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The Tetrakis(carbonyl)dioxoosmium(VI) Cation: *trans*-$[OsO_2(CO)_4]^{2+}$**

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Superacidic reaction media,[1, 2] in particular the Lewis superacid SbF_5 and the conjugate Brønsted Lewis superacid HF/SbF_5, have allowed in recent years the generation of a substantial number of previously unknown homoleptic metal carbonyl cations,[3] for example the octahedral cations $[M(CO)_6]^{2+}$ (M = Fe,[4] Ru, Os[5]). Thermally stable salts are generally obtained with the superacid anion $[Sb_2F_{11}]^-$.[6] Observations made during the synthesis of $[Os(CO)_6][Sb_2F_{11}]_2$ by reductive carbonylation of either $Os(SO_3F)_3$,[5] OsF_6,[7] or OsO_4[8] provide the motivation for this study: In the IR spectra of the products an additional band of varied intensity is observed at 2253 cm^{-1} in addition to the intense CO stretching band (F_{1u}) of $[Os(CO)_6]^{2+}$ at 2190 cm^{-1}. Since the highest intensities of the band at 2253 cm^{-1} are found in samples prepared from OsO_4,[8] we have modified the reaction conditions and intend to show that the high wavenumber band can be attributed to the new cation *trans*-$[OsO_2(CO)_4]^{2+}$.

When the reaction temperature is reduced from 60–90 °C[5] to room temperature and available CO is limited to a modest excess (about 1.4-fold), a yellow product is formed after 10 days. This product is free of $[Os(CO)_6][Sb_2F_{11}]_2$ according to the vibrational spectrum. The only volatile product, CO_2, is formed in a molar ratio of approximately 1:1 (based on OsO_4), as estimated from the intensity of $\nu_{as}(CO_2)$ in the gas-phase IR spectrum.

The new compound, tentatively identified as $[OsO_2(CO)_4]$-$[Sb_2F_{11}]_2$, is extremely sensitive to moisture and turns black in air within seconds. Upon heating in a sealed tube above 80 °C, decomposition to an inhomogeneous violet material and the release of CO are noted. All attempts to obtain single crystals of $[OsO_2(CO)_4][Sb_2F_{11}]_2$ and affect a separation from any

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solid by-products through recrystallization from anhydrous HF or HF/SbF_5 were unsuccessful. In HF decomposition to $[Os(CO)_6][Sb_2F_{11}]_2$[5] with formation of a dark blue solution (possibly OsF_5[9]) occurs within seconds even at −50 °C. In HF/SbF_5 (1:1 to 1:5) the solubility is lower. Solutions are stable at room temperature for several hours, and crystalline $[Os(CO)_6][Sb_2F_{11}]_2$ is eventually obtained from these solutions.

Based on the evidence discussed above, the formation reaction suggested is that shown in Equation (1):

$$OsO_4 + 5\,CO + 5\,SbF_5 \xrightarrow[\lambda\text{-}SbF_5,\ 10\,d]{25\,^{\circ}C,\ 1.5\,atm\ CO} [OsO_2(CO)_4][Sb_2F_{11}]_2 + SbOF_3 + CO_2 \qquad (1)$$

There are three problems with this formulation:

1) A satisfactory elemental analysis is not obtained for this very reactive material, and the mass balance and redox balance (CO_2 determination) are very approximate with errors of 10–20 %.

2) Although the vibrational spectrum of $SbOF_3$ is known,[10] due to extensive overlap with bands of the $[Sb_2F_{11}]^-$ anion, only a single IR band at 407 cm^{-1} can be attributed to this species. (The observed bands below 800 cm^{-1} are listed in the Experimental Section.)

3) At room temperature and with reaction times of 10 days, the reaction is incomplete, and some unchanged OsO_4 is pumped off from the product mixture, which may account for the poor mass balance. Any increase in the reaction temperature results in the formation of substantial amounts of $[Os(CO)_6][Sb_2F_{11}]_2$.

While there is some uncertainty regarding the formation of $[OsO_2(CO)_4][Sb_2F_{11}]_2$, the identity of the cation and its octahedral geometry with *trans* oxygen atoms are clearly established by vibrational spectroscopy. The frequencies of the IR and Raman bands for *trans*-$[OsO_2(CO)_4]^{2+}$ are listed in Table 1 together with estimated intensities and assignments in point group D_{4h}. They are compared to calculated data for gaseous *trans*-$[OsO_2(CO)_4]^{2+}$, obtained from gradient-corrected density functional calculations at the BP86/ECP2 level in analogy to an earlier study.[11] The corresponding vibrational data for *trans*-$[OsO_2(CN)_4]^{2-}$ [12] are listed as well. Salts of the *trans*-tetracyanodioxoosmate(VI) anion have been known since 1928[13] as members of the large family of osmyl complexes.[14, 15] As can be seen in Table 1, there is very good agreement between observed and calculated data for both *trans*-$[OsO_2(CO)_4]^{2+}$ and isoelectronic *trans*-$[OsO_2(CN)_4]^{2-}$.[12]

The vibrational spectrum of $[OsO_2(CO)_4]^{2+}$ has a number of unusual features:

1) As with other metal carbonyl cations,[3] the wavenumbers of CO stretching vibrations are unusually high. The stretching force constant f_{CO}, obtained according to the Cotton–Kraihanzel approximation,[16] is with $20.7 \times 10^2\ Nm^{-1}$ comparable to a reported f_{CO} value of $20.64 \times 10^2\ Nm^{-1}$ for square-planar $[Pt(CO)_4]^{2+}$;[17] $[Sb_2F_{11}]^-$ is the anion in both complex salts. The implication is that the cations Pt^{2+} and *trans*-OsO_2^{2+} exhibit comparable Lewis acidities towards CO. Slightly higher f_{CO} values are reported only for $[Ir(CO)_6]^{3+}$ ($20.8 \times 10^2\ Nm^{-1}$)[18] and $[Hg(CO)_2]^{2+}$($21.0 \times 10^2\ Nm^{-1}$).[19] Evidently in all four complex cations CO is predominantly σ-bonded and the CO ligand is strongly polarized.[3]

2) The three CO stretching vibrations of *trans*-$[OsO_2(CO)_4]^{2+}$ follow the selection rules for the point group D_{4h}, but the band separations of 11 and 27 cm^{-1} for $\nu_1(A_{1g}) - \nu_2(B_{1g})$ and $\nu_1(A_{1g}) - \nu_{16}(E_u)$, respectively, are smaller than the corresponding $\Delta\nu$ values of 27 and 45 cm^{-1} for $[Pt(CO)_4]^{2+}$.[17] Even smaller band separations of 6 and 19 cm^{-1} are reported for the corresponding CN stretching

Table 1. Experimental and calculated vibrational data for *trans*-$[OsO_2(CO)_4]^{2+}$ and *trans*-$[OsO_2(CN)_4]^{2-}$.[a]

Assignment	$[OsO_2(CO)_4]^{2+}$			$[OsO_2(CN)_4]^{2-}$		
(X = O, N)	experimental		calculated[b]	experimental[c]		calculated[b]
	$\tilde{\nu}_{IR}$ [cm^{-1}]	$\tilde{\nu}_{Raman}$ [cm^{-1}]		$\tilde{\nu}_{IR}$ [cm^{-1}]	$\tilde{\nu}_{Raman}$ [cm^{-1}]	
ν_1, A_{1g}, ν(CX)		2280 {20}	2259 {100}[d]		2166 {vs}	2155 {100}[e]
ν_8, B_{1g}, ν(CX)		2269 {16}	2242 {87}		2160 {s}	2144 {63}
ν_{16}, E_u, ν(CX)	2253 (100)		2228 (100)[f]	2147 (s)		2136 (19)
ν^{13}(CX)[h]	2210 (2.7)			–		
ν_2, A_{1g}, ν(OsO)		855 {38}	872 {18}		880 {vs}	869 {11}
ν_5, A_{2u}, ν(OsO)	851 (79)		857 (28)	832 (vs)		824 (100)[g]
ν_{17}, E_u, δ(OsCX)	485[i] (100)		488 (24)	461 (w)		460 (6)
ν_6, A_{2u}, δ(OsCX)	462 (45)		465 (11)	442 (vw)		433 (0.9)
ν_{12}, B_{2u}, δ(OsCX)	–		437 (0)	–		410 (0)
ν_{10}, B_{2g}, δ(OsCX)		411[j]	412 {0.0}		424 {m}	399 {0.8}
ν_{14}, E_g, δ(OsCX)		411 {5}	409 {0.2}		407 {w}	406 {0.02}
ν_3, A_{1g}, ν(OsC)		378 {5}	363 {5}		377 {w}	384 {3}
ν_9, B_{1g}, ν(OsC)		353 {1}	348 {0.7}		364 {w}	377 {1}
ν_4, A_{2g}, δ(OsCX)		–	304 {0}		–	304 {0}
ν_{18}, E_u, ν(OsC)	–[k]		275 (2)	357 (s)		319 (70)
ν_{19}, E_u, δ(OOsO)	–[k]		227 (7)	261/246 (s)		228 (22)
ν_{15}, E_g, δ(COsO)		183 {100}	149 {6}		189/183 {vs}	177 {5}
ν_{20}, E_u, δ(COsC)	–		88 (0.5)	115 (sh)		93 (5)
ν_7, A_{2u}, δ(COsC)	–		87 (0.1)	130 (s)		105 (12)
ν_{11}, B_{2g}, δ(COsC)		128 {43}	86 {3}		127 {s}	93 {3}
ν_{13}, B_{2u}, δ(COsC)	–		68 (0)	–		82 (0)

[a] The relative intensity of a vibration is given after the wavenumber (parentheses for IR-active vibrations and curly brackets for Raman-active vibrations). [b] DFT calculations at the BP86/ECP2 level. [c] $[Me_4N]^+$ salt.[12]). [d] Absolute Raman intensity = 188.1. [e] 457.6 $Å^4\,amu^{-1}$. [f] Absolute IR intensity = 249.1. [g] 242.7 $km\,mol^{-1}$. [h] $[OsO_2(CO)_3(^{13}CO)]^{2+}$. [i] Hidden by a anion band at 493 cm^{-1}. [j] Together with ν_{14}. [k] Hidden by δSbF vibrations (230–346 cm^{-1}).

vibrations in *trans*-$[OsO_2(CN)_4]^{2-}$[12] and for linear $[Hg(CO)_2]^{2+}$, where $\nu_s(CO)$ and $\nu_{as}(CO)$ are separated by only 3 cm^{-1}.[19]

3) A very similar small band separation of 4 cm^{-1} is observed for the two characteristic OsO_2 stretching vibrations in *trans*-$[OsO_2(CO)_4]^{2+}$. This unusually small separation is consistently reproducible in various preparations. In *trans*-$[OsO_2(CN)_4]^{2-}$ a separation of 48 cm^{-1} is observed (see Table 1), which is more typical for neutral or anionic osmyl complexes.[14, 15] The very close proximity of Raman- and IR-active OsO_2 vibrations in the cation could suggest the presence of a single OsO group. However, the OsO stretching vibrations in complexes of this type are commonly found around 1000 cm^{-1}.[14] In addition the observed strict planarity of the $Os(CO)_4$ moiety, in compliance with the mutual exclusion rule, would be difficult to explain for an $[OsO(CO)_4]$ complex.

To understand these unusual observations better, we have calculated the vibrational spectra of two isoelectronic species, molecular $[WO_2(CO)_4]$, which has been observed previously in an Ar matrix,[20] and the still unknown $[ReO_2(CO)_4]^+$. The calculated and available experimental wavenumbers for the CO and MO stretching vibrations for the three isosteric species are listed in Table 2 together with the band separations $\Delta\nu$. With increasing nuclear charge and oxidation state of the central metal the separation between the two MO stretching vibrations (A_{1g} and A_{2u}) gradually decreases. In a similar manner, the band separation between the two $\nu(CO)$ vibrations (A_{1g} and E_u) decreases; however, the trend is less pronounced. It appears that the reduced electron density on osmium in $[OsO_2(CO)_4]^{2+}$ compared to the other two isoelectronic species or other osmyl complexes[14, 15] is responsible for smaller interaction force constants, resulting in narrow band spacings in the MO and CO stretching region. A similar argument can be used to explain the very small separation of 3 cm^{-1} for the CO vibrations of linear $[Hg(CO)_2]^{2+}$. Differences between calculated and experimental wavenumbers (Tables 1 and 2) are usually small and result from systematic errors in the DFT calculations,[11] anharmonicity effects, or interionic interactions in the solid state.

Table 2. Calculated and experimental wavenumbers (in cm^{-1}) of the CO and MO stretching vibrations in the isosteric complexes $WO_2(CO)_4$, $[ReO_2(CO)_4]^+$, and $[OsO_2(CO)_4]^{2+}$.

Assignment	$[WO_2(CO)_4]$ calcd[a]	exp.[b]	$[ReO_2(CO)_4]^+$ calcd[a]	$[OsO_2(CO)_4]^{2+}$ calcd[a]	exp.[c]
$\nu(CO)$ (A_{1g})	2133	2160	2209	2259	2280
$\nu(CO)$ (B_{1g})	2073		2174	2242	2269
$\nu(CO)$ (E_u)	2059	2096	2158	2228	2253
$\Delta\nu(CO)$[d]	60/74	–/64	35/51	17/31	11/27
$\nu(MO_2)$ (A_{1g})	818	850	866	872	855
$\nu(MO_2)$ (A_{2u})	719	751	807	857	851
$\Delta\nu(MO_2)$	99	99	59	15	4

[a] DFT calculations at the BP86/ECP2 level. [b] Ref. [20]. [c] This work. [d] $\nu(CO)(A_{1g}) - \nu(CO)(B_{1g})/\nu(CO)(A_{1g}) - \nu(CO)(E_u)$.

To provide further evidence for the existence of $[OsO_2(CO)_4]^{2+}$ and for its proposed structure, we carried out additional syntheses with ^{13}C-enriched CO and ^{18}O-enriched OsO_4. We subsequently recorded, in addition to the vibrational spectra, ^{13}C magic angle spinning (MAS) NMR and UV/Vis spectra. In the ^{13}C NMR spectrum of $[OsO_2(CO)_4][Sb_2F_{11}]_2$ the isotropic chemical shift is $\delta_c = 134$ with a linewidth of about 5 ppm. The relatively narrow resonance line observed is a strong indication for the high symmetry of the cation (D_{4h}) and its diamagnetism. All osmyl complexes with a d^2 electron configuration are diamagnetic,[14, 15] which is explained by a tetragonal distortion of the octahedral coordination due to the linear O-Os-O moiety.[21]

The ^{13}C chemical shift of $\delta = 134$ for *trans*-$[OsO_2(CO)_4]^{2+}$ is very similar to the value of $\delta = 137$ reported for $[Pt(CO)_4]^{2+}$.[17] This observation, together with the nearly identical CO stretching force constants f_{CO} discussed above and the strong similarity of the vibrational spectra of both *trans*-$[OsO_2(CO)_4]^{2+}$ and $[Pt(CO)_4]^{2+}$,[17] suggests a strictly square-planar arrangement of the four CO ligands in both cations. This has recently been confirmed for $[Pt(CO)_4]^{2+}$ by the determination of the molecular structure of its $[Sb_2F_{11}]^-$ salt.[22] The ^{13}C chemical shift of *trans*-$[OsO_2(CO)_4]^{2+}$ falls between those of $[Os(CO)_6]^{2+}$ ($\delta = 147$)[19] and $[Ir(CO)_6]^{3+}$ ($\delta = 121$)[18]; the chemical shift for the iridium complex is the smallest value so far observed for metal carbonyl cations and their derivatives.[3] For the isoelectronic species *trans*-$[OsO_2(CN)_4]^{2-}$[23] and $[Os(CN)_6]^{4-}$[24] δ_C values of 120 and 142.5 are reported, which correlate well with the ^{13}C chemical shifts for *trans*-$[OsO_2(CO)_4]^{2+}$ and $[Os(CO)_6]^{2+}$.

Since *trans*-$[OsO_2(CO)_4][Sb_2F_{11}]_2$ is unstable in HF and to a lesser extent also in HF–SbF_5, we have not been able to measure UV/Vis spectra in solution. Instead a diffuse reflectance spectrum is obtained on yellow *trans*-$[OsO_2(CO)_4][Sb_2F_{11}]_2$ (Figure 1). However, without reliable extinction coefficients, nothing definitive regarding the nature of the observed electronic transitions can be said, and only qualitative, descriptive comments are appropriate. The spectrum observed is similar to that reported for $[NMe_4]_2[OsO_2(CN)_4]$.[25] Two of the bands have a vibrational fine structure with vibrational wavenumbers of about 730 cm^{-1}, similar to the $[OsO_2(CN)_4]^{2-}$ anion.[25] The origins of the two bands (0–0 transition) at 23100 and 26900 cm^{-1} are red-shifted by about 3000 cm^{-1} relative to the bands of $[OsO_2(CN)_4]^{2-}$.

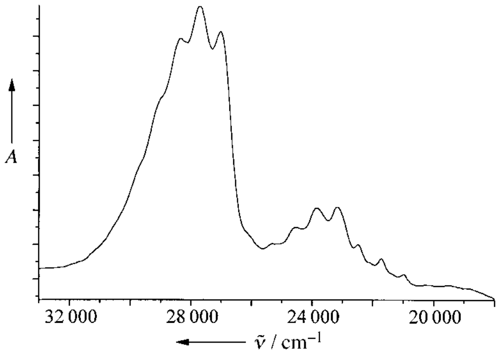

Figure 1. UV Vis spectrum (diffuse reflexion) of $[OsO_2(CO)_4][Sb_2F_{11}]_2$.

In spite of some limitations to the interpretation of the UV/Vis spectra, together with vibrational spectra, DFT calculations, and ^{13}C NMR-MAS spectra they permit the unambiguous identification of the new *trans*-$[OsO_2(CO)_4]^{2+}$ cation. The spectroscopic properties correlate very well not only with those of isoelectronic *trans*-$[OsO_2(CN)_4]^{2-}$,[12, 25] but also with those of the homoleptic carbonyl cations $[Os(CO)_6]^{2+}$[5] and, particularly, square-planar $[Pt(CO)_4]^{2+}$.[17, 22]

The new superelectrophilic[26] cation *trans*-$[OsO_2(CO)_4]^{2+}$ is unusual for two reasons:

1) It is the first oxo derivative of a homoleptic metal carbonyl cation. *trans*-$[OsO_2(CO)_4]^{2+}$ joins a small but growing group of cations such as $[M(CO)_5Cl]^{2+}$ (M = Rh, Ir),[27] $[W(CO)_6(FSbF_5)]^+$,[28] and polymeric $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]^+$.[29] All are generated in superacids, have been structurally characterized, and have $[Sb_2F_{11}]^-$ as counterion. With a number of superacidic media[1, 2] and very versatile synthetic routes available,[3] it should be possible to add more cationic derivatives with the atoms N, O, or F as ligands to this list.

2) *trans*-$[OsO_2(CO)_4]^{2+}$ is the first cationic metal carbonyl complex with the metal in the formal oxidation state +6. Previously the highest oxidation state of the central metal was +4. Examples include the matrix molecule $[WO_2(CO)_4]$[20] and the pentahalo-monocarbonyl-metalate(IV) anions $[PtCl_5(CO)]^-$,[30], $[OsCl_5(CO)]^-$,[31] and $[OsF_5(CO)]^-$.[32]

Experimental Section

A 50-mL glass flask fitted with a PTFE valve and a magnetic stirring bar was dried by heating in vacuo and charged with OsO_4 (0.116 g, 0.46 mmol). SbF_5 (6.34 g, 20 mmol) was added by condensation in vacuo, and the CO pressure was adjusted to 1.5 bar (3.3 mmol). The initially clear solution was vigorously stirred at room temperature. After several days the solution became turbid, and after 10 days a yellow suspension formed. At room temperature all volatile components were removed in vacuo, and a finely powdered, yellowish solid (0.612 g) was obtained. Vibrational bands observed below 800 cm^{-1}: IR: $\tilde{\nu}$ = 760 (m), 704 (vs), 655 (vs), 601 (m), 490 (sh), 407 (m), 346 (m), 311 (s), 276 (s), 240 (vs); Raman: 675 (vs), 645 (m), 605 (m), 296 (s), 232 (m) cm^{-1}.

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A Facile Route to Group 13 Difluorodiorganometalates: $[nBu_4N][R_2MF_2]$ (M = Al, Ga, In)**

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Dedicated to Professor Armin de Meijere
on the occasion of his 60th birthday

Group 13 difluorodiorganometalates have been known since 1955;[1] however, only a few of these were spectroscopically and structurally characterized.[2] Furthermore, the synthesis of these anions was not straightforward. We describe herein the synthesis, X-ray crystal structure,[3] and NMR and IR spectroscopic characterization of some difluorodiorganometalates $[nBu_4N][R_2MF_2]$ (M = Al, Ga, In). The synthesis of these compounds is accomplished through protonolysis of trialkyl derivatives of Group 13 metals with tetra-*n*-butylammonium hydrogen difluoride (TBADF) at room temperature,[4] which induces elimination of methane and addition of two fluoride ions. The compounds **1**–**4** are obtained as colorless, rhombic crystals (Scheme 1).

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