Synthesis, structures, and properties of 3,6-di-*tert*-butyl-*o*-benzosemiquinone complexes of copper(I) with 1,5-diaza-3,7-diphosphacyclooctanes

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Two new 3,6-di-*tert*-butyl-*o*-benzosemiquinone complexes of copper(I) (**2a** and **2b**) with 1,3,5,7-tetraphenyl-1,5-diaza-3,5-diphosphacyclooctane (**1a**) and 1,5-dibenzyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane (**1b**), respectively, were synthesized. Their structures in solution and in the crystalline state were studied. According to the results of X-ray diffraction analysis, the copper(I) atom in molecules **2a** and **2b** is in a pseudotetrahedral environment and is directly coordinated to two P atoms of the diazadiphosphacyclooctane ligand and two O atoms of the benzosemiquinone ligand. In complex **2a**, ligand **1a** adopts a chair-boat conformation typical of all complexes with eight-membered cyclic 1,5-donors studied previously. Unlike ligand **1a**, the ligand in complex **2b** adopts a chair-chair (crown) conformation identical with that of the free ligand. Both complexes are paramagnetic in the solid state and in solutions. The parameters of the isotropic ESR spectra of complexes **2a** and **2b** are typical of four-coordinate *o*-semiquinone copper(I) complexes with bidentate bisphosphine ligands. Based on analysis of the isotropic ESR spectra, it was suggested that compound **2b** in solutions exists as two isomers, which differ in the conformation of the eight-membered heterocycle (chair-boat or chair-chair).

Key words: 1,5-diaza-3,7-diphosphacyclooctanes, copper(I), *o*-semiquinones, complex formation, ESR spectroscopy, X-ray diffraction analysis, conformation.

1,5-Diaza-3,7-diphosphacyclooctanes (**1**) contain both "soft" (phosphine) and "hard" (amine) donor fragments involved in the cyclic system. Previously,[1–3] complexes of transition metals with 1,5-diaza-3,7-diphosphacyclooctanes have been characterized. Coordination to the metal atom (M) in all complexes was demonstrated to occur through the P atoms, the predominant conformation of the free ligand changing from crown (chair-chair) to chair-boat. In addition, the M—P bonds in chelate complexes with these bidentate ligands are distorted because the P atoms of the heterocycle are brought into proximity. Attempts to construct a coordination bond between the metal atom and the heterocyclic ligand involving the N atom have not met with success.

The characteristic feature of copper complexes based on *o*-quinone derivatives is that the redox states of the metal atoms (Cu^{I} or Cu^{II}) and the ligands (the *o*-semiquinone radical anion or the catecholate dianion) are determined by the nature of the neutral ligands bound to the metal atom. In particular, *o*-semiquinone complexes of copper(I) are formed in the case of "soft" phosphines,[4–6] whereas catecholate complexes of copper(II) are formed in the case of "hard" amines.[7] Isotropic ESR spectra of both types of complexes are very characteristic, due to which these compounds can be readily identified in solutions. In addition, the parameters of isotropic ESR spectra of *o*-semiquinone complexes of Cu^{I} are very sensitive to changes in the geometry of the coordination sphere, which allows one to observe changes in the coordination sphere in solutions by ESR spectroscopy.[8]

Results and Discussion

The aim of the present work was to prepare 3,6-di-*tert*-butyl-*o*-benzosemiquinone complexes of copper(I) with 1,5-diaza-3,7-diphosphacyclooctanes and to reveal the character of bonding of the latter with the Cu atom and the effect of the N-substituents in the ligand on the structure of the metal complex.

We synthesized two new 3,6-di-*tert*-butyl-*o*-benzosemiquinone complexes of copper(I) with 1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane (**1a**) and 1,5-dibenzyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane (**1b**) (complexes **2a,b**, respectively) and studied their structures in crystals and solutions.

Complexes **2a** and **2b** were synthesized according to a known procedure[9] starting from copper(I) chloride,

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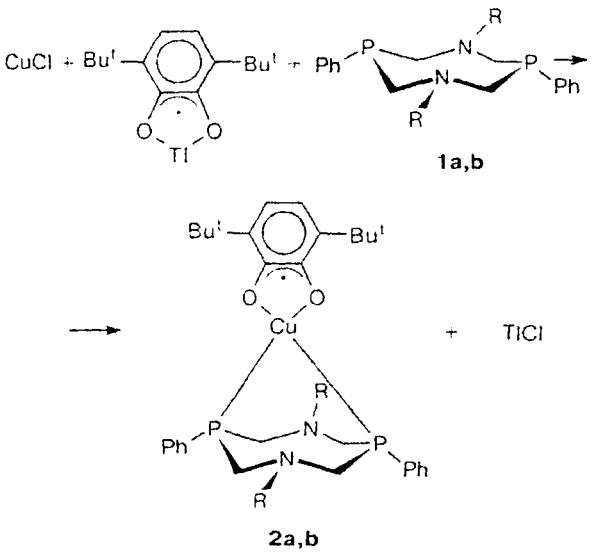
thallium 3,6-di-*tert*-butyl-*o*-benzosemiquinolate (TlSQ), and the corresponding diazadiphosphacyclooctane **1** (Scheme 1).

Scheme 1



R = Ph (**a**), CH_2Ph (**b**)

Complexes **2** were obtained as dark-blue crystals readily soluble in toluene, CH_2Cl_2, and THF and poorly soluble in hexane and methanol. Their solutions in organic solvents withstand oxidation with atmospheric oxygen. The structures of complexes **2** were established by X-ray single-crystal diffraction analysis and ESR, IR, and UV spectroscopy.

According to the data from X-ray diffraction analysis, the environment about the Cu(1) atom in molecules **2a** (Fig. 1) and **2b** (Fig. 2) is a distorted tetrahedron (pseudotetrahedron) and the metal atom is directly bound to two P atoms [P(3) and P(7)] and two O atoms [O(35) and O(36)]. The Cu(1)—P(3) and Cu(1)—P(7) bond lengths in molecule **2a** are somewhat different (2.2036(8) and 2.2319(8) Å, respectively), whereas these bond lengths in molecule **2b** are identical to within the experimental error (2.231(2) and 2.227(2) Å, respectively). These values are slightly larger than those observed in SQ complexes of copper(I).[10,11] The P(3)—Cu—P(7) bond angle in molecule **2a** (90.17(3)°) is noticeably larger than that in molecule **2b** (87.21(8)°). The difference between the Cu(1)—O(35) (1.975(2) Å) and Cu(1)—O(36) (2.072(2) Å) bond lengths in complex **2a** is more pronounced than that observed in complex **2b** (2.062(4) and 2.027(4) Å, respectively).

The geometric parameters of the semiquinone ligands in complexes **2a,b** have standard values. The O(35)—C(35) [1.277(4) Å in **2a** and 1.273(7) Å in **2b**], O(36)—C(36) [1.280(3) and 1.283(8) Å], and C(35)—C(36) [1.474(4) and 1.470(8) Å] bond lengths and the O(35)—Cu(1)—O(36) bond angles [80.98(8)° and 79.8(2)°] are characteristic of *o*-semiquinone metal complexes.[10–12]

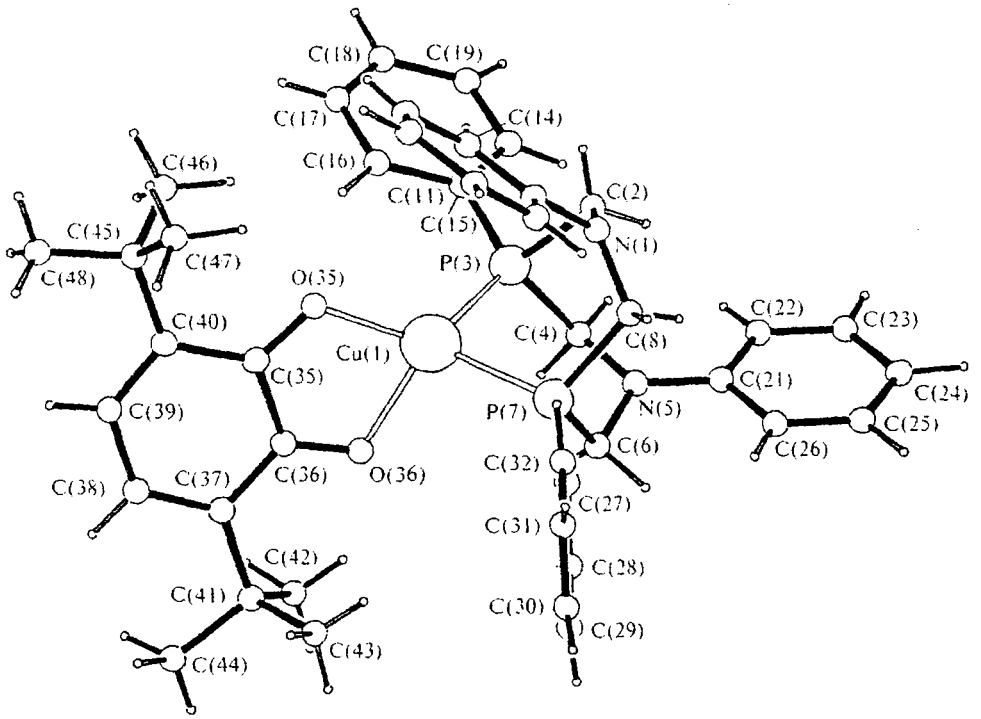


Fig. 1. Crystal structure of complex **2a**.

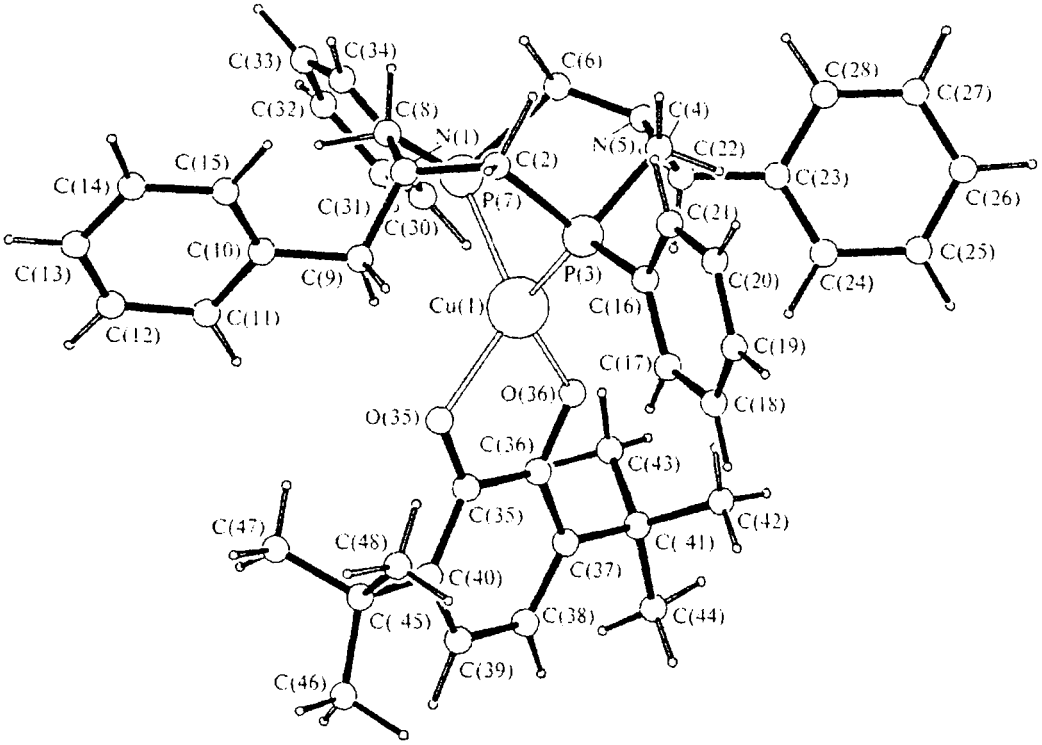


Fig. 2. Crystal structure of complex **2b**.

The cyclic ligand in complex **2a** adopts a chair-boat conformation typical of all complexes of eight-membered heterocyclic 1,5-donors studied previously.[1–3,13,14] Unlike the heterocycles in the chelate complexes of 1,5,3,7-diazadiphosphacyclooctanes,[1–3] 1,5-diphosphacyclooctanes,[13] and 1,5-phosphathiacyclooctanes[14] studied previously, the heterocycle in complex **2b** adopts a chair-chair (crown) conformation, like the free ligand **1b**. The P—Cu—P bond angle (90.17(3)° in **2a** and 87.21(8)° in **2b**), like that in the LCuI(Py) complex reported previously,[2] is substantially smaller than the ideal tetrahedral value (109.5°). In this case, the Cu—P bond substantially deviates from the axis of the lone electron pair of the P atom (this direction is determined by extending the normal from the P atom to the base of the pyramid formed by three P—C bonds), which is associated with a tightening effect of the eight-membered heterocycle. A decrease in the P—Cu—P angle in molecule **2b** compared to that in **2a** agrees with the above-mentioned statement because the P...P distance (3.074(3) Å) in complex **2b** is substantially smaller than that in compound **2a** (3.141(1) Å).

Previously, we have studied free ligands **1a** [15] and **1b** [16] by X-ray diffraction analysis. The heterocycles adopt a chair-chair (crown) conformation, the heterocycle in molecule **1a** being somewhat more flattened compared to that in molecule **1b**. This flattening results from the planar-trigonal coordination of the N atoms in molecule **1a** in contrast to the pyramidal coordination of the N atoms in molecule **1b**. As a result, the phenyl substituents at the N atoms in molecule **1a** are in axial positions. These substituents and the lone electron pairs of the P atoms point in the same direction. Therefore, in the case of the chair-chair conformation of the heterocycle in complex **2a**, the phenyl substituents at the N atoms should experience a strong steric effect of the *tert*-butyl groups of the semiquinone ligand. Apparently, that is why the heterocycle adopts the less hindered chair-boat conformation in which the N(5) atom and the P atoms point in opposite directions and the phenyl substituent at the N atom is remote from the semiquinone ligand. However, the phenyl group at the N(1) atom experiences a noticeable steric effect of the *tert*-butyl groups of the semiquinone ligand, which is manifested in the increase in the O(35)—Cu(1)—P(7) and O(36)—Cu(1)—P(3) bond angles to 142.3° and 124.8°, respectively. In this case, the N(1) atom is located in proximity to the central ion (3.288(2) Å). However, the lone electron pair of the N(1) atom is directed away from the Cu(1) atom.

Unlike all complexes studied previously, the heterocycle in molecule **2b** adopts a chair-chair (crown) conformation. The benzyl substituents at the N atoms are in axial positions. However, the phenyl groups and the *tert*-butyl substituents of the semiquinone ligand are spatially remote from each other due to the presence of the methylene bridge. In molecule **2b**, steric hindrances are absent, resulting in a smaller distortion of the coor-

dination polyhedron about the central ion. In complex **2b**, as in complex **2a**, short contacts exist between the central ion and the N atoms (3.372(6) and 3.411(5) Å, respectively), but no additional coordination bonds are established because the lone electron pairs of both N atoms are directed away from the Cu(1) atom.

It should be noted that the geometric parameters of the heterocyclic ligands in complexes **2a,b** are somewhat different from those observed in **1a,b**. In complexes **2a,b**, the P—C bond lengths are identical, on the average (within the experimental error), to those observed in molecules **1a,b**. However, the lengths of the bonds at the P(3) atom in complex **2a** are somewhat smaller than those at the P(7) atom. The P(7)—C(6) bond in compound **2b** is also noticeably elongated (1.944(7) Å). The bond angles at the P atoms in molecules **2a,b** are also, on the average, equal to those observed in molecules **1a,b**, except for the endocyclic angle at the P(7) atom in molecule **2a**, which is slightly increased (103.2(2)°).

Compounds **2a** and **2b** are paramagnetic both in the solid state and in solutions. The ESR spectrum of a polycrystalline sample of **2a** has a singlet (ΔH = 2.5 mT) with weak anisotropy and g_{eff} = 2.0076. Pronounced anisotropy ($g_{\perp}$ = 2.0037; $g_{||}$ = 2.0138) is seen in the ESR spectrum of a polycrystalline sample of **2b**, but no superfine interactions with magnetic nuclei are observed.

The ESR spectral patterns of solutions of complexes **2a** and **2b** are characteristic of *o*-semiquinone complexes of copper(I) with neutral ligands.[4–6] Hyperfine interactions with the magnetic isotopes ^{63}Cu (69.09%; I = 3/2; μ_N = 2.2206) and ^{65}Cu (30.91%; I = 3/2; μ_N = 2.3790)[17] of the central atom (a 1 : 1 : 1 : 1 quartet), two ^{31}P nuclei (100%; I = 1/2; μ_N = 1.1305)[17] of the heterocyclic ligand (a 1 : 2 : 1 triplet), and two protons of the *o*-semiquinone ligand (a 1 : 2 : 1 triplet) are observed in the ESR spectra of both compounds (Fig. 3, *a*). The parameters of the isotropic ESR spectra (Table 1) are typical of four-coordinate *o*-semiquinone complexes of copper(I) with bidentate bisphosphine ligands[4–6] and indicate that in solution the coordination bond between the ligand and the Cu atom in compounds **2a** and **2b**, as in other known complexes, is also formed through two P atoms.

It is noteworthy that the parameters of the isotropic ESR spectra of complexes **2a** and **2b** depend substantially on the solvent. In acetone, the g_i, $A_i(^{63}Cu)$, $A_i(^{65}Cu)$, and $A_i(^{31}P)$ values increase, which reflects an increase in the spin density on these nuclei (see Table 1).

In the case of complex **2b**, the isotropic ESR spectrum has the major signal along with an additional signal with the same $A_i(H_{SQ})$ value but with a lower g_i value and the constant of hyperfine interaction with the copper and phosphorus magnetic nuclei (see Fig. 3, *b*). The relative intensity of this signal depends on the solvent and is ~25% in toluene and CH_2Cl_2 and 45% in acetone. In toluene, the ratio between the intensities of the signals remains unchanged in the temperature range from 200 to 340 K.

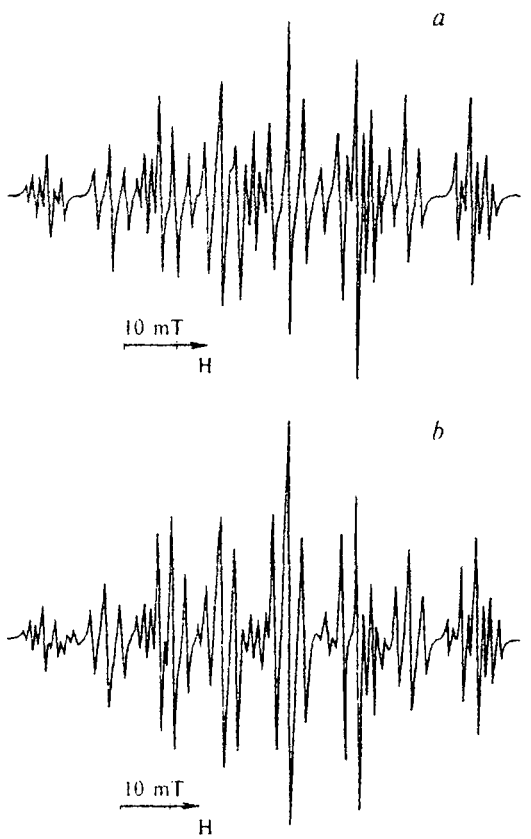


Fig. 3. ESR spectra of complexes **2a** (*a*) and **2b** (*b*).

The X-ray diffraction data indicate that the differences in structure of complexes **2a** and **2b** in the crystalline state are associated with the conformation of the diazadiphosphacyclooctane ligand. Hence, it can be suggested that the benzyl derivative, unlike the phenyl derivative, occurs in solution as two isomers. The additional signal in the ESR spectrum of complex **2b** has parameters close to the corresponding parameters in the ESR spectrum of complex **2a** and should belong to the isomer in which the ligand adopts a chair-boat conformation, as in the case of complex **2a**. The signal with the larger parameters belongs to the isomer in which the

Table 1. Parameters of isotropic ESR spectra of 3,6-di-*tert*-butyl-*o*-benzosemiquinone complexes of copper(I) with 1,5-diaza-3,7-diphosphacyclooctanes

Complex	g_i	$A_i(^{63}Cu)/A_i(^{65}Cu)$	$A_i(^{31}P)$	$A_i(H_{SQ})$	Solvent
		mT			
2a	2.0053	1.401/1.503	2.511	0.292(2H)	Toluene
2a*	2.0050	1.355/1.452	2.275	0.292(2H)	Toluene
2b	2.0054	1.317/1.409	2.307	0.298(2H)	Toluene
2a	2.0062	1.5031/1.603	2.721	0.292(2H)	Acetone
2a*	2.0060	1.432/1.530	2.437	0.292(2H)	Acetone
2b	2.0060	1.403/1.500	2.480	0.292(2H)	Acetone

cyclooctane ligand adopts a chair-chair conformation. The ratio between the concentrations of the isomers in solutions remains unchanged as the temperature changes, which indicates that the enthalpy of their interconversion is equal to zero and the equilibrium concentrations in solutions are completely determined by the entropy contribution to the free energy. Based on the absence of the temperature dynamics in the ESR spectra, it can be concluded that the rate of the interconversion of the isomers is low ($k \leq 10^6$ s^{-1} at 340 K) within the ESR time scale. However, we have demonstrated previously that conformation equilibrium with a rather high rate of conformational transitions is observed in the ^1H NMR spectra of 3,7-diphenyl-1,5-di-*p*-tolyl-1,5,3,7-diazadiphosphacyclooctane at ~20 °C.[2] Hence, other possibilities, for example, the fact that binuclear compounds containing the bridging diazadiphosphaoctane ligand are present in solutions, should not be excluded from consideration.[3]

Experimental

Anhydrous CuCl, thallium 3,6-di-*tert*-butyl-*o*-benzosemiquinolate, 1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane, and 1,5-dibenzyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane were synthesized according to known procedures.[18,19,15,16]

Copper(I) 3,6-di-*tert*-butyl-(1,5-dibenzyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctano)-1,2-benzosemiquinolate (2b). A mixture of anhydrous copper(I) chloride (0.05 g, 0.52 mmol) and ligand **1b** (0.25 g, 0.52 mmol) was placed into a tube and shaken with degassed THF (50 mL) until the copper chloride completely dissolved. A solution of thallium 3,6-di-*tert*-butyl-*o*-benzosemiquinolate prepared from the corresponding *o*-quinone (0.114 g, 0.52 mmol) was added to the reaction mixture and the mixture turned violet. The solvent was replaced by toluene and the thallium chloride that precipitated was filtered off *in vacuo*. The filtrate was concentrated to approximately one-half of the initial volume. After 18—20 h, the dark-violet crystals that precipitated were filtered off, washed with cold toluene, and dried *in vacuo*. The yield was 0.240 g (60%), m.p. 168—169 °C. Found (%): C, 69.13; H, 7.36; Cu, 8.45; P, 8.25. $C_{44}H_{52}CuO_2N_2P_2$. Calculated (%): C, 68.97; H, 6.79; Cu, 8.30; P, 8.10. IR (Nujol mulls), ν/cm^{-1}: 1560, 1440, 1250 (ν_{C-N}), 1130 (ν_{C-C}), 1080 (ν_{C-C}), 1070 (ν_{C-C}), 1030 (ν_{C-C}), 975, 950, 855 ($\delta_{\perp CH}$), 820, 740 ($\delta_{\perp CH}$), 700 ($\delta_{\perp CH}$). The electronic absorption spectrum (PhMe), λ_{max}/nm (ε): 544 (2050), 664 (3450).

Copper(I) 3,6-di-*tert*-butyl-(1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctano)-1,2-benzosemiquinolate (2a) was synthesized analogously. The yield was 0.162 g (75%), m.p. 168—170 °C. Found (%): C, 67.45; H, 6.77; Cu, 9.50; P, 9.49. $C_{42}H_{48}CuO_2N_2P_2$. Calculated (%): C, 68.34; H, 6.51; Cu, 8.61; P, 8.41. IR (Nujol mulls), ν/cm^{-1}: 1600, 1550 (ν_{C-C}), 1515, 1440, 1215 (ν_{C-N}), 1210 (ν_{C-N}), 875, 825, 750 ($\delta_{\perp CH}$), 690 ($\delta_{\perp CH}$). The electronic absorption spectrum (PhMe), λ_{max}/nm (ε): 544 (2425), 640 (3425).

The ESR spectra were recorded on a Bruker ER 200D-SRC spectrometer equipped with an ER 4105DR dual-mode resonator (operating at ~9.5 GHz) and an ER 4111 VT temperature-controlled block. The *g* factors were determined using DPPH as the standard. The IR spectra were measured on a Specord M-80 spectrometer.

Single crystals of compounds **2a,b** suitable for X-ray diffraction study were prepared by crystallization from toluene solutions.

Crystals of complex **2a**, $C_{42}H_{48}CuN_2O_2P_2$, are triclinic. At 20 °C, a = 11.231(8), b = 11.218(9), c = 16.673(9) Å, α = 92.58(5)°, β = 108.07(5)°, γ = 105.01(6)°, V = 1911(2) Å^3, Z = 2, d_{calc} = 1.28 g cm^{-3}, space group $P\bar{1}$.

Crystals of complex **2b**, $C_{44}H_{52}CuN_2O_2P_2$, are monoclinic. At 20 °C, a = 11.116(9), b = 21.47(2), c = 17.24(1) Å, β = 94.49(6)°, V = 4102(5) Å^3, Z = 4, d_{calc} = 1.24 g cm^{-3}, space group $P2_1/c$.

The unit cell parameters and the intensities of 7637 (**2a**) and 11993 (**2b**) reflections (of which 5908 (**2a**) and 5005 (**2b**) reflections were with $I \geq 3\sigma$) were measured on an automated four-circle Enraf-Nonius CAD-4 diffractometer (λ(Cu-Kα) radiation, graphite monochromator, $\omega/2\theta$ scanning technique, $\theta \leq 76°$) at 20 °C. For the crystal structure of complex **2a**, a linear correction was applied to the measured reflections based on the decrease in the intensities of three check reflections (−10% over 76 h). For the structure of **2b**, no decrease in the intensities of the check reflections was observed. An empirical absorption correction was applied (μCu = 18.70 (**2a**) and 17.59 (**2b**) cm^{-1}).

The structures were solved by the direct method using the SIR program[20] and refined first isotropically and then anisotropically. Subsequently, the positions of all hydrogen atoms were located from difference electron density syntheses. In the final stage of the refinement of the structure of **2a**, the hydrogen atoms were refined isotropically. In the structure of **2b**, the contributions of the hydrogen atoms to the structure amplitudes were taken into account with fixed positional and isotropic thermal parameters. The final values of the reliability factors were as follows: R = 0.047, R_w = 0.058 based on 5488 reflections (**2a**) and R = 0.056, R_w = 0.058 based on 3687 reflections (**2b**) with $F^2 \geq 3\sigma$.

All calculations were carried out on an AlphaStation 200 computer using the MolEN program package.[21] The figures were drawn and intermolecular contacts in the crystals were calculated using the PLATON program.[22]

Table 2. Principal bond lengths (d) in molecules **2a,b**

Bond	d/Å	Bond	d/Å
Molecule **2a**		Molecule **2b**	
Cu(1)—P(3)	2.2036(8)	Cu(1)—P(3)	2.231(2)
Cu(1)—P(7)	2.2319(8)	Cu(1)—P(7)	2.227(2)
Cu(1)—O(35)	1.975(2)	Cu(1)—O(35)	2.062(4)
Cu(1)—O(36)	2.072(2)	Cu(1)—O(36)	2.027(4)
P(3)—C(2)	1.869(4)	P(3)—C(2)	1.880(8)
P(3)—C(4)	1.859(4)	P(3)—C(4)	1.869(7)
P(3)—C(15)	1.818(3)	P(3)—C(16)	1.824(7)
P(7)—C(6)	1.886(4)	P(7)—C(6)	1.944(7)
P(7)—C(8)	1.873(4)	P(7)—C(8)	1.880(7)
P(7)—C(27)	1.818(2)	P(7)—C(29)	1.808(7)
O(35)—C(35)	1.277(4)	O(35)—C(35)	1.273(7)
O(36)—C(36)	1.280(3)	O(36)—C(36)	1.283(8)
N(1)—C(2)	1.452(4)	N(1)—C(2)	1.432(9)
N(1)—C(8)	1.454(4)	N(1)—C(8)	1.461(9)
N(1)—C(9)	1.405(4)	N(1)—C(9)	1.47(1)
N(5)—C(4)	1.464(4)	N(5)—C(4)	1.465(8)
N(5)—C(6)	1.455(4)	N(5)—C(6)	1.427(9)
N(5)—C(21)	1.392(5)	N(5)—C(22)	1.469(8)

Table 3. Principal bond angles (ω) and torsion angles (τ) in compounds **2a,b**

Bond angle	ω/deg	Bond angle	ω/deg
Molecule **2a**		Molecule **2b**	
P(3)—Cu(1)—P(7)	90.17(3)	P(3)—Cu(1)—P(7)	87.21(8)
P(3)—Cu(1)—O(35)	119.22(5)	P(3)—Cu(1)—O(35)	120.5(1)
P(3)—Cu(1)—O(36)	125.04(6)	P(3)—Cu(1)—O(36)	128.8(1)
P(7)—Cu(1)—O(35)	142.47(6)	P(7)—Cu(1)—O(35)	123.6(1)
P(7)—Cu(1)—O(36)	101.73(5)	P(7)—Cu(1)—O(36)	122.1(1)
O(35)—Cu(1)—O(36)	80.98(8)	O(35)—Cu(1)—O(36)	79.8(2)
Cu(1)—P(3)—C(2)	109.0(1)	Cu(1)—P(3)—C(2)	107.8(2)
Cu(1)—P(3)—C(4)	110.1(1)	Cu(1)—P(3)—C(4)	109.5(2)
Cu(1)—P(3)—C(15)	123.7(1)	Cu(1)—P(3)—C(16)	130.5(3)
C(2)—P(3)—C(4)	100.9(2)	C(2)—P(3)—C(4)	101.1(3)
C(2)—P(3)—C(15)	104.1(1)	C(2)—P(3)—C(16)	102.4(3)
C(4)—P(3)—C(15)	106.6(2)	C(4)—P(3)—C(16)	101.8(3)
Cu(1)—P(7)—C(6)	98.7(1)	Cu(1)—P(7)—C(6)	109.5(2)
Cu(1)—P(7)—C(8)	110.33(9)	Cu(1)—P(7)—C(8)	108.9(2)
Cu(1)—P(7)—C(27)	130.0(1)	Cu(1)—P(7)—C(29)	128.1(2)
C(6)—P(7)—C(8)	103.2(2)	C(6)—P(7)—C(8)	101.3(3)
C(6)—P(7)—C(27)	104.4(1)	C(6)—P(7)—C(29)	100.8(3)
C(8)—P(7)—C(27)	106.6(1)	C(8)—P(7)—C(29)	105.0(3)
Cu(1)—O(35)—C(35)	114.3(2)	Cu(1)—O(35)—C(35)	112.6(4)
Cu(1)—O(36)—C(36)	110.9(2)	Cu(1)—O(36)—C(36)	113.6(3)
C(2)—N(1)—C(8)	114.4(3)	C(2)—N(1)—C(8)	115.2(5)
C(2)—N(1)—C(9)	118.3(2)	C(2)—N(1)—C(9)	116.2(6)
C(8)—N(1)—C(9)	118.3(2)	P(7)—C(8)—N(1)	115.1(5)
C(4)—N(5)—C(6)	116.2(3)	C(8)—N(1)—C(9)	112.8(5)
C(4)—N(5)—C(21)	122.3(2)	C(4)—N(5)—C(6)	116.2(5)
C(6)—N(5)—C(21)	121.0(2)	C(4)—N(5)—C(22)	114.0(5)
P(3)—C(2)—N(1)	114.7(2)	C(6)—N(5)—C(22)	115.6(5)
P(3)—C(4)—N(5)	110.5(3)	P(3)—C(2)—N(1)	118.9(5)
P(7)—C(6)—N(5)	113.7(3)	P(3)—C(4)—N(5)	116.5(4)
P(7)—C(8)—N(1)	112.3(2)	P(7)—C(6)—N(5)	115.9(5)
Torsion angle	**τ/deg**	**Torsion angle**	**τ/deg**
Molecule **2a**		Molecule **2b**	
C(4)—P(3)—C(2)—N(1)	110.4(3)	C(4)—P(3)—C(2)—N(1)	−119.4(6)
C(2)—P(3)—C(4)—N(5)	−54.4(3)	C(2)—P(3)—C(4)—N(5)	93.1(5)
C(8)—P(7)—C(6)—N(5)	36.7(3)	C(8)—P(7)—C(6)—N(5)	−118.7(5)
C(6)—P(7)—C(8)—N(1)	−106.6(2)	C(6)—P(7)—C(8)—N(1)	94.5(5)
C(8)—N(1)—C(2)—P(3)	−70.8(3)	C(8)—N(1)—C(2)—P(3)	70.6(7)
C(2)—N(1)—C(8)—P(7)	74.2(3)	C(2)—N(1)—C(8)—P(7)	−54.0(7)
C(6)—N(5)—C(4)—P(3)	−65.5(4)	C(6)—N(5)—C(4)—P(3)	−55.3(7)
C(4)—N(5)—C(6)—P(7)	79.4(4)	C(4)—N(5)—C(6)—P(7)	69.1(6)

The atomic coordinates were deposited with the Cambridge Structural Database (CSD). The crystal structures of compounds **2a,b** are shown in Figs. 2 and 3, respectively. The principal geometric parameters of molecules **2a,b** are given in Tables 2 and 3.

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