Unusual copper(II) coordination mode from a potential Schiff-base reaction

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ABSTRACT

The Schiff-base ligands (**1–3**) formed from the reaction of 3-hydroxybenzaldehyde with three alkyl diamines have been synthesised and characterised. They are stable both in solution and in the solid state for several weeks, with no degradation to the starting amines and aldehyde observed. The reactions of the three Schiff-base ligands with various MX_2 salts (M = Cu, Ni or Zn; X = chloride, perchlorate or acetate) resulted in the cleavage of the imine bond and formation of metal–amine complexes, as well as the entrapment of a two coordinate $CuCl_2$ molecule within the lattice in one particular case.

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1. Introduction

Macrocyclic and macroacyclic compounds have attracted much attention in recent years due to their role in furthering the understanding of molecular processes that occur in biochemistry, catalysis and material science to name but a few, and the review by Vigato and Tamburini describes the recent publications relating to these compounds [1]. Molecular architectures featuring the helical arrangements of multidentate ligands around one or more metal centres is one of the goals of supramolecular chemistry [2–5]. Starting from simple dinucleating ligands, complex three-dimensional systems have been prepared using self-assembly, molecular recognition processes and the template effect [6–9]. Although many bi- and tridentate ligands have been prepared with the view of constructing helicates *via* the reaction with metal ions, the complexes usually formed are mono-, bi- or tri-nuclear metal complexes [10–13].

Salen-type ligands are interesting tetradentate ligands with a rich coordination chemistry [1,14–17]. They present versatile electronic, steric and lipophilic properties. They may be prepared easily by the condensation of an aromatic *o*-hydroxyaldehyde and a diamine. The hydrophilic–lipophilic balance can be easily tuned by choosing the appropriate amine precursors and ring substituents of the aromatic aldehyde. Salen complexes of various metal ions are widely used as catalysts for organic transformations [17–19] such as polymerisations, epoxidations and aziridinations, as well

as attracting attention as building blocks for supramolecular chemistry [20–22]. The main disadvantage of Schiff-base ligands is that they can hydrolyse in solution [23]. This instability can be removed by reducing the Schiff-base ligand to give the corresponding amine.

Our interest in this family of ligands was recently aroused by the unusual zwitterionic structures formed between organotin(IV) Lewis acids and various tetradentate Schiff-base ligands [24]. We were particularly intrigued by the fact that there was no account in the literature for the formation of Schiff-base ligands based on the compound 3-hydroxybenzaldehyde, as we believed that such ligands afforded the possibility of binding through the hydroxyl group on the three position in a manner similar to that described in the organotin work of Cunningham et al. [24]. In this paper, we report the synthesis and characterisation of three such Schiff-base ligands (**1**, **2** and **3**, Fig. 1), their reactions with various transition metal salts and the structural characterisations of the products formed.

2. Experimental

2.1. General

^{1}H and ^{13}C NMR (δ ppm; *J* Hz) spectra were recorded on a Bruker Avance 300 MHz NMR spectrometer using saturated $CDCl_3$ solutions with Me_4Si reference, unless indicated otherwise. Infrared spectra (cm^{-1}) were recorded as KBr discs or liquid films between KBr plates using a Nicolet Impact 400D FT-IR spectrometer. All UV/VIS spectra were recorded on a Shimadzu UV-160A spectrometer. Melting point analysis was carried out using a Stewart Scientific SMP 1 melting point apparatus and are uncorrected. Microanalysis was carried out at the Microanalytical

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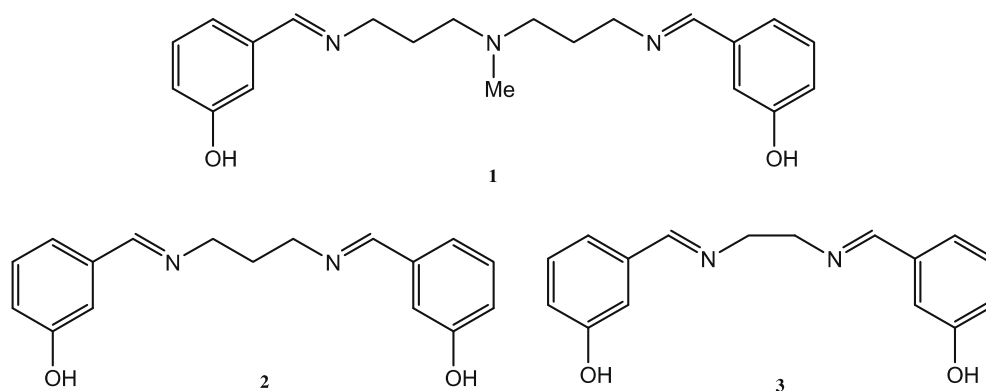
Fig. 1. Schiff-base ligands **1–3**.

Laboratory of either University College, Dublin or the National University of Ireland Cork. Standard Schlenk techniques were used throughout. Starting materials were commercially obtained and used without further purification. The synthesis of the compound 3,3′-(1E,1′E)-ethane-1,2-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)diphenol (**3**) and of the copper(II) acetate monopyridine complex have been described in the literature previously [25,26].

2.2. Synthesis

2.2.1. 3,3′-(1E,1′E)-3,3′-(methylazanediyl)bis(propane-3,1-diyl)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)diphenol (**1**)

A solution of 3-hydroxybenzaldehyde (5.0 g, 40.9 mmol) and 3,3′-diamino-N-methyldipropylamine (2.97 g, 20.4 mmol) in methanol (150 mL) were placed in a round-bottomed flask. The yellow solution was stirred for 3 h. At this point, the solvent was removed under reduced pressure to leave a yellow viscous oil. Yield 95% (6.89 g, 19.5 mmol). *Anal.* Calc. for $(C_{21}H_{27}N_3O_2)_2$ · CH$_3$OH (738.96): C, 69.89; H, 7.91; N, 11.37. Found: C, 69.99; H, 7.55; N, 11.33. ^{1}H NMR (300 MHz, d_6-DMSO, 25 °C): δ = 1.71 [4H, m, CH$_2$CH$_2$CH$_2$], 2.13 [3H, s, NCH$_3$], 2.32 [4H, t, CH$_3$NCH$_2$CH$_2$, J = 7.0 Hz], 3.53 [4H, t, NCH$_2$CH$_2$CH$_2$, J = 7.0 Hz], 6.83 [2H, m, ArH], 7.16 [6H, m, ArH], 8.21 [2H, s, HC=N], 9.55 ppm [2H, br s, OH]. ν_{max} (KBr) 2946, 1645, 1582, 1456, 1375, 1274, 1031, 785, 690 cm^{-1}.

2.2.2. 3,3′-(1E,1′E)-propane-1,3-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)diphenol (**2**)

A solution of 3-hydroxybenzaldehyde (4.0 g, 32.7 mmol) dissolved in acetonitrile (25 mL) and 1,3-diaminopropane (1.21 g, 16.3 mmol) in acetonitrile (25 mL) were placed in a round-bottomed flask, and the resulting yellow solution was stirred at room temperature. After 5 min, a solid started to precipitate and stirring was continued for a further 45 min. At this point, the white solid was filtered, washed with cold acetonitrile and dried in a vacuum oven. Yield 93% (4.29 g, 15.2 mmol). *Anal.* Calc. for $(C_{17}H_{18}N_2O_2)_4$ · H$_2$O (1147.36): C 71.18, H 6.50, N 9.77; found C 71.53, H 6.36, N 9.83. ^{1}H NMR (300 MHz, d_6-DMSO, 25 °C): δ = 2.01 [2H, m, NCH$_2$CH$_2$], 3.68 [4H, t, NCH$_2$CH$_2$, J = 7.0 Hz], 6.92 [2H, m, ArH], 7.24 [6H, m, ArH], 8.33 [2H, s, HC=N], 9.64 ppm [2H, br s, OH]. ν_{max} (KBr) 3056, 2852, 1650, 1596, 1456, 1395, 1275, 1096, 785, 690 cm^{-1}.

2.2.3. 3,3′-(1E,1′E)-ethane-1,2-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)diphenol (**3**)

A solution of 3-hydroxybenzaldehyde (2.0 g, 16.4 mmol) dissolved in acetonitrile (25 mL) and 1,2-diaminoethane (0.49 g, 8.1 mmol) in acetonitrile (50 mL) were placed in a round-bottomed

flask, and the resulting yellow solution was stirred at room temperature. After 5 min, a solid started to precipitate and stirring was continued for a further 45 min. At this point, the white solid was filtered, washed with cold acetonitrile and dried in a vacuum oven. Yield 93% (2.03 g, 7.6 mmol). ^{1}H NMR (300 MHz, d_6-DMSO, 25 °C): δ = 3.84 [4H, s, NCH$_2$], 6.83 [2H, m, ArH], 7.16 [6H, m, ArH], 8.24 [2H, s, HC=N], 9.03 ppm [2H, br s, OH]. ν_{max} (KBr) 3051, 2929, 1647, 1595, 1456, 1275, 1082, 779, 685 cm^{-1}.

All complexation reactions were carried out by a general method using various copper(II), nickel(II) and zinc(II) salts as starting materials.

2.3. General synthesis of metal complexes

A solution of **1**, **2** or **3** (1 mmol) in methanol (10 mL) and the metal salt (1 mmol) in methanol (10 mL) were placed in a round-bottomed flask, and the resulting solution was stirred at room temperature for 45 min. After this time, the solution was allowed to stand and the solvent level was allowed to reduce. On almost complete reduction, acetonitrile (10 ml) was added and a coloured solid precipitated after 5 min. This was removed by filtration and the filtrate was allowed to reduce slowly. After a few days, crystals started to precipitate. The crystals were removed by filtration, washed with cold acetonitrile and dried in a vacuum oven.

2.3.1. Reaction of **1** with CuCl$_2$ · 2H$_2$O (**4**)

A solution of **1** (0.57 g, 1.62 mmol) in methanol (10 mL) and CuCl$_2$ · 2H$_2$O (0.28 g, 1.62 mmol) in methanol (10 mL) were used in the reaction. After standing for several days, dark blue crystals started to precipitate. The crystals were removed by filtration, washed with cold acetonitrile and dried in a vacuum oven. Yield 0.086 g. Single crystals, suitable for X-ray crystallographic analysis, were obtained by the slow evaporation of an acetonitrile solution of **4**. *Anal.* Calc. for $C_{29}H_{79}Cl_9Cu_5N_{12}O_2$ (1264.82): C, 27.54; H, 6.30; N, 13.29. Found: C, 27.34; H, 5.98; N, 12.85. ν_{max} (KBr) 3360, 1666 cm^{-1}.

2.3.2. Reaction of **1** with Cu(ClO$_4$)$_2$ · 6H$_2$O (**5**)

On adding the perchlorate solution, a brown solid precipitated. The suspension was stirred until the brown solid redissolved. After standing for two days, addition of acetonitrile to the solution caused the precipitation of the starting copper(II) perchlorate from the solution.

2.3.3. Reaction of **1** with Cu(OAc)$_2$ · H$_2$O (**6**)

On standing for several days, blue crystals precipitated. The crystals were removed by filtration, washed with cold acetonitrile

and dried in a vacuum oven. The infrared spectrum of the crystals showed that they were the starting copper(II) acetate material.

2.3.4. Reaction of **2** with CuCl₂ · 2H₂O (**7**)

The reaction involved 0.5 g of **2** and 0.30 g of $CuCl_2 \cdot 2H_2O$ in methanol. A dark green solution resulted, from which a dark green solid precipitated after several days. The solid was removed by filtration, washed with cold methanol and dried in a vacuum oven. Analysis revealed that the complex was the 1,3-diaminopropane complex of copper chloride, $Cu(H_2NCH_2CH_2CH_2NH_2)Cl_2 \cdot 2H_2O$. Yield 0.34 g. ν_{max} (KBr) 3435, 3275, 2874, 1572, 1402, 1275, 1164, 1027, 664 cm^{-1}.

2.3.5. Reaction of **2** with Cu(ClO₄)₂ · 6H₂O (**8**)

On standing for several days, purple crystals precipitated. The crystals were removed by filtration, washed with cold acetonitrile and dried in a vacuum oven. The infrared spectrum of the crystals showed that they were the starting copper(II) perchlorate salt.

2.3.6. Reaction of **2** with Cu(OAc)₂ · H₂O (**9**)

The reaction involved 0.48 g of **2** and 0.34 g of $Cu(OAc)_2 \cdot H_2O$. On standing for several days, blue/purple crystals resulted. The crystals were removed by filtration, washed with cold acetonitrile and dried in a vacuum oven. Yield 0.213 g. *Anal.* Calc. $C_{21}H_{50}Cu_3N_6O_{13}$ (785.29): C, 32.12; H, 6.42; N, 10.70. Found: C, 32.37; H, 6.15; N, 10.70. ν_{max} (KBr) 3410, 3259, 2971, 1613, 1571, 1420, 1331, 1188, 1041, 674 cm^{-1}.

2.3.7. Reaction of **3** with CuCl₂ · 2H₂O (**10**)

On standing for several days, light blue solid precipitated. The solid were removed by filtration and dried in a vacuum oven. Analysis of the compound showed that it was the 1,2-diaminoethane complex of copper chloride, $Cu(H_2NCH_2CH_2NH_2)Cl_2 \cdot 2H_2O$. Yield 0.213 g. m_{max} (KBr) 3446, 3299, 2968, 1570, 1270, 1043, 681 cm^{-1}.

2.3.8. Reaction of **3** with Cu(ClO₄)₂ · 6H₂O (**11**)

The reaction was carried out using 0.1 g of **3** and 0.158 g of $Cu(ClO_4)_2 \cdot 6H_2O$ in ethanol. On standing for several days, a purple solid precipitated, which was removed by filtration, washed with cold ethanol and dried in a vacuum oven. Yield 0.055 g. Analysis showed that the purple solid was the 1,2-diaminoethane complex of copper perchlorate, $Cu(H_2NCH_2CH_2NH_2)(ClO_4)_2 \cdot 2H_2O$. m_{max} (KBr) 3348, 2906, 1583, 1470, 1145, 1087, 1042, 626 cm^{-1}.

2.3.9. Reaction of **3** with Cu(OAc)₂ · H₂O (**12**)

The reaction was carried out using 0.1 g of **3** and 0.074 g of $Cu(OAc)_2 \cdot H_2O$ in ethanol. On reducing the solvent after standing for several days, a green/blue solid precipitated. The solid was removed by filtration, washed with cold ethanol and dried in a vacuum oven. The solid was identified as the starting copper acetate material.

2.3.10. Reaction of **1** with NiCl₂ · 6H₂O (**13**)

The resulting green solution was allowed to stand for several days after which time the solvent was reduced under reduced pressure. However, no product was obtained but the starting materials only.

2.3.11. Reaction of **1** with Ni(ClO₄)₂ · 6H₂O (**14**)

The reaction was carried out using 0.64 g of **1** and 0.66 g of $Ni(ClO_4)_2 \cdot 6H_2O$ in ethanol. On standing for several days, a moss green/brown solid precipitated. The solid was removed by filtration, washed with cold ethanol and dried in a vacuum oven. Analysis of the compound showed that it was the 3,3'-diamino-*N*-methyldipropylamine complex of nickel perchlorate, $Ni((H_2NCH_2CH_2CH_2)_2NCH_3)(ClO_4)_2 \cdot 2H_2O$. Yield 0.103 g. ν_{max} (KBr) 3410, 2926, 1602, 1478, 1275, 1095, 625 cm^{-1}.

2.3.12. Reaction of **1** with Ni(OAc)₂ · 4H₂O (**15**)

The resulting green solution was allowed to stand for several days after which time the solvent was reduced under reduced pressure. No product was obtained but starting materials were recovered.

2.3.13. Reaction of **2** with NiCl₂ · 6H₂O (**16**)

The resulting pale green solution was allowed to stand for several days after which time the solvent was reduced under reduced pressure. No product was obtained and only the starting materials were recovered.

2.3.14. Reaction of **2** with Ni(ClO₄)₂ · 6H₂O (**17**)

The reaction was carried out using 0.3 g of **2** and 0.38 g of $Ni(ClO_4)_2 \cdot 6H_2O$ in ethanol. On standing for several days, a light green precipitate resulted. The solid was removed by filtration, washed with cold ethanol and dried in a vacuum oven. Analysis of the compound showed that it was the 1,3-diaminoethane complex of nickel perchlorate, $Ni(H_2NCH_2CH_2CH_2NH_2)_2(ClO_4)_2$. Yield 0.042 g. ν_{max} (KBr) 3423, 2923, 1682, 1282, 1080, 625 cm^{-1}.

2.3.15. Reaction of **2** with Ni(OAc)₂ · 4H₂O (**18**)

The reaction was carried out using 0.1 g of **2** and 0.08 g of $Ni(OAc)_2 \cdot 4H_2O$ in ethanol. On standing the green solution for several days, a light green precipitate resulted. The solid was removed by filtration, washed with cold ethanol and dried in a vacuum oven. Yield 0.1 g. Analysis of the compound showed that it was the 1,3-diaminopropane complex of nickel acetate, $Ni(H_2NCH_2CH_2CH_2NH_2)_2(CH_3CO_2)_2$. ν_{max} (KBr) 3345, 2942, 1558, 1420, 1141, 912, 671 cm^{-1}.

2.3.16. Reaction of **3** with NiCl₂ · 6H₂O (**19**)

After standing the green solution for several days, the remaining solvent was removed under reduced pressure, yielding a mixture of the starting materials, indicating that no reaction had occurred.

2.3.17. Reaction of **3** with Ni(ClO₄)₂ · 6H₂O (**20**)

After standing the green solution for several days, the remaining solvent was removed under reduced pressure, yielding a mixture of the starting materials, indicating that no reaction had occurred.

2.3.18. Reaction of **3** with Ni(OAc)₂ · 4H₂O (**21**)

The reaction was carried out using 0.1 g of **3** and 0.082 g of $Ni(OAc)_2 \cdot 4H_2O$ in ethanol. On standing the green solution for several days, a light green precipitate resulted. The solid was removed by filtration, washed with cold ethanol and dried in a vacuum oven. Yield 0.1 g. Analysis of the compound showed that it was the 1,2-diaminoethane complex of nickel acetate, $Ni(H_2NCH_2CH_2NH_2)_2(CH_3CO_2)_2$. ν_{max} (KBr) 3358, 2924, 1759, 1740, 1551, 1428, 1222, 1024, 680 cm^{-1}.

2.3.19. Reaction of **1** with ZnCl₂ (**22**)

The pale yellow solution was reduced under pressure, after previously standing for several days, resulting in a pale yellow precipitated which decomposed on standing.

2.3.20. Reaction of **1** with Zn(OAc)₂ (**23**)

No reaction occurred in this case, as both stating materials were recovered after allowing the reaction to stand for several days.

2.3.21. Reaction of *2* with ZnCl₂ (*24*)

The pale yellow solution was reduced under pressure, after previously standing for several days, resulting in a pale yellow precipitated which decomposed on standing.

2.3.22. Reaction of *2* with Zn(OAc)₂ (*25*)

No reaction occurred in this case, as both stating materials were recovered after allowing the reaction to stand for several days.

2.3.23. Reaction of *3* with ZnCl₂ (*26*)

On mixing a solution of 0.08 g ZnCl₂ in ethanol (5 ml) with a solution of 0.15 g of **3** in ethanol (5 ml), an immediate white precipitate resulted. The suspension was stirred for a further 30 min. The white solid was removed by filtration, washed with cold ethanol and dried in a vacuum oven. Yield 0.174 g. *Anal.* Calc. for $C_{16}H_{14}Cl_2N_2O_2Zn$ (402.59): C, 47.49; H, 3.99; N, 6.92. Found: C, 47.22; H, 4.03; N, 6.82. ^1H NMR (300 MHz, d_6-DMSO, 25 °C): δ = 3.84 [4H, s, NCH₂], 6.83 [2H, m, ArH], 7.16 [6H, m, ArH], 8.24 [2H, s, HC=N], 9.56 ppm [2H, s, OH]. ν_{max} (KBr) 3336, 2949, 1642, 1584, 1475, 1311, 1039, 795 cm^{-1}.

2.3.24. Reaction of *3* with Zn(OAc)₂ (*27*)

On allowing the colourless solution to stand for several days, a white precipitate formed. This was removed by filtration, washed with acetonitrile and dried in a vacuum oven. The solid was analysed as the starting ligand **3**, indicating that no reaction had occurred.

2.3.25. Reaction of *3* with Cu(OAc)₂ · py (*28*)

On mixing a solution of 0.18 g Cu(OAc)₂·py in pyridine (5 ml) with a solution of 0.15 g of **3** in pyridine (5 ml), an immediate brown solution resulted. The resulting solution was allowed to stand for several days after which time the solvent was reduced under reduced pressure. However, no product was obtained but the starting materials only.

2.4. X-ray structure determination

Crystal Data for **4** and **9**: data collection on a Bruker SMART diffractometer, k (Mo Kα) (0.71073 Å) at *T* = 193 K; structures solved using SHELXS-97[27] and refined using full-matrix least squares in HELXL-97.[27] **4**: $C_{15}H_{41}Cl_{4.5}Cu_{2.5}N_6O$, *M* = 646.92, orthorhombic, space group *Pbcm*, *a* = 11.4150(1), *b* = 18.1840(2), *c* = 25.8210(2) Å, *V* = 5359.67(9) Å^3, *Z* = 8, ρ_{calcd} = 1.603 g cm^{-3}, μ = 2.442 mm^{-1}, *F*(000) = 2668, 81,648 reflections collected, 7936 unique (R_{int} = 0.0789), 5823 with $I > 2\sigma(I)$. Final residuals: R_1 ($I > 2\sigma(I)$) = 0.0312, wR_2 (all data) = 0.0692, GOF = 1.025. **9**: $C_{14}H_{40}Cu_2N_4O_{12}$, *M* = 583.58, monoclinic, space group *P 21/c*, *a* = 16.8610(3), *b* = 9.2650(2), *c* = 16.8760(3) Å, β = 108.354(1)°, *V* = 2502.21(8) Å^3, *Z* = 4, ρ_{calcd} = 1.549 g cm^{-3}, μ = 1.761 mm^{-1}, *F*(000) = 1224, 34,719 reflections collected, 34,728 unique (R_{int} = 0.0000), 28188 with $I > 2r (I)$. Final residuals: R_1 ($I > 2r (I)$) = 0.0462, wR_2 (all data) = 0.1149, GOF = 1.046. Successful refinement was only achieved after accounting for a small amount of non-merohedral twinning about the (1,0,0) reciprocal axis.

3. Results and discussion

3.1. Ligand syntheses

Compounds **1**, **2** and **3** were obtained by reacting either 3,3'-diamino-*N*-methyldipropylamine, 1,3-diaminopropane or 1,2-diaminoethane with 3-hydroxybenzaldehyde in methanol for several hours at ambient temperature to yield the products as either solids or oils. The disappearance of the aldehyde proton signal at 9.8 ppm and the appearance of the imine proton signal at 8.9 ppm in the ^1H NMR spectra of the three compounds was considered to be characteristic of ligand formation. The purity of the ligands was confirmed by both elemental analysis and ^1H NMR spectroscopy. Both materials were air-stable over a period of several weeks, and they were also stable in solution. No decomposition products, i.e. starting materials, were observed in the ^1H NMR spectra which were run after a period of several days. This suggested that these ligands had reasonable stability.

3.2. Complexation reactions

Metal complexation reactions between the three ligands and the metal chloride, metal acetate and metal perchlorate salts $MCl_2 · xH_2O$, $M(ClO_4)_2 · xH_2O$ and $M(CH_3CO_2)_2 · xH_2O$ [M = Cu, Ni or Zn] were carried out in either methanol, ethanol or acetonitrile under nitrogen, respectively. Colour changes from the initial yellow colour of the ligand in methanol to deep blue or blue/green colours were immediately observed, in all cases, for the reactions involving copper and nickel salts. No colour change was observed in any of the zinc reactions, but instead white solids precipitated from the pale yellow solutions within minutes. Table 1 indicates the outcome of the metal complexation reactions involving the three ligands (**1–3**) with the various metal salts $MCl_2 · xH_2O$, $M(ClO_4)_2 · xH_2O$ and $M(CH_3CO_2)_2 · xH_2O$ [M = Cu, Ni, or Zn].

3.3. Copper(II) and nickel(II) reactions

Highly coloured solutions resulted in all complexation reactions involving copper(II) salts and, in several cases, blue or purple crystalline materials precipitated from solution after several days. The solid materials obtained from the reaction solutions were analysed by infrared spectroscopy. In the case of ligand **1**, the solids obtained were the starting copper(II) salts, namely copper(II) perchlorate and copper(II) acetate and there was no indication of any complex being formed involving the Schiff-base **1**. On reducing the remaining solution, a pale yellow solid, corresponding to the starting ligand **1**, was identified in each case. The infrared spectrum of the crystalline material obtained from the reaction involv-

Table 1
Summary of complexation reactions.

Rxn No.	Ligand	Metal salt	Solvent	Outcome
4	1	CuCl₂ · 2H₂O	Methanol	Metal–amine complex
5	1	Cu(ClO₄)₂ · 6H₂O	Methanol	Starters recovered
6	1	Cu(OAc)₂ · H₂O	Methanol	Starters recovered
7	2	CuCl₂ · 2H₂O	Methanol	Metal–amine complex
8	2	Cu(ClO₄)₂ · 6H₂O	Methanol	Starters recovered
9	2	Cu(OAc)₂ · H₂O	Methanol	Metal–amine complex
10	3	CuCl₂ · 2H₂O	Methanol	Metal–amine complex
11	3	Cu(ClO₄)₂ · 6H₂O	Ethanol	Metal–amine complex
12	3	Cu(OAc)₂ · H₂O	Ethanol	Starters recovered
13	1	NiCl₂ · 6H₂O	Methanol	Starters recovered
14	1	Ni(ClO₄)₂ · 6H₂O	Ethanol	Metal–amine complex
15	1	Ni(Oac)₂ · 4H₂O	Methanol	Starters recovered
16	2	NiCl₂ · 6H₂O	Methanol	Starters recovered
17	2	Ni(ClO₄)₂ · 6H₂O	Ethanol	Metal–amine complex
18	2	Ni(Oac)₂ · 4H₂O	Ethanol	Metal–amine complex
19	3	NiCl₂ · 6H₂O	Methanol	Starters recovered
20	3	Ni(ClO₄)₂ · 6H₂O	Methanol	Starters recovered
21	3	Ni(Oac)₂ · 4H₂O	Ethanol	Metal–amine complex
22	1	ZnCl₂	Methanol	Complex decomposed
23	1	Zn(OAc)₂	Methanol	Starters recovered
24	2	ZnCl₂	Methanol	Complex decomposed
25	2	Zn(OAc)₂	Methanol	Starters recovered
26	3	ZnCl₂	Methanol	Metal-complex formation
27	3	Zn(OAc)₂	Methanol	Starters recovered
28	3	Cu(OAc)₂·py	Pyridine	Starters recovered

ing **1** and copper(II) chloride showed that the material was neither the starting copper(II) salt nor was it the starting Schiff-base. The X-ray crystal structure determination of **4** was undertaken and will be discussed in due course.

When ligand **2** or **3** was used instead of ligand **1**, similar results were obtained, that is, in no case was there a reaction between the Schiff-base ligand and the metal salt. Instead what was observed was either no reaction, as in the case of the copper acetate reaction, with the complete return of starting materials, or else the product was the metal complex of the starting diamine compound. The copper–amine complexes were obtained in three separate reactions of **2** or **3** with copper salts, namely, $Cu(H_2NCH_2CH_2CH_2NH_2)Cl_2 \cdot 2H_2O$ (**7**), $Cu(H_2NCH_2CH_2NH_2)Cl_2 \cdot 2H_2O$ (**10**) and $Cu(H_2NCH_2CH_2NH_2)(ClO_4)_2 \cdot 2H_2O$ (**11**). The infrared spectra of the three compounds was identical to that previously reported in all cases [28,29], as well as samples that were prepared in the laboratory for comparison purposes. In fact, crystals suitable for an X-ray crystallographic study were obtained of product **9** from the reaction between **2** and copper acetate and that structure will be discussed in a later section. Again, what is of interest here is that while the ligand **2** itself is stable in both the solid state and in solution as shown by ^{1}H NMR spectroscopy, once the copper(II) salt is added, the Schiff-base ligand breaks down to its starting aldehyde and diamine compounds. We believed that one solution to this conundrum would be to use copper salts which did not contain any water molecules. To this purpose, we prepared the pyridine complex of copper(II) acetate and reacted that with ligand **3**. Interesting enough in this case, no reaction occurred and the starting materials were recovered in this case.

When the reactions were repeated with the three ligands with the same three nickel (II) salts instead of the three copper(II) salts, a similar mixture of reactions giving either amine salts of the nickel starting compounds or else giving no reaction resulted. The nickel–amine complexes were obtained in four separate reactions of either **1**, **2** or **3** with the various nickel salts, namely, $Ni((H_2NCH_2CH_2CH_2)_2NCH_3)(ClO_4)_2 \cdot 2H_2O$ (**14**), $Ni(H_2NCH_2CH_2NH_2)_2(ClO_4)_2$ (**17**), $Ni(H_2NCH_2CH_2CH_2NH_2)_2(CH_3CO_2)_2$ (**18**) and $Ni(H_2NCH_2CH_2NH_2)_2(CH_3CO_2)_2$ (**21**). The infrared spectra of the four compounds was identical to that previously reported in all cases [30–32], as well as samples that were prepared in the laboratory for comparison purposes. We believed that although the reactions were carried out in anhydrous solvents, there was sufficient water present in the metal salts to initiate the breakdown reaction of the Schiff-base ligand. This prompted us to consider the reactions of various zinc salts, which could be obtained commercially in an anhydrous state.

3.4. Zinc(II) reactions

These reactions of the three ligand with either zinc(II) chloride, zinc(II) acetate or zinc(II) perchlorate resulted in the formation of a metal–Schiff base complex which was either air and water stable or which decomposed on standing in either air or in the presence of water. This would suggest that it is water coordinated to the metal salt that is responsible for the break-up of the Schiff-base ligand present in the reaction flask rather than the presence of water in the solvents used. However, only in the case of ligand **3** with $ZnCl_2$ was there a product obtained (**26**) that was sufficiently air-stable enough for analysis to be carried out on the material obtained. In this particular case, a 1:1 metal:ligand complex was obtained. The ^{1}H NMR data for **26** indicate that the hydroxyl proton is still present in the complex and has changed from being a broad singlet in the NMR spectrum of the ligand into a very sharp singlet (see Section 2). This suggests that the zinc metal is involved in coordination through the OH group. However, the signals for the imine proton and also the bridging methylene protons have not shifted, which implies that coordination to the zinc is occurring through only through the hydroxyl group. This NMR information was important to obtain as it also ruled out the possibility that the material we had recovered was only the two recovered starting materials and that no reaction had occurred. Two possibilities exist for the 1:1 complex – one in which the zinc metal binds to the two hydroxyl groups of two different ligand in a dimeric manner or one where the same binding occurs but in a polymeric fashion, to give an overall 1:1 complex, as shown in Fig. 2. Because of the highly insoluble nature of the complex in polar solvents, we believe that the complex has the structure where each zinc atom is bound in a polymeric fashion.

3.5. X-ray crystal structure of **4**

In the case of the copper chloride reaction with **1**, small blue crystals appeared in the reaction vessel within 2 h. The blue crystals were characterised, as being $[\{Cu(H_2NCH_2CH_2CH_2NMeCH_2CH_2CH_2NH_2)(1\text{-}Cl)Cl\}_2] \cdot [CuCl_2] \cdot [Cu(H_2NCH_2CH_2CH_2NMeCH_2CH_2CH_2NH_2)Cl_2]_2 \cdot 2(H_2O) \cdot MeCN$ (**4**, Fig. 3), most probably formed by the concomitant attack of both $CuCl_2$ and H_2O on the Schiff-base **1** to give the starting amine and aldehyde in the reaction mixture. Spectroscopic analysis of the remaining solution showed the presence of the 3-hydroxybenzaldehyde. We have previously observed this type of behaviour involving $CuCl_2$ but with amide bonds rather than amine bonds [33,34], while other groups have observed similar reactions with other Schiff-base compounds [35]. What is unusual here is that the Schiff-base ligand **1** did not decompose when standing in air either as a solid or in solution but that the breakdown products, which turned out to be the starting aldehyde and amine, were only observed when a metal salt was present.

The asymmetric unit of **4** contained two $Cu(H_2NCH_2CH_2CH_2NMeCH_2CH_2CH_2NH_2)Cl_2$ molecules, one $[\{Cu(H_2NCH_2CH_2CH_2NMeCH_2CH_2CH_2NH_2)(1\text{-}Cl)Cl\}_2]^+$ cation, one unusual two-coordinate $Cu(II)Cl_2$ anionic species, two water molecules and one acetonitrile molecule (see Fig. 3). Assignment of one of the
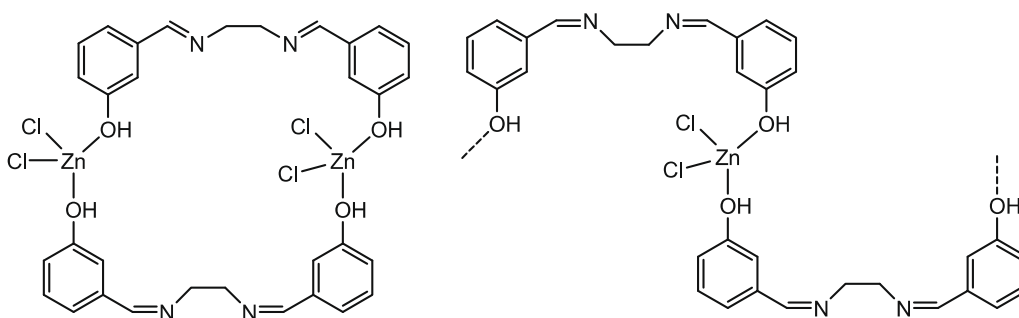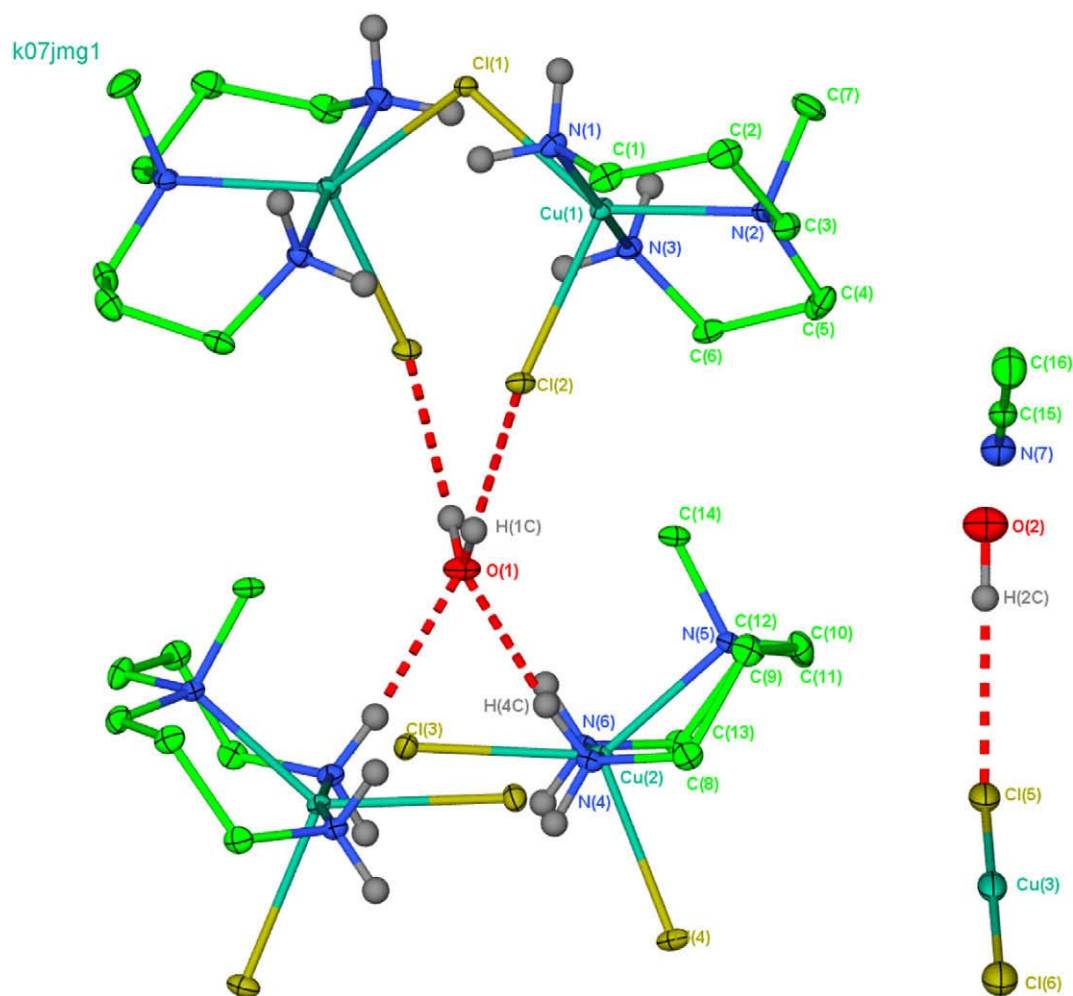

Fig. 2. Possible structures for **26**.

Fig. 3. Molecular structure of **4** showing selected labels. Hydrogens from functionalities that do not contribute to hydrogen-bonding with the asymmetric unit are omitted for clarity. Atoms with primed labels are related to those in the asymmetric unit by the x, $\frac{1}{2} - y$, $1 - z$ symmetry operation. Ellipsoids are displayed at the 30% probability level.

two water molecules, (based on O(1)) was based on the clear identification of the water hydrogens. In the case of the second water molecule, only one hydrogen at O(2) was easily identified, as depicted in Fig. 3. This then suggested that, in order to balance charges in the molecules as a whole, either this was an hydroxyl anion leaving the CuCl$_2$ unit being neutral or else the CuCl$_2$ unit was anionic with a molecule of water present. Given the limitations of X-ray diffraction for the location of hydrogen atoms, electrospray mass spectrometry was chosen to ascertain the identity of the moieties present. This will be discussed in more detail at the end of this section.

The structure also consists of a monochloro-bridged dimeric [{Cu(H$_2$NCH$_2$CH$_2$CH$_2$NMeCH$_2$CH$_2$CH$_2$NH$_2$)(l -Cl)Cl}$_2$]$^+$ cation as well as two Cu(H$_2$NCH$_2$CH$_2$CH$_2$NMeCH$_2$CH$_2$CH$_2$NH$_2$)Cl$_2$ complexes. Monochloro-bridged Cu(II) dimers are unusual, compared with the more common dichloro-bridged Cu(II) complexes [36], and only a few have been reported [37]. The coordination geometry around each Cu(II) atom in both the cation and the complexes contains three nitrogen atoms of the amine and two chlorine atoms. The geometry for both copper centres is midway between trigonal bipyramidal and square pyramidal, with a τ value [38] of 0.45 and 0.56 for Cu(1) and Cu(2), respectively. The Cu(II)–Cl bond length of the monochloro-bridged dimer is 2.4822(4) Å is comparable to the monochloro-bridged Cu(II) dimers previously reported [37], and is significantly shorter than the Cu(II)–Cl bond lengths found in dichloro-bridged Cu(II) dimers, which are usually in the

range of 2.7–3.0 Å [36]. The Cu(II)–Cl–Cu(II) bond angle is 111.11(2)° which is significantly narrower than those previously described [37]. This is most likely accounted for by packing effects. The Cu(H$_2$NCH$_2$CH$_2$CH$_2$NMeCH$_2$CH$_2$CH$_2$NH$_2$)Cl$_2$ complex has been previously characterised by X-ray crystallography and has been previously reported [39]. The data for both structures are very similar, in terms of bond lengths and bond angles. One major difference between the two reactions was that the reaction described by Busch and co-workers [39] showed no evidence for the chloro-bridged dimer. This suggests that the presence of the 3-hydroxybenzaldehyde molecule has an influence on the formation of the chloro-bridged dimer. All attempts to carry out the reaction in acetonitrile failed because a brown, insoluble material resulted from attempts to dissolve the copper(II) chloride in acetonitrile. Indeed, when the reaction between CuCl$_2 \cdot$ H$_2$O and the amine 3,3′-diamino-N-methyldipropylamine is carried out in methanol, a blue solution resulted, from which a blue crystalline material was obtained which is the previously reported Cu(H$_2$NCH$_2$CH$_2$CH$_2$N-MeCH$_2$CH$_2$CH$_2$NH$_2$)Cl$_2$ complex [39].

Analysis of the crystal packing of **4** reveals that the water molecule (O1) has a dual role. In the first instance, the hydrogen atoms therein are involved in hydrogen bonding to a symmetry related pair of Cl(2) atoms in the bis-copper cation. In addition, the oxygen lone pairs form a bridge between two proximate neutral copper complexes based on Cu(2) via hydrogen bonding to a symmetry related pair of amine hydrogen atoms (H(4C)). The second water

molecule (O2) is also involved in hydrogen-bonding with Cl(5), while the lone pair of the hydroxyl oxygen atom is also involved in an interaction with the neighbouring acetonitrile molecule, through the nitrogen atom.

In trying to ascertain whether the CuCl₂ entity was neutral or anionic, the negative electrospray mass spectrum of **4** was obtained. The spectrum showed the presence of the [CuCl₂]⁻ anion, which dominated the spectrum. Nicola et al. have reported that in their copper–phosphine complexes containing the [CuX₂]⁻ anion (X = Cl, Br or I), the predominant peak in the negative ESMS spectrum was for the copper(I) anionic species [40]. There are several examples of the copper(I) species [CuCl₂]⁻ in the literature [41]. One X-ray crystal structure of a copper(II) CuCl₂ species has been reported [42], but, weak interactions between the copper(II) atom and the oxygen atoms of the *N,N'*-di(2-methoxyphenyl)formamidine ligand (Cu···O = 3.157 Å) suggest that, in that case, the copper atom is situated in a highly distorted three coordinate geometry. There are no meaningful interactions (<4 Å) between the copper atom Cu(3) in this structure **4** and any other atom, other than to the two chlorine atoms to which it is bonded. The two Cu–Cl bond distances are slightly asymmetric at 2.1105(12) and 2.1184(12) Å and the Cl–Cu–Cl bond angle of 178.84(4)° suggests a metal geometry which is very close to linear. These bond lengths and angles are in the range of those previously reported.[40,41] Examination of the space filling structure in this case shows that there is no space available around the copper(II) atom for any interaction with another atom and that, in fact, the Cu centre is quite isolated.

Elemental analysis on an oven-dried sample showed that the drying process has resulted in the loss of the molecule of acetonitrile.

3.6. X-ray crystal structure of **9**

In the case of the reaction of **2** with copper(II) acetate, blue crystals (**9**) resulted when the solution was allowed to stand for several hours. Both IR spectroscopy and elemental analysis suggested that the imine bond in ligand **2** had also been broken, resulting in the re-formation of the starting amine and aldehyde, with the metal

salt complexing to the amine. The X-ray crystal structure of **9** revealed the presence of two metal complexes (see Fig. 4). The asymmetric unit consists of one molecule containing a five coordinate copper, half of a dimer containing two five coordinate coppers and three water molecules. There is extensive hydrogen bonding in the lattice.

The synthesis of the monomer unit in **9**, Cu(H₂NCH₂CH₂CH₂NH₂)(CH₃CO₂)₂, has been reported previously [29], but the authors reported that their four coordinate copper(II) compound was highly sensitive to humidity. All their attempts to grow crystals of the acetate material Cu(H₂NCH₂CH₂CH₂NH₂)(CH₃CO₂)₂ resulted in the formation of a copper(II) chloride complex instead, Cu(H₂NCH₂CH₂CH₂NH₂)Cl₂, with the chloride ligands coming from the solvent (carbon tetrachloride) used for crystal growth. The monomer unit in complex **9** does not contain a four coordinate copper(II) species but instead contains a five coordinate species as a result of the coordination of a water molecule. So, the complex Cu(H₂NCH₂CH₂CH₂NH₂)(CH₃CO₂)₂ · H₂O consists of two monodentate acetate anions, a 1,3-diaminopropane ligand as well as the coordinated water molecule in a five coordinate square pyramidal geometry, as denoted by τ = 0 [38]. In the case of the dimer unit, each copper is chelated to one 1,3-diaminopropane ligand, one monodentate acetate group and two bridging monodentate acetate groups, thus making each copper five coordinate, with a τ value of 0.16 for each copper [38]. This implies that the geometry about each copper is a slightly distorted square pyramid.

Numerous crystal structures containing the Cu₂(CH₃CO₂)₂ dimer unit have been reported [43]. Metric data for the dimer in the structure of **9** are comparable to those in the literature. Elemental analysis on an oven-dried sample showed that the drying process has resulted in the loss of the three molecules of water.

We are currently investigating solid state measurements of **4** including magnetic and UV–Vis measurements in order to ascertain the driving force for inclusion of CuCl₂ within this material. Preliminary experiments reveal that the two-coordinate copper complex does not form when the simple amine is reacted with copper chloride itself. Also, we do not want to carry out the magnetic measurement using the Evans method, as we feel that the two-coordinate copper will expand its coordination sphere when in
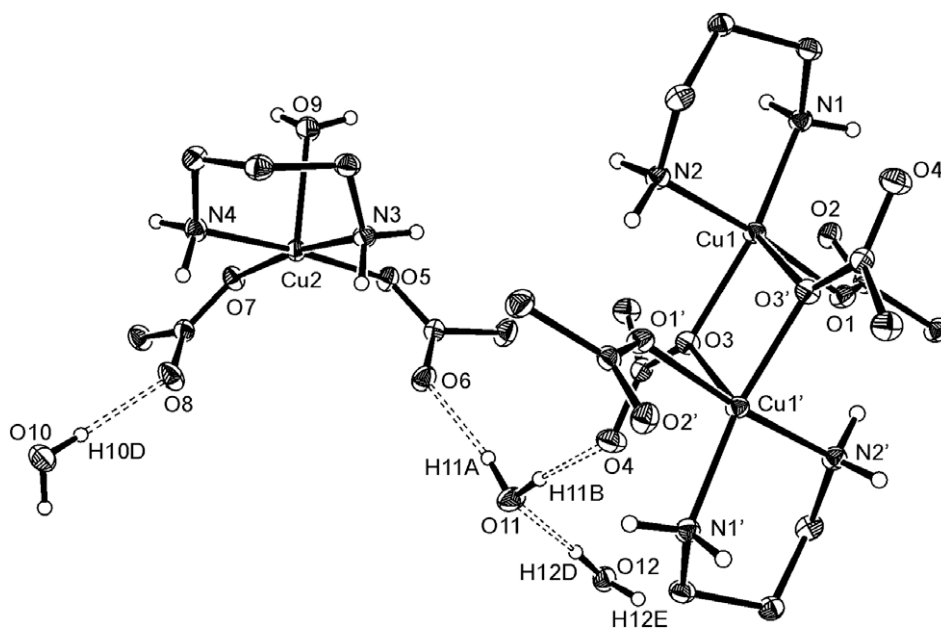

Fig. 4. Molecular structure of **9** showing selected labels. Carbon-bound hydrogens are omitted for clarity. Atoms with primed labels are related to those in the asymmetric unit by the −x, −y, −z symmetry operation.

solution. Initial solid state magnetic measurements of **4** suggest a value of 2.06 B.M. per copper atom. Further variable temperature studies on this complex need to be carried out to ascertain if any antiferromagnetic coupling interactions are occurring between the copper centres.

4. Conclusions

The Schiff-base ligands **1–3** which were synthesised using 3-hydroxybenzaldehyde as starting aldehyde were stable both in solution and in the solid state for several weeks. However, the reactions with various metal salts caused the ligand to break down and return to the starting amine and aldehyde. In several cases, the metal salt then reacted with the free amine to give metal–amine complexes, and X-ray crystal structures of two of these are reported with interesting coordination properties.

5. Supplementary material

CCDC 646341 and 646342 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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