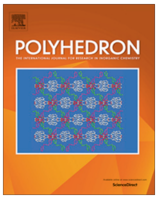
Polyhedron 74 (2014) 113–121

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Mono- and dinucleating Ni(II), Cu(II), Zn(II) and Fe(III) complexes of symmetric and unsymmetric Schiff bases incorporating salicylimine functions – Synthetic and structural studies

Qinghua Meng [a,b], Jack K. Clegg [a,c,*], Aidan J. Brock [c], Katrina A. Jolliffe [a,*], Leonard F. Lindoy [a,*], Gang Wei [d,*]

[a] *School of Chemistry, University of Sydney, NSW 2006, Australia*
[b] *School of Chemistry and Chemical Engineering, Shanghai JiaoTong University, Shanghai 200240, PR China*
[c] *School of Chemistry and Molecular Biosciences, The University of Queensland, Brisbane St Lucia, QLD 4072, Australia*
[d] *CSIRO Materials Science and Engineering, P.O. Box 218, Lindfield, NSW 2070, Australia*

ARTICLE INFO

Article history:
Received 24 April 2012
Accepted 3 March 2014
Available online 12 March 2014

Keywords:
Schiff base
Nickel(II)
Copper(II)
Zinc(II)
Iron(III)

ABSTRACT

The known Schiff base, 3-(2-aminophenylamino)-1-phenylbut-2-en-1-one (**1**), formed by 1:1 condensation of *o*-phenylenediamine and benzoylacetylacetone reacts at its free amine site with salicylaldehyde and 5-*tert*-butylsalicylaldehyde in the presence of Ni(II) and Cu(II) acetates, or with 5-*tert*-butylsalicylaldehyde in the presence of Zn(II) acetate, to generate 1:1 (M:L) diimine complexes (**2**) of the corresponding doubly deprotonated, unsymmetric, O_2N_2-tetradentate ligands. In contrast, reaction of Zn(II) acetate with **1** and salicylaldehyde led to Schiff base exchange (with loss of benzoylacetylacetone) to yield symmetric [ZnL^3] [where L^3 is *N*,*N*′-*o*-phenylenebis(salicyliminato)]. Similarly, when Fe(II) chloride was substituted for metal acetate in the reaction of **1** with 5-*tert*-butyl-salicylaldehyde and the initial product crystallised in the presence of dabco (as base), a related Schiff base exchange reaction occurred along with aerial oxidation of the Fe(II) to produce the neutral dinuclear [$Fe^{III}(L^4)_2(\mu\text{-O})$] species [where L^4 is *N*,*N*′-*o*-phenylenebis(5-*tert*-butylsalicyliminato)] in which Fe(III) centres are linked by an oxo group to produce two 5-coordinate Fe(III) centres; pairs of these (oxo-bridged) dinuclear complex units are further linked via elongated intermolecular Fe–$O_{phenolic}$ contacts (Fe–O, 2.44 Å) to form an unusual tetranuclear supramolecular cluster. This complex was also synthesised directly by the *in situ* reaction of 5-*tert*-butyl-salicylaldehyde, *o*-phenylenediamine and Fe(II) chloride (2:1:1 mol ratio) in air. In an extension of these studies, the *in situ* reaction of the 1,3-aryl linked bis-β-diketone, 1,1-(1,3-phenylene)-bis-butane-1,3-dione), *o*-phenylenediamine, salicylaldehyde and Ni(II) acetate in a 1:2:2:2 ratio yielded [Ni_2L^5], the dinuclear analogue of the unsymmetric mononuclear Ni(II) complex **2**, in which each nickel centre has a square planar environment. Reaction of the above 1,3-phenylene linked bis-β-diketone precursor with *o*-phenylenediamine in a 1:2 M ratio yields 1,3-bis(4-methyl-3H-benzo[*b*][1,4]diazepin-2-yl)benzene as its monohydrate (**3**·H_2O) incorporating two 7-membered diaza heterocyclic rings; thus contrasting with the ‘open’ Schiff base structure observed for **1**. X-ray structures of **1**, **3**·H_2O, [NiL^1]·py, [NiL^1]·EtOH, [NiL^2], [CuL^1]·py, [CuL^1]·0.5$CHCl_3$, [$(FeL^4)_2(\mu\text{-O})]_2$·1.5THF·0.4EtOH·0.6$H_2O$ and [NiL^5]·0.25EtOH·0.125py are reported.

1. Introduction

Symmetrical Schiff bases derived from 2:1 condensation of β-diketone or salicylaldehyde derivatives with a 1,2-diamine moiety represent, not only some of the earliest examples of tetradentate ligand types but also some of the most studied [1–4]. Indeed such species have been known since Alfred Werner’s time. [1] Ligands of this type typically lose two protons and coordinate in a square-planar manner to form neutral metal complexes with a number of divalent metal ions. Individual complexes have been investigated for a number of applications, including as oxygen carriers [5], as non-linear optical materials [6], as catalysts (and especially asymmetric catalysts) [2,7], in inorganic biochemical roles [8] and as components of metallosupramolecular systems [2,9]. In contrast to symmetrical Schiff base systems, unsymmetric

---

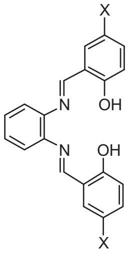
[*] Corresponding authors. Address: School of Chemistry, University of Sydney, NSW 2006, Australia. Tel.: +61 2 93514400; fax: +61 2 9351 3329 (K.A. Jolliffe and L.F. Lindoy).

E-mail addresses: k.jolliffe@chem.usyd.edu.au (K.A. Jolliffe), lindoy@chem.usyd.edu.au (L.F. Lindoy), gang.wei@csiro.au (G. Wei).

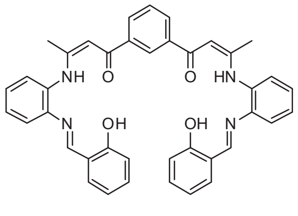
http://dx.doi.org/10.1016/j.poly.2014.03.002

systems have received significantly less attention, in part reflecting that their syntheses are usually [6,10,11] (but not always) [12] somewhat less facile than for related symmetrical systems.

Previous studies [11,13,14] have shown that *o*-phenylenediamine undergoes 1:1 Schiff base condensation with individual *β*-diketones; for example, reaction with benzoylacetylacetone yields 3-(2-aminophenylamino)-1-phenylbut-2-en-1-one (**1**) that incorporates a free amine site [11,13]. As an extension of these prior studies, we now report the metal template syntheses of new Ni(II), Cu(II) and Zn(II) complexes of type **2** (see Fig. 1). These incorporate the deprotonated forms of the unsymmetric ligands, H_2L^1 (R = H) and H_2L^2 (R = *t*-Bu), derived respectively from 1:1 condensation of **1** with salicylaldehyde or 5-*tert*-butylsalicylaldehyde. Related symmetric Zn(II) and Fe(III) complexes incorporating respectively *N,N′*-*o*-phenylenebis(salicyliminato) (L^3) and *N,N′*-*o*-phenylenebis(5-*tert*-butylsalicyliminato) (L^4) (see 3) generated by Schiff base exchange reactions are also reported. The formation of a related dinuclear Ni(II) Schiff base complex([Ni_2L^5]) incorporating the deprotonated form of the difunctional ligand **4** is described, with the latter derived from the condensation of **1** with the 1,3-phenylene-linked bis-*β*-diketone derivative, 1,1′-(1,4-phenylene)bisbutane-1,3-dione.



3
H_2L^3, X = H
H_2L^4, X = t-Bu



4
H_2L^5

2. Experimental

2.1. Materials and instrumentation

All reagents and solvents were obtained from commercial sources and used without further purification. ^1H NMR spectra were recorded on a Bruker Avance DPX200 spectrometer with $(CH_3)_4Si$ as the internal reference. Mass spectra (ESI-MS) were obtained on a Finnigan LCQ-8 spectrometer with the sample dissolved in methanol. UV–Vis spectra of the Ni(II) complexes were recorded on a Cary 1E spectrophotometer; in each case the d–d transition assigned to square planar coordination (due to the $^1A_{1g}$ to $^1B_{1g}$ transition) was partly obscured by the tail of an intense MLCT transition that extended from the UV region into the visible. Unless otherwise stated, all products were dried in air over silica gel before microanalysis.

2.2. Ligand and complex synthesis

3-(2-Aminophenylamino)-1-phenylbut-2-en-1-one (**1**): This was prepared by reaction of *o*-phenylenediamine with benzoylacetone using a similar procedure to that reported previously [13]. Yield 75%. ^1H NMR (δ, ppm /$CDCl_3$): 12.47 (H, br), 7.92 (2H, m), 7.44 (3H, m), 7.06 (2H, m), 6.76 (2H, m), 5.93 (1H, s), 3.87 (2H, br), 1.99 (3H, s). MS(ESI+): 253.0 ($M+H^+$). An X-ray diffraction study on a colourless single crystal of this product confirmed its expected structure.

2.2.1. General procedure for the synthesis of Ni(II), Cu(II) and Zn(II) complexes of type 2 incorporating unsymmetric L^1 and L^2

The procedure is a modified version of that previously reported for [NiL^1] [11] (which was also synthesised in the present study as its ethanol solvate). Intermediate **1** (1 mmol) and salicylaldehyde or 5-*tert*-butyl-salicylaldehyde (1 mmol) (to produce H_2L^1 and H_2L^2 respectively) were dissolved in hot ethanol (15 mL). The mixture was heated under reflux for 1 h, and then 1 mmol of Ni(II) acetate tetrahydrate, Cu(II) acetate monohydrate or Zn(II) acetate dihydrate in ethanol (5 mL) was added dropwise to the warm solution. The reaction mixture was heated at reflux for 2 h and then left overnight at room temperature. In each case the precipitate that formed was removed by filtration and recrystallised from ethanol.

2.2.1.1. [NiL^1]·EtOH and [NiL^1]·py. [NiL^1]·EtOH: yield 78%, dark red-brown crystals. ^1H NMR (*δ*, ppm/$CDCl_3$): 8.18 (1H, s), 7.87 (2H, d), 7.53 (1H, d), 7.35 (6H, m), 7.05 (3H, m), 6.64 (1H, t), 6.02 (1H, s), 2.52 (3H, s). UV–Vis (pyridine): *λ* ~570 (sh) nm. *Anal.* Calc. for $C_{25}H_{24}NiN_2O_3$: C, 65.50; H, 5.24; N, 6.11. Found: C, 65.57; H, 4.71; N, 6.51%. Crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution of the above product and one of these was used for an X-ray structure determination. [NiL^1]·py: A portion of the above product was recrystallised from pyridine (py) to yield brown crystals of [NiL^1]·py; a crystal from this batch was used directly for a structure determination.

2.2.1.2. [NiL^2]·0.33H_2O. Yield 85%, dark red-brown crystals. ^1H NMR (*δ*, ppm/$CDCl_3$) 8.17 (1H, s), 7.86 (2H, s), 7.64 (1H, d), 7.39 (3H, m), 7.36 (2H, m), 7.22 (1H, m), 7.04 (3H, m), 6.02 (1H, s), 2.52 (3H, s), 1.30 (9H, s). UV–vis (pyridine), λ ~570 (sh) nm. *Anal.* Calc. for $C_{27}H_{26.66}NiN_2O_{2.33}$: C, 68.25; H, 5.66; N, 5.90. Found: C, 68.24; H, 5.67; N, 5.93%. Crystals of [Ni(L^2)] suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution of the above product.

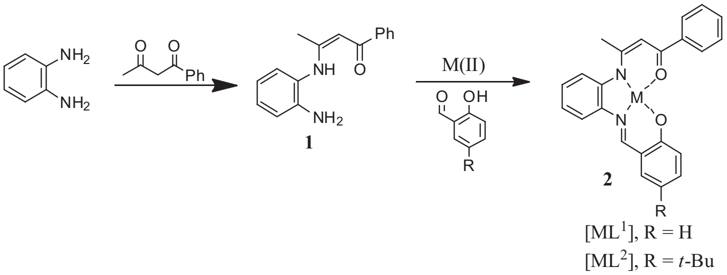


Fig. 1. Synthesis of the 1:1 Schiff base intermediate 3-(2-aminophenylamino)-1-phenylbut-2-en-1-one, **1**, followed by *in situ* reaction with salicylaldehyde or 5-*tert*-butylsalicylaldehyde in the presence of Ni(II), Cu(II) or Zn(II) acetate to produce complexes of type **2**, [ML^1] (M = Ni, Cu) or [CuL^2], that incorporate the doubly deprotonated forms of the unsymmetric ligands H_2L^1 (R = H) and H_2L^2 (R = *t*-Bu).

2.2.1.3. [CuL^1]·0.5CHCl$_3$. Yield 89%, dark green crystals. MS(ESI+): 418.20 (M + H)$^+$. *Anal.* Calc. for $C_{23}H_{18}CuN_2O_2$: C, 66.10; H, 4.34; N, 6.70. Found: C, 65.85; H, 4.35; N, 6.78%. Crystals of composition of [CuL^1]·0.5CHCl$_3$ suitable for X-ray crystal analysis were obtained on slow evaporation of a chloroform solution of the above product. They were used directly for a structure determination. On prolonged drying in air, this product lost chloroform to give the non-solvated product. *Anal.* Calc. for $C_{23}H_{18}CuN_2O_2$: C, 66.10; H, 4.34; N, 6.70. Found: C, 65.85; H, 4.35; N, 6.78%.

2.2.1.4. [CuL^1]·py. Green crystals of composition [CuL^1]·py, suitable for X-ray crystal analysis, were obtained on slow evaporation of a pyridine solution of the above product. *Anal.* Calc. for $C_{28}H_{23}CuN_3O_2$: C, 67.66; H, 4.66; N, 8.45. Found: C, 67.62; H, 4.65; N, 8.55%.

2.2.1.5. [CuL^2]·0.5H$_2$O. Yield 82%, dark green crystals. MS(ESI+): 474.1 (M + H)$^+$. *Anal.* Calc. for $C_{27}H_{27}CuN_2O_{2.5}$: C, 67.13; H, 5.63; N, 5.80. Found: C, 67.17; H, 5.37; N, 5.70%.

2.2.1.6. [ZnL^2]·1.5H$_2$O. Yield 53%, yellow crystals. ^{1}H NMR (δ, ppm/CDCl$_3$) 8.31 (1H, s), 7.72 (2H, d), 7.29 (3H, m), 7.11 (2H, m), 6.90 (2H, m), 5.39 (1H, s), 2.16 (3H, s), 1.24 (9H, s).

MS(ESI+): 475.27(M+H)$^+$. *Anal.* Calc. for $C_{27}H_{29}N_2O_{3.5}Zn$: C, 64.48; H, 5.81; N, 5.57. Found: C, 64.42; H, 5.97; N, 5.50%.

2.2.1.7. [Ni$_2$L^5]·0.25EtOH·0.125py. 1,1′-(1,3-Phenylene)-bis-butane-1,3-dione [15], (1 mmol), *o*-phenylenediamine (2 mmol) and salicylaldehyde (2 mmol) were dissolved in hot ethanol (25 mL). The reaction mixture was refluxed for 1 h and then Ni(II) acetate tetrahydrate (2 mmol) in ethanol (5 mL) was added dropwise to the warm solution. The reaction mixture was refluxed for a further 2 h, and then left overnight at room temperature. The product formed as red-brown crystals. Yield 80%. UV–vis (pyridine), λ ~570 (sh) nm. ^{1}H NMR (δ, ppm/CDCl$_3$) 8.28 (1H, s), 8.20 (2H, s), 7.99 (2H, m), 7.66 (2H, m), 7.36 (5H, m), 7.15 (4H, m), 6.98 (4H, m), 6.66 (2H, m), 6.12 (2H, s), 2.56 (6H, s). MS(ESI+): 768.87 (M+Na)$^+$. Slow evaporation of a pyridine solution of this product yielded crystals suitable for X-ray analysis and a crystal from this batch was used directly for the structure determination.

2.2.2. Schiff base exchange reactions

2.2.2.1. [ZnL^3]·H$_2$O. This complex was obtained from Zn(II) acetate using the general procedure outlined above. The procedure led to Schiff base condensation coupled with imine exchange (with loss of benzoylacetylacetone) to yield the symmetric mononuclear complex [ZnL^3]·H$_2$O (L^3 is the doubly deprotonated form of *N,N′-o*-phenylenebis(salicylimine). Yield 48%, yellow crystals. ^{1}H NMR (δ, ppm/DMSO-d$_6$): 9.04 (2H, s), 7.93 (2H, m), 7.43 (4H, m), 7.24 (2H, t), 6.73 (2H, d), 6.54 (2H, t). MS(ESI+): 379.20 (M+H)$^+$. *Anal.* Calc. for $C_{20}H_{16}N_2O_3Zn$: C, 60.40; H, 4.05; N, 7.04. Found: C, 60.92; H, 4.20; N, 7.05%.

2.2.2.2. [(FeL^4)$_2$(μ-O)]$_2$·3.5H$_2$O (where L^4 is the doubly deprotonated form of N,N’-o-phenylenebis(5-tert-butylsalicylimine). This complex was synthesised by the general procedure outlined in Section 2.2.1 employing intermediate **1**, 5-*tert*-butyl-salicylaldehyde and an ethanol/chloroform (1:1) solvent mixture but with Fe(II) chloride (1 mmol) substituted for the metal acetate. Once again Schiff base condensation coupled with imine exchange (with loss of benzoylacetylacetone) was observed to occur. The initial non-crystalline product obtained was dissolved in a 1:1 mixture of tetrahydrofuran and ethanol containing one equivalent of the difunctional base dabco. Dark red crystals formed on slow evaporation of this solution over several days. Yield, 70%. These were removed from solution and since they tended to lose solvent on standing, a crystal from this batch was used directly for an X-ray structure determination without further drying.

This complex was also synthesised by the more direct *in situ* reaction of 5-*tert*-butyl-salicylaldehyde, *o*-phenylenediamine and iron(II) chloride (2:1:1 mol ratio) in ethanol (thus circumventing the Schiff base exchange step in the above synthesis).

o-Phenylenediamine (1 mmol) and 5-*tert*-butyl-salicylaldehyde (2 mmol) were dissolved in hot ethanol (15 mL). The mixture was heated under reflux for 1 h, then iron(II) chloride tetrahydrate (1 mmol) in ethanol (5 mL) was added dropwise to the warm solution. The reaction mixture was heated at reflux for 2 h and then left overnight at room temperature. The dark brown precipitate that formed was then collected, dissolved in a 1:1 mixture of tetrahydrofuran and ethanol containing one equivalent of dabco as base (note: attempts to isolate the same product without the addition of dabco failed to produce crystalline materials). The resulting dark brown solution was allowed to stand for several days over which time dark red crystals of product formed. These were isolated and allowed to dry in air over several days. Yield 0.233 g (65%). UV–Vis (Nujol): λ 415 nm. MS(ESI+): 1003.3 [(FeL^4)$_2$O + Na]$^+$. *Anal.* Calc. for $C_{112}H_{120}Fe_4N_8O_{10}\cdot 3.5H_2O$: C, 66.44; H, 6.32; N, 5.53. Found: C, 66.35; H, 6.19; N, 5.56%.

2.3. Crystallography

2.3.1. Data collection and structure solution

X-ray structural data were collected on either a Bruker-Nonius APEX2-X8-FR591 diffractometer employing graphite-monochromated Mo Kα radiation generated from a rotating anode (0.71073 Å) with ω and ψ scans [16] or with scans using a Bruker SMART 1000 diffractometer employing graphite-monochromated Mo Kα radiation generated from a sealed tube (0.71073 Å). Data were collected at 150 K to approximately 56° 2θ. Data integration and reduction were undertaken with SAINT and XPREP [17,18] and subsequent computations were carried out using the WinGX-32 graphical user interface [19]. The structures were solved by direct methods using SIR97 [20]. Multi-scan empirical absorption corrections were applied to the data set using the program SADABS [21]. Data were refined and extended with SHELXL-97 [22]. In general, non-hydrogen atoms with occupancies greater than or equal to 0.5 were refined anisotropically. Carbon and alcohol O-bound hydrogen atoms were included in idealised positions and refined using a riding model. Water hydrogen atoms were first located in the difference Fourier map before refinement with bond length and angle restraints as required to facilitate realistic modelling, where they could not be located they were not modelled. X-ray data are summarised in Table 1 and specific refinement details (where required) are given below.

2.3.2. Specific refinement details

2.3.2.1. [NiL^1]·EtOH. Each of the ethanol solvent molecules are disordered and modelled over two positions.

2.3.2.2. [(FeL^4)$_2$(μ-O)]$_2$·1.5THF·0.4EtOH·0.6H$_2$O. One of the THF molecules and the water molecules are disordered and each was modelled over two positions. The water hydrogens could not be located in the difference Fourier map and were not modelled. A number of bond length and angle restraints were required in the modelling of the disordered THF and the ethanol molecule.

2.3.2.3. [Ni$_2$L^5]·0.25EtOH·0.125py. The ethanol and pyridine solvate molecules are disordered across a special position and a number of bond length and angle restraints were required to facilitate realistic modelling.

Table 1
Crystal and structure refinement data.

Compound	**1**	$[\mathrm{Ni}(\mathbf{L}^{1})]\cdot\mathrm{py}$	$[\mathrm{Ni}(\mathbf{L}^{1})]\cdot\mathrm{EtOH}$	$[\mathrm{Ni}(\mathbf{L}^{2})]$	$[\mathrm{Cu}(\mathbf{L}^{1})]\cdot\mathrm{py}$	$[\mathrm{Cu}(\mathbf{L}^{1})]\cdot0.5\mathrm{CHCl_3}$	$[\mathrm{Fe}(\mathbf{L}^{4})_2(\mu_2\text{-}\mathrm{O})]_2\cdot1.5\mathrm{THF}\cdot0.4\mathrm{EtOH}\cdot0.6\mathrm{H_2O}$	$\mathbf{3}\cdot\mathrm{H_2O}$	$[\mathrm{Ni_2}(\mathbf{L}^{5})]\cdot0.25\mathrm{EtOH}\cdot0.125\mathrm{py}$
Formula of refinement model	$C_{16}H_{16}N_2O$	$C_{28}H_{23}N_3NiO_2$	$C_{25}H_{24}N_2NiO_3$	$C_{27}H_{26}N_2NiO_2$	$C_{28}H_{23}CuN_3O_2$	$C_{47}H_{37}Cl_3Cu_2N_4O_4$	$C_{62.80}H_{75.60}Fe_3N_4O_{7.50}$	$C_{26}H_{24}N_4O$	$C_{41.625}H_{32.625}N_{4.125}Ni_2O_{4.25}$
Molecular weight	252.31	492.20	1501.01	469.21	497.03	955.24	1118.17	408.49	776.01
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic
Space group	$C2/c$(#15)	$Pbca$(#61)	Cc(#9)	P^21/c(#14)	P^21/n(#14)	P^21/n(#14)	$P\bar{1}$(#2)	$Pbcn$(#60)	P^21/c(#14)
a (Å)	15.5020(10)	16.209(2)	20.063(3)	12.4950(10)	13.200(3)	18.425(9)	12.083(5)	13.452(3)	11.6715(6)
b (Å)	16.3660(10)	11.9420(15)	19.879(3)	16.2690(13)	9.639(2)	10.912(5)	14.335(6)	16.994(3)	22.0514(12)
c (Å)	11.6720(7)	23.643(3)	22.246(3)	11.7310(10)	17.734(4)	22.707(14)	18.401(8)	9.221(2)	13.4293(7)
α (°)							72.461(8)		
β (°)	111.136(3)		102.714(2)	113.7480(10)	93.023(3)	113.821(6)	86.676(9)		100.232(2)
γ (°)							82.305(7)		
V (Å^3)	2762.0(3)	4576.5(10)	8655(2)	2182.8(3)	508.5(3)	4176(4)	3011(2)	2108.0(7)	3401.4(3)
D_c (g cm^{-1})	1.214	1.429	1.410	1.428	1.465	1.519	1.233	1.287	1.515
Z	8	8	16	4	4	4	2	4	4
Crystal size (mm)	0.30 × 0.25 × 0.10	0.40 × 0.35 × 0.30	0.40 × 0.35 × 0.32	0.40 × 0.35 × 0.30	0.40 × 0.30 × 0.25	0.30 × 0.20 × 0.05	0.40 × 0.30 × 0.05	0.20 × 0.10 × 0.05	03 × 0.2 × 0.05
Crystal colour	colourless	brown	brown	brown	green	green	red	colourless	brown
Crystal habit	plate	block	block	block	prism	plate	plate	plate	plate
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
μ(Mo Kα) (mm^{-1})	0.077	0.879	0.926	0.916	1.001	1.261	0.536	0.081	1.159
T(SADABS)$_{\mathrm{min,max}}$	0.5140, 0.7461	0.6581, 0.7457	0.6323, 0.7457	0.6232, 0.7457	0.6471, 0.7457	0.5191, 0.7457	0.6587, 0.7457	0.6246, 0.7457	0.6454, 0.7457
$2\theta_{\max}$ (°)	60.88	56.64	56.64	56.62	56.74	52.74	54.26	56.50	56.70
hkl range	−22 17, −23 20, −16 16	−20 21, −15 15, −31 31	−26 26, −26 25, −29 29	−16 16, −21 21, −15 15	−17 17, −12 12, −23 23	−21 23, −13 13, −27 28	−15 15, −18 18, −23 23	−17 17, −22 22, −12 12	−15 15, −28 29, −17 17
N	20528	43098	42827	21636	21684	29543	27429	12699	67496
N_{ind} (R_{merge})	4183 (0.0584)	5638 (0.0673)	20032 (0.0339)	5288 (0.0201)	5445 (0.0500)	8489 (0.0948)	13058 (0.0648)	2581 (0.1295)	8355 (0.0431)
N_{obs} ($I > 2\sigma(I)$)	3362	3895	17227	4870	3824	5568	6933	947	6914
N_{var}	183	308	1150	293	308	543	722	146	481
R_1[a] (F) ($I > 2\sigma(I)$)	0.0438	0.0379	0.0415	0.0290	0.0391	0.0982	0.0634	0.0689	0.0711
$wR2$[a] (F^2) (all)	0.1318	0.0854	0.1001	0.0827	0.0975	0.2634	0.2029	0.1630	0.1572
A[a], B[a]	0.0699, 1.2169	0.0354, 2.1618	0.0536, 2.1420	0.0488, 1.1140	0.0490,0.4488	0.0677, 84.4600	0.1099, 0.0000	0.0589, 0.0687	0.0000, 21.23520
Goodness-of-fit	1.032	0.990	1.013	1.004	1.010	1.049	0.969	0.980	1.243
$\Delta\rho_{\mathrm{min,max}}$ (e$^-$ Å^{-3})	−0.291, 0.450	−0.258, 0.536	−0.361, 1.620	−0.248, 0.504	−0.447, 0.462	−1.270, 1.819	−0.935, 0.829	−0.364, 0.258	−0.888, 1.442

[a] $R_1 = \sum||Fo| - |Fc||/\sum|Fo|$ for $Fo > 2\sigma(Fo)$ and $wR_2 = (\Sigma w(Fo^2 - Fc^2)^2/\sum(wFc^2)^2)^{1/2}$ where $w = 1/[\sigma^2(Fo^2) + (AP)^2 + BP]$, $P = (Fo^2 + 2Fc^2)/3$ and A and B are listed in the crystal data su.

3. Results and discussion

Reaction of *o*-phenylenediamine and benzoylacetone in refluxing ethanol yielded the 1:1 Schiff base condensation product **1** whose X-ray structure (Fig. 2) confirmed the previously assigned ‘open’ single imine structure [11,13] (rather than a 7-membered diaza ring structure of the type obtained previously from the 1:1 condensation of acetylacetone and ethylenediamine) [23]. Reaction of **1** with salicylaldehyde or 5-*tert*-butyl-salicylaldehyde *in situ* in the presence of Ni(II), Cu(II), or Zn(II) acetate resulted in metal template syntheses of the corresponding asymmetric Schiff base complexes of type **2**: $[NiL^1]\cdot py$, $[NiL^1]\cdot EtOH$, $[NiL^2]\cdot 0.33H_2O$, $[CuL^1]\cdot 0.5CHCl_3$, $[CuL^1]\cdot py$, $[CuL^2]\cdot 0.5H_2O$ and $[ZnL^2]\cdot 1.5H_2O$.

The X-ray structures of $[NiL^1]\cdot py$ and $[NiL^1]\cdot EtOH$ (Fig. 3a and b) are similar and confirm that the Ni(II) ion has a square planar coordination geometry in each case with the benzene ring from the *o*-phenylenediamine moiety rotated between 14 and 18 degrees with respect to the coordination plane in the respective structures. In both structures, two adjacent molecules pack closely together in a dimeric arrangement (Fig. 3b). There is a moderately close contact between the conjugated γ-carbon and the adjacent Ni(II) centres of 3.3 Å in the case of $[NiL^1]\cdot py$ and 3.2 Å in $[NiL^1]\cdot EtOH$, which may assist with stabilisation of the close (dimeric) packing arrangement. Although such a contact does not seem to have been highlighted in the past, a search of the CSD revealed a number of other low-spin Ni(II), nominally square planar structures, that also show related Ni–π system contacts [24]. These metal-π contacts are reminiscent of those observed previously in a number of Cu(II) complex species [25].

In $[NiL^1]\cdot py$ there are also a number of weak π-π interactions between adjacent dimers and pyridine solvate molecules leading to an overall three dimensional network arrangement. In $[NiL^1]\cdot EtOH$ the disordered solvent is hydrogen bonded to the coordinated oxygens and weak π–π interactions occur between dimers, resulting in a two-dimensional array that extends throughout the lattice.

The crystal structure of $[NiL^2]$ (Fig. 4) shows that the metal is again square planar being bound to the O_2N_2 donor set of the doubly deprotonated form of H_2L^2; adjacent molecules again pack closely to yield a dimeric arrangement. However, in contrast to the structures just discussed, there are no Ni–C distances of less than 3.5 Å (attributable to the steric influence of the bulky *tert*-butyl group); while there is a number of offset face-to-face π–π interactions present. Neighbouring dimers stack in a herringbone-like motif through edge-to-face π–π interactions.

In a similar fashion to the nickel complexes just discussed, the crystal structures of $[CuL^1]\cdot py$ and $[CuL^1]\cdot 0.5CHCl_3$ reveal that the Cu(II) centres adopt square planar geometries (Fig 5). The crystal packing in $[CuL^1]\cdot 0.5CHCl_3$ is quite similar to that occurring for $[NiL^1]\cdot py$, with adjacent molecules forming dimeric species via Cu–π interactions (3.1 Å) that appear similar to those described previously by us and others [25]. If these weak interactions are

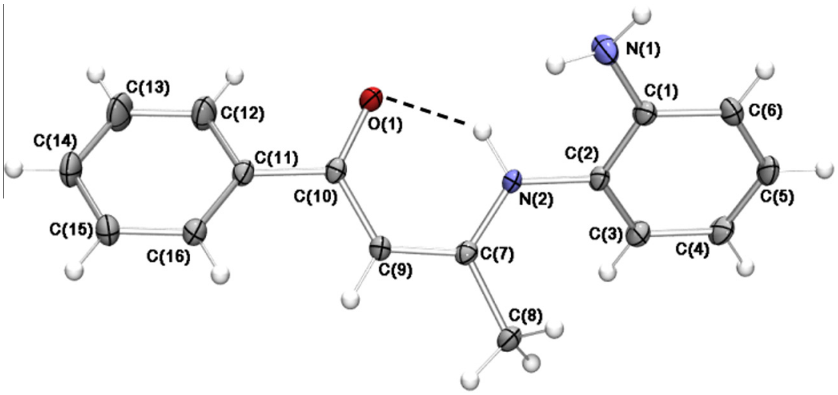


Fig. 2. X-ray structure of the Schiff base intermediate, 3-(2-aminophenylamino)-1-phenylbut-2-en-1-one (**1**), formed by 1:1 condensation of *o*-phenylenediamine and benzoylacetone, shown with 50% probability ellipsoids. The dashed line indicates a hydrogen bond.

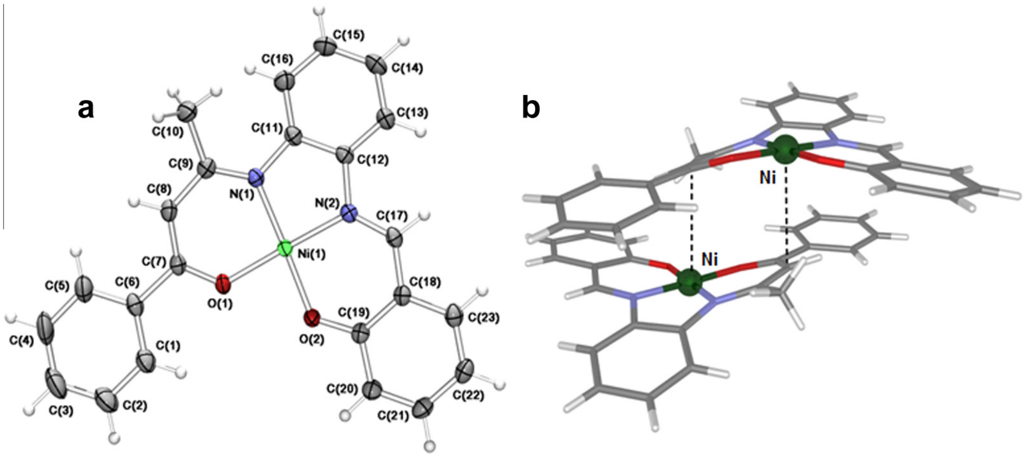


Fig. 3. (a) X-ray structure of the $[NiL^1]\cdot py$ with 50% probability ellipsoids and (b) schematic representation of the dimeric close packing in $[NiL^1]\cdot EtOH$. Both complexes have similar square planar coordination geometries and dimeric packing arrangements. Dashed lines indicate intermolecular contacts between nickel centres and the π-systems of adjacent bound L^1 ligands; solvate molecules not shown.

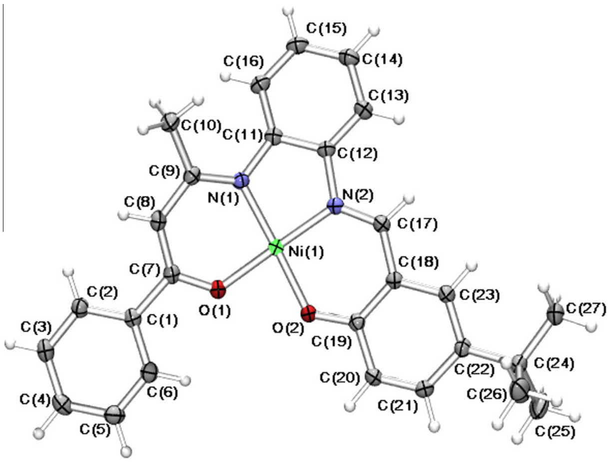


Fig. 4. X-ray structure of $[NiL^2]$ shown with 50% probability ellipsoids.

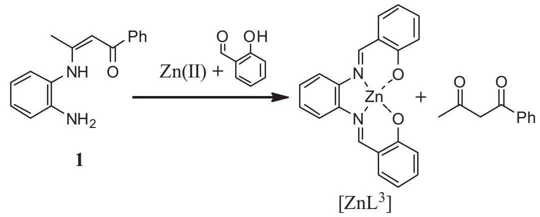


Fig. 6. Schiff base exchange reaction to form $[ZnL^3]$.

included as part of the coordination sphere then the overall coordination geometry can be considered as pseudo-five coordinate; the chloroform solvate molecule is hydrogen bonded to adjacent coordinated oxygens. Neighbouring dimers again interact via a series of weak π–π interactions to form an infinite three-dimensional arrangement. This contrasts slightly with the packing in $[CuL^1]\cdot py$ in which the copper centres interact with *o*-phenylenediamine rings, indicated by Cu-C distances of 3.0–3.3 Å, forming infinite columnar arrays. These π-stack further with adjacent columns and pyridine solvent molecules to yield an infinite three-dimensional lattice.

Unexpectedly, attempts to obtain mononuclear complexes of types $[ZnL^1]$ and $[FeL^2]$ using a similar procedure to that illustrated in Fig. 1, resulted instead in Schiff base exchange to yield the known [26] symmetric Schiff base complex $[ZnL^3]$ [where L^3 is *N*,*N*′-*o*-phenylenebis(salicylimineato)] (see Fig. 6) and the new Fe(III) species $[(FeL^4)_2O]\cdot 1.5THF\cdot 0.4EtOH\cdot 0.6H_2O$ [where L^4 is *N*,*N*′-*o*-phenylenebis(5-*tert*-salicylimineato)], the crystal structure of this iron complex was determined (see below). In these products the benzoylacetonimine moiety in the precursor **1** has been replaced by a salicylaldiminato or 5-*tert*-butylsalicyliminato group, undoubtedly reflecting the inherent solution lability of the imine functions present in **1** [27], with the exchange reaction representing an example of "dynamic covalent chemistry" [28], perhaps driven by the formation of more thermodynamically stable symmetrical Schiff base products. Alternatively, the relative solubilities of the symmetrical versus the non-symmetrical products under the conditions employed could also be important in determining which of these products is isolated.

Crystals of the oxo-bridged species, $[(FeL^4)_2O]\cdot 1.5THF\cdot 0.4EtOH\cdot 0.6H_2O$, suitable for X-ray diffraction were obtained on slow evaporation of an ethanol/chloroform solution of the initial isolated complex in the presence of added dabco as base. In forming this iron complex clearly the Fe(II) employed initially is aerially oxidised to Fe(III) during the course of the reaction which was carried out in air; other examples of such Fe(II)/Fe(III) oxidation in air have been documented [29]. This complex was also synthesised directly by the *in situ* reaction of 5-*tert*-butyl-salicylaldehyde, *o*-phenylenediamine and Fe(II) chloride (2:1:1 mol ratio) in ethanol in air.

Other related oxo bridged Fe(III) species incorporating Schiff base ligands derived from salicylaldehyde or its substituted derivatives have been reported [30-32]. The X-ray structure of the present complex (Fig. 7) shows that the iron centres in each $[Fe^{III}L^4]^+$ unit are bridged by an oxo bridge to form dinuclear $[(FeL^4)_2O]$ units; pairs of these are then further intermolecularly linked via phenoxide oxygen to Fe(III) contacts ($Fe–O_{phenolic}$ distances of 2.44 Å) to form an unusual supramolecular $[(FeL^4)_2O]_2$ tetranuclear cluster. The $Fe–O_{oxo}–Fe$ angle is 153.6°, compared to 176.5° in the related complex, $[\{Fe(3,5\text{-}t\text{-}BuSalphen)\}_2(\mu\text{-}O)]$ (where 3,5-*t*-BuSalphen is the corresponding ligand incorporating *tert*-butyl in both the 3- and 5-positions of its salicyl rings) [31]. Other aspects of the two structures are also quite similar, including the displacement of the five-coordinate iron centres from their respective mean basal planes (0.56 Å in the present structure compared to 0.54 and 0.55 Å in $[\{Fe(3,5\text{-}t\text{-}BuSalphen)\}_2(\mu\text{-}O)]$). However, the present structure differs by the presence of the bridging phenolic oxygens. Each of the resulting tetranuclear

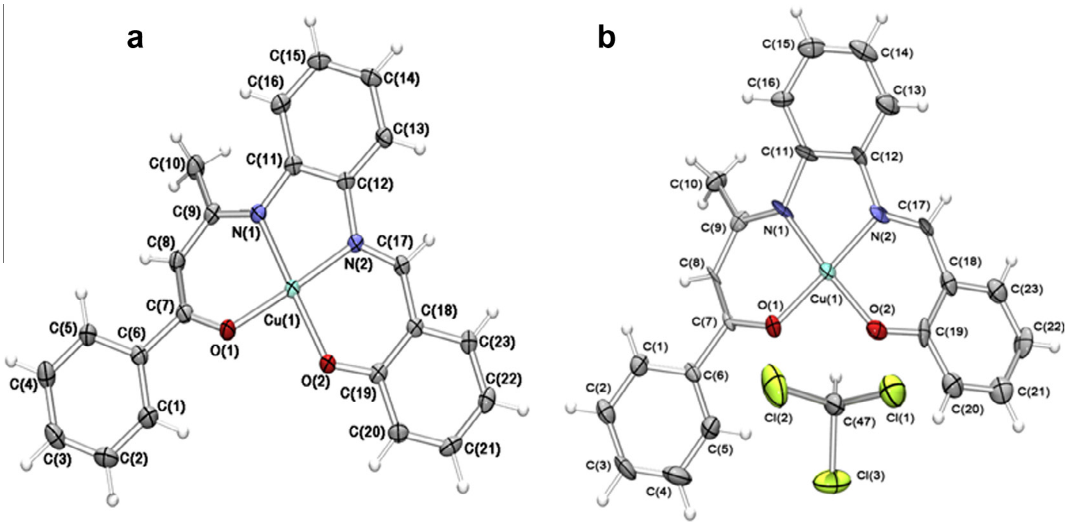


Fig. 5. X-ray structures of (a) $[CuL^1]\cdot py$ and (b) $[CuL^1]\cdot 0.5CHCl_3$ with 50% probability ellipsoids; the pyridine solvate is not shown.

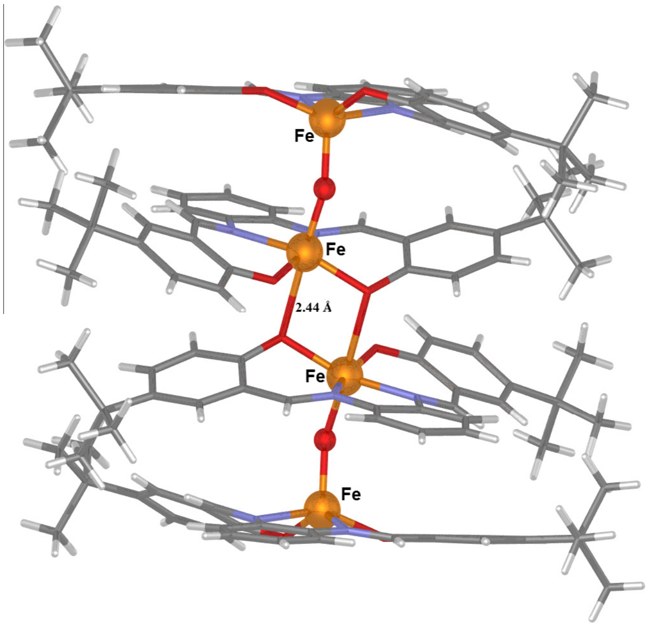


Fig. 7. X-ray structure of the tetrameric complex, $[(FeL^4)_2(\mu\text{-}O)]_2\cdot1.5THF\cdot0.4EtOH\cdot0.6H_2O$; the lattice solvate molecules are not shown.

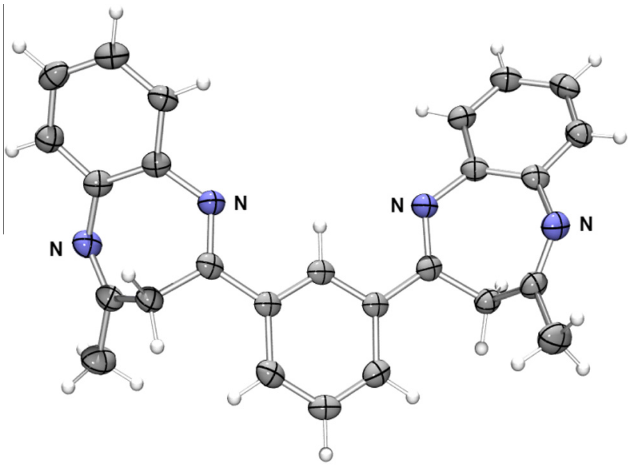
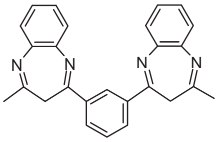


Fig. 8. X-ray structure of **3**·H_2O with 50% probability ellipsoids; the water solvate is not shown.

clusters interacts further with two neighbouring molecules via π–π interactions (indicated by carbon–carbon distances of 3.2–3.4 Å); this results in the formation of an infinite one-dimensional polymer that propagates along the crystallographic *b*-axis.

In an extension of the above investigation (that also extends our past studies involving difunctional *β*-diketone ligands) [33] we have probed the use of the 1,3-phenylene-linked, bis-*β*-diketone derivative, 1,1-(1,3-phenylene)-bis-butane-1,3-dione [22], in place of benzoylacetylacetone, for undertaking related studies to those just described. In an initial attempt to obtain a phenylene-bridged bis-Schiff base analogue of **1** (see Fig. 1) incorporating terminal anilino groups by 1:2 reaction of the above bis-*β*-diketone derivative with *o*-phenylenediamine in hot ethanol resulted instead in the formation of **5**, 1,3-bis(4-(methyl)-3*H*-benzo[*b*][1,4]diazepin-2-yl)benzene, as colourless crystals.



5

The X-ray stucture of this product (Fig. 8), which crystallises as its monohydrate, confirmed that two partially conjugated, 7-membered, diaza-heterocyclic rings had been generated. This arrangement thus contrasts markedly with that obtained (Fig. 2) for the mono-Schiff base **1** discussed earlier, formed by 1:1 condensation of *o*-phenylenediamine and benzoylacetone (see Fig. 1).

The solvent water molecules in the crystal lattice of **3**·H_2O are involved in hydrogen bonding interactions with the 'outermost' nitrogen atoms of the 7-membered rings (O(1 W)H···N(1) 1.99(4) Å) forming an undulating hydrogen bonded polymeric chain that extends along the crystallographic *a*-axis (Fig. 9).

Despite the above result, it was found that an *in situ* (presumably template) reaction in which an ethanol solution of Ni(II) acetate was heated with 1,1-(1,3-phenylene)-bis-butane-1,3-dione), *o*-phenylenediamine and salicylaldehyde in a 1:2.2 ratio resulted in isolation of the target dinuclear Schiff base nickel complex of type $[Ni_2L^5]$ (**6**) whose X-ray structure (Fig. 10) indicated an overall composition of $[Ni_2L^5]\cdot0.25EtOH\cdot0.125py$.

The two Ni(II) centres adopt, in a similar fashion to $[NiL^1]$, a low-spin square planar coordination geometry. The entire molecule is close to planar with only small deviations from planarity occurring for the methyl groups and *o*-phenylenediamine rings. Presumably reflecting steric effects, the coordinating moieties are arranged in a *syn* fashion so that the "salicylimine" aryl rings have maximum separation and lie closest to the 4 and 6 positions on the central 1,3-subsituted phenylene (rather than on the opposite side). This configuration is further stabilised by weak $H_{phenylene}$–O interactions. Interestingly, the *syn* arrangement contrasts with that adopted by the precursor bis-*β*-diketone ligand upon coordination, but parallels the arrangement adopted by the corresponding free ligand in the solid state [22].

As observed in each of the structures reported above, the crystal packing is again dominated by π–π stacking. Adjacent molecules once more form a dimeric arrangement with close Ni–O contacts

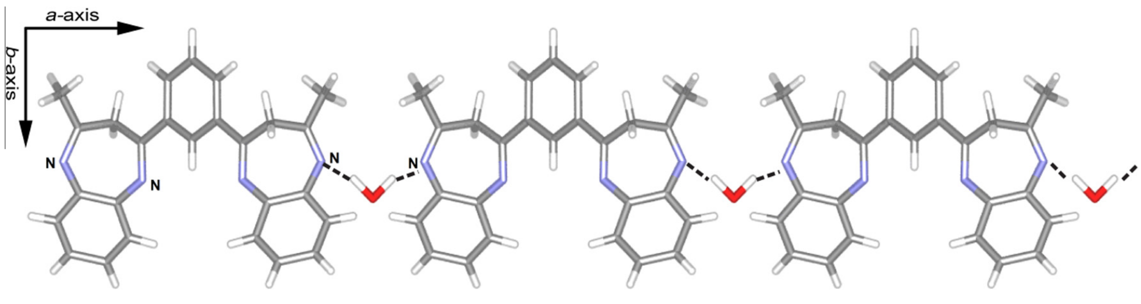
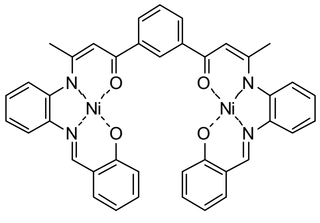


Fig. 9. Part of the infinite hydrogen bonded chain in the X-ray structure of **3**·H_2O.



6; $[Ni_2(L^4)]$

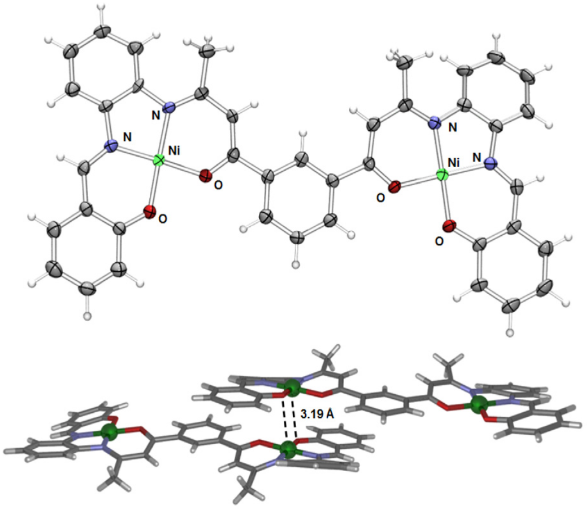


Fig. 10. The X-ray structure of $\{[Ni_2L^5]\cdot0.25EtOH\cdot0.125py$ shown with 50% probability ellipsoids (top) and a schematic representation of the supramolecular interactions between adjacent molecules illustrating the Ni–O contacts (3.19 Å), the corresponding Ni–Ni distance is 3.38 Å; solvate molecules are not shown.

(3.19 Å). Neighbouring dimers undergo further offset face-to-face π–π interactions to form one-dimensional chains. Each of these chains then interact with others to yield a herringbone type motif through edge-to-face π–π stacking, leading to the formation of infinite sheet-like two-dimensional layers. The disordered solvent molecules are located between the layers.

4. Conclusions

The results presented in this study are noteworthy on at least three counts. First, the known range of unsymmetrical tetradentate ligand complexes of Ni(II), Cu(II) and Zn(II) of type **2** has been extended and, in addition, two new Schiff base exchange reactions that yield corresponding doubly deprotonated symmetrical ligands complexes are reported. Secondly, the product of one of the exchange reactions has an unprecedented (as far as we are aware) supramolecular tetranuclear Fe(III) cluster structure incorporating both oxo bridges and longer phenoxo-bridges between iron centres. Finally, $[Ni_2L^5]\cdot0.25EtOH\cdot0.125py$ represents the first example of the new category of dinuclear complexes corresponding to the mononuclear (unsymmetric) Schiff base analogues of type **2**. Further studies on systems of this latter type are planned.

Acknowledgments

This work was supported by China Scholarship Council (2007A18016) and the Science and Technology Commission of Shanghai Municipality (0752nm016). We also acknowledge the Australian Research Council for funding.

Appendix A. Supplementary data

CCDC 849402–849410 contain the supplementary crystallographi data for **1**, **3**$\cdot H_2O$, $[NiL^1]\cdot py$, $[NiL^1]\cdot EtOH$, $[NiL^2]$, $[CuL^1]\cdot py$, $[CuL^1]\cdot0.5CHCl_3$, $[(FeL^4)_2(\mu\text{-}O)]_2\cdot1.5THF\cdot0.4EtOH\cdot0.6H_2O$ and $[NiL^5]\cdot0.25EtOH\cdot0.125py$. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/services/structure_deposit or from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033, or e-mail: deposit@ccdc.cam.ac.uk.

References

[1] A. Combes, C.R. Acad, Sci. Paris 108 (1889) 1252.
[2] C.J. Whiteoak, G. Salassa, A. Kleij, Chem. Soc. Rev. 41 (2012) 622.
[3] (a) See, for example: J. Eilmes, M. Basato, G. Valle, Inorg. Chim. Acta 290 (1999) 14;
(b) L.F. Lindoy, W.E. Moody, J. Am. Chem. Soc. 99 (1977) 5863;
(c) L.F. Lindoy, W.E. Moody, D. Taylor, Inorg. Chem. 1977 (1962) 16;
(d) R.H. Holm, G.W. Everett, A. Chakravorty, Prog. Inorg. Chem. 7 (1966) 183;
(e) P. Pfeiffer, E. Breith, E. Lübbe, T. Tsumaki, Justus Liebig's, Ann. Chem. 503 (1933) 84.
[4] C. Pariya, F.R. Fronczek, A. Maverick, Inorg. Chem. 50 (2011) 2748. and references therein.
[5] (a) D. Chen, A.E. Martell, Y. Sun, Inorg. Chem. 28 (1989) 2647;
(b) A.E. Martell, D.T. Sawyer (Eds.), Oxygen Complexes and Oxygen Activation by Transition Metals, Plenum Press, New York, 1988.
[6] A. Trujillo, M. Fuentealba, D. Carrillo, C. Manzur, I. Ledoux-Rak, J.-R. Hamon, J.-Y. Saillard, Inorg. Chem. 49 (2010) 2750.
[7] (a) M.M. Belmonte, J. Benet-Buchholz, A.W. Kleij, Chem. Commun. 46 (2010) 4580;
(b) A. Decortes, S.I. Vagin, R. Reichardt, S. Klaus, B. Rieger, J. Am. Chem. Soc. 132 (2010) 14367;
(c) A.W. Kleij, Eur. J. Inorg. Chem. 193 (2009) 193;
(d) S. Curreli, E.C. Escudero-Adán, J. Benet-Buchholz, A.W. Kleij, J. Org. Chem. 7 (2007) 7018;
(e) X. Wu, A.V.E. Gorden, Eur. J. Org. Chem. 4 (2009) 503;
(f) F.H. Zelder, J. Rebek Jr., Chem. Commun. (2006) 753;
(g) M. Holbach, X. Zheng, C. Burd, C.W. Jones, M. Weck, J. Org. Chem. 71 (2006) 2903;
(h) A. Wantanabe, K. Matsumoto, Y. Shimada, T. Katsuki, Tetrahedron Lett. 45 (2004) 6229;
(i) A.R. Silva, C. Freire, B. de Castro, New J. Chem. 28 (2004) 253;
(j) P.G. Cozzi, Chem. Soc. Rev. 33 (2004) 410;
(k) I. Kuzniarska-Biernacka, A.R. Silva, R. Ferreira, A.P. Carvalho, J. Pires, M. Brotas de Carvalho, C. Freire, B. De Castro, New J. Chem. 28 (2004) 853;
(l) C.M. Che, J.S. Huang, Coord. Chem. Rev. 242 (2003) 97;
(m) C. Baleizão, B. Gigante, M. Garcia, A. Corme, Tetrahedron Lett. 44 (2003) 6813;
(n) T.P. Yoon, E.N. Jacobsen, Science 299 (2003) 1691;
(o) A. Watanabe, T. Uchida, K. Ito, T. Katsuki, Tetrahedron Lett. 43 (2002) 4481;
(p) M. Bandini, P.G. Cozzi, A.U. Ronchi, Chem. Commun. (2002) 919;
(q) E.N. Jacobsen, Acc. Chem. Res. 33 (2000) 421;
(r) T.S. Reger, K. Janada, J. Am. Chem. Soc. 122 (2000) 6929;
(s) T. Katsuki, Coord. Chem. Rev. 140 (1999) 189.
[8] (a) L. Shi, H.-M. Ge, S.-H. Tan, H.-Q. Li, Y.-C. Song, H.-L. Zhu, R.-X. Tan, Eur. J. Med. Chem. 42 (2007) 558;
(b) P. Panneerselvam, R.R. Nair, G. Vijayalakshmi, S.K. Subramanian, S.K. Sridhar, Eur. J. Med. Chem. 40 (2005) 225.
[9] (a) P.D. Frischmann, G.A. Facey, P.Y. Ghi, A.J. Gallant, D.L. Bryce, F. Lelj, M.J. MacLachlan, J. Am. Chem. Soc. 132 (2010) 3893;
(b) T. Nabeshima, Bull. Chem. Soc. Jpn. 83 (83) (2010) 969;
(c) Q. Meng, J.K. Clegg, K.A. Jolliffe, L.F. Lindoy, M. Lam, G. Wei, Chem. Commun. 13 (2010) 558;
(d) S. Akine, T. Nabeshima, Dalton Trans. (2009) 10395;
(e) Z. Guo, W.L. Tong, M.C.W. Chan, Chem. Commun. (2009) 6189;
(f) S. Akine, F. Utsuno, T. Nabeshima, Chem. Commun. 46 (2010) 1029;
(g) S.J. Wezenberg, A.W. Kleij, Angew. Chem., Int. Ed. 47 (2008) 2354;
(h) T. Nabeshima, H. Miyazaki, A. Iwasaki, S. Akine, T. Saiki, C. Ikeda, Tetrahedron 63 (2007) 3328;
(i) S. Akine, S. Sunaga, T. Taniguchi, H. Miyazaki, T. Nabeshima, Inorg. Chem. 46 (2007) 2959;
(j) T. Nabeshima, H. Miyazaki, A. Iwasaki, S. Akine, T. Saiki, C. Ikeda, S. Sato, Chem. Lett. 35 (2006) 1070;
(k) A.J. Gallant, J.H. Chong, M.J. MacLachlan, Inorg. Chem. 45 (2006) 5248;
(l) S. Akine, T. Taniguchi, T. Nabeshima, Tetrahedron Lett. 42 (2001) 8861;
(m) L.G. Armstrong, H.C. Lip, L.F. Lindoy, M. McPartlin, P.A. Tasker, J. Chem. Soc., Dalton Trans. (1977) 1771.
[10] (a) G.A. Kolawole, A.A. Osowole, J. Coord. Chem. 62 (2009) 1437;
(b) M.S. Ray, R. Bhattacharya, S. Chaudhuri, L. Righi, G. Bocelli, G. Mukhopadhyay, A. Ghosh, Polyhedron 22 (2003) 617;
(c) J.-P. Costes, M.I. Fernandez-Garcia, Inorg. Chim. Acta 237 (1995) 57;

(d) M. Kwiatkowski, G. Bandoli, J. Chem. Soc., Dalton Trans. (1992) 379;
(e) M. Kwiatkowski, E. Kwiatkowski, A. Olechnowicz, D.M. Ho, E. Deutsch, J. Chem. Soc., Dalton Trans. (1990) 2497;
(f) M. Kwiatkowski, E. Kwiatkowski, A. Olechnowiez, D.M. Ho, E. Deutsch, J. Chem. Soc., Dalton Trans. (1990) 3063;
(g) N. Matsumoto, S. Yamashita, A. Ohyoshi, S. Kohata, H. Okawa, J. Chem. Soc., Dalton Trans. (1988) 1943;
(h) T. Nagahara, M. Suzuki, K. Kasuga, Inorg. Chim. Acta 149 (1988) 279;
(i) C.T. Brewer, G. Brewer, J. Chem. Soc., Chem. Commun. (1988) 85.

[11] D. Pawlica, M. Marszałek, G. Mynarczuk, L. Sieroń, J. Eilmes, New J. Chem. 28 (2004) 1615.

[12] E.C. Escudero-Adán, M.M. Belmonte, E. Martin, G. Salassa, J. Benet-Buchholz, A.W. Kleij, J. Org. Chem. 76 (2011) 540 (and refs. therein).

[13] M. Sulca, A.Y. Strakov, I. Hirsbergs, Latv. PSR. Zinat. Akad. Vestis Ser. Chim. 2 (1971) 186.

[14] (a) A. Trujillo, F. Justaud, L. Toupet, O. Cador, D. Carrillo, C. Manzur, J.-R. Hamon, New J. Chem. 35 (2011) 2027;
(b) M. Fuentealba, A. Trujillo, J.R. Hamon, D. Carrillo, C. Manzur, J. Mol. Struct. 881 (2008) 76.

[15] J.K. Clegg, L.F. Lindoy, J.C. McMurtrie, D. Schilter, Dalton Trans. (2005) 857.

[16] Bruker-Nonius, APEX v2.1, SAINT v. 7 and XPREP v.6.14, Bruker AXS Inc., Madison, Wisconsin, USA, 2003.

[17] Bruker-Nonius, SAINT and XPREP. Bruker AXS Inc. Madison, Wisconsin, USA, 2003.

[18] Bruker, SMART, SAINT and XPREP. Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1995.

[19] WinGX-32: System of programs for solving, refining and analysing single crystal X-ray diffraction data for small molecules L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.

[20] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giocavazzo, A. Guagliardi, A.G.C. Moliterni, G. Polidori, S. Spagna, J. Appl. Crystallogr. 32 (1999) 115.

[21] G.M. Sheldrick, SADABS, Empirical Absorption and Correction Software, University of Göttingen, Germany, 1999–2008.

[22] G.M. Sheldrick, SHELXL-97: Programs for Crystal Structure Analysis, University of Göttingen, Germany, 1997.

[23] S. Meicheng, W. Lifeng, Z. Zeying, T. Youqi, Sci. Sin., Ser. B (Engl. Ed.) 27 (1984) 137.

[24] (a) See, for example: D.V. Soldatov, A.T. Henegouwen, G.D. Enright, C.I. Ratcliffe, J.A. Ripmeester, Inorg. Chem. 40 (2001) 1626;
(b) A. Giacomelli, C. Floriani, G. Perego, Chem. Commun. (1982) 650;
(c) M. Mulqi, F. Stephens, R.S. Vagg, Inorg. Chim. Acta. 52 (1981) 73.

[25] (a) K.B. Heine, J.K. Clegg, A. Heine, K. Gloe, K. Gloe, T. Henie, G. Gernhard, Z.-L. Cai, J.R. Reimers, L.F. Lindoy, J. Lach, B. Kersting, Inorg. Chem. 50 (2011) 1498;
(b) S.R. Choudhury, H.M. Lee, T.-H. Hsiao, E. Colacio, A.D. Jana, S. Mukhopadhyay, J. Mol. Struct. 967 (2010) 131;
(c) W.-K. Dong, Y.-X. Sun, X.-N. He, J.-F. Tong, J.-C. Wu, Spectrochim. Acta, Part A 76 (2010) 476;
(d) K. CuHelios, R. Wysokinski, W. Zierkiewicz, L.M. Proniewicz, D. Michalska, J. Phys. Chem. B 113 (2009) 8158;
(e) H. Yorita, K. Otomo, H. Hiramatsu, A. Toyama, T. Miura, H. Takeuchi, J. Am. Chem. Soc. 130 (2008) 15266;
(f) A. Hori, T. Arii, Cryst. Eng. Commun. 9 (2007) 215;
(g) D. CuMichalska, K. Hernik, R. Wysokiński, B. Morzyk-Ociepa, A. Pietraszko, Polyhedron 27 (2007) 4303;
(h) J.K. Clegg, L.F. Lindoy, J.C. McMurtrie, D. Schilter, Dalton Trans. (2006) 3114;
(i) J.K. Clegg, L.F. Lindoy, B. Moubaraki, K.S. Murray, J.C. McMurtrie, Dalton Trans. (2004) 2417;
(j) D. Van der Helm, C.E. Tatsch, Acta Crystallogr., Sect. B 28 (1972) 2307;
(k) W.A. Franks, D. Van der Helm, Acta Crystallogr., Sect. B 27 (1971) 1299.

[26] A.W. Kleij, Dalton Trans. (2009) 4635.

[27] (a) E.C. Escudero-Adán, M.M. Belmonte, J. Benet-Buchholz, A.W. Kleij, Org. Lett. 12 (2010) 4592;
(b) P.T. Corbett, J. Leclaire, L. Vial, K.R. West, J.-L. Wietor, J.K.M. Sanders, S. Otto, Chem. Rev. 106 (2006) 3652;
(c) C. Godoy-Alcantar, A.K. Yatsimirsky, J.M. Lehn, J. Phys. Org. Chem. 18 (2005) 979.

[28] (a) A. Granzhan, C. Schouwey, T. Riis-Johannessen, R. Scopelliti, K. Severin, J. Am. Chem. Soc. 133 (2011) 7106;
(b) A. Granzhan, T. Riis-Johannessen, R. Scopelliti, K. Severin, Angew. Chem., Int. Ed. 49 (2010) 5515;
(c) C.D. Meyer, C.S. Joiner, J.F. Stoddart, Chem. Soc. Rev. 36 (2007) 1705;
(d) S.J. Rowan, S.J. Cantrill, G.R.L. Cousins, J.K.M. Sanders, J.F. Stoddart, Angew. Chem., Int. Ed. 41 (2002) 898.

[29] (a) H.-Y. Xia, Y.-L. Liu, Acta Crystallogr., Sect. E 64 (2008) m1504;
(b) F. Pelascini, M. Wesolek, F. Peruch, A. De Cian, N. Kyritsakas, P.J. Lutz, J. Kress, Polyhedron 23 (2004) 3193;
(c) Y. Nakayama, Y. Baba, H. Yasuda, K. Kawakita, N. Ueyama, Macromolecules 36 (2003) 7953;
(d) G. Wolmershaeuser, G. Wortmann, M. Schnauber, J. Chem. Res. Synopses (1988) 358;
(e) B.J. Hathaway, D.G. Holah, J. Chem. Soc. (1964) 2408.

[30] (a) K. Oyaizu, E.L. Dewi, E. Tsuchida, Inorg. Chim. Acta 321 (2001) 205;
(b) A. Dedieu, M.M. Rohmer, A. Veillard, J. Am. Chem. Soc. 98 (1976) 5789;
(c) P. Coggon, A.T. McPhail, F.E. Mabbs, V.N. McLachlin, J. Chem. Soc. A, (1971) 1014.

[31] W.-J. Ruan, G.-H. Hu, S.-J. Wang, J.-H. Tian, Q.-L. Wang, Z.-A. Zhu, Chin. J. Chem. 23 (2005) 709.

[32] (a) J.M. Becker, J. Barker, G.J. Clarkson, R. van Gorkum, G.K. Johal, R.I. Walton, P. Scott, Dalton Trans. (2010) 2309;
(b) L.N. Rusere, T. Shalumova, J.M. Tanski, L.A. Tyler, Polyhedron 28 (2009) 3804;
(c) S. Konera, S. Iijimab, M. Watanabec, M. Satod, J. Coord. Chem. 56 (2003) 103;
(d) A. Mederos, S. Dominguez, R. Hernandez-Molina, J. Sanchiz, F. Brito, Coord. Chem. Rev. 193–5 (1999) 857;
(e) R.N. Mukherjee, T.D.P. Stack, R.H. Holm, J. Am. Chem. Soc. 110 (1988) 1850.

[33] (a) See, for example: F. Li, J.K. Clegg, R.B. MacQuart, L.F. Lindoy, G.V. Meehan, Nat. Comm. 2 (2011) 205;
(b) J.K. Clegg, F. Li, K.A. Jolliffe, G.V. Meehan, L.F. Lindoy, Chem. Commun. 47 (2011) 6042;
(c) J.K. Clegg, M.J. Hayter, K.A. Jolliffe, L.F. Lindoy, J.C. McMurtrie, G.V. Meehan, S.M. Neville, S. Parsons, P.A. Tasker, P. Turner, F.J. White, Dalton Trans. 39 (2010) 2804;
(d) J.K. Clegg, K. Gloe, M.J. Hayter, O. Kataeva, L.F. Lindoy, B. Moubaraki, J.C. McMurtrie, K.S. Murray, D. Schilter, Dalton Trans. (2006) 3977.