Table III. Electronic Spectrum (cm^{-1}) for $(t\text{-BuPCl}_3)_2(\text{Re}_3\text{Cl}_9)(\text{ReCl}_6)$

295 K	90 K	Assignments[7,8,13]
(5 900)[a]	(6 000)	
(6 600)	(6 600)	
6 700	6 700	ReCl_6^{2-} ($^4A_{2g} \rightarrow {}^2T_{1g}$)?
	(6 800)	
(8 600)	(8 800)	ReCl_6^{2-} ($^4A_{2g} \rightarrow {}^2E_g$)
9 500	9 500	ReCl_6^{2-} ($^4A_{2g} \rightarrow {}^2T_{2g}$)
(10 200)	10 300	Re_3Cl_9
	10 600	
(11 500)	(11 500)	
	(12 100)	
	(12 500)	
	14 200	ReCl_6^{2-} ($^4A_{2g} \rightarrow {}^2T_{2g}$); Re_3Cl_9
15 000	(14 800)	ReCl_6^{2-} ($^4A_{2g} \rightarrow {}^2T_{2g}$)
	(17 500)	
18 300	18 400	Re_3Cl_9
	(21 500)	
	(23 800)	
25 000	25 500	Re_3Cl_9
28 000	27 800	
32 000	32 000	
33 400	33 300	
38 000	37 500	
45 500	45 400	

[a] Parentheses indicate shoulders.

group centred on m/e 878 were the strongest (Re_3Cl_9^+ 877.77) so that 878 was used as the parent peak. This group was analyzed in terms of the isotopic abundances and excellent agreement was found between the calculated and observed intensities for m/e 870–894.

The mass spectrum and assignments agree well with the reported spectra[11,12] for rhenium(III) chloride (Re_3Cl_9) in which several low molecular weight (201–314) fragments containing oxygen have been observed. These were reproduced on handling $(t\text{-Bu})_2\text{P}_2\text{Re}_4\text{Cl}_{21}$ in the air, but if the sample probe was filled under nitrogen, the oxygen-free spectrum was observed. Bromine-containing fragments were also recognized.

Electronic Spectrum (Table III). There was reasonably good agreement between the reflectance spectrum and that expected for ReCl_6^{2-} + Re_3Cl_9.[7,8,13] Most of the low-frequency, spin-forbidden bands for ReCl_6^{2-} were sharp but one (6700 cm^{-1}) was at lower frequency than is usually observed. The spectra[7,8] for Re_3Cl_9 show three or four regions of absorption below 26 000 cm^{-1}. Only the one near 14 000 cm^{-1} was doubtful as ReCl_6^{2-} also absorbs here. There was no evidence to suppose that $\text{Re}_2\text{Cl}_8^{2-}$, Re_2Cl_9^-, or $\text{Re}_2\text{Cl}_9^{2-}$ was present.[14,15] This confirmed the mass and ir spectral assignments.

Preparative Route. The use of phosphorus(III) chloride can result in reduction of the metal ion, e.g., in WCl_6^- prepared from[3] WCl_6 and in our unpublished observations of MoCl_5. In the present work, $\text{Re}_2\text{Cl}_{10}$ was reduced at room temperature to give ReCl_6^{2-} and the Re_3 cluster directly. Thermal methods may be used[16] for the conversion of Re_2X_{10} (X = Cl, Br) to Re_3X_9 which is then followed by reactions which yield other Re_3 cluster compounds.

Acknowledgment. This work was supported in part by grants from the Science Research Council and the Defence Research Board of Canada (Grant No. 9530-102).

Registry No. $(t\text{-BuPCl}_3)_2(\text{Re}_3\text{Cl}_9)(\text{ReCl}_6)$, 59492-78-3.

References and Notes

(1) (a) The University of Surrey. (b) The Royal Military College of Canada.
(2) Part 3: J. I. Bullock, F. W. Parrett, and N. J. Taylor, *Can. J. Chem.*, **52**, 2880 (1974).
(3) J. I. Bullock, F. W. Parrett, and N. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 522 (1973).
(4) J. I. Bullock, F. W. Parrett, and N. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 1843 (1972).
(5) F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, **4**, 59 (1965).
(6) M. Debeau and H. Poulet, *Spectrochim. Acta, Part A*, **25**, 1553 (1969).
(7) F. A. Cotton and J. T. Mague, *Inorg. Chem.*, **3**, 1402 (1964).
(8) M. A. Bush, P. M. Druce, and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 500 (1972).
(9) K. I. Petrov and V. V. Kravchenko, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **16**, 930 (1971).
(10) D. G. Tisley and R. A. Walton, *Inorg. Nucl. Chem. Lett.*, **6**, 479 (1970).
(11) K. Rinke and H. Schafer, *Angew. Chem.*, **77**, 131 (1965).
(12) A. Buchler, P. E. Blackburn, and J. L. Stauffer, *J. Phys. Chem.*, **70**, 685 (1966).
(13) P. B. Dorain, *Transition Met. Chem.*, **4**, 1 (1968).
(14) F. Bonati and F. A. Cotton, *Inorg. Chem.*, **6**, 1353 (1967).
(15) F. A. Cotton, W. R. Robinson, and R. A. Walton, *Inorg. Chem.*, **6**, 223 (1967).
(16) J. E. Fergusson, *Prep. Inorg. React.*, **7**, 137–152 (1971).

Contribution from Bell Laboratories, Murray Hill,
New Jersey 07974 and the Department of Chemistry,
The Chinese University of Hong Kong,
Shatin, N.T., Hong Kong

Linear, Bent, and Triangular M–O$_2$ Bonding in Some Dioxygen Complexes of Cobalt

Boon-Keng Teo* and Wai-Kee Li

Received January 7, 1976 AIC600123

Chemical bonding of dioxygen to five- and four-coordinated metal complexes, using $[\text{Co(CN)}_5\text{O}_2]^{3-}$ (**1**)[1] and $[\text{Co(PR}_3)_4\text{O}_2]^+$ (**2**)[2] as model systems, is explored in this note with the hope of discerning the driving force for bent vs. triangular Co–O$_2$ configurations, respectively. These two geometries are of particular interest in that they are related to the two alternative structures, viz., bent and triangular, first proposed by Pauling[3] and Griffith,[4] respectively, for the Fe–O$_2$ bonding in oxyhemoglobin and oxymyoglobin.

The Fenske–Hall parameter-free MO model[5] was employed in this work. The basis functions were those utilized previously.[5b,c] For phosphorus, only 1s to 3p atomic orbitals are included in the calculations. The pertinent molecular parameters were taken from the known structures of $[\text{Co(CN)}_5\text{O}_2]^{3-}$ [1b] and $[\text{Co(Ph}_2\text{PCH{=}CHPPh}_2)_2\text{O}_2]^+$.[2] In particular, the Co–O and O–O distances chosen are 1.93 and 1.26 Å, and 1.89 and 1.42 Å, for **1** and **2**, respectively. The calculated one-electron molecular orbital energies as a function of the Co–O–O angle (θ) for **1** and **2** are shown in Figures 1 and 2, respectively.

These diagrams indicate that **1** favors a bent structure because of the steep energetic valley of π_x^* at $\theta \approx 132°$ whereas **2** prefers an isosceles triangular structure as a result of the large slope of xz at $\theta \approx 69°$. The reason for this difference is the relative energetic ordering of the metal z^2 orbital with respect to the dioxygen π^* orbitals.[6,7] In **1**, z^2 lies above π^* so that as θ decreases, π_x^* declines rapidly in energy due to both the decrease in its *antibonding* interaction with xz (which lies lower in energy) and the increase in the *bonding* interaction with z^2 (which lies higher in energy).[8] The latter interaction is symmetry forbidden in either linear or triangular configuration. Below $\theta \approx 132°$, π_x^* rises steeply in energy due to the reacquired, enhanced antibonding interaction with xz. The π_y^* orbital exhibits only a slight minimum since π_y^* is perpendicular to the plane of bending. The net result is a Walsh minimum[11a] corresponding to a bent configuration at $\theta \approx 132°$ for $\text{M(d}^6)\text{–O}_2^{(n-2)-}(\pi^{*n})$ where $n = 3$ for [Co-

---

* To whom correspondence should be addressed at Bell Laboratories.

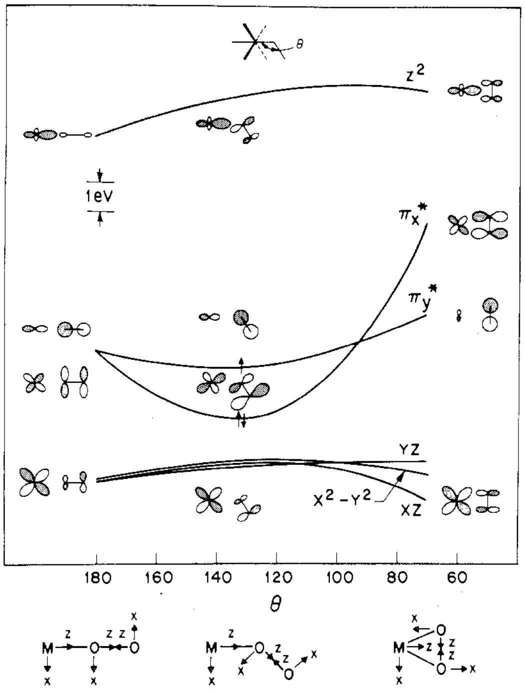


Figure 1. Calculated orbital energies of $[Co(CN)_5O_2]^{3-}$ as a function of bending. The size of individual orbitals corresponds schematically to their percent characters.

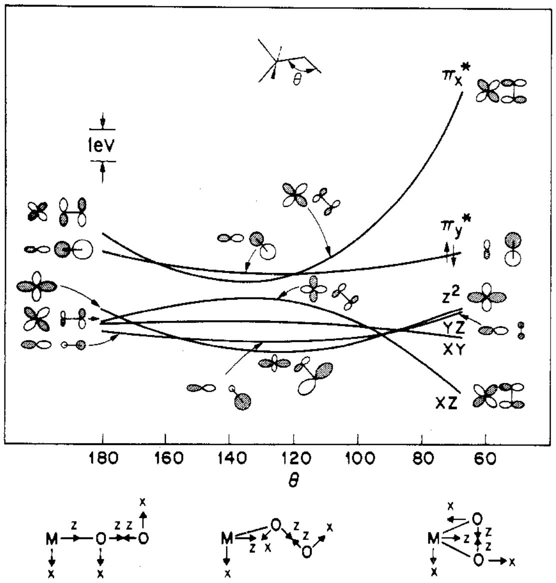
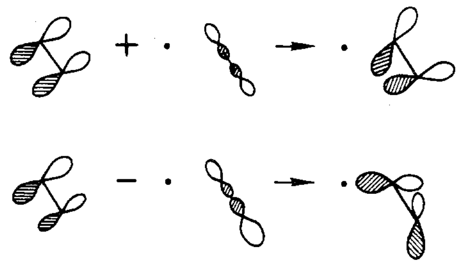


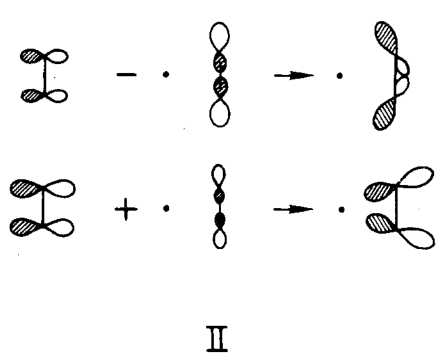
Figure 2. Calculated orbital energies of $[Co(PH_3)_4O_2]^+$ as a function of bending. The size of individual orbitals corresponds schematically to their percent characters.

$(CN)_5O_2]^{3-}$ (obsd $\theta = 153°$),[1b] $Co(acacen)(B)O_2$,[12] Co(bzacen)(py)O_2 ($\theta = 126°$),[13] and $Co(TPP)(B)O_2$[14] (i.e., Co(III)–O_2^-), and $n = 2$ for $Fe(TPP)(B)(O_2)$ ($\theta = 136°$)[15] (i.e., Fe(II)–O_2). On the other hand, for **2**, z^2 generally lies below π^* because of the lack of antibonding interaction associated with the σ orbital on the sixth coordination site as well as the fact that two of the ligands (equatorial with respect to the dioxygen) lie near the nodal surface of z^2. As θ decreases ($180° \gtrsim \theta \gtrsim 132°$), the major energetic factors are the following. (1) z^2 is stabilized by the acquired bonding interaction with π_x^* which is symmetry forbidden in either linear or triangular configuration. This orbital contains substantial dioxygen character (21% z^2 + 11% x + 56% x', x' being on the uncoordinated oxygen, O′) in the bent ($\theta \approx 132°$) configuration.[16] (2) xz is destabilized due to the combined effect of the loss of the bonding interaction with π_x^* and the increase in antibonding interaction with the same dioxygen orbital as a result of the concerted rotation of the metal orbital. At $\theta \approx 132°$, the metal orbital looks like $x^2 - z^2$ (64% ($x^2 - z^2$) + 12% xz + 4% x + 6% x'). (3) π_x^* drops in energy due to the decreasing antibonding interaction with xz and the concomitant change in orbital character (60% xz + 8% x + 10% x' for the bent structure). The consequence of all these factors is that there is no significant energetic difference between the linear and the bent form. Below $\theta \approx 132°$, however, xz declines steeply while π_x^* rises abruptly as a result of the strong interaction between these two orbitals. The z^2 orbital, on the other hand, with its bonding interaction diminishing, raises its energy slightly and regains its identity. Thus, the Walsh diagram favors an isosceles triangular structure[11b] (cf. Figure 2).

Below the filled levels shown in Figures 1 and 2 are the dioxygen π_x, π_y, and σ_g (symmetrical combination of the "lone pairs") orbitals as well as the σ-type Co–L (where L = CN in **1** and PH_3 in **2**) bonding orbitals. Considerable mixing of these orbitals of the same symmetry representation occurs. This presumably provides an effective pathway for both inter- and intra-ligand charge redistribution via the metal orbitals.[5c] Furthermore, the π_x and the σ_g orbitals of the dioxygen exhibit extensive mixing as θ deviates from linearity. The degree of mixing maximizes at the bent configuration for **1** and at the triangular geometry for **2** as shown in I and II, respectively. In I, the *minus* combination, which is somewhat σ_g rich, lies lower in energy and donates electron density to an acceptor orbital (s, z) at the metal, forming the σ-type bond between the metal and the dioxygen group. In II, on the other hand, the *plus* combination, which is π_x abundant, lies lower in energy and donates electron density to the metal. This latter interaction is somewhat different from, albeit similar to, the Dewar–Chatt–Duncanson model[17] for metal-olefin bonding in that the oxygen "lone pairs" play an important role in the formation of the σ-type bond between the filled dioxygen donating orbital and the vacant metal acceptor orbital. In both I and II, however, the blending of π_x and σ_g orbitals serves to optimize the dioxygen–metal σ bonding.



I



II

The preceding discussion can be compared with a bonding model put forth recently by Enemark and Feltham[7] for the structurally analogous cobalt nitrosyl systems $[Co(das)_2(NCS)(NO)]^+$ (**3**) and $[Co(das)_2(NO)]^{2+}$ (**4**). They found that **3** has a bent ($\theta = 132°$) structure whereas **4** has a linear ($\theta = 178°$) Co–N–O configuration. This stereochemical valence control was explained in terms of a qualitative molecular orbital diagram[7b] similar to ours except that only θ between 180 and 120° was considered. The major differences between the two systems are: (1) **3** has two electrons in π^* whereas **1** has three; both, however, conform to a bent structure; and (2) **4**, with no electrons in the π^* of NO, adopts a linear CoNO structure whereas **2**, with two electrons in the π^* of O_2, adopts an isosceles triangular CoO_2 structure. Following Enemark and Feltham's nomenclature, **1** and **2** correspond to the bent $\{CoO_2\}^9$ $(d^6(\pi_x^*)^2(\pi_y^*)^1)$ and triangular $\{CoO_2\}^{10}$ $(d^8(\pi_y^*)^2(\pi_x^*)^0)$ groups, respectively, while **3** and **4** correspond to the bent $\{CoNO\}^8$ $(d^6(\pi_x^*)^2(\pi_y^*)^0)$ and linear $\{CoNO\}^8$ $(d^8(\pi_y^*)^0(\pi_x^*)^0)$ configurations, respectively.

An interesting implication of this work is that *no linear M–O–O linkage is likely even if the two dioxygen π^* orbitals are degenerate and housed with an equal number of electrons unless the π^* (O_2) level is raised much higher in energy with respect to the metal levels* (such that the d_π–π^* back-bonding becomes relatively unimportant)[18] *or severe steric constrain is somehow imposed.* With unequal orbital occupancies, the Jahn–Teller theorem alone rules out linearity.

The calculated Mulliken atomic charges indicate that, in both cases, the O_2 moiety is least negatively charged in the bent configuration but most in the triangular: viz., –0.63, –0.53, –0.76 in **1** and –0.41, –0.30, –0.58 in **2** for linear, bent, and triangular configurations, respectively. The similarity of the dioxygen charge (–0.53 vs. –0.58) for the two drastically different species (**1** vs. **2**), each at their observed geometry, is rather intriguing. Moreover, the results indicate that the noncoordinated oxygen (O′) atom is always substantially more negative than the coordinated one (O): –0.47, –0.44, –0.38 vs. –0.16, –0.09, –0.38 in **1** and –0.28, –0.26, –0.29 vs. –0.13, –0.03, –0.29 in **2** for linear, bent, and triangular configurations, respectively.

The Co–O, Co–O′, and O–O bondings in **1** and **2** exhibit similar trends. The Co–O overlap population (OP) changes very little in going from linear to bent configuration, but decreases drastically as it approaches the triangular structure (viz., 0.364, 0.369, 0.008 in **1** and 0.535, 0.502, 0.252 in **2**). Concomitantly, the Co–O′ overlap population indicates an initial enhancement of the repulsive interaction followed by a reversal in sign and the strengthening of attractive interaction (viz., –0.056, –0.108, 0.008 in **1** and –0.055, –0.092, 0.252 in **2**). On the other hand, the O–O bond first strengthens as the $d_\pi \rightarrow \pi^*$ back-bonding decreases due to the bending but soon weakens significantly as the $d_\pi \rightarrow \pi^*$ back-bonding regains its importance near the triangular configuration. The calculated OP's are: 0.555, 0.639, 0.517 in **1** and 0.580, 0.628, 0.529 in **2** for linear, bent, and triangular configurations, respectively.

Several correlations with experimental observations can be made. First, the approximate O–O bond orders of 1.59 for **1** and 1.35 for **2**, calculated based upon the π and π^* orbital occupancies $(1 + (n_\pi - n_{\pi^*})/2)$,[22] are in reasonable agreement with the values of 1.54 and 1.23, estimated from the "O–O" stretching frequencies of 1138[1a] and 909[2] cm^{-1}, respectively, by linear interpolation assuming a bond order of two for singlet oxygen (1484 cm^{-1}) and of unity for peroxide (738 cm^{-1}).[19]

Second, the calculated orbital character of 10.2% yz + 88.6% π_y^* for the unpaired electron in **1** at $\theta = 132°$ agrees well with the value of 10.3% d character estimated from the observed isotropic ^{59}Co hyperfine splitting of 9.8 G.[1a] Similarly, EPR studies of a series of $Co(Schiff)(B)O_2$[12] or $Co(TPP)(B)O_2$[14] complexes also indicate that the unpaired electron is localized essentially on the dioxygen moiety, suggesting a $Co(III)–O_2^-$ $(d^6(\pi_x^*)^2(\pi_y^*)^1)$ as opposed to a $Co(II)–O_2$ $(d^7(\pi_x^*)^2(\pi_y^*)^0)$ formulation,[20] though the extent of electron delocalization from cobalt to dioxygen may well depend on the electronic environment around the metal atom.[21]

Electrochemical reduction[23] of $Ir(dppe)_2X_2^+$ (X = O, S, Se)[24–27] complexes indicated that the lowest unoccupied molecular orbital is highly antibonding between the metal and the dioxygen. This is consistent with our calculated electronic configuration of $d^8(\pi_y^*)^2(\pi_x^*)^0$ for **2** with a triangular MO_2 structure where the lowest unoccupied in-plane π_x^* orbital contains 47.9% π_x^* + 41.4% xz antibonding character (cf. Figure 2).[28]

Acknowledgment. We would like to thank Professor R. F. Fenske at the University of Wisconsin (Madison) for a copy of his MO program. We are also grateful to Drs. C. J. Weschler and D. W. Murphy at Bell Laboratories for helpful discussions.

Registry No. $[Co(CN)_5O_2]^{3-}$, 12548-02-6; $[Co(PH_3)_4O_2]^+$, 59448-50-9.

References and Notes

(1) (a) D. A. White, A. J. Solodar, and M. M. Baizer, *Inorg. Chem.*, **11**, 2160 (1972). (b) The structure of **1** was initially reported by L. D. Brown and K. N. Raymond, *J. Chem. Soc., Chem. Commun.*, 470 (1974), to possess an essentially linear Co–O–O group. After completion of the present work, further refinements by the same authors (L. D. Brown and K. N. Raymond, *Inorg. Chem.*, **14**, 2595 (1975)) based upon a twofold disorder model gave a bent Co–O–O linkage of 153°. This latter value, though in better agreement with our predicted value of 132°, is, we believe, still too large compared with the range of 119–137° observed in other dioxygen adducts[12–16] containing a bent $M–O_2$ configuration.

(2) N. W. Terry, III, E. L. Amma, and L. Vaska, *J. Am. Chem. Soc.*, **94**, 653 (1972).

(3) L. Pauling, *Nature* (*London*), **203**, 182 (1964).

(4) J. S. Griffith, *Proc. R. Soc. London, Ser. A*, **235**, 23 (1956).

(5) (a) M. B. Hall and R. F. Fenske, *Inorg. Chem.*, **11**, 768 (1972); (b) M. B. Hall and R. F. Fenske, *ibid.*, **11**, 1619 (1972); (c) B. K. Teo, M. B. Hall, R. F. Fenske, and L. F. Dahl, *ibid.*, **14**, 3103 (1975); (d) R. F. Fenske and R. L. DeKock, *ibid.*, **11**, 437 (1972).

(6) Between $\theta = 180$ and 132°, the MO diagram presented here resembles that for metal nitrosyls proposed by several groups.[5d,7–10]

(7) (a) J. H. Enemark, R. D. Feltham, J. Riker-Nappier, and K. F. Bizot, *Inorg. Chem.*, **14**, 3 (1975); (b) J. H. Enemark and R. D. Feltham, *J. Am. Chem. Soc.*, **96**, 5002, 5004 (1974); (c) J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, **13**, 339 (1974).

(8) R. Hoffmann, M. M. L. Chen, M. Elian, A. R. Rossi, and D. M. P. Mingos, *Inorg. Chem.*, **13**, 2666 (1974).

(9) D. M. P. Mingos, *Inorg. Chem.*, **12**, 1209 (1973).

(10) R. Eisenberg and C. D. Meyer, *Acc. Chem. Res.*, **8**, 26 (1975).

(11) The sum of valence orbital energies agrees with the Walsh diagrams: (a) for **1**, the bent structure is 0.10 and 0.63 eV more stable than the linear and triangular ones, respectively; (b) for **2**, the triangular configuration is 0.15 and 0.16 eV more stable than the linear and bent forms, respectively. However, these differences are quite small and such factors as core–core repulsions may be of the same order.

(12) (a) B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Am. Chem. Soc.*, **92**, 61 (1970), and references cited therein; (b) F. Basolo, B. M. Hoffman, and J. A. Ibers, *Acc. Chem. Res.*, **8**, 384 (1975).

(13) G. A. Rodley and W. T. Robinson, *Nature* (*London*), **235**, 438 (1972).

(14) (a) B. B. Wayland, J. V. Minkiewicz, and M. E. Abd-Elmageed, *J. Am. Chem. Soc.*, **96**, 2795 (1974); (b) B. B. Wayland and M. E. Abd-Elmageed, *ibid.*, **96**, 4809 (1974); (c) A. Dedieu and A. Veillard, *Theor. Chim. Acta*, **36**, 231 (1975).

(15) (a) J. P. Collman, R. R. Gagne, C. A. Reed, W. T. Robinson, and G. A. Rodley, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 1326 (1974). (b) A somewhat different description was reported by W. A. Goddard, III and B. D. Olafson, *ibid.*, **72**, 2335 (1975).

(16) We thank one referee for suggesting that the reason there is a large amount of electron density on the far oxygen (O′) in the "middle orbitals" z^2 and yz in the bent form is the consequence of the "allylic" type interactions of the metal orbitals with the dioxygen π and π^* orbitals.

(17) (a) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C79 (1951); (b) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2339 (1953).

(18) For a {MXY} group, the configuration (linear, bent, or triangular) is highly dictated by (1) the relative energies of the π^* orbitals of XY with respect to the d orbitals of the metal complexes and (2) the number of electrons (n) in the π^* orbitals. Since the π^* orbital energies decrease and n generally increases along the sequence XY = CO, NO, O_2, it is not surprising to find that terminal carbonyls adopt only the linear

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.

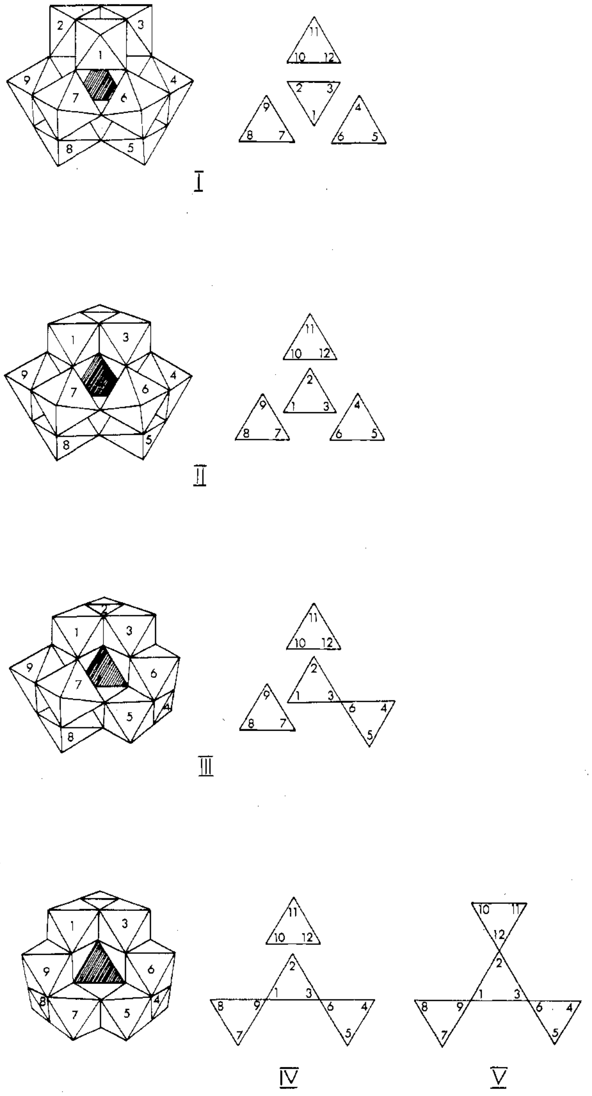


Figure 1. The five isomeric possibilities for $XM_{12}O_{40}$ structures suggested by Baker and Figgis.[1] In the polyhedral representations, the fourth M_3O_{13} group (octahedra 10, 11, and 12) at the back of the structure has been omitted for clarity. Thus IV and V appear to be the same. The numbering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