HSO_4^- appears consistent with a simple anation reaction of Cr^{3+}, whereas the rate of $Cr^{3+} + SO_4^{2-}$ or $CrOH^{2+} + HSO_4^-$ may be set at sulfur, for the rate on either basis seems abnormally high. The charge type is different for this reaction, however, and it is not possible to claim that the sulfate reaction is really anomalous. Precedent for the suggestion of bond breaking at the nonmetal is found in the labile Cr(III) complexes formed by some oxy anions, notably $HCrO_4^-$ [33] and IO_3^-.[34]

The rate constant[12,13] for the reaction of Cr^{3+} and NO_3^- lies in the range of values for Cr^{3+} substitution, but considering its very feeble stability the rate is surprisingly high. This has been ascribed[35] to a possible nitrate–oxygen substitution, which appears to be a reasonable explanation.

Acknowledgment.—The author is indebted to Professors R. G. Pearson and T. W. Swaddle for helpful discussions and comments.

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[36] Fellow of the Alfred P. Sloan Foundation, 1968–1970.

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The Structures of Polyanions

Sir:

Although the formation of polymerized isopolyanions and heteropolyanions in aqueous solutions of vanadium(V), niobium(V), tantalum(V), molybdenum(VI), and tungsten(VI) is well known, a number of important questions remain unanswered.[1] These include why species of the same molecular weight are obtained in each case rather than a complex mixture of polymers, why the extent of polymerization is different for different metals, and what the reasons are for the adoption of the particular structures. Answers to these questions based solely on the size and charge of the metal atoms are presented in this correspondence.

Isopolyanions.—All known isopolyanion structures are constructed at least partly from MO_6 octahedra sharing edges. This introduces unfavorable Coulombic repulsions between the metal atoms, which can be partly accommodated by allowing the metal atoms to move away from the centers of their octahedral cages of oxygen atoms, which will be aided if the metal atom is relatively small. As the size of the polymer increases, it will become increasingly difficult for the electrostatic repulsion to be overcome by such distortion, until eventually polymerization by edge sharing of octahedra will cease. This Coulombic barrier will be reached later for the smaller ions,[2] that is, in the order V^{5+} ($r = 0.59$ Å) < Mo^{6+} ($r = 0.62$ Å) < W^{6+} ($r = 0.68$ Å) < Nb^{5+} ($r = 0.70$ Å) < Ta^{5+} ($r = 0.73$ Å). (This order also parallels the degree of distortion in the oxides.) This order is in agreement with experiment where it is found that the ions formed by edge sharing of octahedra (in contrast to the larger corner-sharing paratungstate Z and metatungstate) are $V_{10}O_{28}^{6-}$, $Mo_8O_{26}^{4-}$ and $Mo_7O_{24}^{6-}$, $HW_6O_{21}^{5-}$ (assuming an edge-shared structure), $Nb_6O_{19}^{8-}$, and $Ta_6O_{19}^{8-}$.

The shapes of the polyanions can also be predicted. If a third octahedron is added to a pair of edge-shared octahedra, the M–M–M angle can be 60, 90, 120, or 180° depending upon the particular edges shared by the central octahedron. The last two cases will be less favorable as the central metal atom is subjected to opposing Coulombic forces, which cannot be readily relieved by distortion. The 60° interaction is clearly the most favorable, and this is the edge-shared structural unit found in metatungstate $H_2(W_3O_{10})_4^{6-}$ and in many heteropolymolybdates and heteropolytungstates.[3]

For four octahedra sharing edges the two most favorable structures are shown in Figure 1. The approximately tetrahedral structure of M_4O_{16} is the most favorable as it again involves only 60° M–M–M interactions, and this is the structure found in $Li_{14}(WO_4)_3(W_4O_{16})\cdot 4H_2O$.[4] All other structures (about 20) involve unfavorable 180 or 120° interactions or more of the moderately unfavorable 90° interactions than occur in M_4O_{18}.

For six octahedra sharing edges, there are only two structures which avoid the unfavorable 180 or 120° interactions (Figure 2). The first is M_6O_{19} which has the six metal atoms in an octahedral arrangement and is the structure observed for $Nb_6O_{19}^{8-}$ and $Ta_6O_{19}^{8-}$.[5] The second is M_6O_{26} which is a continuation of the M_4O_{18} structure. This zigzag polymerization can continue indefinitely without encountering any Coulombic barrier and would result in a complex distribution of high molecular weight polymers. The reason these structures are not observed must be the very favorable entropy change accompanying elimination of water molecules with the formation of more compact structures, for example, M_6O_{19} from M_6O_{26}.

For more than six octahedra sharing edges, some of the unfavorable 120 or 180° M–M–M interactions become inevitable. The largest of the isopolyanions, $V_{10}O_{28}^{6-}$ (Figure 3), has two such 180° interactions, but the structure is considerably distorted due to mutual repulsion of the vanadium atoms so that the vanadium–oxygen bonds range from 1.59 to 2.22 Å, and the central V–V–V angles are reduced from 180 to 175°.[6] The

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Figure 1.—Four octahedra sharing edges.

Figure 2.—Six octahedra sharing edges.

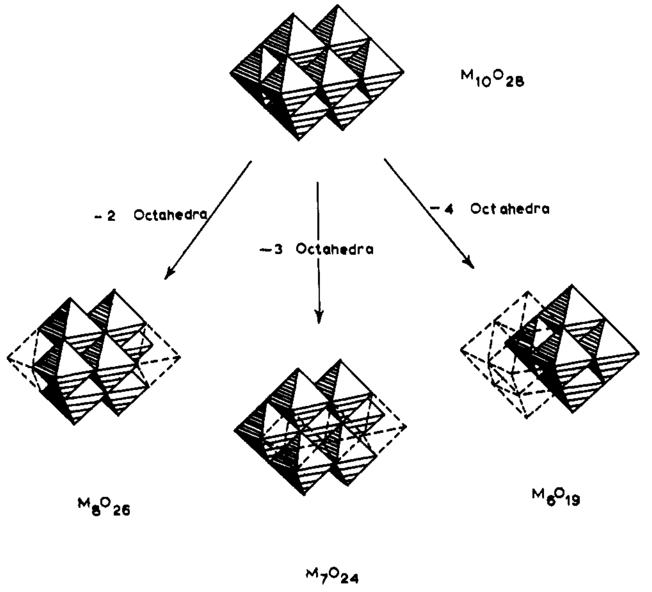

Figure 3.—The structure of isopolyanions showing their relation to the $M_{10}O_{28}$ structure.

structures of $Mo_8O_{26}^{4-}$ [7] and $Mo_7O_{24}^{6-}$ [8] (Figure 3) can be considered to be the fragments of the $M_{10}O_{28}$ structure after removal of octahedra to relieve the electrostatic strain. The central Mo–Mo–Mo angle in $Mo_7O_{24}^{6-}$ is reduced from 180 to 160–170°. (It may also be noted that $Ti^{IV}O_4(OC_2H_5)_{20}$ is isostructural with $Mo_7O_{24}^{6-}$.[9])

Heteropolyanions.—The heteropolyanions can be divided into three structural groups, depending upon the coordination number of the heteroatom.

Group I.—Tetrahedrally coordinated heteroatoms commonly occur in many 1:12[3] and 2:18[10] heteropolymolybdates and heteropolytungstates, and also their reduced, partially hydrolyzed, or substituted derivatives. All contain two or three octahedra sharing edges of the type discussed above as the basic structural units.

Group II.—Octahedrally coordinated heteroatoms occur in the 1:6 anions $Te^{VI}Mo_6O_{24}^{6-}$ [11] and $M^{III}Mo_6O_{24}^{9-}$ (where M is Al, Cr, Fe, Co, Rh, Ga)[12] and in the 1:9 anions $M^{IV}Mo_9O_{32}^{6-}$ (where M is Mn, Ni).[13] The structures of both types can be considered to be fragments of the highly symmetrical 1:12 heteropolyanion $M^{x+}Mo_{12}O_{38}^{(4-x)-}$ formed by addition of an MoO_6 octahedron onto each of the 12 edges of the $M^{x+}O_6$ octahedron and is shown in the upper structures of Figure 4 in both perspective and "exploded" forms.

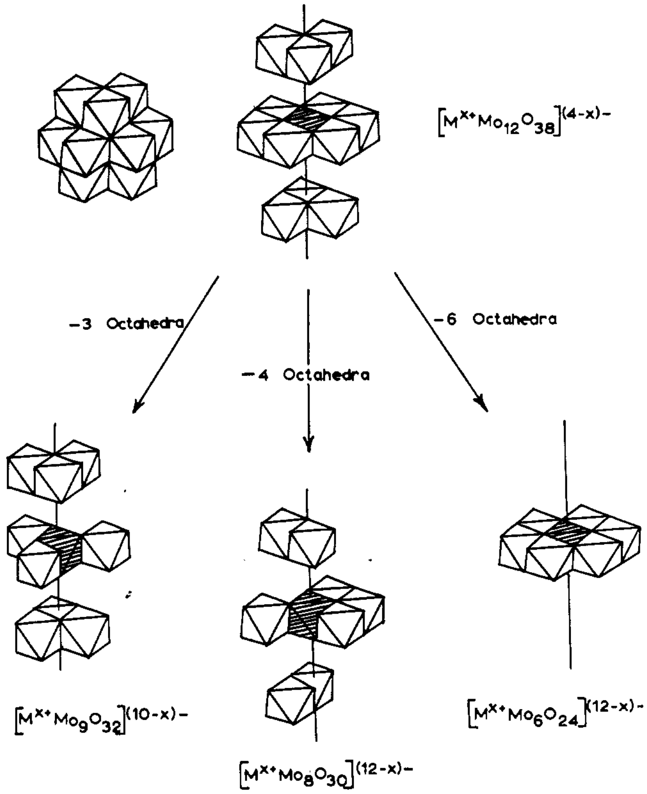

Figure 4.—The structures of heteropolymolybdates and their relation to the hypothetical $M^{x+}Mo_{12}O_{38}^{(4-x)-}$.

This hypothetical 1:12 heteropolyanion would have a uniquely low negative charge for a polyanion and in the extreme case of a high valent heteroatom would even have a highly unfavorable positive charge. However loss of an MoO_6 octahedron from this structure to form the hypothetical $M^{x+}Mo_{11}O_{36}^{(6-x)-}$ increases the negative charge by two, and similarly elimination of two nonadjacent octahedra would form $M^{x+}M_{10}O_{34}^{(8-x)-}$. Elimination of three octahedra leaving vacant sites at the corners of an equilateral triangle which most effectively accommodates any distortions due to molybdenum(VI)–molybdenum(VI) repulsions produces the fragment $M^{x+}Mo_9O_{32}^{(10-x)-}$ (Figure 4). This is the structure found for the manganese(IV) and nickel(IV) complexes above. Loss of four octahedra leaving vacant sites approximately tetrahedrally placed with

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respect to each other leads to $M^{x+}Mo_8O_{30}^{(12-x)-}$ (Figure 4), examples of which are not known. Loss of six metal atoms approximately octahedrally placed leads to $M^{x+}Mo_6O_{24}^{(12-x)-}$ (Figure 4), which is the structure found for the 1:6 heteropolymolybdates listed above.

The formation of large heteropolyanions of this type would be expected to be less favorable with the larger tungsten(VI) atoms, which appears to be in agreement with observation.

Group III.—The structure of $Ce^{IV}Mo_{12}O_{42}^{8-}$ is based on an icosahedrally coordinated cerium atom surrounded by six pairs of face-sharing octahedra.[14] Such face sharing of octahedra produces severe Coulombic interactions, and it is therefore not unexpected that tungsten forms only the 1:8 heteropolyanion $Ce^{IV}W_8O_{28}^{4-}$.[15]

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Association and Hydration Equilibria in NH_4NO_3–$2H_2O$–(AgCl or AgBr)[1]

Recently, from his measurements of the solubilization of silver chloride by excess chloride and of silver bromide by excess bromide in the solvent NH_4NO_3–$2H_2O$, Gal reported association constants for the formation of the associated species AgCl, $AgCl_2^-$, AgBr, and $AgBr_2^-$.[2] Application of the equations of a quasilattice model of anhydrous molten salts[3a] to the "pseudomolten salt" NH_4NO_3–$2H_2O$[3b] seemed to indicate nonlinear rather than linear $AgCl_2^-$ species. Although the absence of data in anhydrous NH_4NO_3 prevents a complete interpretation in terms of a recent aqueous quasilattice model of competition between association and hydration equilibria, it is of interest, nevertheless, to discuss Gal's results in this context.[4]

According to the aqueous quasilattice model, the measured pairwise association constants, K_1 (for AgCl or AgBr), should depend on water content as

$$Z/K_1 = \exp[\epsilon_C/kT] + R_H \exp[(\epsilon_C - \epsilon_H)/kT] \quad (1)$$

where Z is the lattice coordination number (usually assumed to be 6), ϵ_C is the relative silver–halide interaction energy for the exchange $Ag^+NO_3^- + NH_4^+X^- \rightleftharpoons Ag^+X^- + NH_4^+NO_3^-$ in anhydrous molten salt, ϵ_H is the relative hydration energy for $Ag^+NO_3^- + NH_4^+(H_2O) \rightleftharpoons Ag^+(H_2O) + NH_4^+NO_3^-$, R_H is the water concentration expressed as the mole ratio, moles of water per mole of nitrate, k is the Boltzmann constant, and T is the absolute temperature.[4] With eq 1, setting $Z = 6$, it is possible to obtain ϵ_C and ϵ_H from data at two different temperatures although, since ϵ_C is generally of much larger magnitude than ϵ_H, the numerical evaluation of the parameters is imprecise without data for the anhydrous solvent. The model assumes that the hydration energy parameter ϵ_H is the same for the AgCl and AgBr systems. In order to test this, we have inferred reasonable values of ϵ_C for the AgCl and AgBr associations in anhydrous NH_4NO_3 from known values of association energies in molten alkali nitrates.

We also have recalculated the pair equilibrium constants for AgCl and AgBr by graphical extrapolation, since the curve-fitted values often tend to weight the high-concentration data where higher species such as $AgCl_2^-$ or $AgBr_2^-$ predominate.[5] Values of

$$K_1 = \lim_{m_x \to 0} [\partial \ln (Sm_x/\mathrm{KSP})/\partial m_x] = \lim_{m_x \to 0} \{\partial[(Sm_x/\mathrm{KSP}) - 1]/\partial m_x\}$$

were obtained from plots of ln (Sm_x/KSP) and of $[(Sm_x/\mathrm{KSP}) - 1]$ *vs.* m_x for the low concentration data, as in Figure 1. Both plots have the same limiting slope, but at finite concentrations the logarithmic plot is concave downward and the rational plot is concave upward, so that upper and lower limits to the association constant can be estimated. S is the solubility, m_x the molality of ligand, and KSP the solubility product, which was found by successive approximations. It is seen in Figure 2 that the plots of log K_1 *vs.* $1/T$ and of log KSP *vs.* $1/T$ are smoother for the graphically estimated values than for those reported by Gal. These recalculated values in Table I were used in subsequent calculations, although little difference would have resulted from using Gal's values. The values of K in parentheses refer to concentrations expressed as mole ratios (R_x moles of ligand per mole of solvent); all others refer to conventional molality units (in moles of ligand per kilogram of solvent)).

In the absence of measured values of $K_{AgCl(AgBr)}$ or of ϵ_C for AgCl or AgBr (*i.e.*, $\epsilon_{AgCl(AgBr)}$) in anhydrous NH_4NO_3, it seems reasonable to estimate values from association equilibria in molten alkali nitrates.[6] Because the nitrate ion is closer in size to the bromide ion than to the chloride ion, the solvent cation size affects the electrostatic part of the silver–bromide association less than that of the silver–chloride association, and ϵ_{AgBr} is therefore subject to less uncertainty than ϵ_{AgCl} in estimating the parameters in NH_4NO_3. In dilute aqueous solution at 25° K^+ and NH_4^+ have the same effective radii and mobilities, and their chlorides have nearly identical activity coefficients.[7] However, at elevated temperatures and high salt concentrations, water

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corp.

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