

Carbonyl Derivatives of Mercury: Synthesis, Vibrational and ^{13}C MAS NMR Spectra

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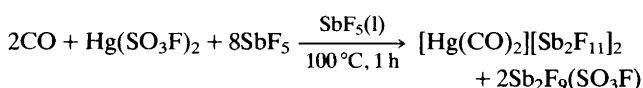
The syntheses of the previously unknown mercury carbonyl compounds $[\text{Hg}(\text{CO})_2][\text{Sb}_2\text{F}_{11}]_2$ and $[\text{Hg}_2(\text{CO})_2][\text{Sb}_2\text{F}_{11}]_2$ and their characterization by FT-Raman, FT-IR, and ^{13}C NMR spectroscopy are reported.

The ability to form thermally stable metal carbonyl species has so far been limited to d-block elements (groups 4–11) in low oxidation states, because π -back donation of metal d-electrons into the empty $2\pi_g$ orbitals of CO is generally viewed as an essential component of synergic M–CO bonding.

Very recently a number of binary carbonyl cations and cationic derivatives of group 10 and 11 metals have been generated in strong protonic acids (HSO_3F) or superacids ($\text{HSO}_3\text{F}\cdot\text{SbF}_5$), where π -back bonding appears to be insignificant. In the solid state the carbonyl cations are stabilized by very weakly basic anionic groups or anions like SO_3F^- , $\text{Sb}_2\text{F}_{11}^-$ or $[\text{B}(\text{OTeF}_5)_4]^-$. Examples are the linear cations $[\text{M}(\text{CO})_n]^+$, $\text{M} = \text{Au}$ or Ag , $n = 1$ or 2 , and square planar $[\text{M}(\text{CO})_4]^{2+}$, $\text{M} = \text{Pd}$ or Pt .^{5,6}

The compound $[\text{Au}(\text{CO})_2][\text{Sb}_2\text{F}_{11}]_2$ may serve as an example: the white solid is thermally stable up to 130°C and C–O stretching vibrations $\bar{\nu}\text{CO}_{\text{avg}}$ are at 2235.5 cm^{-1} , more than 90 wavenumbers higher than in free CO. In HSO_3F solution $\delta^{13}\text{C}$ is 174, well outside the range $\delta 190$ – 2107 of classical carbonyls. The $[\text{Au}(\text{CO})_2]^+$ cation is isoelectronic and isostructural with the well characterized cyanides $[\text{Au}(\text{CN})_2]^-$ and $\text{Hg}(\text{CN})_2$,^{8,9} and the so far unknown cation $[\text{Hg}(\text{CO})_2]^{2+}$. We have now adopted with modification the synthetic route to $[\text{Au}(\text{CO})_2][\text{Sb}_2\text{F}_{11}]_2$ to the preparation of bis(carbonyl)mercury(II) undecafluorodiantimonate(v), $[\text{Hg}(\text{CO})_2][\text{Sb}_2\text{F}_{11}]_2$, to our knowledge the first thermally stable carbonyl derivate of a post-transition metal.

Solvolysis of $\text{Hg}(\text{SO}_3\text{F})_2$ in a large excess of liquid antimony(v) fluoride at 100°C and CO pressures between 0.8 and 0.9 bar, proceeds according to:



After repeated washing of the reaction mixture with perfluoro *n*-butyl sulfonyl fluoride, $\text{C}_4\text{F}_9\text{SO}_2\text{F}$, a white solid of the composition $[\text{Hg}(\text{CO})_2][\text{Sb}_2\text{F}_{11}]_2$ is isolated. The compound is identified by microanalysis, the mass balance of the reaction and by CO-uptake measurements. The yield of isolated product is 95%. On heating, $[\text{Hg}(\text{CO})_2][\text{Sb}_2\text{F}_{11}]_2$ melts at 160°C with some loss of CO (about 10%). In HSO_3F or liquid SO_2 , CO evolution occurs and only in $\text{HSO}_3\text{F}\cdot\text{SbF}_5$ are solutions of $[\text{Hg}(\text{CO})_2]^{2+}$ stable.

The corresponding mercury(I) carbonyl compound $[\text{Hg}_2(\text{CO})_2][\text{Sb}_2\text{F}_{11}]_2$ is obtained by a similar procedure. The starting material is produced by the treatment of Hg_2F_2 with HSO_3F at 80°C . After all volatiles are removed *in vacuo*, the solvolysis in SbF_5 is carried out at 60°C and a CO pressure of 0.7 bar. After a reaction time of 1 h, workup and product characterization as described above, $[\text{Hg}_2(\text{CO})_2][\text{Sb}_2\text{F}_{11}]_2$ is obtained as a pale yellow solid in nearly quantitative yield.

The compound shows lower thermal stability than the $[\text{Hg}(\text{CO})_2]^{2+}$ salt. At 50°C all CO is removed *in vacuo* within 30 min to yield a solid of the composition $\text{Hg}_2[\text{Sb}_2\text{F}_{11}]_2$. In a sealed capillary melting, with decomposition, occurs at 140°C . Both mercurous compounds show a single intense Raman line attributed to Hg–Hg stretching at 169 cm^{-1} for the $[\text{Hg}_2(\text{CO})_2]^{2+}$ cation and at 190 cm^{-1} for Hg_2^{2+} . Previously $\bar{\nu}\text{Hg–Hg}$ has been found to be substituent dependent.⁹ The isoelectronic cyanide $\text{Hg}_2(\text{CN})_2^+$ appears to be unknown,⁸ or of transient existence.¹⁰

The use of ^{13}C in synthesis allows the formation of the isotopomeric cations $[\text{Hg}(^{13}\text{CO})_2]^{2+}$ and $[\text{Hg}_2(^{13}\text{CO})_2]^{2+}$ for use in vibrational spectroscopy and ^{13}C -MAS NMR. ^{13}C NMR data: $[\text{Hg}_2(^{13}\text{CO})_2][\text{Sb}_2\text{F}_{11}]_2$, $\delta 168.8 \pm 0.1$; $^1J(^{13}\text{C–}^{199}\text{Hg}) 5206 \pm 5\text{ Hz}$. In magic acid ($\text{HSO}_3\text{F}\cdot\text{SbF}_5$) solution only a single line resonance at $\delta 171.4 \pm 0.1$ is observed. $[\text{Hg}(^{13}\text{CO})_2][\text{Sb}_2\text{F}_{11}]_2$, $\delta 188.7 \pm 0.2$; $^1J(^{13}\text{C–}^{199}\text{Hg}) 3350 \pm 20\text{ Hz}$; $^2J(^{13}\text{C–}^{199}\text{Hg}) 850 \pm 50\text{ Hz}$.

The chemical shifts observed for both compounds are similar to those previously reported for other nonclassical noble-metal carbonyls,^{2,4,5,11} however $^1J(^{13}\text{C–}^{199}\text{Hg})$ for $[\text{Hg}(^{13}\text{CO})_2]^{2+}$ is considerably higher than data reported for various organomercury compounds.¹²

The FT-IR and FT-Raman spectra are, for both mercury carbonyl compounds in the region below 750 cm^{-1} , dominated by intense anion bands, very similar to those reported for $[\text{Au}(\text{CO})_2][\text{Sb}_2\text{F}_{11}]_2$ and $[\text{Pt}(\text{CO})_4][\text{Sb}_2\text{F}_{11}]_2$.⁶ The data in the CO stretching range are tabulated (Table 1) and compared to corresponding data for $[\text{Au}(\text{CO})_2]^{2+}$, $[\text{Au}(\text{CN})_2]^-$,¹³ and $\text{Hg}(\text{CN})_2$.

The CO stretching vibrations observed for $[\text{Hg}(\text{CO})_2]^{2+}$ occur at the highest wavenumbers so far reported for any metal carbonyl species. The calculated C–O stretching force constant, f_r , of $21.0 \times 10^2\text{ Nm}^{-1}$ is slightly lower than a value of 21.3 obtained for HCO^+ ,² where π -back donation is not possible. The increase of metal ion and hence complex ion charge for the isoelectronic pair $[\text{Au}(\text{CO})_2]^+$ and $[\text{Hg}(\text{CO})_2]^{2+}$ increases $\bar{\nu}\text{CO}_{\text{avg}}$ by 44 cm^{-1} and f_r by $0.9 \times 10^2\text{ Nm}^{-1}$. The corresponding values for $[\text{Hg}_2(\text{CO})_2]^{2+}$ of 2247.5 cm^{-1} and $20.4 \times 10^2\text{ Nm}^{-1}$ fall in between. The separation between $\bar{\nu}_{\text{sym}}\text{CX}$ and $\bar{\nu}_{\text{asym}}\text{CX}$, $\text{X} = \text{O}$ or N , is for all mercury species very small, which reflects weak bonding and ineffective vibrational coupling in the C–Hg–C framework. With the molecular structures for $[\text{Au}(\text{CN})_2]^-$,¹⁴ $\text{Hg}(\text{CN})_2$ ¹⁵ and very recently¹⁶ $[\text{Hg}(\text{CO})_2]^{2+}$ known, there is little doubt that all species discussed here are linear, consistent with the observation of $\bar{\nu}\text{Hg–Hg}$ for $[\text{Hg}_2(\text{CO})_2][\text{Sb}_2\text{F}_{11}]_2$ in the Raman spectrum only.

When the ease of synthesis and the relatively high thermal stability of the new mercury carbonyl cations are considered, it may be surprising that no post-transition metal carbonyls have been reported previously. It appears to us that adherence to the classical synergic bonding model, the noble-gas formalism (rule of 18) and the reluctance to use highly acidic reagents

Table 1 Vibrational spectra in the CO and CN stretching range for mercury and gold carbonyl and cyanide species

M(CX) ₂ species ^a	$\Delta\bar{\nu}\text{CX}_{\text{sym}}^{b,c}$ cm^{-1}	$\bar{\nu}\text{CX}_{\text{asym}}^c$ cm^{-1}	f_r^d 10^2 Nm^{-1}	Ref.
$[\text{Hg}(\text{CO})_2]^{2+}$	2281 (2228)	2278 (2225)	21.0	e
$[\text{Au}(\text{CO})_2]^+$	2254 (2194.5)	2217 (2160)	20.1	2
$\text{Hg}(\text{CN})_2$	2197.4 (2148.3)	2197.2 (2149)	18.07	13
$[\text{Au}(\text{CN})_2]^-$	2164 (2115.6)	2146 (2099)	17.64	13
$[\text{Hg}_2(\text{CO})_2]^{2+}$	2248 (2197)	2247 (2196)	20.4	e

^a M = Hg, Au, X = O, N. ^b Raman shifts. ^c Wavenumbers in parentheses refer to data for the ^{13}C isotopomers. ^d f_r , CX stretching force constants, obtained in this study by the two mass model. The remaining f_r values are calculated according to Jones.¹³ ^e This work.

like liquid SbF_5 or $\text{HSO}_3\text{F}\cdot\text{SbF}_5$ in metal carbonyl synthesis, have provided conceptual and practical barriers which should now be overcome.

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