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Synthesis and solid state structures of copper(II) complexes of Schiff bases derived from cyclopropyl and cyclobutylamine

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Abstract

The Schiff base copper(II) complexes (**1**)–(**6**) were prepared and characterised by mass, IR, and electronic spectra. Their solid states structures, determined by X-ray crystallography, indicate that the geometry around copper is determined by a combination of steric and electronic effects, as well as crystal packing forces. Thus, complex (**1**) is the only one in the series to have a square planar geometry. In contrast, complexes (**2**) and (**3**) display deformed square planar geometries, despite the small steric effect of the *N*-cyclopropyl and cyclobutyl groups. Furthermore, a purely electronic argument, based on which complexes (**5**) and (**6**) must have deformed tetrahedral structures, fails to account for the observed stepped square planar structures. Finally, complex (**4**) also has a stepped square planar geometry.

Keywords: Copper chelates; Schiff base ligands; Solid state structures

1. Introduction

There has been continuous interest in *bis*-bidentate Schiff base Cu(II) complexes derived from salicyl and naphthalenecarboxaldehydes because in the solid state the ligands display a wide range of geometric arrangements around copper, going from the ideal *trans*-square planar structure to deformed tetrahedral geometry [1–6]. It has been proposed that the extent of distortion from the square planar geometry in such molecules and the nickel(II) analogues depends on the volume of the substituent at the coordinating nitrogen atom [2]. In some cases, however, both electronic effects [3,6,7] and crystal packing [6,8,9] have been invoked as the driving forces responsible for the distortion. The presence of a small substituent bound to the nitrogen atom such as a cyclopropyl or cyclobutyl group should have a small steric effect on the geometric arrangement of the ligands around the copper centre. Therefore, Schiff base complexes derived from cyclopropylamine and cyclobutylamine would allow us to focus on the relevance of electronic effects and crystal packing forces in these systems.

We had previously reported the synthesis and solid state structures of copper(II) Schiff base complexes prepared from the condensation products of salicylaldehyde, 2-hydroxy-1-naphthalenecarboxaldehyde, and 3-hydroxy-2-naphthalenecarboxaldehyde, and the series of amines substituted with cycloalkyl groups from cyclopentyl to cyclooctyl [9–11]. Despite the instrinsic electronic differences among the aromatic groups of the Schiff base ligands, which correspond to a larger negative charge on the oxygen atom of the 3-oxo-2-naphthalenecarboxaldiminate ligand, an

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intermediate one on that of salicylaldiminate, and a smaller one on that of the 2-oxo-1-naphthalenecarboxaldiminate ligand [7], the expected electronic effects are not reflected in the structural features of the coordination geometry of copper. Therefore, it is reasonable to assume that crystal packing forces play a significant role in the coordination geometry around copper in the solid state structures.

In order to determine the importance of crystal packing forces in these systems, and to complete a systematic study of the geometric arrangement of bidentate Schiff base ligands around copper in the solid state structures, we have undertaken the synthesis and solid state structure determination of copper(II) Schiff base complexes which include the two smaller members of the cycloalkyl-substituted series of primary amines, cyclopropyl and cyclobutylamine. Thus, we herein report the preparation and single crystal X-ray diffraction studies of the compounds *bis*-{(cyclopropyl)[(2-oxo-1H-benzo-1-ylidene)methyl]aminato}copper(II) (**1**), *bis*-{(cyclobutyl)[(2-oxo-1H-benzo-1-ylidene)methyl]aminato}copper(II) (**2**), *bis*-{(cyclopropyl)[(2-oxo-1H-naphth-1-ylidene)methyl]aminato}copper(II) (**3**), *bis*-{(cyclobutyl)[(2-oxo-1H-naphth-1-ylidene)methyl]aminato}copper(II) (**4**), *bis*-{(cyclopropyl)[(3-oxo-2H-naphth-2-ylidene)methyl]aminato}copper(II) (**5**), and *bis*-{(cyclobutyl)[(3-oxo-2H-naphth-2-ylidene)methyl]aminato}copper(II) (**6**), which are obtained from the corresponding Cu(II) *bis*-aldehydate precursors and the appropriate cycloalkylamine.

2. Experimental

2.1. Reagents and techniques

Cyclopropylamine, cyclobutylamine, copper(II) acetate monohydrate, salicylaldehyde, and 2-hydroxy-1-naphthalenecarboxaldehyde were purchased from Aldrich Chemical Co. Inc., and were used without further purification. 3-hydroxy-2-naphthalenecarboxaldehyde was prepared as described in the literature [12]. Methanol (MeOH) and ethanol (EtOH) were distilled prior to use from magnesium, while CH_2Cl_2 was distilled from CaH_2.

Melting points were determined on a Fisher–Johns melting point apparatus and are uncorrected. Infrared spectra (KBr disks) were recorded on a Perkin–Elmer 203-B spectrometer, and UV-visible spectra on a Shimadzu UV-160U spectrophotometer. Positive ion fast atom bombardment (FAB) mass spectra were obtained on a JEOL JMS-SX-102A mass spectrometer operated at an accelerating voltage of 10 kV. Samples were desorbed from a nitrobenzyl alcohol matrix by using xenon atoms at 6 keV.

2.2. Synthetic procedures

The copper *bis*-aldehydate precursors were prepared by a method analogous to that of Tyson and Adams [13]. Complexes (**1**)–(**6**) were synthesized by treating CH_2Cl_2 suspensions (solution in the case of copper *bis*-salicylaldehydate) of the corresponding Cu(II) *bis*-aldehydate precursors with a small excess of the appropriate cycloalkylamine. The following preparation represents a typical example.

To a solution of salicylaldehyde (0.25 g, 2.05 mmol) in 50 ml of EtOH was added an equimolar amount of KOH (0.11 g, 2.05 mmol), and the reaction mixture was stirred for an hour. A solution containing $Cu(OAc)_2$. H_2O (0.20 g, 1.03 mmol) in 7 ml of H_2O was then added, and the resulting brownish-green suspension was heated to reflux for 2 hours. The green copper(II) *bis*-aldehydate obtained was concentrated to dryness with a rotary evaporator, and dissolved in 100 ml of CH_2Cl_2. A small excess of cyclopropylamine (0.16 ml, 2.26 mmol) was then added, and the mixture was heated to a gentle reflux to avoid loss of the amine by evaporation overnight. During the course of the reaction the solution changed colour from green to brown, indicative of the formation of the copper Schiff base complex. The volatile materials were removed with a rotary evaporator, and the brown solid obtained was washed with 3 × 20 ml portions of H_2O/MeOH (9:1), until the washings appeared colourless. The products were dissolved in 20 ml of CH_2Cl_2, and slow diffusion of 80 ml of MeOH afforded deep brown crystalline (**1**) in 83 % yield (0.33 g, 0.85 mmol).

*Bis-{(cyclopropyl)[(2-oxo-1H-benzo-1-ylidene)methyl]aminato}copper(II) (**1**)*. Deep brown crystals were obtained by recrystallization from CH_2Cl_2/MeOH (1:4) in 83 % yield (0.33 g, 0.85 mmol). Mp 145–147 °C. FAB-MS *m/z*: M^+ 384 (base peak 154).

IR (KBr): ν(C=N) 1614 cm^{-1}. UV/vis ($CHCl_3$) λ/nm (ε/M^{-1} cm^{-1}): 254 (30089), 372 (10626).

*Bis-{(cyclobutyl)[(2-oxo-1H-benzo-1-ylidene)-methyl]aminato}copper(II) (**2**).* Dark brown crystals were obtained by recrystallization from CH_2Cl_2/-MeOH (1:4) in 97 % yield (0.42 g, 1.02 mmol). Mp 167–169 °C. FAB-MS *m/z*: M^+ 412 (base peak 154). IR (KBr): ν(C=N) 1621 cm^{-1}. UV/vis ($CHCl_3$) λ/nm (ε/M^{-1} cm^{-1}): 251 (28153), 308 (8686), 368 (10197).

*Bis-{(cyclopropyl)[(2-oxo-1H-naphth-1-ylidene)-methyl]aminato}copper(II) (**3**).* Deep brown crystals were obtained by recrystallization from CH_2Cl_2/EtOH (1:2) in 84 % yield (0.25 g, 0.52 mmol). Mp 193–196 °C. FAB-MS *m/z*: M^+ 484 (base peak 274). IR (KBr): ν(C=N) 1611 cm^{-1}. UV/vis ($CHCl_3$) λ/nm (ε/M^{-1} cm^{-1}): 252 (51304), 318 (34170), 385 (15101).

*Bis-{(cyclobutyl)[(2-oxo-1H-naphth-1-ylidene)-methyl]aminato}copper(II) (**4**).* Dark brown crystals were obtained by recrystallization from CH_2Cl_2/EtOH (1:1) in 64 % yield (0.20 g, 0.39 mmol). Mp 232–234 °C. FAB-MS *m/z*: M^+ 512 (base peak 154). IR (KBr): ν(C=N) 1613 cm^{-1}. UV/vis ($CHCl_3$) λ/nm (ε/M^{-1} cm^{-1}): 254 (50921), 316 (35095), 396 (15081).

*Bis-{(cyclopropyl)[(3-oxo-2H-naphth-2-ylidene)-methyl]aminato}copper(II) (**5**).* Deep brown crystals were obtained by slow evaporation of a concentrated CH_2Cl_2 solution in 65 % yield (0.24 g, 0.49 mmol). Mp 208 °C. FAB-MS *m/z*: M^+ 484 (base peak 154). IR (KBr): ν(C=N) 1603 cm^{-1}. UV/vis ($CHCl_3$) λ/nm (ε/M^{-1} cm^{-1}): 267 (73272), 307 (45207), 439 (51130).

*Bis-{(cyclobutyl)[(3-oxo-2H-naphth-2-ylidene)-methyl]aminato}copper(II) (**6**).* Brown crystals were obtained by slow evaporation of a concentrated CH_2Cl_2 solution in 71 % yield (0.45 g, 0.88 mmol). Mp > 300 °C (dec). FAB-MS *m/z*: M^+ 512 (base peak 154). IR (KBr): ν(C=N) 1617 cm^{-1}. UV/vis ($CHCl_3$) λ/nm (ε/M^{-1} cm^{-1}): 264 (71690), 442 (5460).

2.3. X-ray crystallography data collection and processing

The crystals were each mounted on a glass fiber. Measurements were performed on a Siemens P4/PC four-circle diffractometer for complexes (**1**) and (**2**). A Bruker SMART Apex CCD area detector diffractometer was employed for collecting the diffraction data of complexes (**3**)–(**6**). In both cases the diffractometers operated with graphite-monochromated Mo Kα radiation. In the case of complexes (**1**) and (**2**), orientation matrices and unit-cell constants were obtained from the least-squares refinements of the setting angles of 40 reflections, collected by using the XSCANS program [14]. Lorentz and polarization corrections were applied [15]. For complexes (**3**)–(**6**), unit-cell constants were obtained from the least-squares refinements of the observed reflections in the range ($2.2° < 2\theta < 32.0°$), using the Bruker SMART program [16]. Data were corrected for crystal decay with the Bruker SAINT Plus program [17]. All data sets were collected using the ω scan mode. Additional crystallographic data are collected in Table 1.

2.4. Structure solution and refinement

Structures of complexes (**1**) and (**2**) were solved by direct methods by using the SHELXS-97 program [18], and refined with the SHELXL-97 program [19]. In the case of complexes (**3**)–(**6**), the Bruker SAINT Plus program was used [17]. In all cases, the refinements were carried out by full matrix least-squares on F^2. Weighted *R*-factors, *R*w, and all goodness of fit indicators, *S*, were based on F^2. The observed criterion of ($F^2 > 2\sigma F^2$) were used only for calculating the *R*-factors. The number of observed reflections is presented in Table 1. All non-hydrogen atoms were refined with anisotropic thermal parameters in the final cycles of refinement. Hydrogen atoms were placed in idealised positions, with C–H distances of 0.93 Å and 0.98 Å for sp^2 and sp^3 hybridised carbon atoms, respectively. The isotropic thermal parameters of the hydrogen atoms were assigned the values of $U_{\mathrm{iso}} = 1.2$ times the thermal parameters of the parent non-hydrogen atom. Neutral atomic scattering factors were taken from the International Tables for X-ray Crystallography [20].

3. Results and discussion

3.1. Spectroscopic studies

Initial preparation of the copper(II) *bis*-aldehydate complexes Cu(salicylaldehydate)$_2$,

Table 1
Crystal data and structure refinement for compounds (**1**)–(**6**)

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_{20}H_{20}CuN_2O_2$	$C_{22}H_{24}CuN_2O_2$	$C_{28}H_{24}CuN_2O_2$	$C_{30}H_{28}CuN_2O_2$	$C_{28}H_{24}CuN_2O_2$	$C_{30}H_{28}CuN_2O_2$
Molecular weight	383.92	411.97	484.03	512.08	484.03	512.08
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pbca*	*C*2/*c*	*P*1bar	$P2_1/c$	$P2_1/n$	$P2_1/n$
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal color	Brown	Brown	Brown	Brown	Red	Brown
T (K)	291(2)	291(2)	291(2)	291(2)	291(2)	291(2)
Crystal dimensions (mm)	0.36 × 0.22 × 0.06	0.36 × 0.20 × 0.14	0.33 × 0.27 × 0.06	0.36 × 0.16 × 0.14	0.33 × 0.17 × 0.04	0.30 × 0.10 × 0.08
a (Å)	8.5976(7)	21.434(2)	9.3225(12)	9.6234(6)	9.0436(7)	9.7792(8)
b (Å)	13.8379(14)	8.7412(5)	10.4481(14)	12.7504(8)	5.6897(5)	5.6979(4)
c (Å)	14.6574(9)	21.177(3)	12.1392(16)	10.1370(6)	21.7238(18)	21.2508(16)
α (°)	90	90	72.273(3)	90	90	90
β (°)	90	90.513(1)	77.675(3)	107.849(1)	91.306(2)	91.766(2)
γ (°)	90	90	84.361(3)	90	90	90
V (Å^3)	1743.8(3)	3967.6(7)	1099.6(3)	1183.96(13)	1117.52(16)	1183.55(16)
hkl ranges	$0 \le h \le 10$ $0 \le k \le 16$ $0 \le l \le 17$	$0 \le h \le 30$ $0 \le k \le 12$ $-29 \le l \le 29$	$-11 \le h \le 11$ $-12 \le k \le 12$ $-14 \le l \le 14$	$-11 \le h \le 11$ $-15 \le k \le 15$ $-12 \le l \le 12$	$-10 \le h \le 10$ $-6 \le k \le 6$ $-25 \le l \le 25$	$-11 \le h \le 11$ $-6 \le k \le 6$ $-25 \le l \le 25$
ρ_{calc} (g cm^{-3})	1.462	1.379	1.462	1.436	1.438	1.437
Z	4	8	2	2	4	4
F(000)	796	1720	502	534	502	534
μ (mm^{-1})	1.268	1.120	1.022	0.954	1.006	0.954
θ range (°)	2.78–25.00	1.92–30.00	1.80–25.00	2.22–25.00	1.88–25.00	1.92–24.99
Absorption correction	Analytical	Analytical	None	None	None	None
T_{max}, T_{min}	0.9239, 0.7276	0.8516, 0.7819	N/A	N/A	N/A	N/A
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Independent reflections	1541	5796	3873	2088	1967	2091
Data/restraints /parameters	1541/0/116	5796/0/246	3873/0/298	2088/0/160	1967/0/151	2091/0/160
Goodness -of-fit on F^2	0.843	0.752	0.992	0.956	1.000	0.950
R	0.0370	0.0388	0.0400	0.0348	0.0497	0.0365
R_w	0.0747	0.0644	0.0829	0.0883	0.0938	0.0828
Largest diff. peak and hole (e Å^{-3})	0.212 and −0.219	0.239 and −0.318	0.555 and −0.189	0.699 and −0.154	0.737 and −0.271	0.523 and −0.186

Cu(2-oxo-1-naphthalenecarboxaldehydate)$_2$, and Cu(3-oxo-2-naphthalenecarboxaldehydate)$_2$ was required in order to synthesize the desired Schiff base complexes (**1**)–(**6**). The former complexes were obtained upon treatment of copper(II) acetate monohydrate with ethanolic solutions of potassium salicylaldehydate, 2-oxo-1-naphthalenecarboxaldehydate, and 3-oxo-2-naphthalenecarboxaldehydate, respectively. Suspensions of the Cu(II) *bis*-aldehydates in CH_2Cl_2 were treated with a small excess of cyclopropyl or cyclobutylamine, and heated to a gentle reflux to avoid loss of the amine by evaporation. Complexes (**1**)–(**6**) were obtained in good to moderate yields after recrystallization from the appropriate solvent systems, as shown in Scheme 1.

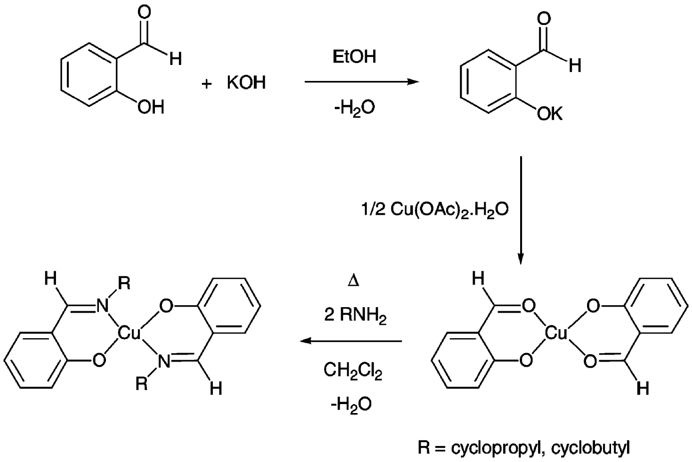
The dichloromethane and chloroform soluble copper Schiff base complexes were characterised by spectroscopic methods. FAB mass spectra of (**1**)–(**6**) confirm the presence of the expected molecular ions with a 2:1 ligand-to-metal stoichiometric ratio. Molecular ions with the characteristic copper isotopic distribution were detected as well as the $[M^+ + H]$ ions which are commonly observed in FAB mass spectra [21]. The main feature of the infrared spectra consists of the ν(C=N) vibration at 1614, 1621, 1611, 1613, 1603, and 1617 cm^{-1} for (**1**)–(**6**), respectively. Thus, the stretching frequencies for all complexes are close to the mean value of 1612 cm^{-1}, which is characteristic of these systems [22]. In the electronic spectra of all complexes (**1**)–(**6**), bands associated with d → d transitions were not detected, perhaps due to the intensity of the charge transfer and intraligand transitions [23].

3.2. Crystallographic studies

The X-ray crystal structures of (**1**)–(**6**) reveal four coordinate copper centres bound to both nitrogen and oxygen atom donors. The usual N,O-*trans* arrangement of ligands is observed in all cases, as well as *N*-cycloalkyl substituents and aryl groups in a cisoid position. A list of selected bond distances and angles is presented in Table 2, and the molecular structures of compounds (**1**)–(**6**), which were generated with the XP feature of SHELX, are presented with atom numbering schemes in Figs. 1–6, respectively. Thermal ellipsoids in all figures are shown at the 40% probability level.

Complex (**1**) has square planar geometry, while complexes (**4**)–(**6**) have stepped square planar geometries with relatively small step values of 0.49, 0.36, and 0.60 Å, respectively. Based on steric considerations, such planar coordination environments are expected for Schiff base Cu(II) complexes with small substituents at the coordinating nitrogen atoms. Nonetheless, complexes (**2**) and (**3**) display deformed square planar geometries with dihedral angles between the two coordination planes of 21.99 (average) and 30.26°, respectively.

The asymmetric unit of complex (**2**) is defined by 2 independent molecules which possess Cu–O bond lengths of 1.885(2) and 1.881(2) Å, and Cu–N bond lengths of 1.996(2) and 1.998(2) Å. The dihedral angles of the planes defined by O(1)–Cu(1)–N(1) and O(1a)–Cu(1)–N(1a) in one molecule, and O(2)–Cu(2)–N(2) and O(2a)–Cu(2)–N(2a) in the other molecule of compound (**2**), are very similar, with values of 22.02(5) and 21.96(5)°. Complex (**3**) has only one molecule in the asymmetric unit, but the two ligands are inequivalent with slightly different Cu–O and Cu–N bond distances of 1.892(2), 1.902(2), and 1.956(2), 1.946(2) Å, respectively. In contrast,



Scheme 1. Synthesis of *N*-cycloalkyl copper(II) Schiff base complexes.

Table 2
Selected bond lengths (Å) and angles (°) for complexes (**1**)–(**6**)

Complex (**1**)			
Cu(1)–O(1)	1.892(3)	O(1)–Cu(1)–O(1a)	180.000(1)
Cu(1)–O(1a)	1.892(3)	O(1)–Cu(1)–N(1)	91.02(13)
Cu(1)–N(1)	2.004(3)	O(1)–Cu(1)–N(1a)	88.98(13)
Cu(1)–N(1a)	2.004(3)	O(1a)–Cu(1)–N(1)	88.98(13)
O(1)–C(2)	1.299(5)	O(1a)–Cu(1)–N(1a)	91.02(13)
N(1)–C(7)	1.286(5)	N(1)–Cu(1)–N(1a)	180.000(1)
N(1)–C(8)	1.460(5)	C(2)–O(1)–Cu(1)	128.9(3)
C(1)–C(7)	1.439(5)	C(7)–N(1)–Cu(1)	124.2(3)
C(1)–C(2)	1.402(6)	C(8)–N(1)–Cu(1)	117.9(3)
C(2)–C(3)	1.413(6)	O(1)–C(2)–C(1)	124.1(4)
C(3)–C(4)	1.372(6)	N(1)–C(7)–C(1)	126.5(4)
Complex (**2**)			
Cu(1)–O(1)	1.885(2)	O(1)–Cu(1)–O(1a)	162.9(1)
Cu(1)–O(1a)	1.885(2)	O(1)–Cu(1)–N(1)	93.1(1)
Cu(1)–N(1)	1.996(2)	O(1)–Cu(1)–N(1a)	89.0(1)
Cu(1)–N(1a)	1.996(2)	O(1a)–Cu(1)–N(1)	89.0(1)
O(1)–C(2)	1.302(3)	O(1a)–Cu(1)–N(1a)	93.1(1)
N(1)–C(7)	1.279(3)	N(1)–Cu(1)–N(1a)	165.3(1)
N(1)–C(8)	1.467(3)	C(2)–O(1)–Cu(1)	128.4(2)
C(1)–C(7)	1.438(3)	C(7)–N(1)–Cu(1)	122.8(2)
C(1)–C(2)	1.422(3)	C(8)–N(1)–Cu(1)	119.9(2)
C(2)–C(3)	1.407(3)	O(1)–C(2)–C(1)	124.2(2)
C(3)–C(4)	1.371(4)	N(1)–C(7)–C(1)	127.8(2)
Cu(2)–O(2)	1.881(2)	O(2)–Cu(2)–O(2a)	162.7(1)
Cu(2)–O(2a)	1.881(2)	O(2)–Cu(2)–N(2)	93.1(1)
Cu(2)–N(2)	1.998(2)	O(2)–Cu(2)–N(2a)	89.1(1)
Cu(2)–N(2a)	1.998(2)	O(2a)–Cu(2)–N(2)	89.1(1)
O(2)–C(22)	1.304(3)	O(2a)–Cu(2)–N(2a)	93.1(1)
N(2)–C(27)	1.280(3)	N(2)–Cu(2)–N(2a)	165.6(1)
N(2)–C(28)	1.473(3)	C(22)–O(2)–Cu(2)	128.2(2)
C(21)–C(27)	1.434(4)	C(27)–N(2)–Cu(2)	122.5(2)
C(21)–C(22)	1.411(4)	C(28)–N(2)–Cu(2)	119.6(2)
C(22)–C(23)	1.410(4)	O(2)–C(22)–C(21)	124.3(3)
C(23)–C(24)	1.369(4)	N(2)–C(27)–C(21)	127.6(2)
Complex (**3**)			
Cu(1)–O(1)	1.8917(18)	O(1)–Cu(1)–O(2)	158.86(9)
Cu(1)–O(2)	1.9020(18)	O(1)–Cu(1)–N(1)	91.62(8)
Cu(1)–N(1)	1.956(2)	O(1)–Cu(1)–N(2)	91.39(9)
Cu(1)–N(2)	1.946(2)	O(2)–Cu(1)–N(1)	93.01(8)
O(1)–C(2)	1.304(3)	O(2)–Cu(1)–N(2)	92.03(8)
O(2)–C(22)	1.308(3)	N(1)–Cu(1)–N(2)	157.90(9)
N(1)–C(11)	1.290(3)	C(2)–O(1)–Cu(1)	128.71(18)
N(1)–C(12)	1.453(3)	C(11)–N(1)–Cu(1)	124.59(19)
N(2)–C(31)	1.290(3)	C(12)–N(1)–Cu(1)	117.73(16)
N(2)–C(32)	1.463(4)	O(1)–C(2)–C(1)	124.0(3)
C(1)–C(11)	1.424(3)	N(1)–C(11)–C(1)	127.8(3)
C(1)–C(2)	1.409(4)	C(22)–O(2)–Cu(1)	127.05(17)
C(2)–C(3)	1.422(4)	C(31)–N(2)–Cu(1)	124.71(19)
C(3)–C(4)	1.349(4)	C(32)–N(2)–Cu(1)	116.53(19)
C(21)–C(31)	1.427(4)	O(2)–C(22)–C(21)	124.5(3)
C(21)–C(22)	1.405(4)	N(2)–C(31)–C(21)	127.4(3)
C(22)–C(23)	1.425(4)		
C(23)–C(24)	1.346(4)		
Complex (**4**)			
Cu(1)–O(1)	1.895(2)	O(1)–Cu(1)–O(1a)	180.0(1)
Cu(1)–O(1a)	1.895(2)	O(1)–Cu(1)–N(1)	90.2(1)
Cu(1)–N(1)	1.993(2)	O(1)–Cu(1)–N(1a)	89.8(1)
Cu(1)–N(1a)	1.993(2)	O(1a)–Cu(1)–N(1)	89.8(1)
O(1)–C(2)	1.301(3)	O(1a)–Cu(1)–N(1a)	90.2(1)
N(1)–C(11)	1.294(3)	N(1)–Cu(1)–N(1a)	180.0(1)
N(1)–C(12)	1.470(3)	C(2)–O(1)–Cu(1)	129.7(1)
C(1)–C(11)	1.428(3)	C(11)–N(1)–Cu(1)	123.4(2)
C(1)–C(2)	1.404(3)	C(12)–N(1)–Cu(1)	119.7(1)
C(2)–C(3)	1.427(3)	O(1)–C(2)–C(1)	124.4(2)
C(3)–C(4)	1.349(3)	N(1)–C(11)–C(1)	128.4(2)
Complex (**5**)			
Cu(1)–O(1)	1.866(2)	O(1)–Cu(1)–O(1a)	180.00(11)
Cu(1)–O(1a)	1.866(2)	O(1)–Cu(1)–N(1)	91.55(11)
Cu(1)–N(1)	2.026(3)	O(1)–Cu(1)–N(1a)	88.45(11)
Cu(1)–N(1a)	2.026(3)	O(1a)–Cu(1)–N(1)	88.45(11)
O(1)–C(3)	1.313(4)	O(1a)–Cu(1)–N(1a)	91.55(11)
N(1)–C(11)	1.291(4)	N(1)–Cu(1)–N(1a)	180.00(13)
N(1)–C(12)	1.464(4)	C(3)–O(1)–Cu(1)	129.9(2)
C(2)–C(11)	1.435(4)	C(11)–N(1)–Cu(1)	122.3(2)
C(1)–C(2)	1.387(4)	C(12)–N(1)–Cu(1)	119.7(2)
C(2)–C(3)	1.421(4)	O(1)–C(3)–C(2)	121.6(3)
C(3)–C(4)	1.383(5)	N(1)–C(11)–C(2)	126.8(3)
C(1)–C(9)	1.399(4)		
Complex (**6**)			
Cu(1)–O(1)	1.876(2)	O(1)–Cu(1)–O(1a)	180.00(9)
Cu(1)–O(1a)	1.876(2)	O(1)–Cu(1)–N(1)	91.76(8)
Cu(1)–N(1)	2.018(2)	O(1)–Cu(1)–N(1a)	88.24(8)
Cu(1)–N(1a)	2.018(2)	O(1a)–Cu(1)–N(1)	88.24(8)
O(1)–C(3)	1.314(3)	O(1a)–Cu(1)–N(1a)	91.76(8)
N(1)–C(11)	1.289(3)	N(1)–Cu(1)–N(1a)	180.00(11)
N(1)–C(12)	1.468(3)	C(3)–O(1)–Cu(1)	129.26(17)
C(2)–C(11)	1.441(3)	C(11)–N(1)–Cu(1)	122.35(17)
C(1)–C(2)	1.383(3)	C(12)–N(1)–Cu(1)	120.21(16)
C(2)–C(3)	1.434(3)	O(1)–C(3)–C(2)	122.0(2)
C(3)–C(4)	1.382(4)	N(1)–C(11)–C(2)	127.4(2)
C(1)–C(9)	1.399(3)		

compounds (**1**) and (**4**)–(**6**) have crystallographically equivalent bidentate ligands with Cu–O bond lengths of 1.892(3), 1.895(2), 1.866(2), and 1.876(2) Å. The corresponding Cu–N bond lengths are 2.004(3), 1.993(2), 2.026(3), and 2.018(2) Å.

The average Cu–O bond lengths of 1.892(3), 1.883(2), 1.897(2), 1.895(2), 1.866(2), and 1.876(2) Å for compounds (**1**)–(**6**), respectively, are all similar to those observed in related copper(II) complexes, 1.868(4)–1.901(4) Å [9–11,24]. The Cu(1)–O(2) distance of 1.902(2) Å in complex (**3**), and

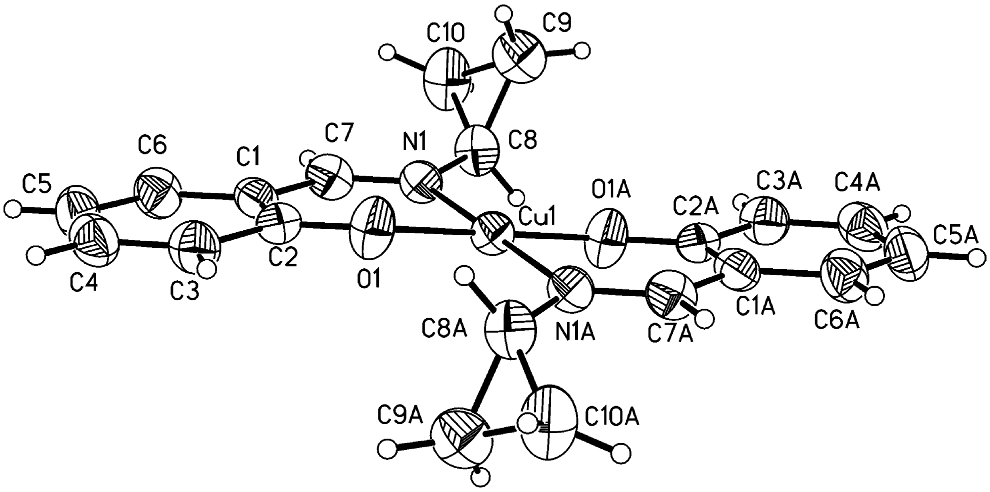


Fig. 1. Molecular structure of (**1**) with atom numbering Scheme.

the Cu(1)–O(1) distance of 1.866(2) in complex (**5**), however, represent the longest and shortest Cu–O bond lengths reported to date for the series of known N-cycloalkyl substituted copper(II) Schiff base complexes. The average Cu–N bond distances of 2.004(3), 1.997(2), 1.951(2), 1.993(2), 2.026(3), and 2.018(2), are also similar to those of related copper(II) complexes, 1.962(4)–2.034(2) Å. It is important to notice, however, that both Cu–N bond lengths in (**3**) [Cu(1)–N(1) 1.956(2) Å, and Cu(1)–N(2) 1.946(2) Å] are shorter than those reported to date for the series of complexes with *N*-cycloalkyl

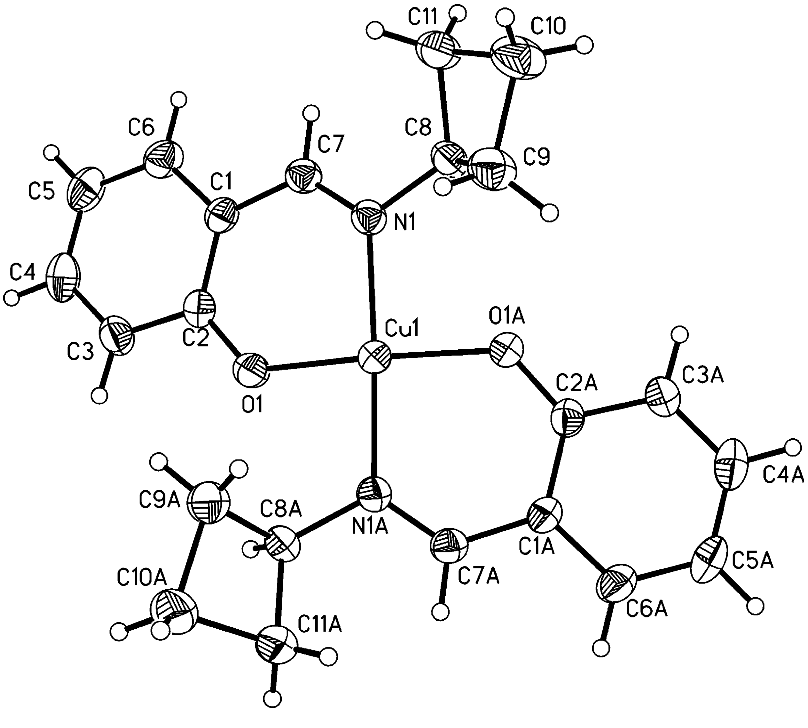


Fig. 2. Molecular structure of (**2**) with atom numbering Scheme.

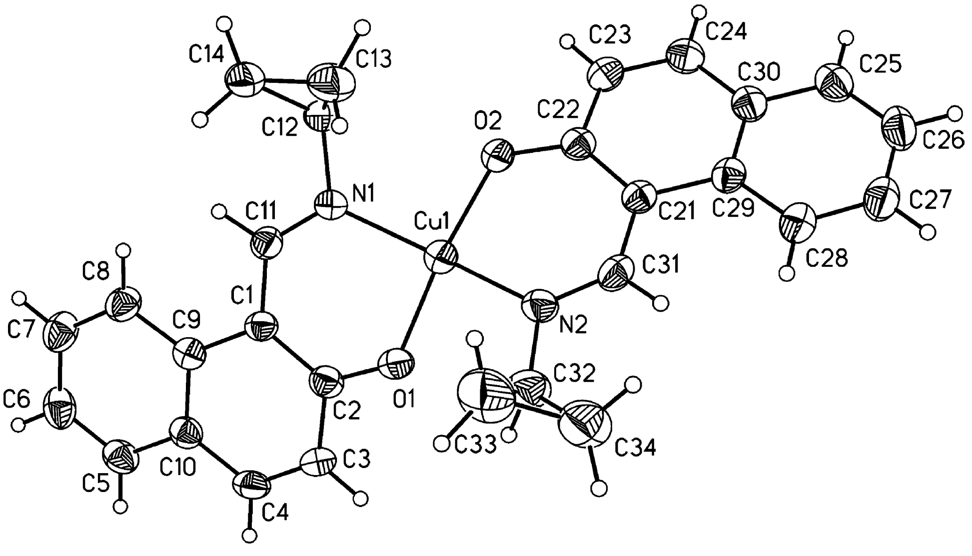


Fig. 3. Molecular structure of (**3**) with atom numbering Scheme.

substituents [9–11,24]. Moreover, the shortest Cu(1)–N(2) bond distance in (**3**) is associated with the longest Cu(1)–O(2) bond distance of 1.902(2) Å mentioned above. Likewise, the long Cu(1)–N(1) bond distance in compound (**5**) is associated with the short Cu(1)–O(1) bond distance of 1.866(2) Å.

The deformed square planar geometry of (**2**) is characterised by O(1)–Cu(1)–O(1a) and O(2)–Cu(2)–O(2a) bond angles of 162.9(1) and 162.7(1)°, and N(1)–Cu(1)–N(1a) and N(2)–Cu(2)–N(2a) bond angles of 165.3(1) and 165.6(1)°, respectively. The geometric parameters of (**3**) are characterised by the O(1)–Cu(1)–O(2) and N(1)–Cu(1)–N(2) bond angles of 158.9(1) and 157.9(1)°, respectively. Other bond lengths and angles within the ligand framework of all complexes show expected values.

In order to search for intra- and intermolecular interactions in the solid state structures of compounds (**1**)–(**6**), a geometric analysis was carried out with the PLATON program [25]. The type of interactions that

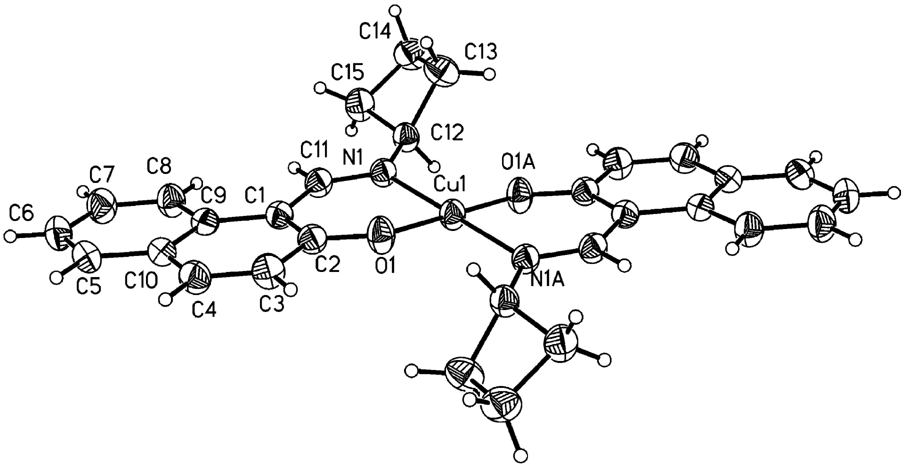


Fig. 4. Molecular structure of (**4**) with atom numbering Scheme.

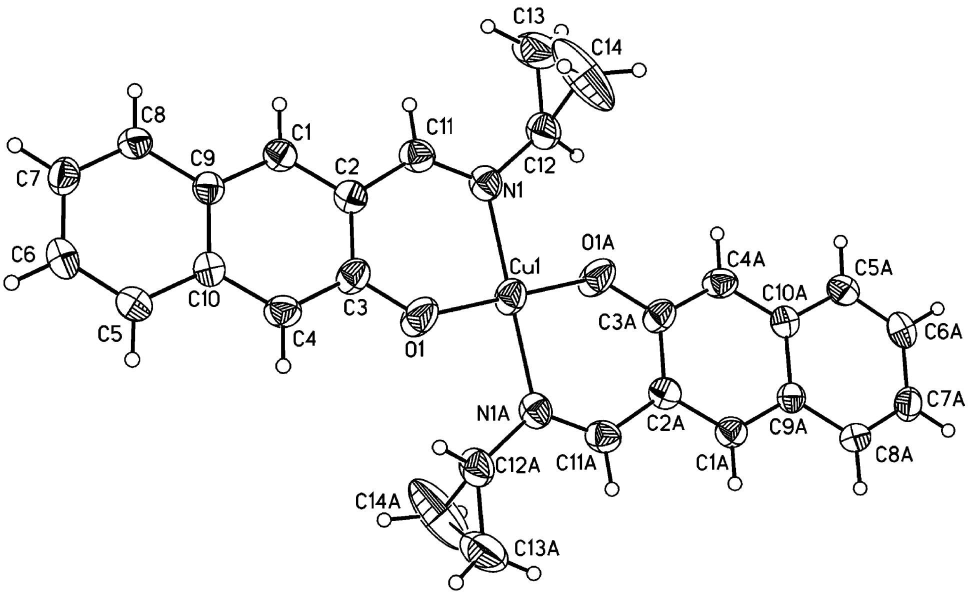


Fig. 5. Molecular structure of (**5**) with atom numbering Scheme.

have been described as being relevant in determining the packing of molecules in a lattice include weak C–H···O and C–H···N hydrogen bonds [26], C–H···π [26], and π···π interactions [27], among others. In the crystal structure of square planar (**1**), an intermolecular interaction between the copper atoms and H(5) from adjacent molecules appears to exist. This interaction must be relatively weak since the H(5) atoms, which are directed towards the axial positions of the Cu, are at a distance of 3.07 Å. No

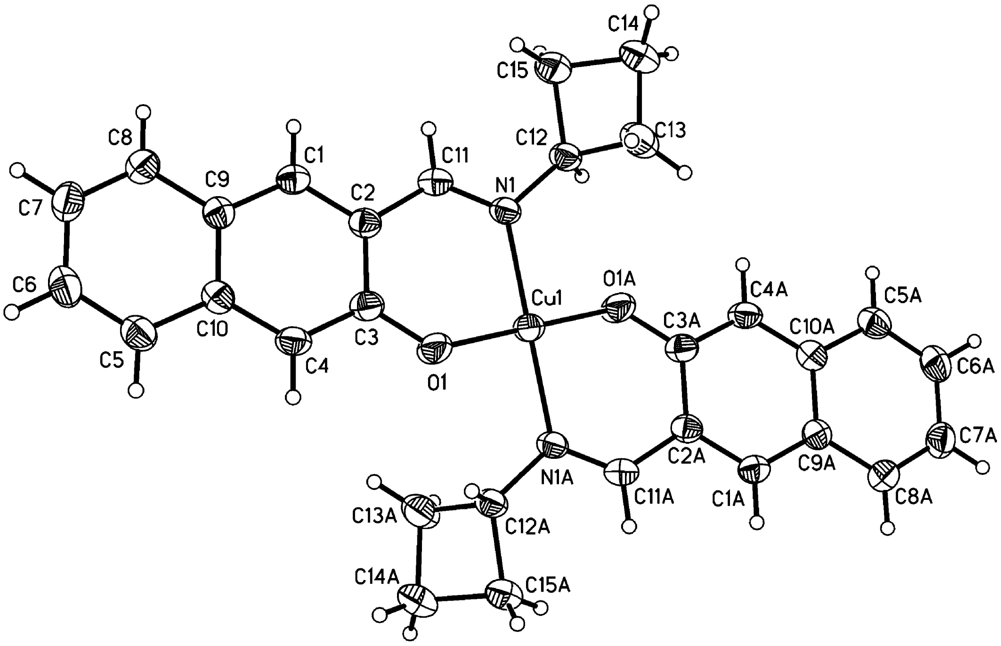


Fig. 6. Molecular structure of (**6**) with atom numbering Scheme.

significant $\pi\cdots\pi$ interactions are present in the solid state structure of (**1**), perhaps due to the small size of the aromatic ring.

In the distorted square planar structures of (**2**) and (**3**), there is no axial position in the copper coordination sphere. Despite the fact that no Cu···H interaction can take place, there are other intra- and intermolecular interactions that need comment. Thus, the pair of intramolecular C–H···O hydrogen bonds [C(8)–H(8)···O(1), 2.61 Å, and C(19)–H(19)···O(2), 2.59 Å] could be responsible for the distortion in compound (**2**). A similar hydrogen bond exists in the structure of complex (**3**), characterised by a C(32)–H(32)···O(1) distance of 2.46 Å. This interaction, together with the $\pi\cdots\pi$ interaction (3.43 Å) between the aromatic rings defined by C(1)–C(4), C(9), C(10), and C(5)–C(10) from an adjacent molecule, could be responsible for the distortion in the latter compound.

In the structures of complexes (**4**)–(**6**), the presence of the large naphthalenic rings seems to favour $\pi\cdots\pi$ interactions [3.04 Å, and 3.44 Å for complexes (**4**) and (**5**), respectively], with the exception of compound (**6**). There are also intramolecular hydrogen bonds involving C(12)–H(12)···O(1) in all 3 complexes (**4**)–(**6**) [with H···O distances of 2.44, 2.23, and 2.43 Å], although the factor that appears to determine the observed geometries is the intermolecular Cu···H(axial) interaction [at 3.10, 3.05, and 2.93 Å for (**4**)–(**6**), respectively], which is absent in the deformed tetrahedral structures of (**2**) and (**3**).

4. Conclusions

In the solid state structures of complexes (**1**)–(**6**), the steric influence of the small cyclopropyl and cyclobutyl substituent at the coordinating nitrogen atom must play a minor role in determining the geometric arrangement of the ligands around the copper centres, for which a square planar coordination environment is expected. Based on an electronic argument, it seems plausible that the more electron rich ligands, which by donation create a copper centre resembling Cu(I), can favour the deformed tetrahedral structure [3,7,28,29]. Although this kind of distortion was therefore expected for compounds (**5**) and (**6**), which incorporate the relatively electron rich 3-oxo-2-naphthalenecarboxaldiminate ligand, it was instead observed in compounds (**2**) and (**3**). Thus, the electronic influence of the aromatic portion of the ligands does not seem to be so strong as to determine the geometry of the complexes. The apparent lack of correlation between a steric or electronic parameter and the observed molecular structures of the series of *N*-cycloalkyl substituted copper (II) Schiff base complexes, indicates that crystal packing forces are at least as important as steric and electronic effects in determining the solid state structures of such complexes.

5. Supplementary material

Crystallographic data for compounds (**1**)–(**6**) have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, and are available free of charge from the Director upon request quoting the CCDC deposition numbers 202414–202419.

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