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Cu(II) and Cd(II) complexes with a new symmetrical
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Amel Ghames, Tahar Douadi, Djahida Haffar, Salah Chafaa, Magali Allain, et al.. Structural and electrochemical studies of Co(II), Ni(II), Cu(II) and Cd(II) complexes with a new symmetrical N₂O₂ Schiff base: Crystal structure of the ligand 1,2-di[4-(2-imino 4-oxo pentane)phenyl]ethane. *Polyhedron*, Elsevier, 2006, 25 (16), pp.3201-3208. 10.1016/j.poly.2006.05.019 . hal-03230394

HAL Id: hal-03230394

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Structural and electrochemical studies of Co(II), Ni(II), Cu(II) and Cd(II) complexes with a new symmetrical N₂O₂ Schiff base: Crystal structure of the ligand 1,2-di[4-(2-imino 4-oxo pentane)phenyl]ethane

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Received 28 March 2006; accepted 22 May 2006

Available online 3 June 2006

Abstract

The crystal structure of a new Schiff base: 1,2-di[4-(2-imino 4-oxo pentane)phenyl]ethane (H₂L) is described. This molecule undergoes tautomerism with three tautomers: keto-imine, enol-imine and keto-amine. It acts mainly as a tetradentate ligand. Its complexes with cobalt(II), nickel(II), copper(II) are characterised using spectroscopic determinations and cyclic voltammetry. These new complex species are formulated as [CoL]·(H₂O)₃, [(NiCl₂)₂(H₂L)], [CuCl₂(H₂L)] and [CdCl₂(H₂L)], respectively. The coordination occurs through the N₂O₂ system, using various tautomers.

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Keywords: Schiff base; Complexes; Crystal structure; Cyclic voltammetry

1. Introduction

Since the first report of their metal complexes, symmetrical as well as non-symmetrical Schiff bases have been extensively studied and used as ligands in many complex species [1]. Among them, tetradentate symmetrical N₂O₂ Schiff bases are the more common ligands. Recently, some symmetrical Schiff bases with carbonyl functional groups have been described by Anthonysamy and Balasubramanian [2]. In the corresponding nickel(II) complexes, the coordination occurs through the N₂O₂ system. The cyclic voltammetry shows in each complex two quasi-reversible one electron waves.

Symmetrical tetradentate Schiff bases derived from substituted salicylaldehyde and ethylenediamine could coordinate manganese(II) and copper(II) chlorides, giving 2:1 and 1:1 complex species, respectively [3].

Very few papers dealt with symmetrical Schiff base bearing a ketonic group near the imino part of the molecule. Karmakar et al. described a Schiff base with only one pendant arm by reacting 2-picolylamine and acetylacetone [4]. They have obtained 1:1 complex with CuBr₂ in which the metal ion is bound through N-pyridine, N-imine and O from ionised enol tautomer. Mukherjee et al. have prepared a new copper(II) complex using a multidentate Schiff base ligand [*N,N'*-(2-hydroxypropane-1,3-diyl)bis-(pyridine-2-aldimine)] where they observed the formation of the amido moiety as a reactive intermediate from the kinetic studies in solution using infrared spectroscopy [5].

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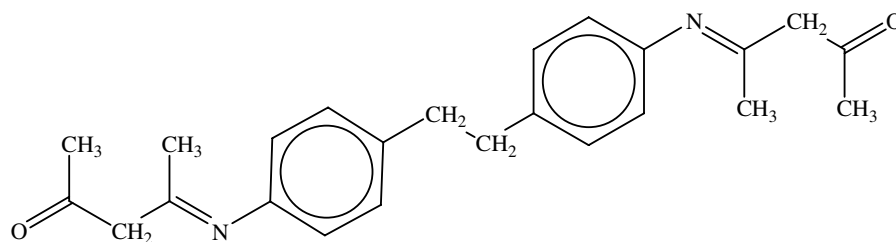


Fig. 1. Chemical structure of the ligand.

The keto-amine and enol-imine equilibrium of the Schiff base, 2-deoxy-2-(2-hydroxybenzaldimino)-D-glucopyranose was described in methanolic and dimethyl sulfoxide solutions. It reacts with nickel acetate to give a bidentate mononuclear Ni(II) complex [6].

Recently, Cerchiaro et al. reported some copper(II) complexes with isatin or imine ligands derived from isatin. In some derivatives, the metal ion is bound through the keto oxygen atom [7].

In our continuous work about symmetric Schiff bases built around 4,4'-diaminodiphenyl [8,9] we present here the crystal structure of a new symmetrical compound: 1,2-bis[4-(2-imino 4-oxo pentane)phenyl]ethane (see Fig. 1) obtained by reacting 4,4'-diaminodiphenyl with acetylacetonone. In addition, we discuss the structure and the electrochemical behaviour of its complexes with cobalt(II), nickel(II), copper(II) and cadmium(II).

2. Experimental

2.1. Reactants

All reactants and solvents were analytical grade. 4,4'-Diaminodiphenyl ethane and acetylacetonone were purchased from Sigma–Aldrich, France. All the metals were used as hydrated chlorides and were used as received.

2.2. Preparation of the ligand

The ligand is obtained by reacting 4,4'-diaminodiphenyl ethane and acetylacetonone in MeOH with a 1:2 ratio as previously described [10,11]. To a solution of diaminodiphenyl ethane (1 mmol, 0.21 g, 40 mL) was added a solution of acetylacetonone (2 mmol, 0.2 g, 7 mL). The mixture was refluxed for 3 h and cooled. The yellow product was filtered, washed twice with EtOH (10 mL) and finally recrystallised from a mixture EtOH/CHCl₃ (30/70 v/v) and dried under vacuum. The single crystals for X-ray diffraction were obtained by slow evaporation from toluene.

2.3. Syntheses of the complexes

All the complexes were prepared by mixing in EtOH equimolar amounts of ligand (0.2 g, 4 mL) and hydrated chlorides (10 mL). After standing under reflux conditions for 8 h, the mixture was kept overnight at room tempera-

ture. After the addition of toluene (30 mL), the complex precipitated. It was removed by filtration, washed several times with hot EtOH, dried under vacuum.

Besides this operating mode we have obtained these complexes by template synthesis without isolating the ligand [12]. In a first step, we have mixed 4,4'-diaminodiphenyl ethane and acetylacetonone as indicated above (see Section 2.2), after an 8-h reflux, the hydrated metal chloride (EtOH, 10 mL) in stoichiometric amount, was added. Finally, the complex species was obtained and purified, in the same way than previously described.

2.4. Measurements

All elemental analysis were carried out at the Service d'Analyse du C.N.R.S. de l'I.C.S.N., Gif sur Yvette (France). The melting points were determined with a Kofler bank and are uncorrected. The i.r. spectra were recorded with a Perkin–Elmer 1000 series FTIR spectrophotometer, using KBr disks. The UV–Vis spectra were obtained with a UNICAM UV300 spectrophotometer in DMF solutions. The ¹H NMR spectra were recorded on a Jeol GSX WB spectrometer at 270 MHz in CDCl₃ or DMSO-D₆, the chemical shifts are given in ppm, using TMS as internal reference. Electrochemical measurements were recorded on a Radiometer VOLTALAB 32 (DEA 332 type); the working electrode was a Pt rotating disk (2 mm diameter) and the auxiliary electrode a Pt wire. A saturated calomel electrode was used as the reference electrode and measurements were carried out at 25 ± 0.2 °C. DMF was used as solvent and the ionic strength was maintained at 0.1 mol L⁻¹, with Bu₄NPF₆ as supporting electrolyte. The concentration of all species was 2.5 × 10⁻³ mol L⁻¹.

2.5. Crystal data collection and processing

Crystals of H₂L are monoclinic with space group *P*2₁/*c*. The crystal and instrumental parameters used in the unit-cell determination and data collection are summarised in Table 1. X-ray single-crystal diffraction data were collected at 293 K on a STOE-IPDS diffractometer, equipped with a graphite monochromator utilising Mo K α radiation ($\lambda = 0.71073$ Å) (CIMMA, UMR CNRS 6200, Angers). The structure was solved by direct methods using SIR92 [13] and the refinement was performed on *F*² by full matrix

Table 1
Crystallographic data for the ligand

Formula	C ₁₂ H ₁₄ NO
Formula weight	188.24
Crystal system	monoclinic
Space group	P2 ₁ /c
a (Å)	10.632(2)
b (Å)	6.2615(6)
c (Å)	16.370(2)
α (°)	90
β (°)	98.09(2)
γ (°)	90
V (Å ³)	1078.9(3)
Z	4
Color	yellow
D _{calc} (g cm ⁻³)	1.159
F(000)	404
μ (mm ⁻¹)	0.074
hkl limits	-12 ≤ h ≤ 13, -7 ≤ k ≤ 7, -20 ≤ l ≤ 19
θ _{min} , θ _{max} (°)	2, 26
Number of data with I > 2σ(I)	1295F _o
Weighting scheme	w = 1/[σ ² (F _o ²) + (0.1714P) ²] with P = (F _o ² + 2F _c ²)/3
Number of variables	127
R ₁	0.0759
wR ₂	0.2288

least-squares techniques using SHELX-97 package [14]. All non-H atoms were refined anisotropically and the H atoms were included in the calculation without refinement. Absorption was corrected by Gaussian technique.

3. Results and discussion

3.1. Crystal structure of the ligand

The main crystal parameters are reported in Table 1. The bond distances and their angles are given in Table 2.

Table 2
Bond lengths (Å) and angles (°)

Bond lengths (Å)		Bond angles (°)	
C01—C'01	1.500(6)	C'01—C01—C02	114.3(3)
C01—C02	1.516(3)	C07—C02—C03	117.0(2)
C02—C07	1.374(4)	C07—C02—C01	120.9(3)
C02—C03	1.403(4)	C03—C02—C01	122.2(3)
C03—C04	1.386(3)	C04—C03—C02	121.6(2)
C04—C05	1.379(4)	C05—C04—C03	120.4(2)
C05—C06	1.385(4)	C04—C05—C06	118.8(2)
C05—N01	1.436(3)	C04—C05—N01	118.5(2)
C06—C07	1.394(4)	C06—C05—N01	122.6(2)
C08—N01	1.346(3)	C05—C06—C07	120.3(2)
C08—C10	1.375(3)	C02—C07—C06	121.9(2)
C08—C09	1.500(4)	N01—C08—C10	120.9(2)
C10—C11	1.421(4)	N01—C08—C09	118.2(2)
C11—O01	1.244(3)	C10—C08—C09	120.8(2)
C11—C12	1.507(3)	C08—C10—C11	124.4(2)
		O01—C11—C10	122.0(2)
		O01—C11—C12	119.3(2)
		C10—C11—C12	118.6(2)
		C08—N01—C05	127.9(2)

The molecule presents a symmetrical structure with two identical independent half-molecules. The structure, with the atoms numbering scheme, is given in Fig. 2. The angles and the distances around C11 are typical of a keto functional group. The bond distances between C05 and N01 correspond to a double bond length as already observed in similar compounds [15]. The C08—C10 (1.375 Å) and C08—N01 (1.346 Å) bond distances are close to that published by Nathan and Traina (1.368 Å and 1.365 Å, respectively) [15] but in our ligand, we note a shorter bond distance for C10—C11 (1.421 instead of 1.502 Å). These results are in good agreement with keto-imine or keto-amine tautomers.

All angles are close to 120°, showing sp² hybridisation of all atoms without taking into account the methyl groups. The azomethine moiety presents an E configuration around the carbon–nitrogen double bond.

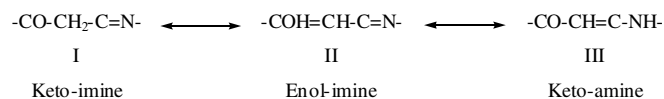
In a molecule, the two aromatic rings are in parallel planes and the two carbonyl oxygen atoms lie on the two sides of these planes. The packing along b-axis (Fig. 3) shows that the molecules lie in parallel planes. In a cell, there are four half-molecules giving two independent complete symmetrical ligands. The half-molecules lie in two planes with a 77° angle between them as presented in Fig. 4.

3.2. Complexes formulae

The analytical data are reported in Table 3. The purity of each species was verified using t.l.c. The complexes are formulated as [CoL]·(H₂O)₃, [(NiCl₂)₂(H₂L)], [CuCl₂·(H₂L)] and [CdCl₂(H₂L)], respectively. The cobalt complex is the only complex obtained through the ionised hydroxyl enol-imino tautomer. The compounds 4 and 5 are slightly unstable as indicated by higher errors in elemental analysis. So, all spectroscopic and electrochemical determinations were performed using freshly prepared compounds.

3.3. Spectroscopic results

The main spectroscopic data are given in Table 4. We have to take into account the tautomeric equilibria giving three tautomers [15,16]:



As indicated by crystallographic data, a keto tautomer was observed in the solid state in the case of the ligand. The hydroxyl stretching vibration band appearing in the infrared spectra of the complex with cobalt is due to coordination water molecules [17]. In the case of the nickel(II) complex, the band centred at 3380 cm⁻¹ is due to ν(N—H) from keto-amine tautomer [18]. The aromatic cycle vibrations at ca. 1270, 1030 and 825 cm⁻¹ [19] and

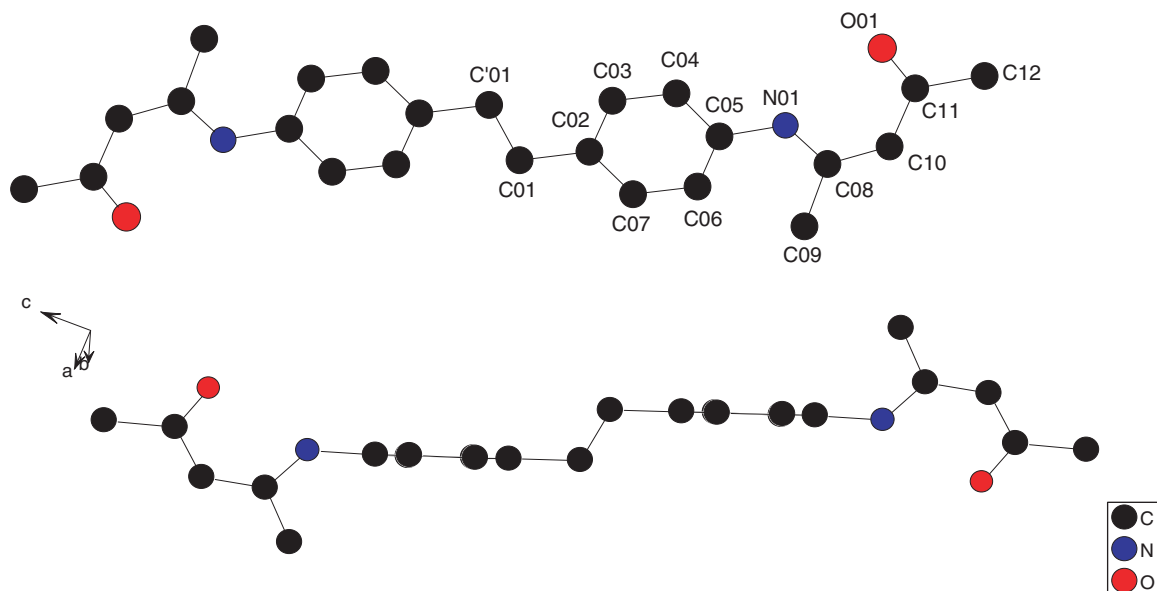


Fig. 2. Perspective view of the ligand with atom numbering (in the second identical part of the molecule, the atoms are noted C', N' and O', respectively).

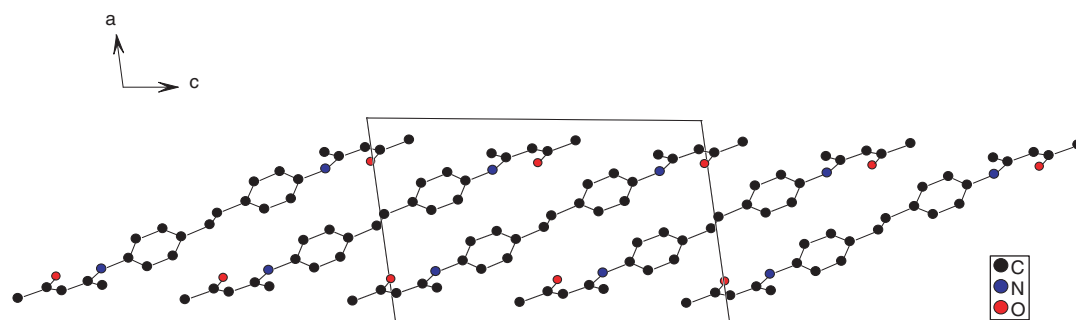


Fig. 3. Packing of the molecules along *b*-axis.

the CH₃ and CH₂ vibration band around 2925 cm⁻¹ are not modified by coordination. The stretching vibration band $\nu(\text{C}=\text{N})$ appearing at 1625 cm⁻¹ is in good agreement with the values published for similar compounds [18]. In the complexes, this band is slightly shifted down as already observed by Losada et al. [20].

The electronic spectra in DMF solutions (see Table 4) show one absorption band at 332 nm in the case of the ligand. The Co^{II} compound absorbs at 315 nm and with a weak molar absorption coefficient. In Ni(II) complex, two bands are located at 305 and 270 nm while two shoulders are observed at 350 nm ($\epsilon = 49000 \text{ L mol}^{-1} \text{ cm}^{-1}$) and 330 nm ($\epsilon = 65000 \text{ L mol}^{-1} \text{ cm}^{-1}$). In the case of the cupric complex, a weak shoulder at 330 nm appears together with the absorption band at 300 nm. In the UV region three new bands are located at 265 ($\epsilon = 14200 \text{ L mol}^{-1} \text{ cm}^{-1}$), 250 ($\epsilon = 10600 \text{ L mol}^{-1} \text{ cm}^{-1}$) and 230 nm ($\epsilon = 9000 \text{ L mol}^{-1} \text{ cm}^{-1}$). As expected, the spectra of the cadmium complex and of the free ligand are similar. These results agree with previous published results ([20–22] and references cited therein).

3.4. ¹H NMR

The ¹H NMR data for the ligand (in CDCl₃) and the cadmium complex (in DMSO-D₆) is given in Table 5. Though the ligand crystallises in keto-imine tautomer I, the solution NMR spectra of both compounds show signals corresponding to keto-amine tautomer III: the singlet at 12.3 ppm corresponds to the N–H proton [16] (the hydroxyl proton of the enol-imino tautomer leads to a singlet in the 8–9 ppm range [23]). This signal could be also observed in the spectrum of the cadmium complex with the same chemical shifts as it has been observed in similar compounds [24,25]. The signal of the aromatic protons, of the ethylene moiety and of the methyl groups are not modified by coordination. The only change is observed in the methyl groups signals: in the ligand, the terminal methyl groups give a singlet at 2.0 ppm and the methyl attached to C08 and C'08 a second signal at 2.1 ppm while the four methyl groups appear as a singlet corresponding to 12 hydrogen atoms in the cadmium complex.

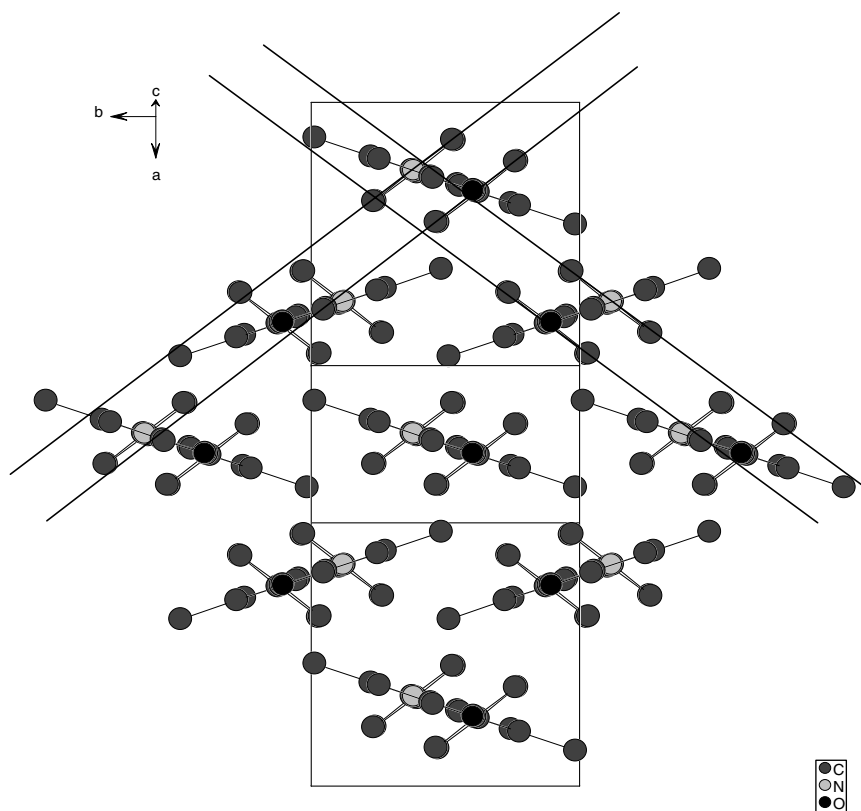


Fig. 4. Angles of 77° between the two types of aromatic planes.

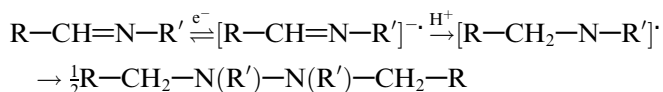
Table 3
Analytical data

Compound	Color	Yield (%)	m.p. (°C)	Elemental analysis found (Calc.)		
				C (%)	H (%)	N (%)
Ligand H ₂ L (1)	yellow	65	152	76.0 (76.6)	7.4 (7.5)	7.4 (7.4)
[CoL]·(H ₂ O) ₃ (2)	green	42	183	58.1 (59.1)	6.6 (6.6)	6.1 (5.8)
[(NiCl ₂) ₂ (H ₂ L)] (3)	yellow	45	>260	45.5 (45.3)	5.5 (4.4)	5.5 (4.4)
[CuCl ₂ (H ₂ L)] (4)	brown	51	>260	53.2 (56.4)	5.0 (5.5)	6.8 (5.5)
[CdCl ₂ (H ₂ L)] (5)	tan	65	>260	50.8 (54.9)	6.0 (5.4)	5.8 (5.3)

3.5. Cyclic voltammetry

The main electrochemical data are given in Table 6 and some representative voltammograms are presented in Fig. 5.

For the ligand, a cyclic sweep in the –1.80 to +0.00 V range shows a cathodic peak at –1.05 V and an anodic peak at –1.15 V. The peak at –1.05 V is due to the reduction of the imino moiety of the molecule as suggested by Gilli et al. [26] and Andrieu and Savéant [27]:



When the sweep is performed between 0.00 and +1.80 V, two anodic peaks are obtained at +0.91 and +1.37 V, respectively. The reoxidation of the last product in the above mechanism occurs at +1.37 V. In the range

–1.80 to +1.80 V, a cathodic peak is located at –1.05 V together with a new anodic peak at –0.05 V. When performing a second sweep in the same range, a new cathodic peak is observed at –0.42 V and the peak at –1.05 V is shifted to higher potential values (–0.97 V).

In the case of the cobalt(II) complex, and in the –2.00 to +1.80 V, a cathodic peak appears at –0.98 V while three anodic peaks are observed at –0.17, +0.80 and +1.32 V, respectively. When the sweep is limited to the –1.00 to 0.00 V range, the peak at –0.17 V is lacking. This peak should be attributed to the reoxidation of the ligand previously reduced [26]. In addition, when performing a second sweep (–1.00 to 0.00 V), a new peak is observed at –0.36 V due to the reoxidation of cobalt reduced at –0.98 V [28]. The intensity of the anodic peak at +1.32 V is a linear function of the square root of sweep speed showing a slow electron transfer.

Table 4
Spectroscopic data

Compound	Infrared					UV–Vis	
	$\nu(\text{O–H})$	$\nu(\text{N–H})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	Aromatic ring	λ (nm)	$[\epsilon (\text{L mol}^{-1} \text{cm}^{-1})]$
1			1625	1565	1275	330	[152000]
					1015	255	[55000]
					850	235	[95000]
2	3420		1615	1567	1280	315	[11000]
					1030		
					850		
3		3380	1615	1560	1245	350	[49000]
					1030	330	[65000]
					825	305	[120000]
						270	[160000]
4			1580	1522	1275	300	[13600]
					1015	265	[14200]
					820	255	[10600]
						230	[9000]
5		3460	1615	1550	1280	330	[200000]
					1020		
					820		

Table 5
 ^1H NMR data, chemical shifts in ppm (TMS); ligand in CDCl_3 , complex in $\text{DMSO-}D_6$

	Ligand (1)	Cd(II) complex (5)
H (C10)	5.2	5.2
CH_3 (C12)	2.1	2.0
CH_3 (C9)	2.0	2.0
$\text{CH}_2\text{—CH}_2$ (C01—C'01)	2.8	2.9
Aromatic	7.1	7.1
NH (keto amine)	12.3	12.4

The cyclic voltammogram of nickel(II) species shows one cathodic peak located at -1.31 V when sweeping from -1.80 to $+1.80$ V. During the reverse sweep, we observe three anodic peaks at $+0.04$ V, $+0.83$ V and $+1.35$ V. When performing successive sweeps in the same range, the peak at -1.35 V and its corresponding reoxidation peak disappear (Fig. 5c) while a new one appears at

-1.10 V. The peak at $+0.83$ V has been reported by Pereira et al. [29] for nickel(II) complexes of asymmetric tetradentate Schiff bases.

A sweep from -1.80 to $+1.80$ V for copper(II) complex shows three cathodic peaks (-1.60 V, -0.78 V, $+0.15$ V) and the back sweep ($+1.80$ to -1.80 V) shows five anodic peaks at -0.16 , $+0.10$, $+0.63$, $+0.88$ and $+1.38$ V, respectively. The peak at -0.88 V has already been observed by Losada et al. [20] in similar compounds. A second sweep shows that the peak at -1.60 V disappears, the peak at $+1.38$ V is slightly shifted to $+1.36$ V while its intensity diminishes. In the -2.00 to $+0.30$ V range, a peak is observed at $+0.10$ V. If the studied range is limited from -0.10 to $+0.80$ V, we observed the oxidation of Cu^{II} into Cu^{III} at $+0.55$ V while the reduction peak is located at $+0.37$ V [30]. The variation of the scan rate from 200 to 10 mV s^{-1} shows that the curve E_{pc} as a function of $\log \nu$, for this reduction peak, is a straight line (Fig. 5g) and it does not depend upon the sweep speed.

Table 6
Voltamperometric results at 25°C in DMF, ionic strength 0.1 mol L^{-1} (Bu_4NPF_6), results in V vs. SCE, sweep speed: 100 mV s^{-1} , E_a : anodic; E_c : cathodic

Compound	E range (V)	E_{pa1}	E_{pa2}	E_{pa3}	E_{pa4}	E_{pa5}	E_{pc1}	E_{pc2}	E_{pc3}
1	$-1.8/0$	-1.15					-1.05		
	$0/1.8$				$+0.91$	$+1.37$			
	$-1.8/+1.8$	-0.05					-1.05		
2	$-2.0/+1.8$	-0.17			$+0.80$	$+1.32$	-0.98		
	$-1.0/0$				$+0.80$	$+1.32$	-0.98		
3	$-1.8/+1.8$	$+0.43$			$+0.83$	$+1.35$		-1.31	
4	$-1.8/+1.8$	-0.17	$+0.10$	$+0.63$	$+0.88$	$+1.38$	$+0.15$	-0.78	-1.6
	$-2.0/+0.3$		$+0.10$						
	$-0.1/+0.8$			$+0.54$					
5	$-1.8/+1.8$					$+1.45$	-0.92	-1.18	

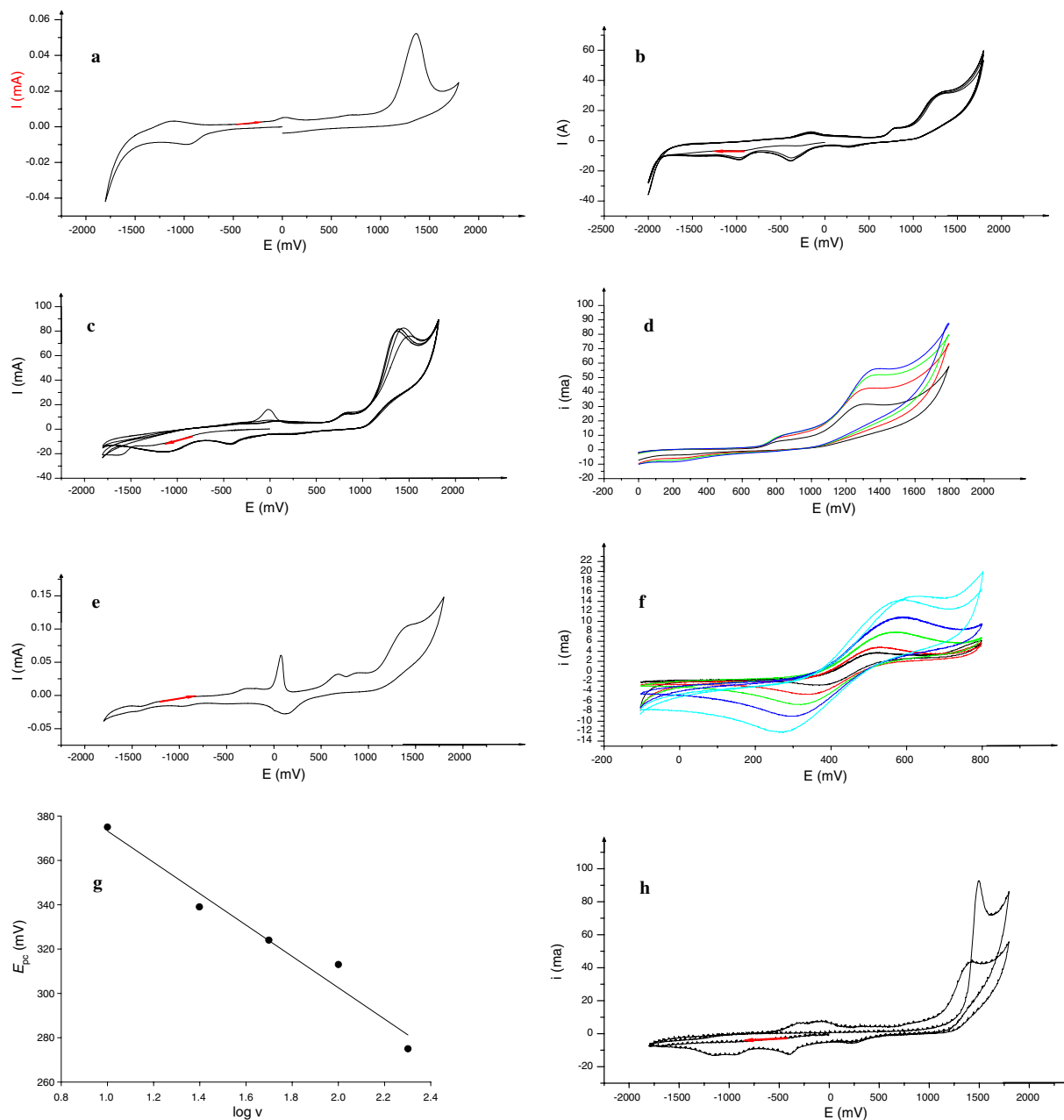


Fig. 5. Representative cyclic voltammograms in DMF (25 °C, ionic strength: 0.1 mol L⁻¹, Bu₄NPF₆, i in μ A, $v = 100$ mV s⁻¹): (a) ligand; (b) Co(II) complex, successive sweeps; (c) Ni(II) complex, successive sweeps; (d) Co(II) with variable speed; (e) Cu(II) complex; (f) Cu(II) complex, variable speed; (g) Cu(II) complex $E_{pc} = f(\log v)$; (h) Cd(II) complex.

Finally, for the cadmium(II) compound, when sweeping from -1.80 to $+1.80$ V, two cathodic waves at -1.18 and -0.92 V and one anodic peak at $+1.45$ V are obtained (Fig. 5h). We note that, in this case, the reoxidation of the imino moiety occur at higher potential values in the other compounds ($+1.45$ V instead of $+1.37$ V). A second sweep leads to three oxidation peaks at -0.78 and -0.33 V together with two reduction ones located at -0.95 and -1.15 V.

3.6. Proposed structures for the complexes

The proposed structures for the complexes are given in Fig. 6. As indicated along the discussion, some differences have been noted between solid state and solution because of the tautomeric equilibria. The cobalt complex is obtained with ionised enol-imine tautomer. In this compound, two water molecules are bounded to Co(II). In addition this cation is linked to N (imino) and O⁻ (ionised

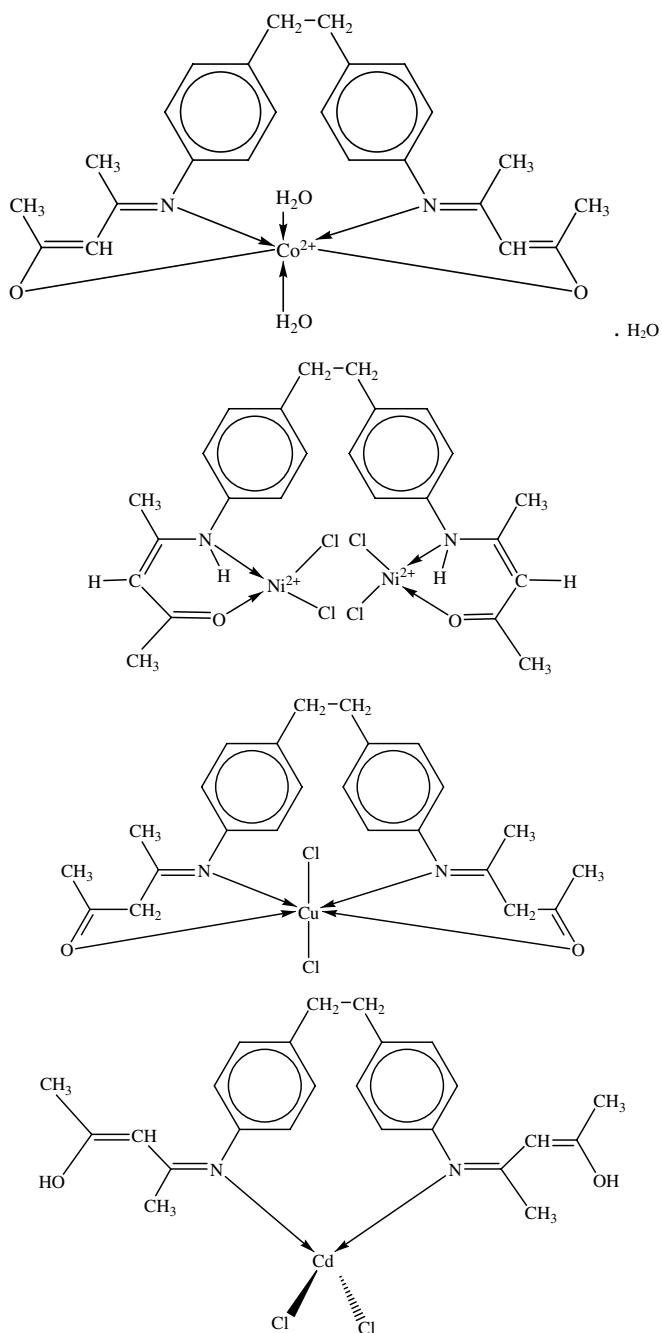


Fig. 6. Proposed structures for the complexes.

enol). So this metal ion shows an octahedral geometry. Finally, a third water molecule is in the outer coordination sphere.

The nickel(II) compound is a binuclear complex in which each nickel(II) ion presents a square planar arrangement and the Schiff base acts as a symmetrical tetradentate ligand through the keto-amine tautomer.

The copper(II) is the only compound obtained with the non-ionised keto-imine tautomer. The copper(II) ion shows a distorted octahedral geometry with O atoms (keto), N atoms (imine) in a plane and two chloride ions located on the orthogonal axis.

In the cadmium complex, the geometry around the metal cation is tetrahedral. It is linked to the keto-amine tautomer of the ligand through N (amine) atom.

4. Supplementary data

Crystallographic data have been deposited with the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or at <http://www.ccdc.cam.ac.uk>), and are available on request quoting the deposition number CCDC 287415.

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