The square-planar structure of bis[N-(i-propyl)-3-oxy-2-naphthaldiminato]copper(II)

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The stepped square planar Schiff base copper(II) complex bis[N-(i-propyl)-3-oxy-2-naphthaldiminato]copper(II) was synthesized and characterized by chemical analysis, UV–visible, mass spectrometry, IR, far IR, X-ray crystallography and EPR. In addition was complemented with computational methods.

The stepped square-planar Schiff base copper(II) complex bis[N-(i-propyl)-3-oxy-2-naphthaldiminato]copper(II) (I) is presented. This compound was synthesized and characterized by chemical analysis, mass spectrometry, UV–visible, IR, far-IR, and X-ray crystallography. In addition, EPR studies were carried out for I. In this complex, the geometry around the copper ion is stepped square planar. EPR spectra in toluene, chloroform, and DMF solutions at 77 K suggest that the geometry of I is similar to that observed in the solid state by X-ray crystallography. Kohn–Sham geometry optimizations on this complex are in good agreement with the experimental data. Additionally, we show that a square planar structure for the bis-(N-i-Pr-3-oxy-2-naphthaldiminato)copper(II) complex can also be found in gas phase and not only in the solid state, result that challenges the hypothesis that packing effects are crucial for obtaining this structure.

Keywords: X-ray structure; EPR; Computational methods; Electronic structure; Packing effects

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Introduction

There is a continuous interest on bis-bidentate Schiff base metal complexes; they have recently been used as polymerization catalysts [1], in molecular hyperpolarizability studies [2], or in self-assembly systems and aggregation phenomena [3]. Copper-complexed Schiff bases with aromatic imines have been studied because of their ability to intercalate between the bases of DNA, and to participate in catalytic cycles with reducing and oxidizing agents in biological media [4, 5]. The cytotoxicity of some Schiff-base copper(II) complexes toward tumor cells was reported [6, 7]. Understanding the interaction of these kinds of complexes with DNA will help in designing new drugs and developing new, selective, and efficient DNA recognition, as well as DNA-cleaving agents [8].

Metal ions present in Schiff base complexes accelerate their drug action and the efficiency of some therapeutic agents depending on the geometry of the complexes [9, 10], a property that can make a stereoisomer either inert or biologically useful. So, an intriguing feature that has received considerable attention is the wide range of stereochemistry that is exhibited by bis-bidentate Schiff base copper(II) complexes derived from salicylaldehyde [11] in the solid state [12, 13], ranging from perfect square-planar to pseudo-tetrahedral. It has been argued that this structural variety is the result of steric effects [14], electronic effects [15], or crystal packing forces [16–19].

Characterization of the Schiff base copper(II) complex bis[N-(i-propyl)-3-oxy-2-naphthal-diminato]copper(II) (1) is reported here (scheme 1). Single-crystal X-ray analysis of 1 was undertaken to elucidate its conformation and structure and to correlate the crystal structure with other Schiff base copper(II) complexes reported [11]. The molecular structure of 1 including atom-numbering scheme is shown in figure 1. Furthermore, we compared 1 with analogous Schiff base copper(II) complexes, i.e. bis-(N-isopropyl-salicylidenameinato)copper (II) [18], bis-(N-isopropyl-2-oxy-1-naphthylideneaminato) copper(II) [19] and the recently described crystal isomer of 1, bis-(N-isopropyl-3-oxy-2-naphthylideneaminato) copper(II) [20]. In addition, EPR studies of 1 in toluene, chloroform, and DMF frozen solutions at 77 K were performed in order to investigate the influence of the solvent polarity on the geometry of this complex and whether the geometry of 1 in solution is different to that observed in the solid state by X-ray crystallography. The study is complemented with electronic structure calculations within the Kohn–Sham approach.
Experimental

Copper(II) acetate monohydrate, isopropylamine, methanol LC-MS CHROMASOLV (MeOH), ethyl ether, phosphorus pentachloride, tin(II) chloride anhydrous, naphthol AS, acetone, n-hexane, and dichloromethane were all obtained from Aldrich Chemical Co. Inc. and were used without purification. Spectroscopic grade solvents such as toluene, chloroform, deuterochloroform (CDCl₃), and N,N-dimethylformamide (DMF) were obtained from the same source. In addition, hydrogen chloride was acquired from Matheson and 3-hydroxy-2-naphthalencarboxaldehyde was prepared as described in the literature [21].

The melting point was determined on a Fisher-Johns apparatus and is uncorrected, i.e. it was not inserted in a calibration curve. IR (KBr disks) and far-IR (CsI disks) spectra were recorded on a Bruker Tensor-27 FT spectrophotometer. The UV–vis spectrum was acquired on a Shimadzu UV-160U recording spectrophotometer using chloroform as solvent. Mass spectrum was obtained on a JEOL Mod. JMS-SX-102A mass spectrometer operated at an accelerating voltage of 70 kV. The EPR measurements were performed on a JEOL JES TE300 spectrometer. A nitrogen-based cryogenic attachment JEOL DVT unit was used. An external NMR precision field-meter JEOL ES-FC5 was used for calibration of the magnetic field. Compound 1 shows EPR response in 1 × 10⁻² M toluene, DMF, and chloroform frozen solutions at 77 K. TGA analysis of 1 was determined on a General V4.1C Dupont 2100 apparatus with a heating speed of 10 °C min⁻¹ under nitrogen. Elemental analysis was performed by Galbraith Laboratories, Inc. Knoxville, Tenn. 37921-1750 USA.

The copper complex 1 was prepared by a method described in the literature [22]. The following preparation is typical: to a stirred cold solution of 0.006 M (0.51 mL) of isopropylamine in 30 cm³ of methanol was added a solution of 0.002 M (0.344 mg) of 2-hydroxy-3-naphthalencarboxaldehyde in 250 cm³ of methanol followed by the addition of a cold solution of 0.001 M Cu(OAc)₂H₂O (0.200 mg) in 10 cm³ of H₂O, then the mixture was boiled under reflux for 2 h and concentrated until a precipitate was observed; the brilliant brownish-orange solid was filtered with suction, washed with cold water, and dried. Recrystallization from dichloromethane-methanol gave 0.328 g of 1 as deep brownish-orange crystals.

Figure 1. Structure of 1 with atom labeling.
Bis-(N-isopropyl-3-oxo-2-naphthylideneamino)copper(II) (I), (Yield 0.328 g, 67%); deep brownish-orange crystals, m.p. 209 °C; mass spectrum (m/z) M⁺ 487 (base peak 213); IR (KBr) ν(C=N) 1620 cm⁻¹; UV/vis (solvent CHCl₃; in nm; ε in cm² M⁻¹) 262 (ε = 74 730), 302 (ε = 44 870), 436 (ε = 4 830). EPR at 77 K, (DMF) A||(in mT) 17.00 (±0.15), g|| 2.2497, g⊥ 2.053; (CHCl₃) A||(in mT) 17.18 (±0.15), g|| 2.2316, g⊥ 2.0717; (Toluene) A||(in mT) 17.30 (±0.15), g|| 2.2363, g⊥ 2.0468. Found: C, 69.0; H, 5.80; N, 5.70. Calcd for C₂₈H₂₈N₂O₂Cu: C, 68.88; H, 5.78; N, 5.74%.

X-ray crystallography

Suitable X-ray quality crystals of I were grown by slow layer diffusion of MeOH into a saturated CH₂Cl₂ solution of I at room temperature.

The crystal was mounted on a glass fiber and diffraction experiments were performed on a Bruker Smart APEX AXS CCD area detector/omega with MoKα radiation. Orientation matrices and lattice parameters were obtained from least-squares refinements of the setting angles of 40 reflections 1.89° < θ < 24.99°. Data-sets were collected from 3.00° to 50.00° using the θ scan mode at 293(2) K. The observed extinctions and subsequent refinements confirmed the space group (see table 1).

The structure was solved by direct methods using the SHELXS-97 programs [23]. The refinements were carried out by full-matrix least-squares on F². Weighted R-factors Rw and all goodnesses of fit S were based on F². The observed criterion of (F² > 2σF²) was used only for calculating the R factors. No absorption corrections were applied. In the final cycles of refinement, all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogens were included in calculated positions (C–H = 0.93 Å for aromatic H, C–H = 0.98 Å for methyne, and C–H = 0.96 Å for methyl H) and refined using a riding model, with Uiso(H) = 1.2 Ueq for H aromatic and methyne and Uiso(H) = 1.5 Ueq for H of the methyl group of the carrier atoms. Neutral atomic scattering factors were taken from the international tables for X-ray crystallography [24].

Table 1. Crystallographic data for I.

| Description                              | Value                                      |
|------------------------------------------|--------------------------------------------|
| Chemical formula                         | C₂₈H₂₈CuN₂O₂                               |
| CCDC deposit no.                         | 269972                                     |
| Formula weight                           | 488.06                                     |
| Crystal system                           | Monoclinic                                 |
| Crystal color                            | Brownish-orange                            |
| Space group                              | P2₁/n                                     |
| μ (MoKα)                                 | 0.71073 mm⁻¹                               |
| T of data collection (K)                 | 293(2)                                    |
| Unit cell dimensions                     |                                           |
| a (Å)                                    | 8.9528(7)                                  |
| b (Å)                                    | 6.0240(5)                                  |
| c (Å)                                    | 21.5772(17)                                |
| β (°)                                    | 91.260(2)                                  |
| Unit cell volume (Å³)                    | 1163.41(2)                                 |
| Density (Calcd) g/cm³                    | 1.393                                      |
| Absorption coefficient                   | 0.967 mm⁻¹                                 |
| F(0 0 0)                                 | 510                                        |
| Z                                        | 2                                          |
| θ Range (°)                              | 1.89 < θ < 24.99                           |
| Max. and min. transmission               | 0.9621 and 0.7917                         |
| Goodness of fit on F²                    | 0.873                                      |
| Measured/independent reflections and R (int) | 9253/2118; 0.0453           |
| Final R indices [I > 2σ(I)]              | R₁ = 0.037, wR₂ = 0.086                    |
| Largest diff. peak and hole              | 0.448 and –0.167                          |
**Computational methods**

For the geometry optimizations, initial structures were constructed in Molden [25]. The first geometry optimization calculation was performed on the X-ray structure; another was initiated from a distorted tetrahedral arrangement. The minima were characterized by vibrational analysis. The calculations in this work were performed using Kohn–Sham theory as implemented in deMon2 k [26]. For comparison, we used either the DZVP basis set [27] within the local spin density approximation using Dirac’s exchange [28] and VWN [29] correlation or the DZVP-GGA basis set [30] in conjunction with the generalized gradient approximation functional PBE [31]. These functionals were selected because they are non-empirical and belong to the first two rungs of Jacob’s ladder [32]. The results provided by this computational strategy allow us to analyze the role of the functional in the description of these molecular systems. For the SCF settings, we used a tight-binding start density, an initial SCF convergence criterion of $0.5 \times 10^{-9}$, an adapted grid tolerance of $1 \times 10^{-5}$ for the numerical integration, an auxiliary density convergence criterion of $5 \times 10^{-6}$, and DIIS was turned off. For the inversion of the Coulomb matrix, the analytical calculation of the fitting coefficients in the diagonal basis was used through a singular value decomposition analysis with tolerance of $0.1 \times 10^{-6}$. Finally, for the variational fitting of the electronic density, the automatically generated auxiliary function sets GEN-A2 [33, 34], which contain $s$, $p$, and $d$ functions, were employed. The evaluation of four center integrals was avoided by invoking the variational fitting of the Coulomb energy.

**Results and discussion**

**Crystal study**

A selection of bond lengths and angles is given in table 2. The molecular structure of 1 including atom-numbering schemes is shown in figure 1. The X-ray diffraction analysis of 1 shows that copper(II) is in a special position lying on a center of inversion and is bonded to the oxygen and nitrogen donors of the two bidentate ligand molecules in the usual trans arrangement. As depicted in figure 2, the geometry around copper(II) is stepped square planar with a step value (S) of 0.947(7) Å. While for the complexes bis-(N-ipr-salicylaldiminato) copper(II) [18], bis(N-ipr-2-oxy-1-naphthylidene-aminato)copper(II) [19], and the polymorph of 1, bis(N-ipr-3-oxy-2-naphthylideneaminato)copper(II) [20], the geometries around the copper(II) ion are distorted square planar with dihedral angle values between the planes defined by O1–Cu–N1 and O1A–Cu–N1A of 59.7°, 38.6°, and 51.5°, respectively. It is interesting to point out that for the copper(II) complex derived from diphenylmethanamine and

| Bond lengths       | Bond angles |
|--------------------|-------------|
| Cu(1)–N(1)        | 2.0307(19)  |
| Cu(1)–O(1)        | 1.8769(17)  |
| O(1)–C(3)         | 1.316(3)    |
| N(1)–C(11)        | 1.278(3)    |
| N(1)–C(12)        | 1.491(3)    |
| C(1)–C(2)         | 1.383(3)    |
| C(2)–C(3)         | 1.430(3)    |
| N(1)–Cu(1)–O(1)   | 91.02(7)    |
| N(1)–Cu(1)–O(1A)  | 88.98(7)    |
| C(3)–O(1)–Cu(1)   | 125.86(16)  |
| C(11)–N(1)–Cu(1)  | 121.06(17)  |
| C(12)–N(1)–Cu(1)  | 119.63(15)  |
| C(3)–O(1)–Cu(1)   | 125.86(16)  |
| C(11)–N(1)–Cu(1)  | 121.06(17)  |
| C(12)–N(1)–Cu(1)  | 119.63(15)  |
the same aldehyde, despite the bulkiness of the original amine, the geometry is planar \[35\], whereas other Schiff base copper(II) complexes derived from the same 3-hydroxy-2-naphthalenecarboxaldehyde with the 1-ethylpropyl \[36\] or (R)(−)-secbutyl \[37\] substituents on the imine nitrogen show geometries intermediate between square planar and tetrahedral with dihedral angle values between the corresponding OCuN planes of 50.1° and 49.0°, respectively. The data suggest that despite volume or electronic considerations, the geometry of 1 could be explained predominantly in terms of crystal packing forces. To explore the role of packing effects, we have carried out a series of electronic structure calculations on complexes of the series bis-(N-R-salicylaldiminato)copper(II), bis-(N-R-2-oxy-1-naphthylidene-aminato)copper(II), and bis-(N-R-3-oxy-2-naphthylideneaminato)copper(II), where R = H, Me, Et, Pr, iPr, Bu, secBu, and tertBu, and they show that packing effect in the crystal is not necessarily the driving force responsible for the existence of planar arrangements. As it will be discussed elsewhere, structural versatility could be obtained with very strict calculations.

Due to the symmetry of 1, the geometry about the copper in 1 is square planar, with a slight deviation of ideal square-planar geometry, where the O(1)–Cu–N(1) bite angle is 91.02(7)°.

The Cu–O bonds (1.8769(17) Å) in 1 have similar lengths and are in the same range as those reported for their analogs with diphenylmethyl substituents \[35\], bis(N-ipr-salicylidienaminato)copper(II) \[18\], bis(N-ipr-1,2-naphthaldiminato)copper(II) \[19\], and bis(N-ipr-3,2-naphthaldiminato)copper(II) \[20\], i.e. Cu–O distances have values between 1.870 and 1.903(6) Å, the Cu–N bond length, 2.0307(19) Å, is in the range of Cu–N distances with values of bond lengths between 1.963 and 2.033 Å. Again, Cu–N and Cu–O bond lengths in 1 are in the same range as other similar square-planar Schiff base copper(II) complexes derived from salicylaldehyde, 4-methylacetophenone, and 3,4,5-trimethoxybenzaldehyde \[38–41\], for instance, in bis(5-chloro-N-ipr-salicylidienaminato)copper(II) \[42\], where the corresponding bond lengths are Cu–N 2.032(3) and Cu–O 1.891(2) Å. Other bond lengths and angles show the expected values. It is interesting to point out that the bond lengths Cu–O and Cu–N in the pseudo-tetrahedral polymorph \[17\] are 1.873(1) and 2.005(2) Å, respectively.

In 1, there is an intermolecular hydrogen contact between C(8)–H(8) and the C(1) of a sub-adjacent molecule \([-x + 0.5, y + 0.5, -z + 0.5]\), where the H⋯C_acceptor and C_donor⋯C_acceptor centroid distance is 2.717 Å and the angle C_donor–H⋯C_acceptor is 127.2°.

**Physical and spectroscopic study**

The elemental analysis was satisfactory and this complex shows a ligand to metal ratio of 2 : 1. The electronic impact mass spectra of 1 show the expected molecular ion, other ions
were also recorded at \((M^+ + 2) m/z\), which are characteristic of copper isotopic distribution. The molecular ion \(\text{CuL}_2\) decomposes to a \(\text{CuL}\) fragment being present as well as a fragment corresponding to the mass of \(L\) (base peak). The absorption electronic spectra of \(1\) showed only absorptions to be attributed to intraligand transitions \((n-\pi^*, \pi-\pi^*)\) or charge transfer bands were observed [43]. No bands corresponding to transitions in the ligand field region, i.e. \(d^x-d\) transitions, were observed. The IR spectrum of \(1\) displays the characteristic absorption band attributed to the \(\nu-\text{(C=N)}\) vibration around 1615 cm\(^{-1}\) as described in similar complexes [44], the \(\nu-\text{OH}\) band is absent in \(1\). By correlating the far-IR spectrum of \(1\) with other Schiff base copper(II) complexes [45], it was possible to assign the \(\nu-\text{Cu–O}\) vibration at 588 cm\(^{-1}\) and the \(\nu-\text{Cu–N}\) vibration bands at 395 cm\(^{-1}\), which are in agreement with analogous N-(alkyl-salicylaldiminato)copper(II) complexes [45].

**EPR study**

The X band in the EPR solution spectrum of \(1\) allows measurement of \(g∥, g⊥, \text{and } A∥\); the sample shows axial symmetry for the paramagnetic copper center. The magnitude of the coupling constant \(A∥\) usually is taken as a measure of distortion, in the sense that \(A∥\) values diminish as the geometry departs from axial configuration, i.e. distortion grows [16, 46, 47]. The \(A∥\) values of \(1\) in DMF, chloroform, and toluene frozen solutions have essentially the same magnitude: 17.00 (±0.15 mT), 17.18 (±0.15 mT), and 17.30 (±0.15 mT), respectively, consistent with a square planar copper(II) complex [48]. Furthermore, the empirical relationship \(f = g∥/A∥\) [39] shows values of 126, 124.7, and 123.8 cm for each of the frozen solutions, respectively, which are in the range for square-planar copper(II) complexes \((f = 105-135 \text{ cm})\) [49] and confirms that in solution, the coordination geometry of copper in \(1\) is square planar [50].

**TGA study**

The TGA curve (25–350 °C) of \(1\) shows an inflection point at 208.8 °C, which corresponds to its melting point followed by a constant steady decomposition. Nevertheless, the IR spectrum of the residue of the TGA study shows some absorption bands attributable to \(1\), which indicates that not all the complex was decomposed.

**Electronic structure analysis**

To the best of our knowledge, there is only one theoretical study on the polymorph bis-(N-i-pr-3-oxy-2-naphthaldiminato)copper(II) [20], and it possesses a pseudo-tetrahedral copper coordination geometry where there is an angle between the planes O(1)–Cu(1)–N(1) and O(1A)–Cu(1)–N(1A) of 58.7°. With our methodology described above, we found this same arrangement with angles between the planes O(1)–Cu(1)–N(1) and O(1A)–Cu(1)–N(1A) of 48.4° (VWN) and 49.7° (PBE). The authors of reference 20 claim that with DFT, a planar structure for the bis-(N-i-pr-3-oxy-2-naphthaldiminato)copper(II) cannot be found because of the bulkiness of the i-Pr group; its presence in the crystal is explained in terms of packing pressure. Nevertheless, we were able to characterize, also as a minimum, a stepped square-planar arrangement for both functionals. Structures are presented in figures 3 (stepped planar) and 4 (pseudo-tetrahedral). For the functional PBE, the energy difference between the two arrangements is only 0.4 kcal M\(^{-1}\); the pseudo-tetrahedral one having the
lowest energy. The Cu–O bonds in the stepped planar structure have lengths of 1.906 and 1.964 Å for VWN and PBE, respectively. Cu–N distances are 1.978 and 2.047 Å for VWN and PBE, respectively. Again, it is interesting to compare these lengths with the theoretical pseudo-tetrahedral polymorph where the distances are: Cu–O(1) 1.964 Å, Cu-O(1A) 1.966 Å, Cu–N(1) 1.998 Å, Cu–N(1A) 2.014 Å. Bond angles of one of our calculations also show that the coordination geometry about copper is like in 1, square planar, with O(1)–Cu–N(1), O(1)–Cu–N(1A), N(1)–Cu–N(1A) and O(1)–Cu–O(1A) angles of 90.2, 89.8, 179.9, 180.0, respectively, for PBE and 91.0, 89.0, 179.8, 179.8 for VWN.

Conclusion

The isopropyl group in the solid state structure of 1 has a stepped square-planar coordination around the copper ion structure that probably is stabilized by crystal packing forces. This substituent usually is found as part of a pseudo-tetrahedral arrangement as in the corresponding copper(II) Schiff base structures with salicylaldehyde or in 2-hydroxy-1-naphthalenecarboxaldehyde and 3-hydroxy-2-naphthalenecarboxaldehyde derivatives [17, 18, 20].
EPR data indicate that in the liquid phase, 1 has the same geometry as that observed in the solid state. Theoretical calculations predict two structures in the gas phase; one of them is also square-planar and the other is a pseudo-tetrahedral structure. So, as the same stepped square-planar structure of this Cu(II) complex can be found in gas, liquid, and solid state, we conclude that packing effects are not the main reason to observe this structure. On the contrary, we think that, experimentally, the conditions to obtain the crystal and, theoretically, the tightness on several calculation thresholds are the factors responsible to obtain this structure.

Summarizing in this work we have shown, experimentally and theoretically, that the bulkiness of the isopropyl group is not a necessary condition to obtain a planar arrangement around the copper ion in these Cu(II) Schiff base complexes.

**Supplementary material for compound 1**

Crystallographic files in cif format have been deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2-1EZ, UK (Fax: + 44 1223/336–033; E-mail for inquiry: fileserv@ccdc.cam.uk) with CCDC deposition number 269972. EPR spectrum of 1. UV–vis. spectrum of 1. TGA study of 1.

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