Correspondence

Heteropoly and Isopoly Anions as Oxo Complexes and Their Reducibility to Mixed-Valence "Blues"[1]

Sir:

The structures of isopoly and heteropoly anions[2] are customarily described as assemblages of metal–oxygen polyhedra or as fragments of metal–oxide lattices.[3] This communication draws attention to the fact that, in many respects, poly anions behave like conventional mononuclear oxo complexes of molybdenum, vanadium, *etc.* Such a viewpoint leads to a classification of structural types and to a rationalization of heteropoly blue formation.

Although all known poly anion structures contain each nonhetero metal atom M (Mo^{VI}, V^{V}, *etc.*) in an octahedron of six oxygen atoms, the metal atom is always found to be displaced from the center of its octahedron toward a corner or an edge.[4] The resulting short M–O bonds link M to either one or two nonbridging oxygens on the exterior of the anion. Such "terminal" M–O bond lengths in poly anions are very close to those observed for normal oxo complexes, *e.g.*, Mo–O in $Mo_7O_{24}^{6-}$ is 1.72 Å,[5] and in $MoO_2F_4^{2-}$ it is 1.71 Å.[6] Metal–oxygen stretching frequencies are also similar; *cf.* the terminal W–O stretch (940–980 cm^{-1})[7,8] in several 12-tungstates, $XW_{12}O_{40}^{n-}$, with that (961–968 cm^{-1})[9] in $WOCl_5^-$. Furthermore, it has recently been shown that the uv charge-transfer spectra of poly anions are comparable to those of mononuclear oxo complexes.[10]

In Table I, known poly anion structures have been divided into categories according to the number of unshared oxygen atoms attached to each M atom. Type I structures correspond to mononuclear MOL_5 species and have the M atom in an approximately tetragonal (C_{4v}) site with a single unshared oxygen atom. Type II structures have each M atom with two mutually cis unshared oxygens (*cf.* mononuclear MO_2L_4 species). Type III anions have both sorts of M atom sites. Only one structure, that of the 12-paratungstate ion, $H_2W_{12}O_{42}^{10-}$, is known[11] to be of the last type, although the 1:11 and 2:17 heteropoly anions,[12] formed by partial hydrolysis of $XM_{12}O_{40}^{n-}$ and $X_2M_{18}O_{62}^{6-}$ complexes, probably have type III structures.[13]

Table I

Structural Types of Poly Anions

General formula[a]	Type[b]	No. of known examples[c]
$XM_{12}O_{40}^{n-}$ ($n = 3–7$)	I	>30[d]
$X_2M_{18}O_{62}^{6-}$	I	*Ca.* 10[d]
$M'_6O_{19}^{n-}$ ($n = 2–8$)	I	*Ca.* 6
$V_{10}O_{28}^{6-}$	I[e]	1
$XM^*_6O_{24}^{n-}$ ($n = 5–8$)	II	5
$XM^*_6O_{24}H_6^{n-}$ ($n = 3–4$)	II	*Ca.* 12
$Co_2Mo_{10}O_{38}H_4^{6-}$	II	1
$XMo_9O_{32}^{6-}$	II	2
$XMo_{12}O_{42}^{8-}$	II	3
$Mo_7O_{24}^{6-}$	II[e]	1
$Mo_8O_{26}^{4-}$	II	1
$H_2W_{12}O_{42}^{10-}$	III	1

[a] M = W, Mo, W + V, Mo + V; M′ = W, Mo, W + V, Mo + V, Nb, Ta; M* = Mo, W. [b] For original structure determinations see ref 2 and 14: type I, monooxo terminal groups; type II, cis dioxo terminal groups; type III, both monooxo and cis dioxo terminal groups. [c] Excluding "mixed" Mo + W and Nb + Ta complexes. [d] Including isomeric (α and β) forms but excluding the large numbers of 1:1:11 and 1:2:17 complexes in which an M atom of the 1:12 and or 2:18 structures has been replaced by another "central" atom: see, for example, L. C. W. Baker, *et al., J. Amer. Chem. Soc.*, **88**, 2329 (1966). [e] $V_{10}O_{28}^{6-}$ contains two metal atoms with no oxo-type oxygens; $Mo_7O_{24}^{6-}$ contains one such metal atom.

Evans[2,14] and Bachmann and Barnes[15] have noted the prevalence of the cis MO_2 group in poly anion structures, and more recently, Lipscomb[16] has proposed that the structures of isopoly and heteropoly anions might be limited to those in which each M atom is coordinated to no more than two unshared oxygens. Lipscomb's proposal would limit poly anion structures to the three types listed in Table I. However, mononuclear trioxo complexes of Mo(VI) and W(VI), *e.g.*, MoO_3dien[17] and $WO_3F_3^{3-}$,[18] are not unknown. It seems possible, therefore, that poly anions incorporating MO_3 or $M(OH)_xO_{3-x}$ groups might be formed. Indeed, structures proposed[19] for the metastable species $H_4W_4O_{16}^{4-}$ and "paratungstate-A," $H_3W_6O_{22}^{5-}$, are of this type. Although the tetratungstate anion is detectable only by fast-reaction techniques,[20] isolation of sodium paratungstate-A has recently been claimed.[21]

The reduction of certain poly anions to mixed-valence heteropoly blues is well known and has been recently

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[2] For a recent review of poly anion structures see H. T. Evans, Jr., *Perspect. Struct. Chem.*, **4**, 1 (1971).

[3] L. C. W. Baker, "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, p 604.

[4] Baker[3] has rationalized these displacements in terms of polarization of the external oxygens by the highly charged M cations.

[5] H. T. Evans, Jr., *J. Amer. Chem. Soc.*, **90**, 3275 (1968).

[6] D. Grandjean and R. Weiss, *Bull. Soc. Chim. Fr.*, 3049 (1967).

[7] G. Lange, H. Hahn, and K. Dehnicke, *Z. Naturforsch. B*, **24**, 1498 (1969).

[8] D. R. Wexell, Ph.D. Thesis, Georgetown University, 1971; H. So, unpublished results; C. M. Flynn, Jr., and M. T. Pope, *Inorg. Chem.*, **10**, 2745 (1971).

[9] G. W. A. Fowles and J. L. Frost, *J. Chem. Soc. A*, 1631 (1966).

[10] H. So and M. T. Pope, *Inorg. Chem.*, **11**, 1441 (1972).

[11] R. Allman and G. Weiss, *Acta Crystallogr., Sect. A*, **25**, S106 (1969); R. Allman, *Acta Crystallogr., Sect. B*, **27**, 1393 (1971).

[12] F. Kehrmann and M. Freinkel, *Chem. Ber.*, **25**, 1966 (1892); P. Souchay, *Ann. Chim.*, **20**, 73 (1945); G. Schwarzenbach, G. Geier, and J. Littler, *Helv. Chim. Acta*, **45**, 2601 (1962). The last paper reports the unit cell dimensions of $K_7PW_{11}O_{39}\cdot 30H_2O$.

[13] Such structures can result from the effective loss of an MO^{4+} group from the parent type I anions, *e.g.*, the structure of a 1:11 complex would therefore contain 7 monooxo and 4 cis dioxo M atoms. See also C. M. Flynn, Jr., and M. T. Pope, *J. Amer. Chem. Soc.*, **92**, 85 (1970), for another type III structure.

[14] H. T. Evans, Jr., *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **114**, 257 (1960); *Inorg. Chem.*, **5**, 967 (1966).

[15] H. G. Bachmann and W. H. Barnes, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **115**, 215 (1961).

[16] W. N. Lipscomb, *Inorg. Chem.*, **4**, 132 (1965).

[17] F. A. Cotton and R. C. Elder, *ibid.*, **3**, 397 (1964).

[18] O. Schmitz-Dumont and P. Opgenhoff, *Z. Anorg. Allg. Chem.*, **275**, 21 (1954).

[19] K. H. Tytko and O. Glemser, *Chimia*, **23**, 494 (1969); *Z. Naturforsch. B*, **26**, 658 (1971); K. H. Tytko, private communication, 1971.

[20] O. Glemser and K. H. Tytko, *Z. Naturforsch. B*, **24**, 648 (1969).

[21] C. M. Wolff and J. P. Schwing, *C. R. Acad. Sci., Ser. C*, **272**, 1974 (1971).

studied by several groups.[22–24] The formation of heteropoly blues appears to involve the stepwise reduction of d^0 M atoms to the d^1 oxidation state without a change in the structure of the anion.[10,25,26] It is noted here that the formation of heteropoly blue anions appears to be restricted to complexes with type I or type III structures.[27] Thus, each of the type I structures listed in Table I is known to be reducible,[28] but there are no instances of the reduction of type II anions.[29] As far as type III structures are concerned, although the 12-paratungstate ion has such a structure in the solid state, there is little evidence for other than the hexatungsto (type II?) form in most solutions,[30] and there have been no reports of a paratungstate "blue." On the other hand, the demonstrated reducibility[31] of $PW_{11}O_{39}^{7-}$, $SiW_{11}O_{39}^{8-}$, and $P_2W_{17}O_{61}^{10-}$ is consistent with the view of these complexes as type III species.

Conclusions regarding the structures of poly anions not listed in Table I may be drawn from considerations of their redox behavior. Recent polarographic investigations of the isopoly "pseudometatungstate"[32] and "polytungstate-Y"[33] anions indicate that these complexes are easily reduced, from which it may be inferred that they have type I (or type III) structures.[34] Since the true formulas of these complexes are not known at present, further speculation is inappropriate. In molybdate solutions, the isopoly anions which are the predominant solute species at pH 3–5, *viz.*, $Mo_7O_{24}^{6-}$ and $Mo_8O_{26}^{4-}$, are not reducible, although more acidic solutions of Mo(VI) are easily reduced to blue species. The anion responsible for the blue color in such solutions has been formulated[35] as $Mo_6O_{18}^{2-}$. Recent work[36] shows that this species is better written as $H_2Mo^V{}_2Mo_4O_{19}^{2-}$, a reduced form of the type I hexamolybdate anion, first reported by Fuchs and Jahr.[37]

Most of the approximately 75 anions representing the structures listed in Table I are tungstates and molybdates. At present count, all poly anions containing octahedral vanadium, niobium, or tantalum have type I structures.[38] This is to be expected for electrostatic reasons; type II structures for pentavalent atoms would tend to have high overall charges. Among molybdates and tungstates there appears to be a tendency for the former to adopt type II structures and the latter, type I structures. Thus, the only type I molybdates are a few 1:12 and 2:18 complexes with central atoms that strongly favor tetrahedral coordination (P^V, Si, etc.), together with the hexamolybdate anion, $Mo_6O_{19}^{2-}$. Type II tungstates are even less common than type I molybdates and are based on "octahedral" central atoms I^{VII}, Te^{VI}, Ni^{II}, and N^{IV}.[39] In this connection, the structues of the 10-tungstolanthanates, $Ln^{III}W_{10}O_{35}^{7-}$, recently described by Peacock and Weakley[40] will prove interesting. Since no observations of heteropoly blue formation were made, it is possible that these complexes have type II structures. Further discussion of the significance or even the existence of the tungstate-type I *vs.* molybdate-type II dichotomy must therefore await the results of more structural studies.

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(22) P. Souchay, "Ions Minéraux Condensés," Masson et Cie, Paris, 1969, pp 326–339; R. Massart and G. Hervé, *Rev. Chim. Miner.*, **5**, 521 (1968).

(23) M. T. Pope and G. M. Varga, Jr., *Inorg. Chem.*, **5**, 1249 (1966).

(24) P. Stonehart, J. G. Koren, and J. S. Brinen, *Anal. Chim. Acta*, **40**, 65 (1968).

(25) G. M. Varga, Jr., E. Papaconstantinou, and M. T. Pope, *Inorg. Chem.*, **9**, 662 (1970).

(26) M. T. Pope, D. P. Smith, J. J. Altenau, and J. Bender, *Proc. Int. Conf. Coord. Chem., 13th*, **1**, 127 (1970).

(27) The nonreducibility of type II anions is consistent with the observation that there are no authenticated examples of *cis*-$MO_2L_4^{n-}$ complexes where M has a d^1 configuration: W. P. Griffith, *Coord. Chem. Rev.*, **5**, 459 (1970). Griffith has suggested that this may be a consequence of the participation of the metal's t_{2g} orbitals in π bonding to the cis oxo groups.

(28) See ref 23–27 ($XM_{12}O_{40}^{n-}$ and $X_2M_{18}O_{62}^{6-}$); C. M. Flynn, Jr., H. So, and M. T. Pope, in preparation ($M_6O_{19}^{n-}$); S. Ostrowetsky, *Bull. Soc. Chim. Fr.*, 1018 (1964) ($V_{10}O_{28}^{6-}$).

(29) Although $Mo_7O_{24}^{6-}$ cannot be chemically reduced without decomposition, γ irradiation of the ammonium salt produces NH_3^+ and Mo(V) centers. Since the esr signal due to the latter species is isotropic at liquid nitrogen temperatues and shows superhyperfine structure, it is possible that the anion structure remains more or less intact following irradiation at these temperatures: I. Pascaru, O. Constantinescu, M. Constantinescu, and D. Arizan, *J. Chim. Phys.*, **62**, 1283 (1965).

(30) D. L. Kepert, *Progr. Inorg. Chem.*, **4**, 199 (1962); J. Aveston, *Inorg. Chem.*, **3**, 981 (1964); O. W. Rollins, Ph.D. Thesis, Georgetown University, 1965.

(31) P. Souchay and A. Tézé, *C. R. Acad. Sci., Ser. C*, **268**, 804 (1969).

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(33) F. Chauveau, M. Boyer, and B. Le-Meur, *C. R. Acad. Sci., Ser. C*, **268**, 479 (1969); F. Chauveau, private communication, 1971.

(34) Both of these anions are isolated from relatively acidic solutions. For this reason also, type I structures (since they contain fewer oxygen atoms per M atom than do type II) are likely.

(35) S. Ostrowetsky, *Bull. Soc. Chim. Fr.*, 1003 (1964).

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(37) J. Fuchs and K. Jahr, *Z. Natursforsch. B*, **23**, 1380 (1968).

(38) The structure proposed for the (reducible) heteropolyvanadate $MnV_{13}O_{38}^{7-}$ is type III, however: C. M. Flynn, Jr., and M. T. Pope, *J. Amer. Chem. Soc.*, **92**, 85 (1970).

(39) K. Eriks, private communication, 1970; H. H. K. Hau and K. Eriks, Abstracts, American Crystallographic Association Meeting, New Orleans, La., 1970, No. P10.

(40) R. D. Peacock and T. J. R. Weakley, *J. Chem. Soc. A*, 1836 (1971).

(41) A sabbatical leave (1970–1971) spent in the Department of Inorganic Chemistry, Technical University of Vienna, was supported in part by a Type D grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Hückel-Type Rules and the Systematization of Borane and Heteroborane Chemistry

Sir:

This correspondence deals with some theoretical justification for two empirical concepts which in our opinion allow for a conceptually simple systematization of boranes, carboranes, and heteroboranes. One concept correlates the structures of the known boranes and heteroboranes to a "parent" series of closo molecules[1] whose geometries are closely approximated by regular deltahedra (Figure 1, column 1)[2] and from which the nido[1] and arachno[1] series can be derived (Figure 1, columns 2 and 3, respectively). The second concept

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(1) R. E. Williams, *Inorg. Chem.*, **10**, 210 (1971).

(2) A deltahedron is a polyhedron whose faces are equilateral triangles.