

Table I. C₆F₆⁺ Excitation Spectrum in Solid Argon

cm^{-1}			cm^{-1}		
$\bar{\nu}$	$\Delta\nu$	assignment	$\bar{\nu}$	$\Delta\nu$	assignment
21 372	0	ν_{0-0}	22 606	1234	$\nu_{17} + 3\nu_{18}$
21 642	270	ν_{18}	22 659	1287	$3\nu_{17}$
21 800	428	ν_{17}	22 764	1392	$2\nu_{17} + 2\nu_{18}$
21 908	536	$2\nu_{18}$	22 775	1403	$\nu_2 + 2\nu_{17}$
21 919	547	ν_2	22 883	1511	
22 012	640		22 933	1561	ν_1
22 068	696	$\nu_{17} + \nu_{18}$	22 975	1603	$\nu_{15}?$
22 185	813	$\nu_2 + \nu_{18}$	22 996	1624	$\nu_{16} + \nu_{17}?$
22 231	859	$2\nu_{17}$	23 200	1828	$\nu_1 + \nu_{18}$
22 337	865	$\nu_{17} + 2\nu_{18}$	23 356	1984	$\nu_1 + \nu_{17}$
22 346	974	$\nu_2 + \nu_{17}$	23 476	2104	$\nu_1 + \nu_2$
22 456	1084	$2\nu_2$	23 625	2253	$\nu_1 + \nu_{17} + \nu_{18}$
22 495	1123	$2\nu_{17} + \nu_{18}$	23 785	2413	$\nu_1 + 2\nu_{17}$
22 568	1196	$\nu_{16}?$	23 896	2524	$\nu_1 + \nu_2 + \nu_{17}$

studies of electronic spectra of relatively large matrix isolated ions, providing insight both into the guest spectroscopy and into the ion-host interactions. Similar studies involving other ions as well as the effects of various hosts are in progress.

References and Notes

- (1) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **46**, 4562 (1967).
- (2) D. E. Milligan, M. E. Jacox, and W. A. Gullory, *J. Chem. Phys.*, **52**, 3864 (1970).
- (3) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **55**, 3404 (1971).
- (4) M. E. Jacox and D. E. Milligan, *J. Mol. Spectrosc.*, **52**, 363 (1974).
- (5) B. S. Ault and L. Andrews, *J. Am. Chem. Soc.*, **97**, 3824 (1975).
- (6) M. E. Jacox and D. E. Milligan, *J. Chem. Phys.*, **54**, 3935 (1971).
- (7) F. T. Prochaska and L. Andrews, *J. Chem. Phys.*, **67**, 1091 (1977).
- (8) L. Andrews, *J. Am. Chem. Soc.*, **98**, 2147 (1976).
- (9) D. W. Green, S. D. Gabelnick, and G. T. Reedy, *J. Chem. Phys.*, **64**, 1697 (1976).
- (10) M. Allan and J. P. Maier, *Chem. Phys. Lett.*, **34**, 442 (1975).
- (11) M. Allan, J. P. Maier, and O. Marthaler, *Chem. Phys.*, **26**, 131 (1977).
- (12) D. G. Streets and G. P. Ceasar, *Mol. Phys.*, **26**, 1037 (1973).
- (13) A. Gedanken, B. Raz, and J. Jortner, *J. Chem. Phys.*, **58**, 1178 (1973).
- (14) V. E. Bondybey and T. A. Miller, unpublished work.
- (15) T. A. Miller and V. E. Bondybey, *Chem. Phys. Lett.*, in press.
- (16) S. Abramowitz and I. W. Levin, *Spectrochim. Acta, Part A*, **26**, 2261 (1970).
- (17) L. Åsbrink, E. Lindholm, and O. Edqvist, *Chem. Phys. Lett.*, **5**, 609 (1970).

V. E. Bondybey,* J. H. English, Terry A. Miller

Bell Laboratories
Murray Hill, New Jersey 07974

Received May 8, 1978

A Trinuclear Molybdenum(IV) Cluster Compound Having an Unusual Structure and Unusual Stability

Sir:

The chemistry of molybdenum(IV) was relatively late and slow to develop and still remains imperfectly understood.¹ This is particularly true of its aqueous chemistry; only in 1966 was it shown² that Mo^{IV} is stable in aqueous media and only in 1973 did some firm information as to the identity of the species become available.³ There is also a very limited amount of information about its solid-state chemistry. We report here a discovery that bears significantly on both the aqueous and solid state chemistry of molybdenum(IV).

A solution of Mo^{IV} prepared by the method of Ardon and Pernick^{3a} was adsorbed on a Dowex 50W × 2 cation-exchange column and was eluted with 0.5 M oxalic acid. CsCl was added to the eluate, and, upon slow evaporation of this red-purple solution, red-purple crystals were obtained. These crystals are monoclinic and belong to space group $P2_1/n$ with cell dimensions $a = 12.082$ (2), $b = 16.764$ (3), $c = 12.529$ (2) Å; $\beta = 91.31$ (2)°; $V = 2537$ (2); and $Z = 4$. Using 2500 unique reflections with $I > 3\sigma(I)$, the structure was solved and refined

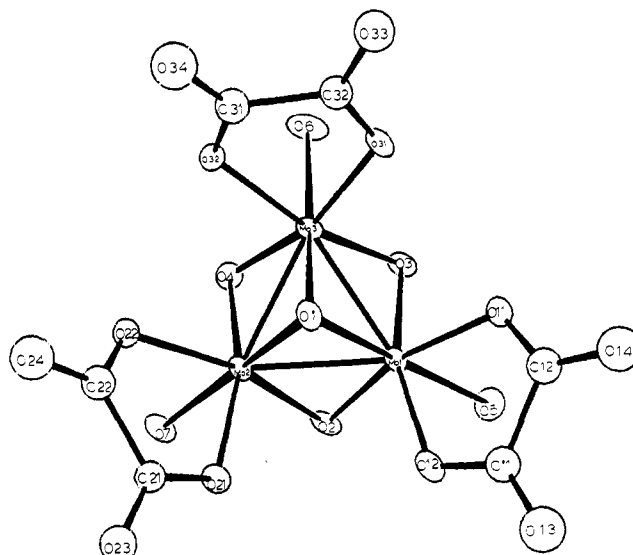


Figure 1. The structure of $[\text{Mo}_3\text{O}_4(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_3]^{2+}$.

to convergence. Anisotropic temperature factors were used for the Mo and Cs atoms and for the oxygen atoms in the coordination sphere. The final residuals obtained are $R_1 = 0.041$, $R_2 = 0.061$. From the structure the complete formula is found to be $\text{Cs}_2[\text{Mo}_3\text{O}_4(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_3] \cdot 4\text{H}_2\text{O} \cdot 1/2\text{H}_2\text{C}_2\text{O}_4$.

The molecular structure and atom labeling scheme is shown in Figure 1. Each molybdenum atom is surrounded by six oxygen atoms in a distorted octahedral geometry. The average bond distance of Mo—O(1) (2.019 (6) Å) is slightly longer than that of Mo—O(*a*) (1.921 (7) Å) ($a = 2, 3, 4$; these atoms are chemically equivalent) as is expected for a triply bridging oxygen atom. The average Mo—O(H₂O) distance (2.154 (7) Å) and the average Mo—O(ox) distance (2.091 (7) Å) are as expected for these ligands. Other results are available as supplementary material.⁴

The most interesting distance in the structure is that between the molybdenum atoms, 2.486 (1) Å. This is clearly indicative of the presence of Mo—Mo bonds and, on the simple basis that Mo^{IV} has two d electrons with which a single bond could be formed to each of its neighbors, we believe that these Mo—Mo bonds are single bonds. They are considerably shorter than nearly all other previously recognized Mo—Mo single bonds⁵ and comparable in length with several recently discovered examples of what *may be* Mo=Mo double bonds, viz., Mo₂(OPrⁱ)₆(CO)₆ (2.489 Å) and Mo₂(OPrⁱ)₈⁷ (2.523 Å). It must be kept in mind, however, that the lengths of all bridged M—M bonds, but especially when the bonds are of lower order, depend not only the bond order but also *strongly* on the number, size, arrangement, and character of the bridging groups.

The most pertinent structural comparison involving this structure is with the Mo₃O₁₃ unit found in a series of compounds with the general formula MM'Mo₃O₈ where M and M' are two cations with charge totaling +4, e.g., Zn₂, Co₂, or LiSc.⁸ The Mo₃O₁₃ unit, shown in Figure 2, is not discrete in these compounds, many of the oxygen atoms being shared between such units. In fact, this type of trinuclear cluster structure, which also occurs in the lower halides⁹ of niobium, Nb₃X₈ and CsNb₄X₁₁, has never before been found as a discrete entity. The present structure is, however, essentially the same, except that some of the 13 oxygen atoms are now supplied by oxalate ions and water molecules. It is the bridging oxygen atoms of the Mo₃O₁₃ structure which are still simple oxygen atoms in the present case.

It is noteworthy that the electronic structure of the Mo₃O₁₃ unit was analyzed many years ago¹⁰ and it was shown that a

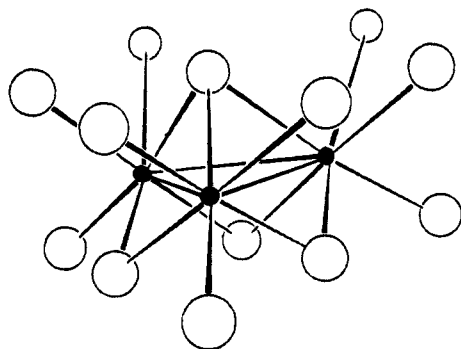


Figure 2. The structure of the Mo_3O_{13} unit that occurs in $\text{Zn}_2\text{Mo}_3\text{O}_8$ and related compounds.

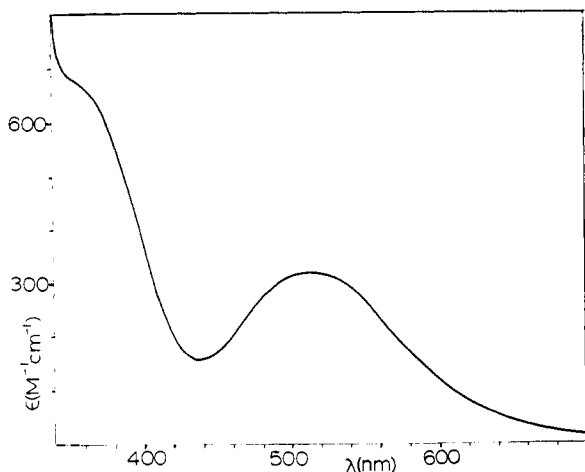


Figure 3. Absorption spectrum of $[\text{Mo}_3\text{O}_4(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_3]^{2-}$.

symmetry-based molecular orbital treatment leads naturally to the conclusion that the metal atoms are linked by single bonds since the occupied MO's having metal-metal character give the electron configuration a^2e^4 . The Mo-Mo distance in $\text{Zn}_2\text{Mo}_3\text{O}_8$ (2.524 \AA) is not very different from the one found here.

Ardon and co-workers^{3a,b} have presented evidence that the Mo^{IV} aquo ion is dinuclear, with a charge of +4 and, hence, most likely $[(\text{H}_2\text{O})_4\text{Mo}(\mu\text{-O})_2\text{Mo}(\text{H}_2\text{O})_4]^{4+}$. Thus, in the presence of oxalate a structural transformation occurs. It is true that both species, Ardon's and ours, are red, but the spectra are different, as a comparison of Figure 3 with the spectrum of the aquo ion^{3a} will show. The formation of the trinuclear oxalato ion is irreversible and this new species is stable indefinitely in aqueous solution without reverting to the Ardon species.

The compound described here is the first example of a structurally characterized complex containing Mo^{IV} isolated from aqueous solution of molybdenum(IV). It is also one of the most stable and easily prepared Mo^{IV} complexes known. It suggests that the aqueous (and other) chemistry of this oxidation state of molybdenum may be more extensive than previously supposed.¹²

Supplementary Material Available: A table of atomic positional and thermal parameters, a more complete list of interatomic distances and angles, and a list of structure factors (16 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) E. I. Steifel, *Prog. Inorg. Chem.*, **22**, 100 (1977).
- (2) P. Souchay, M. Cadot, and M. Duhamel, *C. R. Hebd. Seances Acad. Sci.*, **262**, 1524 (1966).
- (3) (a) M. Ardon and A. Pernick, *J. Am. Chem. Soc.*, **95**, 6871 (1973); (b) M. Ardon, A. Bino, and G. Yahav, *ibid.*, **98**, 2338 (1976); (c) T. Ramasami, R. S. Taylor, and A. G. Sykes, *ibid.*, **97**, 5918 (1975).

- (4) See paragraph at end of paper.
- (5) F. A. Cotton, *J. Less-Common Metals*, **54**, 3 (1977).
- (6) M. H. Chisholm, R. L. Kelly, F. A. Cotton, and M. W. Extine, *J. Am. Chem. Soc.*, **100**, 2257 (1978).
- (7) M. H. Chisholm, F. A. Cotton, M. W. Extine, and W. W. Reichert, *Inorg. Chem.*, in press.
- (8) Cf. W. H. McCarroll, *Inorg. Chem.*, **16**, 3351 (1977), and earlier papers cited therein.
- (9) A. Simon and H. G. von Schnering, *J. Less-Common Metals*, **11**, 31 (1966); A. Bröll, A. Simon, H. G. von Schnering, and H. Schäfer, *Z. Anorg. Allg. Chem.*, **367**, 1 (1969).
- (10) F. A. Cotton, *Inorg. Chem.*, **3**, 1217 (1964).
- (11) G. B. Ansell and L. Katz, *Acta Crystallogr.*, **21**, 482 (1966).
- (12) We thank the National Science Foundation for support.
- (13) Visiting Professor, on leave from the Technion-Israel Institute of Technology, Haifa, Israel.

Avi Bino, F. Albert Cotton,* Zvi Dori*¹³

Department of Chemistry, Texas A&M University
College Station, Texas 77843

Received May 8, 1978

Interaction of Vicinal and Nonvicinal Amino-Hydroxy Group Pairs in Aminoglycoside-Aminocyclitol Antibiotics with Transition Metal Cations. Selective N Protection

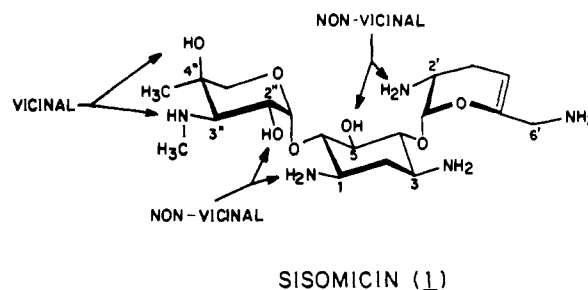
Sir:

We wish to report a novel, general, and high yielding method of selective N protection of aminoglycoside-aminocyclitol antibiotics via divalent transition metal complexing of vicinal and nonvicinal amino-hydroxy group pairs.¹

We define a nonvicinal amino-hydroxy group pair as one in which the two groups might be located on different rings, yet are in proximity owing to a unique stereochemical consequence as a result of conformational preference about the glycosidic linkage and possible further stabilization of the conformation by hydrogen bonding between the two groups.²⁻⁵

It was thought that, under suitable conditions, both vicinal and nonvicinal amino-hydroxy group pairs might form reversible complexes with divalent transition metal cations, the extent to which these cation complexes are formed being dependent on the type and amount of transition metal, availability of the pair for complexing, stability of the complex, and nature of the solvent. Conventional N blocking of amino groups not complexed in a similar manner would then lead to, after removal of the metal, selectively N-protected derivatives.

Treatment of sisomicin (**1**) with cobaltous acetate tetrahydrate (3 equiv) in Me_2SO (0.005 mol %) for 30 min, fol-



SISOMICIN (**1**)

lowed by acetic anhydride (3 equiv), and subsequent removal of the metal with hydrogen sulfide afforded 3,2',6'-tri-N-acetylsisomicin (**4**) in 95% yield.⁶ The results of similar selective 3,2',6'-tri-N protection of sisomicin (**1**) and related antibiotics using a variety of N-blocking agents and transition metal salts are given in Table I. As seen, for the antibiotics listed in Table I, Co^{2+} ions appear to give best yields of the tri-N-blocked products.⁶