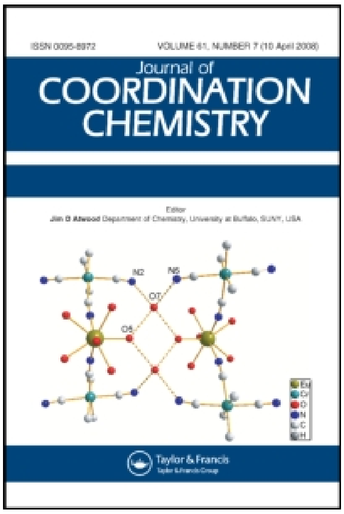

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SHORT COMMUNICATION
Dimolybdenum(II) Trifluoromethanesulfonates. The Coordination of Mo_2^{+4} by Weak Bidentate Ligands

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INTRODUCTION

It is now apparent that there is a substantial coordination chemistry of binuclear cations M_2^{+4} where M is one of several second row transition metals. The existence of a large number of tetra-μ-carboxylates of Mo_2^{+4} and the ability to substitute various ligands for the carboxylates are reflections of this.[1–7] As indicated by both theoretical and structural studies, the bond between two molybdenum(II)'s is a quadruple bond and is very strong.[2,8,9] A striking indication that the bond maintains its integrity in solution is in the proof of the existence of Mo_2^{+4} as a stable ion in aqueous solution.[3]

We have been interested in the coordination chemistry of binuclear metal ions, particularly in the ways that this chemistry may differ from the chemistry of mononuclear metal ions. In this paper we wish to report on a remarkable chelate effect which occurs with appropriate weak bidentate ligands when they bind the binuclear metal ions Mo_2^{+4}

EXPERIMENTAL

Tetraacetatodimolybdenum(II) (Mo_2Ac_4) was the starting material for the Mo_2^{+4} compounds and was prepared according to published procedures.[10] Trifluoromethanesulfonic acid (HTFMS) was obtained from Willow Brook Laboratories and distilled before use. It was stored in grease-free glassware in a dessicator. Ethylacetate was purified by the method of Perrin *et al*[11] other reagents were of the highest purity readily obtainable. All reactions were performed in Schlenk type apparatus with the careful exclusion of air and water.

Tetra(ethylacetate)dimolybdenum(II) trifluoromethanesulfonate [$Mo_2(EtOAc)_4(TFMS)_4$]

This compound was prepared by dissolving with stirring 3.6 g of Mo_2Ac_4 in a solution containing 6 ml HTFMS and 100 ml dry ethylacetate. This yields a red-orange solution. The product can be isolated by adding 50 ml heptane and leaving the resulting solution to stand in an ice bath for an hour. The yield is 2.4 g fine, yellow-orange crystals. Calculated for $C_{20}H_{32}O_{20}F_{14}S_4Mo_2$: C = 21.0%, H = 2.81%, F = 20.0%, Mo = 16.75%. Found: C = 21.04%, H = 2.95%, F = 19.58%, N = 0.0%.

Dimolybdenum(II) Trifluoromethanesulfonate · Trifluoromethanesulfonic Acid.

In a small Schlenk tube 10 ml HTFMS were added to 1.0 g Mo_2Ac_4 with stirring. An intensely red solution formed. Heating to 100°C. dissolved remaining Mo_2Ac_4. The acetic acid formed and about one half of the HTFMS were distilled off under vacuum. Upon cooling, a bright red solid formed. It was filtered off and dried in a stream of nitrogen. This compound contains variable amounts of HTFMS, as discussed below, and gradually loses weight under a stream of nitrogen.

Tetrakis(trifluoromethanesulfonato)dimolybdenum(II) [$Mo_2(TFMS)_4$]

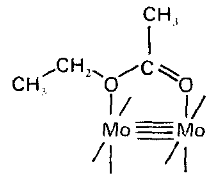
10 ml HTFMS were added to 1g. Mo_2Ac_4 with stirring. The resulting red solution was heated to 100° C. until all of the acetate dissolved. The solvent was distilled off yielding a pink solid which was dried at 100° C. until it became uniformly tan. Purification was achieved by sublimation at a vacuum of

10^{-8} mm Hg and 175°C. This yielded a light yellow-red solid which is exceedingly air-sensitive. Analysis was achieved by mass spectrometry which showed the molecular ion with isotope ratios as anticipated for two molybdenums.

RESULTS

Our initial object in undertaking this work was to prepare true salts of the cation Mo_2^{+4}. We reasoned that in the appropriate non-coordinating solvent, an acid, HX, whose conjugate base, X^-, is a sufficiently poor nucleophile would protonate the acetate ligands of Mo_2Ac_4,[1 1] removing them. We could thus be left with the salt Mo_2X_4. Inasmuch as HTFMS is strongest monobasic acid known and since TFMS is a very non-reactive anion, we reacted HTFMS with Mo_2Ac_4 in many solvents. Only the solvent ethylacetate yielded a solid product; however, it was not the desired compound. Elemental analysis and the infrared data in Table 1 support the formulation $Mo_2(EtOAc)_4(TFMS)_4$ as a complex in which four ethylacetates have coordinated the Mo_2^{+4} unit as in I. Both the C–OEt and C=O stretching frequencies are found at much lower frequency than in the free ethylacetate indicating that both oxygens are bound in a bridging, bidentate fashion analogous to the tetraacetatodimolybdenum(II) case. The trifluoromethanesulfonate frequencies are essentially identical to those in sodium trifluoromethanesulfonate and so this ion is present only to balance charge.

The compound $Mo_2(EtOAc)_4(TFMS)_4$ as isolated above is always found to be contaminated with acetate ion. This is revealed by the presence of a band at 675 cm^{-1} which has been attributed to the rocking of an acetate bound to two molybdenums.[1] At first we believed that the acetate arose from impurities in the ethylacetate or from saponification of coordinated ethylacetate by residual water. However, rigorous purification of the ethylacetate did not improve the product. Likewise attempts to recrystallize the compound from ethylacetate did not improve the purity. In fact it was found that the longer the product remained in contact with the mother liquor the worse the acetate impurity. The reverse procedure of precipitating the product with heptane at low temperature as soon as the acidic ethylacetate dissolved the Mo_2Ac_4 yielded a sticky precipitate of the desired compound which though quite hard to handle, was shown by infrared to contain virtually no coordinated acetate. On this basis we conclude that the Mo_2^{+4} unit causes and possibly catalyzes the decomposition of ethyl acetate in solution.



I

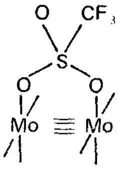
Heating $Mo_2(EtOAc)_4(TFMS)_4$ at 100° C. *in vacuo* for five hours causes a weight loss. Nmr of the effluent shows it to be pure ethylacetate. The infrared data in Table 1 also show that all the ethylacetate has been removed. In addition these data indicated that TFMS has replaced the ethylacetate as a bridging bidentate ligand. This is revealed in the

TABLE 1

Comparison of ethylacetate and various trifluoromethanesulfonate salts. Frequencies are in cm^{-1}, spectra were recorded as nujol mulls except for ethylacetate which was a thin film. Abbreviations: EtOAc = ethylacetate. NaTFMS = sodium trifluoromethanesulfonate, $Mo_2(EtOAc)_4(TFMS)_4$ = tetra(ethylacetate)dimolybdenum trifluoromethanesulfonate, $Mo_2(TFMS)_4$ = tetrakis(trifluoromethanesulfonate)-dimolybdenum(II), $(CH_3)_3Sn(TFMS)$ = Trimethyltin trifluoromethanesulfonate. $(CH_3)_3Sn(TFMS)$ data was taken from reference 5. NaTFMS band assignments were taken from M. G. Miles, G. Doyle, R. P. Cooney and R. S. Tobias *Spectrochim. Acta*, **25A**, 1515 (1969).

Assignment	ETOAc	NaTFMS	$Mo_2(EtOAc)_4(RFMS)_4$	$Mo_2(TFMS)_4$	$(CH_3)_3Sn(TFMS)$
C=O stretch	1740	–	1660, 1680	–	–
C–OEt stretch	1230	–	1210	–	–
CO–Et stretch	1040	–	1045	–	–
C–F stretch	–	1280 E	1250	1200	1226 (E)
		1240 A_1	1240		1179 (A_1)
S–O stretch	–	1175 (E)	1180 (E)	1350 (A″)	1319 (A″)
		1035 (A_1)	1030 (A_1)	1110 (A′)	1145 (A′)
				990 (A′)	1026 (A′)

splitting of the E mode of the S–O stretch into an A′ mode at 1110 cm^{-1} and an A″ mode at 1350 cm^{-1} while the A_1 mode becomes an A′ mode shifted down to 990 cm^{-1}. The magnitudes of the shifts and splitting are much too great to be attributed to reduction of crystal symmetry alone but are in keeping with an Mo_2^{+4} ion bridged by four bidentate TFMS ligands as in II.



II

Table I also includes data for the $(CH_3)_3SnTFMS$ complex, in which the TFMS has been shown to be bidentate in the solid state, bridging adjacent tin atoms[1 2]. The TFMS frequencies we observe in $Mo_2(TFMS)^4$ are shifted substantially further than those in the tin compound, indicating a stronger interaction.

The presence of a prominent 675 cm^{-1} bond in the infrared shows that the problem of acetate impurities is made even more severe when $Mo_2(TFMS)_4$ is prepared from $Mo_2(EtOAc)_4(TFMS)_4$. Evidently some further decomposition of ethylacetate to acetate occurs on heating. Elemental analyses, though variable, agree fairly well with a formulation of two molybdenums, three TFMS and one acetate. This raised the possibility that the molybdenum trifluoromethanesulfonate prepared under these conditions had three bridging TFMS's and one bridging acetate. Mass spectroscopy, however, showed it to be mixtures of $Mo_2(TFMS)_4$, $Mo_2(TFMS)_3$(acetate), and $Mo_2(TFMS)_2$(acetate)$_2$.

To prepare $Mo_2(TFMS)_4$ free of coordinated acetate, it is necessary to eliminate ethylacetate from the synthesis altogether. This was achieved by reacting the Mo_2Ac_4 with pure HTFMS and distilling off the acetic acid which is formed. Such a procedure leads to a bright red solution which on cooling precipitates a solid of similar color. The solid evidently contains HTFMS of crystallization which is gradually liberated in vacuum or a stream of nitrogen. Infrared shows the same ionic TFMS bands observed in NaTFMS or $Mo_2(EtOAc)_4(TFMS)_4$ and nothing else. The reactivity of HTFMS is so high, however, that the infrared plates may have reacted with any $Mo_2(TFMS)_4$ present to liberate free TFMS.

On heating at 100°C. in a vacuum the red solid turns light pink and finally tan, with loss of HTFMS. This product is $Mo_2(TFMS)_4$, free of acetate, as is shown by the absence of a 675 cm^{-1} band in the infrared. It may be purified by sublimation. The $Mo_2(TFMS)_4$ stoichiometry was proven by mass spectroscopy which showed the molecular ion as the most prominent ion the spectrum.

DISCUSSION

The significance of this work is that it illustrates a remarkable chelate effect resulting from the fact that in the binuclear ion Mo_2^{+4} two positive metal ions are firmly held a short distance from one another. Ethylacetate and TFMS are normally expected to be exceedingly poor ligands because of the low bascity of their oxygens. Our infrared data show that both ligands bind the Mo_2^{+4} cation quite strongly, in stark contrast to their binding of mononuclear metal ions. The ready sublimation of $Mo_2(TFMS)_4$ at 200° further supports a strong covalence. We attribute this binding to the fact that the donor atoms on the ligands are about as far apart as the two molybdenums in Mo_2^{+4}. One may then take advantage of metal-ligand chelate ring formation to form an unstrained five-membered ring whereas if a mononuclear ion were bound, the ligand would either be bound in a monodentate fashion or to form a relatively strained 4 membered chelate ring. It would seem that many molecules with weakly negative atoms the appropriate distance apart should bind binuclear ions strongly. Since there is a substantial variation in bond lengths of binuclear metal ions thus reported, there should be an important and selective coordination chemistry of such species.

A second point of this paper is that $Mo_2(TFMS)_4$ readily dissolves in anhydrous ethanol to give a bright yellow solution. Any ligand which is soluble in ethanol will react immediately with such a solution to form Mo_2^{+4} complexes. For example, tetraformatodimolybdenum(II), which has not yet been reported, forms virtually instantaneously when 90% formic acid is added to a concentrated solution of $Mo_2(TFMS)_4$ in anhydrous ethanol. The reaction proceeds rapidly at temperatures as low as –70°C. We are currently utilizing this method to prepare a number of novel Mo_2^{+4} complexes and will report on them in due time.

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REFERENCES

1. T. A. Stephenson, E. Bannister, and G. Wilkinson, *J. Chem. Soc.* 2538, 2541 (1964).
2. J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, 8, 7 (1968).
3. A. R. Bowen and H. Taube *J. Amer. Chem. Soc.*, 93 3287 (1971).
4. F. A. Cotton and J. G. Norman, *J. Coord. Chem.*, 1 161 (1972).
5. J. San Filippo jr., *Inorg. Chem.* **11**, 3140 (1972).
6. D. F. Steele and T. A. Stephenson *Inorg. Nucl. Lett.*, 9, 771 (1973).
7. C. L. Angell, F. A. Cotton, B. A. Frenz, and T. R. Webb, *Chem. Comm.* 399 (1973).
8. D. Lawton and R. Mason, *J. Amer. Chem. Soc.*, 87, 921 (1965).
9. F. A. Cotton and C. B. Harris, *Inorg. Chem*, 6, 924 (1967).
10. A. B. Brignole and F. A. Cotton, *Inorg. Synth.* McGraw-Hill, New York, p. 81 (1972).
11. D. D. Perrin, W. L. F. Armarego, and D. D. Perrin *Purification of Laboratory Chemicals* Pergamon, Oxford 1966 pp. 158.
12. P. A. Yeates, J. R. Sams, and F. Aubke, *Inorg. Chem.*, **10**, 1877 (1971).