triplet at τ 7.51 is split into two double doublets and the multiplet at τ 9.67 split into two multiplets of approximately equal areas, one of which is shifted downfield and the other upfield to τ 10.6. Such signals are consistent only with the paracyclophane structure **4**. Benzocyclooctene is eliminated as a possibility by a simple comparison of spectra[7] and [6]metacyclophane would be expected to show neither so simple a pmr spectrum nor so complex an ultraviolet spectrum.[5]

As **4** is a liquid, the determination of the amount of bending in the "benzene" ring must await X-ray analysis of an appropriate derivative. However, comparisons can be made with the estimates of Allinger and his coworkers. Early calculations[8] using the method of Pariser and Parr gave an angle of *ca.* 25–30° for θ. More recently an angle of 22.4° has been suggested[9] on the basis of force-field calculations which reproduce well the structures of [7]- and [8]paracyclophanes. Using this angle, an ultraviolet spectrum closely approximating the experimental was calculated.[9] There can be no doubt that **4** is substantially deformed.

The question of aromaticity of [6]- and [7]paracyclophanes requires most careful scrutiny, but the pmr spectrum clearly reveals a ring current and thus within the limits of this single criterion, these paracyclophanes are still aromatic.

We suspect the mechanism of formation of **4** involves radicals similar to those recently implicated in the formation of *p*-xylene from 4,4-dimethylcyclohexadienylidene.[10] We have not yet explicitly tested this surmise, however.

(7) W. R. Moore, E. Marcus, S. F. Fenton, and R. T. Arnold, *Tetrahedron*, **5**, 2217 (1964); C. M. Humby, G. P. Semeluk, and R. D. S. Stevens, *Spectrosc. Lett.*, 99 (1970).
(8) N. L. Allinger, L. A. Freiberg, R. B. Hermann, and M. A. Miller, *J. Amer. Chem. Soc.*, **85**, 1171 (1963).
(9) N. L. Allinger, J. T. Sprague, and T. Liljefors, *J. Amer. Chem. Soc.*, in press.
(10) T. E. Berdick, R. H. Levin, A. D. Wolf, and M. Jones, Jr., *J. Amer. Chem. Soc.*, **95**, 5087 (1973).
(11) Petroleum Research Fund Postdoctoral Fellow, 1972–1973.

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Equivalence of Metal Centers in the Iron–Sulfur Protein Active Site Analogs $[Fe_4S_4(SR)_4]^{2-}$

Sir:

The synthetic clusters $[Fe_4S_4(SR)_4]^{2-}$ [1,2] serve as close structural[2–4] and electronic[1,5,6] representations of the $[Fe_4S_4(S\text{-Cys})_4]$ active sites of oxidized ferredoxin (Fd$_{ox}$) and reduced "high-potential" (HP$_{red}$) proteins.[7]

(1) T. Herskovitz, B. A. Averill, R. H. Holm, J. A. Ibers, W. D. Phillips, and J. F. Weiher, *Proc. Nat. Acad. Sci. U. S.*, **69**, 2437 (1972).
(2) B. A. Averill, T. Herskovitz, R. H. Holm, and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 3523 (1973).
(3) C. W. Carter, Jr., J. Kraut, S. T. Freer, R. A. Alden, L. C. Sieker, E. Adman, and L. H. Jensen, *Proc. Nat. Acad. Sci. U. S.*, **69**, 3526 (1972).
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(6) B. V. DePamphilis, B. A. Averill, T. Herskovitz, L. Que, Jr., and R. H. Holm, *J. Amer. Chem. Soc.*, in press.
(7) J. C. M. Tsibris and R. W. Woody, *Coord. Chem. Rev.*, **5**, 417 (1970); W. H. Orme-Johnson, *Annu. Rev. Biochem.*, **42**, 159 (1973).

The structures of the analogs $(Et_4N)_2[Fe_4S_4(SCH_2Ph)_4]^2$ and $(Me_4N)_2[Fe_4S_4(SPh)_4]^8$ reveal noncrystallographically imposed D_{2d} anion symmetry. Formal oxidation state considerations[1,2] imply a possible mixed valence [2Fe(II) + 2Fe(III)] property for the dianions. In view of the same total oxidation level for Fd$_{ox}$, HP$_{red}$, and $[Fe_4S_4(SR)_4]^{2-}$,[1,5,6] their structural similarities, and the current interest in mixed valence compounds,[9] the equivalence of all irons apparent in the crystalline state at ambient temperature[2,8] has been further investigated under different conditions in several laboratories. Techniques capable of detecting widely variant electronic state lifetimes (τ) have been employed in order to differentiate trapped valence (integral oxidation states) *vs.* delocalized properties of the dianions.

Pmr spectra of some 12 dianions (R = alkyl, aryl) obtained over a wide temperature interval in several solvents consistently reveal one set of contact-shifted R signals.[5] For example, single CH$_2$ resonances downfield of TMS are found for $[Fe_4S_4(SEt)_4]^{2-}$ at $-78°$ (-9.82 ppm, acetone-d_6) and at 118° (-14.4 ppm, DMSO-d_6). From these and similar data $\tau \lesssim 10^{-4}$ sec is estimated for a distinct Fe(II, III) valence state.

Mössbauer spectra of $[Fe_4S_4(SCH_2Ph)_4]^{2-}$ at room temperature, 77, 4.2, and 1.5°K in zero field (Figure 1a) are characterized by a single quadrupole doublet. The isomer shift $\delta = +0.36$ mm/sec (relative to iron metal), quadrupole splitting $\Delta E_Q = 1.10$ mm/sec, and line width $\Gamma = 0.23$ mm/sec at room temperature. At the two lower temperatures $\Delta E_Q = 1.26$ mm/sec, $\Gamma = 0.28$ mm/sec,[10] and δ is unchanged. Both components of the doublet are of equal intensity and width at all temperatures and have the expected Lorentzian line shape. Spectra obtained in external magnetic fields were compared with computer-generated spectra (Figure 1b). For all values of the applied field H_0, the spectra indicate a single iron site with the magnetic field at the nucleus $H_n = H_0$, the sign of the principal component of the electric field gradient positive, and the asymmetry parameter $\eta < 0.4$. These results provide strong evidence that all iron sites are structurally and electronically equivalent at temperatures down to 1.5°K; *i.e.*, $\tau \lesssim 10^{-7}$ sec. Similar conclusions follow from frozen solution measurements on several dianions at 77 and 4.2°K. For $[Fe_4S_4(SCH_2Ph)_4]^{2-}$ δ is intermediate between the values given by Reiff, *et al.*,[11] for tetrahedral Fe(II)–S$_4$ (*ca.* $+0.60$ mm/sec) and Fe(III)–S$_4$ (*ca.* $+0.20$ mm/sec).

The existence of trapped valence states (class I, II species[9,12]) requires electronic spectral properties of distinct Fe(II,III)–S$_4$ chromophores. Tetrahedral Fe(II) is spectrally characterized by one or more ligand field bands of $^5E \rightarrow \,^5T_2$ parentage in the near-infrared region. For the Fe(II)–S$_4$ chromophore such bands

(8) L. Que, Jr., M. A. Bobrik, J. A. Ibers, and R. H. Holm, *Annu. Rev. Biochem.*, in press.
(9) D. O. Cowan, C. Le Vanda, J. Park, and F. Kaufman, *Accounts Chem. Res.*, **6**, 1 (1973), and references therein.
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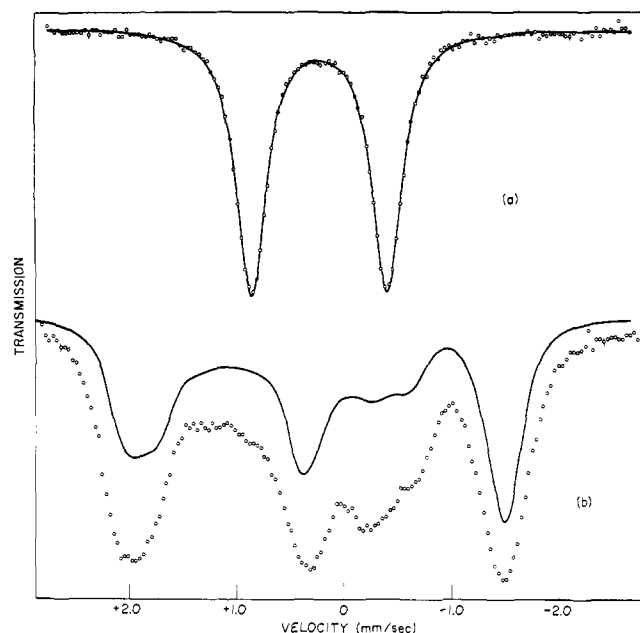(12) M. B. Robin and P. Day, *Advan. Inorg. Chem. Radiochem.*, **10**, 247 (1967).

Figure 1. Mössbauer spectra of $(Et_4N)_2[Fe_4S_4(SCH_2Ph)_4]$ at (a) 1.5°K, $H_0 = 0$; (b) 4.2°K, $H_0 = 80$ kOe applied longitudinally. Solid lines in (a) and (b) are respectively theoretical least-squares fit to the data assuming Lorentzian line shape and theoretical computer-generated spectrum assuming $H_n = 80$ kOe, $\Delta E_Q = 1.26$ mm/sec, $\eta = 0$, and the sign of the principal component of electric field gradient positive.

Figure 2. Visible and near-infrared electronic absorption spectra at 5°K. $(n\text{-}Pr_4N)_2[Fe_4S_4(SEt)_4]$: (a) thin film, 440–1000 nm; (b) film, 1000–2500 nm. (c) $(n\text{-}Pr_4N)(FeCl_4)$, KBr pellet, 2000–2500 nm, illustrating cation vibrational overtones. $(Et_4N)_2[Fe_4S_4-(SCH_2Ph)_4]$: (d) thin film, 430–900 nm; (e) TlCl pellet, 800–2400 nm. In solution the bands near 500 and 600 nm are less well resolved and that near 800 nm is not observable.

have been found in the ca. 2500–6000 cm^{-1} region of the spectra of reduced adrenodoxin and rubredoxin,[13] spinach Fd$_{red}$,[13] Fe[(SPMe$_2$)$_2$N]$_2$,[14,15] and Fe(II) in inorganic sulfide lattices.[16,17] Careful examination of the spectra of $[Fe_4S_4(SEt)_4]^{2-}$ and $[Fe_4S_4(SCH_2Ph)_4]^{2-}$ in evaporated films and pellets at 5°K to 2500 nm has been conducted (Figure 2). Considerable vibrational overtone structure due to the cations is encountered at ca. 2000–2500 nm. No features clearly attributable to the Fe(II)–S$_4$ chromophore were detected nor were bands found which appeared characteristic of an intervalence transition. Absorption below ca. 800 nm in the solid[14] and solution[6] phases appears to arise only from excitation of the Fe(III)–S$_4$ unit. Regardless of the precise nature of these transitions, it is concluded that the electronic spectra of $[Fe_4S_4(SR)_4]^{2-}$ do not satisfy the criteria for class I or II mixed valence compounds and that $\tau \lesssim 10^{-12}$ sec.

The X-ray photoelectron spectrum of a film sample of $(n\text{-}Pr_4N)_2[Fe_4S_4(SEt)_4]$ was determined under conditions to minimize irradiative decomposition.[18] At 250°K the Fe 2p(3/2) binding energy is 710.4 eV with the C 1s standard (methylene carbons of $n\text{-}Pr_4N^+$) being 285.2 eV. The spectrum showed no evidence of inequivalent Fe atoms, implying $\tau \lesssim 10^{-16}$ sec.

Hence, the collective body of spectroscopic results, together with the X-ray structure determinations,[2,8] conclusively establish that $[Fe_4S_4(SR)_4]^{2-}$ are not trapped valence complexes. One rationalization of these results is that intracluster electron exchange, $Fe(II)(e^3t^3_2) \rightleftharpoons Fe(III)(e^2t^3_2)$, is extraordinarily rapid ($k > 10^{16}$ sec^{-1}). This process would require little structural reorganization due to interchange of essentially nonbonding e-type electrons. This same feature should be operative in external electron exchange and may have been important in evolutionary selection of tetrahedral Fe–S$_4$ groups found in all characterized sites of iron–sulfur proteins.[7,19] The delocalized nature of $[Fe_4S_4(SR)_4]^{2-}$ may be compared to the trapped valence nature of solid $[Co_4(OMe)_4(acac)_4(OAc)_2]$, which also contains weak field ligands and has a cubane-type stereochemistry with 2Co(II) + 2Co(III) octahedral metal sites.[20] Here intracluster exchange, $Co(II)(t^5_{2g}e^2_g) \rightleftharpoons Co(III)(t^6_{2g})$, should have a larger reorganization barrier.[21]

Lastly, while $[Fe_4S_4(SR)_4]^{2-}$ complexes are concluded to possess a fully delocalized Fe_4S_4 core, the present results do not necessarily establish a fractional valence (2.5, class III[9,12]) description, although isomer shifts are not inconsistent with this description. The possibility of an electron distribution resulting in, effectively, 4Fe(III) and two delocalized ligand-based electrons remains. Structural and spectroscopic results for HP$_{red}$ and Fd$_{ox}$ proteins, while unquestionably similar to those of $[Fe_4S_4(SR)_4]^{2-}$, are not yet precise enough to indicate whether the inequivalence in metal sites necessarily imposed by the protein structure is sufficiently pronounced to alter significantly the electron distribution from that in the synthetic analogs.

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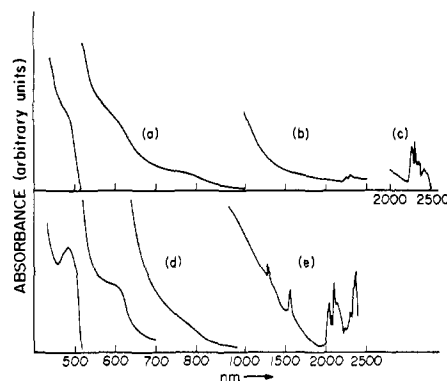
(19) J. J. Mayerle, R. B. Frankel, R. H. Holm, J. A. Ibers, W. D. Phillips, and J. F. Weiher, *Proc. Nat. Acad. Sci. U. S.*, **70**, 2429 (1973).

(20) J. A. Bertrand and T. C. Hightower, *Inorg. Chem.*, **12**, 206 (1973).

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The Bis(dimethylamido)phosphinium Cation with a p_π-p_π Multiple Bond between Phosphorus and Nitrogen Atoms

Sir:

In 1964 Dimroth and Hoffman[1] synthesized the first authentic compound containing a p_π-p_π phosphorus–carbon double bond. This type of substance named as a phosphamethinecyanine, was represented as
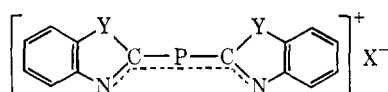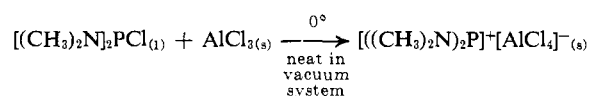

where $X^- = ClO_4^-$ and BF_4^- and Y is S or NR. Unstable tris(hydroxymethyl)phosphine and *N*-ethyl-2-chlorobenzothiazolium tetrafluoroborate served as starting materials.

We have found that the reaction between bis(dimethylamino)chlorophosphine and aluminum(III) chloride gives a one to one adduct which has an unexpected ionic structure $[((CH_3)_2N)_2P]^+[AlCl_4]^-$. The compound also contains a two-coordinate phosphorus cation which shows unequivocal evidence for a multiple p_π-p_π bond between phosphorus and nitrogen atoms. The corresponding $[(R_2N)_2P]^+[PF_6]^-$ and $[(R_2N)_2P]^+[B_2F_7]^-$ have also been prepared and characterized. An analogous cyclic cation was first reported in a definitive paper by Fleming, Lupton, and Jekot;[2] the cyclic and noncyclic structures represented below show marked formal similarities but rather striking differences in product properties.
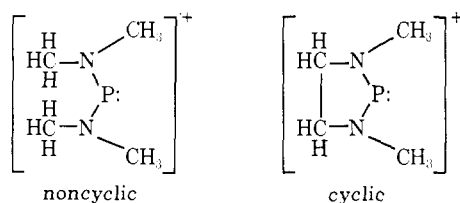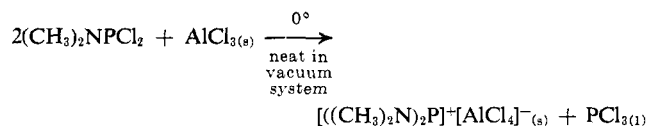

noncyclic   cyclic

The noncyclic compound $[((CH_3)_2N)_2P]^+[AlCl_4]^-$ can be prepared by either of the following reactions.

$$[(CH_3)_2N]_2PCl_{(l)} + AlCl_{3(s)} \xrightarrow[\substack{\text{neat in}\\\text{vacuum}\\\text{system}}]{0°} [((CH_3)_2N)_2P]^+[AlCl_4]^-_{(s)}$$

(1) K. Dimroth and P. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **3**, 384 (1964); R. A. Allman, *Angew. Chem.*, **77**, 134 (1965); *Angew. Chem., Int. Ed. Engl.*, **4**, 150 (1965).
(2) S. Fleming, M. K. Lupton, and K. Jekot, *Inorg. Chem.*, **11**, 2534 (1972).

$$2(CH_3)_2NPCl_2 + AlCl_{3(s)} \xrightarrow[\substack{\text{neat in}\\\text{vacuum}\\\text{system}}]{0°}$$

$$[((CH_3)_2N)_2P]^+[AlCl_4]^-_{(s)} + PCl_{3(l)}$$

The product is a homogeneous white waxy solid which is extremely sensitive to attack by water at both the P–N and the Al–Cl bonds. The compound decomposes above 65° to give equiformal quantities of Cl_2-PNR_2 and $(Cl_2AlNR_2)_n$ in a nonreversible reaction. Although some crystals of (this compound) have been obtained in a vacuum system, we have not yet been able to load a crystal for X-ray study. Even though the gross features of the structure are unambiguously established by the data noted below, an X-ray structure would still provide very significant details and is being pursued.

The adduct is soluble in CH_2Cl_2. The conductivity of the adduct is approximately 50% of that of a similar solution of $[N(CH_3)_4]^+[AlCl_4]^-$ and more than 100 times greater than a CH_2Cl_2 solution of either $AlCl_3$ or $[(CH_3)_2-N]_2PCl$. An ionic structure is clearly indicated. The ionic formulation is also indicated by the infrared spectrum. The N_2P–Cl stretching vibration (mostly P–Cl) is clearly apparent in a CH_2Cl_2 solution of $ClP[N(CH_3)_2]$ at 670 cm^{-1}. In a methylene chloride solution containing equimolar quantities of dissolved $[(CH_3)_2N]_2PCl$ and $AlCl_3$ the P–Cl stretching frequency at 670 cm^{-1} disappears and a strong frequency at 490 cm^{-1}, attributable to the nonsymmetric Al–Cl stretching frequency of $AlCl_4^-$ (ν_3), appears. Other details of the spectrum are also consistent with the ionic formulation.

The nmr spectra for ^1H, ^{31}P, and ^{13}C (and ^{19}F for $[PF_6]^-$) are all consistent with the ionic structure and provide unequivocal evidence for restricted rotation about the P–N bond in the cation and thus for a delocalized electronic structure involving a clear p_π-p_π P–N multiple bond. The free energy for rotation is 14.2 kcal based upon the variation of the ^1H spectrum with temperature.[3] The $\Delta H^{\ddagger}$ is about 10.3 kcal/mol. The $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ values are also confirmed by the variation of the ^{13}C spectrum with temperature. The proton spectrum at $-50°$ consists of two equal area doublets at δ 2.13 (CH_2Cl_2) ($J_{PNCH} = 14.1$ Hz) and δ 1.97 ($J_{PNCH} = 5.0$ Hz). As the temperature is raised to 30° this becomes a single doublet at δ 2.06 ($J_{PNCH} = 9.6$ Hz). The carbon-13 spectrum shows two doublets at $-20°$, δ 52.46, ($J_{PNCH} = 6.25$ Hz) and δ 54.64, $J = 19.5$ Hz, that collapses to one doublet at 57°, δ 53, $J = 12.9$ Hz. The onset of rotation about the P–N bond is blocked in the cyclic cation
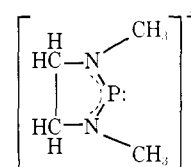
and the cyclic ion spectrum is not temperature dependent in the range $-30°$ to $+30°$. It is significant that the cyclic cation shows a doublet for CH_2 at δ 2.10 ($J_{PNCH} = 11.0$ Hz) and a doublet for CH_3 δ 1.37 ($J_{PNCH} = 5$ Hz). Both cyclic and noncyclic cations show a ^{31}P singlet at

(3) Max T. Rogers and James C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).