



Synthesis, Characterization, and Electrochemical Study of Complexes with 4,4'-Bis(Salicylideneimino) Diphenylether and Cobalt(II), Copper(II), Zinc(II), and Cadmium(II)

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Synthesis, Characterization, and Electrochemical Study of Complexes with 4,4'-Bis(Salicylideneimino) Diphenylether and Cobalt(II), Copper(II), Zinc(II), and Cadmium(II)

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The 4,4'-bis(salicylideneimino) diphenyl ether is a N_2O_3 Schiff base but it acts as a tetradentate ligand. Its complexes with cobalt (II), copper(II), zinc(II), and cadmium (II) were characterised using spectroscopic determinations, d.s.c. and cyclic voltammetry. In these compounds, the coordination occurs through the non-ionised phenolic hydroxyl of the ligand and the nitrogen atom of the azomethine moiety. These new complexes should be formulated $[CuCl_2(H_2L)] \cdot H_2O$, $[(CoCl_2)_2(H_2L)(H_2O)_4] \cdot 2H_2O$, $[Zn_2Cl_2(H_2L)]$ and $[Cd(H_2L)]Cl_2$ respectively. The copper(II) and cadmium(II) complexes are mononuclear while the cobalt(II) and zinc(II) appeared to be binuclear species. The anodic oxidations of cobalt (II), zinc(II), and cadmium(II) compounds show only one peak attributed to the oxidation of the phenolic moiety of the ligand. In addition, the copper complex $[CuCl_2(H_2L)] \cdot H_2O$ exhibits two peaks at +680 mV (ECS) and +965 mV (ECS) corresponding to the complexed couples Cu^{II}/Cu^{III} and Cu^I/Cu^{II} .

Keywords Complexes, cyclic voltammetry, Schiff base, tetradentate

INTRODUCTION

Among metal complexes, Schiff bases coordination compounds showing an imino moiety in their structure were widely used in medicine, for corrosion prevention, metal recovery, as well as to treat nuclear wastes. As these bases

show a great ability to complex many metal ions, they also may be useful for water treatment (Wilkinson, 1987).

Since the pioneering work of (Feiffer et al., 1933) a large series of Schiff bases coordination compounds was described. More recently, (Yudhvir et al., 1994) have published the synthesis and the characterisation of bis(2,5-dihydroxyacetophenone ethylenediamine (daen), a tetradentate Schiff base, and of its monomeric and dimeric copper(II) complexes. In both cases, the cupric ion showed a tetrahedral arrangement binding through O and N atoms of the ligand.

S. Samal et al. (2002) have prepared Schiff's bases resins by reacting o-hydroxyacetophenone 4,4'-diamino diphenylether with successively ethanal and 2-furaldehyde. They were able to isolate copper (II) from a mixture of Cu(II) and Ni(II) ions. Starting from 4,4-bis[2-(aminomethyl) pyridylisonitrosoacetyl]diphenylmethane and 4,4-bis(2-hydroxy-5-methylphenylaminoisonitrosoacetyl)diphenylmethane, (Karipcin et al., 2002) obtained a series of complexes with Co(II), Ni (II), and Cu(II). The phenolic hydroxyl was not deprotonated in the case of Ni(II) complex, which is a mononuclear species. The binuclear complexes with cobalt and copper are coordinated through deprotonated phenolic hydroxyl.

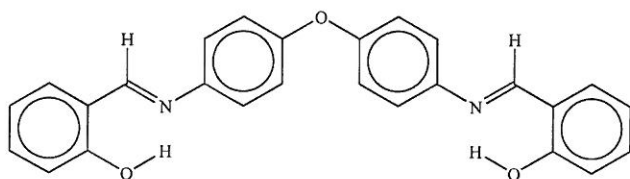
Two heptadentate ligands were described (Keypour et al., 2002): the ligand tris(3-salicylideneimino) propylamine and tris(3-(4'-hydroxysalicylideneimino)-propyl)amine coordinated through the three phenolic hydroxyls, but two of them were ionised. All these complexes were insoluble in aqueous media. (Keypour et al., 2003, 2004) reported the coordination of zinc(II) and magnesium(II) by macrocyclic heptaaza Schiff-base with two aminoethyl pendant arms.

The tetradentate ligands 4,4'-bis(salicylideneimino)diphenylmethane (sal-dadpmX) lead to complexes of general formula: $[M_2(sal-dadpmX)_2]$ where $X = H, CH_3, OCH_3, Cl$ and $M = Cu(II), Ni(II), Co(II), dioxoranium(VI)$ (Ramachandraith et al., 1989). While the copper(II) complexes were found to

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FIG. 1. Chemical structure of the ligand H_2L .

be pseudotetrahedral species, the Co(II), Ni(II) and dioxoranium(VI) exhibited an octahedral geometry. Tetradentate Schiff base ligands deriving from 4-aminoantipyrine and 2-aminophenol or 2-aminothiophenol chelated Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Vo(II) ions. The corresponding complexes exhibited a higher antimicrobial activity than the ligands alone (Raman, 2001).

(Ando et al., 2004) have recently reported the characterisation of a series of pentadentate Schiff base derived from salicylaldehyde and their complexes with oxovanadium(IV).

In this paper, we report the synthesis and the characterisation of new complexes with Co(II), Cu(II), Zn(II) and Cd(II) of a tetradentate Schiff base: 4,4'-bis(salicylèneimino) diphenyl ether (H_2L) whose structure is given on Figure 1. Their electrochemical behaviour in organic media is described.

RESULTS AND DISCUSSION

The main analytical data are given in Table 1. The copper (II) compound synthesised as described above, differs from the complex obtained by (Yoshida et al., 1999) in DMF as solvent, which was found to be a polymeric species $[CuL]_n$. The spectral data of our complexes is summarised in Table 2.

Infrared Spectra

In the ligand and in all complexes the phenolic O–H stretching vibration is located between 3500 and 3100 cm^{-1} . Some differences are observed: in the spectrum of the ligand H_2L (1) the low intensity band located at 3444 cm^{-1} is narrow. The spectrum of the complex (2) exhibits a very large and intense band with a maximum at 3407 cm^{-1} . This band is unsymmetrical in the case of the copper complex (3) with

small shoulders at lower wavenumbers. The zinc compound (4) shows a smaller band around 3440 cm^{-1} and in the case of the cadmium(II) compound (5) this band is shifted to 3483 cm^{-1} .

As expected, the aromatic ring vibrations are not modified when passing from ligand to complexes. The stretching vibration band of the C=N bond is observed at c.a. 1620 cm^{-1} as a single sharp band in the case of the ligand (1) and the complex (3). In the other spectra, this band appears with one or two close shoulders. This indicates that the nitrogen atoms of the two azomethine groups are coordinating atoms.

The stretching vibration band of the ether moiety remained unchanged in the whole series. Consequently, this oxygen atom is not involved in the coordination and the 4,4'-bis(salicylèneimino) diphenyl ether H_2L acts as a tetradentate ligand.

$^1\text{H-N.M.R.}$ Spectra

The ^1H n.m.r. spectrum of the ligand (Table 2) shows the singulet corresponding to the two phenolic protons at 13.3 p.p.m. (Sanmartin et al., 2000). In the case of the diamagnetic Zn(II) and Cd(II) compounds we note that this signal is slightly shifted down due to complexation. In the mean time, we note that the peak of the proton relative to CH–N group is slightly shifted to higher values. These observations are in agreement with the structures proposed for the corresponding complexes.

Thermal Analysis

The d.s.c. data is reported in Table 3. The melting point of the ligand (1), with a very thin symmetric endothermic peak, is observed at 212°C .

The d.s.c. diagram of the compound (2) presents a very weak endothermic peak at 159°C followed by an important unsymmetrical endotherm at 188°C , a feeble endotherm at 217°C and finally a strong endothermic peak at 241°C . The first peak corresponds to the departure of the unbounded water molecules. In the same experimental conditions, the hexahydrated cobalt(II) chloride exhibits a wide endothermic peak at c.a. 185°C due to loss of coordinated water molecules.

TABLE 1
Analytical data

| Compounds | | Yield (%) | Color | M.P. ($^\circ\text{C}$) | C % (cald.) | H % | N % |
|---|-----|-----------|--------|---------------------------|-------------|-----------|-----------|
| Ligand (H_2L) | (1) | 90 | Yellow | 212 | 76.4 (76.5) | 4.6 (4.9) | 7.0 (6.9) |
| $[(\text{CoCl}_2)_2(\text{H}_2\text{L})(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ | (2) | 40 | Green | >260 d | 39.5 (40.2) | 4.9 (4.2) | 3.6 (3.6) |
| $[\text{CuCl}_2(\text{H}_2\text{L})] \cdot \text{H}_2\text{O}$ | (3) | 40 | Brown | >240 d | 57.4 (55.7) | 3.9 (3.9) | 6.0 (5.0) |
| $[\text{Zn}_2\text{Cl}_2(\text{H}_2\text{L})]$ | (4) | 45 | Orange | >260 d | 51.7 (51.2) | 3.7 (3.3) | 4.7 (4.6) |
| $[\text{Cd}(\text{H}_2\text{L})]\text{Cl}_2$ | (5) | 70 | Orange | >260 d | 52.2 (52.2) | 3.4 (3.4) | 4.8 (4.7) |

d: decomposition.

TABLE 2
Spectral data

| Compound | | (1) | (2) | (3) | (4) | (5) |
|---|--------------------------|---------|--------|------|---------|---------|
| I.R. spectra ^a | Vibration | | | | | |
| | $\nu(\text{OH})$ | 3444 w | 3407 b | 3448 | 3443 | 3483 |
| | Benzene rings | 3053 | 3065 | 3050 | 3064 | 3056 |
| | | 835 | 836 | 835 | 837 | 833 |
| | | 750 | 750 | 750 | 759 | 749 |
| | | 1621 | 1620 | 1620 | 1633 | 1619 |
| | $\nu(\text{C}-\text{N})$ | 1263 | 1262 | 1262 | 1252 | 1260 |
| | $\delta(\text{OH})$ | 1283 | 1283 | 1283 | — | 1283 |
| | $\nu(\text{C}-\text{O})$ | 1189 | 1188 | 1188 | 1178 | 1188 |
| | $\nu(\text{C}-\text{N})$ | | | | | |
| NMR ¹ H spectra ^b | Chemical shift | | | | | |
| | H phenol | 13.3 s | — | — | 13.1 | 13.1 |
| | CH=N | 8.7 | — | — | 9.0 | 9.0 |
| | H aromatic | 7.5–6.9 | — | — | 7.7–6.6 | 7.7–6.9 |

^aKBr disk, cm^{-1} ; b = broad, w = weak, sh = shoulder.^bChemical shift in ppm (TMS); s = singlet.

The same phenomenon is observed in the case of the complex (2) for the endotherm at 188°C. The last exothermic peak is due to the decomposition of the molecule.

In the case of the copper complex (3), the first exothermic peak at 133°C is due to the release of the water molecules as previously described (Haffar, 2004; Bouet et al., 1996). The

other peaks, due to its decomposition, are observed at 214°C (endothermic) and 284°C (very large exotherm).

The zinc complex (4) is stable until 320°C. A narrow endothermic peak is observed at 323°C, followed immediately by an exothermic one at 330°C. The first is due to the breaking of the binuclear species and the second to a decomposition process.

Finally, the d.s.c. diagram of the cadmium complex (5), shows two peaks located at 209°C and 382°C showing a weak endothermic effect. The first is unsymmetrical with a shoulder at the beginning due to the break of the coordination bonds and the melting of the free ligand.

TABLE 3
D.s.c. data

| Compound | Peaks (°C) | ΔH ($\text{kJ} \cdot \text{mol}^{-1}$) |
|---|------------|--|
| (1) | 212 | +55 |
| (2) | 159 | +3 |
| | 188 | +144 |
| | 217 | +4 |
| | 241 | +122 |
| (3) | 133 | −71 |
| | 214 | +14 |
| | 284 | −42 |
| (4) | 323 | +63 |
| | 330 | −178 |
| (5) | 209 | +29 |
| | 382 | +24 |
| $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ | 62 | −125 |
| | 185 | endo |
| $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}^a$ | 138 | −133 |
| | 185 | +30.7 |

^aFrom reference Haffar et al. (2004) and Bouet et al. (1996).

Cyclic Voltammetry

The cyclic voltammograms were recorded at $25 \pm 0.2^\circ\text{C}$ in DMF and the ionic strength was maintained at $0.1 \text{ mol} \cdot \text{L}^{-1}$ with Et_4NClO_4 (TEAP) as supporting electrolyte. The data are reported in Table 4 and the voltammograms are given in Figure 2.

The cyclic voltammetric study of H_2L (1) from +1700 mV to −1600 mV (vs. SCE) shows an anodic peak at +1180 mV and a cathodic one at −1020 mV. The oxidation peak corresponds to the oxidation of the phenolic group, while the second peak is attributed to the reduction of the imine moiety (Gili et al., 1996). During the second sweep, the reduction of the oxidised phenolic group occurs at +400 mV.

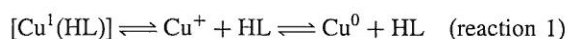
During a sweep from −1600 to +1700 mV, the cobalt compound (2) exhibits a cathodic peak at −1270 mV and two anodic peaks at −150 and +1330 mV respectively. When the scan is limited from 0 to −1000 mV, the first anodic peak at −150 mV is absent and consequently this

TABLE 4
Voltamperometric results in DMF at 25°C, ionic strength 0.1 mol · L⁻¹ (TEAP), results in mV vs SCE., *E*_a: anodic; *E*_c: cathodic

| Compound | Sweep | Oxidation | | Reduction | |
|----------|-------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| | | <i>E</i> _{pa} (mV) | <i>E</i> _{pc} (mV) | <i>E</i> _{pa} (mV) | <i>E</i> _{pc} (mV) |
| (1) | 1 | +1480 | | | -1020 |
| | 2 | | | | -400 |
| (2) | 1 | +1330 | | -150 | -1270 |
| | 2 | | -400 | | |
| (3) | 1 | +1460 | +380 | -140 | -1450 |
| | | +960 | | | |
| | | +680 | | | |
| | | +210 | | | |
| | 2 | | | | -600 |
| (4) | 1 | +1570 | | -670 | -900 |
| | 2 | | | | -110 |
| (5) | 1 | +1560 | | -340 | -1400 |
| | 2 | | | | -1080 |
| | | | | | -250 |

peak corresponds to the reoxidation of the phenolic reduced species obtained at -1270 mV. The following sweeps (-1600 to +1700 mV) show a new peak at -400 mV with growing intensity. Under similar experimental conditions, CoCl₂ shows a cathodic peak at -1500 mV (SCE) and an anodic one at -100 mV (Djebbar-Sid et al., 2001).

The copper(II) complex (3) shows two cathodic peaks at -1450 and 380 mV and five anodic peaks located at -140, +210, +680, +960 and +1460 mV respectively. The anodic peaks at +680 and 960 mV correspond to the oxidation of the cupric ions (Djebbar-Sid et al., 2001; Gullotti et al., 1972; Fernandez-G et al., 2002; Pereira et al., 1998; Nicholson and Schain, 1964; Djebbar-Sid et al., 1997). A new study between 0 to +750 mV shows that the peak at 380 mV is due to the reduction of the previously oxidised copper(III) (Raman et al., 2001). When several sweeps between -1600 mV and +1700 mV are performed successively, we note that the intensities of the peaks located at -1450 and +210 mV are diminishing. It is well known that the Cu^{II}/Cu^I reaction in most CuN₂O₂ coordination complexes is quasi-reversible in nature due to the fact that the [Cu^IL₂] species are chemically decomposed to a copper ion (reaction 1), which subsequently is reduced to copper metal (Aguilar-Martinez et al., 2001).



Finally, a new sweep, limited from -1000 to +1000 mV leads to the disappearing of two peaks at -140 and +210 mV, respectively. These two peaks are due to the reoxidation of

the species obtained from the phenolic moiety at -1450 mV (Samal et al., 2002; Raman et al., 2001; Gullotti et al., 1972; Anderson et al., 1984).

A scan in the range 0 to -1600 mV in the case of the compound (4) with zinc, shows a reduction cathodic peak at -900 mV and an anodic peak at -670 mV due to the oxidation of the metallic zinc previously formed. A new scan from 0 to +1700 mV leads to a single anodic peak at +1570 mV (phenol group oxidation). Successive sweeps from -1660 mV to +1700 mV show the appearance of a new cathodic peak at -110 mV, which results of the reoxidation of the reduced phenolic group. In this cyclic voltammograms, the oxidation curve and the reduction one cross over; this may be due to the deposition of reduced material on the surface of the electrode (Yudhuir et al., 1994) and to the presence of bridging chloride in the structure of this binuclear complex. A similar behaviour with very poorly defined peaks was observed in some zinc complexes obtained from Schiff bases (Lutta and Kagwanja, 2001).

Finally, in the range -1600 to +1700 mV, the cyclic voltammogram of the cadmium complex (5) exhibits two cathodic peaks: -1400 mV and -1080 mV and two anodic peaks at -340 mV and +1560 mV. The peak corresponds to the oxidation of the phenolic part of the Schiff base. At a second sweep shows that the peak at -1400 mV is absent and that the two peaks at -1080 mV and -340 mV are slightly shifted to higher potential values; in the mean time, their intensities decrease because of a partial blocking of the electrode (Nicholson and Schain, 1964).

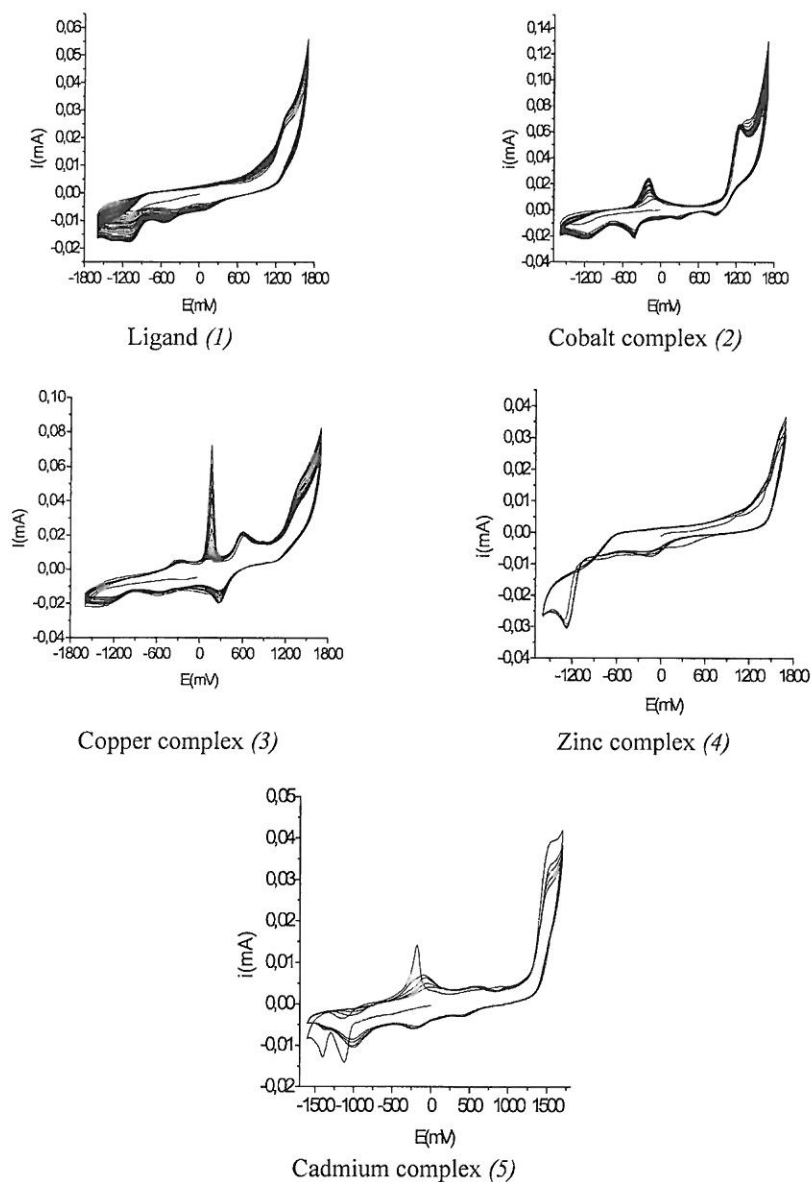


FIG. 2. Cyclic voltammograms.

Proposed Structures

Though the ligand H_2L is a potent N_2O_3 pentadentate ligand, only the two symmetrical azomethine systems could coordinate metal ions and this compound finally acts as a N_2O_2 tetradentate ligand.

In the complex (2), the cobalt ions show an octahedral environment (Figure 3). Two water molecules are located outside the complexes and four molecules are bounded to the metal ions. These two types of molecules lead to the two endothermic peaks at 159 and 188°C observed in the d.s.c. diagram. This

feature is also correlated with the shape of the O–H stretching band in the infrared spectrum (Sanmartin et al., 2001).

The cupric species (3) shows a typical distorted octahedral geometry. The presence of outer water molecule is confirmed by the exothermic peak at 133°C in the d.s.c. diagram as well as the shape of the $\nu(O-H)$ vibration band (Boca et al., 2003).

The zinc complex (4) is a binuclear halogen bridging species: $[Zn_2Cl_2(H_2L)]$. The infrared spectrum show a broad band corresponding to the hydroxyl stretching vibration and in the 1H NMR spectra, the signal at 13.1 p.p.m. remains

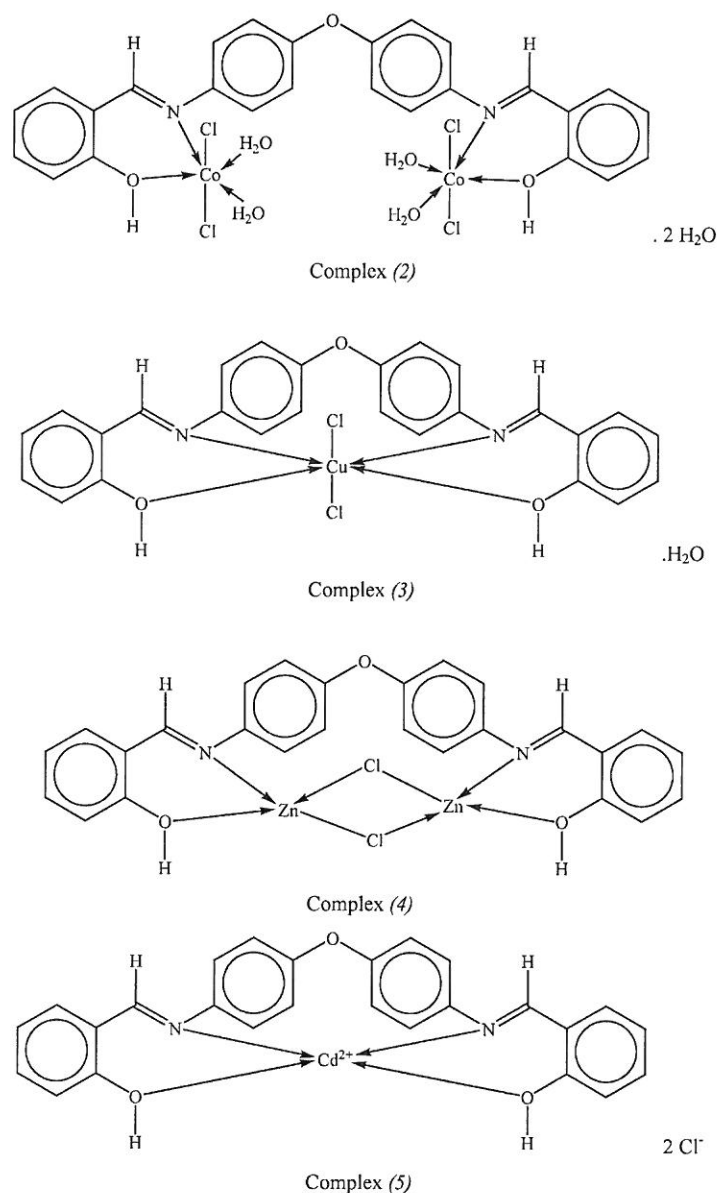


FIG. 3. Proposed structures for the complexes.

quite unchanged when passing from the ligand to the complex and consequently the phenolic hydroxyl is not ionised. The number of relative proton is less than 2 as it has been observed in cobalt(II) complexes (Felicio, 2001). The molecule is very stable without any thermal phenomenon under 320°C in d.s.c. study. The two Zn(II) ions present a tetrahedral geometry.

The cadmium complex (5) $[\text{Cd}(\text{H}_2\text{L})]\text{Cl}_2$ shows a tetrahedral arrangement around the cadmium ion with two chloride ions in the outer sphere of the complex. In the NMR spectra, the phenolic protons give a singlet at 13.1 p.p.m. like in ligand with a slightly modified intensity, like in zinc complex (4).

EXPERIMENTAL

Chemicals

All reagents and solvents were analytical grade and used without further treatment.

Physical Measurements

The measurements were done as previously described (Haffar et al., 2004). The ^1H NMR spectra were recorded using a Bruker Avance DRX 500 MHz spectrometer (Service Commun d'Analyses Spectroscopiques, Université d'Angers).

Synthesis of the Ligand

The ligand was prepared according to the methods previously reported by Sharma (Yudhuir, 1994) and Gili (1996) by mixing 4,4'-diamino diphenylether and salicylaldehyde in MeOH at 50°C in a 1:2 ratio. The product was recrystallised from MeOH-CHCl₃ (50% V/V). The main analytical data are reported in Table 1; they are in good agreement with that previously described (Yoshida et al., 1999).

Synthesis of the Complexes

To a solution of 1 mmole of the ligand (CHCl₃, 40 mL) was added drop-wise a solution of 1 mmole of the hydrated chlorides (EtOH, 10 mL). After heating at 50°C for 7 h, the solution was kept at room temperature for a night. Then the complexes precipitated down and were removed by filtration, washed with a hot mixture of methanol and chloroform (60/40 V/V). Their purity was verified using t.l.c. with toluene/EtOH (50/50 V/V) as solvent. They were finally dried under reduced pressure.

CONCLUSION

We have described four new complexes obtained with 4,4'-bis(salicyleneimino) diphenyl ether. This compound is a N₂O₃ Schiff base but acts as a N₂O₂ tetradentate ligand towards cobalt(II), copper(II), zinc(II) and cadmium(II) ions. In every case, the coordination occurs through the N azomethine atom and the oxygen atom of the phenolic hydroxyl, which is not ionised. Each complex presents its own structure. The cobalt and the zinc species are binuclear while copper and cadmium complexes are mononuclear. Only Co(II) and Cu(II) compounds are hydrated species.

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