The implication from these comparisons is that there is appreciable metal character in the unpaired electron density. Some radical character is implied indirectly from the limited chemical stability of the cobalt(I) species, since such species are likely to undergo irreversible chemical reactions with solvent.[19,21,22] The ability to delocalize some electron density onto the thioether donors is also likely to be the key to the different redox chemistry between CoN_6 and CoN_3S_3 macrobicyclic complexes.

Acknowledgment. We thank Dr. M. Gunter for assistance in recording the ESR spectrum at liquid-helium temperature.

Registry No. II, 81505-65-9; IIIa, 81505-68-2; IIIb, 92490-30-7; IV, 81600-15-9; $Co(ten)^{2+}$, 92490-31-8; Co(ten), 92524-60-2; $Co(azacapten)^{2+}$, 86161-69-5; $Co(azacapten)^{+}$, 92490-36-3; $Co((NH_3^+)capten)^{3+}$, 92490-34-1; $Co((NH_3^+)capten)^{2+}$, 92490-35-2; $Co((NO_2)capten)^{2+}$, 92490-32-9; $Co((NO_2)capten)^{+}$, 92490-33-0; $Co((NO)capten)^{3+}$, 92490-37-4; $Co((NHOH)capten)^{3+}$, 92490-38-5; $NaClO_4$, 7601-89-0; $Me_4NOSO_2CF_3$, 25628-09-5.

Notes

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On the Nonobservability of Cubic P_8

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One of the more perplexing features of the chemistry of elemental phosphorus is the absence of any P_6 or P_8 species from the manifold of its allotropic forms.[2] This point has been underscored in a recent photoelectron spectroscopic investigation of the equilibrium $P_4 \rightleftharpoons 2P_2$.[3] No other species was detected in the vapor phase up to 1470 K. Specifically, P_8, the expected product of the dimerization of P_4, and P_6, which might be formed by the addition of P_2 to P_4, were conspicuously absent.

Exploratory semiempirical computations, using MNDO,[4] disclosed a number of P_6 and P_8 species, each at a minimum in the potential energy surface; several of them are calculated to be thermodynamically more stable than their dissociation products. The failure to observe any particular one of them could arise from either of two causes: (1) An insurmountable kinetic barrier prevents its formation. (2) Although it may be formed with relative ease, it is immediately converted to some more stable species; in the present instance, this would presumably be $(P_4)_n$, i.e. common red phosphorus.

In this paper we consider the most stable of these molecules, cubic (O_h) P_8. Possible pathways leading to other P_8 and P_6 species are presently being explored.

Ground-State Energies and Geometries

The calculated energies and geometries of P_2, P_4, and P_8 are summarized in Table I.

The reliability of the computational method is confirmed by the good agreement of the value ($\Delta H°$ = 43 kcal/mol) calculated for the equilibrium $P_4 \rightleftharpoons 2P_2$. The temperature dependence of the equilibrium constant yields $\Delta H°$ = 55 kcal/mol over the range 1170–1470 K,[3] whereas the best thermochemical value in this temperature range is 53 ± 1 kcal/mol.[5]

The value ($\Delta H°$ = −68 kcal/mol), calculated for the equilibrium $2\,P_4 \rightleftharpoons P_8$, leaves no doubt that cubic P_8 is substantially more stable than two tetrahedral P_4 molecules, as simple considerations of steric strain would suggest. Our results are confirmed to some extent by Trinquier, Malrieu, and Daudey,[6] who performed ab initio pseudopotential SCF calculations employing doubleζ basis sets and found (without inclusion of d polarization functions) cubic P_8 to be more stable than two P_4 by 10 kcal/mol. They are in conflict with those of Fluck, Pavlidou, and Janoschek,[7] who find P_8 to be unstable with respect to two P_4 molecules by some 47 kcal/mol. These authors did not optimize the P–P distance for P_8 but used the experimental value in P_4 for both molecules. It is clear from the table that, although bond lengths calculated by MNDO are consistently shorter than the experimental ones, the P–P bond is appreciably longer in P_8 than in P_4. It follows that the energy calculated for the former at the experimental bond length of the latter is necessarily too high.

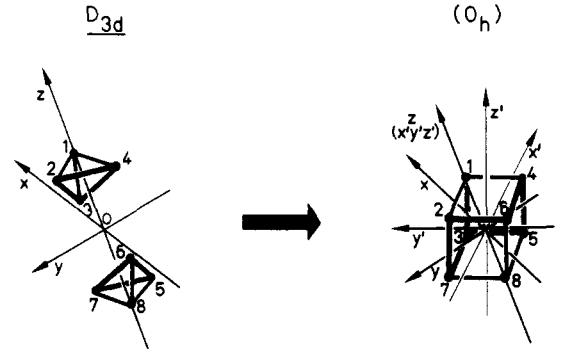

Figure 1. Highest symmetry reaction path (D_{3d}) for dimerization of tetrahedral P_4 to cubic P_8. Bonds broken: (23), (34), (42), (56), (67), (75). Bonds made: (26), (64), (45), (53), (37), (72).

Table I. Calculated Enthalpies of Formation and Bond Lengths of Various Species of Elemental Phosphorus

species	symmetry	ΔH_f, kcal	r_{PP}, Å calcd	r_{PP}, Å exptl
P_2	$D_{\infty h}$	40.7	1.693	1.894
P_4	T_d	36.2	2.052	2.21
P_8	O_h	4.1	2.074	

Qualitative Symmetry Analysis (OCAMS)

The cubic P_8 molecule has O_h symmetry. If it is stretched along one of its diagonals, its symmetry is reduced to D_{3d}. Further elongation of the diagonal, with retention of D_{3d} symmetry, eventually produces two P_4 molecules, so orbital correspondence analysis in maximum symmetry (OCAMS)[8] is carried out in D_{3d}, the highest symmetry compatabile with

(1) (a) Technion—Israel Institute of Technology. (b) University of Frankfurt.
(2) See, e.g., Figure 8 of: Corbridge, D. E. C. "The Structural Chemistry of Phosphorus"; Elsevier: Amsterdam, 1974; p 22.
(3) Bock, H.; Müller, H. *Inorg. Chem.*, companion article in this issue.
(4) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.
(5) "JANAF Thermochemical Tables"; Dow: Midland, MI 1960.
(6) Trinquier, G.; Malrieu, J.-P.; Daudey, J.-P. *Chem. Phys. Lett.* **1981**, *80*, 552.
(7) Fluck, E.; Pavlidou, C. M. E.; Janoschek, R. *Phosphorus Sulfur* **1979**, *6*, 469.
(8) (a) Halevi, E. A. *Helv. Chim. Acta* **1975**, *58*, 2136. (b) Katriel, J.; Halevi, E. A. *Theor. Chim. Acta* **1975**, *40*, 1.

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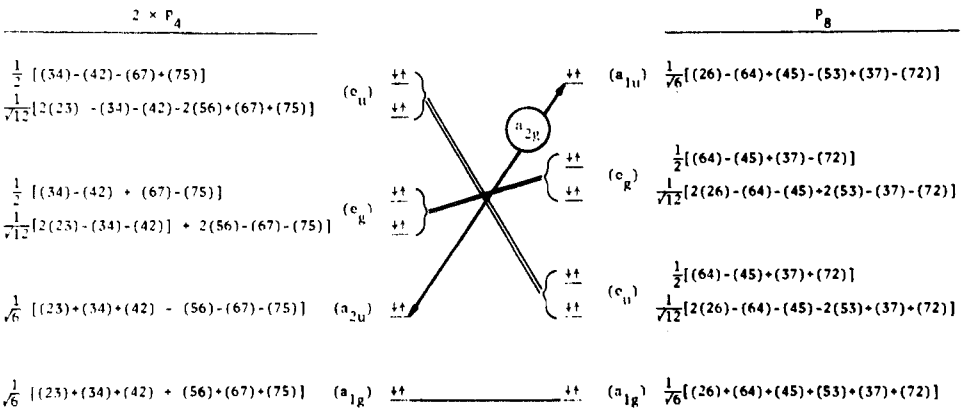

Figure 2. Correspondence diagram for dimerization of P_4 in D_{3d}. The localized bond orbitals are as indicated in Figure 1.

the fragmentation of P_8 to two P_4 units. The reverse reaction, the dimerization of two P_4 tetrahedra in the staggered face-to-face (D_{3d}) orientation, is illustrated in Figure 1. Three of the six bonds of each reactant molecule are ruptured, and a six-membered ring, reminiscent of chair cyclohexane, is formed to complete the cube.

The reaction can thus be discussed as if it involves only 12 electrons in six bonding orbitals, since the remaining 14 doubly occupied molecular orbitals retain their identity along the reaction path. Therefore, for the construction of the OCAMS correspondence diagram in Figure 2, we require two sets of six molecular orbitals; those on the left are linear combinations of the six bonding orbitals of the two P_4 that are broken, and those on the right are LCBOs of the newly formed bond orbitals in P_8.

Five pairs of LCBOs are seen to be in direct correspondence across the diagram. The sixth pair is not, the nonmatching irreducible representations being a_{2u} on the left and a_{1u} on the right. By the rules of OCAMS,[8] a *correspondence* can be *induced* between these two orbitals by distorting the elongated cube along an a_{2g} ($=a_{2u} \times a_{1u}$) symmetry coordinate, thereby reducing the symmetry along the reaction path to S_6, the subgroup of D_{3d} that is the *kernel* of a_{2g}.

However, as a conventional vibrational analysis[9] will confirm, the 18 internal symmetry coordinates of P_8—like its 18 normal modes—transform in D_{3d} as $[3a_{1g} + a_{1u} + 2a_{2u} + 3e_g(2) + 3e_u(2)]$. There is *no* symmetry coordinate of the species, a_{2g}, such as would be required in order to "allow" the reaction. The dissociation reaction and its inverse, the dimerization of P_4, are thus both strictly "forbidden" at the molecular orbital level.

To be sure, a more drastic reduction of symmetry, for example the simultaneous displacement along an a_{1u} and an a_{2u} coordinate, would bring the two offending orbitals into correspondence, since both would have the same irreducible representation (a) in the ensuing subgroup of S_6 (C_3), but any such distortion would be opposed by a large restoring force. The same could be said about the still more drastic reduction of symmetry to C_i, in which both orbitals would map on to a_u. We therefore conclude that any pathway retaining D_{3d} symmetry will be blocked by a massive barrier which, moreover, cannot be circumvented by any reduction of symmetry that does not present excessive energetic demands.

Semiempirical Pathway Computations (MNDO)

The P_8 molecule has three independent geometric degrees of freedom in D_{3d}, as can be determined from a simple algorithm[10] or from the vibrational analysis just cited, which specifies—equivalently—that there are three totally symmetric normal modes.

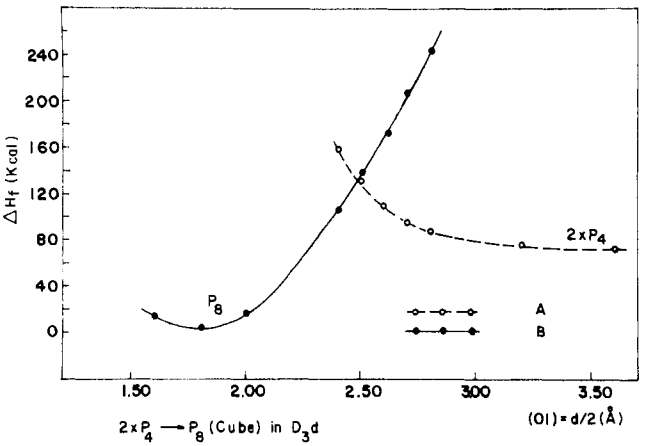

Figure 3. Attempted calculation of D_{3d} reaction path: (A) compression of the two P_4; (B) stretching of P_8.

Half the length of the diagonal (01) was chosen to be the "reaction coordinate"; as it was varied, the other two independent parameters, chosen to be the length of the endge (12) and the angle between (01) and (12), were optimized. The result of two such calculations is shown in Figure 3. In the first, two separated P_4 molecules are pushed together by decreasing (01); in the second, P_8 is stretched by gradually increasing (01).

The curves in Figure 3 appear to cross at (01) = 2.475 Å, but they represent two distinct species, with different values of (12) and ∠012. One, which we recognize to be "compressed two P_4", has the electronic configuration A($[4a_{1g}^2, 4a_{2u}^2, 3e_g^4, 3e_u^4]$). The other, "stretched P_8", is B ($[4a_{1g}^2, 1a_{1u}^2, 3a_{2u}^2, 3e_g^4, 3e_u^4]$). In agreement with Figure 2, the two configurations differ only with respect to the symmetry species of a single pair of occupied orbitals, a_{2u} in A and a_{1u} in B. This mismatch suffices to separate the two molecular species by a high ridge on the potential energy hypersurface.

A crossing from A to B can be forced by fixing (01) at 2.475 Å and varying (12) from 1.9 to 2.3 Å. A smooth transition is effected only when the minimal amount of configuration interaction available in the MNDO program is included. Its effect on the energy is small—only a few kilocalories—but it rescues the calculations from being discontinued on the grounds of being "unable to achieve self-consistency".

A three-dimensional plot is shown in Figure 4. The energy maximum (ΔH_f = 175 kcal at (12) = 2.05 Å) lies more than 100 kcal above the two P_4 and nearly 170 kcal above P_8. The region around this point was not explored thoroughly enough to characterize it firmly as "the transition state" for the reaction. However, the number of points that were calculated near it was sufficient to confirm the presence of a long energy ridge separating the two species. Moreover, reducing the symmetry to C_3 or to C_i, the low-symmetry subgroups of D_{3d} in which a_{1u} and a_{2u} map onto the same irreducible representation, does not lower the energy near the barrier. One can be confident that distortion of the reacting system along a coordinate that reduces the symmetry to any of the other subgroups of D_{3d}, in which a_{1u} and a_{2u} map onto different irreducible representations, will be completely ineffective.

(9) See e.g.: Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. "Molecular Vibrations"; McGraw-Hill: New York, 1955; p 105 ff.
(10) Pople, J. A.; Sataty, Y. A.; Halevi, E. A. *Isr. J. Chem.* **1980**, *19*, 290.

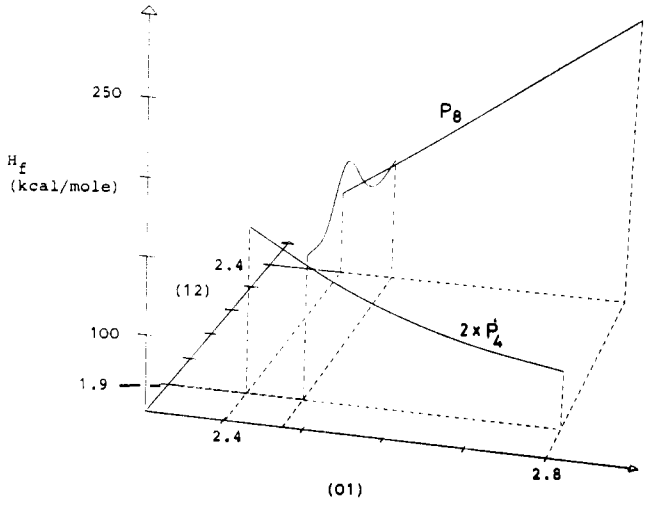

Figure 4. Crossing from A to B in D_{3d} at (01) = 2.475 Å.

Conclusions

The presence of a barrier some 100 kcal high to the dimerization of tetrahedral P_4 to cubic P_8 has been established computationally. The calculations confirm the results of the orbital symmetry analysis, which predicts the presence of such a barrier, ascribing it to the incompatibility of one doubly occupied LCBO of the two P_4 (a_{2u}) with one of P_8 (a_{1u}), which cannot be overcome by any reduction of symmetry below D_{3d}, which is both geometrically feasible and energetically convenient.

An energy barrier of this magnitude should be sufficient to prevent the formation of cubic P_8 at temperatures below that at which P_4 is fully dissociated to P_2, particularly if routes to more stable species such as red $(P_4)_n$ are available. The possible formation of noncubic P_8 species, which can serve as possible intermediates in the polymerization process, is presently being explored.[11]

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(11) Bock, H.; Roth, B.; Halevi, E. A. unpublished results.

Contribution from the Chemistry Departments, State University of New York, Albany, New York 12222, and State University of New York, Plattsburgh, New York 12901

EPR of Copper(II) Complexes with Tripodal Ligands: Dynamical Properties

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A major theme in bioinorganic chemistry is the understanding of the role played by metal ions in metalloenzymes with particular focus on their unique characteristics. Many of the iron proteins can be successfully modeled because they contain extrinsic active sites which may be reasonably reproduced outside of the actual protein. By contrast, copper proteins possess intrinsic active sites which are uniquely defined by the interactions of the ligating protein residues with the copper ions.[2] Thus, much of the activity in generating model systems for copper proteins has focused on small, well-defined structural or spectroscopic analogues that allow a particular feature(s) to be examined in detail. Many of the studies heretofore have examined the static spectral characteristics because these aspects may (or even must) be understood before additional dynamical features can be explored. Nevertheless, it is clear that a detailed understanding of the motional adjustments of the metalloprotein are needed to provide information on reaction rates and other dynamical properties.[3] Indeed, since changing structural properties are believed to be important in influencing the chemistry of real copper-containing enzymatic systems,[4-7] a further step in modeling enzyme active sites and reactivity should be to examine the possible roles of dynamical distortions in physcially realistic model systems.

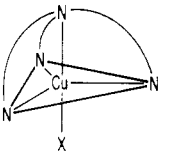

Figure 1.

This paper provides a vehicle for examining dynamical behavior by EPR spectroscopy on trigonal-bipyramidal (TBP) systems of the type $[Cu(TMPA)X]PF_6$, TMPA = tris(2-pyridylmethyl)amine and X = Cl^- and N_3^-, in frozen solutions and as a single crystal for X = Cl^-. The latter material has been characterized by X-ray crystallography[8] and has in-plane bonding very close to the 120° expected in the ideal TBP geometry.[8] A schematic drawing is shown in Figure 1. The usefulness of some tripod ligands in studying and modeling certain aspects of the coordination chemistry and structural properties of five-coordinate copper(I) and copper(II) complexes is well established.[8-13] Furthermore, the general features of many EPR spectra of five-coordinate Cu(II) covering the full range from TBP to square pyramidal are also now reasonably well understood within the framework of the C_{2v} model.[14] Of course, the well-known tendency of the Cu(II) ion to prefer a square-pyramidal geometry has greatly limited the number of examples that approach the trigonal-bipyramidal limit. Thus Cu(II) complexes near this limit might be expected to exhibit a rhombic EPR pattern and some do. On

(1) (a) State University of New York, Plattsburgh. (b) State University of New York, Albany. (c) Permanent address: Institute of Chemistry, Wrocław, Poland.

(2) Solomon, E. I.; Penfield, K. W.; Wilcox, D. E. *Struct. Bonding (Berlin)* **1983**, *53*, 1-57 and references cited therein.
(3) Gurd, F. R. N.; Rothgeb, T. M. *Adv. Protein Chem.* **1979**, *33*, 77-166.
(4) An example of this kind is the dramatic structural changes expected and observed at Cu(I)-Cu(II) centers in redox-active copper metalloproteins.
(5) Gray, H. B.; Solomon, E. I. In "Copper Proteins"; Spiro, T. G., Ed.; Wiley: New York, 1981; pp 1-40. Solomon, E. I. *Ibid.* pp 41-108.
(6) Bacci, M. *Struct. Bonding (Berlin)* **1983**, *55*, 67.
(7) Karlin, K. D.; Zubieta, J., Eds. "Copper Coordination Chemistry: Biochemical and Inorganic Perspectives"; Adenine Press: Guilderland, NY, 1983.
(8) Karlin, D. D.; Hayes, J. C.; Juen, S.; Hutchinson, J.; Zubieta, J. *Inorg. Chem.* **1982**, *21*, 4106 and references cited therein.
(9) Padula, F.; Goldstein, C.; Orsini, J.; Kokoszka, G.; Karlin, K. D. *Inorg. Chim. Acta* **1983**, *79*, 198-199.
(10) Zubieta, J.; Karlin, K. D.; Hayes, J. C. In ref 5, pp 97-108.
(11) Sorrell, T. N.; Jameson, D. L. *Inorg. Chem.* **1982**, *21*, 1014.
(12) Addison, A. W.; Hendriks, H. M. J.; Reedijk, J.; Thompson, L. K. *Inorg. Chem.* **1981**, *20*, 103.
(13) Thompson, L. K.; Ball, R. G.; Trotter, J. *Can. J. Chem.* **1980**, *58*, 1566-1576.
(14) Bencini, A.; Bertini, I.; Gatteschi, D.; Scozzafava, A. *Inorg. Chem.* **1978**, *17*, 3194.

0020-1669/84/1323-4378$01.50/0