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Complex of N,N′,N″,N‴-Tetrakis[2-Diphenylphosphorylethyl]-1,4,7,10-tetraazacyclododecane with Copper(II) Perchlorate. Synthesis, Structure, and Conformational Analysis

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ABSTRACT

1,4,7,10-Tetraazacyclododecane having β-ethylphosphoryl pendant groups on the nitrogen atoms can form a complementary ligand for the Cu cation. It gives rise to a square pyramidal complex of [CuL]$^{2+}$ compositions, the ligand entering this complex with a slight energy strain. © 1996 John Wiley & Sons, Inc.

Earlier we reported [1,2] a synthesis of organophosphorus cyclopendant ligands based on the cyclene with ethylphosphoryl pendant groups.

The complex-forming ability for the compound with PO_3H_2 groups has been characterized by the stability constants for complexes with several metal cations [1] and by the molecular mechanics calculations using the "floating point" technique [3,4].

In the present article, we report the X-ray structure analysis of the $\{Cu[O{=}P(Ph_2)CH_2CH_2\text{–}N\text{–}CH_2CH_2\text{–}]_4\}^{2+}(ClO_4^-)_2\cdot 6H_2O$ complex and the result of a molecular mechanics calculation of a ligand contour strain energy.

EXPERIMENTAL

The crystalline complex $CuL(ClO_4)_2\cdot 6H_2O$ (I) was isolated from an equimolar mixture of $Cu(ClO_4)_24H_2O$ and ligand (*L*) solutions in alcohol (concentrations of components being 6×10^{-2} mole/L) in the presence of an excess of $LiClO_4\cdot 2H_2O$ (0.1 mole/L). The precipitate was filtered off, washed with alcohol, and dried in the air. If more concentrated solutions are mixed in the absence of $LiClO_4$, an oil-like viscous precipitate is formed that cannot be converted into a crystalline form. Being left in a vacuum over P_2O_5 and heated to 110°C, the complex loses water, which is evidence for the water of crystallization molecules bound in the complex. Physicochemical and spectral characteristics of the complex were described in Ref. [5].

X-ray diffraction data were collected on a CAD-4 automated diffractometer utilizing M_0 K_α radiation, the ω/θ-scan technique, $2\theta \leq 47°$.

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TABLE 1 Nonhydrogen Atom Coordinates in the Structure I. Atoms C(17)–C(64) belong to the Phenyl Rings; O(W1–W6) belong to Crystalline Water Molecules.

TABLE 1 (*Continued*) Nonhydrogen Atom Coordinates in the Structure I. Atoms C(17)–C(64) belong to the Phenyl Rings; O(W1–W6) belong to Crystalline Water Molecules.

Atom	*x*	*y*	
Cu	0.1267(1)	0.24565(8)	0.35399(8)
P(1)	0.1831(2)	0.2355(2)	0.1619(2)
P(2)	0.5143(3)	0.0634(2)	0.2246(2)
P(3)	0.3329(3)	0.5031(2)	0.2199(2)
P(4)	−0.1728(3)	0.5156(2)	0.3675(2)
O(1)	0.1921(5)	0.2805(4)	0.2291(4)
O(2)	0.5641(6)	0.1392(5)	0.1655(5)
O(3)	0.4154(6)	0.4316(5)	0.1957(5)
O(4)	−0.0934(6)	0.5405(5)	0.3958(5)
N(1)	0.0726(6)	0.1257(5)	0.3508(5)
N(2)	0.2467(6)	0.1738(5)	0.3794(5)
N(3)	0.1509(7)	0.3429(5)	0.4124(5)
N(4)	−0.0258(6)	0.2917(5)	0.3915(5)
C(1)	0.0559(9)	0.1079(7)	0.2750(7)
C(2)	0.1515(9)	0.1193(6)	0.1959(7)
C(3)	0.1443(8)	0.0541(6)	0.3720(7)
C(4)	0.1927(9)	0.0892(7)	0.4264(7)
C(5)	0.3375(8)	0.1571(7)	0.3036(6)
C(6)	0.4244(9)	0.0961(7)	0.3221(7)
C(7)	0.2750(9)	0.2235(7)	0.4362(7)
C(8)	0.1824(9)	0.2880(7)	0.4782(7)
C(9)	0.2333(9)	0.4088(7)	0.3669(7)
C(10)	0.2111(9)	0.4620(7)	0.2912(7)
C(11)	0.0500(8)	0.3910(7)	0.4537(7)
C(12)	−0.0364(9)	0.3282(7)	0.4701(7)
C(13)	−0.0531(8)	0.3604(7)	0.3314(6)
C(14)	−0.1681(9)	0.3956(7)	0.3659(7)
C(15)	−0.0931(9)	0.2132(7)	0.1087(8)
C(16)	−0.0273(8)	0.1283(6)	0.4207(7)
C(17)	0.2991(8)	0.2374(6)	0.0758(6)
C(18)	0.3052(9)	0.2090(8)	0.0013(7)
C(19)	0.397(1)	0.2164(8)	−0.0646(7)
C(20)	0.485(1)	0.2505(8)	−0.0603(8)
C(21)	0.477(1)	0.2773(8)	0.0146(8)
C(22)	0.3837(8)	0.2726(7)	0.0844(7)
C(23)	0.0868(8)	0.2919(7)	0.1271(6)
C(24)	0.0883(9)	0.3864(7)	0.1161(7)
C(25)	0.0116(9)	0.4356(8)	0.0924(7)
C(26)	−0.065(1)	0.3926(9)	0.0825(8)
C(27)	−0.067(1)	0.2968(9)	0.0927(8)
C(28)	0.0099(9)	0.2490(8)	0.1158(7)
C(29)	0.6049(8)	−0.0198(7)	0.2464(7)
C(30)	0.669(1)	−0.0617(9)	0.181(1)
C(31)	0.748(1)	−0.1234(9)	0.189(1)
C(32)	0.755(1)	−0.1413(9)	0.269(1)
C(33)	0.689(1)	−0.098(1)	0.335(1)
C(34)	0.611(1)	−0.0358(9)	0.3244(9)
C(35)	0.4395(8)	0.0063(7)	0.1857(7)
C(36)	0.4362(9)	0.0346(8)	0.1086(7)
C(37)	0.374(1)	−0.0112(8)	0.0787(7)
C(38)	0.318(1)	−0.0817(8)	0.1256(8)
C(39)	0.321(1)	−0.1113(8)	0.2041(8)
C(40)	0.3843(9)	−0.0682(7)	0.2342(7)
C(41)	0.3022(9)	0.5581(7)	0.1333(7)
C(42)	0.356(1)	0.5189(8)	0.0585(7)
C(43)	0.338(1)	0.560(1)	−0.0126(8)
C(44)	0.274(1)	0.638(1)	−0.0067(9)
C(45)	0.224(1)	0.679(1)	0.0663(9)
C(46)	0.236(1)	0.6338(9)	0.1422(9)
C(47)	0.3683(8)	0.5877(6)	0.2649(6)
C(48)	0.2939(9)	0.6429(7)	0.3200(7)
C(49)	0.330(1)	0.7078(7)	0.3527(7)
C(50)	0.435(1)	0.7170(7)	0.3293(8)
C(51)	0.507(1)	0.6621(8)	0.2753(8)
C(52)	0.4742(9)	0.5973(7)	0.2424(7)
C(53)	−0.3002(8)	0.5513(7)	0.4325(7)
C(54)	−0.3535(9)	0.5001(9)	0.5058(7)
C(55)	−0.444(1)	0.537(1)	0.5613(8)
C(56)	−0.477(1)	0.6262(9)	0.5422(8)
C(57)	−0.425(1)	0.6758(8)	0.4703(8)
C(58)	−0.3354(9)	0.6392(7)	0.4145(7)
C(59)	−0.1591(9)	0.5669(7)	0.2662(7)
C(60)	−0.0821(9)	0.6287(7)	0.2301(7)
C(61)	−0.073(1)	0.6740(8)	0.1496(8)
C(62)	−0.142(1)	0.6525(9)	0.1114(9)
C(63)	−0.216(1)	0.5900(9)	0.1505(8)
C(64)	−0.226(1)	0.5456(8)	0.2287(7)
Cl(1)	0.3496(3)	0.8801(3)	0.5218(2)
Cl(2)	0.9692(3)	0.1707(2)	0.6752(2)
O(5)	0.337(1)	0.7831(8)	0.540(1)
O(6)	0.340(2)	0.8875(8)	0.4470(8)
O(7)	0.441(1)	0.883(1)	0.530(1)
O(8)	0.2654(9)	0.8181(8)	0.5801(8)
O(9)	0.930(1)	0.1288(9)	0.7532(6)
O(10)	0.929(2)	0.1524(9)	0.6240(9)
O(11)	0.956(2)	0.2594(9)	0.6722(9)
O(12)	1.0672(9)	0.160(2)	0.647(1)
O(W1)	0.4522(9)	0.6969(6)	0.7727(7)
O(W2)	0.292(1)	0.719(1)	0.7171(8)
O(W3)	0.171(1)	0.889(1)	0.766(1)
O(W4)	0.220(1)	0.868(1)	0.916(1)
O(W5)	0.127(2)	0.030(2)	0.014(2)
O(W6[a])	0.009(3)	0.010(2)	0.857(2)
O(W6[a])	0.036(3)	0.886(2)	0.043(3)

[a] Disordered water molecule.

Crystals are triclinic (at 20°C):

a = 14.016(4) Å α = 82.51(2) V = 3470 Å^3
b = 15.229(4) Å β = 68.23(2) Z = 2
c = 17.682(4) Å γ = 84.36(2) space group P1

From 9811 measured reflections, only 4180 reflections with $|F| \geq 4\sigma(F)$ were used in calculations and refinement of the structure. The structure was solved by direct methods and refined by least-squares techniques with anisotropic thermal parameters for nonhydrogen atoms, to residuals R = 0.069 and R = 0.079. Because of the poor quality of the single crystals, no attempts were made to locate hydrogen atoms.

All calculations were carried out on an IBM-11/23 PLUS computer using the SDP-PLUS package of

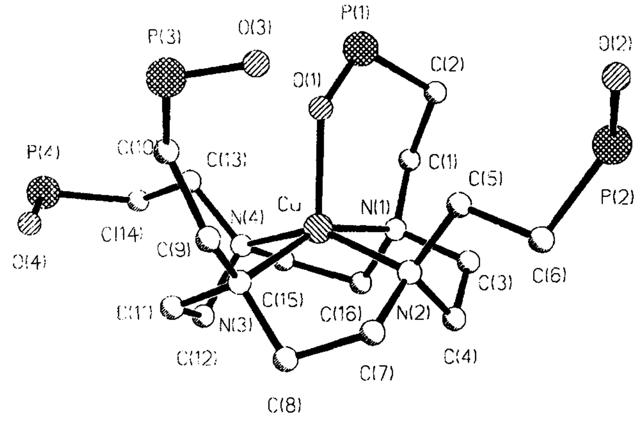

FIGURE 1 Structure of complex $\{Cu[O=P(Ph_2)CH_2CH_2-N-CH_2CH_2-]_4\}^{2+}(ClO_4^-)2\cdot 6H_2O$.

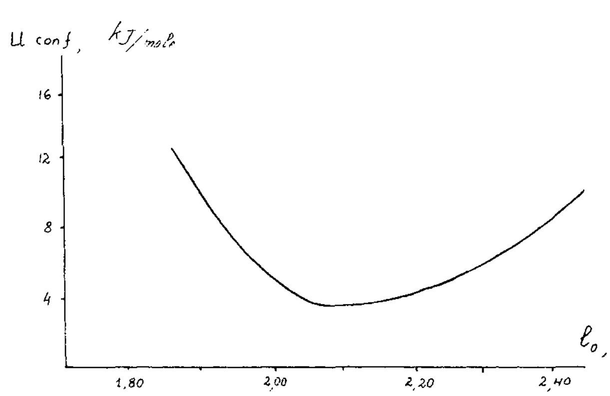

FIGURE 2 Dependence of potential energy of ligand molecule on the distance l_o.

programs [6]. Coordinates for the nonhydrogen atoms are listed in Table 1. A perspective view of the $[CuL]^{2+}$ cation is shown in Figure 1.

DISCUSSION OF THE STRUCTURE

The crystal structure I consists of $[CuL]^{2+}$ cations, two CLO_4^- anions, and six molecules of water of crystallization. There is a branched system of H bonds between the H_2O molecules, the oxygen atoms of the phosphoryl groups, and ClO_4^- anions. One of the six water molecules appears to be disordered over two positions [atoms O(W5) and O(W6); see Table 1].

The copper atom in the $[CuL]^{2+}$ unit has a square-pyramidal coordination (Figure 1) with five donor atoms of the macrocyclic pendant ligand *L*-[4N + O]. Four N atoms are in the base of the square pyramid and are coplanar to within +0.02 Å. The macrocycle has a monoplanar conformation (nitrogen atoms are on one side of the conventional plane). Atom O(1) of one of the four phosphoryl groups occupies the apical position of the pyramid. Other phosphoryl donor oxygen atoms do not participate in the metal coordination and are directed outward from the plane of the four N atoms. The deviation of the atom Cu from the plane of the N atoms toward O(1) is rather large and amounts to 0.502 Å. The lengths of coordination bonds Cu–N are close and range from 2.050 Å to 2.072(8) Å. These values are near to 2.08 Å, the characteristic value for the nonstrained bonds of this type in a Cu^{2+} complex with N-donor atoms in a macrocycle [7]. The coordination bond length Cu–O(1) is 2.070(6) Å (Table 2). This distance is somewhat longer than the Cu–O bonds in all of the Cu complexes with the square-pyramidal coordination of the metal atom studied earlier [8].

It should be noted that the P(1)–O(1) bond 1.497(8) Å for the oxygen atom participating in the metal coordination is somewhat longer as compared with P–O bond distances in noncoordinated phosphoryl groups of the ligand. Other geometric parameters of the structure have the expected values.

Estimation of the strain energy of the pentadentate ligand contour, identical with that experimentally determined for the $[CuL]^{2+}$ cation structure, was calculated by the molecular mechanics method. Contributions to the molecular potential function and penalty limitations were taken from Ref. [2]; namely,

$$U_{\text{conformational}} = U_{\text{nonvalent}} + U_{\text{torsional}} + U_{\text{penalty}}$$

Results of the conformational analysis are represented in Figure 2 as a dependence $U_{\text{conf.}}(l_o)$. This curve corresponds to the searched topology of the pentadentate ligand.

As may be seen, the function minimum of the curve differs by 3 kJ/mole from the free ligand energy (the global minimum) due to a small distortion of the macrocycle, which is evidence for a slight strain in the ligand contour in question.

The position of the local minimum corresponds to the coordination bond length 2.10 Å; this value may be considered as a satisfactory approximation to that determined by X-ray structure analysis, especially if one takes into account calculations of the complex model where all bond lengths M–O and M–N are assumed to be equal. The optimal calculated value 2.10 Å is obtained as a result of competition between the pendant chain and the macrocycle conformations; the strain increases with decreasing l_o due to changes in the phosphoryl group conformation, while an increase in this distance results in the torsional strain in the macrocycle.

The coordination polyhedron is formed in the area of the minimum of the $U_{\text{conf.}}(l_o)$ curve. It has

TABLE 2 Important Bond Lengths (Å) and Bond Angles (deg.) in the Cation of the Structure I.

Bond	*d, Å*	*Angle*	*Deg.*
Cu–N(1)	2.061(8)	0(1)CuN(1)	98.3(3)
Cu–N(2)	2.072(9)	O(1)CuN(2)	102.4(3)
Cu–N(3)	2.030(9)	O(1)CuN(3)	108.3(3)
Cu–N(4)	2.068(8)	O(1)CuN(4)	107.5(3)
Cu–O(1)	2.070(6)	N(1)CuN(2)	87.1(3)
P(1)–O(1)	1.497(8)	N(1)CuN(3)	153.4(3)
P(2)–O(2)	1.489(7)	N(1)CuN(4)	85.5(3)
P(3)–O(3)	1.487(8)	N(2)CuN(3)	86.5(4)
P(4)–O(4)	1.48(2)	N(2)CuN(4)	150.0(4)
Mean N–C	1.51(1)	N(3)CuN(4)	87.3(4)
Mean O–C	1.81(2)		

the shape of a regular square pyramid whose base is occupied by four nitrogen atoms and the apex by the phosphoryl oxygen. The calculated structure of such a ligand contour shows that the coordination type, the macrocycle configuration, and position of the cation above the macrocycle plane coincide.

According to calculations, the distance of the foregoing plane deviation of the cation changes, depending on l_o. For the optimal value, $l_o = 2.10$ Å; h is 0.45 Å, which is close to the value obtained from the X-ray analysis (0.502 Å).

It should be noted that the conformational analysis data are reported for calculations of molecules having hypothetical carbon atoms instead of phenyl groups with phosphorus atoms. Earlier we showed that such an approach slightly effects the position of the potential function minimum [9]; if there are no stacking interactions between phenyl group pairs, it also has little effect on its relative depth. Nevertheless, to be correct, we carried out a calculation for the molecules with phenyl groups using three l_o values (1.95, 2.10, and 2.25 Å). As should be expected, the absolute value for the conformational energy differs from that obtained from the previous calculation; however, the relative value and position of the minimum are nearly the same. Thus, steric interactions between phenyl rings are not essential if only one phosphoryl group is coordinated; however, for the hexadentate structure, the energy of nonvalent interactions between phenyl rings becomes significant.

The character of the strain energy changes provides evidence for a high stability of complexes in the area $l_o = 2.10$ Å; it is also defined by the cation's requirement to form the structure in the shape of a regular square pyramid.

The latter differs somewhat from opinions expressed in Ref. [5], where the authors arrived at conclusions about a disordered symmetry of the inner sphere of the complex. The value of the extinction coefficient, too high for a copper(II) compound, was attributed to a low symmetry at the $[CuN_4O]$ chromophore. In contrast to that, the result of the X-ray and conformational analysis only point to a low complex symmetry on the whole, and a distortion of the macrocycle.

Thus, the tetraazacyclododecane has been examined with ethylphosphoryl pendant groups on the nitrogen atoms that can form a complementary ligand for the Cu cation. It gives rise to a square-pyramidal complex of $[CuL]^{2+}$ compositions, the ligand entering this complex with a slight energy strain.

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