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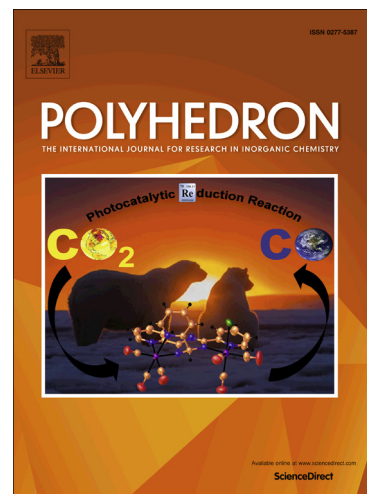
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Synthesis, characterization and crystal structures of Ni(II) and Cu(I) complexes with the condensation product of 2-(diphenylphosphino)benzaldehyde and 1-hydrazinophthalazine

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Abstract

A square-pyramidal Ni(II) complex (**1**) with the composition [Ni**L**(**HL′**)]ClO$_4$·H$_2$O was synthesized in the reaction of nickel(II) perchlorate and 2-[2-(diphenylphosphino)benzylidene]-1-phthalazinylhydrazone (**HL**). The coordination surrounding the Ni(II) ion consist of a PNN coordinated deprotonated **HL** ligand and its corresponding oxidation product - phosphine oxide **HL′** - coordinated via two nitrogen atoms of the hydrazinophthalazine moiety. The structure of Ni(II) complex **1** was determined by X-ray analysis, IR spectroscopy, elemental analysis and magnetic measurements. In the reaction of copper(II) perchlorate with **HL**, a binuclear phthalazine bridged Cu(I) complex (**2**) was obtained with the composition [Cu$_2$(**HL**)$_2$](ClO$_4$)$_2$·C$_2$H$_5$OH. The structure of Cu(I) complex **2** was determined by X-ray analysis, IR and NMR spectroscopy, elemental analysis and magnetic measurements.

Keywords Ni(II) complex, Cu(I) complex, 2-(diphenylphosphino)benzaldehyde, hydralazine, crystal structure

1. Introduction

Hydralazine (1-hydrazinophthalazine hydrochloride) is a known antihypertensive drug [1], which has also been used as a building block for the synthesis of various hydrazones [2-11]. 1-Hydrazinophthalazine hydrazones of mono- and dicarbonyl compounds are versatile chelating agents due to their conformational flexibility, possibility of tautomerism and coordination in either the neutral or anionic form [2-11]. Also, in some of the reported binuclear metal complexes with these ligands, the phthalazine ring act as an NN′ donor bridge between the two metal centers [7,8,12-16]. Researcher's interest for metal complexes with 1-hydrazinophthalazine hydrazone ligands is mainly associated with their magnetic properties [6-8,12-16] and biological activity [3-5]. Hydrazone ligands derived from 2-(diphenylphosphino)benzaldehyde, which contain significantly different types of "hard" and "soft" donor atoms, have attracted considerable attention due to their interesting coordination properties [17-19], catalytic [20-23] and biological activity [24-26]. There is a relatively small number of papers concerning copper complexes with 2-(diphenylphosphino)benzaldehyde hydrazones [27-31]. In most of them the presence of the "soft" phosphorus donor atom stabilizes the copper ion in the +1 oxidation state [28-31]. The reported Ni(II) complexes with 2-(diphenylphosphino)benzaldehyde acylhydrazones possess significant antitumor and antimicrobial activity [32-36]. Square-planar Ni(II) complexes with 2-(diphenylphosphino)benzaldehyde acylhydrazones consist of the PNO coordinated deprotonated phosphine ligand and different monodentate anionic ligands at the fourth coordination place [33-36]. Tetrahedral [32] and octahedral [18] Ni(II) complexes with 2-(diphenylphosphino)benzaldehyde acylhydrazones are rare. In these complexes the hydrazone ligands are PNO coordinated and the remaining coordination places are occupied with cyanate [32] or thiocyanate anions [18]. Ni(II) complexes with 2-(diphenylphosphino)benzaldehyde hetarylhydrazones are much less studied [37,38]. Until now, only square-planar Ni(II) complexes with 2-(diphenylphosphino)benzaldehyde 2-pyridyl [37] and 2-quinolinylhydrazone [38] have been described in the literature. As a continuation of the investigation of the coordination behavior of 1-hydrazinophthalazine hydrazones, the present work reports the synthesis and characterization of Ni(II) and Cu(I) complexes with the 2-[2-(diphenylphosphino)benzylidene]-1-phthalazinylhydrazone ligand.

2. Experimental

2.1. Materials and methods

All chemicals used for the preparative work were of reagent grade. Solvents were dried and distilled before use according to standard procedures. 2-(Diphenylphosphino)benzaldehyde and 1-hydrazinophthalazine hydrochloride were purchased from Aldrich and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin–Elmer 240C Analyzer. IR spectra were recorded on a Varian Scimitar 1000 FT-IR spectrophotometer in the range 4000-400 cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra of the ligand **HL** and the ^{1}H NMR spectrum of complex **2** were recorded on a 300 MHz Varian Unity-300 spectrometer in DMSO-d^6. Magnetic susceptibilities of powdered samples of complexes **1** and **2** were measured in the temperature range 300-77.4 K using a Faraday magnetometer and employing a magnetic field strength of 0.9 T.

2.2. Synthesis

2.2.1. Synthesis of 2-[2-(diphenylphosphino)benzylidene]-1-phthalazinylhydrazone (HL)

The ligand **HL** was obtained by the condensation reaction of 2-(diphenylphosphino)benzaldehyde and 1-hydrazinophthalazine hydrochloride according to the previously reported method [39].

Elemental analysis calcd for $C_{27}H_{21}N_4P$: C 74.99, H 4.89, N 12.96, found: C 75.08, H 5.14, N 12.87%. IR (KBr, cm^{-1}): ν(N–H) 3250, ν(C=N)$_{azomethine}$ 1621, ν(C=N)$_{phthalazine}$ 1600, ν(C–P) 1435. ^{1}H NMR (300 MHz, DMSO-d_6) (numbering of the atoms according to Scheme 1a) δ (ppm): 11.92 (s, 1H, N-H), 8.99 (d, 1H, J = 6 Hz, H-1), 6.79 (m, 1H, H-3), 7.30 (m, 1H, H-4), 7.50 (m, 1H, H-5), 8.54 (m, 1H, H-6), 7.21 (m, 4H, H-9), 7.39 (m, 4H, H-10), 7.39 (m, 2H, H-11), 8.12 (s, 1H, H-13), 7.75 (m, 1H, H-16), 7.67 (m, 1H, H-17), 7.78 (m, 1H, H-18), 8.24 (d, 1H, J = 9 Hz, H-19). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 151.5 (d, J = 25 Hz, C-1), 136.5 (d, J = 12 Hz, C-2), 133.6 (C-3), 129.5 (C-4), 130.1 (C-5), 128.9 (d, J = 5 Hz, C-6), 139.0 (d, J = 22 Hz, C-7), 135.9 (d, J = 22 Hz, C-8), 133.9 (d, J = 23 Hz, C-9), 129.4 (d, J = 8 Hz, C-10), 129.6 (C-11), 149.2 (C-12), 138.6 (C-13), 126.2 (C-14), 127.5 (C-15), 127.0 (C-16), 132.3 (C-17), 132.9 (C-18), 124.4 (C-19).

2.2.2. Synthesis of [NiL(HL')]ClO$_4$ · H$_2$O (1)

The ligand **HL** (0.86 g, 2.00 mmol) was dissolved in ethanol (10 mL) with heating, then a solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.36 g, 1.00 mmol) in hot ethanol (10 mL) was added. After refluxing for 3 h, a brown precipitate was formed. After cooling, the precipitate was filtered off and recrystallized from ethanol. Yield 30%. The same reaction product was obtained when the reaction between **HL** and $Ni(ClO_4)_2 \cdot 6H_2O$ was performed in a molar ratio of 1:1. Elemental analysis calcd for $C_{54}H_{43}ClN_8NiO_6P_2$: C 61.41, H 4.10, N 10.61, found: C 61.73, H 4.01, N 10.47%. IR (KBr, cm^{-1}): ν(N–H) 3251, ν(C=N)$_{azomethine}$ 1624, ν(C=N)$_{phthalazine}$ 1592, ν(C–P) 1434, ν(P=O) 1208, ν(ClO$_4$) 1108. μ_{eff} (B.M.): 2.98 (295 K), 2.96 (77.4 K).

2.2.3. Synthesis of [Cu$_2$(**HL**)$_2$](ClO$_4$)$_2$ · C$_2$H$_5$OH (2)

Into a hot solution of **HL** (0.43 g, 1.00 mmol) in ethanol (10 mL), a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.37 g, 1.00 mmol) in hot ethanol (10 mL) was added. After refluxing for 3 h, a red precipitate appeared. After cooling, the product was filtered off and recrystallized from ethanol. Yield 25%. Due to the insolubility of complex **2** in non-coordinating solvents, we recorded its ^{1}H NMR spectrum in DMSO-d_6. Low solubility and the observed solvolysis of complex **2** in DMSO-d^6 are the reasons why its ^{13}C NMR spectrum was not recorded. Elemental analysis calcd for $C_{56}H_{48}Cl_2Cu_2N_8O_9P_2$: C 54.37, H 3.91, N 9.06, found: C 54.63, H 4.12, N 9.35%. IR (KBr, cm^{-1}): ν(N–H) 3242, ν(C=N)$_{azomethine}$ 1619, ν(C=N)$_{phthalazine}$ 1591, ν(C–P) 1435, ν(ClO$_4$) 1110. ^{1}H NMR (DMSO-d_6) (numbering of the atoms according to Scheme 1a) δ (ppm): 12.70 (bs, 2H, N-H), 9.39 (s, 2H, H-1), 8.08-8.56 (m, 10H, H-13, H-16, H-17, H-18, H-19), 6.93-7.85 (m, 28H, H-3, H-4, H-5, H-6, H-9, H-10, H-11).

2.3. Crystallographic structure determination

X-Ray diffraction experiments were carried out with a Bruker APEX-II CCD in the case of Cu(I) complex and Bruker SMART 1000 CCD in the case of Ni(II) complex, using graphite Mo-Kα radiation (λ = 0.71073 Å). The initial array of measured intensities was processed by the SAINT [40] and SADABS [41] programs. The structures were solved by direct methods (SHELXTL) and refined by the full-matrix least-squares method on F^2 in anisotropic approximation for non-hydrogen atoms. All calculations were performed by using the SHELXTL software [42]. Crystal data and structure refinement parameters for both complexes are given in Table 1.

<Table 1>

Hydrogen atoms attached to oxygen and nitrogen atoms were found in the difference Fourier synthesis and normalized at standard X-ray values of 0.85 /A for O and 0.9 /A for N. The H(C) atom positions were calculated. All the hydrogen atoms were refined in isotropic approximation within the riding model with the $U_{iso}(H)$ parameters equal to $1.5U_{eq}(Ci)$, $1.2U_{eq}(Cj)$, $1.2U_{eq}(Nj)$ and $1.5U_{eq}(Ok)$ where $U(Ci)$ are the equivalent thermal parameters of the methyl carbon atoms, $U(Cj)$ are the equivalent thermal parameters of the other carbons, $U(Nj)$ are the equivalent thermal parameters of the nitrogen atom and $U(Ok)$ are the equivalent thermal parameters of the oxygen atom to which the corresponding H atoms are bonded.
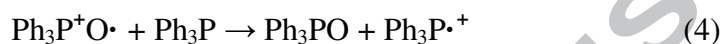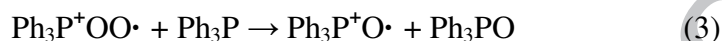
3. Results and discussion

3.1. Chemistry

The ligand 2-[2-(diphenylphosphino)benzylidene]-1-phthalazinylhydrazone (**HL**) was synthesized in the condensation reaction of 2-(diphenylphosphino)benzaldehyde and 1-hydrazinophthalazine hydrochloride using the previously reported method [39] (Scheme 1a). The reaction of **HL** with nickel(II) perchlorate in a molar ratio of 2:1 resulted in the formation of the square-pyramidal Ni(II) complex **1** (Scheme 1b). The coordination surrounding of the Ni(II) ion consists of a PNN coordinated deprotonated **HL** ligand and NN′ coordinated oxidized **HL** ligand (**HL′**). A similar oxidation of the phosphine ligand was observed in the case of the square-planar Ni(II) complex obtained in the reaction of $Ni[BF_4]_2 \cdot 6H_2O$ with 2-(diphenylphosphino)benzaldehyde thiosemicarbazone [43]. Reactions of Ni(II) complexes with molecular oxygen are generally unusual, but in some cases ligand coordination to the Ni(II) ion reduces the high Ni(III)/Ni(II) redox potential and makes it thermodynamically allowed. The reported reactions of Ni(II) complexes with O_2 resulted in ligand oxidation [43-45] or catalytic oxidation of exogenous substrates [46-48].

<Scheme 1>

In the reaction of the ligand **HL** and copper(II) perchlorate in a 1:1 molar ratio, the binuclear Cu(I) complex **2** was obtained (Scheme 1c). In complex **2** each Cu(I) ion is tetracoordinated with PNN donor atoms from one **HL** ligand and a phthalazine nitrogen atom from another **HL** ligand.

Triphenylphosphine oxidation by copper(II) perchlorate in the presence of molecular oxygen proceeds through a radical mechanism with triphenylphosphine oxide and the Cu(I) ion as reaction products (equations 1-4) [49-51].

$$Ph_3P + Cu(II) \rightarrow Ph_3P^{\cdot +} + Cu(I) \qquad (1)$$

$$Ph_3P^{\cdot +} + O_2 \rightarrow Ph_3P^+OO^{\cdot} \qquad (2)$$

$$Ph_3P^+OO^{\cdot} + Ph_3P \rightarrow Ph_3P^+O^{\cdot} + Ph_3PO \qquad (3)$$

$$Ph_3P^+O^{\cdot} + Ph_3P \rightarrow Ph_3PO + Ph_3P^{\cdot +} \qquad (4)$$

Complex **2** and the other reported Cu(I) complexes with 2-(diphenylphosphino)benzaldehyde hydrazones are stable towards air oxidation [28-31]. In these complexes the phosphorus donor atom, which is a "soft" base, stabilizes the Cu(I) ion, which is a typical "soft" acid [52]. Similar to complex **2**, in the previously reported binuclear Cu(II) complexes the NN′ coordinated phthalazine ring acts as a bridge between the two metal centers [7,8,12-16].

3.2.IR spectra

The presence of a band at 3251 cm^{-1} in the IR spectrum of complex **1**, corresponding to the ν(N–H) vibration, confirms the coordination of the ligand **HL′** in the non-deprotonated form. In the IR spectrum of complex **2** a band observed in the ν(N–H) vibration range at 3242 cm^{-1} indicates that the ligand **HL** is coordinated in the neutral form [17]. A band at 1621 cm^{-1}, originating from the ν(C=N) vibration of the azomethine group from an uncoordinated ligand **HL**, is shifted to 1624 cm^{-1} in the spectrum of complex **1** and 1619 cm^{-1} in the spectrum of complex **2**, suggesting coordination of the azomethine nitrogen atom [18]. Coordination of the nitrogen atoms from the phthalazine ring in complexes **1** and **2** results in a bathochromic shift of the ν(C=N) vibration [53] from 1600 cm^{-1} in the spectrum of **HL** to 1592 cm^{-1} in the spectrum of complex **1** and 1591 cm^{-1} in the spectrum of complex **2**. In the IR spectra of the ligand **HL** and complexes **1** and **2** the positions of the bands assigned to the ν(C–P) vibration [54] are almost constant (1435 cm^{-1} in the spectrum of **HL**, 1434 cm^{-1} in the spectrum of **1** and 1435 cm^{-1} in the spectrum of **2**). The band at

1208 cm^{-1} in the spectrum of complex **1** corresponds to the ν(P=O) vibration [46] of the uncoordinated triphenylphosphine oxide group from the **HL′** ligand. Strong bands at 1108 cm^{-1} in the spectrum of complex **1** and 1110 cm^{-1} in the spectrum of complex **2** originate from perchlorate anions in the outer sphere of the complexes [55].

3.3. NMR spectra

In the ^{1}H NMR spectrum of complex **2** in DMSO-d^6 the signals were broadened due to the oxidation of the Cu(I) ion and the formation of a small amount of paramagnetic Cu(II) species, indicating that solvolysis of complex **2** in DMSO solution is accompanied by Cu(I) oxidation with air oxygen. Nevertheless, from the ^{1}H NMR spectrum of complex **2** it can be seen that the **HL** ligands are coordinated in the non-deprotonated form since a signal at 12.70 ppm corresponding to the hydrazone NH group is present. Coordination through the azomethine nitrogen atoms results in a downfield shift of the H-1 atoms (numbering of the atoms according to Scheme 1a). In the ^{1}H NMR spectrum of complex **2** signals of the hydrogen atoms from the phthalazine rings are shifted downfield, suggesting coordination of the phthalazine nitrogen atoms.

3.4. Magnetic measurements

The effective magnetic moment of complex **1**, μ$_{eff}$ (295 K) = 2.98 B.M., is almost independent of temperature (μ$_{eff}$ (77.4 K) = 2.96 B.M.) The measured value of the effective magnetic moment is slightly higher than the spin-only value for the Ni^{2+} ion (μ$_{eff}$ = 2.82 B.M.), but in good agreement with the literature data for high-spin pentacoordinated Ni(II) complexes [56]. The results of the magnetic measurements showed that complex **2** is diamagnetic in the solid state.

3.5. X-ray crystallographic analysis

The formula unit of compound **1** is formed by a heteroleptic coordinated monocation, a perchlorate anion and a crystallization water molecule. The complex cation is formed by interaction of the nickel(II) ion with the tridentate PNN deprotonated anionic ligand **L$^-$** (through P1, N4, N1 donor atoms) and the neutral phosphine oxide **HL′**, being the corresponding oxidation product of **HL**, coordinated in bidentate manner through nitrogen atoms N8 and N5 of

the hydrazone and phthalazine moieties, correspondingly (see Fig.1 for the molecular view and numbering scheme and Table 2 for selected geometric parameters of **1**). The phosphine oxide group of **HL′** is left uncoordinated. The closest description of the nickel ion coordination polyhedron is square-pyramidal, with atoms P1, N1, N4 of the ligand **L⁻** and N5 of the ligand **HL′** in the basal plane and N8 of the ligand **HL′** in the axial position (distance to the basal least square plane (l.s.p.) of the pyramid defined by atoms P1, N1, N4, N5 for the donor and metal atoms are: P1 -0.0618(14) Å, N1 -0.074(4) Å, N4 0.072(4) Å, N5 0.064(4) Å, Ni1 0.1841(7) Å, N8 2.491(4) Å). The axial coordination of the nitrogen atom of the hydrazine moiety is rather weak and the interatomic distance Ni1–N8 is obviously elongated (2.463(4) Å).

<Table 2>

<Fig. 1>

The tridentate ligand **L⁻** forms two chelate cycles with the Ni ion, of which the five-membered "envelope"-shaped one (Ni1 ion in the apical position) adopts a close to planar conformation, with the Ni1 ion deviation from the l.s.p. of the cycle's members being 0.074(1) Å, while the six-membered one is significantly folded around the P1···N4 and P1···C9 lines. In the case of the **HL′** ligand, only the five-membered chelate cycle is close to planar (max deviation from the l.s.p. is 0.053(1) Å).

The crystallization water molecule participates in the formation of three intermolecular hydrogen bonds, whose characteristics are listed in the supplementary data table. The first one (O1W–H1W2···O4S) is formed by a water OH bond and the perchlorate anion's O4S oxygen atom in the same crystallographic position. The other two hydrogen bonds, O1W–H1W1···N2 and N7$^{(i)}$–H7$^{(i)}$···O1W (symmetry code (i): 1 - x, -y, 1 - z), bind the water molecule with two complex cations, one in the same crystallographic position (the water oxygen O1W acting as the donor and the N2 nitrogen atom of phthalazine moiety of **L⁻** as the acceptor) and the second in a neighboring centrosymmetric position (the water oxygen atom O1W as the acceptor part and the nitrogen atom N7$^{(i)}$ of the hydrazone moiety of the ligand **HL′** as the donor).

The water molecule in crystallographic position (i) is also bound to the same complex molecules by similar hydrogen bonds, O1W$^{(i)}$–H1W1$^{(i)}$···N2$^{(i)}$ and N7–H7···O1W$^{(i)}$, thus forming a centrosymmetric macrocycle comprising of alternating two water and two complex molecules.

The perchlorate anion is disordered over two positions with a ratio of 521(6):479(6), as is the benzene ring C50-C51-C52-C53-C54-C55, the ratio being 51(6):49(6) in this case.

The relatively high value of the R-factor obtained in refinement procedure can be connected with the partial random replacement of the phosphine-oxide ligand with a non-oxidized one in the molecules of complex **1** in the crystal structure. Differences in the values of the C-P-C bond angles and the P-C bond lengths of the oxidized and non-oxidized ligands (the corresponding values for triphenylphosphine are 102°, 1.83 Å and for triphenylphosphine oxide - 106°, 1.80 Å) can cause the abovementioned disorder in the benzene ring position, in conjugation with two different orientations, or the perchlorate ion, depending on the oxidation state of the phosphorus atom.

The formula unit of compound **2** consists of a complex dication, two perchlorate anions and a solvate ethanol molecule. The binuclear Cu(I) complex cation can be considered as the dimerization product of the mononuclear units [Cu(**HL**)]$^+$, formed by Cu coordination with the tridentate PNN neutral ligand **HL** through **the** P1, N4, N5 donor atoms, and possesses C2 symmetry (see Fig.2 for the molecular view and numbering scheme, Table 2 for selected geometric parameters). Dimerization occurs due to coordination of the copper centers with the ring nitrogen atoms in position 3 of the phthalazine moieties, which results in the formation of a doubly NN′ bridged binuclear Cu(I) core. Each copper ion has the same distorted tetrahedral coordination environment, consisting of the phosphorus P1 (d(Cu1–P1) = 2.1831(10) Å), hydrazone N4 (d(Cu1–N4) = 2.125(3) Å) and phthalazine N1 (d(Cu1–N1) = 2.063(3) Å) donor atoms of one neutral ligand and N2# nitrogen donor atom of the second ligand molecule (d(Cu1–N2#) = 2.019(3) Å) (symmetry code: (#) -x, y, 1/2-z). The interesting fact that the coordination Cu1–N4 bond length between the Cu(I) ion and the phthalazine nitrogen atom in position 2 (within monomer [Cu(**HL**)]$^+$) is significantly longer than the Cu1–N2# bond length with the nitrogen atom in position 3 (between monomers) can be explained by the strong *trans*-influence of the phosphorus atom.

In the monomeric units the five-membered chelate cycle with an envelope conformation is close to planar, the Cu(I) ion deviates by only 0.050(1) Å from the least square plane (l.s.p.) defined by the 5 ring atoms. The six-membered chelate cycle is heavily distorted by folding of the cycle's plane around the lines P1···C9 and P1···N4. The binuclear metallocycle adopts a "bath"

conformation with the copper centers in apical positions with a rather short interatomic distance (d(Cu1–Cu1[(i)]) = 3.1323(6) Å). Due to that, the overall shape of the complex is "roof-like", the dihedral angle between the l.s. planes defined by ten atoms of the phthalazine moieties of the ligands is 78.49(10)°.

<Fig. 2>

In the crystal each coordination dication is bound by a strong intermolecular hydrogen bond through the NH unit of the hydrazine moiety with the closest perchlorate anion: N3–H3B···O3S[(ii)] (symmetry code: (ii) x, 2 - y, -1/2 + z), with the following characteristics: d(N3–O3S[(ii)]) = 2.854(4) Å), angle in the fragment N3–H3B–O3S equals 160°.

The position of the crystal ethanol molecule is disordered.

4. Conclusion

In this work we investigated the coordination properties of 2-[2-(diphenylphosphino)benzylidene]-1-phthalazinylhydrazone (**HL**) towards Ni(II) and Cu(II) ions. In the reaction of nickel(II) perchlorate and **HL**, a square-pyramidal Ni(II) heteroleptic complex was obtained. The coordination environment surrounding the Ni(II) ion consists of a PNN coordinated deprotonated **HL** ligand and an NN′ coordinated oxidized **HL** ligand (**HL'**). In the Ni(II) complex, the coordination of the ligand reduces the Ni(III)/Ni(II) redox potential and allows its reaction with molecular oxygen, which results in **HL** ligand oxidation. A binuclear phthalazine bridged Cu(I) complex was obtained in the reaction of copper(II) perchlorate with **HL**. According to the previously reported results [49-51], it can be proposed that the reduction of the Cu(II) ion with the triphenylphosphine **HL** ligand in the presence of air oxygen gives the Cu(I) ion and the corresponding phosphine oxide of **HL**. The remaining non-oxidized **HL** ligand coordinates to the Cu(I) ion affording the stable binuclear Cu(I) complex.

Appendix A. Supplementary data

CCDC 853331 and CCDC 853332 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data

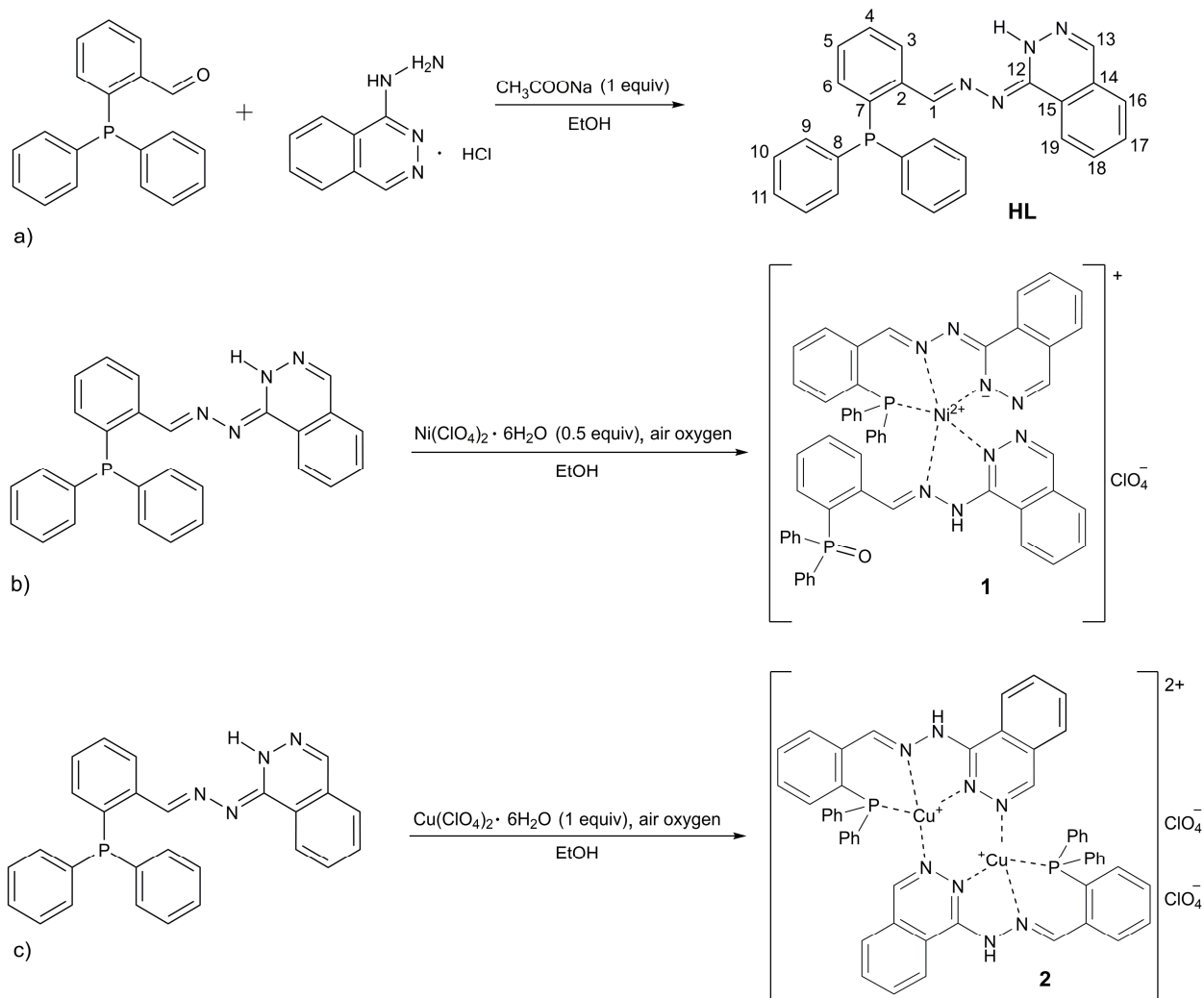Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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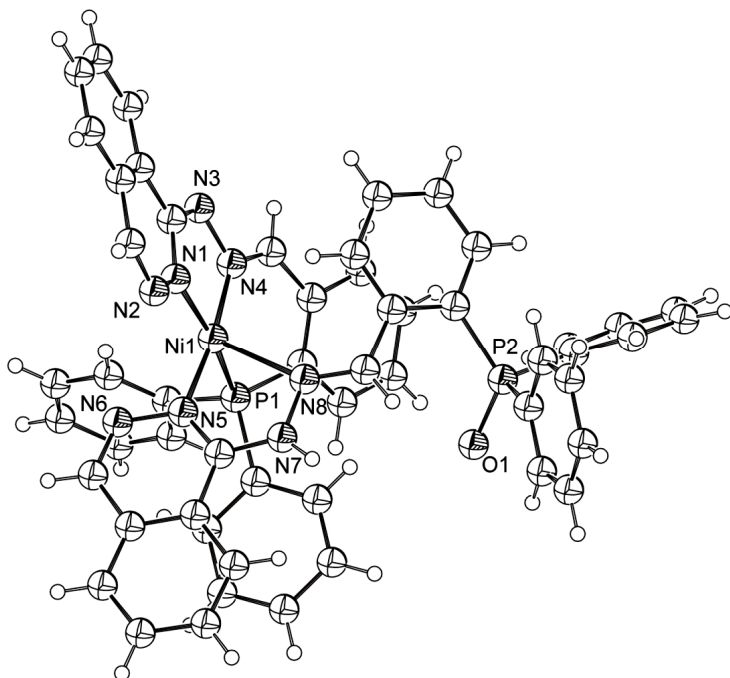**Scheme 1.** Synthesis of the **HL** ligand and complexes **1** and **2**.

Fig. 1. Structure of the monocation in complex **1** with labelling and thermal ellipsoids drawn at the 50% probability level
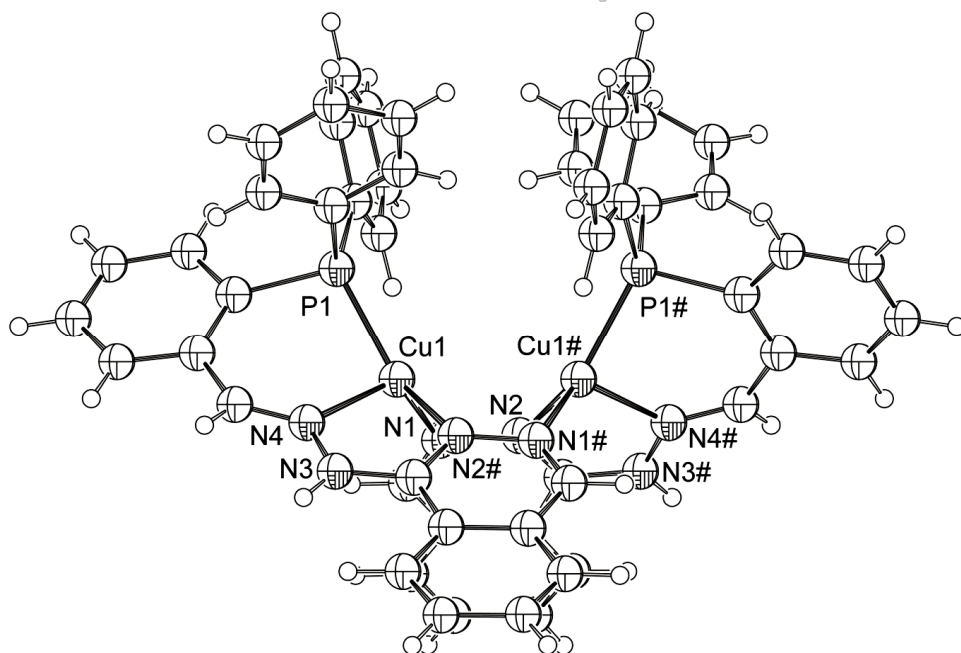

Fig. 2. Structure of the dication in complex **2** with labelling and thermal ellipsoids drawn at the 50% probability level

Table 1. Crystal data and structure refinement details for complexes **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{54}H_{43}ClN_8NiO_6P_2$	$C_{56}H_{48}Cl_2Cu_2N_8O_9P_2$
Fw (g mol^{-1})	1056.06	1236.97
Crystal size (mm)	$0.16 \times 0.13 \times 0.04$	$0.43 \times 0.13 \times 0.12$
Temperature (K)	120(2)	120(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	P-1	Pbcn
a (Å)	11.686(3)	20.1667(19)
b (Å)	13.257(4)	11.7428(11)
c (Å)	16.967(5)	22.214(2)
α (º)	74.306(5)	90.00
β (º)	75.907(6)	90.00
γ (º)	85.571(6)	90.00
V (Å^3)	2454.2(12)	5260.7(9)
Z	2	4
Density $_{calcd}$ (Mg/m^3)	1.429	1.562
μ, mm^{-1}	0.576	1.039
F(000)	1092	2536
$2\theta_{max}$ (º)	54	55
Number of measured reflections	31084	32922
Number of independent reflections	10645	6027
Number of reflections with $I > 2\sigma(I)$	5080	4168
Ranges of reflection indices	$-14 < h < 14$ $-16 < k < 16$ $-21 < l < 21$	$-26 < h < 26$ $-15 < k < 12$ $-26 < l < 28$
Number of refined parameters	600	348
R$_1$ ($I > 2\sigma(I)$)	0.0973	0.0502
wR$_2$ (all reflections)	0.2912	0.1518
Goodness of fit on F^2	1.183	1.000

| Largest diff. peak and hole (eÅ^{-3}) | 1.628 and −1.146 | 1.289 and −0.926 |

Table 2. Selected bond lengths and angles for complexes **1** and **2**.

Complex **1**			
Bond lengths (Å)			
Ni1–N4	1.883(4)	N1–N2	1.363(6)
Ni1–N1	1.899(5)	N3–N4	1.409(6)
Ni1–N5	1.901(4)	N5–N6	1.385(6)
Ni1–P1	2.1689(16)	N7–N8	1.389(5)
Ni1–N8	2.463(5)	P2–O1	1.571(3)
Bond angles (º)			
N4–Ni1–N1	82.51(18)	N5–Ni1–P1	90.47(13)
N4–Ni1–N5	172.66(18)	N2–N1–Ni1	126.7(3)
N1–Ni1–N5	94.58(17)	N3–N4–Ni1	114.4(3)
N4–Ni1–P1	90.69(14)	N6–N5–Ni1	113.5(3)
N1–Ni1–P1	164.46(13)	N7–N8–Ni1	103.69(13)
Complex **2**			
Bond lengths (Å)			
Cu1–N2	2.019(3)	Cu1–P1	2.1831(10)
Cu1–N1	2.063(3)	N1–N2	1.386(4)
Cu1–N4	2.125(3)	N3–N4	1.376(4)
Bond angles (º)			
N2–Cu1–N1	98.37(11)	N4–Cu1–P1	90.34(8)
N2–Cu1–N4	122.46(12)	N2–N1–Cu1	123.0(2)
N1–Cu1–N4	76.48(10)	N1–N2–Cu1#	107.7(2)
N2–Cu1–P1	124.50(9)	N3–N4–Cu1	111.73(19)
N1–Cu1–P1	134.61(8)		

Complexes of Ni(II) and Cu(I) ions with the condensation derivative of 2-(diphenylphosphino)benzaldehyde and 1-hydrazinophthalazine were synthesized and characterized by X-ray analysis, spectroscopic methods and magnetic measurements.