Polish J. Chem., **75**, 751–754 (2001) **COMMUNICATION**

Structure of O,O-Diethylthonophosphorylhydrazine *o*-Vanillin Schiff Base Copper(II) Complex: $Cu[(C_2H_5O)_2PSNHNCHPh(o\text{-}O)OMe]_2$

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There is considerable interest in the coordination chemistry of transition metals with the hydrazine family of ligands [1–4]. Hydrazines, functionalized with the main group units (*e.g.*; P(S) or P(O)) in addition to the nitrogen hard bases, can be used in heteroatomic chelation of a variety of transition metals. The transition metal chemistry of hydrazines functionalized with main group backbones not only is of fundamental importance in understanding the organometallic and coordination chemistries of hydrazine ligands but also may enhance the scope and the subsequent utility of hydrazines in transition metal chemistry [5]. Although hydrazine frameworks with main group functionalities in their backbone have been described [6,7], there is a scarcity of hydrazines Schiff base with main group functionalities in their backbone.

As we know, phosphorylhydrazine complexes exhibit insecticidal activities to parasites, fly, beetle, ladybug, and underground pest, *etc.* [8,9]. We select phosphorydrazine Schiff base as ligand, because it could promote chelation and provide extra stability of the centers. We expect that the phosphorydrazine Schiff base metal complexes are also biological active. In this paper, the synthesis of the Schiff base of O,O-diethylthonophosphorylhydrazine with *o*-vanillin and its Cu(II) complex, and the crystal structure of O,O-diethylthonophosphorylhydrazine *o*-vanillin Schiff base copper(II) complex are described. Fig. 1 shows the title compound with atom labeling. Selected bond distances and angles are listed in Table 1. The crystal structure contains two centrosymmetric molecules of $Cu[(Et_2O)_2PSNHNCHPh(o\text{-}O)OMe]_2$. The copper(II) ion is coordinated in a slightly distorted trans square-planar configuration, the distortion consisting of a reduction of the N–Cu–O angle with the chelate rings from the ideal value of 90°

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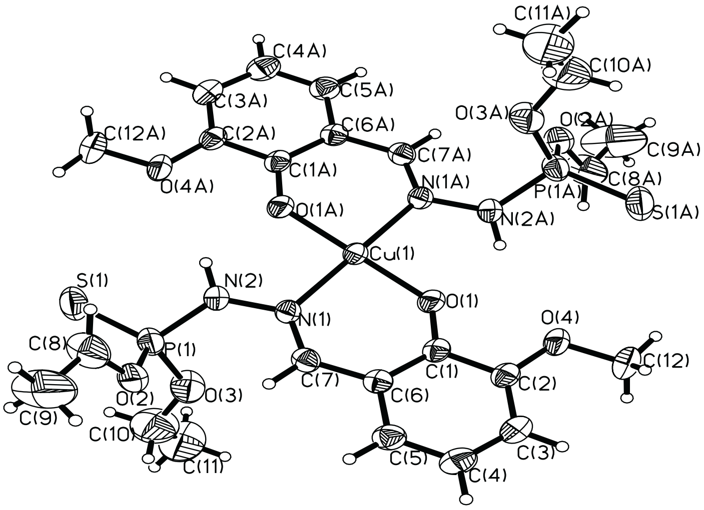

Figure 1. The molecular structure of Cu[$(C_2H_5O)_2$PSNHNCHPh(*o*-O)OMe$]_2$ showing the atom labeling scheme. Atoms are represented as thermal ellipsoids at 30% level, the H-atoms as small circles of arbitrary reduces.

Table 1. Selected bond lengths (Å) and angles (°).

Cu1–O1	1.867(2)	Cu1–O1	1.867(2)
Cu1–N1	2.009(3)	Cu1–N1	2.009(3)
P1–O2	1.576(3)	P1–O3	1.577(4)
P1–N2	1.651(3)	P1–S1	1.9112(17)
N1–C7	1.300(5)	N1–N2	1.403(4)
O1–C1	1.308(4)	O2–C8	1.470(6)
O3–C10	1.366(7)	O4–C2	1.371(5)
O1–Cu1–O1	180.0	O1–Cu1–N1	87.98(12)
O1–Cu1–N1	92.02(12)	O2–P1–O3	101.03(19)
O2–P1–N2	107.52(17)	O3–P1–N2	101.82(18)
O2–P1–S1	115.13(13)	O3–P1–S1	117.77(15)

Symmetry transformations used to generate equivalent atoms: #1: –x, –y, –z.

The coordination geometry of copper(II) is square planar with two equivalent Cu–N and Cu–O bonds. The Schiff base loses a proton from the hydroxyl group and acts as a single charged bidentate ligand coordinating to copper(II) through the hydroxyl O and hydrazination N atoms. The six-member chelate ring is plane with the mean deviation from the best plane of 0.093(1)°. The copper atom is located in the center of the coordination plane defined by O(2), N(1), C(5), C(6), C(7) and O(2)a, N(1)a, C(5)a, C(6)a, C(7)a. The least-squares plane composed of O(1), O(2), N(1), N(2), C(1), C(2), C(3), C(4), C(5), C(6) C(7) and C(8), with maximum deviation not greater than 0.05 Å is nearly parallel to that of Cu, N(1), N(2), C(4), C(5), C(6), C(7); the dihedral angle between them is only 4.67°. The two phenyl rings and the coordination moieties are in one plane forming an extensive electronic delocalization system. The bond distances of Cu–O(2) and Cu–N(1) for $Cu[(C_2H_5O)_2PSNHNCHPh(o\text{-}O)OMe]_2$ are 1.867(2), 2.009(3) Å, respectively. All these parameters are in close agreement with those reported for square-planar copper(II) compound [10–12]. The P–O, P–S and P–N bond lengths of the diethylthonophosphorylhydrazine correspond with those in other dialkylthonophosphoryl derivatives [13–15]. Atoms C(9) and C(10) of the ethyl groups were found to be slightly disordered.

Intramolecular N–H···O hydrogen-bonding interaction exists between the two ligands of each molecule as indicated by the geometric parameters; the donor and acceptor distances are N(2)–H(2A)···O(1) 2.643 (1) Å [symmetry codes: –x, –y, –z]. The title compound was synthesized by mixing copper(II) acetate with excess O,O-diethylthonophosphorylhydrazine *o*-vanillin Schiff base in ethanol, brown-green solid precipitated was recrystallized from EtOH/CH_3Cl mixture solution. Single crystal suitable for X-ray analysis was obtained by slow evaporation of acetic ether solution at room temperature.

Crystal data and structure refinement: $Cu[(C_2H_5O)_2PSNHNCPh(o\text{-}O)OMe]_2$; Mr = 698.17; Monoclinic; $P2_1/c$; $a = 15.458(3)$ Å; $b = 7.314(1)$ Å; $c = 15.874(3)$ Å ; $\beta = 118.11(3)°$; $Z = 2$; V = 1583.0 $Å^3$; $D_x = 1.318\ Mg/m^3$; MoK_α radiation; $\lambda = 0.71073$ Å; $\theta = 2.57–27.52°$; $\mu = 0.961/mm$; 0.28×0.26×0.12 mm^3; T = 293 K; Prism; Brown. Four-circle CAD-4 diffractometer; $\omega/2\ \theta$ scans; Absorption correction; Semi-empirical; 3202 Reflections collected; 2142 Independent reflections with $I > 2\sigma(I)$; $R_{int} = 0.0343$; $h = 0 \rightarrow 20$ $k = -9 \rightarrow 9$ $l = -20 \rightarrow 18$; Refinement on F^2; R = 0.0531; $wR = 0.1219$; GOF = 1.055; 188 parameter; $w = 1/[\sigma^2(F^2) + (0.0678P)^2 + 0.1777P]$, where $P = (F^2 + 2Fc^2)/3$; $(\Delta/\sigma)_{max} = 0.0009$; $\Delta\rho_{max} = 0.334\ e/A^3$; $\Delta\rho_{min} = -0.337\ e/A^3$. Extinction correction: none.

Data were collected with SADABS program [16]. The structure was solved by direct methods using the *SHELXTL* software package [17]. All non-H atoms were anisotropically refined. The hydrogen atoms were located by difference synthesis and refined isotropically. The molecular graphics were plotted using SHELXTL [17]. Atomic scattering factors and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography [18]. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number CCDC152951).

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