Intramolecular hydrogen bonds in the copper(II) complex with *cis,cis*-1,3,5-tri[2-(diphenylphosphoryl)ethylamino]cyclohexane

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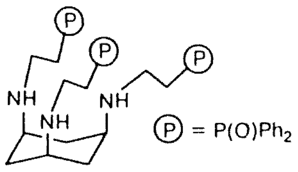
The formation of intramolecular hydrogen bonds in the complex of *cis,cis*-1,3,5-tri[2-(diphenylphosphoryl)ethylamino]cyclohexane with the Cu^{2+} cation in different solvents has been studied by IR spectroscopy. Conformational analysis of the complex has been performed.

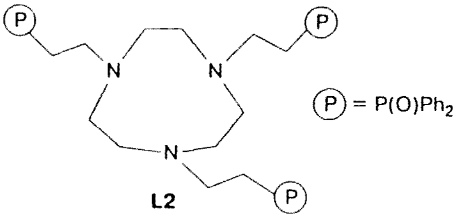
Key words: cyclopendant organophosphorus ligands, complexation with the Cu^{2+} cation, intramolecular hydrogen bond; conformational analysis.

Studies of reactions of *cis,cis*-1,3,5-tri[2-(diphenylphosphoryl)ethylamino]cyclohexane (**L1**) with the Cu^{2+} ion



L1

have demonstrated that the five-coordinate square-pyramidal $[CuL1]X_2$ complex (X = Cl or Br) is formed in different solvents with an equimolar metal—ligand ratio. The metal ion is bonded to three nitrogen atoms and two oxygen atoms of the ligand, whereas one phosphoryl group remains free.[1] Although the coordination polyhedron does not contain solvent molecules, the structure of this polyhedron depends on the nature of the solvent. Two types of the $[CuL1]X_2$ complex with different spectral parameters are observed in aprotic (chloroform, DMSO, and acetone) and hydroxyl-containing (methanol and acetone—water and DMSO—water mixtures) media. Thus, in the electronic spectrum, the d—d transition band is observed at 710 and 740 nm for solutions of the complex in chloroform and methanol, respectively, whereas in the acetone—water mixture, the corresponding doublet is observed. In a hydroxyl-containing solvent, the value of $g_{\|}$ (2.281 and 2.331) is smaller and the value of $a_{\|}$ (161 and 142) is higher in the ESR spectra than in an aprotic solvent, while the degree of covalence of coordination σ-bonds remains unchanged ($\alpha^2 = 0.81$). The IR spectra of the complex in aprotic solvents show an absorption band of coordinated P=O phosphoryl groups at lower frequencies (1135 cm^{-1}) than those observed in hydroxyl-containing solvents (1150 cm^{-1} in methanol).[1] This relationship between the spectral characteristics of the complex and the nature of the solvent was not observed when the analogous copper complex with 1,4,7-tris(2-diphenylphosphorylethyl)-1,4,7-triazacyclononane (**L2**), which is isomeric to **L1**, was studied (see Ref. 2).



L2

Unlike **L2**, the **L1** ligand contains secondary rather than tertiary amino groups. For this reason, it can be assumed that the differences observed in the behavior of copper complexes result from the formation of intramolecular hydrogen bonds in the $[CuL1]X_2$ complex with the participation of amine hydrogen atoms and phosphoryl groups. These bonds may exist in aprotic media, but they are broken in hydroxyl-containing media.

In this work, to check this assumption, the IR spectra of solutions of the $[CuL1]Cl_2$ complex in aprotic and hydroxyl-containing solvents (in chloroform, methanol, and in deuterium-substituted analogs) were studied in detail. To compare the spectral characteristics, the IR spectra of copper complexes of model compounds containing, as in the case of **L1**, secondary amino and phosphoryl groups (diphenylphosphorylmethylcyclo-

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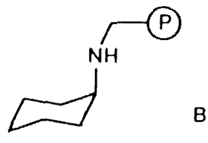
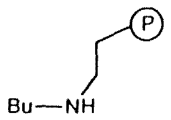
hexylamine (**L3**) and (2-diphenylphosphorylethyl)butylamine (**L4**)) were studied under the same conditions.



L3



L4

Ⓟ = P(O)Ph$_2$

The **L3** and **L4** ligands differ, in particular, in the length of the alkylene bridge between the chelating groups, which should be variously reflected in their ability to form intramolecular hydrogen bonds.

To assess the potential possibility of intramolecular H-cycles being closed in the [CuL1] complex, conformational analysis was performed by molecular mechanics.

Results and Discussion

Complexation of the L1 ligand with CuCl$_2$. Analysis of the IR spectra of the **L1**—**L4** ligands and their complexes with CuCl$_2$ in the region of ν(P=O) stretching vibrations demonstrated that absorption bands of both free and coordinated phosphoryl groups are observed in the spectra of all complexes (Table 1). It should be noted that when the **L1** and **L2** ligands react with CuCl$_2$, individual complexes of 1 : 1 composition are formed,[1,2] whereas under analogous conditions, the **L3** and **L4** ligands show variable dentation and form a mixture of complexes of different compositions and different structures (complexation of **L3** and **L4** with CuCl$_2$ is discussed below). Thus, for solutions of the complexes with the **L1** and **L2** ligands, the frequencies given in Table 1 correspond to the ν(P=O) vibrations of one type of [CuL]Cl$_2$ complex in which two phosphoryl groups are coordinated and one group is free.[1,2] In the case of solutions containing complexes with the model **L3** and **L4** ligands, different frequencies correspond to different complexes in which the phosphoryl group of the ligand is either coordinated or free.

Table 1. The ν(P=O) stretching vibration frequencies (ν/cm^{-1}) of the phosphoryl group of the **L1**—**L4** ligands and their complexes with CuCl$_2$ in chloroform and methanol

Compound	CHCl$_3$		MeOH	
	Ligand	Complex	Ligand	Complex
L1	1180	1135 s,[a] 1180 m[a]	1160	1148,[a] 1160 sh[a]
L2	1175	1145 s,[a] 1175 m[a]	1160	1150,[a] 1160 sh[a]
L3	1180	1145 w,[b] 1170 s,[b] 1190 sh[b]	1160	1150 br[b]
L4	1180	1175 br[b]	1160	1150 br[b]
L4	1180	1145,1170 br[c]		

[a] Complex of composition [CuL]Cl$_2$. [b] The solution with a CuCl$_2$: **L** ratio of 1 : 2 contains complexes of different composition and with different structures (see p. 1470), [c] A mixture of the complexes in the presence of excess CuCl$_2$, Cu : **L** > 3 : 1 (see p. 1470).

As is evident from Table 1, the ν(P=O) absorption band of the phosphoryl group of the **L1** and **L2** ligands shifts equally from 1160 to 1148—1150 cm^{-1} upon formation of complexes in methanol, whereas upon complexation of the **L1** ligand in chloroform, this ν(P=O) band shifts from 1180 to 1135 cm^{-1}; this shift far exceeds those observed for the analogous [CuL2]Cl$_2$ complex (from 1175 to 1145 cm^{-1}) and for the complexes of the model compounds (from 1180 to 1145—1150 cm^{-1}). This "additional" lowering of the ν(P=O) frequency of coordinated P=O groups in the spectrum of the [CuL1]Cl$_2$ complex in chloroform suggests that a bifurcated interaction of the oxygen atom of the phosphoryl group with the metal cation and the hydrogen atom of the N—H group occurs in this complex.

The high-frequency regions of the IR spectra of solutions of the **L1**, **L3**, and **L4** ligands and their complexes with CuCl$_2$ are given in Fig. 1. In the spectrum of the solution of the **L1** ligand in deuterochloroform, the ν(N—H) vibration occurs as a rather broad absorption band with a maximum at 3330 cm^{-1}. In the spectra of the **L3** and **L4** model compounds, the analogous absorption band is observed. The shoulder at ~3400 cm^{-1} does not correspond to the N—H stretching vibration, but is determined by absorption by traces of water present in deuterochloroform used without precision drying.*

When the [CuL1]Cl$_2$ complex is formed in deuterochloroform, the spectrum changes substantially: two maxima at 3220 and 3130 cm^{-1} appear and, in addition, the absorption intensity in the 3200—2800 cm^{-1} region increases substantially; the bands corresponding to C—H vibrations stand out against the background of this absorption (see Fig. 1, *a*, spectrum *2*). The shift of ν(NH) absorption bands to the lower-frequency region and the increase in their intensity may be a result of the formation of the metal—nitrogen coordination bond[3,4] without any other interactions. Therefore, spectrum *2* (see Fig. 1, *a*) is not an unambiguous indication of the

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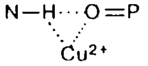
* In the spectrum in deuterochloroform, weak absorption bands at 3620 and 3690 cm^{-1} attributable to free molecules of residual water are observed. When dissolved in CDCl$_3$, the compounds studied form aquacomplexes with residual water, which results in a change in the absorption bands of water (3400 cm^{-1}) and of the N—H groups of the ligands (broadening of the band in the 3300 cm^{-1} region). Note that when the concentration of the solution of **L2** is changed from 0.5 to 0.01 mol L^{-1}, the N—H band shows no changes either in position or intensity (*Cd* = const), which supports the validity of the interpretation made.

nate [CuL1]Cl_2 complex in chloroform: two out of three groups have additional interactions and one group is involved only in coordination. Both coordinated phosphoryl groups are also involved in additional interactions, which may be two intramolecular hydrogen bonds in the complex


$N{-}H\cdots O{=}P$, Cu^{2+}

One phosphoryl group of the ligand moiety remains free.

The IR spectrum of the [CuL1]Cl_2 complex in deuterochloroform is no more intense in the 3150—2800 cm^{-1} region than that of the ligand (see Fig. 1, *b*, spectra *1* and *2*). Therefore, the NH vibration band occurs at higher frequencies and is hidden by the broad intense band with the maximum at 3350 cm^{-1}. Besides NH absorption, this band includes the OH absorption of the water molecule that is contained in commercial samples of deuteromethanol. The spectra of the **L3** ligand and the CuL3 complex (see Fig. 1, *b*, spectra *3* and *4*) may be characterized analogously. The differences observed between the spectra of the [CuL1]Cl_2 complex in methanol (and in any hydroxyl-containing solvent) and the spectra of this compound in chloroform (an aprotic solvent) are reasonably attributable to the absence of intramolecular hydrogen bonds in methanol, which solvates mainly through H bonding. Apparently, when the solvation shell of the complex is formed in methanol, the donor groups of the ligand moiety form intermolecular H-bonds with the solvent molecules, whereas when the complex is dissolved in methanol, intramolecular H-bonds appear to be more energetically favorable.

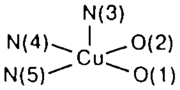
Note that formation of intracomplex H-bonds may result in slight changes in the character of the planar coordination bonds as well as in a slight distortion of the structure of the coordination polyhedron. Both these factors may produce changes in the spectral parameters of the complex, which occur when the solvent is changed.[1]

Therefore, of the three ligands studied (**L1**, **L3**, and **L4**), which have the same functional groups (N—H and P=O), only **L1** forms an intramolecular hydrogen bond when it coordinates with the Cu^{2+} cation in aprotic solvents. In the case of the **L3** and **L4** model compounds, regardless of the length of the alkylene bridge between the P=O and N—H groups, no hydrogen bond in the complex is formed. It may be suggested that formation of the [CuL1] complex cause two pairs of P=O and N—H groups to be brought into proximity; in this case, interactions between these groups do not require additional expenditure of energy. Apparently, the copper complexes of the **L3** and **L4** ligands have different (less rigid) structures; in this case, formation of the H-cycle is not favored by the conformation.

Conformational analysis of the [CuL1] complex. The conformation energy of the [CuL1] complex was calculated by molecular mechanics (the MMX-88 program, PC Model, Serena Software, Bloomington, IN). The geometry of the metal polyhedron was based on the experimental data on the square-pyramidal structure of the complex with one hydrogen atom in an axial position, two oxygen atoms in equatorial positions, and two nitrogen atoms in equatorial positions.[1] Because one phosphoryl group remains uncoordinated, the complex may occur as two isomers that differ in the position of the free phosphoryl group. In the first case, the uncoordinated phosphoryl group is attached to the equatorial nitrogen atom, whereas in the second isomer, this group is bonded to the axial nitrogen atom. Calculations were performed for both isomers.

The structures of the complexes were optimized with the given copper—donor atom distances (see Ref. 5): the lengths of the equatorial Cu—N bonds, the axial Cu—N bond, and the equatorial Cu—O bonds are 2.029 Å, 2.299 Å, and 1.947 Å, respectively. The bond lengths were fixed with the elastic constant equal to 20. Calculations demonstrated that the absolute energy minima corresponding to stable conformations of the complexes differ by only 1.1 kcal mol^{-1}, which gives no way of choosing reasonably between the models. However, the coordination polyhedra of the complexes differ substantially. The polyhedron of the first model of the complex with the uncoordinated phosphoryl group in an equatorial position is a distorted square pyramid, which is in agreement with the results of the experiment,[1] whereas the polyhedron of the second model is close to a trigonal bipyramid: the N(3)—Cu—O(1) angle (Scheme 1) is 150°.

Scheme 1



This structure of the polyhedron contradicts the experimental data, therefore, hereinafter we analyze the first model of the complex.

The values of the angles of the coordination polyhedron of the complex, which is a distorted square pyramid in which the copper atom is above the plane of the base (see Scheme 1), are as follows: N(3)—Cu—O(2) 107.17°; N(3)—Cu—O(1) 83.01°; N(3)—Cu—N(4) 87.70°; N(3)—Cu—N(5) 94.14°; N(4)—Cu—O(1) 167.70°; N(5)—Cu—O(2) 158.37°; O(2)—Cu—O(1) 88.21°; N(4)—Cu—O(2) 86.85°; N(4)—Cu—N(5) 90.45°; O(1)—Cu—N(5) 112.42°. The bond lengths remain equal to the given values (see above).

The conformation of the complex in the region around the absolute minimum is shown in Fig. 2. The uncoordinated phosphoryl group and the nitrogen atom bonded to this group are separated by 3.35 Å. The distances between the pairs of the coordinated nitrogen

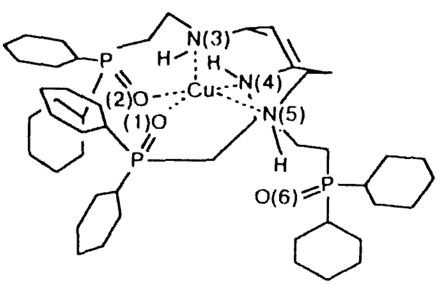


Fig. 2. Conformation of the [CuL1] complex in the region around the absolute minimum. The O(1)—N(4), O(2)—N(3), and O(6)—N(5) distances are 2.76 Å, 2.84 Å, and 3.35 Å, respectively.

and oxygen atoms are 2.76 and 2.84 Å, which is optimum for hydrogen bonding. The typical N—O distances in the N—H...O bonds are 2.90±0.10 Å.[6] Therefore, because of coordination requirements of the metal atom, ideal conditions for the formation of two intraligand (intracomplex) hydrogen bonds occur during complexation of the copper cation with the **L1** ligand. For the third hydrogen bond to be formed, it is necessary that the oxygen atoms of the uncoordinated phosphoryl group and the nitrogen atom come within a distance of 2.90 Å. The strain energy of this conformer is 4.4 kcal mol^{-1}. Therefore, formation of the third intramolecular H-bond is energetically less favorable, which is in agreement with the experimental results.

The case of the formation of intramolecular hydrogen bonds in the complex, which we discussed, is one example of the mutual influence of two effects: coordination and hydrogen bonding. The best-known example is the formation of an H-bond in metal dioximates in which coordination of the ligand is favorable for forming an H-bond, which affects the structure and, therefore, the properties of the complex compound.[7—9]

Complexation of the L3 and L4 model compounds with $CuCl_2$. When the **L3** and **L4** ligands react with $CuCl_2$ in deuterochloroform, stable coordination occurs mainly through the nitrogen atom. This is evidenced by the appearance of the N→Cu charge transfer in the 280—290 nm region of the UV spectrum as well as by the change in the CH stretching absorption bands in the IR spectrum. It is known that the stretching vibration frequencies of the CH groups bonded to the nitrogen atom increase upon coordination of this atom. For the compounds considered, the disappearance of the absorption band at ~2800 cm^{-1} (see Fig. 1, *a*, spectra *4* and *6*) is most readily noted. Previously, we observed analogous evidence of coordination of the nitrogen atom.[1,2]

Coordination of the phosphoryl group is less stable and depends on the metal : ligand ratio in the reaction mixture. An intense rather broad absorption band with a maximum at 1180 cm^{-1}, which corresponds to the phosphoryl group vibration, is observed in the spectra of the free **L3** and **L4** ligands. With the metal : ligand (M : L) ratio of 1 : 1, complexes in which the ligand is coordinated only through the nitrogen atom are observed spectroscopically. In the spectrum of the solution of the $CuCl_2$ complex with **L3** with M : L = 1 : 2, three bands are observed: 1145 (a medium intensity band), 1170 (an intense band), and ~1190 cm^{-1} (a shoulder). The first of these bands corresponds to a coordinated phosphoryl group; the value of the shift of $\nu(P=O)$ is typical of copper complexes (see, for example, [Cu**L2**], Table 1). The second split band indicates that the solution contains complexes in which coordination occurs through the nitrogen atom, while the phosphoryl group remains free. In chloroform, free coordination sites in complexes of this type may be occupied by the Cl^- anion. In the UV spectrum, the absorption band in the 350 nm region corresponds to Cu—Cl coordination. The d—d transition band is observed at 750 nm.

In the case of the **L4** ligand, coordination of the phosphoryl group to the copper cation becomes noticeable only with the ratio M : L > 2 : 1; in this case, the absorption band of the P=O groups broadens and has a maximum at 1170 cm^{-1} and a shoulder at 1145 cm^{-1}. In the UV spectrum, the d—d transition band is observed at 710 nm with the ratio M : L = 1 : 2; this band shifts to 780 nm in the presence of excess $CuCl_2$.

Therefore, when the **L3** and **L4** ligands react with $CuCl_2$ in chloroform solutions, complexes of different composition and/or with different structures are formed. In all complexes, the nitrogen atom of the ligand is coordinated, whereas the phosphoryl group may be coordinated or free. In the **L3** ligand, coordination of the P=O group occurs more readily than in the **L4** ligand. Instead of the P=O group, the Cl^- anion is incorporated into the coordination polyhedron.

During complexation in methanol, a mixture of different complexes also forms; in these complexes coordination of the nitrogen atom of the ligand is always observed, whereas the phosphoryl group may remain free (see Table 1). Unlike chloroform solutions, the coordination sphere of the copper cation in methanol solutions contains solvent molecules rather than the Cl^- anion. A change in the composition and/or in the structure of the complex according to the M : L ratio was noted from the shift of the d—d band to the long-wave region within 740—780 nm when the concentration of $CuCl_2$ was increased.

Therefore, studies of the model **L3** and **L4** compounds and their complexes with $CuCl_2$ demonstrated that none of the spectral changes that are observed in the case of the [Cu**L1**] complex occur upon coordination of the nitrogen atom. It was also demonstrated that the presence of coordinated N—H and P=O groups does not necessarily lead to the formation of intramolecular H-bonds in the complex.

Experimental

IR spectra of solutions of the ligands and their complexes with different concentrations (C = 0.5—0.0018 mol L^{-1}) were recorded on a Specord M-80 or UR-20 spectrometer. Cells with different path lengths (d) were used to keep the value of the Cd product constant. Electronic spectra were measured on a Specord M-40 spectrometer with the use of quartz cells with a 1 cm or 0.1 cm path length. The ^{31}P NMR spectrum was obtained on a Bruker WP 200 SY instrument (80.3 MHz) in $CDCl_3$ (85 % H_3PO_4 solution was used as the external standard).

The solvents, deuterochloroform and deuteromethanol (both of reagent grade, the concentration of the isotope was 99.3 %), were used without additional purification using standard procedures. Reagent-grade methanol and chloroform were purified using standard procedures.

Synthesis and purification of the **L1** ligand were described previously.[10]

Diphenylphosphorylmethylcyclohexylamine (**L3**) was synthesized and purified using the known procedure.[11] M.p. 90—92 °C. Found (%): N, 4.3; P, 10.0. $C_{19}H_{24}NOP$. Calculated (%): N, 4.5; P, 10.0.

(2-Diphenylphosphorylethyl)butylamine (L4) was synthesized using the procedure described previously[12] and recrystallized from a benzene—pentane mixture. M.p. 141—143 °C. Found (%): C, 71.5; H, 8.1; N, 4.6; P, 10.2. $C_{18}H_{24}NOP$. Calculated (%): C, 71.7; H, 8.0; N, 4.6; P, 10.3. ^{31}P NMR, δ: 28.34.

Chemically pure anhydrous copper chloride, $CuCl_2$, was additionally dried at 100 °C *in vacuo*.

Solutions of the complexes in deuterochloroform were prepared by the addition of the calculated amount (using the ratio M : L = 1 : 1 or 1 : 2) of the crystalline anhydrous salt $CuCl_2$ to a solution of the ligand with a concentration of 0.5 —0.0018 mol L^{-1}. Complexes in deuteromethanol were obtained by mixing solutions of the ligand and $CuCl_2$ with known concentrations.

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