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Tungsten and Molybdenum Nitrosyl Cations in Fluorosulfonic Acid

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The tungsten and molybdenum hexacarbonyls, $M(CO)_6$ (M = W, Mo), dissolve in fluorosulfonic acid, HSO_3F, to generate the tungsten and molybdenum carbonyl cations, $[M(CO)_4]^{2+}$(solv), which are transformed, by exposure to an NO atmosphere, into the tungsten and molybdenum carbonyldinitrosyl cations, $[M(CO)(NO)_2]^{2+}$(solv), respectively. These complexes have been characterized by NMR (^{183}W, ^{13}C, and ^{15}N), IR, and Raman spectroscopy, and they are the first well-characterized metal nitrosyl cations in strong acids or superacids although the spectroscopic techniques do not address the number or coordination mode of the solvent molecules. Their formation suggests that strong acids and superacids can hopefully be used to generate a number of metal nitrosyl cations as they have been successfully used for preparing a series of metal carbonyl cations.

Nitrogen monoxide, NO, is an important bioregulatory molecule, and metal nitrosyl adducts, including metal nitrosyl cations, are implicated as pivotal intermediates in biological systems.[1] Significant attention has been focused on the important role that cationic metal−NO species have played in the environmentally significant nitrogen oxide processing using metal exchanged zeolites.[2] However, the direct observation of metal nitrosyl cations remains very limited, usually as adsorption species in zeolites[3] or species isolated in rare-gas matrixes.[4] So far, there is no evidence for the formation of metal nitrosyl cations in strong acids or superacids with the only exception being $[CuNO]^{2+}$(solv),[5,6] whereas over the past decade, there has been a rapid development in the synthesis and characterization of metal carbonyl cations and their derivatives from groups 6−12, usually generated in strongly acidic or superacidic media or with weakly coordinating anions.[7−9]

We now report the preparation[10] and spectroscopic study[11] of the first well-characterized tungsten and molybdenum nitrosyl cations, $[M(CO)(NO)_2]^{2+}$(solv) (M = W, Mo) and $[Mo(NO)_2]^{2+}$(solv), in fluorosulfonic acid, HSO_3F.[12] According to Scheme 1, the dissolution of $M(CO)_6$ (M = W, Mo) in HSO_3F leads to the release of 2 mol of CO per mol of $M(CO)_6$ to produce $[W(CO)_4]^{2+}$(solv) (**1**) and [Mo-

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(10) For the preparation, use was made of the equipment similar to that previously described (see: Xu, Q.; Heaton, B. T.; Jacob, C.; Mogi, K.; Ichihashi, Y.; Souma, Y.; Kanamori, K.; Eguchi, T. *J. Am. Chem. Soc.* **2000**, *122*, 6862−6870.). Standard cannula transfer techniques were used for all sample manipulations. Compounds **1** and **2**: $W(CO)_6$ (1 mmol) and $Mo(CO)_6$ (1 mmol) in HSO_3F (3 mL) were stirred for 3−5 h under CO or Ar, whereupon both clear yellow solutions were obtained, respectively. The ^{13}CO-enriched complexes of **1** and **2** were prepared by repeating the substitution with 99% ^{13}CO. Compound **3**: **1** was rapidly transformed into **3** (ca. 30 min) upon exposure to a NO atmosphere producing a green solution. The ^{13}C- and ^{15}N-enriched complexes of **3** were similarly prepared from the ^{13}CO enriched complex of **1**. The solution is indefinitely stable under an Ar atmosphere. Compounds **4** and **5**: **2** was rapidly transformed into **4** (ca. 30 min) by exposure to NO producing a dark green solution. Compound **4** is stable under a CO atmosphere even without gas-phase NO. Compound **4** gradually changed to **5** (>2 days) under a NO or Ar atmosphere with the dark green color unchanged. The solution of **5** is indefinitely stable under an Ar atmosphere.

(11) For the ^{183}W NMR measurements (16.5 MHz), saturated Na_2WO_4 in D_2O prepared using the substitution method (see: Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947−2960) was contained as an external reference and a lock in 10-mm-o.d. sample tubes, in which coaxial inserts containing liquid samples were placed. For the ^{13}C (100.4 MHz) and ^{15}N (40.4 MHz) NMR measurements, CD_3CN was contained as an external reference and a lock in 5-mm-o.d. sample tubes, in which coaxial inserts containing liquid samples were placed. The infrared spectra were obtained on thin films between two silicon discs. The Raman spectra were recorded on liquid samples contained in a 5-mm-o.d. NMR tube.

(12) For sake of brevity, a solvated cation that should exist in the form of $[M(CO)_m(NO)_n(L)_x]^{a+}$ (L denotes the weakly coordinating ligand probably being the conjugate base of the solvent acid or a closely related species) is hereafter simply formulated as $[M(CO)_m(NO)_n]^{a+}$(solv).

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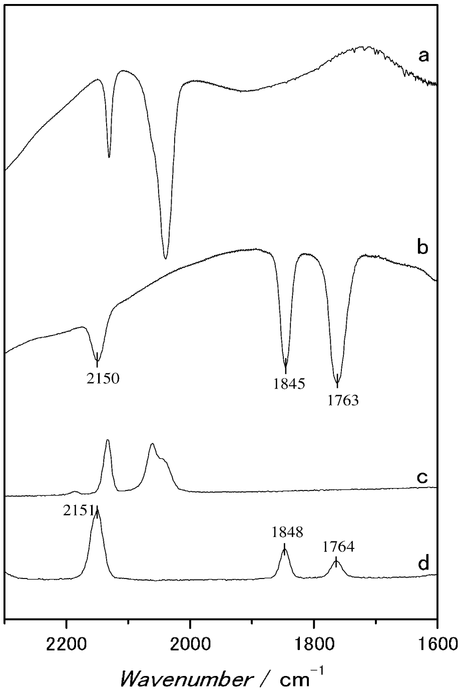

Figure 1. IR spectra of the carbonyl and nitrosyl regions of (a) **1** and (b) **3** in HSO_3F, and the corresponding Raman spectra of (c) **1** and (d) **3**.

Scheme 1

$$M(CO)_6 \xrightarrow[-\,2CO]{HSO_3F} [M(CO)_4]^{2+}(solv) \xrightarrow[-\,3CO]{+\,2NO} [M(CO)(NO)_2]^{2+}(solv)$$

(M = W, Mo)

$(CO)_4]^{2+}$(solv) (**2**), which exhibit band distributions in the CO stretching range similar to those reported for $[\{W(CO)_4\}_2(F_2SbF_4)_3]_x[Sb_2F_{11}]_x$, formed as the decomposition product of $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$,[13] and for $[\{Mo(CO)_4\}_2$-(*cis*-μ-$F_2SbF_4)_3]_x[Sb_2F_{11}]_x$,[14] respectively (Figures 1 and 2). $[W(CO)_4]^{2+}$(solv) shows a single ^{183}W resonance at -1120 ppm, which splits into a quintuplet with approximately 1:4:6:4:1 relative intensities ($^1J_{W-C} = 115$ Hz) in $[W(^{13}CO)_4]^{2+}$-(solv), indicating the presence of four equivalent CO ligands coordinating to W. We believe that the tungsten and molybdenum ions in complexes **1** and **2** are similarly seven coordinate including a pyramidal $M(CO)_4$ group with the three other coordination sites occupied by weakly coordinating solvent ligands. Upon exposure to NO, the three CO ligands are readily replaced by two NOs to form $[W(CO)(NO)_2]^{2+}$(solv) (**3**) and $[Mo(CO)(NO)_2]^{2+}$(solv) (**4**), respectively (Scheme 1).

The formulation of **3** results from ^{13}C, ^{15}N, and ^{183}W NMR studies at natural abundance and ^{13}C and ^{15}N enrichment. As shown in Figure 3, $[W(CO)(NO)_2]^{2+}$(solv) shows a single ^{183}W resonance at -1317.7 ppm, which splits into a doublet with $^1J_{W-C} = 180$ Hz in $[W(^{13}CO)(NO)_2]^{2+}$(solv) and further splits into two triplets with $^1J_{W-N} = 108$ Hz in $[W(^{13}CO)(^{15}NO)_2]^{2+}$(solv), in agreement with the presence of one CO ligand and two equivalent NO ligands coordinating to W. These observations are consistent with the ^{13}C NMR (190.7 ppm, $^1J_{W-C} = 180$ Hz) and ^{15}N NMR (70.3 ppm, $^1J_{W-N} = 108$ Hz) measurements on the unenriched and ^{13}C- and ^{15}N-enriched complexes of **3**. We favor the six-coordinate W having an octahedral geometry involving an axial CO ligand and two equatorial NO ligands in a *cis*-configuration with the three other coordination sites occupied by weakly coordinating solvent ligands; this is consistent with the IR and Raman measurements (Figure 1). The infrared spectrum shows a CO stretching band at 2150 cm^{-1} along with its corresponding Raman counterpart at 2151 cm^{-1}. The IR absorption at 1845 cm^{-1} along with its Raman counterpart at 1848 cm^{-1} is assigned to the symmetric NO stretch, and the IR absorption at 1763 cm^{-1} along with its Raman

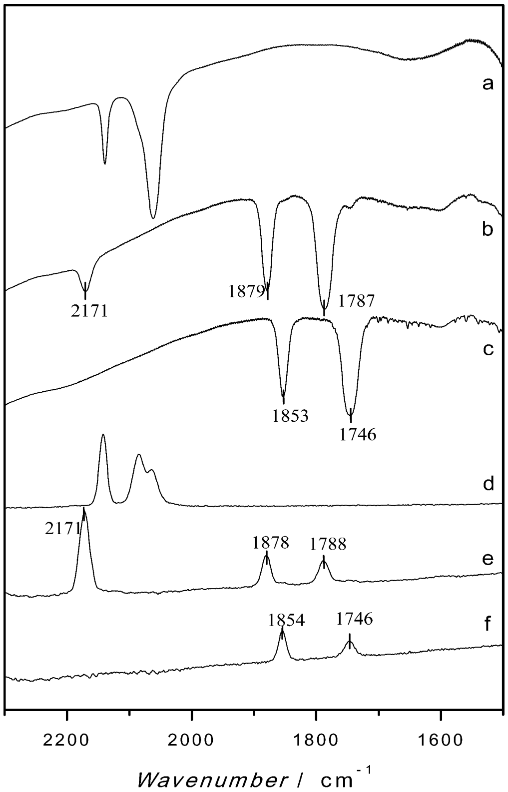

Figure 2. IR spectra of the carbonyl and nitrosyl regions of (a) **2**, (b) **4**, and (c) **5** in HSO_3F, and the corresponding Raman spectra of (d) **2**, (e) **4**, and (f) **5**.

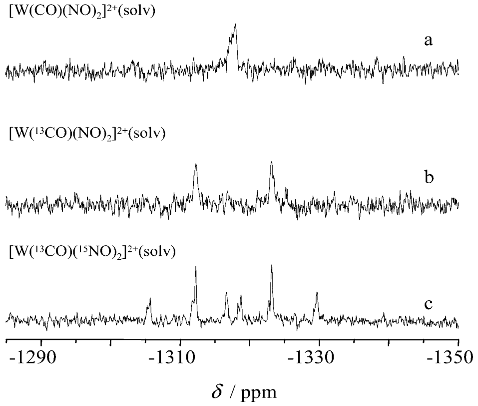

Figure 3. ^{183}W NMR spectra (16.5 MHz) of **3** in HSO_3F (a) at natural abundance, (b) with ^{13}CO enrichment, and (c) with ^{13}CO and 99% ^{15}NO enrichment.

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counterpart at 1764 cm^{-1} is assigned to the asymmetric NO stretch. This is compared with the related tungsten dinitrosyl cations stabilized by the donating CH_3CN ligands, $[W(CH_3CN)_4(NO)_2]^{2+}$ and $[W(CH_3CN)_3(CO)(NO)_2]^{2+}$, generated in the CH_3CN solution, which exhibit nitrosyl bands at 1730−1870 cm^{-1}, and a single carbonyl band, if having a CO ligand, at around 2160 cm^{-1}.[15] Other related complexes include $[LW(CO)_3(NO)]^+[SbF_6]^-$ (L = Me_2PhP, 2102, 2012, 1690 cm^{-1}; Me_3P, 2102, 2010, 1690 cm^{-1} (IR)), which results from the reaction of $LW(CO)_5$ with $NO^+SbF_6^-$ in CH_2Cl_2.[16]

The infrared and Raman spectra for **4** are similar to those for **3** (Figure 2). The CO stretching wavenumbers observed at 2171 (IR) and 2171 (Raman) cm^{-1} are to our knowledge the highest for any molybdenum carbonyl species. The ν(NO) values are observed at 1879, 1787 (IR) and 1878, 1788 (Raman) cm^{-1}. Compound **4** is stable in HSO_3F under a CO atmosphere even without gas-phase NO but gradually releases CO to form $[Mo(NO)_2]^{2+}$(solv) (**5**) (1853, 1746 (IR) and 1854, 1746 (Raman) cm^{-1}) under an NO or argon atmosphere (eq 1). The ν(NO) values for **4** and **5** are close to those of the related molybdenum dinitrosyl cations stabilized by the donating CH_3CN ligands, $[Mo(CH_3CN)_4(NO)_2]^{2+}$, generated in the CH_3CN solution.[15] Interestingly, CO can be involved in the molybdenum dinitrosyl cation stable under a CO atmosphere in the superacid, HSO_3F, whereas only $[Mo(CH_3CN)_4(NO)_2]^{2+}$, but not $[Mo(CH_3CN)_3(CO)(NO)_2]^{2+}$, is formed in the CH_3CN solution.[15]

$$[Mo(CO)(NO)_2]^{2+}(\text{solv}) \underset{+CO}{\overset{-CO}{\rightleftarrows}} [Mo(NO)_2]^{2+}(\text{solv}) \quad (1)$$

The CO stretching wavenumbers observed at 2150 (IR) and 2151 (Raman) cm^{-1} for **3** and at 2171 (IR) and 2171 (Raman) cm^{-1} for **4**, much higher than those of the corresponding $[M(CO)_4]^{2+}$(solv) (M = W, Mo) cations, indicate a much more positive charge on the central metal, M, in **3** and **4** than in **1** and **2**, probably originating from a charge transfer from M to NO, consistent with the observation of the partially negative NO species as their observed ν(NO) values are lower than 1876 cm^{-1}, the value for free NO.[17] The ν(NO) values for the tungsten and molybdenum nitrosyl cations are much lower than the ν(NO) values for $[CuNO]^{2+}$(solv) in strong acids and superacids;[6] a similar trend is observed for metal carbonyl cations such that much higher ν(CO) values are observed for the late-transition metals than for the early-transition metals.[7−9] It is found that CO and NO are much more strongly coordinated to W in **3** than to Mo in **4** and **5**. Significant $^{12}CO \leftrightarrow {}^{13}CO$ and $^{14}NO \leftrightarrow {}^{15}NO$ exchanges with free CO and NO were not observed for **3** but were observed for **4** and **5**.

In summary, we have found that the tungsten and molybdenum nitrosyl cations, $[W(CO)(NO)_2]^{2+}$(solv), $[Mo(CO)(NO)_2]^{2+}$(solv), and $[Mo(NO)_2]^{2+}$(solv), are formed in HSO_3F; these are the first well-characterized metal nitrosyl cations in strong acids and superacids although the spectroscopic techniques do not address the number or coordination mode of the solvent molecules. The present finding suggests that strong acids and superacids can hopefully be used to generate a number of metal nitrosyl cations as they have been successfully used for preparing a series of metal carbonyl cations. Attempts will be made to obtain the new complexes as crystalline salts, and further studies will be extended to a number of transition metals.

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