Fluxional Polyoxoanions

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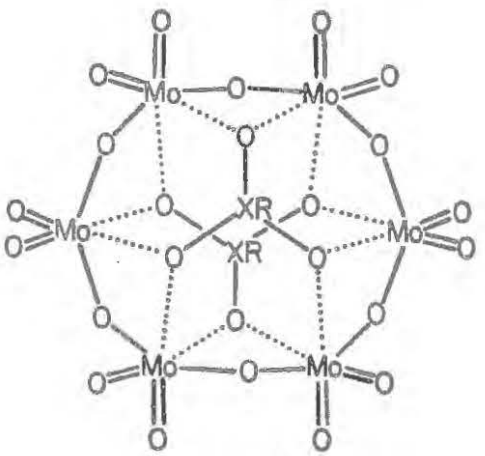
Although the structural chemistry of the early transition metal polyoxoanions is well established [1], virtually nothing is known about the mechanistic aspects of their chemistry [2]. Despite extensive speculation on the subject, little experimental data is available due largely to the general complexity of polyoxoanion structures as well as the difficulty in synthesizing specific compounds to test mechanistic hypotheses. In order to gain insight into some mechanistic aspects of polyoxoanion transformations, ^{17}O dynamic NMR line shape analysis, ^{17}O spin saturation transfer techniques, and ^{17}O label crossover experiments have been applied to the study of three polyoxoanions: α-$Mo_8O_{26}^{4-}$, $C_6H_5AsMo_7O_{25}^{4-}$, and $(C_6H_5As)_2Mo_6O_{24}^{4-}$.

These three anions share the common $[(RXO_3^{2-})_2(Mo_6O_{18})]$ structure shown in a, in which RXO_3^{2-} units are the tetrahedral $C_6H_5AsO_3^{2-}$ and/or $OMoO_3^{2-}$ anions connected by weak molybdenum-oxygen bonds to opposite sides of an $Mo_6(VI)O_{18}$ ring. The $C_6H_5AsMo_7O_{25}^{4-}$ anion shows two distinct types of fluxional behavior



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that can be related to the anions structure, a puckered Mo_6O_{18} ring capped on opposite sides by tridentate tetrahedral MoO_4^{2-} and $C_6H_5AsO_3^{2-}$ units. The low temperature process involves Mo_6O_{18} ring inversion accompanied by twisting of the $C_6H_5AsO_3^{2-}$ subunit and twisting or flipping of the MoO_4^{2-} subunit. Only weak (>2.2 Å) molybdenum oxygen bonds are broken and reformed. The higher temperature process, although mechanistically undefined, involves cleavage of stronger (1.7-2.0 Å) molybdenum-oxygen bonds. Evidence is presented for related processes in the α-$Mo_8O_{26}^{4-}$ and $(C_6H_5As)_2Mo_6O_{24}^{4-}$ anions.

Two structural features in a are of central importance since they are features observed in numerous other early transition metal polyoxoanion structures. First, the tetrahedral PO_4^{3-} ion is a subunit of the Keggin anion $PMo_{12}O_{40}^{3-}$ [3],

the Dawson anion $P_2Mo_{18}O_{62}^{6-}$ [4], and numerous related species. Second, neutral Mo_nO_{3n} rings are found in many structures such as the $P_2Mo_5O_{23}^{6-}$ [5], and $(CH_3)_2AsMo_4O_{15}H^{2-}$ anions [6]. Therefore, an understanding of the dynamic behavior in the structure shown in a has direct relevance to numerous other systems, and will be discussed.

References

1. Pope, M. T., "Heteropoly and Isopoly Oxometalates," Springer Verlag Berlin: Heidelberg, 1983; pp. 18-30.

2. Ibid., pp. 136-140.

3. Ibid., pp. 23.

4. Ibid., pp. 69.

5. Ibid., pp. 28.

6. Ibid., pp. 119.