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Structures of *o*-hydroxy Schiff-base copper(II) complexes derived from *p*-benzylamines

Juan M. Fernández-G^a; Janeth Xochitiotzi-Flores^a; Simón Hernández-Ortega^a; Virginia Gómez-Vidales^a; Ma. Del Rocío Patiño-Maya^a

^a Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán 04510, México D.F., México

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Structures of *o*-hydroxy Schiff-base copper(II) complexes derived from *p*-benzylamines

JUAN M. FERNÁNDEZ-G*, JANETH XOCHITIOTZI-FLORES,
SIMÓN HERNÁNDEZ-ORTEGA, VIRGINIA GÓMEZ-VIDALES
and MA. DEL ROCÍO PATIÑO-MAYA

Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior,
Ciudad Universitaria, Coyoacán 04510, México D.F., México

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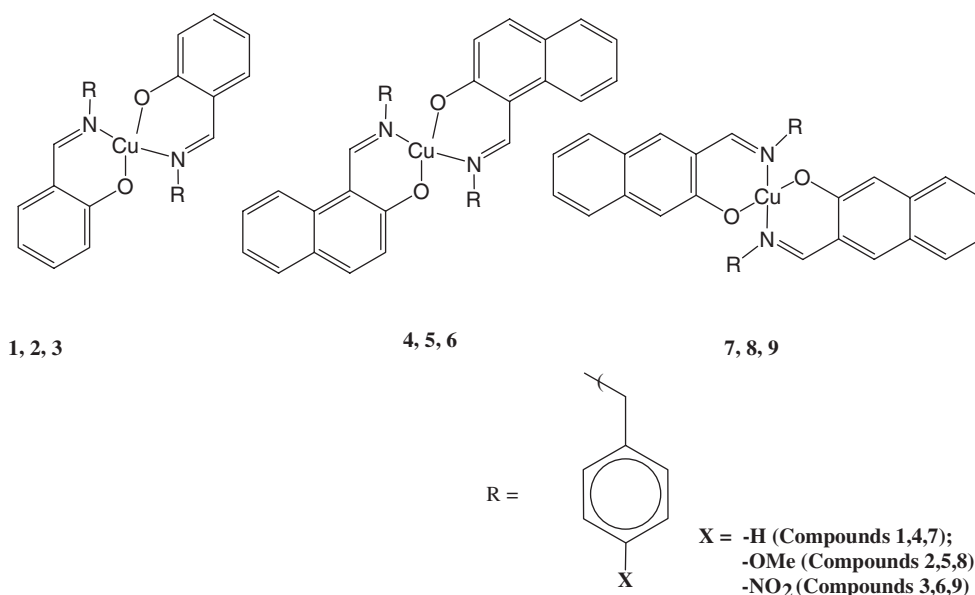
Nine copper(II) complexes of *o*-hydroxy Schiff bases derived from benzylamine, *p*-methoxybenzylamine, *p*-nitrobenzylamine, salicylaldehyde, 2-hydroxy-1-naphthalenecarboxaldehyde, and 3-hydroxy-2-naphthalenecarboxaldehyde were synthesized and characterized by chemical analysis, mass spectrometry, UV-Vis, infrared and electron paramagnetic resonance (EPR) spectroscopy, and seven X-ray crystal structures. The X-ray diffraction studies of these compounds showed that the geometry around the copper is square planar in six of the seven complexes. EPR studies of all the complexes in DMF solution at 77 K suggest that their geometries in solution are square planar as well.

Keywords: Synthesis Schiff-base copper(II) complexes; X-ray structures; EPR

1. Introduction

Interest in Schiff-base metal complexes has seen a continuous growth and two reviews about the structural properties and biological studies of transition metal complexes derived from 4-aminoantipyrine and molecular design of mononuclear complexes have recently been published [1, 2]. Additionally, Schiff-base metal complexes have been used as polymerization catalysts [3, 4], in molecular hyperpolarizability studies [5], or as antimicrobial agents [6]. To continue our comparative studies [7, 8] of the geometry of bis-bidentate Schiff-base copper(II) complexes in solution and crystalline state, which result from steric effects [9], electronic effects [10], or crystal packing forces [11] and to establish the importance of a *p*-substituent on benzylic moiety of a ligand, in relation to electronic effects in this kind of Cu(II) complex, we have prepared and characterized some bis-bidentate Schiff-base copper(II) complexes derived from benzylamine, *p*-methoxybenzylamine, and *p*-nitrobenzylamine with salicylaldehyde, 2-hydroxy-1-naphthalenecarboxaldehyde, and 3-hydroxy-2-naphthalenecarboxaldehyde (scheme 1). We chose those amines considering that their pK_a values of 9.2, 9.5, and 8.3, respectively, could be related to the nitrogen donor ability, perhaps obtaining a slightly

*Corresponding author. Email: jmanuel@servidor.unam.mx



Scheme 1. General structures of the Schiff base copper(II) complexes 1–9.

different arrangement around copper in the obtained complexes (i.e., extent of distortion).

Therefore, this work focuses on finding links between distortion in the crystalline state and the magnitude of the so-called electronic effect considering that there are electron acceptors or electron donors in the *-p*- position of the original amines. Herein, the preparation of the following bis-bidentate Schiff base copper(II) complexes is reported: bis{(benzyl)[(2-oxo-1H-benzo-1-ylidene)methyl]aminato}copper(II) (**1**) [12], bis{(*p*-methoxybenzyl)[(2-oxo-1H-benzo-1-ylidene)methyl]aminato}copper(II) (**2**), bis{(*p*-nitrobenzyl)[(2-oxo-1H-naphth-1-ylidene)methyl]aminato}copper(II) (**3**), bis{(benzyl)-[(2-oxo-1H-naphth-1-ylidene)methyl]aminato}copper(II) (**4**), bis{(*p*-methoxybenzyl)[(2-oxo-1H-naphth-1-ylidene)methyl]aminato}copper(II) (**5**), bis{(*p*-nitrobenzyl)[(2-oxo-1H-naphth-1-ylidene)methyl]aminato}copper(II) (**6**), bis{(benzyl)[(3-oxo-2H-naphth-2-ylidene)methyl]aminato}copper(II) (**7**), bis{(*p*-methoxybenzyl)[3-oxo-2H-naphth-2-ylidene)methyl]aminato}copper(II) (**8**), and bis{(*p*-nitrobenzyl)[(3-oxo-2H-naphth-2-ylidene)methyl]aminato}copper(II) (**9**) (scheme 1), which were synthesized by an *in situ* method and characterized by elemental analysis, infrared (IR), electronic, electron paramagnetic resonance (EPR), and mass spectra. Furthermore, the crystal structures of **1–5**, **7**, and **8** were determined.

2. Experimental

2.1. Materials, measurements, and methods

Phosphorous pentachloride, naphthol AS, anhydrous tin(II) chloride, anhydrous ethyl ether, benzylamine, *p*-methoxybenzylamine, *p*-nitrobenzylamine hydrochloride,

copper(II) acetate monohydrate, KOH, KBr, salicylaldehyde, 2-hydroxy-1-naphthalenecarboxaldehyde, and the solvents *N,N*-dimethylformamide (DMF), ethanol, and dichloromethane spectroscopic grade were purchased from Aldrich Chemical Co. Inc. 3-Hydroxy-2-naphthalenecarboxaldehyde was prepared as described in [13].

Melting points were determined on a Fisher–Johns melting point apparatus and are uncorrected; IR spectra (KBr disks) were recorded on a Perkin-Elmer Mod. 203-B spectrophotometer; UV-Vis spectra on a Shimadzu UV-160U recording spectrophotometer in dichloromethane; electron impact (EI) mass spectra were obtained on a JEOL Mod. JMS-SX-102A mass spectrometer operated at 75 eV. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn. 37921-1750, USA.

EPR measurements were performed on a JEOL JES TE300 spectrometer. An external NMR precision field-meter JEOL ES-FC5 was used for the calibration of the magnetic field. Compounds **1–9** showed an EPR response in a 1×10^{-2} M DMF solution at 77 K.

Suitable X-ray-quality crystals of **1–5**, **7**, and **8** were grown by slow layer diffusion of EtOH or MeOH into a saturated CH_2Cl_2 solution. Data collection was performed on a Bruker Smart APEX AXS CCD area detector/omega scans diffractometer using $\text{Mo-K}\alpha$ radiation ($\lambda = 0.7173$) with a graphite monochromator. Structures were solved by direct methods using SHELXS-97 [14] and were refined by SHELXL-97 [15]. In the final cycles of refinement all the non-hydrogen atoms were refined with anisotropic thermal parameters. Neutral atomic scattering factors were taken from the International Tables of X-Ray Crystallography [16].

2.2. Synthesis of the copper complexes

Complexes **1–9** were prepared by methods described elsewhere [17]. The following preparation is typical of the general method: a solution of benzylamine (0.002 mol) in EtOH (200 cm^3) followed by $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.0011 mol) in H_2O (10 cm^3) was added to a solution of the appropriate aldehyde (0.002 mol) in EtOH (200 cm^3). The mixture was refluxed under nitrogen for 6 h and then concentrated until a precipitate was observed. It was then cooled in an ice bath until precipitation was completed; the green solid was suction filtered, washed with a mixture of cold $\text{H}_2\text{O}:\text{EtOH}$ 9:1, and dried. Recrystallization from CH_2Cl_2 to EtOH gave brownish red crystals.

In the case of the complexes with *p*-nitrobenzylamine, the hydrochloride of *p*-nitrobenzylamine was first neutralized with an equimolecular amount of KOH dissolved in ethanol.

2.2.1. Bis{(benzyl)[(2-oxo-1H-benzo-1-ylidene)methyl]aminato}copper(II) (1) [12]. (Yield 0.265 g, 55%); brownish red crystals; m.p. 208°C (Found (%): C, 69.5; H, 5.1; N, 5.70. Calcd (%) for $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_2\text{Cu}$: C, 69.3; H, 5.0; N, 5.8); EI mass spectrum (m/z) M^+ 483 (base peak 274); IR (KBr) $\nu\text{-C}=\text{N}$ 1613 cm^{-1} ; UV-Vis. (CH_2Cl_2 , in nm), 240 ($\epsilon = 52,625$), 271 ($\epsilon = 26,850$), 305 ($\epsilon = 10,240$), 370 ($\epsilon = 11,790$). EPR at 77 K (DMF), A_{\parallel} in mT (± 0.01 mT) 18.06, g_{\parallel} 2.2351, g_{\perp} 2.0542.

2.2.2. Bis{(p-methoxybenzyl)[(2-oxo-1H-benzo-1-ylidene)methyl]aminato}copper(II) (2). (Yield 0.293 g, 54%); green crystals; m.p. 185°C (Found (%): C, 66.1; H, 5.2; N,

5.2. Calcd (%) for $C_{30}H_{28}N_2O_4Cu$: C, 66.2; H, 5.2; N, 5.1; EI mass spectrum (m/z) M^+ 543 (base peak 121); IR (KBr) $\nu-C=N$ 1613 cm^{-1} , $\nu_{\text{asym}}-C-O-C$ 1250 cm^{-1} ; UV-Vis. (CH_2Cl_2 , in nm), 235 ($\epsilon = 50,830$), 273 ($\epsilon = 27,570$), 370 ($\epsilon = 9800$). EPR at 77 K (DMF), A_{\parallel} in mT (± 0.01 mT) 18.22, g_{\parallel} 2.2296, g_{\perp} 2.0645.

2.2.3. Bis{(p-nitrobenzyl)[(2-oxo-1H-benzo-1-ylidene)methyl]aminato}copper(II) (3). (Yield 0.275 g, 48%); green crystals; m.p. $225^{\circ}C$ (Found (%): C, 58.5; H, 3.8; N, 9.8. Calcd (%) for $C_{28}H_{22}N_4O_6Cu$: C, 58.6; H, 3.9; N, 9.7); EI mass spectrum (m/z) M^+ 573 (base peak 319); IR (KBr) $\nu-C=N$ 1614 cm^{-1} , $\nu-NO_2$ 1344 cm^{-1} ; UV-Vis. (CH_2Cl_2 , in nm), 243 ($\epsilon = 44,645$), 275 ($\epsilon = 42,790$), 373 ($\epsilon = 10,545$); (CH_2Cl_2 , in nm), 243 ($\epsilon = 44,490$), 276 ($\epsilon = 42,645$), 373 ($\epsilon = 10,505$). EPR at 77 K (DMF), A_{\parallel} in mT (± 0.01 mT) 18.36, g_{\parallel} 2.2347, g_{\perp} 2.0612.

2.2.4. Bis{(benzyl)[(2-oxo-1H-naphth-1-ylidene)methyl]aminato}copper(II) (4). (Yield 0.320 g, 55%); green crystals; m.p. $229^{\circ}C$ (Found (%): C, 74.7; H, 5.2; N, 4.6. Calcd (%) for $C_{36}H_{28}N_2O_2Cu$: C, 74.0; H, 4.8; N, 4.8); EI mass spectrum (m/z) M^+ 583 (base peak 324); IR (KBr) $\nu-C=N$ 1614 cm^{-1} ; UV-Vis. (CH_2Cl_2 , in nm), 243 ($\epsilon = 59,905$), 317 ($\epsilon = 35,345$), 383 ($\epsilon = 14,360$). EPR at 77 K (DMF), A_{\parallel} in mT (± 0.01 mT) 18.21, g_{\parallel} 2.2378, g_{\perp} 2.0561.

2.2.5. Bis{(p-methoxybenzyl)[(2-oxo-1H-naphth-1-ylidene)methyl]aminato}copper(II) (5). (Yield 0.328 g, 51%); green crystals; m.p. $205^{\circ}C$ (Found (%): C, 71.0; H, 5.0; N, 4.3. Calcd (%) for $C_{38}H_{32}N_2O_4Cu$: C, 70.6; H, 5.0; N, 4.3); EI mass spectrum (m/z) M^+ 643 (base peak 121); IR (KBr) $\nu-C=N$ 1612 cm^{-1} , $\nu_{\text{asym}}-C-O-C$ 1246 cm^{-1} ; UV-Vis. (CH_2Cl_2 , in nm), 233 ($\epsilon = 63,010$), 317 ($\epsilon = 32,030$), 384 ($\epsilon = 13,465$). EPR at 77 K (DMF), A_{\parallel} in mT (± 0.01 mT) 18.26, g_{\parallel} 2.2388, g_{\perp} 2.0635.

2.2.6. Bis{(p-nitrobenzyl)[(2-oxo-1H-naphth-1-ylidene)methyl]aminato}copper(II) (6). (Yield 0.323 g, 48%); brownish red crystals; m.p. $243^{\circ}C$ (Found (%): C, 64.0; H, 4.0; N, 8.3. Calcd (%) for $C_{36}H_{26}N_4O_6Cu$: C, 64.1; H, 3.9; N, 8.3); EI mass spectrum (m/z) M^+ 673 (base peak 306); IR (KBr) $\nu-C=N$ 1612 cm^{-1} , $\nu-NO_2$ 1368 cm^{-1} ; UV-Vis. (CH_2Cl_2 , in nm), 240 ($\epsilon = 65,140$), 251 ($\epsilon = 65,460$), 311 ($\epsilon = 36,290$), 385 ($\epsilon = 14,770$). EPR at 77 K (DMF), A_{\parallel} in mT (± 0.01 mT) 17.52, g_{\parallel} 2.2403, g_{\perp} 2.0485.

2.2.7. Bis{(benzyl)[(3-oxo-2H-naphth-2-ylidene)methyl]aminato}copper(II) (7). (Yield 0.245 g, 42%); brownish red crystals; m.p. $243^{\circ}C$ (Found (%): C, 74.3; H, 5.0; N, 4.7. Calcd (%) for $C_{36}H_{28}N_2O_2Cu$: C, 74.0; H, 4.8; N, 4.8); EI mass spectrum (m/z) M^+ 583 (base peak 261); IR (KBr) $\nu-C=N$ 1612 cm^{-1} ; UV-Vis. (CH_2Cl_2 , in nm), 265 ($\epsilon = 7620$), 276 ($\epsilon = 8055$), 304 ($\epsilon = 5650$), 439 ($\epsilon = 6435$). EPR at 77 K (DMF), A_{\parallel} in mT (± 0.01 mT) 17.47, g_{\parallel} 2.2448, g_{\perp} 2.0501.

2.2.8. Bis{(p-methoxybenzyl)[3-oxo-2H-naphth-2-ylidene)methyl]aminato}copper(II) (8). (Yield 0.270 g, 42%); brownish red crystals; m.p. $209^{\circ}C$ (Found (%): C, 70.7; H, 5.1; N, 4.4. Calcd (%) for $C_{38}H_{32}N_2O_4Cu$: C, 70.6; H, 5.0; N, 4.3); EI mass spectrum (m/z) M^+ 643 (base peak 121); IR (KBr) $\nu-C=N$ 1612 cm^{-1} , $\nu_{\text{asym}}-C-O-C$ 1269 cm^{-1} ;

UV-Vis. (CH_2Cl_2 , in nm), 233 ($\epsilon = 64,610$), 276 ($\epsilon = 86,685$), 304 ($\epsilon = 61,295$), 439 ($\epsilon = 7340$). EPR at 77 K (DMF), A_{\parallel} in mT (± 0.01 mT) 17.54, g_{\parallel} 2.2390; g_{\perp} 2.0562.

2.2.9. Bis(*p*-nitrobenzyl)(3-oxo-2H-naphth-2-ylidene)methylaminato)copper(II) (9). (Yield 0.276 g, 41%); deep brown crystals; m.p. 249°C (Found (%): C, 63.9; H, 4.0; N, 8.2. Calcd (%) for $\text{C}_{36}\text{H}_{26}\text{N}_4\text{O}_6\text{Cu}$: C, 64.1; H, 3.9; N, 8.3); EI mass spectrum (m/z) M^+ 673 (base peak 306); IR (KBr) $\nu\text{-C=N}$ 1619 cm^{-1} , $\nu\text{-NO}_2$ 1345 cm^{-1} ; UV-Vis. (DMF, in nm), 261 ($\epsilon = 102,390$), 304 ($\epsilon = 59,620$), 441 ($\epsilon = 3760$). EPR at 77 K (DMF, A_{\parallel} in mT (± 0.01 mT) 16.903, g_{\parallel} 2.247, g_{\perp} 2.057.

3. Results and discussion

Except for **6** and **9** that are quite insoluble, all compounds are reasonably soluble in chlorinated solvents. The elemental analyses were satisfactory with a ligand-to-metal ratio of 2:1. Mass spectra of the complexes show the expected molecular ions $[\text{M}]^+$, displaying the characteristic copper isotopic distribution, which agrees with the 2:1 ligand to metal stoichiometric ratio. The fragmentation patterns of these complexes are similar to those described elsewhere [5], in addition to the molecular ion $[\text{CuL}_2]^+$, ions were also recorded at $[\text{M}-\text{H}]^+$ m/z . The molecular ion gives $[\text{CuL}]^+$ fragment, as well as fragments that correspond to $[\text{L}]^+$. IR spectra showed a $\nu\text{-C=N}$ vibration band around 1612 cm^{-1} , which is characteristic of these systems [18]. In **3**, **6**, and **9** the symmetric stretching band -C-NO_2 is at 1344, 1368, and 1345 cm^{-1} , respectively [19]. The asymmetric stretching band that corresponds to the functional ether in **2**, **5**, and **8** was also assigned to bands at 1250, 1246, and 1269 cm^{-1} , respectively [19]. The electronic absorption spectra of **1-9** showed no definite bands corresponding to transitions in the ligand field region, that is, $d \leftarrow d$ transitions; only absorptions attributed to intraligand transitions ($\pi\text{-}\pi^*$, $n\text{-}\pi^*$) or charge transfer bands were observed [20]. In addition, at higher dichloromethane concentration solutions of **1-5** and **6-8**, we were unable to observe absorptions that could be related to $d \leftarrow d$ transitions, probably due to the broad charge transfer bands [6, 20, 21].

3.1. Structural studies

Crystal and additional data collection parameters and refinement details for **1-5**, **7**, and **8** are given in table 1. A selection of bond lengths and angles is given in table 2. The molecular structure of **1**, **2**, **3**, **5**, and **7**, including atom-numbering schemes, are illustrated in figures 1-5.

The X-ray diffraction analyses of **1-5**, **7**, and **8** show that copper is bonded to oxygen and nitrogen of two ligands in the usual *trans* arrangement of four-coordinate copper. Except for **1**, which is slightly distorted with a dihedral angle (θ) between the two coordination planes defined by $\text{O}(1)\text{-Cu-N}(1)$ and $\text{O}(1a)\text{-Cu-N}(1a)$ of 6.7°, the other complexes, **2-5**, **7**, and **8**, have very similar structures with stepped square planar and planar geometries (**5**). Their magnitude of the step values (S) are 0.37, 0.41, 0.10, 0.00, 1.42, and 0.59 Å, respectively. However, the magnitude of the step in **7** (1.42 Å), with a hydrogen in the *-p*- position of the benzylic moiety of the ligand, is unexpected because

Table 1. Crystallographic data for **1–5**, **7**, and **8**.

	1	2	3	4	5	7	8
Chemical formula	C ₂₈ H ₂₄ CuN ₂ O ₂	C ₃₀ H ₃₈ CuN ₂ O ₄	C ₂₈ H ₂₂ CuN ₄ O ₆	C ₃₆ H ₃₈ CuN ₂ O ₂	C ₃₈ H ₃₂ CuN ₂ O ₄	C ₃₆ H ₃₈ CuN ₂ O ₂	C ₃₈ H ₃₂ CuN ₂ O ₄
Formula weight	512.08	544.08	574.04	584.14	644.20	584.14	644.20
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2(<i>1</i>) ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2(<i>1</i>) ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2(<i>1</i>) ₁ / <i>c</i>	<i>P</i> 2(<i>1</i>) ₁ / <i>c</i>	<i>P</i> 2(<i>1</i>) ₁ / <i>c</i>
Wavelength (Mo-K α) (Å)	0.71069	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Absorption coefficient (mm ⁻¹)	1.011	0.898	0.944	0.847	0.774	0.820	0.774
Temperature (K) of data collection	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Calculated density (g cm ⁻³)	1.446	1.420	1.555	1.438	1.427	1.392	1.379
Index ranges	-14 ≤ <i>h</i> ≤ 14 -11 ≤ <i>k</i> ≤ 11 -24 ≤ <i>l</i> ≤ 24	-7 ≤ <i>h</i> ≤ 7 -10 ≤ <i>k</i> ≤ 10 -12 ≤ <i>l</i> ≤ 12	-5 ≤ <i>h</i> ≤ 5 -13 ≤ <i>k</i> ≤ 13 -29 ≤ <i>l</i> ≤ 29	-27 ≤ <i>h</i> ≤ 27 -6 ≤ <i>k</i> ≤ 6 -26 ≤ <i>l</i> ≤ 26	-20 ≤ <i>h</i> ≤ 20 -6 ≤ <i>k</i> ≤ 6 -20 ≤ <i>l</i> ≤ 20	0 ≤ <i>h</i> ≤ 15 0 ≤ <i>k</i> ≤ 7 -21 ≤ <i>l</i> ≤ 21	0 ≤ <i>h</i> ≤ 14 0 ≤ <i>k</i> ≤ 6 -27 ≤ <i>l</i> ≤ 26
Unit cell dimensions (Å, °)	<i>a</i> = 12.333(5) <i>b</i> = 9.271(5) <i>c</i> = 20.342(5) β = 107.094(5)	<i>a</i> = 6.4991(6) <i>b</i> = 9.2534(1) <i>c</i> = 10.9147(10) α = 88.420(2) β = 79.898(2) γ = 79.880(2)	<i>a</i> = 4.2901(2) <i>b</i> = 11.6195(12) <i>c</i> = 24.595(5) β = 90.312(2)	<i>a</i> = 23.096(2) <i>b</i> = 5.2470(4) <i>c</i> = 22.5652(19) β = 99.279(2)	<i>a</i> = 16.9216(2) <i>b</i> = 5.1959(4) <i>c</i> = 17.1748(13) β = 96.7780(10)	<i>a</i> = 13.155(3) <i>b</i> = 5.972(3) <i>c</i> = 17.775(5) β = 93.55(2)	<i>a</i> = 12.3235(11) <i>b</i> = 5.6141(9) <i>c</i> = 23.224(3) β = 105.153(8)
Unit cell volume (Å ³)	2223.1(16)	636.16(10)	1226.0(2)	2698.8(4)	1499.5(2)	1393.8(9)	1550.9(3)
<i>Z</i>	4	1	4	4	2	4	4
<i>F</i> (000)	1004	283	590	1212	670	606	670
Measured/independent reflection	17,596/3913	5229/2236	9718/2139	3130/2614	10,423/2380	11,716/2746	2867/2732
<i>R</i> _(int)	0.0749	0.0327	0.0683	0.0427	0.0530	0.0686	0.0396
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0520, <i>wR</i> ₂ = 0.1076	<i>R</i> ₁ = 0.0490, <i>wR</i> ₂ = 0.1261	<i>R</i> ₁ = 0.0498, <i>wR</i> ₂ = 0.0979	<i>R</i> ₁ = 0.0477, <i>wR</i> ₂ = 0.1082	<i>R</i> ₁ = 0.0431, <i>wR</i> ₂ = 0.0667	<i>R</i> ₁ = 0.0423, <i>wR</i> ₂ = 0.0862	<i>R</i> ₁ = 0.0522, <i>wR</i> ₂ = 0.1085

Table 2. Selected bond lengths (Å) and angles (°) for 1–5, 7, and 8.

Compound 1			
Cu–O(1)	1.887(3)	O(1)–Cu–O(2)	173.82(13)
Cu–O(2)	1.888(3)	O(1)–Cu–N(2)	88.41(12)
Cu–N(1)	2.009(3)	O(2)–Cu–N(2)	91.47(13)
Cu–N(2)	2.010(3)	O(2)–Cu–N(1)	88.75(13)
O(1)–C(2)	1.304(5)	O(1)–Cu–N(1)	91.66(13)
O(2)–C(16)	1.306(5)	N(1)–Cu–N(2)	177.20(13)
N(1)–C(7)	1.279(5)	C(2)–O(1)–Cu	130.6(3)
N(1)–C(8)	1.484(5)	C(7)–N(1)–Cu	123.7(3)
C(1)–C(7)	1.442(5)	C(8)–N(1)–Cu	121.0(3)
C(1)–C(2)	1.416(5)	O(1)–C(2)–C(1)	123.5(4)
C(2)–C(3)	1.394(5)	N(1)–C(7)–C(1)	128.1(4)
Compound 2			
Cu–O(1)	1.887(2)	O(1)–Cu–O(2)	180.000(1)
Cu–O(2)	1.887(2)	O(1)–Cu–N(1A)	88.62(9)
Cu–N(1)	2.011(2)	O(1A)–Cu–N(1)	88.62(9)
Cu–N(2)	2.011(2)	O(1A)–Cu–N(1A)	91.38(9)
O(1)–C(2)	1.302(4)	O(1)–Cu–N(1)	91.38(9)
O(2)–C(15)	1.278(8)	N(1)–Cu–N(1A)	180.000(1)
N(1)–C(7)	1.284(4)	C(2)–O(1)–Cu	130.6(2)
N(1)–C(8)	1.474(4)	C(7)–N(1)–Cu	123.6(2)
C(1)–C(7)	1.427(4)	C(8)–N(1)–Cu	121.0(2)
C(1)–C(2)	1.413(4)	O(1)–C(2)–C(1)	123.2(3)
C(2)–C(3)	1.412(4)	N(1)–C(7)–C(1)	127.3(3)
Compound 3			
Cu–O(1)	1.885(3)	O(1)–Cu–O(1a)	180.00(15)
Cu–O(1A)	1.885(3)	O(1)–Cu–N(1a)	89.23(12)
Cu–N(1)	2.013(3)	O(1a)–Cu–N(1a)	90.77(12)
Cu–N(1A)	2.013(3)	O(1)–Cu–N(1)	90.77(12)
O(1)–C(2)	1.316(4)	O(1a)–Cu–N(1)	89.23(12)
N(1)–C(7)	1.280(4)	N(1)–Cu–N(1a)	180.00(5)
N(1)–C(8)	1.497(5)	C(2)–O(1)–Cu	131.2(3)
C(1)–C(7)	1.427(5)	C(7)–N(1)–Cu	124.0(3)
C(1)–C(2)	1.409(5)	C(8)–N(1)–Cu	121.0(2)
C(2)–C(3)	1.393(5)	O(1)–C(2)–C(1)	122.8(4)
Compound 4			
Cu–O(1)	1.893(2)	O(1)–Cu–O(1A)	180.000(1)
Cu–O(1A)	1.893(2)	O(1)–Cu–N(1)	90.75(10)
Cu–N(1)	1.990(3)	O(1)–Cu–N(1A)	89.25(10)
Cu–N(1A)	1.990(3)	O(1A)–Cu–N(1)	89.25(10)
O(1)–C(2)	1.306(4)	O(1A)–Cu–N(1A)	90.75(10)
N(1)–C(11)	1.284(4)	N(1)–Cu–N(1A)	180.000(1)
N(1)–C(12)	1.497(4)	C(2)–O(1)–Cu	130.6(2)
C(1)–C(11)	1.425(4)	C(11)–N(1)–Cu	124.2(2)
C(1)–C(2)	1.397(4)	C(12)–N(1)–Cu	121.8(2)
C(2)–C(3)	1.426(4)	O(1)–C(2)–C(3)	116.5(3)
C(3)–C(4)	1.345(4)	N(1)–C(11)–C(1)	128.9(3)
Compound 5			
Cu–O(1)	1.8868(18)	O(1)–Cu–O(1A)	180.00(9)
Cu–O(1A)	1.8868(18)	O(1)–Cu–N(1)	90.92(9)
Cu–N(1)	1.994(2)	O(1)–Cu–N(1A)	89.08(9)
Cu–N(1A)	1.994(2)	O(1A)–Cu–N(1)	89.08(9)
O(1)–C(2)	1.300(3)	O(1A)–Cu–N(1A)	90.92(9)
N(1)–C(11)	1.294(3)	N(1)–Cu–N(1A)	180.00(11)
N(1)–C(12)	1.490(3)	C(2)–O(1)–Cu	131.13(18)
C(1)–C(11)	1.425(3)	C(11)–N(1)–Cu	123.54(19)
C(1)–C(2)	1.403(3)	C(12)–N(1)–Cu	121.96(18)
C(2)–C(3)	1.428(3)	O(1)–C(2)–C(3)	116.5(3)
C(3)–C(4)	1.347(4)	N(1)–C(11)–C(1)	129.1(3)

(Continued)

Table 2. Continued.

Compound 7			
Cu–O(1)	1.879(3)	O(1)–Cu–O(1a)	180.0
Cu–O(1a)	1.879(3)	O(1)–Cu–N(1)	91.16(13)
Cu–N(1)	2.016(3)	O(1)–Cu–N(1a)	88.84(13)
Cu–N(1a)	2.016(3)	O(1a)–Cu–N(1)	88.84(13)
O(1)–C(3)	1.325(4)	O(1a)–Cu–N(1a)	91.16(13)
N(1)–C(11)	1.280(5)	N(1)–Cu–N(1a)	180.0
N(1)–C(12)	1.475(4)	C(3)–O(1)–Cu	128.1(2)
C(2)–C(11)	1.446(5)	C(11)–N(1)–Cu	123.3(2)
C(1)–C(2)	1.388(5)	C(12)–N(1)–Cu	119.7(3)
C(2)–C(3)	1.448(5)	O(1)–C(3)–C(2)	121.8(4)
C(3)–C(4)	1.386(5)	N(1)–C(11)–C(2)	127.3(3)
Compound 8			
Cu–O(1)	1.884(3)	O(1)–Cu–O(1a)	180.0
Cu–O(1a)	1.884(3)	O(1)–Cu–N(1)	91.22(13)
Cu–N(1)	2.015(3)	O(1)–Cu–N(1a)	88.78(13)
Cu–N(1a)	2.015(3)	O(1a)–Cu–N(1)	88.78(13)
O(1)–C(3)	1.322(5)	O(1a)–Cu–N(1a)	91.22(13)
N(1)–C(11)	1.295(5)	N(1)–Cu–N(1a)	180.0
N(1)–C(12)	1.479(5)	C(3)–O(1)–Cu	128.7(2)
C(2)–C(11)	1.445(6)	C(11)–N(1)–Cu	122.7(2)
C(1)–C(2)	1.379(6)	C(12)–N(1)–Cu	121.1(3)
C(2)–C(3)	1.425(6)	O(1)–C(3)–C(2)	122.6(4)
C(3)–C(4)	1.391(5)	N(1)–C(11)–C(2)	126.7(4)

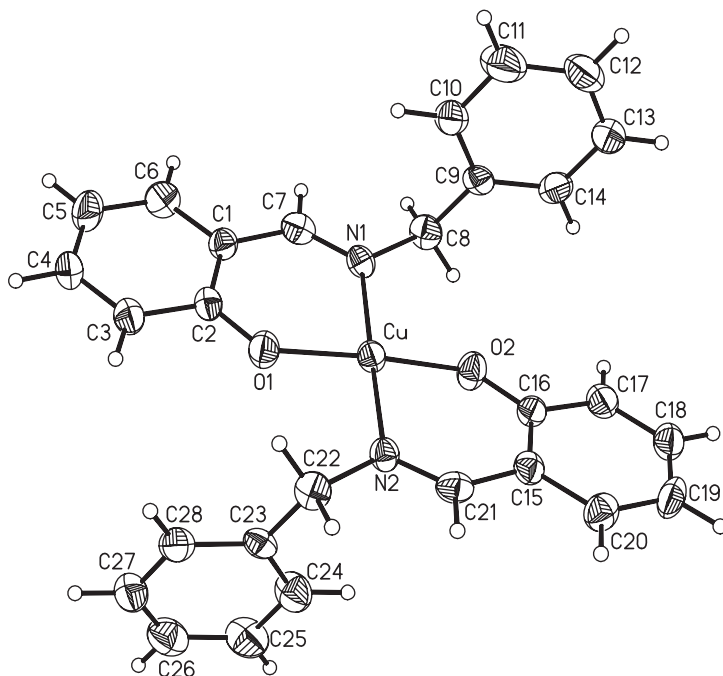


Figure 1. Molecular structure of **1** in the solid state with atom numbering scheme. Thermal ellipsoids are drawn at 50% probability.

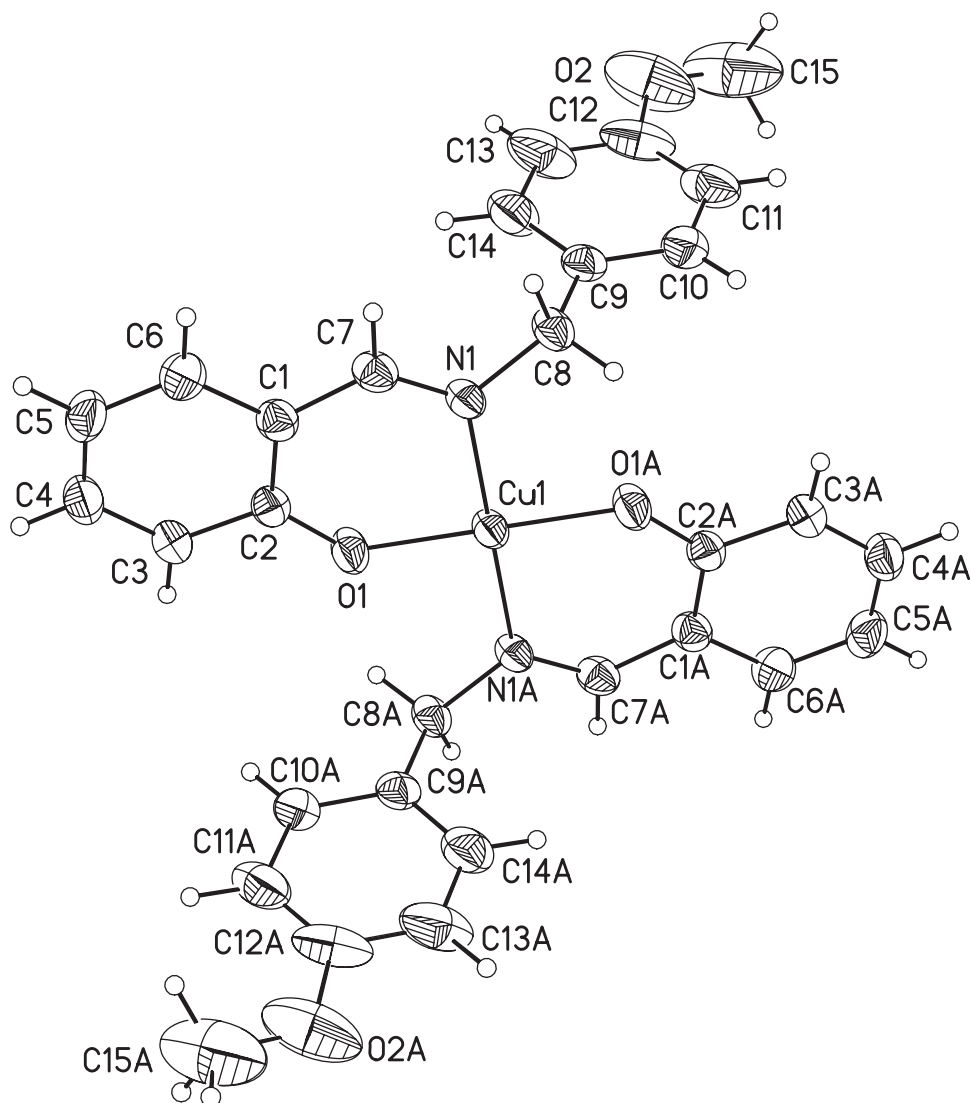


Figure 2. Molecular structure of **2** in the solid state with atom numbering scheme. Thermal ellipsoids are drawn at 50% probability.

in its isomer **4** the value is 0.10 \AA and in **1** there is a slight distortion to tetrahedral geometry (6.7°). Thus, **2–5**, **7**, and **8** show square-planar geometry similar to analogous Schiff base copper(II) complexes described [22, 23].

Bond angles in these complexes also show that the coordination geometry around the copper atom is square planar, with $\text{N}(1)\text{--Cu--N}(1a)$ and $\text{O}(1)\text{--Cu--O}(1a)$ angles very close to 180° . The values of other angles are within the expected range. The Cu--O and Cu--N bonds in **1**, **3**, **5**, and **6** have similar lengths in the same range reported for similar copper(II) complexes [6, 22–26], that is, Cu--O distances of $1.87\text{--}1.91 \text{ \AA}$ and Cu--N between 1.96 and 2.02 \AA . The Cu--N bond distances in the four complexes are slightly

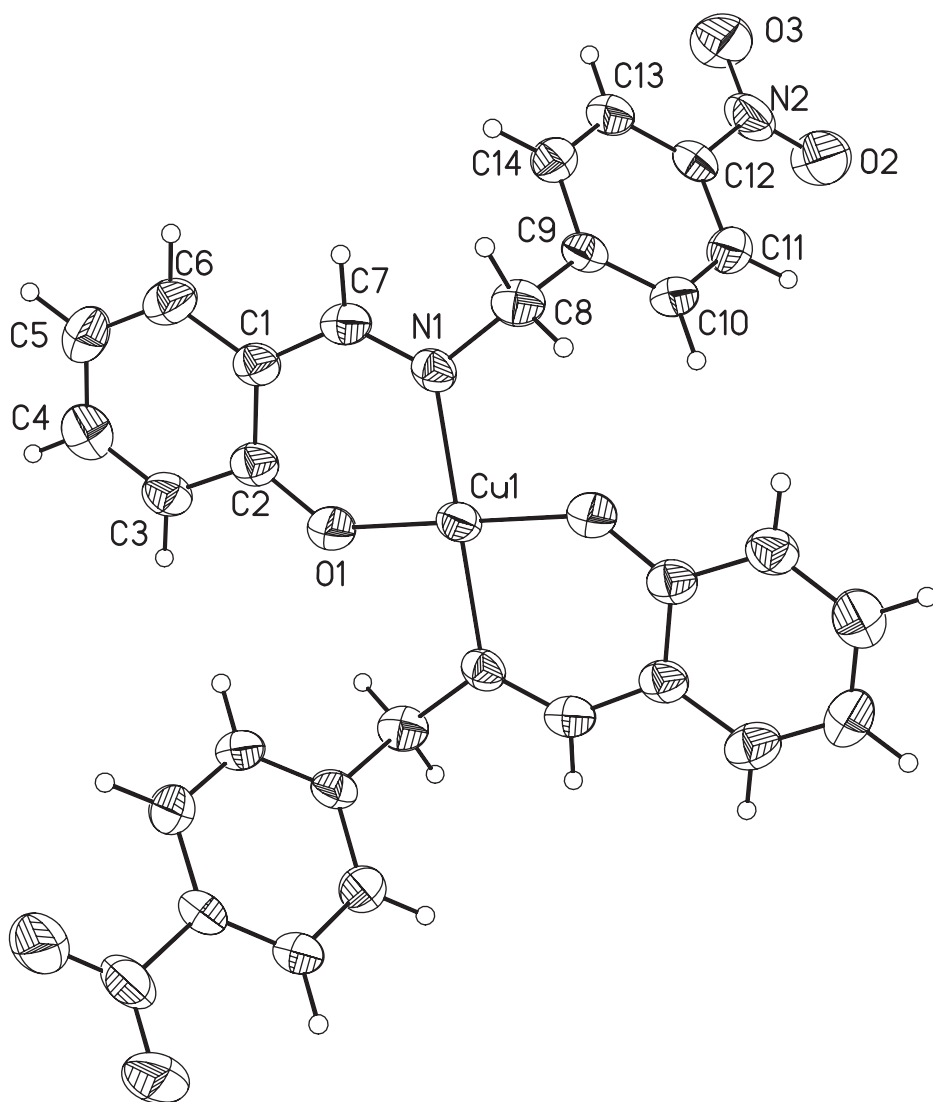


Figure 3. Molecular structure of **3** in the solid state with atom numbering scheme. Thermal ellipsoids are drawn at 50% probability.

shorter than those found in similar Schiff-base, square-planar copper(II) complexes, 2.025(4) [27] and 2.032(3) Å [28], where it was proposed that the Cu–N distance is slightly lengthened by steric interference between the nitrogen substituent and the opposite ligand [27].

Compounds **1–5** and **7–8** show weak H intramolecular contacts between O(1) of a ligand and a hydrogen of the benzylic methylene of the other ligand, the $D \cdots H$ lengths are 2.338, 2.316, 2.266, 2.278, 2.267, 2.288, and 2.337 Å, respectively, while $D \cdots A$ distances are 2.811, 2.800, 2.826, 2.826, 2.826, 2.803, and 2.861 Å, respectively, and the magnitude of the DHA angle is between 109.29 and 115.82°. In addition, there are other

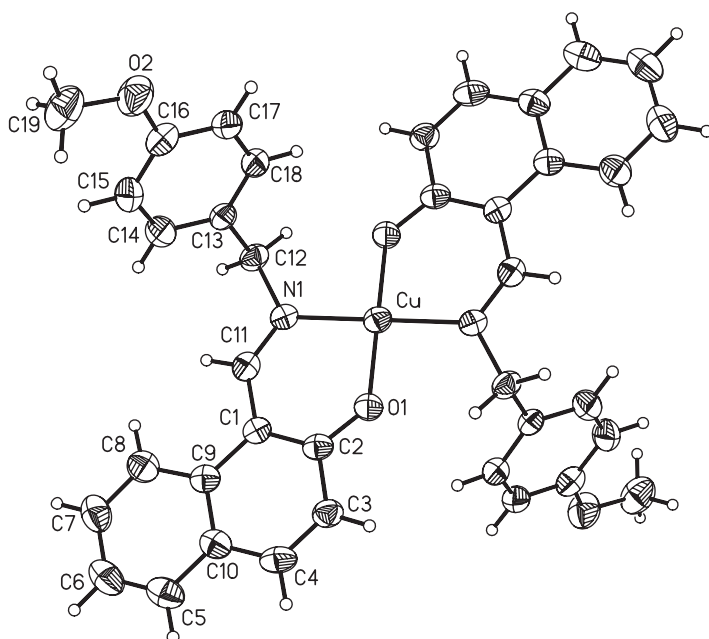


Figure 4. Molecular structure of **5** in the solid state with atom numbering scheme. Thermal ellipsoids are drawn at 50% probability.

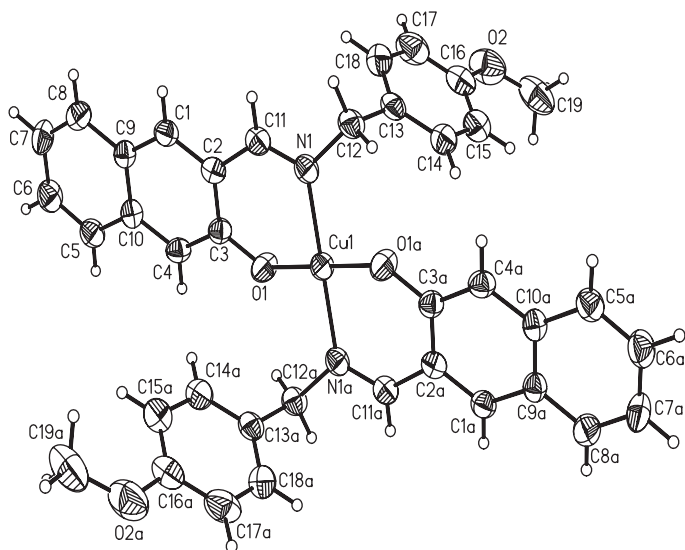


Figure 5. Molecular structure of **7** in the solid state with atom numbering scheme. Thermal ellipsoids are drawn at 50% probability.

Table 3. Coupling constants (A_{\parallel}), parallel tensors (g_{\parallel}), perpendicular tensors (g_{\perp}), factor f at 77 K, and magnitude of the step (S) in the solid state for **1–9**.

Compound	A_{\parallel} (± 0.15 mT)	g_{\parallel}	g_{\perp}	f (cm)	S (\AA)
1	18.06	2.2351	2.0542	118	–
2	18.22	2.2296	2.0645	118	0.37
3	18.36	2.2347	2.0612	117	0.41
4	18.21	2.2378	2.0561	118	0.10
5	18.26	2.2388	2.0635	117	0.00
6	17.52	2.2403	2.0485	122	s.n.d. ^a
7	17.47	2.2448	2.0501	123	1.42
8	17.54	2.2390	2.0562	122	0.59
9	18.36	2.2395	2.0625	127	s.n.d. ^a

^as.n.d.: structure not determined.

intermolecular contacts and/or electronic π – π stacking interactions among the aromatic rings of the ligands.

3.2. EPR studies

The frozen solution EPR spectra allowed us to measure both g_{\parallel} and A_{\parallel} for **1–9**. Complexes **1–9** showed axial symmetry for the paramagnetic copper center. The magnitude of the coupling constant A_{\parallel} was used as the measurement for the degree of distortion toward a tetrahedral coordination geometry in the sense that A_{\parallel} values diminish as the geometry departs from axial configuration, that is, the distortion grows [11, 29, 30]. Therefore, EPR data at 77 K in DMF for **1–9** (table 3) agree with square-planar geometry. Furthermore, the empirical index of tetrahedral distortion f ($g_{\parallel}/A_{\parallel}$ in cm^{-1}) [31, 32] for the frozen solutions show values of 118, 118, 117, 118, 117, 122, 123, 122, and 127 cm, which are in the range of square planar copper(II) complexes ($f=105$ – 135 cm) [33].

4. Concluding remarks

The X-ray study of **1** shows that the geometry around the metal atom is slightly distorted square planar with a dihedral angle (θ) of 6.7° and despite bulkiness or inductive electronic factors of the substituent in the *-p*- position of the benzylic moiety of the ligand, the other complexes **2–5**, **7**, and **8** show square-planar geometry around copper. This might indicate that for these complexes, in the solid state, electronic effect has no influence on the geometry, but crystalline packing forces could be responsible for that geometry which is stabilized by intermolecular contacts and/or electronic π – π stacking interactions among the aromatic rings of the ligands. EPR studies of **1–9** in DMF solution at 77 K suggest that their geometry in solution is similar to that observed in the solid state by X-ray crystallography.

Supplementary material

Crystallographic files in cif format have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2-1EZ, UK (Fax: +44 1223/336-033; Email for inquiry: fileserv@ccdc.cam.ac.uk) with CCDC deposition numbers 738777–738783.

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