2204 cm^{-1}) suggested little or no π-backbonding, a situation that is virtually unprecedented in metal carbonyl chemistry.[4] It was also found that $[Ag(CO)][B(OTeF_5)_4]$ *reversibly* took up another equivalent of CO at pressures >200 Torr.[1]

We have now succeeded in isolating extremely hygroscopic, thermally labile crystals of $[Ag(CO)_2][B(OTeF_5)_4]$[5] and have determined that it contains two-coordinate, roughly linear $[Ag(CO)_2]^+$ complex ions.[6] This is the first structural evidence for a simple two-coordinate $M(CO)_2$ complex of any metal, although manometric and spectroscopic data have suggested the existence of solvated $[Ag(CO)_2]^+$ [2c,f,g] and $[Au(CO)_2]^+$ [4d] ions in highly acidic media, $[Au(CO)_2]^+$ ions in the solid state,[4a,b] and neutral $M(CO)_2$ species in carbon monoxide matrices.[7] The triclinic ($P\bar{1}$) unit cell of $[Ag(CO)_2][B(OTeF_5)_4]$ contains two symmetry-related pairs of $B(OTeF_5)_4^-$ anions at general positions, one symmetry-related pair of $[Ag(CO)_2]^+$ cations at general positions, and two $[Ag(CO)_2]^+$ cations at inversion centers. The structures of the two independent $B(OTeF_5)_4^-$ anions are unremarkable: bond distances and angles are similar to those found in other structures containing this anion.[1,3,8] Figure 1 shows a view of one of the $[Ag(CO)_2]^+$ ions and its four closest counterions.

The $[Ag(CO)_2]^+$ complex cation at a general position has a five-atom O1–C1–Ag1–C2–O2 array that deviates slightly from linearity. The O1–C1–Ag1, C1–Ag1–C2, and Ag1–C2–O2 bond angles are 173(3), 169(1), and 178(3)°, respectively. The cations located at inversion centers have Ag–C–O bond angles of 174(4)° (Ag2–C3–O3) and 179(2)° (Ag4–C4–O4). These compare favorably with the Ag–C–O bond angle of 176(1)° found in $[Ag(CO)][B(OTeF_5)_4]$.[1] In addition, the Ag–C and C–O bond distances in $[Ag(CO)_2][B(OTeF_5)_4]$ are similar to those found in $[Ag(CO)][B(OTeF_5)_4]$ (2.10(1) and 1.08(2) Å, respectively): Ag1–C1, Ag1–C2, Ag2–C3, and Ag3–C4 are 2.20(4), 2.16(4), 2.06(5), and 2.14(3) Å, respectively; C1–O1, C2–O2, C3–O3, and C4–O4 are 1.07(5), 1.09(5), 1.09(6), and 1.08(4) Å, respectively. While the esd's for these distances are high, the $[Ag(CO)_2]^+$ cations may very well contain shorter, stronger C–O bonds than in free CO (1.12822(7) Å[9]).

Each of the $[Ag(CO)_2]^+$ cations is very weakly bonded to two or more $B(OTeF_5)_4^-$ anions. For example, Ag1 makes contact with seven fluorine atoms from several different anions, with Ag···F distances ranging from 2.75(1) to 3.19(1) Å. The other two silver ions have fewer Ag···F contacts: Ag2 has two at 3.02(1) Å and Ag3 (Figure 1) has two at 2.96(1) Å (F9 and F9′) and two more at 3.09(2) Å (F35 and F35′). For comparison, the Ag–F distances in $AgSbF_6$[10] and AgF[11] are 2.62 and 2.467(3) Å, respectively, and the sum of the van der Waals radii for silver and fluorine is 3.15 ± 0.08 Å.[12]

Despite our success in crystallizing $[Ag(CO)_2][B(OTeF_5)_4]$, it is not suitable for detailed spectroscopic study because it decomposes at room temperature (as does $[Ag(CO)][B(OTeF_5)_4]$[1]) by the following reaction:

$$[Ag(CO)_2][B(OTeF_5)_4] \rightarrow Ag(CO)OTeF_5 + B(OTeF_5)_3 + CO$$

However, we have found that the salts $Ag_2Zn(OTeF_5)_4$[13] and $Ag_2Ti(OTeF_5)_6$[14] form more stable 1:1 and 1:2 (Ag:CO) adducts when subjected to subambient pressures of CO.[15] The values of $\nu(CO)$ for $[Ag(CO)]_2[Zn(OTeF_5)_4]$ and $[Ag(CO)]_2[Ti(OTeF_5)_6]$ from IR spectra are 2203 and 2207 cm^{-1}, respectively, while $\nu_{asym}(CO)$ for $[Ag(CO)_2]_2[Zn(OTeF_5)_4]$ and $[Ag(CO)_2]_2[Ti(OTeF_5)_6]$ are both 2198 cm^{-1}. All of these values are much higher than in free CO (2143 cm^{-1}), an indication of an *increase* in C–O bond order upon coordination to Ag(I). We propose that

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[†] Dedicated to Professor R. H. Holm on the occasion of his 60th birthday.

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(5) Conditions: The compound $[Ag(CO)_2][B(OTeF_5)_4]$ was crystallized from a solution of $AgB(OTeF_5)_4$ in 1,1,2-trichlorotrifluoroethane at −15 °C under ~350 Torr CO. Since CO is reversibly bound, the crystals were never allowed to reach temperatures above −15 °C.

(6) Crystal data for $[Ag(CO)_2][B(OTeF_5)_4]$: $C_2AgBF_{20}O_6Te_4$, $M_r = 1129.1$, triclinic, space group $P\bar{1}$, $a = 10.367(5)$ Å, $b = 13.146(7)$ Å, $c = 16.56(1)$ Å, $\alpha = 87.77(5)°$, $\beta = 76.38(4)°$, $\gamma = 89.06(4)°$, $V = 2192(2)$ Å^3, $Z = 4$, $\rho_{calc} = 3.422$ g cm^{-1}, $F(000) = 2000$, λ(Mo Kα) = 0.710 73 Å, $\mu = 63.3$ cm^{-1}, $T = -100$ °C, crystal dimensions 0.15 × 0.40 × 0.50 mm, Siemens *R*3m diffractometer, θ–2θ scan technique. Of 11812 reflections measured ($4° \leq 2\theta \leq 60°$), 7571 were used in the refinement ($F \geq 2.5\sigma(F)$). Anisotropic refinement was used for all atoms. A semiempirical absorption correction was applied. Final $R = 0.078$ and final $R_w = 0.102$. Total number of parameters = 616.

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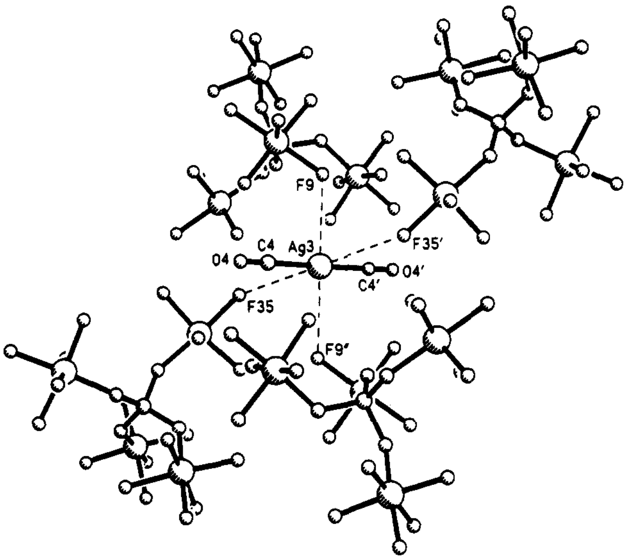

Figure 1. Structure of one of the centrosymmetric $[Ag(CO)_2]^+$ cations and the four $B(OTeF_5)_4^-$ anions that surround it in $[Ag(CO)_2]$-$[B(OTeF_5)_4]$. Each $B(OTeF_5)_4^-$ anion consists of a central B atom, four B–O–Te linkages, and 20 Te–F bonds (this is most clearly seen in the anion containing F35′). Selected distances (Å) and angles (deg): Ag3–C4, 2.14(3); C4–O4, 1.08(4); Ag3···F9, 2.96(1); Ag3···F35, 3.09(2); B–O, 1.45(2)–1.4(2); Te–O, 1.81(1)–1.84(1); Te–F, 1.80(1)–1.87(1); C4–Ag–C4′, 180; Ag3–C4–O4, 179(2); C4–Ag3–F9, 92.1(7); C4–Ag3–F35, 67.2(7); F9–Ag–F35, 109.3(4).

discrete, two-coordinate, linear $[Ag(CO)_2]^+$ cations are also present in $[Ag(CO)_2]_2[Zn(OTeF_5)_4]$ and $[Ag(CO)_2]_2[Ti(OTeF_5)_6]$. Raman spectroscopy may confirm this prediction, but so far fluorescence has prevented adequate spectra from being recorded.

Room-temperature ^{13}C NMR spectra of dichloromethane solutions of ^{13}CO and $AgB(OTeF_5)_4$ exhibited only one resonance at $\delta \sim 174$ (i.e., no silver–carbon coupling was observed; a single resonance at δ 184 was observed for ^{13}CO alone).[16] Since our silver salts bind CO reversibly, it is reasonable that $[Ag(CO)_n]^+$ complexes are labile in solution and that free and bound CO were undergoing rapid exchange in these experiments. To slow down the exchange, we recorded solid-state ^{13}C NMR spectra of five stable silver carbonyl complexes. A typical spectrum of two broad lines is shown in Figure S-1 (supplementary material), in which the splitting is assigned as $J_{Ag^{13}C}$. Since ^{107}Ag and ^{109}Ag are nearly equally abundant and the ratio of their magnetogyric ratios is 0.870,[17] we assume that the expected four line spectrum is partially unresolved and that the observed peak-to-peak separation corresponds to the average of $J_{^{107}Ag^{13}C}$ and $J_{^{109}Ag^{13}C}$. The data are (compd, δ, $J_{^{109}Ag^{13}C}$) as follows: $Ag(CO)OTeF_5$, 172.8(2), 247(6) Hz; $[Ag(CO)]_2[Zn(OTeF_5)_4]$, 171.4(2), 264(6) Hz; $[Ag(CO)]_2[Ti(OTeF_5)_6]$, 170.8(2), 245(6) Hz; $[Ag(CO)_2]_2[Zn(OTeF_5)_4]$, 172.3(2), 189(6) Hz; $[Ag(CO)_2]_2[Ti(OTeF_5)_6]$, 171.7(2), 177(6) Hz.

Despite the long, weak Ag–C bonds, the $J_{^{109}Ag^{13}C}$ values are large, indicating a significant amount of covalent Ag–C bonding involving the silver 5s orbital. For comparison, $J_{^{109}Ag^{13}C}$ for $Li[Ag(C_6H_5)_2]$[18] and $[Ag(CH_2PPh_3)_2]Cl$[19] are only 132 and 103 Hz, respectively. A more relevant comparison can be made with four-coordinate Rh(I) carbonyls: the reduced coupling constant, $K_{^{109}Ag^{13}C}$,[20] for $[Ag(CO)]_2[Ti(OTeF_5)_6]$ is 17.3×10^{21} N A^{-2} m^{-3}, while $K_{^{103}Rh^{13}C}$ for $Rh_2Cl_2(CO)_4$ is only 7.2×10^{21} N A^{-2} m^{-3} ($J_{^{103}Rh^{13}C} = 69$ Hz).[21] Note that $J_{^{109}Ag^{13}C}$ decreases on going from $[Ag(CO)]^+$ to $[Ag(CO)_2]^+$, which suggests a smaller amount of silver 5s character in each of the Ag–C bonds in the latter complex relative to the Ag–C bond in the former complex.

A theoretical study has led to the prediction that if a Cr(0)–CO bond was stretched ~0.25 Å longer than its equilibrium distance, Cr–C π-bonding would be negligible and CO would act as a σ-only ligand.[22] Significantly, the Ag(I)–CO distances in $[Ag(CO)][B(OTeF_5)_4]$ and $[Ag(CO)_2][B(OTeF_5)_4]$, ~2.1 Å, are ~0.3 Å longer than typical Rh(I)–CO distances, which are ~1.8 Å.[23] Therefore, on the basis of the structural data (relatively long Ag–C bonds) as well as spectroscopic data, we conclude that little or no π-backbonding occurs in the $[Ag(CO)_2]^+$ complex.[24] This conclusion is not in conflict with the fact that $\nu_{asym}(CO)$ for $[Au(CO)_2]^+$, 2236 cm^{-1},[4a] is higher by 38 cm^{-1} than our value of 2198 cm^{-1} for $[Ag(CO)_2]^+$. We believe that the higher value for the gold compound is the result of stronger Au–C σ-bonding, not less π-backbonding: the CO ligands in $[Au(CO)_2][Sb_2F_{11}]$ are not labile[4a] and hence are probably *more* strongly bound than the CO ligands in $[Ag(CO)_2][B(OTeF_5)_4]$.

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Supplementary Material Available: Figures S-1 and S-2, showing the solid-state ^{13}C NMR spectrum of $Ag(CO)OTeF_5$ and the asymmetric unit of $[Ag(CO)_2][B(OTeF_5)_4]$, respectively, and Tables S-I–S-V, listing crystallographic data, atomic coordinates and isotropic thermal parameters, bond distances, bond angles, and anisotropic thermal parameters for $[Ag(CO)_2][B(OTeF_5)_4]$ (19 pages). Ordering information is given on any current masthead page.

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(16) Others have observed single resonances at $\delta \sim 174$ for solutions of silver salts and carbon monoxide. See refs 2b,f,g.

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