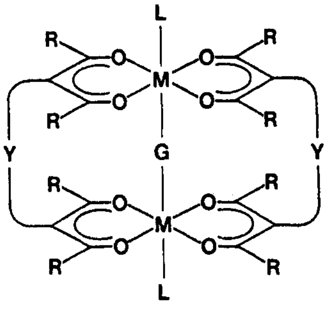
Cofacial Binuclear Copper Complexes of a Bis(β-diketone) Ligand[1]

Sir:

The adaptation of chelating ligands to the synthesis of binuclear metal complexes has been an area of intense activity. The objectives of these experiments have included modeling active sites in metalloproteins as well as promoting and catalyzing multielectron redox reactions. Various ligands have been used in the synthesis of such complexes: "face-to-face" porphyrins,[2] planar polyketones and related macrocycles,[3] and cyclic polyaza compounds, both saturated[4] and unsaturated.[5] Exploration of the elegant chemistry of these complexes, particularly those of the diporphyrins and the saturated polyaza compounds, has often been inhibited by the complexity of the ligand syntheses. Our work has therefore concentrated on the development of binuclear complexes that are derived from simpler polydentate ligands; these complexes should still be capable of great versatility in physical and chemical properties. We now report the preparation, structural characterization, and adduct formation reactions of the first cofacial binuclear complex of a readily synthesized bis(β-diketone) ligand.

The general structure **1** of our complexes is illustrated. Bis(β-diketones) with suitable bridging groups Y were prepared by Martin and co-workers.[6] Our initial experiments with one of these, *p*-XBAH$_2$ (Y = 1,4-C$_6$H$_4$(CH$_2$)$_2$; R = CH$_3$), and various divalent first-row metal ions yielded largely polymeric materials.[7] (Discrete binuclear complexes of Rh and Ir containing only one *p*-XBA^{2-} ligand have recently been described by Whitmore and Eisenberg.[8]) Thus, we turned next to the corresponding meta isomer, *m*-XBAH$_2$ (3,3′-[1,3-phenylenebis(methylene)]bis(2,4-pentanedione)).[9] Dichloromethane solutions of *m*-XBAH$_2$ rapidly turn green on treatment with aqueous Cu(NH$_3$)$_4$$^{2+}$, and small crystals of Cu$_2$(*m*-XBA)$_2$ can be grown from the resulting CH$_2$Cl$_2$ solutions by layering with 2-propanol.[10]



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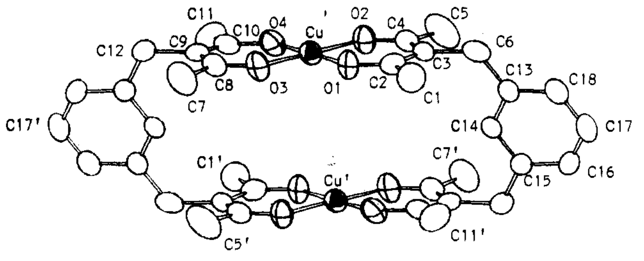

Figure 1. ORTEP[12] view of the Cu$_2$(*m*-XBA)$_2$ molecule, with ellipsoids at the 50% probability level. Hydrogen atoms omitted for clarity.

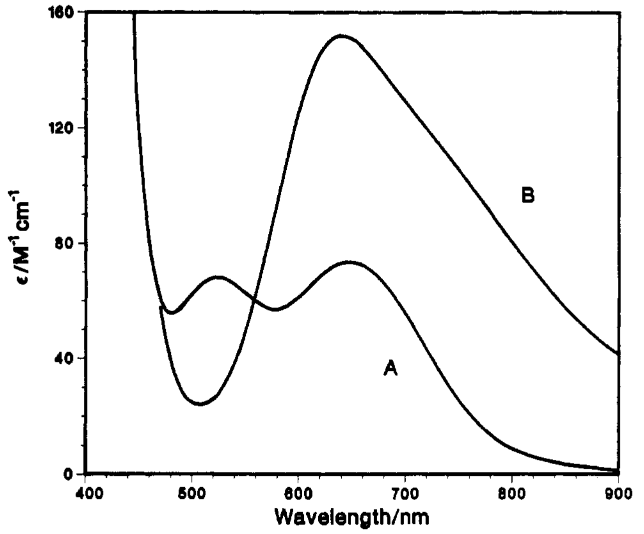

Figure 2. Room-temperature electronic absorption spectra: (A) Cu$_2$(*m*-XBA)$_2$ in chloroform; (B) Cu$_2$(*m*-XBA)$_2$(py)$_2$ in pyridine–chloroform (1:1, v/v). The two spectra are approximately coincident between 400 and 460 nm.

The crystal structure of Cu$_2$(*m*-XBA)$_2$[11] (see the ORTEP[12] drawing in Figure 1) consists of binuclear molecules with

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(1) Presented in part at the 187th National Meeting of the American Chemical Society, St. Louis, MO, April 8–13, 1984.

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(3) See, for example: Lintvedt, R. L.; Ranger, G.; Schoenfelner, B. A. *Inorg. Chem.* **1984**, *23*, 688. Gagné, R. R.; Spiro, C. L.; Smith, T. J.; Hamann, C. A.; Thies, W. R.; Shiemke, A. K. *J. Am. Chem. Soc.* **1981**, *103*, 4073.

(4) Motekaitis, R. J.; Martell, A. E.; Dietrich, B.; Lehn, J.-M. *Inorg. Chem.* **1984**, *23*, 1588. Coughlin, P. K.; Martin, A. E.; Dewan, J. C.; Watanabe, E.-I.; Bulkowski, J. E.; Lehn, J.-M.; Lippard, S. J. *Inorg. Chem.* **1984**, *23*, 1004.

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(6) Martin, D. F.; Fernelius, W. C.; Shamma, M. *J. Am. Chem. Soc.* **1959**, *81*, 130.

(7) Yeager, M. A., unpublished work. See also: Korshak, V. V.; Krongauz, E. S.; Sheina, V. E. *Vysokomol. Soedin.* **1960**, *2*, 662; *Chem. Abstr.* **1961**, *55*, 7898*b*.

(8) Whitmore, B. C.; Eisenberg, R. *Inorg. Chem.* **1984**, *23*, 1697. We thank Professor Eisenberg for communicating these results to us prior to publication.

(9) The crude ligand *m*-XBAH$_2$ was prepared by the method used in ref 6 for *p*-XBAH$_2$. It has since been prepared in crystalline form by condensation of benzene-1,3-dicarboxaldehyde with 2,4-pentanedione and subsequent ctalytic hydrogenation: Fishbain, J. T., unpublished work.

(10) The chemical composition of the complex was verified by mass spectroscopy (parent ions, *m/e* 726–731). Anal. Calcd for Cu$_2$C$_{36}$H$_{40}$O$_8$: C, 59.41; H, 5.54; Cu, 17.5. Found: C, 59.41; H, 5.57; Cu, 17.8, 16.5.

(11) The olive green crystals are monoclinic blades elongated along *b*: space group $P2_1/c$ (No. 14); a = 12.002 (5), b = 7.434 (2), c = 19.431 (9) Å; β = 99.47 (3)°; Z = 2; Nicolet P3 diffractometer; Mo Kα radiation, graphite monochromator, ω scan with variable scan rate. A crystal of approximate dimensions 0.05 × 0.1 × 0.5 mm was used in the collection of intensity data for 2549 independent reflections ($-h,-k,\pm l$) at ca. 20 °C. The structure was solved with the Enraf-Nonius VAXSDP system of programs. A Patterson map located the unique Cu atom, and subsequent difference Fourier syntheses revealed the remaining non-hydrogen atoms and many of the hydrogen atoms. Positional parameters for H5–H16 (methyl) and H17–H20 (aromatic ring) derived from the difference maps did not refine well. Those for H17–H20 were calculated to give equal C–C–H angles. For the methyl groups the refined coordinates suggested a conformation in which one hydrogen atom approximately eclipsed the adjacent carbonyl oxygen. This H–C–C–O eclipsed conformation was therefore assumed, along with tetrahedral bond angles, in calculating positions for H5–H16. Results of full-matrix least-squares refinement: based on 1262 reflections with $I > 3\sigma(I)$ and 220 variables (anisotropic thermal parameters for all non-hydrogen atoms; fixed isotropic thermal parameters for H1–H4), R = 0.044 and R_w = 0.051.

(12) Johnson, C. K. "ORTEP-II: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations", Report ORNL-5138; National Technical Information Service, U.S. Department of Commerce: Springfield, VA, 1976.

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crystallographically imposed inversion symmetry. There are no short intermolecular contacts in the structure. The Cu–Cu distance is 4.908 (2) Å; other distances and angles are approximately as expected. The "Cu(acac)$_2$" (acacH = 2,4-pentanedione) moieties are essentially planar and make an angle of 89.8° with the bridging aromatic rings, giving the molecule approximate overall D_{2h} symmetry.

Additional details concerning electronic structure and reactivity for the complex may be seen from the electronic absorption spectra in Figure 2, taken on solutions of Cu$_2$(*m*-XBA)$_2$ in chloroform with and without added pyridine. Spectrum A, in pure chloroform, shows two d–d absorption bands with maxima at 518 (ϵ = 68) and 646 nm (ϵ = 73 M^{-1} cm^{-1}). These bands are very similar in energy to those for Cu(acac)$_2$ ($\lambda_{\max}$ = 532 (ϵ = 26) and 658 nm (ϵ = 34 M^{-1} cm^{-1})),[13] but about twice as intense. Thus, the copper atoms in Cu$_2$(*m*-XBA)$_2$ behave electronically much like isolated Cu(acac)$_2$ units. The room-temperature effective magnetic moment (Gouy method, powdered sample) for Cu$_2$(*m*-XBA)$_2$ of approximately 1.8 μ_B per copper atom suggests that the magnetic coupling between the copper atoms is also relatively weak.

Solutions of Cu$_2$(*m*-XBA)$_2$ change color from olive green to bright yellow-green on addition of pyridine (Figure 2B), and the principal d–d absorption now occurs at 635 nm. As estimated from spectral data at intermediate concentrations, the formation of the new species is essentially complete in 50% pyridine. The position and intensity (ϵ = 152 M^{-1} cm^{-1}) of the new band again compare favorably with those of Cu(acac)$_2$(py) (py = pyridine) ($\lambda_{\max}$ = 654 nm; ϵ = 73 M^{-1} cm^{-1}).[14] This evidence, combined with the observation that the space between the copper atoms is to small to accommodate pyridine, leads to the formulation of the new species as Cu$_2$(*m*-XBA)$_2$(py)$_2$, with pyridine molecules in the axial positions L of **1**.

Evidence for association of solvent molecules with Cu$_2$(*m*-XBA)$_2$ comes from ^{1}H NMR data as well. Solutions of Cu$_2$(*m*-XBA)$_2$ in CHCl$_3$/CDCl$_3$ mixtures show significant broadening of the CHCl$_3$ resonance even for [Cu$_2$(*m*-XBA)$_2$] values in the millimolar range. The effect is more pronounced for CHCl$_3$ than for Me$_4$Si under similar conditions, suggesting a specific outer-sphere interaction with chloroform. Broadening is also observed in solutions of Cu$_2$(*m*-XBA)$_2$ containing pyridine, the amount being greatest for the pyridine α protons.[15]

Thus, we have structurally and spectroscopically characterized the first cofacial binuclear complexes of simple bis(β-diketone) ligands. A more detailed study of EPR spectra and magnetic susceptibility of Cu$_2$(*m*-XBA)$_2$ is currently under way. We are also exploring the affinities of these and related complexes for small diatomic molecules G of **1** and the redox activity of the resulting adducts, as well as variations in these properties as a function of the bridging bis(β-diketone) ligand.

Acknowledgment. We thank Professor G. G. Stanley for assistance with the X-ray structure determination. This research was supported in part by grants from the Research Corp. and the Monsanto Co. and by Grant BRSG S07 RR07054-17 awared by the Biomedical Research Support Grant Program, Division of Research Resources, National Institutes of Health. F.E.K. was a participant in the Summer Undergraduate Research Program at Washington University.

Registry No. Cu$_2$(*m*-XBA)$_2$, 93040-31-4; Cu$_2$(*m*-XBA)$_2$(py)$_2$, 93040-33-6; *m*-XBA, 93040-32-5; Cu(NH$_3$)$_4^{2+}$, 16828-95-8.

Supplementary Material Available: Stereoscopic view of the unit cell (Figure 3) and listings of atomic positional and thermal parameters, interatomic distances and angles, and observed and calculated structure factors for Cu$_2$(*m*-XBA)$_2$ (14 pages). Ordering information is given on any current masthead page.

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[13] The data for Cu(acac)$_2$, with absorption maxima and intensities calculated by deconvolution of the observed CHCl$_3$ spectra, are from: Belford, R. L.; Calvin, M.; Belford, G. *J. Chem. Phys.* **1957**, *26*, 1165.

[14] Graddon, D. P.; Schulz, R. A. *Aust. J. Chem.* **1965**, *18*, 1731. These workers resolved an additional absorption band ($\lambda_{\max}$ = 800 nm; ϵ = 32 M^{-1} cm^{-1}) in the Cu(acac)$_2$(py) spectrum; a similar feature can be identified in the spectrum of Figure 2B here, although it is difficult to determine accurately its location and intensity. The authors in ref 13 assigned the band at 654 nm to the sum of two closely spaced bands, but the simpler approach is taken here.

[15] The formulation Cu$_2$(*m*-XBA)$_2$(py)$_2$, with axial ligation of pyridine to Cu, is consistent with the observed broadening of the pyridine resonances. For chloroform a more likely model is weak hydrogen bonding to the oxygen atoms of the ligand, as has been suggested for Cu(acac)$_2$: Kitaigorodskii, A. N.; Nekipelov, V. M.; Zamaraev, K. I. *J. Struct. Chem.* (*Engl. Transl.*) **1978**, *19*, 686. See also: Langford, C. H.; Stengle, T. R. In "NMR of Paramagnetic Molecules: Principles and Applications"; La Mar, G. N., Horrocks, W. D., Jr., Holm, R. H., Eds.; Academic Press: New York, 1973; p 372.

Synthesis of Novel Organo(silyl)phosphine Synthons and Their Conversion to New Organophosphines

Sir:

Organo(silyl)phosphines [e.g., Me$_3$SiPR$_2$ and (Me$_3$Si)$_2$PR], because they contain highly reactive Si–P bonds, offer considerable potential for novel organophosphorus and organophosphorus–metal compound systhesis,[1] e.g. the recent preparation of [Co$_4$(μ_3-PPh$_3$)$_4$] from the reaction of CoCl$_2$·2PPh$_3$ with (Me$_3$Si)$_2$PPh.[2] Unfortunately, because the available organo(silyl)phosphines have been limited to cases where R = alkyl or aryl,[3] the derived organophosphorus products have been limited. Recently, we have studied Me$_3$SiPH$_2$–olefin radical reactions and found they yield selectively and cleanly new classes of Me$_3$Si-substituted products. These synthons are converted hydrolytically to new primary and secondary phosphines, thus demonstrating a widely exploitable new two-step phosphine synthesis.

Reactions of Me$_3$SiPH$_2$[4] with the olefins **1**–**4** listed in Table I, in benzene or toluene at 85 °C and initiated by AIBN [AIBN = 2,2′-azobis(isobutyronitrile)], occur cleanly to yield the new silylphosphines, **5**–**8**. Hydrolysis of **5**–**8** by their reaction with excess (typically 20%) deoxygenated H$_2$O in benzene yields the primary and secondary organophosphines **9**–**12** quantitively. Products from both the phosphine–olefin and hydrolysis reactions were handled in vacuo and separated by low-temperature fractional distillation. Me$_3$SiPH$_2$ with excess 1,4-pentadiene (**1**) yields **5**; only tentative ^{31}P NMR spectral evidence was obtained for intermediate pentenyl(silyl)phosphine formation. Excess norbornadiene (**2**) with Me$_3$SiPH$_2$ yields intractable oligomeric/polymeric products; however, with excess Me$_3$SiPH$_2$, **6** predominates. Further conversion of **6** to Me$_3$SiP(C$_7$H$_9$)$_2$ is not observed. Di-

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[1] Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: Berlin, 1983.

[2] Fenske, D.; Basoglu, R.; Hachgenei, J.; Rogel, F. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 160.

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[4] Me$_3$SiPH$_2$ is prepared as described previously: Norman, A. D. *Inorg. Chem.* **1970**, *9*, 870.

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