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Synthesis and characterization of copper(II) complexes with dissymmetric tetradentate Schiff base ligands derived from aminothioether pyridine. Crystal structures of [Cu(pytIsal)]$ClO_4 \cdot 0.5CH_3OH$ and [Cu(pytAzosal)]ClO_4

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Abstract

Five dissymmetric tetradentate Schiff base ligands, containing a mixed donor set of NSNO were prepared by the reaction of aminothioether pyridine with the appropriate salicylaldehyde and characterized by FTIR, ^1H and ^{13}C NMR and elemental analysis methods. The complexes of these ligands were synthesized by treating an ethanolic solution of the appropriate ligand with an equimolar amount of $Cu(ClO_4)_2 \cdot 6H_2O$ and methanolic NaOH or alternatively by a more direct route in which the two reactants are added to a solution of the ligand immediately after formation of the ligand and prior to any isolation. The copper(II) complexes, [Cu(pytXsal)]ClO_4 (4-X-2-{[2-(2-pyridin-2-yl-ethylsulfanyl)ethylimino]methyl}phenol copper(II)) (X=iodo (I), bromo (Br), nitro (NO_2), methoxy (OMe), phenylazo (Azo)) were characterized by FTIR, elemental analysis, electronic spectra and molar conductivity. The ligand functions as a monobasic tetradentate ligand bonding through the thiolate sulfur, azomethine and pyridine nitrogens and phenolate oxygen. All of the complexes were found to be 1:1 electrolyte systems in acetonitrile. Electronic spectra show that the copper complexes have a tetrahedrally distorted square planar environment. The single crystal X-ray diffraction is reported for [Cu(pytIsal)]$ClO_4 \cdot 0.5CH_3OH$ (**A**) and [Cu(pytAzosal)]ClO_4 (**B**). The copper atom in both complexes lies in a slightly tetrahedrally distorted square planar coordination. Cyclic voltammetry indicates that complexes of [Cu(pytXsal)]ClO_4 (X=NO_2, Azo) have a quasi-reversible redox behavior and complexes of [Cu(pytXsal)]ClO_4 (X=I, OMe) undergo irreversible reduction under the experimental conditions.

Keywords: Dissymmetric Schiff base; Mixed donor set; Copper complexes; X-ray structures; Cyclic voltammetry

1. Introduction

Salen type ligands, one of the oldest classes of ligands in coordination chemistry, have been used extensively to complex transition and main group metals [1]. Schiff base complexes containing different metal ions such as Ni and Cu have been studied in great details for their various crystallographic feature, structure–redox relationships and enzymatic reactions, mesogenic characteristics and catalysis properties [2–6]. Recent interest in the design, synthesis and characterization of dissymmetrical Schiff base ligands derived from appropriate amines for transition metal ion complexes has come from the realization that the coordinated ligands around central metal ions in natural systems are unsymmetric [7]. Dissymmetrical Schiff base ligands can clearly offer many advantages over their symmetrical counterparts in the elucidation of the composition and geometry of metal ion binding sites in metalloproteins, and selectivity of natural systems with synthetic materials [8]. Dissymmetric Schiff base complexes as chiral analogues become more effective and prevalent in asymmetric catalysis; an

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inexpensive, large-scale production of these materials would be highly desirable [7–13]. The synthesis of transition metal complexes containing thiolate coordination is an important area of study with implications in bioinorganic chemistry, catalysis, and medical chemistry [14]. In recent years, considerable interest has developed in copper complexes with mixed donor ligands as structural models for the active site of copper proteins. In copper proteins a distorted metal ion environment of low symmetry with mixed donor sets is present [14,15]. This information prompted us to synthesize copper complexes with a mixed donor atoms environment incorporating nitrogen, oxygen and sulfur as ligand donors. We describe here, some copper(II) complexes and their spectroscopic characterizations as shown in Scheme 1. We also report the crystal structures of the complexes $[Cu(pytIsal)]ClO_4 \cdot 0.5CH_3OH$ and $[Cu(pytAzosal)]ClO_4$ as determined by single crystal X-ray diffraction.

2. Experimental

2.1. Materials

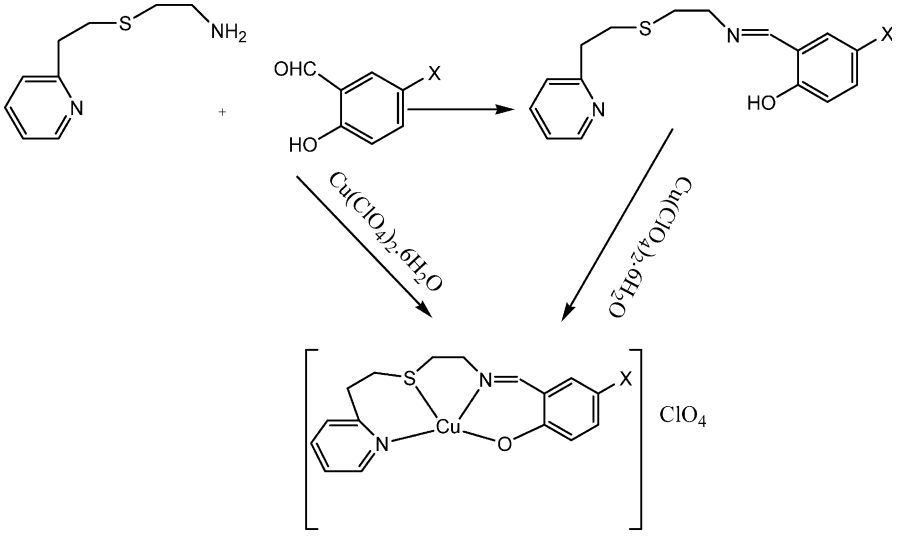
All of the chemicals and solvents were of analytical reagent grade and were obtained commercially from Merck with the exception of metal salts which were obtained from Aldrich. The solvents were purified by standard methods [16]. 5-Phenylazo salicylaldehyde, 5-iodo-salicylaldehyde and 1-(2-pyridyl)-3-thia-5-amino pentane (pyta) were synthesized according to known procedures [17–19] and 2-vinyl pyridine was distilled in vacuo before using.

2.2. Physical measurements

Elemental analyses for CHN were performed using a Heraeus CHN-O-RAPID elemental analyzer. Infrared (FTIR) spectra were recorded using KBr discs on a FTIR Unicam 4600. ^1H and ^{13}C NMR spectra were taken in $CDCl_3$ on a Bruker Spectrospin Avance 400 MHz ultrashield spectrometer and chemical shifts are indicated in ppm relative to tetramethylsilane. The electronic spectra in the 200–900 nm range were obtained in acetonitrile on a Shimadzu UV-265 FW spectrophotometer. The conductivity measurements were carried out in acetonitrile at room temperature using a Hanna conductometer HI 8828N instrument. Cyclic voltammograms were performed using an AMEL instrument Model 2053 as potentiostat connected with a function generator (AMEL Model 568). All solutions were deoxygenated by passing a stream of Ar into the solution for at least 10 min prior to recording the voltammogram. All potentials reported herein were measured at room temperature and referenced to the saturated calomel electrode with ferrocene as an internal standard. A platinum wire was used as counter electrode and a glassy carbon disc with a diameter of 3 mm was used as the working electrode. Before each experiment the working electrode was cleaned perfectly by polishing with alumina and rinsed thoroughly with distilled water and acetone. The electrolytic medium consisted of 0.1 M $LiClO_4$ in acetonitrile. Under these conditions the ferrocenium–ferrocene couple was located at 371 mv with a peak separation of 89 mv.

2.2.1. X-ray crystallography

Crystallographic data for complexes of $[Cu(pytIsal)]ClO_4 \cdot 0.5CH_3OH$ (**A**) and [Cu(pytAzo-



X=I, Br, NO_2, OCH_3, N_2Ph

Scheme 1. Schematic representation of Schiff base ligands and their complexes formation.

sal)]ClO_4 (**B**) are given in Table 5. Single crystals of the complexes were acquired by slow evaporation from a methanol solution for complex **A** and from an acetonitrile solution for complex **B** at room temperature and mounted in sealed glass capillaries. Diffraction data were collected on a Bruker SMART CCD diffractometer at 110 K. Intensity data were obtained using Mo Kα radiation (0.7107 Å) monochromatized from graphite and π and ω scan modes were used. The data were reduced and the structures were solved by direct methods using the program SHELXTL version 5.1 and refined by the full-matrix least-squares on F^2, using all the unique data and the weighting scheme $W=[\sigma^2(F_o)^2+(0.0729P)^2+6.4767P]^{-1}$ for complex **A** and $W=[\sigma^2(F_o)^2+(0.0419P)^2]^{-1}$ for complex **B**, where $P=(F_o^2+2F_c^2)/3$. Atomic scattering factors are from the international tables for X-ray crystallography volume C.

3. Synthesis

3.1. Synthesis of Schiff base ligands

General procedure: All ligands were prepared in a similar manner (Scheme 1). A solution of 1 mmol of pyta in 5 ml absolute ethanol was added to a solution of 1 mmol of the required salicylaldehyde in 5 ml absolute ethanol to give clear yellow or orange solutions which were gently refluxed for about 60 min. Evaporation of the solution in vacuo gave viscous liquids. The ligands 4-X-2-{[2-(2-pyridin-2-yl-ethylsulfanyl)-ethylimino]-methyl}phenol [X = I, Br, NO_2, OMe and N_2ph] which will abbreviated as pytIsalH, pytBrsalH, pytNO_2salH, pytOMesalH and pytAzosalH, respectively, were obtained as microcrystals with the exception of pytAzosalH which gave a viscous oily liquid and was dried in vacuo. The microcrystals were filtered off, washed with 5 ml of cooled absolute ethanol and then recrystallized from ethanol–chloroform (2:1, v/v). The analytical and physical data of the ligands are given in Table 1.

3.2. Synthesis of metal complexes

General procedure: a solution of the appropriate ligand was prepared by either dissolving the required amount (1 mmol) of the ligand in absolute ethanol (10 ml) or by preparing the ligand in situ from its precursors as follows; a solution of 1 mmol of pyta in 5 ml absolute ethanol was added to solution of 1 mmol of the required salicylaldehyde in 5 ml absolute ethanol and the mixture was refluxed for 40 min and then 1 ml of 1 M methanolic NaOH was added and reflux and stirring were continued for a further 5 min. Then 1 mmol of $Cu(ClO_4)_2\cdot 6H_2O$ in 5 ml absolute ethanol was added to the ligand solution with stirring and the reaction mixture was stirred under reflux for 25 min. The

Table 1
Analytical and physical data of the ligands and their complexes

Compound	Empirical formula (formula weight)	Yield (%)	Color	M.p. (°C)	Molar conductivity [a] (μs)	Analyses found (Calc.) (%)		
						C	H	N
PytIsalH	$C_{16}H_{17}IN_2OS$ (412.294)	70	yellow	71		46.70(46.61)	4.20(4.15)	6.80(6.79)
PytBrsalH	$C_{16}H_{17}BrN_2OS$ (365.293)	83	yellow	69		52.50(52.60)	4.70(4.69)	7.60(7.66)
PytNO_2salH	$C_{16}H_{17}N_3O_3S$ (331.395)	78	orange	90		57.70(57.99)	5.20(5.17)	12.50(12.67)
PytOMesalH	$C_{17}H_{20}N_2O_2S$ (316.424)	75	orange	59–60		64.00(64.50)	6.30(6.37)	8.70(8.85)
PytAzosalH	$C_{22}H_{22}N_4OS$ (390.501)	65	dark brown			67.35(67.70)	5.85(5.67)	14.50(14.35)
[Cu(pytIsal)]$ClO_4\cdot 0.5CH_3OH$	$C_{16.5}H_{18}ClCuIN_2O_{5.5}S$ (590.298)	64	black	231(°)	145	34.20(33.57)	3.0(3.07)	5.06(4.75)
[Cu(pytBrsal)]ClO_4	$C_{16}H_{16}BrClCuN_2O_5S$ (527.276)	68	dark green	229(°)	146	36.40(36.44)	3.10(3.06)	5.20(5.31)
[Cu(pytNO_2sal)]$ClO_4\cdot 1CH_3CN$	$C_{18}H_{19}ClCuN_4O_7S$ (534.432)	60	dark green	251(°)	140	40.30(40.45)	3.50(3.58)	10.00(10.48)
[Cu(pytOMesal)]ClO_4	$C_{17}H_{19}ClCuN_2O_6S$ (478.408)	62	dark brown	202(°)	153	42.70(42.68)	4.10(4.00)	5.80(5.85)
[Cu(pytAzosal)]ClO_4	$C_{22}H_{21}ClCuN_4O_5S$ (552.492)	58	dark red	236(°)	142	48.30(47.83)	3.80(3.83)	10.10(10.14)

[a] Conductivity.

obtained colored solution was left at room temperature. The product was removed by filtration, washed with cooled absolute ethanol, recrystallized from acetonitrile or methanol and dried in vacuo. The analytical and physical data of the complexes are given in Table 1.

Safety note: Perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small quantities of material should be prepared, and they should be handled with great caution.

4. Results and discussion

The reaction of pyta with several salicylaldehyde derivatives containing donor, withdrawing and bulky groups in absolute ethanol gave the desired dissymmetric tetradentate Schiff base ligands in good yield and purity (Scheme 1).

Mononuclear copper(II) complexes were prepared by treating an ethanolic solution of the appropriate ligand with equimolar amounts of $Cu(ClO_4)_2\cdot 6H_2O$ and methanolic NaOH, or alternatively by a more direct route in which the two reactants are added to a solution of the ligand immediately after formation of the ligand and prior to any isolation. Both routes gave identical products but the latter was less time consuming and gave higher yields (Scheme 1).

The Schiff base ligands and complexes were characterized by elemental analysis (Table 1), molar conductivity (Table 1), ^1H and ^{13}C NMR (Table 2), FTIR (Table 3), electronic spectra (Table 4) and crystal structure determinations of two of the complexes. All of the complexes are very stable at room temperature in air and are insoluble in water and nonpolar solvents. However, they are soluble in acetonitrile, methanol, DMF and DMSO, completely. Solution conductivity measurements were performed to establish the electrolyte type of the complexes. The molar conductivities at 10^{-3} M concentration for the complexes in acetonitrile are in the range expected for their formulation as 1:1 electrolytes [20] as shown in Table 1.

The ^1H and ^{13}C NMR spectra data of the ligands in $CDCl_3$ solvent (Table 2) confirm the proposed structures of the ligands (Scheme 1). In the ^1H NMR spectra of ligands, the signal for proton of the –NH group was not found and it is suggested that the Schiff base ligands do not undergo keto-enol tautomerism [21,22]. The spectrum of the pytOMesalH ligand shows one signal at 59.33 ppm and this can be attributed to the carbon atom of the methoxy group [22]. Most of the IR characteristic bands of all ligands are given in Table 3. The FTIR spectra of all complexes compared with those of the ligands, indicate that the ν(C=N) band at 1634–1655 cm^{-1} is shifted to lower frequency by 8–30 cm^{-1} in the complexes, indicating that the ligands are coordinated to the metal ions through the nitrogen atom of the azomethine group. On the other hand, the disappearance of the OH bands of the free ligands in the complexes indicates that the OH group has been deprotonated and bonded to metal ions as O^-. The spectra of the $pytNO_2salH$ ligand and its complex show two bands at 1325 and 1557 cm^{-1} and these can be attributed to ν(N=O) nitro group [22]. The appearance of a broad intense band in the spectra of the complexes at 1094–1101 cm^{-1} compared to those of ligands is assigned to ν(Cl–O) perchlorate group [23]. A medium broad absorption with a maximum at 3620 cm^{-1} in the spectrum of $[Cu(pytIsal)]ClO_4\cdot 0.5CH_3OH$ indicates the presence of methanol in the complex. The elemental analysis of the complex also shows the presence of half mole of methanol per mole of complex (Table 1).

The electronic absorption spectral data for all of the complexes are given in Table 4. The spectra were recorded using CH_3CN as solvent. The appearance of broad intense absorption bands at 578, 576, 584, 568 and 573 nm in the spectra of the complexes of $[Cu(pytXsal)]ClO_4$ (X=I, Br, NO_2, OMe, Azo), respectively, which are assigned to d–d transitions, seems to be little influenced by the different substitutions on the salicylaldehyde, and suggests that the coordination geometry at the metal ion could be distorted from square planar [7,24–26]. The broad, slightly intense and poorly resolved bands between 320–400 nm may be assigned to O(phenolate)$\leftrightarrow Cu^{II}$ LMCT or MLCT [7,27–29].

4.1. Crystal structures of $[Cu(PytIsal)]ClO_4\cdot 0.5CH_3OH$ (A) and $[Cu(PytAzosal)]ClO_4$ (B)

Both structures consist of complex mononuclear cations and perchlorate anions, complex **A** includes half a solvent molecule, but complex **B** does not include any solvent molecule. Details of data collection procedures and structures are given in Table 5. The crystal structures of **A** and **B** complexes and their unit cell diagrams are shown in Figs. 1–4. The relevant distances and angles are listed in Table 6. In both complexes, the copper ion has a N_2OS coordination sphere, bound by deprotonated phenolate oxygen, imine and pyridine type nitrogens and the thioether sulfur atoms. The Cu–O (1.881, 1.908 Å), Cu–N(1) (2.022, 1.992 Å) and Cu–N(2) (1.947, 1.933 Å) bond lengths for complexes **A** and **B**, respectively, are in the range found for similar Cu–O (phenolate), Cu–N (pyridine) and Cu–N (imine) interactions, and the Cu–S (2.3202, 2.3492 Å) bond lengths are slightly shorter (0.098, 0.069 Å, respectively) than the mean Cu–S (2.4185 Å) distance found in related Schiff base complexes [8,15,30,31]. The Cu–N(2) distance is slightly longer than that of Cu–O. In complex **B** the Cu–O and Cu–S distances are little longer (0.027 and 0.029 Å), while the Cu–N(2) and Cu–N(1) distances are little shorter (0.014 and 0.03 Å) than those of

Table 2
^{1}H and ^{13}C NMR data for Schiff base ligands

	Compounds				
	PytIsalH	PytBrsalH	$PytNO_2salH$	PytOMesalH	PytAzosalH
^{1}H NMR (ppm)					
	13.35 (br s, 1H, OH)	13.20 (br s, 1H, OH)	14.55 (br s, 1H, OH)	12.75 (br s, 1H, OH)	13.80 (br s, 1H, OH)
	8.54 (d, 1H, pyridinic)	8.55 (d, 1H, pyridinic)	8.55 (d, 1H, pyridinic)	8.52 (d, 1H, pyridinic)	8.54 (d, 1H, pyridinic)
	8.23 (s, 1H, iminic)	8.26 (s, 1H, iminic)	8.35 (s, 1H, iminic)	8.29 (s, 1H, iminic)	8.39 (s, 1H, iminic)
	7.64 (t, 1H, pyridinic)	7.67 (t, 1H, pyridinic)	8.22–8.16 (m, 2H, aromatic)	7.58 (t, 1H, pyridinic)	7.98 (d, 1H, aromatic)
	7.55–7.17 (m, 4H, aromatic)	7.39–7.21 (m, 4H, aromatic)	7.65 (t, 1H, pyridinic)	7.20–7.11 (m, 4H, aromatic)	7.89–7.86 (m, 3H, aromatic)
	6.74 (d, 1H, aromatic)	6.85 (d, 1H, aromatic)	7.19 (m, 2H, aromatic)	6.76 (d, 1H, aromatic)	7.61 (t, 1H, pyridinic)
	3.78 (t, 2H, CH_2 aliphatic)	3.80 (t, 2H, CH_2 aliphatic)	3.84 (t, 2H, CH_2 aliphatic)	3.77 (m, 5H, aliphatic)	7.51–7.41 (m, 3H, aromatic)
	3.09 (t, 2H, CH_2 aliphatic)	3.13 (t, 2H, CH_2 aliphatic)	3.10 (t, 2H, CH_2 aliphatic)	3.08 (t, 2H, CH_2 aliphatic)	7.18–7.13 (m, 2H, aromatic)
	2.98 (t, 2H, CH_2 aliphatic)	3.00 (t, 2H, CH_2 aliphatic)	3.00 (t, 2H, CH_2 aliphatic)	2.98 (t, 2H, CH_2 aliphatic)	7.05 (d, 1H, aromatic)
	2.84 (t, 2H, CH_2 aliphatic)	2.86 (t, 2H, CH_2 aliphatic)	2.88 (t, 2H, CH_2 aliphatic)	2.83 (t, 2H, CH_2 aliphatic)	3.80 (t, 2H, CH_2 aliphatic)
					3.08 (t, 2H, CH_2 aliphatic)
					2.98 (t, 2H, CH_2 aliphatic)
					2.85 (t, 2H, CH_2 aliphatic)
^{13}C NMR (ppm)	(12C, aromatic)	(12C, aromatic)	(12C, aromatic)	(12C, aromatic)	(18C, aromatic)
	164.55, 160.90	164.61, 160.16	169.22, 164.98	165.55, 159.77	165.67, 164.94
	159.67, 149.33	159.66, 149.32	159.48, 149.25	155.21, 152.00	159.54, 152.56
	140.68, 139.56	136.45, 134.92	138.72, 136.62	149.29, 136,48	149.12, 145.02
	136.52, 123.31	133.46, 123.25	128.41, 128.21	123.27, 121.54	136.77, 130.45
	121.60, 120.79	121.56, 119.96	123.35, 121.69	119.38, 118.30	129.09, 127.50
	119.57, 79.15	119.02, 109.95	119.02, 116.65	117.23, 114.95	126.96, 123.45
					122.53, 121.71
					118.27, 118.05
	(4C, aliphatic)	(4C, aliphatic)	(4C, aliphatic)	(5C, aliphatic)	(4C, aliphatic)
	58.93, 38.36	58.93, 38.36	57.04, 38.21	59.33, 55.93	58.38, 38.24
	32.97, 31.84	32.94, 31.82	32.72, 31.70	38.44, 33.09	32.94, 31.83
				31.905	

Table 3
Characteristic IR bands of the ligands and their complexes as KBr discs (cm^{-1})

Compound	ν(O–H)/CH_3OH	ν(C–H) aromatic	ν(C–H) aliphatic	ν(C=N)	ν(N=O)	ν(Cl–O)
PytIsalH	3485	3053	2853–2930	1634	–	–
PytBrsalH	3447	3015–3050	2850–2930	1634	–	–
$PytNO_2salH$	3447	3053	2922–2940	1655	1325–1541	–
PytOMesalH	3447	3053	2850–2937	1641	–	–
PytAzosalH	3400	3069	2850–2930	1641	–	–
$[Cu(pytIsal)]ClO_4 \cdot 0.5CH_3OH$	3620	3079	2937–2984	1626	–	1094
$[Cu(pytBrsal)]ClO_4$	–	3007–3076	2850–2937	1634	–	1094
$[Cu(pytNO_2sal)]ClO_4$	–	3076	2937–2999	1641	1325–1557	1094
$[Cu(pytOMesal)]ClO_4$	–	3030	2860–2937	1618	–	1101
$[Cu(pytAzosal)]ClO_4$	–	3059	2850–2930	1634	–	1094

Table 4
The electronic spectra of the copper(II) complexes

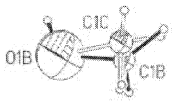
Compound	λ_{max} (nm) (ε) [a]
$[Cu(pytIsal)]ClO_4$	578(470), 385(4162), 330(10 937), 235(42 975)
$[Cu(pytBrsal)]ClO_4$	576(404), 384(4400), 329(10 400), 229(34 225)
$[Cu(pytNO_2sal)]ClO_4$	584(413), 360(21 375), 253(23 175), 240(20 583)
$[Cu(pytOMesal)]ClO_4$	568(459), 410(4737), 329(9725), 251(25 337), 226(28 700)
$[Cu(pytAzosal)]ClO_4$	573(480), 370(4102), 270(sh), 245(29 350)

[a] $Mol^{-1}\ cm^{-1}$.

complex **A**. Incorporation of the metal ion into the ligand in complex **A** has appeared to lead the chelating ring containing Cu(1), N(2), C(10), C(11), C(16) and O(1), being delocalized. The C(10)–C(11) distance of 1.430 Å is much shorter than the normal $C(sp^2)$–$C(sp^2)$ single bond (1.51 Å) [8], the C(10)–N(2) distance of 1.292 Å is a little longer than the normal imine C=N double bond (1.28 Å) and the C(16)–O(1) bond length of 1.309 Å is shorter than the normal $C(sp^2)$–O single bond (1.34 Å) [8]. All these changes in bond lengths indicate delocalization of the donating ring of the aromatic Schiff base portion, so this chelating ring tends to remain planar as a result of this delocalization to form a stable conjugation structure. On the other hand, for the complex **B**, in the chelating ring containing Cu(1), N(2), C(10), C(11), C(16) and O(1), the C(10)–C(11), C(16)–O(1) and C(10)–N(2) distances are 1.437, 1.292 and 1.273 Å, respectively. These changes in bond lengths, also indicate delocalization of the aromatic Schiff base portion, mainly in the phenoxide site [8]. Within the ligand–metal fragment, the four adjacent bond angles about the Cu center are unevenly distributed from the ideal 90°, except for the O(1)–Cu(1)–N(1) bond angle of the open sector in complex **A** that is

Table 5
Crystal and structure refinement data for the copper complexes

	$[Cu(PytIsal)]ClO_4 \cdot 0.5CH_3OH$	$[Cu(PytAzosal)]ClO_4$
Empirical formula	$C_{16.5}H_{18}ClCuIN_2O_{5.5}S$	$C_{22}H_{21}ClCuN_4O_5S$
Formula weight	590.28	552.48
Temperature (K)	110(2)	110(2)
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/c$
Unit cell dimension		
a (Å)	12.519(4)	19.199(3)
b (Å)	16.409(5)	7.8004(14)
c (Å)	20.033(6)	14.862(3)
α (°)	90	90
β (°)	107.207(5)	100.632(6)
γ (°)	90	90
V (Å^3)	3931(2)	2187.5(7)
Z	8	4
D_{calc} (Mg m^{-3})	1.995	1.678
Absorption coefficient (mm^{-1})	2.959	1.261
$F(0\,0\,0)$	2320	1132
Crystal size (mm)	$0.34 \times 0.32 \times 0.2$	$0.43 \times 0.08 \times 0.03$
θ Range for data collection (°)	2.11–30.05	2.16–28.02
Index ranges	$-17 \le h \le 17$, $-23 \le k \le 23$, $-26 \le l \le 28$	$-25 \le h \le 22$, $-10 \le k \le 10$, $-19 \le l \le 10$
Reflections collected	22 896	10 734
Independent reflections	5738 [$R_{int} = 0.0323$]	5208 [$R_{int} = 0.0741$]
Reflection observed	4196	2115
Data/restraints/parameters	5738/26/293	5208/0/305
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0496$, $wR_2 = 0.1192$	$R_1 = 0.0538$, $wR_2 = 0.1048$
R indices (all data)	$R_1 = 0.0710$, $wR_2 = 0.1303$	$R_1 = 0.1413$, $wR_2 = 0.1268$
Goodness-of-fit on F^2	1.068	0.779
Largest difference peak and hole (e Å^{-3})	3.702 and −0.665	0.753 and −0.437



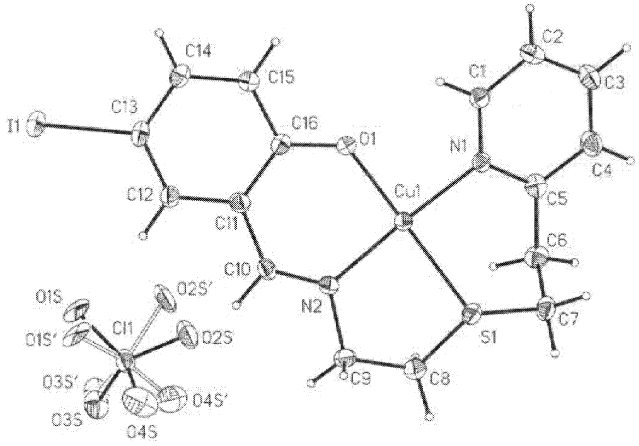


Fig. 1. The structure of $[Cu(pytIsal)]ClO_4 \cdot 0.5CH_3OH$.

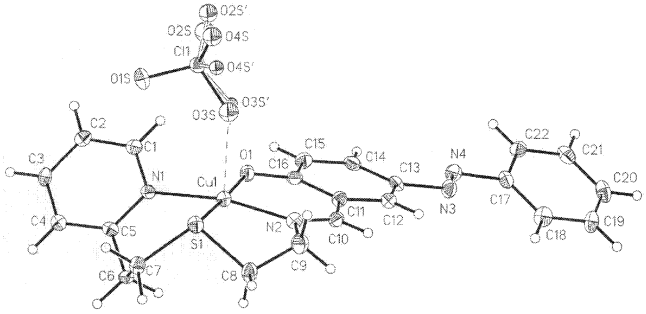


Fig. 2. The structure of $[Cu(pytAzosal)]ClO_4$.

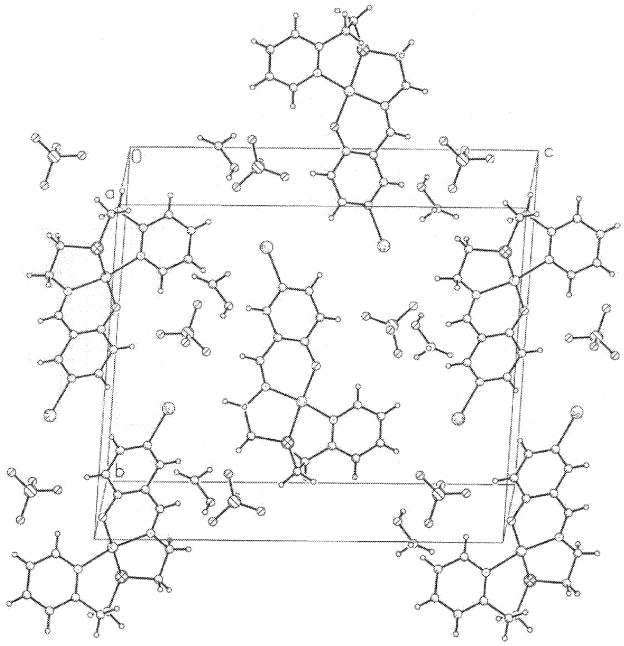


Fig. 3. Stereoview of the unit cell of $[Cu(pytIsal)]ClO_4 \cdot 0.5CH_3OH$.

perfectly 90°. It should be noticed that the deviation for the O(1)–Cu(1)–N(1) (89.33°) and N(1)–Cu(1)–S(1) (90.78°) bond angles in complex **B** are minor. The N–Cu–S bond angles in six membered rings are bigger than those of five membered rings in the complexes of **A** and **B**, the same results have been obtained in related complexes [15]. The N(2)–Cu(1)–O(1) bond angles in the complexes are comparable with corresponding angles in related complexes [8,30,31], while these angles are much smaller than the 97.2° reported bond angle in Ref. [15]. In complex **B** in comparison with complex **A**, the N(1)–Cu(1)–S(1) bond angle is much smaller (4.01°)

Table 6
Selected bond lengths (Å) and angles (°) for the complexes

	$[Cu(PytIsal)]ClO_4 \cdot 0.5CH_3OH$	$[Cu(PytAzosal)]ClO_4$
Cu(1)–O(1)	1.881(3)	1.908(3)
Cu(1)–N(2)	1.947(3)	1.933(4)
Cu(1)–N(1)	2.022(3)	1.992(4)
Cu(1)–S(1)	2.3202(12)	2.3492(15)
O(1)–C(16)	1.309(5)	1.292(5)
N(2)–C(10)	1.291(5)	1.273(6)
C(10)–C(11)	1.430(6)	1.437(7)
Cu(1)–O(3S)	–	2.473(16)
O(1)–Cu(1)–N(2)	93.89(13)	94.64(16)
O(1)–Cu(1)–N(1)	90.00(13)	89.33(14)
N(2)–Cu(1)–N(1)	166.50(14)	168.63(17)
O(1)–Cu(1)–S(1)	165.36(10)	176.18(11)
N(2)–Cu(1)–S(1)	84.63(10)	85.97(13)
N(1)–Cu(1)–S(1)	94.79(10)	90.78(11)

while the N(2)–Cu(1)–O(1) and N(2)–Cu(1)–S(1) bond angles are slightly bigger (0.75° and 1.34°, respectively). The copper(II) ion displays tetrahedrally distorted square planar coordination characterized by *trans* O(1)–Cu(1)–S(1) and N(1)–Cu(1)–N(2) angles of 165.36° and 166.5° for complex **A** and 176.18° and 168.63° for complex **B**, respectively, which are comparable with those of related complexes [31,32]. Complex **A** has solvate methanol disordered in the vicinity of the twofold axis. Atom O(2s′) from the anion is hydrogen bonded to methanol at an O(2s′)···H(O(1B)) distance of 1.74 Å. The O(2s′)···O(1B) distance is 2.619 Å. The ClO_4^- anions are disordered in both structures. The copper atom in the complexes carries no axial ligands, but in crystal **B**, both sites are remotely occupied by c-glide related perchlorate oxygen at distances longer than 2.47 Å.

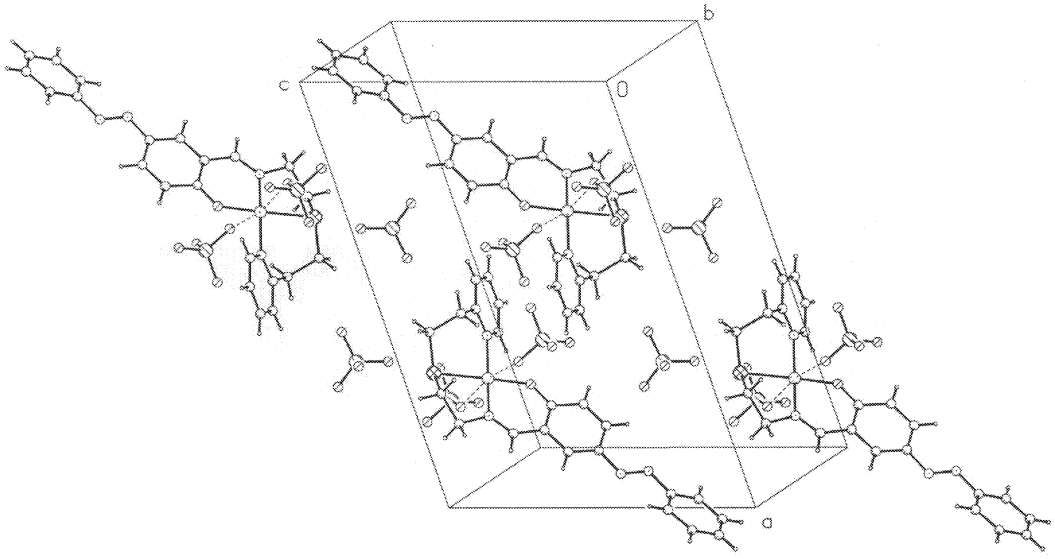


Fig. 4. Stereoview of the unit cell of $[Cu(pytAzosal)]ClO_4$.

Table 7
Cyclic voltammetry data for the copper(II) complexes

Complex	E_{pc} (V)	E_{pa} (V)	ΔE (V)	i_{pa}/i_{pc}
[Cu(pytAzosal)]ClO_4	−0.228	−0.120	0.108	0.73
[Cu(pytNO_2sal)]ClO_4	−0.248	−0.068	0.180	0.90
[Cu(pytIsal)]ClO_4	−0.255	–	–	–
[Cu(pytOMesal)]ClO_4	−0.285	–	–	–

4.2. Cyclic voltammetry

The voltammetric parameters obtained for the complexes are listed in Table 7. Moreover, one of the voltammograms of the copper(II) complexes is shown in Fig. 5. On the basis of the voltammetric data, the complexes of [Cu(pytIsal)]ClO_4 and [Cu(pytOMesal)]ClO_4 undergo irreversible reduction processes in a potential range of −0.7 to +0.5 V under the experimental conditions. The peak separation ΔE ($=E_{pc}-E_{pa}$) for the complexes [Cu(pytNO_2sal)]ClO_4 and [Cu(pytAzosal)]ClO_4 are 0.180 and 0.108 V, respectively, at a scan rate of 0.1 V s^{-1}, thus the redox process for both complexes is quasi-reversible [33]. The voltammetric responses are assignable to the Cu(II)/Cu(I) couple. For the dissymmetric Schiff base complexes herein studied, E_{pc} becomes less negative in the sequence of $OCH_3 < I < NO_2 <$ Azo with increasing electron-withdrawing effect of the substituent at the *para* position respect to the phenolic hydroxyl group. Similar results have been reported previously for copper(II) complexes of symmetric tetradentate Schiff base ligands [34] and have been interpreted by assuming that the strong electron-withdrawing effects stabilize the lower oxidation state[35]. It should be noticed that the E_{pc} variation in our complexes are minor. As can be noticed in Table 7 the E_{pc} values for the complexes are less negative and these indicate that, for dissymmetric Schiff base ligands herein studied, the chelate of copper(I) complexes are more stable than the respective chelates of copper(II), probably due to the presence of the sulfur donor atom in the ligands [36]. With continuing the scan in the negative direction beyond −0.8 V a narrow anodic peak with a large current around −0.3 V appears, which probably corresponds to oxidation of copper deposited at the electrode [23b].

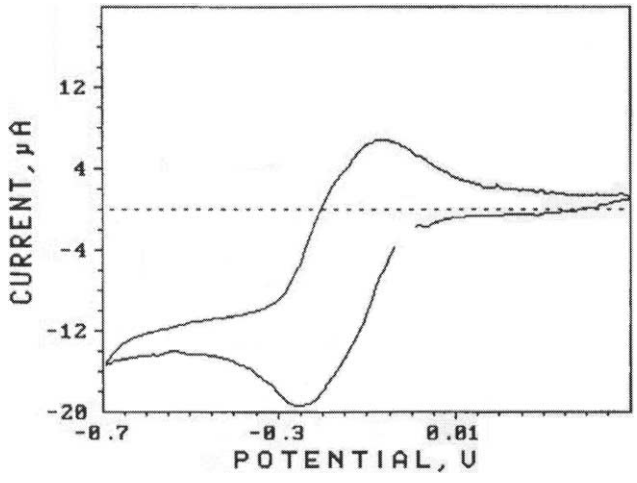


Fig. 5. The cyclic space voltammogram of [Cu(pytNO_2sal)]ClO_4.

4.3. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 197821 for complex **A** and CCDC 197822 for complex **B**. Copies of this information may be obtained free of charge from the The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) on request.

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