Synthesis and Structure of $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$: An Ionic Coordination Polymer

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The oxidation of molybdenum hexacarbonyl, $Mo(CO)_6$, by antimony(V) fluoride, SbF_5, at 60 °C in an excess of liquid SbF_5, produces polymeric $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$ as the main product. Recrystallization from HF−SbF_5 produces orange prismatic crystals, suitable for a single-crystal X-ray diffraction study. Crystals of $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$ are monoclinic, space group $P2_1/c$ (No. 14), $a = 9.234(4)$ Å, $b = 13.858(3)$ Å, $c = 25.790(3)$ Å, $\beta = 90.532(2)°$, $V = 3300.1(12)$ Å^3, and $Z = 4$. The structure was solved by the Patterson method and refined with anisotropic thermal parameters to $R = 0.048$ and $R_w = 0.047$ (on F, 472 variables, 5116 observations with $I \geq 3\sigma(I)$). In the polymeric cation, two pyramidal $Mo(CO)_4$ groups are linked by bridging, iso-bidentate F_2SbF_4 groups first into eight-membered rings, which are then further linked into polymeric chains. The bridging F_2SbF_4 groups and the $[Sb_2F_{11}]^-$ anion are involved in significant intermolecular and interionic F···C contacts to the C atoms of the $Mo(CO)_4$ groups.

Introduction

Since the first report of the generation of $[Au(CO)_2]^+$ in the Brønsted superacid HSO_3F in 1990,[1] the field of thermally stable, homoleptic carbonyl cations of electron-rich metals and their derivatives has grown rapidly and includes examples from groups 8−12. Both a highlight[2] and a review article[3] on the subject have appeared recently. The Lewis superacid[4,5] SbF_5 has emerged as the ideal reaction medium for the solvolytic, oxidative, or reductive carbonylations of metal salts.[3] The superacid anion $[Sb_2F_{11}]^{-}$ [6] is found invariably as an ideal counterion to produce salts of surprisingly high thermal stability.[3] In addition a number of related metal carbonyl derivatives, where one or more CO ligands are replaced by anions have been obtained. Three of these, *cis*-$Pd(CO)_2(SO_3F)_2$, *mer*-$Ir(CO)_3(SO_3F)_3$, and the cation $[Ir(CO)_5Cl]^{2+}$ with $[Sb_2F_{11}]^-$ as anion are structurally characterized.[3] We describe here our first successful attempt to extend the existence range of the predominantly σ-bonded homoleptic metal carbonyl cations[2,3] and their derivatives to molybdenum, a group 6 metal.

Experimental Section

(a) Synthetic Procedure. Freshly sublimed $Mo(CO)_6$ (1 mmol, 264 mg) (Pressure Chemicals) and about 15 mL of freshly distilled SbF_5 (Atochem North America) were allowed to react for 24 h at 60 °C in a glass reactor of 50-mL internal volume. The reaction mixture turned yellow immediately. The progress of the reaction may be monitored by the CO evolution. Removal of all volatiles in vacuo produces a mixture of $SbF_3{\cdot}SbF_5$ and the $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$. The latter is dissolved at 50 °C in anhydrous HF (Air Products) with about 20 vol % SbF_5 added and contained in a KEL-F reactor. Lowering the temperature at a rate of 10 °C per hour produces yellow-orange crystals on the reactor wall. All volatiles are then removed in vacuo. Carbon analysis: expected 6.09%, found 3.88%.

(b) X-ray Crystallography. A Rigaku/ADSC CCD diffractometer and Mo Kα, graphite-monochromated radiation are used: Mo Kα ($\lambda = 0.710\ 69$ Å), ω scans at −93 °C, 21 454 reflections with $2\theta = 4.0{-}60.2°$, unique 8081. The data were processed and corrected for Lorentz polarization and absorption (empirical, based on a three-dimensional analyses of symmetry-equivalent data using fourth order spherical harmonics, relative transmission factors: 0.7809−1.0000). The structure was solved by the Patterson method. The heavy atom positions were determined from the Patterson function, and the remaining atoms were positioned from subsequent difference Fourier syntheses. Sb(3) and Sb(4) lie on crystallographic centers of symmetry. All atoms were refined with anisotropic thermal parameters to $R = 0.048$ and $R_w = 0.047$ (on F, 472 variables, 5116 observations with $I \geq 3\sigma(I)$). No secondary correction was necessary. Neutral atom scattering factors and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography*.[21] All calculations were performed using TeXsan (Molecular Structure Corporation, The Woodlands, TX, 1996). Ad-

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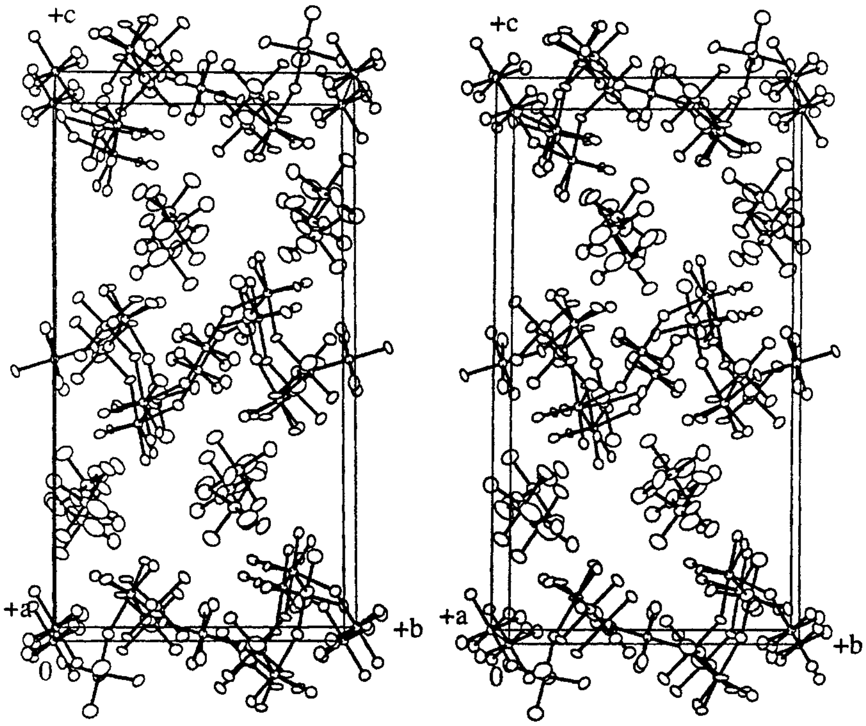

Figure 1. Stereoview of the unit cell of $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$.

Table 1. Crystallographic Data

emp form	$C_8F_{29}Mo_2O_8Sb_5$	
form wt	1575, 67	
lattice param	$a = 9.234(4)$ Å	space group $P2_{1/c}$ (No. 14)
	$b = 13.858(3)$ Å	T −93 °C
	$c = 25.790(3)$ Å	δ calcd, 3.171 g cm^{-3}
	$\beta = 90.532(2)°$	$\lambda = 0.710\ 69$ Å
	$V = 3300.1(12)$ Å^3	$\mu = 49.5$ cm^{-1}
	$Z = 4$	$2\theta = 4.0-60.2°$
	R, R_w (on F, $I \geq 3\sigma(I))^{a,b}$	0.048, 0.047

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2}$.

ditional crystallographic data are collected in Table 1. Selected structural parameter (bond lengths and bond angles) together with vibrational data are summarized in Table 2. A stereoview of the unit cell is shown in Figure 1. A repeat unit of the polymeric $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]^+$ cation is depicted in Figure 2.

Results and Discussion

We report here the synthesis and the molecular structure of a new type of predominantly σ-bonded metal carbonyl derivative, polymeric $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$ (see Figure 1), which has no precedent among known CO-containing organometallic cations[7,8] or coordination compounds of molybdenum[9−12] on three accounts: (i) all known homoleptic metal carbonyl cations and their derivatives[3] are mononuclear or occasionally like $[Pd_2(\mu\text{-}CO)_2]^{2+}$ binuclear.[3] Likewise, previously reported molybdenum(II) carbonyl derivatives are either monomers or ligand-bridged di-, tri-, or tetramers.[9−12] (ii) The existence range of predominantly σ-bonded cationic metal carbonyl derivatives is now extended to group 6. The range of coordination geometries and d-electron configurations includes in addition to d^{10} (linear), d^8 (square planar), and d^6 (octahedral),[3] also d^4 with a seven-coordinate geometry for the metal ion. Molybdenum becomes, together with iridium,[3] the only other metal for which presently typical,[13,14] highly reduced,[15] and predominantly σ-bonded cationic carbonyl derivatives[3] are reported. (iii) The simultaneous presence of two extremely weakly nucleophilic fluoroantimonate(V) anions, $[SbF_6]^-$ and $[Sb_2F_{11}]^-$ in the same compound is highly unusual. The former is found here as *cis*-F-bridging, iso-bidentate ligand. The *cis*-bridging $[F_2SbF_4]^-$ ligands are responsible for two unusual structural features: eight-membered *trans*-$Mo_2F_2Sb_2F_2$ rings with fluoro bridges between alternating Mo and Sb atoms. The metallocycles are further linked into chains, again by *cis*-F_2-SbF_4 bridges.

Another feature, secondary contacts which are about 0.20−0.40 Å shorter than the sum of the van der Waals radii,[16] between F atoms of the $[Sb_2F_{11}]^-$ anion or the *cis*-SbF_6 ligands, and O or C atoms of the carbonyl groups are found also previously for $[Ir(CO)_5Cl][Sb_2F_{11}]_2$[17] while for $[Hg(CO)_2][Sb_2F_{11}]_2$[18] F···C contacts dominate. The observed formation of a metallocycle and polymerization, of the cyclic moieties both via F_2-SbF_4 bridges as well as the interionic and intramolecular contacts described above, reflect the enormous electrophilicity and Lewis acidity of the pyramidal Mo(II)$(CO)_4$ moiety.

The synthetic route to $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$ has evolved from prolonged and ultimately unsuccessful attempts to synthesize a binuclear compound, containing the quadruply bonded cation $[(CO)_4MoMo(CO)_4]^{4+}$. In the binuclear metallocycle which is formed in these attempts, the two Mo$(CO)_4$ moieties are separated by intervening SbF_6^- anions with the shortest Mo−Mo separation of 5.776 Å. The formation reaction, formulated for a single formula unit is deceptively simple:

$$2Mo(CO)_6 + 9SbF_5 \xrightarrow[SbF_3(l),\ -4CO]{60\ °C,\ 24\ h} [\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3][Sb_2F_{11}] + 2(SbF_3{\cdot}SbF_5) \quad (1)$$

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Table 2. Internal Bond Parameters and Vibrational Wavenumbers (C−O Stretching Range) for $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$

(a) Bond Parameter

group	bond length range obsd [Å]	group	bond angles range obsd [deg]
Mo−C	2.021(10)−2.052(10)	C−Mo−C	70.2(4) and 75.3(4) 111.6(4) and 113.9(4)
C−O	1.089(11)−1.136(11)	Mo−C−O	174.8(9)−178.7(9)
Mo−μF	2.140(5)−2.196(5)	F−Mo−F	74.2(2)−77.6(2)
Sb−μF−(Sb)[a]	2.014(6) and 2.056(5)	Sb−F−Sb[a]	150.0(3)
Sb−μF−(Mo)	1.933(6)−1.988(6)	Sb−F−Mo	142.1(3)−162.8(3)
Sb−$F_{(t)}$[b]	~1.85 ± 0.02	$F_{(t)}$−Sb−F_t	91 ± 1°

(b) Vibrational Data

fundamental and assignment[c]	IR Wavenumbers $\bar{\nu}$ [cm^{-1}] and esd intensities	fundamental and assignment[c]	Raman shifts $\Delta\bar{\nu}$ [cm^{-1}] and esd intensities
ν(CO) A_1	2156 ms	ν(CO) A_1	2156 vs
ν(CO) A_1	2105 m, sh	ν(CO) A_1	2105 vs
ν(CO) B_1	2092 s, sh	ν(CO) B_1	2088 m, sh
ν(CO) B_2	2086 vs	ν(CO) B_2	2085 m
$\bar{\nu}CO_{av}$	2110	f_{CO}	18.0×10^2 N m^{-1}

[a] Data pertain to $[Sb_2F_{11}]^-$. [b] Denotes terminal F atom in *cis*-SbF_6^- and in $[Sb_2F_{11}]^-$. [c] Assignment is based on C_{2v} local symmetry.

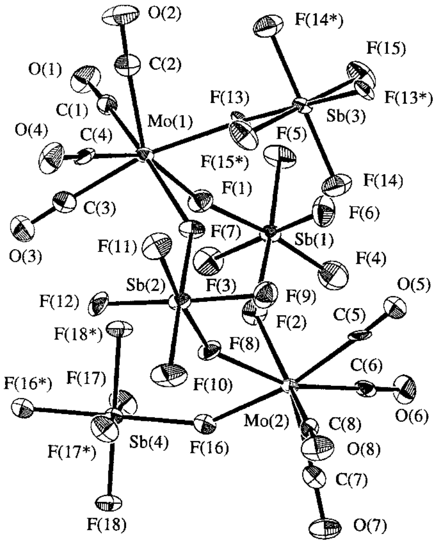

Figure 2. ORTEP plot with 50% probability thermal ellipsoids of the repeat unit of the polymeric cation $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]^+$.

Separation of the two solid products and recrystallization of the title compound is achieved with the help of the conjugate superacid[4,5] HF−SbF_5, wherein $SbF_3{\cdot}SbF_5$[19] is found to be insoluble. The general synthetic method appears to be extendable to tungsten hexacarbonyl. In this new approach, liquid SbF_5 plays an expanded role: as in all other carbonylation reactions reported by us[3] it is the reaction medium and source for the counterion $[Sb_2F_{11}]^-$. In addition it functions as oxidizing agent, provides the bidentate ligand $F_2SbF_4^-$, which facilitates elimination of CO.

Yellow-orange crystals of $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x$-$[Sb_2F_{11}]_x$ are, in a sealed glass tube, stable up to 140 °C. At ~150 °C melting with decomposition occurs. CO, BF_3, and SiF_4 are observed in gas-phase IR spectra. In addition to liquid SbF_5, colorless sublimable crystals form, which are tentatively identified as $MoOF_4$. An olive residue is left. The reduced byproduct, formulated as $SbF_3{\cdot}SbF_5$(A),[19] is recrystallized from anhydrous HF and is identified according to its cell constants as $6SbF_3{\cdot}5SbF_5$ whose structure is known.[20] This finding confirms that SbF_5 functions as oxidizing agent toward $Mo(CO)_6$.

The new complex is unambiguously characterized by single-crystal X-ray diffraction.[21] Support comes from IR and Raman spectra, which are readily interpreted in the CO-stretching range only. A repeat unit of the polymeric cation $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]^+$ is shown in Figure 2. Important bond parameters for the cation as well as for $[Sb_2F_{11}]^-$ are summarized in Table 2, together with vibrational wavenumbers ($\bar{\nu}$CO) for the Mo^{II}-$(CO)_4$ moiety. As can be seen both molybdenum ions are seven-coordinate, which is rather common for Mo(II) complexes.[9−12] The coordination polyhedron is best described as a square antiprism or 4:3 geometry,[9] where a trigonal MoF_3 and an approximately square $Mo(CO)_4$ pyramid share a common apex. For the latter, observed bond angle alternation and coincidence of $\bar{\nu}$CO in the IR and Raman spectra (see Table 1) suggest the local symmetry of the $Mo(CO_4)$ moiety to be approximately C_{2v}.

As can be seen from the data collected in Table 1, the molecular structure of the cyclic repeat unit $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]^+$ is very regular. Variations within a bond group are small, often within the quoted esd values. As observed for the homoleptic metal carbonyl cations,[3] C−O bond lengths are rather short and are near or below the q_l value of 1.132 Å in the Cambridge data index.[22] Correspondingly the Mo−C distances are long and above the q_u value of 2.007 Å. While the C−Mo−C angles alternate between acute and rather wide by about 40°, the Mo−C−O angles depart from linearity by 1.3−5.2°, as found in $[Hg(CO)_2]^{2+}$.[18] This is, in our opinion, due to the observed interionic and intermolecular contacts which involve both O and C atoms of the carbonyl groups.

The average $\bar{\nu}$CO wavenumber of 2110 cm^{-1} and consequently the stretching force constant f_{CO} of 18.0×10^2 Nm^{-1} obtained by the Cotton-Kraihanzel method[23,24] are slightly lower than in free CO (2143 cm^{-1} and 18.6×10^2 N m^{-1} respectively[3]). There are two reasons for this: (a) the net charge on each Mo is $+1/2$ compared to +2 in $[Hg(CO)_2]^{2+}$ where $\bar{\nu}$CO is 2279.5 cm^{-1}. By comparison for neutral $Mo(CO)_6$ f_{co} is 17.1 × 10^2 N m^{-1};[25] (b) some π-back-bonding and secondary interionic and intramolecular contacts combine to weaken the C−O bond. Nevertheless, the CO stretching wavenumbers observed here are to our knowledge the highest for any molybdenum(II) carbonyl species. They are even higher than the $\bar{\nu}$CO values for otherwise poorly characterized carbonyl

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fluorides of Mo(III) and Mo(IV) reported some time ago.[26,27] The remaining bond parameters are clear-cut and merit little discussion.

Conclusions

In summary, following early pioneering studies on $[M(CO)_6]^+$ (M = Mn,[28,29] Tc,[30] Re[31,32]) by E. O. Fischer[28,29] et al. and W. Hieber et al.,[30−32] the field of thermally stable homoleptic carbonyl cations and their derivatives has grown substantially in recent years.[3] The systematic use of superacid media[4,5] in synthesis and product isolation[3] has made it possible to include now in this group the first cationic derivative formed by an early transition metal with a d^4 configuration, a coordination polymer with a very unusual structure.

We are not aware of any other synthetic method that produces any thermally stable, homoleptic metal carbonyl cations and their derivatives with metals in +2 or +3 oxidation states.[3,33]

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Supporting Information Available: An X-ray crystallographic file in CIF format for complex $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$ is available on the Internet only. This material is available free of charge via the Internet at http://pubs.acs.org.

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