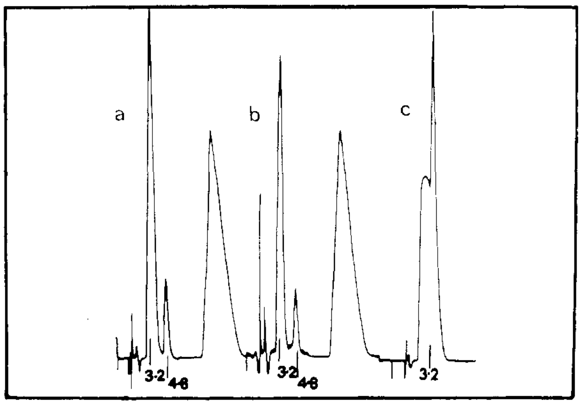

Figure 6. Chromatograms showing the effects of loading ratios and overloading (2.5% MeOH/H_2O (isocratic); 5 mM tosylate, pH 3.5): (a,b) independence of Δt_R (and t_R) of the relative amounts of Λ-$[Co(en)_2(Gly)]I_2$ ((a) 511 nmol, (b) 102 nmol) and Δ-$[Co(en)_2(Val)]I_2$ ((a) 2065 nmol, (b) 2479 nmol) loaded (45-μL samples); (c) "normal" overloading for a single species, Λ-$[Co(en)_2(Gly)]I_2$ (2410 nmol, 40 μL).

4 demonstrates this with decreasing tosylate concentration (from 30 to 15 mM) at a fixed $[Co(en)_2(AA)]^{2+}$ loading (AA = Gly (1640 nmol) + Pro (1616 nmol)). Thus, the effect is also dependent on the concentration of the ion-pairing reagent.

The degree of splitting, Δt_R, increases linearly with amount of sample loaded (n) (Figure 5a) but nonlinearly with ion-pairing concentration ([T]) (Figure 5b), and the combined effect shows as a nonlinear correlation between n and [T] at a fixed Δt_R (Figure 5c). This suggests the onset of saturation of the stationary phase by ion-paired species. From the above data it can be shown that, for a tosylate mobile phase (2.5% MeOH/97.5% H_2O), peak splitting can be avoided ($\Delta t_R <$ 12 s) if $n/[T] < 1.0 \times 10^{-4}$ dm^3. This is a useful guide for this system, but other results[5] show varying $n/[T]$ minima for other solvent systems and for other ion-pairing reagents.

The phenomenon is not restricted to chiral complexes, as it has been observed for mixtures of the achiral $[Co(NH_3)_5OCOR]^{2+}$ ions (R = CH_3, C_2H_5),[6] but it is independent of the nature of the accompanying anion (I^-, Cl^-, ClO_4^- salts) and of the *ratios* of the complex ions making up the sample. This last point is demonstrated by Figure 6a,b where the Δ-Gly:Δ-Val ratio changes from 0.25 to 0.04 (the total amount loaded remaining constant), but Δt_R remains the same at 96 s. This experiment also allowed the recovery of the separated Λ-Gly peaks, and these were shown to have identical molecular rotations ($[M]_D$ = 1465 ± 15° mol^{-1} dm^3 cm^{-1}) characteristic of pure Λ-$[Co(en)_2(Gly)]^{2+}$;[7] their identity was also confirmed by RP-HPLC of the recovered fractions under conditions where normal behavior obtained. Figure 6c gives the chromatogram of AA = Λ-Gly alone at a much higher loading, and comparisons with peaks a and b show the dramatic difference between the two overloading phenomena.

These experiments show that there must be an interaction between the two (or more) complex ions that influences their distribution ratios with the stationary phase, in addition to the normal pairing-ion depletion effect encountered with high concentrations of sample.[8] Such interactions between the complex cations and pairing anions apparently lead to species of different counterion stoichiometry, or geometry, which have sufficient lifetime on the matrix of the stationary phase to allow their separation as discrete entities.

As mentioned above, this abnormal effect can be avoided by increasing the pairing-ion concentration,[9] but it can also be avoided by using radial-compression columns.[5] In the latter, the distribution of the sample over an annular ring in the loading zone results in an even distribution over a large surface area, whereas for the unsupported stainless-steel columns the sample is highly concentrated in the middle of the zone.

Experimental Section

HPLC was carried out by using a Varian 5000 microprocessor-controlled pump assembly equipped with a Waters Associates C_{18}-μ-Bondapak column (10 μm, 30 cm × 3.9 mm i.d.). Procedures for sample and eluent preparation are detailed elsewhere.[6,10]

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Contribution from the Departments of Chemistry,
Montana State University, Bozeman, Montana 59717,
and City University of New York,
Hunter College, New York, New York 10021

Preparation of Octakis(acetonitrile)dimolybdenum(II) Trifluoromethanesulfonate, Bis(trifluoromethanesulfonato)tetraaquodimolybdenum(II) Trifluoromethanesulfonate, and Molybdenum(III) Trifluoromethanesulfonate

J. M. Mayer† and E. H. Abbott*

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In recent years there has been a great deal of interest in complexes with strong multiple metal–metal bonds,[1] especially the quadruply bonded d^4–d^4 systems.[2] Much of the work has been on the group 6 metals, and a variety of chromium, molybdenum, and tungsten compounds have been made. These seem to fall into a few basic types: complexes with negatively charged bridging ligands (carboxylates), complexes with anionic monodentate ligands (halides and pseudohalides), and mixed compounds with both anionic and neutral donors, of the type $M_2X_4L_4$. One of the more curious aspects is that almost all of the compounds are neutral or negatively charged. If complexes with cationic ligands are excluded, to our knowledge there are only three known cationic dinuclear molybdenum(II) species.

Bowen and Taube have reported Mo_2^{4+}(aq), from which they made $Mo_2(en)_4^{4+}$, precipitated as its chloride salt[3] (en = ethylenediamine). Mo_2^{4+}(aq) has so far defied all attempts at isolation with a noncoordinating anion.[1] $[Mo_2(en)_4]Cl_4$ can also be prepared directly by substitution of $Mo_2Cl_8^{4-}$; this is the only known example of a substitution reaction of a neutral ligand with binuclear molybdenum halides that leaves the quadruple bond intact and does not stop at the neutral species.

Experimental Section

All manipulations were performed by standard Schlenk techniques. Trifluoromethanesulfonic acid (HTFMS) was obtained from the 3M Co. and was distilled prior to use. Trifluoromethanesulfonic anhydride was prepared by distilling the acid from P_2O_5. Formic acid (90%; 10% water) was obtained from Aldrich and was distilled from excess phthalic anhydride; 100% formic acid was stored at 5 °C. Acetonitrile

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* To whom correspondence should be addressed at Montana State University.

† Present address: Central Research and Development Department, E. I. du Pont de Nemours & Co., Wilmington, DE 19898.

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Table I. Infrared Stretching Frequencies for $CF_3SO_3^-$ Ligands (cm^{-1})

	ionic		bridging		
	$NaTFMS^a$	$[Mo_2(CH_3CN)_8](TFMS)_4$	$[Mo_2(H_2O)_4(TFMS)_2](TFMS)_2$	$Mo_2(TFMS)_4$	$(CH_3)_3SnTFMS^b$
CF_3 str	1280	1270	1240	1200	1226
	1240	1230 (w)	1205		1179
SO_3 str	1175	1160	1150, 1110	1110	1145
	1035	1030	1030, 990	990	1026
			1340	1350	1319

[a] Spectra and assignments taken from M. B. Miles, G. Doyle, R. P. Cooney, and R. S. Tobias, *Spectrochim. Acta, Part A*, 25A, 1515 (1969). [b] Data for trimethyltin trifluoromethanesulfonate taken from P. A. Yeats, J. R. Sams, and F. Aubke, *Inorg. Chem.*, 10, 1877 (1971).

was triply distilled from P_2O_5 and stored under nitrogen. Diglyme was distilled from CaH_2. All other reagents were used without additional purification. Infrared spectra were taken as Nujol mulls. Analyses were performed by Galbraith Laboratories.

$Mo_2(O_2CH)_4$ (2). This compound has already been reported, and two synthetic routes have been described, one from molybdenum(II) acetate[4] and one from **1**.[4] This procedure is a one-step route from $Mo(CO)_6$, and it seems to yield an identical product by infrared and analytical data. A 1-mL portion of 100% formic acid and 1 g of $Mo(CO)_6$ were refluxed in 25 mL of diglyme for 3 h with nitrogen passing through the apparatus. Several 0.5-mL portions of formic acid were added over this period until all the $Mo(CO)_6$ had dispersed. The yellow needles were filtered, washed with diethyl ether, and dried in vacuo; yield 0.45 g (65%). Anal. Calcd. for $Mo_2O_8C_4H_4$: Mo, 51.61; C, 12.90; H, 0.93. Found: Mo, 51.84; C, 13.06; H, 1.07. This reaction can be scaled up by a factor of 10, and if care is taken to return the sublimed $Mo(CO)_6$ to the reaction mixture, the yield is only slightly lower. The yellow needles are air sensitive, especially when moist.

$[Mo_2(H_2O)_4(TFMS)_2](TFMS)_2$ (3). A 1.29-g sample of **2** was placed in a Schlenk flask, and 32 mL of HTFMS with 32 mL of trifluoromethanesulfonic anhydride was added. The solution was stirred for 6 days and the liquid distilled off at reduced pressure. The solid was dried for 1 h at about 90 °C under vacuum; yield 2.3 g (77%). Anal. Calcd for $MoC_2H_4O_8S_2F_6$: Mo, 22.33; C, 5.58; H, 0.93. Found: Mo, 21.91; C, 5.57; H, 0.96. In addition to the IR bands listed in Table I, the compound exhibited strong bands at 3430, 3180, and 1650 cm^{-1} (coordinated water), 720 cm^{-1} (CF_3 deformation), and 625 cm^{-1} (SO_3 deformation). The long reaction time and the acid anhydride are not crucial to the preparation—the reaction is complete in a few hours with only HTFMS—but a purer product is obtained with this procedure. The solid varies from an orange to a pink-tan color and is very air and moisture sensitive. It is soluble only in coordinating solvents, and then always with a change in color, indicating a reaction. The solid is, however, recoverable from diethyl ether by evaporation of the solvent. Crystalline products could not be obtained, but the infrared spectrum was identical with that which was obtained by direct synthesis.

$[Mo_2(CH_3CN)_8](TFMS)_4$ (4). A 0.50-g sample of **3** was placed in a Schlenk flask and 20 mL of acetonitrile added. After the mixture was stirred a few minutes, some of the CH_3CN was evaporated off and the solution left in a refrigerator overnight. The resulting blue crystals were filtered and washed with diethyl ether; yield 0.34 g (52%). Anal. Calcd for $MoC_{10}H_{12}N_4F_6O_6S_2$: Mo, 17.18; C, 21.51; H, 2.17; N, 10.04. Found: Mo, 17.08; C, 21.23; H, 2.33; N, 9.98. In addition to the IR bands listed in Table I, **4** exhibits bands at 2320 and 2295 cm^{-1} (CN stretch) and at 720 and 630 cm^{-1}. The visible spectrum shows one band at 555 nm, and the NMR spectrum (acetone-d_6) shows a singlet at 1.55. Compound **4** is recrystallized from acetonitrile. It reacts with acetic acid to form tetraacetate, as shown by infrared spectroscopy.

$Mo(TFMS)_3$. $Mo(CO)_6$ (2.0 g) was added to 20 mL of HTFMS under N_2. The suspension was refluxed for 4 h, during which time a yellow solution formed and then changed to green and an off-white precipitate formed. This solid was filtered under N_2 and washed with 10 mL of HTFMS. The compound is paramagnetic. It was dried at 100 °C in vacuo with KOH. Anal. Calcd for $MoC_3F_9O_9S_3$: C, 6.66; H, 0.00; Mo, 17.67. Found: C, 6.73; H, 0.16; Mo, 17.25.

Results and Discussion

Several years ago we reported the synthesis of tetrakis(trifluoromethanesulfonato)dimolybdenum(II), $Mo_2(TFMS)_4$[5] (**1**). While **1** showed promise as a precursor of complexes of Mo_2^{4+}, it was extremely difficult to purify in our hands. The present work was initiated to find a better route to **1** and to use it to prepare a variety of new complexes of the Mo_2^{4+} unit.

The original synthesis of **1** involved the reaction of $Mo_2(O_2CCH_3)_4$ with trifluoromethanesulfonic acid (HTFMS), but the product is plagued with an acetate impurity, which is very difficult to remove.[5] We attempted to avoid this problem by starting with tetrakis(formato)dimolybdenum(II), $Mo_2(O_2CH)_4$ (**2**), utilizing the decomposition of formate in strong acid to carbon monoxide and water. This reaction does not, however, produce **1**: it proceeds quantitatively as shown by eq 1.

$$\underset{\mathbf{2}}{Mo_2(O_2CH)_4} + HTFMS \rightarrow \underset{\mathbf{3}}{[Mo_2(H_2O)_4(TFMS)_2](TFMS)_2} + CO \qquad (1)$$

The formulation of **3** is based on spectral, chemical, and physical evidence. Unlike the parent compound **1**, **3** shows no tendency to sublime: heating under vacuum instead induced decomposition at about 100 °C. Compound **3** is insoluble in nonpolar solvents and reacts with coordinating solvents. It yields yellow powders on treatment with carboxylic acids, the product with acetic acid being identified as $Mo_2(O_2CCH_3)_4$ by its IR spectrum.[6]

Infrared spectroscopy provides the most useful information about the compound, as tabulated in Table I. Band splitting through symmetry reduction and band shifts can provide clear proof of bridging, as we have shown elsewhere.[5] Compound **3** shows both bridging trifluoromethanesulfonate modes (as in **1** or $Me_3SnTFMS$) and also ionic modes as in NaTFMS. Together with the water bands this clearly indicates a structure with coordinated water molecules, bridging coordinated $TFMS^-$, and ionic $TFMS^-$. The stoichiometry is confirmed by the analytical data.

The presence of four water molecules is surprising: HTFMS and especially trifluoromethanesulfonic anhydride, which can also be used in the above reaction, should be excellent scavengers for water. By analogy to the acid decomposition of bidentate carbonate,[7] it is expected that the bound formate ion might decompose without breaking both metal–oxygen bonds, leaving a water molecule attached to the molybdenum. The water must be extremely resistant to substitution in strong acid because **3** can be stirred in a 1:1 mixture of HTFMS and $(F_3CSO_2)_2O$ for 6 days without change. Heating these solutions leads to oxidation. The failure of **3** to be dehydrated by

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$(F_3CSO_2)_2O$ was rationalized as a reflection of kinetic inertness to water substitution rather than thermodynamic stability, because **1** does not dehydrate HTFMS to make **3** and $(F_3CSO_2)_2O$. Our failure to dehydrate **3** has caused us considerable concern as to whether it is correctly formulated. In light of this, we were again surprised to find that the water is readily expelled when acetonitrile is added to **3**, as shown by eq 2. We believe this to be the first isolated tetracation of binuclear molybdenum(II) with a unidentate ligand.

$$\underset{\mathbf{3}}{[Mo_2(H_2O)_4(TFMS)_2](TFMS)_2} + 8CH_3CN \rightarrow \underset{\mathbf{4}}{[Mo_2(CH_3CN)_8](TFMS)_4} \quad (2)$$

The deep blue compound **4** is formed instantly when **3** is dissolved in acetonitrile and precipitates as large crystals upon cooling. It is very air sensitive and loses acetonitrile on exposure to vacuum or other solvents—the low stability relative to other Mo_2^{4+} complexes may be due to the 4+ charge. San Filippo and co-workers have reported the preparation of $Mo_2(CH_3CN)_4Cl_4$ from acetonitrile and $Mo_2[S(CH_3)_2]Cl_4$;[8] there is no evidence for further substitution to a cationic species.

In the course of studying these complexes of TFMS, we carried out the reaction of $Mo(CO)_6$ with HTFMS. The product is the Mo(III) complex $Mo(TFMS)_3$. In view of the poor coordinating ability of TFMS, this complex may be of value as a precursor to the synthesis of other Mo(III) complexes. Complexes of this valence state are generally quite unstable to oxidation except in the presence of rather special ligands.[9]

In conclusion, we have prepared two new cationic complexes of Mo_2^{4+}, and they seem somewhat less stable than the neutral or anionic derivatives. Their formation raises questions about the poorly understood substitution behavior of the binuclear ion. The acetonitrile complex **4** is the first isolated example of a quadruple-bonded dimer coordinated only to monodentate neutral ligands. The trifluoromethanesulfonate derivative **3** is a very labile and reactive compound, and it seems to be a good starting material to prepare new complexes of binuclear molybdenum(II). However, it should be noted that solutions that we believe contain **3** were used by DeSimone in reactions with macrocycles. Both Mo(II) and Mo(IV) complexes were formed, but the Mo(II) complex no longer had a quadruple metal-metal bond.[10]

Registry No. 2, 51329-49-8; **3**, 86527-40-4; **4**, 86527-42-6; $Mo(TFMS)_3$, 86527-43-7; $Mo(CO)_6$, 13939-06-5.

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Contribution from the Chemistry Department,
University of Western Ontario, London, Canada N6A 5B7

Carbon-13 Line Width Criterion for the *lel* Conformation of Chelated Diamine Ligands

R. Garth Kidd

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In 1976, Baggar and Bang[1] discovered a dramatic ^{13}C NMR line width difference between diastereotopic methyl groups in (±)-2,3-butanediamine chelated to cobalt(III). While unable to explain the phenomenon, they recognized a convenient method for distinguishing the *lel* from the *ob* conformation of a five-member chelate ring, and since then a methyl ^{13}C line width in the range 15-25 Hz has become the accepted criterion[2] for recognizing an *lel* conformation. It is highly probable that the observed broadening has its origin not in nuclear shielding as has been suggested[2] but in nuclear relaxation and that scalar coupling of the second kind[3] to ^{59}Co is the source.

When chelated in a tris(diamine) complex, the five-member ring can adopt either the *lel* conformation in which the HC-CH axis is paral*lel* to the pseudo-C_3 molecular axis or the *ob* conformation in which the HC-CH axis is *ob*lique to the pseudo-C_3 axis by about 60°. The 15-25-Hz line width observed for the *lel* conformation distinguishes it from the *ob* conformation with a 5-10-Hz line width showing little if any anomalous broadening. By comparison, methyl or methine ^{13}C chemical shift differences between *lel* and *ob* conformations of 1 ppm or less[2] provide only a tenuous criterion for making the distinction.

In the absence of fluxional motion or chemical exchange that can limit the lifetime of a nuclear spin state, the natural ^{13}C line width is determined by the rate of transverse relaxation, R_2, according to the equation $\Delta\nu_{1/2} = R_2/\pi$. Most ^{13}C relaxation occurs through magnetic dipole-dipole coupling to bonded protons, modulated by molecular rotation; and this relatively inefficient relaxation mechanism places an upper limit of about 1 Hz on the line width in situations where the molecular motion is normal. If ^{13}C is scalar coupled to a nucleus with spin I whose relaxation rate is less than the coupling constant, a $2I + 1$ multiplet is observed. If, however, the other nucleus is undergoing rapid relaxation at a rate that exceeds the coupling constant, the multiplet is collapsed and the coupling is manifest only as a relaxation mechanism for ^{13}C, the efficiency of which can be considerably greater than that of the dipole-dipole mechanism. The scalar coupling contribution to the rate of ^{13}C relaxation is given by[4]

$$R_2^{SC}(^{13}C) = 21\pi^2[J(^{59}Co-^{13}C)]^2[R_1(^{59}Co)]^{-1}$$

^{59}Co is 100% abundant and has a spin $I = {}^7/_2$ and an electric quadrupole moment of 0.5 b. In sites having symmetry lower than O_h, the cobalt nucleus can experience a significant electric field gradient that promotes quadrupolar relaxation, and ^{59}Co relaxation rates in tris(diamine) complexes as high as 280 s^{-1} have been observed.[3]

Two- and three-bond coupling constants are highly sensitive to dihedral angle, and $^{205}Tl-^{13}C$ couplings[5] in a thallium adduct of bicyclo[3.2.1]octadiene are known to obey a Karplus-type[6] relationship. As a result, not only can $^3J(^{205}Tl-^{13}C)$ vary by a factor of 20 depending upon dihedral angle but $^3J(^{205}Tl-^{13}C)$ can exceed $^2J(^{205}Tl-^{13}C)$ by a factor of 3. These two facts taken together and placed in the context of tris(diamine)cobalt(III) complexes provide an angle-dependent relaxation mechanism that is of the correct magnitude to explain the atypically broad ^{13}C lines observed in some tris((±)-2,3-butanediamine)cobalt(III) isomers.

Where it is to be used as a diagnostic test for the presence of an *lel* conformation, several features of this relaxation-induced broadening are worth noting.

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