Crystal Structure and Magnetic Studies of Bis(μ-dibutylphosphinato)-copper(II)

R. CINI,[1a] P. COLAMARINO,[1a] P. L. ORIOLI,*[1a] L. S. SMITH,[1b] P. R. NEWMAN,[1b] H. D. GILLMAN,*[1c] and PIERO NANNELLI[1c]

The structure of $Cu[OP(C_4H_9)_2O]_2$ in the solid state has been determined by three-dimensional single-crystal x-ray techniques. The compound crystallizes in the triclinic space group $P\bar{1}$ with two formula units in a cell of dimensions $a = 12.245$ (6) Å, $b = 9.863$ (5) Å, $c = 9.819$ (5) Å, $\alpha = 101.18$ (4)°, $\beta = 105.78$ (5)°, $\gamma = 93.77$ (4)°, $V = 1110.7$ Å³, and $d_c = d_m = 1.25$ g cm⁻³. The structure was solved by the heavy-atom technique, and least-squares refinement gave an R factor of 0.061. The structure consists of polymeric chains of copper atoms linked by double phosphinate bridges. The coordination around each copper atom can be described as a very flattened tetrahedron. The Cu–Cu distance was 4.94 Å. The **g** tensors for oriented single crystals were determined by ESR and range from 2.07 to 2.41, with the larger value in a direction nearly normal to a plane formed by the flattened tetrahedron. The spin–orbit coupling constant suggests considerable mixing of metal and ligand orbitals in this polymer.

Introduction

The poly(metal phosphinates), which are inorganic coordination polymers consisting of metal ions linked by phosphinate (OPO) bridges, have been extensively studied because of their potential in a variety of high-temperature applications including coatings and grease thickeners.[2] Recently we have become interested in the magnetic properties of these unique one-dimensional inorganic complexes and initiated an investigation of these properties. In this regard we studied the temperature-dependent magnetic susceptibilities of a number of these materials and found that the OPO bridges provided a path for antiferromagnetic superexchange $J/K \sim 0$–5 K.[3,4] In addition, more extensive studies of some chromium phosphinates also indicated that disorder plays an important role in determining the magnetic properties of these polymers by limiting the range of spin correlation.[3] In order to extend our understanding of this system further, we report here a single-crystal study of $Cu[OP(C_4H_9)_2O]_2$ including its complete crystallographic structure and the orientation of the electronic **g** tensor relative to the atomic configuration.

Experimental Section

The preparation of $Cu[OP(C_4H_9)_2O]_2$ has previously been reported.[5] Some crystals were obtained from dilute aqueous solutions, whereas other larger crystals were obtained from dilute ethanol solutions.

Crystal Structure Data Collection. The title compound crystallizes in the triclinic space group $P\bar{1}$ with two formula units in a cell with dimensions [λ(Mo Kα) 0.7107 Å, μ(Mo Kα) 11.40 cm⁻¹] $a = 12.245$ (6) Å, $b = 9.863$ (5) Å, $c = 9.819$ (5) Å, $\alpha = 101.18$ (4)°, $\beta = 105.78$ (5)°, $\gamma = 93.77$ (4)° and $V = 1110.7$ Å³. The calculated density of 1.249 g/cm³ agrees well with that of 1.253 g/cm³ measured by flotation in potassium tetraiodomercurate. Intensity data were collected on a Philips automatic diffractometer with the ω–2θ scan technique, at a scan speed of 0.05°/s and a scan width of 1.20° in ω. The crystal used had approximate dimensions 0.12 × 0.12 × 0.20 mm parallel to [100], [001], and [010], respectively. Stationary-counter, stationary-crystal background counts of 15 s were taken at each end of the scan range. The 2462 reflections having $I > 2\sigma(I)$ were collected in the range $6 < 2\theta < 50°$ and used for the structure determination and refinement. The standard deviation $\sigma(I)$ of the corrected intensity I was taken as $\sigma(I)[P + 0.25(B_1 + B_2)(T_p/T_b)^2 + (KI)^2]^{1/2}$ where P is the peak count, B_1 and B_2 are the background counts, and T_p and T_b are the count times on the peak and background, respectively. The factor K was found to be 0.02 by a least-squares fit of three standard reflections monitored at regular intervals. Intensities were corrected for Lorentz–polarization effects; absorption effects were neglected because transmission factors ranged only from 0.80 to 0.86.

Structure Solution and Refinement. The structure was solved by the heavy-atom technique with the use of Patterson and Fourier

syntheses, which gave all the nonhydrogen atom positions. Two cycles of least-squares refinement with isotropic temperature factors for all the atoms, followed by two cycles with anisotropic temperature factors for Cu, P, and O atoms reduced the R factor to 0.061. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights taken as $w = 4F_o^2/\sigma(F_o^2)$. At this point a difference electron density synthesis showed 26 out of 36 hydrogen atoms. The positions of the other hydrogen atoms were calculated. Introduction of hydrogen atoms with the temperature factors of the carbon atoms to which they are attached, followed by two cycles of least-squares refinement, gave final values for R and R' factors of 0.050 and 0.053, respectively (R' is defined as $[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. Atomic scattering factors were taken from Cromer and Waber[6] for Cu, P, O, and C atoms and from Stewart et al.[7] for H atoms. Cu and P scattering factors were corrected for the real and imaginary parts of anomalous dispersion effects. All the calculations were performed with the use of the X-RAY 72 system of programs, adapted for the C11 10070 computer of the University of Florence. Final atomic parameters with their estimated standard deviations are listed in Table I.

Electron Spin Resonance. Single crystals were selected after observation under cross polarizers to eliminate twinned samples. Alignment was accomplished by using x-ray precession photographs of the zero-level reflections $(hk0)$ and $(0kl)$. The aligned crystal was then fixed to the wall of a rectangular TE_{102} cavity which was cooled to 77 K and operated at 10 GHz. The magnitude of the resonant field was calibrated by inserting a small amount of diphenylpicrylhydrazyl (DPPH) in the cavity. The resonant magnetic fields as a function of magnet angle were measured for three orthogonal rotations. The resulting data for each rotation (see Figure 1) were fit to the expression

$$\bar{g}^2 = \alpha + \beta \cos^2 \theta + \gamma \sin 2\theta$$

with

$$\alpha = (g_+^2 + g_-^2)/2$$
$$\beta = [(g_+^2 - g_-^2)/2] \cos 2\theta_+$$
$$\gamma = [(g_+^2 - g_-^2)/2] \sin 2\theta_+$$

where g_+ and g_- are the maximum and minimum g values occurring at θ_+ and θ_- for each rotation. The parameters α^i, β^i, and γ^i (i denotes the rotation axis) are then used to define a matrix, **w**. The eigenvalues of the **w** matrix are the squares of the principal values of the **g** tensor. In addition the eigenvectors are composed of the directional cosines of the principal axes of the **g** tensor relative to the fixed (laboratory) coordinates used to index the external magnetic field orientation. The previous alignment of the crystal was then used to relate the orientation of the principal axes of the **g** tensor to the atomic coordination surrounding each Cu^{2+} ion.[8]

Magnetic Susceptibility. Approximately 11 mg of polycrystalline material was used for measurement of the magnetic susceptibility in a Faraday balance over the temperature range $77 \leq T \leq 300$ K. The details of the experimental apparatus are described elsewhere.[9]

Table I. Positional Parameters ($\times 10^4$), Thermal Parameters^a ($A^2 \times 10^3$), and Estimated Standard Deviations for the Atoms of Bis(dibutylphosphinate)copper(II)

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	113 (1)	257 (1)	2588 (1)	46 (0)	51 (0)	24 (0)	15 (0)	19 (0)	12 (0)
P(1)	1389 (1)	−938 (2)	5235 (2)	51 (1)	51 (1)	27 (1)	21 (1)	20 (1)	13 (1)
P(2)	1598 (1)	−480 (2)	381 (2)	43 (1)	65 (1)	27 (1)	15 (1)	18 (1)	16 (1)
O(1)	1097 (3)	−858 (4)	3647 (4)	66 (3)	78 (3)	28 (2)	41 (2)	28 (2)	20 (2)
O(2)	378 (3)	−1164 (4)	5799 (4)	54 (3)	56 (3)	29 (2)	18 (2)	25 (2)	9 (2)
O(3)	1058 (3)	452 (4)	1350 (4)	54 (3)	62 (3)	32 (2)	12 (2)	28 (2)	17 (2)
O(4)	1307 (3)	−319 (4)	−1184 (4)	49 (3)	94 (3)	32 (2)	19 (2)	21 (2)	24 (2)

Atom	x/a	y/b	z/c	U, A^2	Atom	x/a	y/b	z/c	U, A^2
C(1)	2180 (5)	−2399 (6)	5388 (6)	51 (2)	C(9)	3133 (6)	−42 (7)	1097 (7)	60 (2)
C(2)	1522 (6)	−3740 (7)	4512 (7)	70 (2)	C(10)	3490 (7)	1458 (8)	1104 (8)	79 (2)
C(3)	2221 (7)	−4985 (9)	4540 (9)	96 (3)	C(11)	4771 (8)	1901 (10)	1636 (10)	115 (3)
C(4)	1555 (9)	−6289 (11)	3660 (11)	133 (4)	C(12)	5094 (9)	3395 (11)	1639 (11)	133 (4)
C(5)	2318 (5)	582 (6)	6328 (6)	52 (2)	C(13)	1255 (5)	−2268 (7)	400 (7)	59 (2)
C(6)	3373 (6)	962 (7)	5870 (7)	64 (2)	C(14)	1749 (6)	−3316 (8)	−561 (8)	81 (2)
C(7)	4113 (7)	2236 (8)	6797 (9)	90 (3)	C(15)	1417 (8)	−4788 (10)	−503 (10)	114 (3)
C(8)	5170 (8)	2611 (10)	6323 (10)	120 (3)	C(16)	1855 (9)	−5867 (11)	−1442 (12)	146 (4)
H(1)	2521	−2361	6448	51	H(19)	3305	−172	2150	60
H(2)	2899	−2195	5119	51	H(20)	3468	−676	532	60
H(3)	974	−3825	3573	70	H(21)	3303	1586	0	79
H(4)	826	−4027	4835	70	H(22)	3323	2555	1710	79
H(5)	2884	−4586	4153	96	H(23)	4847	1507	2513	115
H(6)	2513	−5077	5733	96	H(24)	5151	1316	1005	115
H(7)	717	−6367	3173	133	H(25)	4656	3861	2355	133
H(8)	1945	−6617	2911	133	H(26)	4969	3592	743	133
H(9)	1693	−6995	4266	133	H(27)	6180	3703	2082	133
H(10)	1834	1223	6203	52	H(28)	528	−2310	0	59
H(11)	2621	548	7358	52	H(29)	1583	−2366	1400	59
H(12)	3723	0	5761	64	H(30)	1424	−3124	−1522	81
H(13)	3223	712	4800	64	H(31)	2503	−3216	−135	81
H(14)	3861	3061	7370	90	H(32)	587	−4986	−739	114
H(15)	4508	1826	7619	90	H(33)	1716	−4926	476	114
H(16)	4774	2981	5587	120	H(34)	2627	−5573	−1086	146
H(17)	5601	1753	6348	120	H(35)	1280	−5816	−2553	146
H(18)	5656	3395	7077	120	H(36)	1636	−6812	−1343	146

^{a} Anisotropic thermal factors are of the form $\exp(-2\pi^2(^3\Sigma_{i=1}\ ^3\Sigma_{j=1}h_ih_ja_i{}^*a_j{}^*U_{ij}))$.
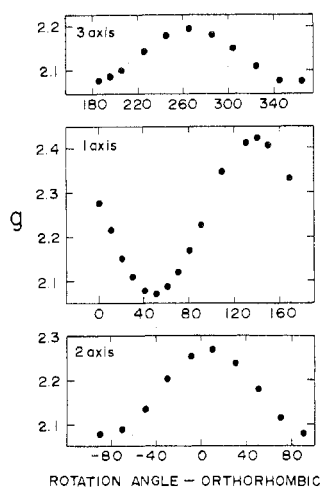
Figure 1. Measured g values as a function of magnet angle for three orthogonal rotations.

Figure 2. ORTEP drawing showing the polymeric chain of bis(dibutylphosphinato)copper(II).

Results and Discussion

Description of the Structure. The overall structure of bis(dibutylphosphinato)copper(II) is similar to that of the analogous bis(diphenylphosphinato)lead(II);[10] i.e., it consists of polymeric chains in which the phosphinate groups form double bridges between copper atoms (Figure 2). The endless chains wind around the crystallographic c axis. The coordination around the copper atom can be described as a very flattened tetrahedron with approximate D_{2d} symmetry (Figure 3). This type of coordination geometry is rather common in four-coordinate copper(II) compounds. The average Cu–O distance is 1.920 (4) Å, a value in agreement with other Cu–O
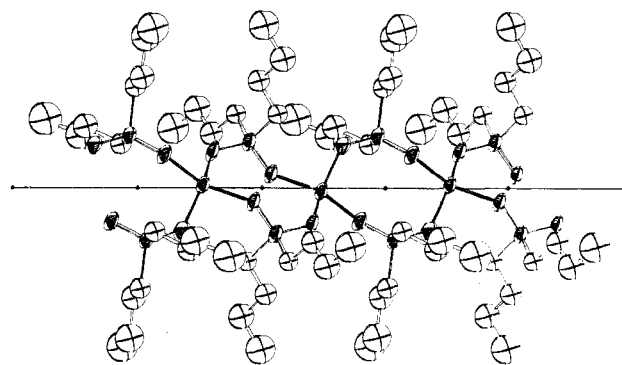
bond lengths in four-coordinate copper compounds. The Cu–Cu distance along the chain is 4.938 (2) Å. Bond lengths and angles in the phosphinate group are in agreement with the values found in bis(diphenylphosphinato)lead(II) (Table II).

The single-crystal x-ray studies of a few zinc phosphinates showed them all to consist of tetrahedral metal atoms linked by alternating single and triple phosphinate bridges.[11] Some cobalt phosphinates have been shown to be isomorphous with their zinc analogues,[12] and x-ray fiber studies have indicated that a beryllium phosphinate also has the single–triple bridged structure.[13] This copper phosphinate is the first definitively characterized poly(metal phosphinate) with tetrahedral metal centers (albeit distorted) and double phosphinate bridging.

ESR and the g Tensor. The x-ray precession photographs were used to relate the principal g values and orientation of the **g** tensor to the atomic coordination of the Cu^{2+} ions as
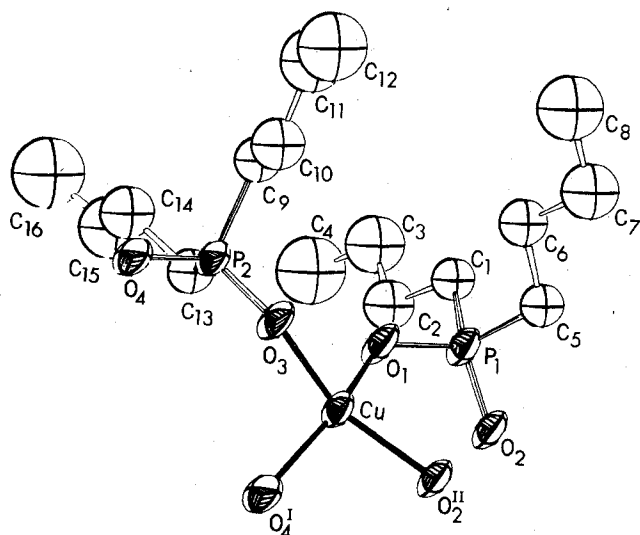
Figure 3. ORTEP drawing of the bis(dibutylphosphinato)copper(II) moiety. The numbering scheme is the same as that used in the tables. Superscripts 1 and 11 refer respectively to atoms related through the centers of symmetry at 0, 0, 0 and 0, 0, $^1/_2$.

Table II. Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses

Cu–O(1)	1.919 (4)	O(1)–Cu–O(2)	95.7 (2)
Cu–O(2)	1.926 (4)	O(1)–Cu–O(3)	93.7 (2)
Cu–O(3)	1.919 (4)	O(1)–Cu–O(4)	147.2 (2)
Cu–O(4)	1.916 (4)	O(2)–Cu–O(3)	145.8 (2)
		O(2)–Cu–O(4)	93.7 (2)
		O(3)–Cu–O(4)	96.0 (2)
		Cu–O(1)–P(1)	130.8 (3)
		Cu–O(2)–P(1)	135.8 (2)
		Cu–O(3)–P(2)	137.9 (3)
		Cu–O(4)–P(2)	132.4 (3)
P(1)–O(1)	1.521 (4)	O(1)–P(1)–O(2)	115.4 (2)
P(1)–O(2)	1.508 (5)	O(1)–P(1)–C(1)	105.8 (3)
P(1)–C(1)	1.780 (7)	O(1)–P(1)–C(5)	109.6 (3)
P(1)–C(5)	1.783 (5)	O(2)–P(1)–C(1)	107.9 (3)
		O(2)–P(1)–C(5)	110.3 (3)
		C(1)–P(1)–C(5)	107.5 (3)
P(2)–O(3)	1.507 (4)	O(3)–P(2)–O(4)	115.7 (2)
P(2)–O(4)	1.522 (4)	O(3)–P(2)–C(9)	107.8 (2)
P(2)–C(9)	1.809 (6)	O(3)–P(2)–C(13)	110.5 (3)
P(2)–C(13)	1.790 (7)	O(4)–P(2)–C(9)	105.4 (3)
		O(4)–P(2)–C(13)	109.2 (3)
		C(9)–P(2)–C(13)	108.0 (3)
C(1)–C(2)	1.48 (1)	P(1)–C(1)–C(2)	113.6 (4)
C(2)–C(3)	1.54 (1)	C(1)–C(2)–C(3)	114.1 (5)
C(3)–C(4)	1.45 (1)	C(2)–C(3)–C(4)	112.9 (7)
C(5)–C(6)	1.53 (1)	P(1)–C(5)–C(6)	116.3 (4)
C(6)–C(7)	1.48 (1)	C(5)–C(6)–C(7)	114.5 (6)
C(7)–C(8)	1.54 (1)	C(6)–C(7)–C(8)	114.1 (7)
C(9)–C(10)	1.51 (1)	P(2)–C(9)–C(10)	111.0 (5)
C(10)–C(11)	1.52 (1)	C(9)–C(10)–C(11)	114.6 (7)
C(11)–C(12)	1.50 (2)	C(10)–C(11)–C(12)	113.1 (8)
C(13)–C(14)	1.53 (1)	P(2)–C(13)–C(14)	115.1 (6)
C(14)–C(15)	1.50 (1)	C(13)–C(14)–C(15)	112.1 (7)
C(15)–C(16)	1.50 (2)	C(14)–C(15)–C(16)	114.8 (9)

shown in Figure 4. The largest *g* value, 2.41, is found in a direction nearly in the *bc* plane of the crystal, approximately normal to a plane formed by completely flattening the tetrahedron of four oxygens surrounding the copper.

This **g** tensor is consistent with those normally seen for Cu^{2+} in an approximate square-planar ligand field. For Cu^{2+} in a tetragonal field the principal *g* values are given by:

$$g_{zz} = 2 - (8\lambda/\Delta_0)$$

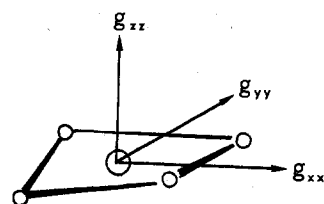$$g_{xx} = g_{yy} = 2 - (2\lambda/\Delta_1)$$

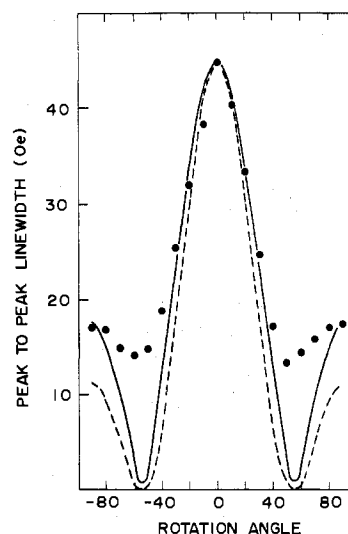**Figure 4.** The orientation of the principal *g* values.

Figure 5. Line width variation as a function of angle of rotation. The best fit of data points (●) for magnetic dipolar interactions in one dimension (—) and for three dimensions (- - -).

in which Δ_0 is the splitting between $d_{x^2-y^2}$ and d_{xy} and Δ_1 is the difference in energy between $d_{x^2-y^2}$ and the (degenerate) d_{xz} and d_{yz} orbitals. Thus the largest *g* value should occur along the *z* axis or perpendicular to the square-planar arrangement. If we assume Δ_0 is approximately equal to $\Delta = 13\,000$ cm^{-1} (estimated from absorption spectra), we calculate a value of $\lambda = -500 \pm 100$ cm^{-1} (with the variation due to anisotropy). This is somewhat less than the free ion value of -830 cm^{-1} and indicates significant mixing of metal and ligand orbitals.

ESR Line Width. The resonance line was a single, well-resolved absorption at all temperatures in the range $1.1 \leq T \leq 300$ K. The line width and *g* value are both anisotropic but nearly temperature independent. Figure 5 shows the range of line width anisotropy for a typical rotation. The angular dependence is reminiscent of magnetic dipolar interaction with functional dependence closer to $(3\cos^2\theta - 1)^{4/3}$ as occurs in one dimension than $(3\cos^2\theta - 1)^2$ which occurs in three dimensions. The solid and dash lines show the best fits of these functions to the data.[14] This indication of a one-dimensional magnetic interaction is consistent with the linear crystal structure. However, in order to explain the nonzero line width at 54 °C a weak (isotropic) exchange mechanism is needed,[15] in addition to the magnetic dipolar interaction.

Magnetic Susceptibility. The high-temperature magnetic susceptibility is Curie-like with $C = 0.485$ (1). The *g* value of $\bar{g}_{susc} = 2.18$ (1) derived from the Curie constant compares well with the geometric average of the ESR *g* values.

References and Notes

(1) (a) Università di Siena. (b) University of Pennsylvania. (c) Pennwalt Corporation.
(2) B. P. Block, *Inorg. Macromol. Rev.*, **1**, 115 (1970).
(3) J. C. Scott, A. F. Garito, A. J. Heeger, P. Nannelli, and H. D. Gillman, *Phys. Rev. B*, **12**, 356 (1975).
(4) T. S. Wei, J. C. Scott, A. F. Garito, A. J. Heeger, H. D. Gillman, and P. Nannelli, *Phys. Rev. B*, **12**, 5297 (1975).
(5) W. C. Drinkard and G. M. Kosolapoff, *J. Am. Chem. Soc.*, **74**, 5520 (1952).
(6) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(7) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(8) W. G. Waller and M. T. Rogers, *J. Magn. Reson.*, **9**, 92 (1973).
(9) J. C. Scott, A. F. Garito, and A. J. Heeger, *Phys. Rev. B*, **10**, 3131 (1974).
(10) P. Colamarino, P. L. Orioli, W. D. Benzinger, and H. D. Gillman, *Inorg. Chem.*, **15**, 800 (1976).
(11) F. Giordano, L. Randaccio, and A. Ripamonti, *Chem. Commun.*, 19, 1239 (1967); *Acta Crystallogr., Sect. B*, **25**, 1057 (1969).
(12) V. Giancotti and A. Ripamonti, *J. Chem. Soc. A*, 706 (1969).
(13) V. Giancotti, F. Giordano, and A. Ripamonti, *Makromol. Chem.*, **120**, 96 (1968).
(14) R. E. Dietz, F. R. Merritt, R. Dingle, D. Hone, B. G. Silbernagel, and P. M. Richards, *Phys. Rev. Lett.*, **26**, 1186 (1971).
(15) M. J. Hennessy, C. D. McElwee, and P. M. Richards, *Phys. Rev. B*, **7**, 930 (1973).

Contribution from the Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210

Structure of an Iron(II) Complex with a Novel Sexadentate Ligand Derived from a Tetraaza Macrocycle

KRISTIN BOWMAN MERTES, P. W. R. CORFIELD, and DARYLE H. BUSCH*

Recent investigations of a series of low-spin iron(II) complexes with macrocyclic ligands have yielded a new sexadentate iron(II) chelate formed by the electrophilic attack of two coordinated acetonitrile molecules at the apical carbons of the parent macrocycles. In this way the acetonitriles form appended iminoethyl groups that are well oriented for chelation. A three-dimensional x-ray crystallographic structural determination has confirmed and clarified the unique nature of the complex. *cis*-3,11-Bis(1-iminoethyl-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraeneiron(II) hexafluorophosphate crystallizes in the orthorhombic space group $P2_12_12_1$ with cell dimensions $a = 21.647$ (19), $b = 11.077$ (11), and $c = 11.115$ (9) Å. The structure was solved by Fourier and least-squares techniques to a conventional $R = 0.064$ for 2787 reflections. The six nitrogens form a slightly trigonal distorted octahedron and the iron nitrogen distances vary from 1.936 to 1.971 Å. The average C–N bond length of 1.256 Å coincides with double bond localization in these rings. The coordination sphere therefore consists of six imine nitrogen donors. The macrocycle is folded and the nitrogens of the iminoethyl groups are coordinated in cis positions.

Introduction

Recent studies on the chemistry of complexes of synthetic macrocyclic ligands have tended to focus on those reactions which mimic the behavior of natural systems such as heme-iron proteins and on the changes in the chemical and physical properties which are attendant upon systematic variations in the structure of the ring. The former are well illustrated by the considerable progress in the development of oxygen-carrying chelates[1-3] while the latter include the dependence of redox properties[4,5] and ligand field strengths[6] on such structural parameters as ring size, extent and arrangement of unsaturated groups, and ligand charge. Structures derived from macrocyclic ligands that have been modified by appended groups are of increasing importance. The function of the metal ion in complicated natural molecules, such as heme proteins and vitamin B_{12}, is controlled in part by the extracyclic part of the structure. Studies on synthetic O_2 carriers have exploited this theme. Traylor and his associates appended an imidazole to a porphyrin ring;[2] Collman et al. produced a "picket fence" porphyrin,[3] and Baldwin and Huff provided a structure wherein a hydrophobic moiety shields one coordination site above a porphyrin.[1] Studies in these laboratories are directed toward the use of extracyclic groups to control the total environment about the metal atom in synthetic, nonporphyrin macrocycles. Earlier reports have included the attachment of a fifth donor atom so placed that it filled a coordination site and the appending of other functional and hydrophobic groups.[7] Cytochrome *c* exemplifies the case where the two coordination sites not filled by a tetradentate macrocyclic ligand are occupied by donor groups propitiously arrayed for chelation by the protein portion of a natural product. We report in a separate paper[8] the fortuitous synthesis and characterization of a series of complexes of the latter class. The structure of one of these is reported here.

Results and Discussion

When macrocycles of general structure I react with solvated

Ia, X = (CH$_2$)$_2$; Y = (CH$_2$)$_2$
b, X = (CH$_2$)$_2$; Y = (CH$_2$)$_3$
c, X = (CH$_2$)$_3$; Y = (CH$_2$)$_3$
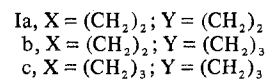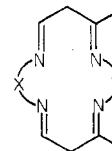
ferrous iron in acetonitrile solution, complexes are formed that can be isolated as the hexafluorophosphate salts.[8] These salts uniformly have the composition of bis(acetonitrile) solvates, i.e., Fe(MAC)(PF$_6$)$_2$·2CH$_3$CN. Only the 14-membered ring derivative, however, involves the most obvious possible structure wherein the macrocycle is coordinated in a planar fashion about the Fe^{2+} ion with the acetonitrile molecules coordinated at the two axial sites. Application of the usual physical and chemical methods of characterization to the bis(acetonitrile) adducts of the iron complexes with the 15- and 16-membered rings revealed disquieting chemical and physical properties. Most striking among the physical properties were the absence