configuration, whereas nitrosyls can exist in either a linear or a bent structure and metal dioxygen adducts can exhibit either a bent or a triangular structure.

(19) The larger discrepancy for **2** can be attributed to the mixing of the symmetrical Co–O stretching mode into the O–O stretching frequency which has been suggested for other triangular MO_2 bonding. See A. Nakamura, Y. Tatsuno, M. Yamamoto, and S. Otsuka, *J. Am. Chem. Soc.*, **93**, 6052 (1971).

(20) (a) B. S. Tovrog and R. S. Drago, *J. Am. Chem. Soc.*, **96**, 6766 (1974); (b) B. M. Hoffman, T. Szymanski, and F. Basolo, *ibid.*, **97**, 673 (1975).

(21) J. H. Burness, J. G. Dillard, and L. T. Taylor, *J. Am. Chem. Soc.*, **97**, 6080 (1975).

(22) The dioxygen π_x, π_y, π_x^*, π_y^* orbital occupancies (n) are 1.962, 2.000, 1.684, 1.108 for **1** and 1.677, 1.994, 0.981, 1.998 for **2**, respectively.

(23) B. K. Teo, A. P. Ginsberg, and J. C. Calabrese, *J. Am. Chem. Soc.*, **98**, 3027 (1976).

(24) L. Vaska and D. L. Catone, *J. Am. Chem. Soc.*, **88**, 5324 (1966).

(25) (a) J. A. McGinnety, N. C. Payne, and J. A. Ibers, *J. Am. Chem. Soc.*, **91**, 6301 (1969); (b) M. J. Nolte, E. Singleton, and M. Laing, *ibid.*, **97**, 6396 (1975).

(26) W. D. Bonds and J. A. Ibers, *J. Am. Chem. Soc.*, **94**, 3413 (1972).

(27) A. P. Ginsberg and W. E. Lindsell, *Chem. Commun.*, 232 (1971).

(28) A different description of the isosceles triangular PtO_2 bonding in $Pt(PH_3)_2O_2$ based on SCF-Xα-SW calculations was reported by J. G. Norman, Jr., *J. Am. Chem. Soc.*, **96**, 3327 (1974). It was found that "a buildup of extra antibonding electron density in the π^* orbitals arises not through direct Pt d$\pi \rightarrow O_2\ \pi^*$ back-donation but in some more subtle reorganization of electrons throughout the Pt, PH_3 and O_2 components".

Correspondence

Structural Isomers of 1:12 and 2:18 Heteropoly Anions. Novel and Unexpected Chirality

AIC50813Q

Sir:

A few years ago Baker and Figgis[1] suggested a number of structural possibilities that could account for the reported existence of pairs of isomers of 1:12 (Keggin[2]) and 2:18 (Dawson[3]) heteropoly anions. More recently Sasaki and co-workers[4,5] have shown that the structures of the so-called β isomer of $SiW_{12}O_{40}^{4-}$ and the so-called α (or A) isomer of $P_2W_{18}O_{62}^{6-}$ were among those suggested by Baker and Figgis. The purposes of the present communication are (1) to comment on the relative stability of two of the five Baker–Figgis structures for the 1:12 anions, (2) to recommend reversing the α–β nomenclature of the two known isomers of $P_2W_{18}O_{62}^{6-}$ in order to avoid confusion, and (3) to point out that a highly unusual and subtle type of chirality is exhibited by the 1:9 ("half-unit") and α 2:18 anions, and that the β 2:18 isomer is a meso (*dl*) species.

The five Baker–Figgis structures (I–V) are illustrated in Figure 1. Structure I is the well-known Keggin anion observed in α-$K_4SiW_{12}O_{40}\cdot 17H_2O$[6] and numerous other 12-molybdo and 12-tungsto salts and acids.[7-9] Structure II, in which one edge-shared M_3O_{13} group has been rotated by 60°, is the structure of the β isomer of $SiW_{12}O_{40}^{4-}$ determined by Yamamura and Sasaki.[4] In structures III–V, two, three, and four M_3O_{13} groups, respectively, have undergone 60° rotations. As a consequence of these rotations, the M_3O_{13} groups, which in I and II are linked by corner sharing only, become linked by edges. The tungsten and molybdenum atoms in poly anions are always strongly displaced toward the unshared vertices of their respective octahedra. Such displacements can be regarded as alleviating electrostatic repulsions between neighboring metal ions or as facilitating terminal oxygen–metal π bonding.[10] The gradual replacement of 12 corner-shared links in I and II with one to six edge-shared links in III–V has the effect of forcing the metal atoms closer together in the latter structures. The differences are significant: typical metal–metal separations in Keggin anions are 3.42 Å (edge-shared octahedra) and 3.70 Å (corner-shared octahedra).[8] On electrostatic grounds, therefore, structures III–V are much less favorable than I and II which should be of approximately equal energy. It is noteworthy that all reported isomerisms of 1:12 heteropoly anions,[11-15] with one possible exception,[16] involve structures I and II. Structure I, corresponding to the so-called α isomer, appears to be thermodynamically more stable than structure II (the β isomer) inasmuch as all observed isomerizations of nonreduced[17] anions proceed in the direction β → α. It also appears to be generally true that the β isomers undergo reduction at potentials that are more positive (by ca. 50 mV) than those of the corresponding α isomers.

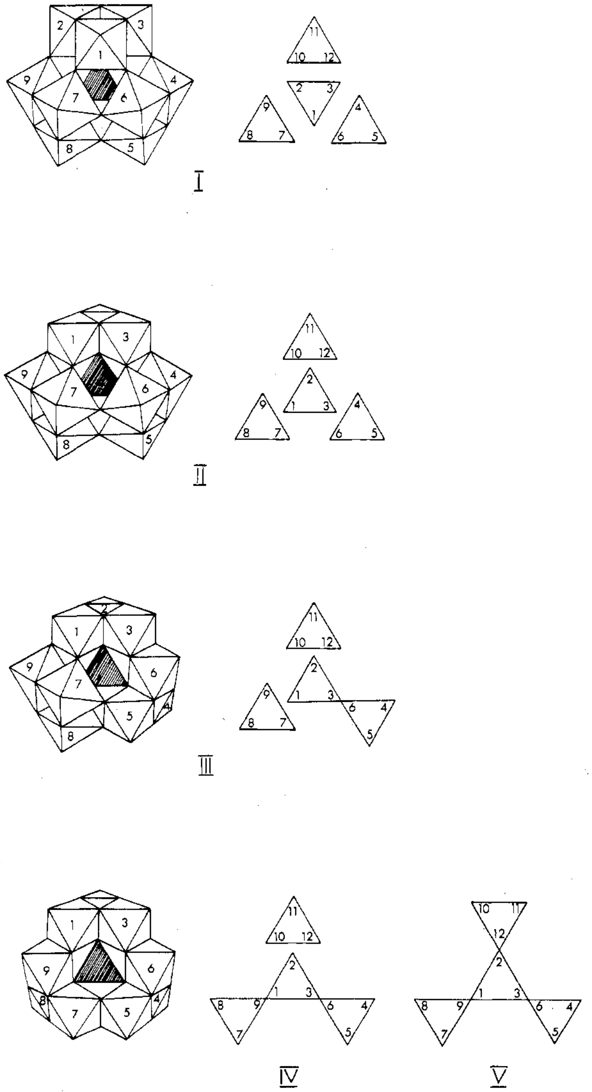

Figure 1. The five isomeric possibilities for $XM_{12}O_{40}$ structures suggested by Baker and Figgis.[1] In the polyhedral representations, the fourth M_3O_{13} group (octahedra 10, 11, and 12) at the back of the structure has been omitted for clarity. Thus IV and V appear to be the same. The numbering system and the representations of unfolded structures in terms of edge-shared octahedral links are taken from ref 29.

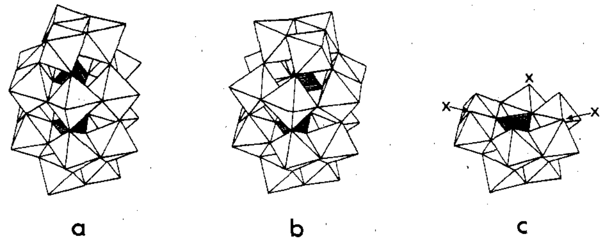

Figure 2. (a) Structure of α-$X_2M_{18}O_{62}$ anions (Dawson;[3] Wu's B form). (b) Structure of β-$X_2M_{18}O_{62}$ anions (Matsumoto and Sasaki;[5] Wu's A form). (c) Structure of $PMo_9O_{31}(OH_2)_3^{3-}$ (Strandberg[21]). Vertices marked by crosses indicate the locations of the coordinated water molecules that impart chirality to the anion.

With the 2:18 series of heteropoly anions the situation is a little more confusing. Isomers of $P_2W_{18}O_{62}^{6-}$ were labeled "A" and "B" by Wu and earlier workers,[18] but unfortunately these labels have recently been transliterated into α and β. The structure of B-$P_2W_{18}O_{62}^{6-}$ in $K_6P_2W_{18}O_{62}\cdot 14H_2O$ was determined by Dawson[3] and is identical with the structure of the stable form of $P_2Mo_{18}O_{62}^{6-}$ in $Na_6P_2Mo_{18}O_{62}\cdot 24H_2O$ recently determined by Strandberg.[19] Souchay, Contant, and Fruchart[14] have shown that unstable isomers of $P_2Mo_{18}O_{62}^{6-}$ and $As_2Mo_{18}O_{62}^{6-}$ exist and that these are reduced at more positive potentials than the stable forms (to which they spontaneously isomerize in solution). Following the accepted nomenclature for the 1:12 anions, the stable and unstable isomers were labeled α and β, respectively. Clearly the Dawson and Strandberg structures are of α isomers (the Dawson anion is reduced at a more negative potential than the "A" isomer[20]), and I therefore propose that the A and B forms of $P_2W_{18}O_{62}^{6-}$ be relabeled β and α, respectively, so that both molybdate and tungstate 1:12 and 2:18 series have a consistent nomenclature.

The structure of the β 2:18 isomer[4] is shown in Figure 2b and it differs from that of the α isomer[3,19] (Figure 2a) by rotation of half of the structure by 60°. As is well known,[3] the half-unit for the 2:18 structure is formally derived from the α 1:12 structure by removal of one MO_6 octahedron from each of three M_3O_{13} edge-shared groups; see Figure 2c. Strandberg[21] and d'Amour and Allman[22] have independently reported the crystal structure of the sodium salt of a 9-molybdophosphate anion, $Na_3H_6PMo_9O_{34}\cdot xH_2O$, crystallizable from acidic solutions, which has just this structure. Three of the terminal Mo–O bonds in this anion are abnormally long (2.21 Å) and this indicates to me that water molecules are coordinated at these sites.[23] Such a feature has never before been observed in a heteropoly or isopoly anion but would account for the ready dimerization

$$2[PMo_9O_{31}(OH_2)_3]^{3-} \rightarrow [P_2Mo_{18}O_{62}]^{6-} + 6H_2O$$

It is significant that both 1:9 and 2:18 anions can be crystallized from solutions of the same composition and acidity.

It does not seem to have been noted that the nondisordered locations of the coordinated water molecules in $PMo_9O_{31}(OH_2)_3^{3-}$ render the anion chiral (Figure 2c).[24] The chirality of the anion is reinforced by a sequence of oxygen atom displacements (cooperative trans effects?) that can be considered to have been induced by protonation at any one of the vertices labeled × in Figure 2c. These displacements result in a significant alternation in bond lengths for the three sequences of trans-related Mo–O bonds that run from any vertex, ×, to the corresponding unlabeled vertex on the opposite side of the ring of six edge- and corner-shared octahedra. The lengths of the Mo–O bonds are 2.21 (vertex with H_2O), 1.81, 2.07, 1.83, 2.08, 1.78, 2.26, and 1.70 Å (vertex without H_2O). That water molecules are attached only to alternate octahedra is therefore seen to be no accident.[25] In order to form the α 2:18 structure two *d* or two *l* enantiomers must be coupled, and it is interesting to note that the resulting dimer remains chiral. The six oxygen atoms common to both halves of the structure do not lie in a plane but are displaced alternately about 0.18 Å on either side,[19] and each is part of a continuous loop of trans-related Mo–O bonds that are alternately "short" and "long" as in the 1:9 structure.[26] The effective symmetry of the anion is thereby reduced from D_{3h} to D_3.

The β 2:18 structure is now seen to be a meso form which results from the combination of both enantiomers of the 1:9 anions. The $d + l$ (β) combination is less favorable than $d + d$ and $l + l$ because of the uneven matching between edge- and corner-shared MoO_6 octahedra of the two half-units.

Baker and Figgis considered other possibilities for isomerism of 2:18 anions in which one or both half-units had been derived from the β 1:12 structure. These structures have not been observed, most probably for kinetic reasons. Isomerization rates for β 1:12 anions increase with the extent of protonation of the anion.[27] Since the 2:18 anions must be synthesized in strongly acid solutions, it is unlikely that significant concentrations of a β form of the 1:9 precursor anion would survive.[28]

Note Added in Proof. A recent determination of the structures of $Na_4H_2[P_2Mo_{18}O_{62}]\cdot nH_2O$ and $(NH_4)_6[P_2W_{18}O_{62}]\cdot 9H_2O$ (α isomer) confirms Strandberg's results for the molybdate, but shows that the "chiral" distortion of the tungstate is much less pronounced.[30]

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References and Notes

(1) L. C. W. Baker and J. S. Figgis, *J. Am. Chem. Soc.*, **92**, 3794 (1970).
(2) J. F. Keggin, *Proc. R. Soc. London, Ser. A*, *A***144**, 75 (1934).
(3) B. Dawson, *Acta Crystallogr.*, **6**, 113 (1953).
(4) K. Yamamura and Y. Sasaki, *J. Chem. Soc., Chem. Commun.*, 648 (1973).
(5) K. Y. Matsumoto and Y. Sasaki, *J. Chem. Soc., Chem. Commun.*, 691 (1975).
(6) P. M. Smith, Ph.D. Thesis, Georgetown University, 1972; *Diss. Abstr. Int. B*, **32**, 5136 (1972).
(7) H. T. Evans, Jr., *Perspect. Struct. Chem.*, **4**, 1 (1971), and references cited therein.
(8) R. Strandberg, *Acta Chem. Scand., Ser. A*, **29**, 359 (1975).
(9) A. Kobayashi and Y. Sasaki, *Kagaku To Kogyo (Tokyo)*, **48**, 885 (1975).
(10) M. T. Pope, *Inorg. Chem.*, **11**, 1973 (1972).
(11) "Gmelins Handbuch der Anorganischen Chemie", System No. 54, Verlag Chemie, Berlin, 1933, pp 327–328, 340–345.
(12) P. Souchay, *Bull. Soc. Chim. Fr.*, 365 (1951).
(13) J. D. H. Strickland, *J. Am. Chem. Soc.*, **74**, 868 (1952).
(14) P. Souchay, R. Contant, and J. M. Fruchart, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **264**, 976 (1967); J. M. Fruchart and P. Souchay, *ibid.*, **266**, 1571 (1968); R. Contant, *ibid.*, **267**, 1479 (1968).
(15) J. P. Launay, M. Boyer, and F. Chauveau, *J. Inorg. Nucl. Chem.*, **38**, 243 (1976).
(16) The second (non-α) isomer of 12-tungstoboric acid does not appear to have structure II according to recent solution studies: G. Herve and A. Tézé, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **278**, 1417 (1974). It was provisionally labeled *h*-$BW_{12}O_{40}^{5-}$ by these authors, and the possibility exists that, if this compound proves to be a true isomer, it has one of the structures III–V.
(17) With the reduced (heteropoly blue) anions the β structure appears to become the more stable form.
(18) H. Wu, *J. Biol. Chem.*, **43**, 189 (1920); F. Kehrmann, *Ber. Dtsch. Chem. Ges.*, **20**, 1805 (1887).
(19) R. Strandberg, *Acta Chem. Scand., Ser. A*, **29**, 350 (1975).
(20) M. T. Pope and E. Papaconstantinou, *Inorg. Chem.*, **6**, 1147 (1967).
(21) R. Strandberg, *Acta Chem. Scand., Ser. A*, *A***28**, 217 (1974).
(22) H. d'Amour and R. Allman, *Naturwissenschaften*, **61**, 31 (1974).
(23) The other (12) terminal Mo–O bond lengths in this structure fall in the range 1.70–1.71 Å. The bond length for Mo–OH_2 in $MoO_3\cdot 2H_2O$ is 2.288 Å: B. Krebs, *Acta Crystallogr., Sect. B*, **28**, 2222 (1972). Bond lengths for Mo–OH and Mo–OH_2 in $[MoO(OH)(CN)_4]^{3-}$ and $[MoO(OH_2)(CN)_4]^{2-}$ anions are 2.077 and 2.271 Å, respectively: P. R. Robinson, E. O. Schlemper, and R. K. Murmann, *Inorg. Chem.*, **14**, 2035 (1975).

(24) The salt crystallizes in the chiral space group $P6_3$ but Strandberg[21] did not record whether he determined the absolute configuration of the anion in the crystal he studied.

(25) The three trans Mo(IV) complexes $MoO_2(CN)_4^{4-}$, $MoO(OH)(CN)_4^{3-}$, and $MoO(OH_2)(CN)_4^{2-}$ illustrate the principle involved. Protonation of one oxygen increases the Mo–O(–H) bond length and shortens the bond to the trans oxygen, thereby decreasing the basicity of the latter. Consequently the second proton becomes bound to the hydroxo oxygen: P. R. Robinson et al., *Inorg. Chem.*, **14**, 2035 (1975). The structure of $PMo_9O_{34}H_6^{3-}$ is such that similar bond length changes can be transmitted through several metal atoms.

(26) Starting at one of the "equatorial" oxygen atoms the sequence of Mo–O bond lengths is 2.12, 1.78, 2.07, 1.83, 2.03, 1.77, 2.14, 1.75, 2.12, 1.78, 2.06, 1.84, 2.05, 1.77, 2.14, and 1.76 Å. There are three such sequences in the whole structure.

(27) R. Massart, *Ann. Chim. (Paris)*, **3**, 507 (1968).

(28) Other 1:9 anions, which are *not* the same as the precursor species described here, have been reported recently: R. Contant, J. M. Fruchart, G. Hervé, and A. Tézé, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **278**, 199 (1974). The new anions (two isomers of each) are obtained by *alkaline* hydrolysis of α and β isomers of 1:12 anions and may have structures resulting from removal of a complete M_3O_{13} group.

(29) M. T. Pope and T. F. Scully, *Inorg. Chem.*, **14**, 953 (1975).

(30) H. d'Amour, *Acta Crystallogr., Sect. B*, **32**, 729 (1976).

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Interpretation of Isosbestic Points

AIC50883X

Sir:

The significance of the existence, or lack thereof, of an isosbestic point in systems containing three or more absorbing species is deceptively complex. In a recent article[1] incorrect criteria were offered for recognizing systems in which an isosbestic point exists. [We ignore the possibility of accidental occurrence of isosbestic points due to fortuitous combinations of extinction coefficients at some wavelength. A consideration of this problem, conditions under which it occurs, and a method for determining if the isosbestic point is accidental by the method of forming ξ curves from the sum of spectral lines with shifted wavelength axes have been discussed by Kwiatkowski.[5]] The stated criteria for the existence of an isosbestic point are that "2 + N species may be present providing there are N relations between the concentrations of these species and these relations are independent of the parameter being varied". A series of consecutive equilibria

$$A + B \rightarrow AB \tag{1}$$

$$AB + B \rightarrow AB_2 \tag{2}$$

provides the classic example in which the lack of an isosbestic point is used to infer[2] the simultaneous existence of more than two absorbing species, A, AB, and AB_2. Yet this system satisfies the above criteria offered[1] for the existence of an isosbestic point. In this system, there are three absorbing species, so we need find only one relation ($N = 1$) which is independent of B. This relation is given by the ratio of the two equilibrium constants for eq 1 and 2

$$K_1/K_2 = [AB]^2/[A][AB_2] \tag{3}$$

Clearly, the above criteria would predict an isosbestic point in this classic example where one is not obtained.

Another example of the failure of the Stynes criteria[1] is a system in which two different acids A and A′ are competing for a single base B

$$A + B \rightarrow AB \tag{4}$$

$$A' + B \rightarrow A'B \tag{5}$$

The four absorbing species are A, A′, AB, and A′B. A series of solutions is investigated in which the initial concentrations of A and A′ are held constant and B is varied. With four absorbing species, N equals 2 and the two relationships independent of the quantity being varied, B, are

$$[A'] + [A'B] = k'$$

$$[A] + [AB] = k \tag{6}$$

An isosbestic point will not result as B is varied even though there are two "relationships between the absorbing species".[1]

A correct set of criteria for the existence of an isosbestic point can be best illustrated by considering an ambidentate donor, the system treated by Stynes.[1] For example, if a basic molecule containing nitrogen and oxygen donor atoms were able to coordinate to an acid, A, to produce either an oxygen-bound complex or a nitrogen-bound complex, the mixture of complexes AN (nitrogen bound), AO (oxygen bound), and free A (an absorbing Lewis acid) would give rise to an isosbestic point. The absorbance (A) for such a system is given by

$$A = \epsilon_A[A] + \epsilon_N[AN] + \epsilon_O[AO] \tag{7}$$

The equilibrium constant expressions are given by

$$K_O = [AO]/[A][B]$$

$$K_N = [AN]/[A][B]$$

$$K_O + K_N = \frac{[AO] + [AN]}{[A][B]} = \frac{[AB]}{[A][B]} \tag{8}$$

where we define $[AO] + [AN] = [AB]$. The fraction of complex, X_O, which is oxygen coordinated, is given by

$$X_O = \frac{K_O}{K_O + K_N} = \frac{[AO]/[A][B]}{[AB]/[A][B]} = \frac{[AO]}{[AB]} \tag{9}$$

The fraction which is nitrogen coordinated is similarly derived to be

$$X_N = [AN]/[AB] \tag{10}$$

Now the total absorbance becomes

$$A = \epsilon_A[A] + \epsilon_O X_O[AB] + \epsilon_N X_N[AB]$$

or

$$A = \epsilon_A[A] + (\epsilon_O X_O + \epsilon_N X_N)[AB] = \epsilon_A[A] + \epsilon'[AB] \tag{11}$$

Since the sum of [A] and [AB] is a constant and there must be a place in overlapping spectra where $\epsilon_A = \epsilon'$, an isosbestic point will be obtained even though three absorbing species exist.

We have taken two absorbing species whose ratio is a constant independent of the parameter being varied and translated them to what is effectively a single absorbing species via eq 11. The general criteria thus are that 2 + N absorbing species will give rise to an isosbestic point if there are N *independent* equations of the form

$$[Y]/[Z] = k$$

where Y and Z are two of the absorbing species in the system and the value of k is independent of the parameter being varied.

As an example of the application of these criteria, consider an acid which can form two isomers with a base AB and A^*B—e.g., $Cu(hfac)_2$[3] which forms basal and apical adducts—forming an adduct with a base that can form two isomers with an acid AB and AB^*—e.g., N-methylimidazole[4] bound through the amine and imine nitrogen. Five absorbing species (A, AB, A^*B, AB^*, A^*B^*) can exist