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Synthesis, characterisation and electrochemical study of 4,4'-bis(salicylideneimino)diphenylethane and its complexes with cobalt(II), copper(II) and cadmium(II)

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Abstract

We have prepared and characterised a new series of metal complexes obtained from 4,4'-bis(salicylideneimino)diphenylethane (saldipH₂) and cobalt(II), copper(II) and cadmium(II) chlorides. In every case, the coordinating atoms are N and O. However, each compound has its own structure: [Co(saldip)]·2 H₂O is monomeric and a mononuclear species, [Cu₂(saldip)₂(H₂O)] is a binuclear complex and finally the cadmium complex is formulated as: [(CdCl₂)₂(saldipH₂)]·CdCl₂. An electrochemical study (cyclic voltammetry) indicates that the reduction, as well as the oxidation, of copper in [Cu₂(saldip)₂(H₂O)] proceeds in two steps. For the reduction of the two other complexes, two steps are indicated out: the first is attributed to the reduction of the metal and the second to the reduction of the coordinated ligands.

Introduction

Schiff bases are widely used as ligands to coordinate various metal ions because of their good solubility in common solvents and the high stability of their complexes [1, 2]. These compounds, with several donor atoms, have potential analytical applications in water treatment, due to their ability to readily form transition metals complexes [3–6]. These complex species are also involved in enzymatic reactions and are present in proteins from conjunctive tissue [7–9]. They can also be used as selective membranes [10, 11] or as compounds to prevent corrosion [12].

Ramachandraiah *et al.* described the synthesis of tetradentate ligands from 4,4'-bis(salicylideneimino)diphenyl methane (sal-dadpmX, with X = H, Me, OMe and Cl). These ligands led to [M₂(sal-dadpmX)₂] complexes, where M is cobalt(II), nickel(II), copper(II) or dioxouranium (IV) [13]. The copper complexes are pseudo-tetrahedral binuclear species while other complexes in this series are polynuclear octahedral species. The voltamperometric study of [Cu₂(sal-dadpmX)₂] complexes indicated the presence of two redox couples: copper(II)/copper(I) at –0.35 V (*versus* s.c.e) and copper(III)/copper(II) at +0.45 V (*versus* s.c.e).

Sharma *et al.* have synthesised and characterised some monomeric and dimeric copper(II) complexes with bis(2,5-dihydroxyacetophenone) (Daen). E.p.r studies

of these complexes in DMSO solution, indicated the binding of a tetradentate ligand with two N and two O donor sites, with a near square-planar arrangement of N₂O₂ donor groups in a monomeric species. The authors also found [Cu(Daen)CuCl₂] complexes, suggesting the formation of a dimeric species [14].

Recently, a series of [M(Phca2en)X₂] complexes, where Phca2en is *N,N'*-bis(β -phenylcinnamaldehyde)-1,2-diiminoethane and M = Co, Ni or Zn and X = Cl, Br, I or NCS, have been synthesised and characterised. These compounds were found to be pseudo-tetrahedral species, coordinating through N atoms [15]. Manganese(III) complexes of Schiff bases such as bis(salicylaldehyde)ethylenediamine and its substituted derivatives show biological activity as catalytic scavengers of hydrogen peroxide and cytoprotective agents [16]. L.C. Nathan *et al.* studied the effect of the chain between the azomethine groups on the structure of complexes obtained with copper(II) [17].

Schiff bases obtained from *N,N'*-(1R,2R)-1,2-cyclohexanediamine and 2-hydroxy-3-methylbenzaldehyde, and 2-hydroxy-5-methylbenzaldehyde, have been used as ligands for complexing copper(II), cobalt(II) and nickel(II) and the results of spectral analysis indicated that central ions were in a distorted square-planar geometry, with the N₂O₂ chromophore group [18]. Reactions between the non-ionised form of the Schiff base, *NN'*-propane-1,3-diyl bis(salicylideneimine) and hydrated zinc, cadmium and mercury ion gave complexes where the Schiff base is coordinated through the

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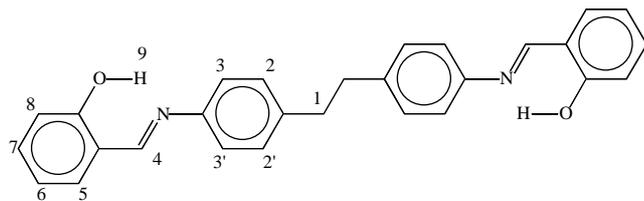


Fig. 1. Chemical structure of the ligand saldipH₂.

phenolic oxygen atoms and not the nitrogen atoms of the azomethine groups. Halide and sulphate were covalently bonded to the central metal ion, whereas the nitrate group showed ionic character in the mercury nitrate compound but not in zinc and cadmium nitrate complexes. The i.r. spectra confirmed the dimeric nature of the complexes and therefore the coordination number suggested would be four in the halo and sulphato or six in nitrate complexes, with possible tetrahedral or octahedral arrangements around these metal cations [18]. In the case of cadmium complexes with tripodal Schiff bases, Jäntti *et al.* reported an unusual eight-coordinated structure [19].

In this paper, we describe the synthesis of a new tetradentate Schiff base: 4,4'-bis(salicylideneimino)diphenylethane (saldipH₂) whose chemical structure is given in Figure 1. This compound was complexed with cobalt(II), copper(II) and cadmium(II) chlorides. The products structures are discussed on the basis of i.r. and n.m.r. spectra and thermal analysis. In addition, the electrochemical behaviour of these complexes in dimethylformamide (DMF) is described.

Experimental

Physical measurements

All elemental analysis were carried out at the Service Central d'Analyse du C.N.R.S., Vernaison (France). The melting points were determined with a Kofler bank and are uncorrected. The i.r. spectra were recorded with a Bruker Vector 22 FT-IR system. The u.v.-vis. spectra were obtained with a UNICAM UV300 spectrophotometer. The n.m.r. spectra were recorded on a Jeol FT-NMR at 270 MHz in CDCl₃. D.s.c. diagrams were recorded in the 25–350 °C range with a Mettler DSC 30 unit, with the help of Mettler Toledo STAR^c System software (Équipe INSERM ERIT-M 0104, Faculté de Pharmacie, Angers, Prof. J. P. Benoit); the heating rate

was 10 °C per min. All measurements were made in 40 mm³ closed Al crucibles. Electrochemical measurements were recorded on a VOLTALAB 32 (DEA 332 type): the working electrode was made of Pt (2 mm diameter) and so was the auxiliary electrode. 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 Et₄NClO₄ (TEAP) as supporting electrolyte.

Chemicals

All chemical products and solvents were of analytical grade and were used without further treatment.

Synthesis of the ligand

The ligand 4,4'-bis(salicylideneimino) diphenylmethane was synthesised according to previously reported procedures [1, 13], starting from 4,4'-diaminodibenzyl (1 mmol) and salicylaldehyde (2 mmol). The solvent was EtOH and the mixture was kept at 60 °C for 2 h. The Schiff base precipitated on cooling. After recrystallisation (Me₂CO 40%/CH₂Cl₂ 60%, V/V) its purity was verified by t.l.c. and the ligand was obtained in 83% yield. Its analytical data are reported in Table 1.

Synthesis of the complexes

The three complexes were prepared in the same way: 1 mmol of saldipH₂ was dissolved in hot EtOH (20 cm³), then 1 mmol of metal chloride (EtOH, 20 cm³) was added with stirring. After refluxing for 5 h, the mixture was cooled and the complex precipitated. It was filtered, recrystallised and finally dried under reduced pressure. Its purity was verified by t.l.c. Analytical data are given in Table 1.

Results and discussion

The analytical data are summarised in Table 1 and spectral data are given in Table 2.

I.r. spectra

As expected, the vibrations of the aromatic rings (*e.g.*, 1174, 838, 753 cm⁻¹) are not modified when passing

Table 1. Analytical data for the ligand and the complexes

Compound	Yield (%)	Colour	M.p. (°C)	Found (Calcd.) (%)			
				C	H	N	Cl
SaldipH ₂ (1)	83	yellow	228	79.4 (80.0)	5.5 (5.75)	6.8 (6.7)	–
[Co(saldip)] · 2 H ₂ O (2)	53	green	223	66.6 (65.2)	5.0 (5.5)	5.7 (5.4)	–
[Cu ₂ (saldip) ₂ (H ₂ O)] (3)	47	brown	208	68.85 (68.7)	4.7 (4.7)	5.7 (5.7)	–
[(CdCl ₂) ₂ (saldipH ₂)] · CdCl ₂ (4)	43	orange	260	34.4 (34.65)	2.6 (2.5)	2.9 (2.9)	21.9 (21.9)

Table 2. Spectral data

Compound	(1)	(2)	(3)	(4)
I.r. spectra ^a (cm ⁻¹)				
ν (O—H) ass	3441 (b)	3425 (b)	3449	3444 (b)
ν (C=N)	1618	1618	1619 (sh)	1635
ν (C—O)	1287	1286	1284	—
δ (O—H)	1231	1238	—	1236
Aromatic cycles	1174	1174	1180	1173
	838	838	826	834
	753	754	760	754
ν (M—O)	—	588	548	515
ν (M—N)	—	—	—	490
N.m.r. spectra (ppm) ^b				
H (9)	13.35 (sg)			—
H (8)	6.98 (dd)			7.02
H (7)	7.39			7.39
H (6)	6.88 (m)			6.98
H (5)	7.22 (sg)			7.22
H (4)	8.63			8.64
H (2,2',3,3')	1.56			1.56
	1.26			1.26
CH ₂ (1)	2.99 (sg)			2.98

^aKBr disk: b: broad, s: sharp, sh: shoulder; ^bchemical shifts in ppm, TMS as internal reference, sg: singlet, d: doublet and dd: double doublet.

from the ligand to the complexes. In the ligand (1) and complexes (2) and (4), the O—H stretching vibration gave a single broad band in the 3425–3444 cm⁻¹ range. In the case of the ligand, a hydrogen bond occurs between N and H9 (see Figure 1 for the numbering). Complex (2) exhibits lattice water molecules [20]. The copper complex (3) shows several bands of mid intensity at 3349, 3303, 3230 and 3118 cm⁻¹ respectively. After recrystallisation in D₂O, the bands at 3349 and 3118 cm⁻¹ exhibit a very low intensity. These bands are assigned to the intercalated bridging water molecule [20], and this hypothesis is further confirmed by d.s.c. data given elsewhere in this publication. The ν (C=N) vibration appeared at 1618 cm⁻¹ for (1), (2) and at 1612 cm⁻¹ for (3). In the case of compound (4), this band is slightly shifted to 1620 cm⁻¹ and becomes a shoulder.

The spectrum of complex (2) exhibits two bands at 643 and 626 cm⁻¹ corresponding to the asymmetric and symmetric stretching Co—O (phenol) vibration [21], the (Co—N) occurs at 445 cm⁻¹ [22]. In the case of (3), this vibration gives a sharp, weak band at 466 cm⁻¹. The Cd—N vibration in (4) is located at 432 cm⁻¹ [23, 24]. Hence, the i.r. data favour the chelating mode of Schiff bases and four-coordinated central ions, with a near square planar geometry for (2) and (3) and a tetrahedral arrangement for cadmium ions in (4).

Electronic spectra

The spectra were recorded in DMF solution. The ligand only exhibits a band at 348 nm. The cobalt complex (2) shows a peak at 310 nm and two peaks in the visible region at 607 and 671 nm (16,475 and 10,300 cm⁻¹)

corresponding to pseudo-tetrahedral geometry [15, 25]. Compound (3) leads to an intense absorption at 300 nm followed by two weak peaks at 800 and 1015 nm (12,500 and 9,850 cm⁻¹) typical of square planar and/or tetrahedral species [24–26].

¹H-n.m.r. spectra

¹H-n.m.r. spectra of diamagnetic (1) and (4) were recorded in CDCl₃. The signal assignments are in good agreement with those previously reported [21, 27].

Thermal analysis

The d.s.c. data is reported in Table 3. The ligand (1) exhibits a single endothermic peak at 228 °C, corresponding to its melting point.

The d.s.c. diagram of complex (2) presents two endothermic peaks: the first at 223 °C and the second at 299 °C, immediately followed by an important exotherm at 304 °C. The endothermic peaks may be attributed to the breaking-up of the coordination bonds while the exothermic peak is due to the decomposition of the ligand. Two very prominent endotherms appear at *c.a.* 140 °C and are due to the departure of the water molecules.

The copper(II) complex (3) successively leads to one exotherm located at 140 °C, two endothermic peaks at 154 and 247 °C and, finally, an intense exothermic peak at 325 °C with a shoulder at 300 °C. An exothermic peak is also observed at 138 °C in the diagram of CuCl₂·2H₂O under the same experimental conditions [24] which is due to the release of the intercalated water molecule and this confirms the molecular formula of this compound.

The diagram of complex (4) shows a weak endotherm at 163 °C which may be attributed to the loss of a CdCl₂ molecule, followed by a large endothermic peak beginning at *c.a.* 300 °C as the complex decomposes exothermically.

Electrochemical behaviour

The cyclic voltammetric data are reported in Table 4 and some representative voltammograms are given in Figure 2.

Table 3. D.s.c. data

Compound	Peak (°C)	ΔH (kJ · mol ⁻¹)
(1)	228	+53.2
(2)	223	+15.5
	299	+31.2
	304	-44.5
	304	-44.5
(3)	140	-45.8
	154	+17.9
	247	+11.0
(4)	163	+4.6

Table 4. Voltamperometric results in DMF at 25 °C, ionic strength 0.1 mol.l⁻¹ (TEAP), results in V versus SCE, E_a: anodic; E_c: cathodic

Compound	Sweep	Oxidation		Reduction	
		E _a (V)	E _c (V)	E _a (V)	E _c (V)
(1)	1	1.38	0.18	-0.92	-1.67
	2		-0.40		0.91
(2)	1	1.32		-0.56	-1.65
	2	0.89			-0.96
(3)	1	1.46	0.14	-0.25	-1.68
		0.90			-0.88
		0.58			-0.46
		0.10			
	2	1.46	0.14	-0.25	-1.68
		0.90			-0.88
(4)	1	1.41	0.21	-0.36	-1.57
		0.42		-0.54	-1.32
					-1.07
					1.10
	2		-0.41		

The cyclic voltammetric study of *saldipH₂* (1) shows two cathodic peaks at -1.67 and +0.18 V respectively and two anodic peaks at -0.92 and +1.38 V. A second sweep in the same range (-1.80 to +1.80 V), leads to two new cathodic peaks at -0.40 and +0.91 V and then the reduction waves disappear. When limiting a new sweep in the -1.80 to 1.00 V range, the reduction peaks which appeared during the second sweep are absent. So these reductions peaks could be attributed to the oxidation product of the phenolic moiety obtained at 1.38 V. The peak at -1.67 V corresponds to the reduction of the imino part of the molecule [28], while its reoxidation occurs at -0.92 V.

When exploring the -2.00 to 1.90 V region, the cobalt(II) complex (2), shows two cathodic peaks: -1.65 and -0.96 V and three anodic peaks at -0.56 mV, +0.89 V and 1.32 V respectively. A second sweep, in the same range, leads to the appearance of two new cathodic peaks located at -0.41 and 1.08 V while a

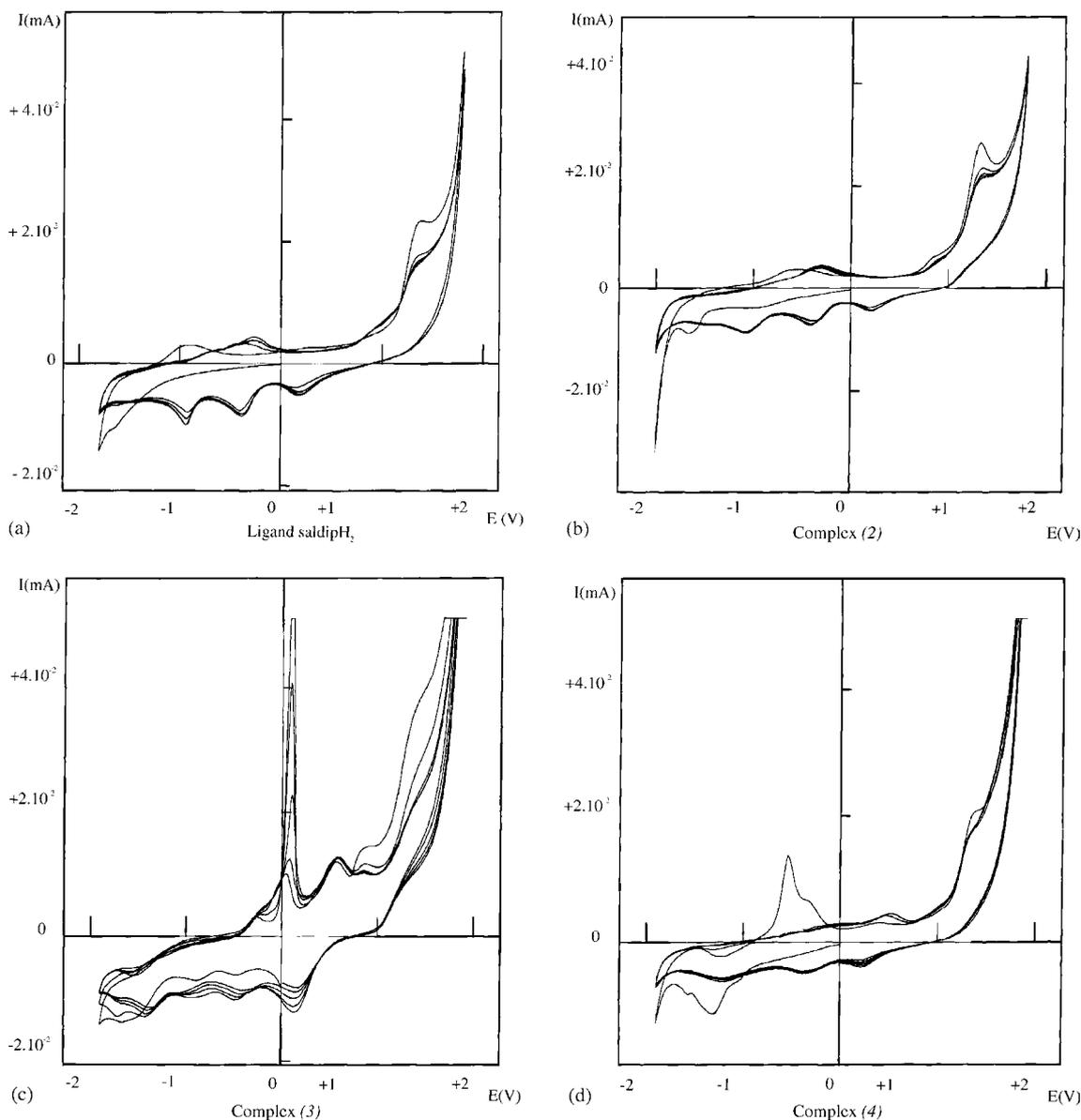


Fig. 2. Cyclic voltammograms.

third sweep from -2.00 to 1.00 V shows the disappearance of these two waves. The waves at -1.65 and $+1.32$ V (first sweep) are attributed to the ligand as well as the one at -0.41 V (second sweep). The couple $[\text{Co}^{\text{III}}(\text{saldip})]/[\text{Co}^{\text{II}}(\text{saldip})]$ produces two waves at -0.56 and 0.89 V respectively.

Under comparable experimental conditions (-1.90 to 1.90 V), the copper(II) complex (3), shows four cathodic peaks: -1.68 , -0.88 , -0.46 and 0.14 V and five anodic peaks located at -0.25 , 0.10 , 0.58 , 0.90 and 1.46 V. A new sweep in the range -1.20 to 1.20 V leads to the disappearance of the peak at 0.10 V. This indicates that the peak at -1.68 V is due to reduction of the coordinated copper ion while the peak at 0.10 V corresponds to oxidation of the metallic copper previously obtained. The anodic peak at -0.25 V results from the reoxidation of the reduced product obtained at -0.46 V [29–31]. The couple $[\text{Cu}_2^{\text{III}}(\text{saldip})]/[\text{Cu}_2^{\text{II}}(\text{saldip})]$ gives the anodic peak at 0.58 V [27] while the two waves at -0.46 and -0.88 V can be attributed to the successive reduction of the couples $[\text{Cu}_2^{\text{II}}(\text{saldip})]/[\text{Cu}_2^{\text{I}}(\text{saldip})]$ and $[\text{Cu}_2^{\text{I}}(\text{saldip})]/[\text{Cu}_2^{\text{0}}(\text{saldip})]$ [32].

Three cathodic peaks corresponding to the successive reduction steps of the complex species are observed in the cyclic voltammetric curves (recorded between -1.90 and 1.90 V) of compound (4) at -1.57 , -1.32 and -1.07 V respectively. In the meantime, the oxidation waves of the reduced products occur at -0.36 and -0.54 V. The electrochemical oxidation of this complex shows two peaks at 0.42 and 1.41 V. Finally, the oxidised compound obtained at this stage, is reduced at 0.21 V. A second sweep in the same range shows the appearance of two new cathodic peaks, as described above for the compound (2).

These results show unambiguously that the waves relative to the ligand are shifted in all complexes. Moreover, some new waves appear in the voltammograms of the complexes. This behaviour is consistent with those described for similar complex species [33, 34]. For instance, Gili *et al.* pointed out similar electrochemical results for Schiff bases copper(II) complexes [28]: the oxidation wave occurs at 1.03 V for the free ligand and at 0.84 V in a cupric complex. In addition, we note that this electrochemical behaviour is consistent with the chemical structures below.

Proposed structures

On the basis of the structural and electrochemical studies the following structures are proposed. In the mononuclear cobalt(II) complex $[\text{Co}(\text{saldip})] \cdot 2\text{H}_2\text{O}$ (2), the cobalt is linked to the ionised hydroxyl and coordinated to the N atoms, with a quite square planar geometry, and the two water molecules being considered as lattice molecules. In the case of compound (3), $[\text{Cu}_2(\text{saldip})_2(\text{H}_2\text{O})]$, the water molecule acts as a bridge between the two symmetric parts of the complex molecule. Finally, the complex $[(\text{CdCl}_2)_2(\text{saldipH}_2)] \cdot \text{CdCl}_2$ (4) in which a CdCl_2 molecule is intercalated

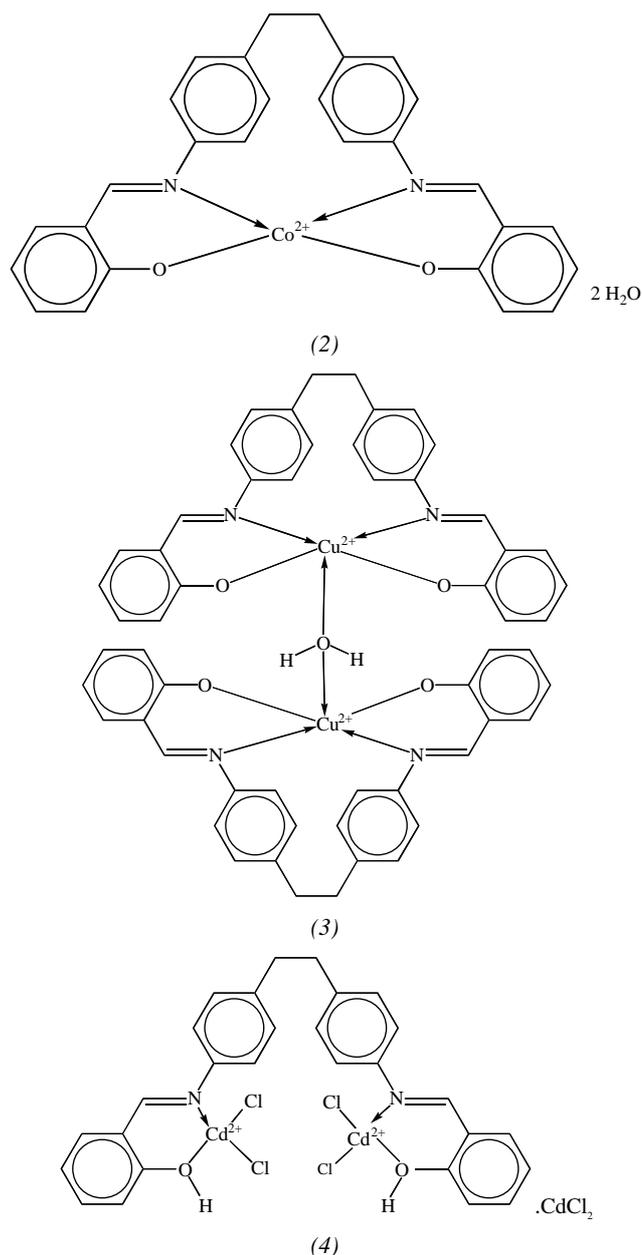


Fig. 3. Proposed structures for the complexes.

inside the complex species while two Cd^{2+} ions are linked to the non-deprotonated ligand and the cadmium ions showing a tetrahedral environment (Figure 3).

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