COMPLEX FORMATION OF 1,4,7-TRIS(β-DIPHENYLPHOSPHINYLETHYL)-1,4,7-TRIAZACYCLONONANE WITH DIVALENT COPPER SALTS

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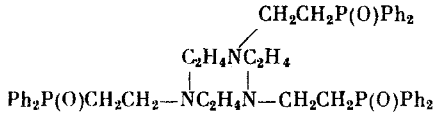
UDC 541.124.7

An investigation of the monoligand complex of 1,4,7-tris(β-diphenylphosphinylethyl)-1,4,7-triazacyclononane with divalent copper has been carried out in various solvents using electronic, IR, and ESR spectroscopy. It was found that the five-coordination polyhedron formed in the complex involves only donor atoms of the ligand and has the structure of a tetragonally elongated square pyramid with two nitrogen atoms and two oxygen atoms at the base and a nitrogen atom at the apex. Compared with the copper(II) complex with the corresponding acid, 1,4,7-tris(β-dihydroxyphosphinylethyl)-1,4,7-triazacyclononane, the coordination compound studied has a higher order of symmetry. The absence of observable distortions in the case of the acid is probably connected with steric interaction of the bulky phenyl substituents in the test ligand.

Keywords: *complex formation, cyclopendant ligands, structure, phosphoryl groups, ESR.*

Derivatives of 1,4,7-triazacyclononane containing organophosphorus pendants form 1:1 complexes with metal cations, the pendant donor centers coordinating the metal ion on an equal footing with nitrogen atoms of the macrocycle [1]. Owing to the small dimensions of triazacyclononane its cavity cannot enclose cations and therefore the properties of these ligands depend considerably on the stereochemistry of the pendants involved in forming the coordination polyhedron [2]. Previously electronic, IR, and ESR spectroscopy have been used to study the complexing properties of 1,4,7-tris(dihydroxyphosphinylmethyl)-1,4,7-triazacyclononane (**1**, H_6L^1) and 1,4,7-tris(β-dihydroxyphosphinylethyl)-1,4,7-triazacyclononane (**2**, H_6L^2) with respect to divalent copper. Protonated and deprotonated complexes of these compounds have a pentacoordinate structure of the tetragonal type, such that two phosphone groups and two nitrogen atoms form the base of the pyramid and a third nitrogen atom is its apex. The difference lies in a different degree of distortion and the mobility of the pyramidal polyhedron [3].

Introduction of substituents at the phosphorus atoms in pendants while keeping the length of the pendant fixed is also able to alter their donor properties and the stereochemistry of the ligand contour. The present paper describes a study of the interaction of the cyclopendant structure



$$\begin{array}{c} CH_2CH_2P(O)Ph_2 \\ C_2H_4NC_2H_4 \\ Ph_2P(O)CH_2CH_2-NC_2H_4N-CH_2CH_2P(O)Ph_2 \end{array}$$

(3, L^3)

with divalent copper in methanol, a methanol—water mixture (1:1 by volume), and chloroform using ESR, electronic, and vibrational spectroscopy.

The ESR spectra of frozen solutions of the complexes characterize the electronic state of the copper atom and yield information on the structure of the immediate coordinate environment of the cation.

The ESR spectra of the complex of ligand (**3**) with copper(II) chloride and perchlorate in methanol and the methanol—water mixture, and with copper chloride and bromide in chloroform are the same. The anisotropic parameters of the complex are shown in Table 1.

A study of the dependence of the anisotropic ESR spectrum of Cu^{2+} on ligand concentration in methanol showed that for $0 < [L^3]:[CuCl_2] < 1$ the spectrum contains lines corresponding to solvated copper(II) which has not reacted with the ligand, as well as the absorption lines of the complex. For $[L^3]:[CuCl_2] \geq 1$ only the spectrum of the complex is recorded and its parameters do not depend on the excess of ligand. This indicates that the composition of the complex is ligand:metal = 1:1.

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TABLE 1. Parameters of the ESR Spectra of Complexes of Divalent Copper with L^1-L^6

Complex	$g_\parallel$	$g_\perp$	$A_\parallel$ (10^{-4}) cm^{-1}	g_{iso}	g_{av}
CuH_4L^1 (cryst.) [3]	2.256	2.059	–	–	2.125
(CuH_3L^2) solution in H_2O [3]	2.314	2.081	142.1	–	2.159
[CuL^3]X_2 *	2.339	2.082	135.2	2.164	2.168
[CuL^4]Cl_2 [6]	2.342	–	135	–	–
[CuL^5]Cl_2 [6]	2.346	2.081	139	–	2.169
[CuL^6]Cl_2	2.346	–	143	–	–

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*X = Cl^-, Br^-, ClO_4^-, solutions in MeOH, MeOH—H_2O, and $CHCl_3$.

TABLE 2. Parameters of Absorption Bands in Electronic Spectra of Cu^{2+} Complexes with L^1-L^3

Complex	Solvent	λ, nm (ε, $cm^{-1}\cdot M^{-1}$)	
		d–d band	CTB
$(CuH_3L^1)^-$	H_2O [3]	725(60)	270(3500)
$(CuH_3L^2)^-$	H_2O [3]	750(40), 650 sh	270(5000)
CuL^3Cl_2	MeOH	820(48)	280sh 225
»	MeOH–H_2O	820(45)	280sh
»	$CHCl_3$	820(40)	280sh
*	»	710 sh	310 sh 400 con
*	»		
CuL^3Br_2	$CHCl_3$	810(33)	280 sh

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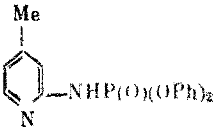
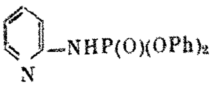
*A complex of unknown composition formed by interaction of CuL^3Cl_2 with $CuCl_2$ (solid) in chloroform.

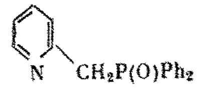
A symmetrical singlet is observed when the solutions are frozen and the g-factor (g_{iso}) is the same as the average value $g_{av} = (g_\parallel + 2g_\perp)/3$ within the uncertainty of the measurements (see Table 1). This indicates an identical structure for the CuL^3X_2 complexes (X = Cl^-, Br^-, ClO_4^-) at 293 K and 77 K.

Ligand **3** in chloroform at ~20°C forms two types of complex with $CuCl_2$: g_{iso} for one of them corresponds to g_{iso} for the CuL^3Cl_2 complex described and the parameters of the other could not be determined because of the weak intensity of the signal compared with the CuL^3Cl_2 singlet.

The ESR spectra of copper(II) complexes with simpler ligands were studied for comparison (see Table 1):


(L^4),


(L^5);


(L^6).

For all the complexes $g_\parallel > g_\perp > 2.04$, i.e., the unpaired electron is in a $d_{x^2-y^2}$ orbital and the CuL^3X_2 complexes are tetragonally elongated [4].

Attention is drawn to the similarity of the ESR parameters of the complexes with ligands L^3-L^6. Compounds L^4-L^6 are known to react with transition metals to form six-membered chelate rings involving coordination of an oxygen atom of the phosphoryl group and a nitrogen atom of the pyridine ring. Square-planar $Cu(N_2O_2)$ chromophores are formed in the bisligand complexes [5, 6]. The similarity in magnetic properties of the complexes with ligands L^3-L^6 provides corroboration that the equatorial plane in CuL^3X_2 is formed by two nitrogen atoms and two oxygen atoms. Slight differences in the ESR parameters are due in our opinion to differences in donor—acceptor properties of substituents at the atoms involved in coordination with the metal:

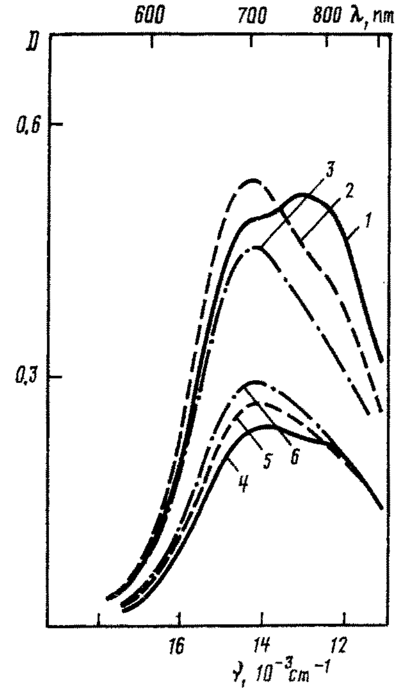


Fig. 1. Spectra for *d—d* absorption of $CuCl_2$ complexes with L^3 in chloroform: 1) $T = 300$ K, $C_L = 0.05$ M, $d = 0.19$ cm, exp (*y*) = 0.5; 2) $T = 300$ K, $C_L = 0.01$ M, $d = 1$ cm, exp (*y*) = 0.5; 3) $T = 300$ K, $C_L = 0.002$ M, $d = 1$ cm, exp (*y*) = 0.2; 4) $T = 273$ K, $C_L = 0.01$ M, $d = 1$ cm, exp (*y*) = 1; 5) $T = 310$ K, $C_L = 0.01$ M, $d = 1$ cm, exp (*y*) = 1; 6) $T = 330$ K, $C_L = 0.01$ M, $d = 1$ cm, exp (*y*) = 1.

it is known that increasing the donor properties of ligands entering into equatorial coordination tends to cause a decrease in $g_{\|}$ [7].

The electronic spectra of solutions of the complexes contain bands for *d—d* transitions and charge-transfer bands (CTBs). For comparison Table 2 gives parameters of the corresponding absorption bands for copper complexes with acids **1** and **2** in aqueous solution. The complexes of ligand **3** in methanol and aqueous-methanol solutions with copper chloride and in chloroform with $CuBr_2$ give similar spectra: a *d—d* band is observed in the region of 820 nm and a CTB is superimposed on the strong absorption of the ligand in the region of 250-275 nm, but a shoulder (280 nm) belonging to the complex can be identified on the long-wavelength side of this absorption. A band for the complex can also be detected in the region of 225 nm in the case of MeOH.

A double-peaked *d—d* band is observed when ligand **3** interacts with $CuCl_2$ in chloroform, a long-wavelength shoulder also occurring in the 800-820 nm region. The ratio of intensities of the maxima depends on the concentration of the complex solution and temperature. In Fig. 1 spectra 1-3 show the absorption as a function of concentration and spectra 4-6 as a function of temperature: the intensity of the short-wavelength shoulder at 710 nm increases with dilution of the solution and on heating. Besides the absorption at 280 nm there are also weak bands around 310-320 nm and 400 nm which may be attributed to Cu—Cl coordination [8]. These results are consistent with the ESR data and indicate that there are at least two complex forms present in the chloroform solution. One of them (710, 400, and 320 nm) probably contains a chlorine atom in the first coordination sphere and may be due to formation of binuclear or dimeric complexes from the heterophase reaction $CuL^3Cl_2 \xrightarrow{CuCl_2} Cu_2Cl_4L_n^3$, where $n = 1$ or 2. The other form (820 and 280 nm) is the same as in methanol and the methanol—water mixture during reaction with $CuCl_2$, and in chloroform during reaction with $CuBr_2$.

Comparison with the ESR results makes it possible to attribute the bands at 820 and 280 nm to the spectrum of $[CuL^3]X_2$, where X is the anion of the salt used to obtain the complex in solution. Since the position of the *d—d* band and the ESR parameters of this complex are practically independent of solvent and anion, it follows that the coordination polyhedron is formed solely by donor atoms of the ligand.

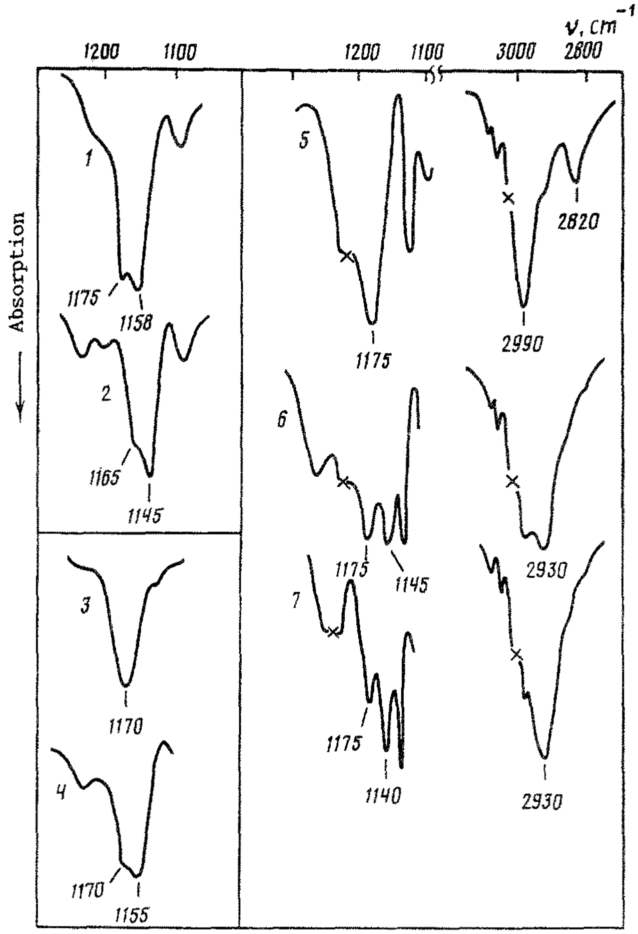


Fig. 2. IR spectra: 1) L^3, MeOH; 2) $CuCl_2$—L^3, MeOH; 3) L^3, MeOH—H_2O; 4) $CuCl_2$—L^3, MeOH—H_2O; 5) L^3, $CHCl_3$; 6) $CuCl_2$—L^3, $CHCl_3$; 7) $CuBr_2$—L^3, $CHCl_3$ (regions of solvent absorption denoted by "x").

Note that a CTB in the 280-nm region has been observed in the spectra of complexes of acids **1** and **2** and was attributed to $N_a \rightarrow Cu_{d_{x^2-y^2}}$ charge transfer [3]. It can be assumed that the equatorial plane in complex **3** also contains nitrogen atoms. The absorption at 225 nm is probably due to P(O) → Cu charge transfer. The position of the *d—d* band at a longer wavelength than that in the case of the acids indicates weaker interaction in the equator, which is consistent with the difference in donor properties of dihydroxyphosphinyl and diphenylphosphinyl groupings for equatorial coordination and retention of a strong axial bond.

Thus analysis of the electronic spectra leads to the same conclusions regarding the structure of the complexes as the analysis of ESR data.

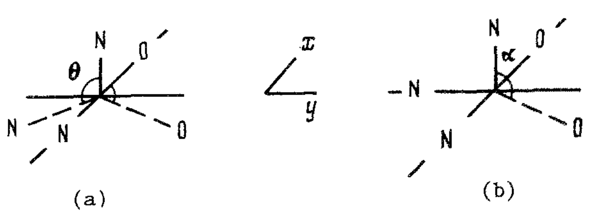
Infrared spectra of solutions of complexes and ligand were measured to determine the coordination of the ligand functional groups (Fig. 2). The $\nu(P{=}O)$ band of the ligand in methanol is split into 1175 and 1160 cm^{-1} components, perhaps due to association of some of the groups with solvent molecules. This may explain the broadening of the ligand $\nu(P{=}O)$ in water. In chloroform the ligand gives a narrow intense band at 1175 cm^{-1}. Complex formation leads to the emergence of low-frequency $\nu(P{=}O)$ components at 1145 cm^{-1} (1155 cm^{-1} in the methanol—water mixture), indicating coordination of diphenylphosphinyl groups by the Cu^{2+} ion, but bands corresponding to uncoordinated P=O groups (1170 cm^{-1}) are also retained (Fig. 2, spectra 2, 4, 6, 7). According to the ESR data, a free ligand is not present in polar solvents with an equimolar [L]:[$CuCl_2$] ratio, and so the $\nu(P{=}O)$ bands at 1170 cm^{-1}indicate that not all the P=O groups of the ligand are coordinated. Complex formation in chloroform takes place at the boundary of the solid and liquid phases and therefore the solution may also contain free ligand. Infrared spectra of the ligand and the complex were compared in the region of $\nu(CH)$ valence vibrations (spectra 5-7) in order to check this. It is known that the frequencies of valence vibrations of CH groups bound to a nitrogen atom are increased when the nitrogen is coordinated [9]. The presence of the large number of CH_2 groups in the molecule of 3 hinders comparison of the spectra; however, analysis of the spectra of simpler compounds containing methylene groups bound to a nitrogen atom and study of spectral criteria for protonation of nitrogen atoms in acids **1** and **2** showed that protonation and coordination of nitrogen atoms leads to disappearance of bands in the 2800-2820 cm^{-1} range [10]. Precisely this effect is observed during complex formation of ligand **3** in chloroform (spectra 5, 6, and 7); this indicates both that the solution contains no free ligand and that all the nitrogen atoms are coordinated.

Comparison of the intensities of $\nu(P{=}O)$ bands of free and coordinated phosphinyl groups is hindered by the proximity of intense ligand and solvent bands and it is impossible, therefore, to estimate the number of coordinated groups solely on the basis of IR spectra. Thus, analysis of IR spectra indicates that all the nitrogen atoms and some of the phosphinyl groups are coordinated by the metal.

Comparison of results from different spectroscopic methods, together with comparison of the physicochemical properties of the complexes and model compounds **1, 2a, 4-6** shows that the complex formed in the solutions under consideration is a five-coordinate compound with a square-pyramid structure, two nitrogen atoms and two phosphinyl groups lying in the equatorial plane and one nitrogen atom in the axial position with one $P{=}O$ group free. In its main features this complex is similar to the complexes of acids **1** and **2**, but the substitution of dihydroxyphosphinyl groups in **2** by diphenylphosphinyl in **3** leads to certain differences in the stereochemistry of the complexes of these two ligands.

The complex CuH_3L^2 has a pentacoordinate structure similar to CuH_4L^1 [3]. According to data from x-ray structural analysis, CuH_4L^1 is a tetragonally elongated square pyramid with two oxygen atoms and two nitrogen atoms lying at the base and a third nitrogen atom on the axial axis of the complex [11]. The complex with ligand **2** has an increased value of $g_{\parallel}$ compared with that for CuH_4L^1 (see Table 1), probably due to structural differences in the complexes.

Theoretical conformational analysis showed that the geometry of the coordination polyhedron of the copper(II) complex with ligand **2** in five-coordinate complexes should be close to a trigonal bipyramid [2]. Nevertheless, as shown by experiment, this structure is not realized (see Table 1), since $g_{\parallel} < g_{\perp}$ for a trigonal bipyramid [4]. It could be suggested that the complex $(CuH_3L^2)^-$ has a structure that is intermediate between a square pyramid and a trigonal bipyramid. The description of an intermediate structure requires the introduction of a distortion parameter which in the limit converts the tetragonal conformation into a trigonal bipyramid. An actual physical model of intermediate geometry has been considered by Saraev and Shmidt [7]. It is described by an angular distortion θ such that $\pi/2 < \theta < 2\pi/3$: when $\theta = \pi/2$ the complex has tetragonal symmetry and when $\theta = 2\pi/3$ it has trigonal symmetry (a). It was found that small deviations from tetragonal symmetry scarcely affect $g_{\parallel}$ but with further increase in the degree of distortion $g_{\parallel}$ decreases. Consequently, such distortions cannot lead to the observed increase in $g_{\parallel}$ in $(CuH_3L^2)^-$ compared with CuH_4L^1. Moreover, such distortions would be accompanied by a change in the position of one of the nitrogen atoms relative to the other two, which would lead to considerable strain in the ring. It is possible that the increased g-factor of the copper complex of **2** compared with CuH_4L^1 is due to more complicated distortions, the principal feature of which is displacement of one of the oxygen atoms out of the plane of the base of the pyramid (b). For small angular distortions there is little delocalization of the $d_{x^2-y^2}$ orbital which contains the unpaired electron and the change in $g_{\parallel}$ is mainly due to the splitting $\Delta = E_{x^2-y^2} - E_{xy}$. Since displacement of the oxygen atom out of the plane reduces overlap of the $d_{x^2-y^2}$ orbital of the copper ion and ligand orbitals, this leads to a decrease in the splitting Δ and, consequently, to an increase in $g_{\parallel}$ [12]. Evidence for this type of distortion is also provided by IR data, according to which the three phosphone groups in the complex with **2** are nonequivalent; one is firmly bound to the cation, the second less firmly, and the third is not coordinated to the metal atom [3]:



Note that the distortion (b) is not, strictly speaking, trigonal but a structure which is intermediate between tetragonal and trigonal conformations since increasing the degree of distortion α from $\pi/2$ to π gives a distorted tetragonal pyramid.

At the same time the similarity between the ESR spectrum parameters of $[CuL^3]^{2+}$ and those of the complexes of the model compounds L^4-L^6 suggests that the $Cu(N_2O_2)$ chromophore in the compound under investigation does not have appreciable deviations from square-planar geometry.

In the complex with **3** the lack of the "trigonal" distortions observed in the complex with **2** may be due to interaction of the bulky phenyl fragments during the approach of phosphinyl groups when $[CuL^3]X_2$ is formed. As a result of this interaction (repulsion), the volume of the cavity formed by ligand **3** during complex formation may be greater than that for **2** and therefore it is possible that ligand **3**, compared with ligand **2**, will be characterized by a higher selectivity toward cations of a somewhat greater radius during formation of tetragonally elongated five-coordinated complexes.

EXPERIMENTAL

1,4,7-Tris(β-diphenylphosphinylethyl)-1,4,7-triazacyclononane. To a solution of 0.15 g (1.16 mmoles) of 1,4,7-triazacyclononane in benzene was added a solution of 0.8 g (3.5 mmoles) of vinyldiphenylphosphine oxide in benzene. The mixture was heated for 6 h in a sealed ampul on an oil bath at 160°C. The precipitate formed on cooling was filtered off, washed with cooled benzene, and dried under vacuum using a water pump. Recrystallization from CH_3CN yielded 0.45 g (47.6%) of 1,4,7-tris(β-diphenylphosphinylethyl)-1,4,7-triazacyclononane, mp 171-173°C. Found, %: C 70.4, H 6.8, N 5.2. $C_{48}H_{54}N_3O_3P_3$. Calculated, %: C 70.9, H 6.6, N 5.2. Ligand L^6 was obtained using the published procedure [13].

Equimolar mixtures of solutions of ligand **3** and $CuCl_2$ were prepared to obtain complexes in methanol and the 1:1 methanol—water mixture. When recording spectra in the visible region their concentration varied over the range 0.03-0.002 M and the path length *d* from 0.19-1 cm. The positions and shapes of the bands were not dependent on concentration. Ultraviolet spectra were measured for a complex concentration in solution of 0.0001 M.

Complexes with $CHCl_3$ were produced by adding $CuCl_2$ or $CuBr_2$ anhydrous salts to a 0.05 M ligand solution; after the color of the solution was established the salt residue was filtered off and the concentration and temperature of the resulting solution were varied.

Electronic spectra were recorded on a Specord M-40 spectrometer.

The IR spectra were obtained using 0.03 M solutions (MeOH, MeOH—H_2O) and 0.05 M ($CHCl_3$), CaF_2 cuvettes $d = 0.121$ mm, NaCl $d = 0.17$ mm, UR-20 and Specord M-80 spectrophotometers.

The ESR spectra were recorded at 20 and —196°C on a Radiopan E/X 2544 spectrometer using an NMR magnetometer and a microwave frequency meter to measure the spectrum parameters. Parameters of the CuL^6Cl_2 complex were obtained in a study of stepwise complex formation in solution similar to that described in [6].

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