

# 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



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## ABSTRACT

The known Schiff base, 3-(2-aminophenylamino)-1-phenylbut-2-en-1-one (**1**), formed by 1:1 condensation of *o*-phenylenediamine and benzoylacetone 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<sub>2</sub>N<sub>2</sub>-tetradentate ligands. In contrast, reaction of Zn(II) acetate with **1** and salicylaldehyde led to Schiff base exchange (with loss of benzoylacetone) to yield symmetric [ZnL<sup>3</sup>] [where L<sup>3</sup> 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<sup>III</sup>(L<sup>4</sup>)<sub>2</sub>(μ-O)] species [where L<sup>4</sup> 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<sub>phenolic</sub> 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<sub>2</sub>L<sup>5</sup>], 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<sub>2</sub>O) 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<sub>2</sub>O, [NiL<sup>1</sup>].py, [NiL<sup>1</sup>].EtOH, [NiL<sup>2</sup>], [CuL<sup>1</sup>].py, [CuL<sup>1</sup>].0.5CHCl<sub>3</sub>, [(FeL<sup>4</sup>)<sub>2</sub>(μ-O)]<sub>2</sub>·1.5THF·0.4EtOH·0.6H<sub>2</sub>O and [NiL<sup>5</sup>].0.25EtOH·0.125py are reported.

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## 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

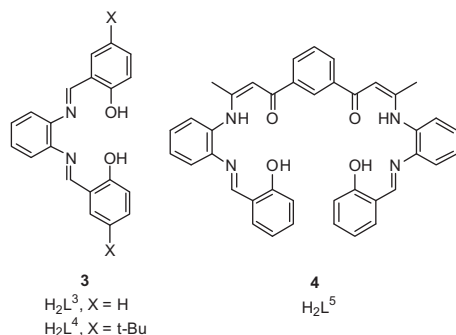
tetradentate ligand types but also some of the most studied [1–4]. Indeed such species have been known since Alfred Werner's time. [1] Ligands of this type typically lose two protons and coordinate in a square-planar manner to form neutral metal complexes with a number of divalent metal ions. Individual 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

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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  $\beta$ -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- $\beta$ -diketone derivative, 1,1'-(1,4-phenylene)bisbutane-1,3-dione.



## 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

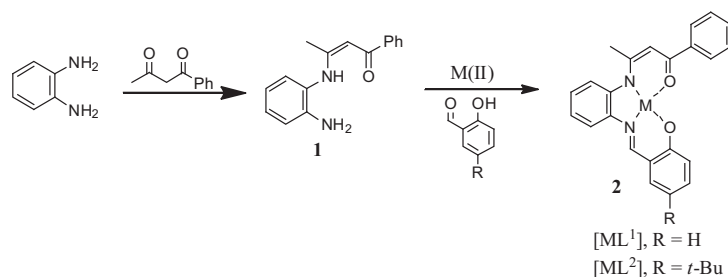
**3-(2-Aminophenylamino)-1-phenylbut-2-en-1-one (1)**: This was prepared by reaction of *o*-phenylenediamine with benzoylacetylacetone using a similar procedure to that reported previously [13]. Yield 75%.  $^1H$  NMR ( $\delta$ , ppm/ $CDCl_3$ ): 12.47 (H, br), 7.92 (2H, m), 7.44 (3H, m), 7.06 (2H, 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*-butylsalicylaldehyde (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.  $[NiL^1] \cdot EtOH$  and  $[NiL^1] \cdot py$ .**  $[NiL^1] \cdot EtOH$ : yield 78%, dark red-brown crystals.  $^1H$  NMR ( $\delta$ , 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):  $\lambda \sim 570$  (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.  $[NiL^1] \cdot py$ : A portion of the above product was recrystallised from pyridine (py) to yield brown crystals of  $[NiL^1] \cdot py$ ; a crystal from this batch was used directly for a structure determination.

**2.2.1.2.  $[NiL^2] \cdot 0.33H_2O$ .** Yield 85%, dark red-brown crystals.  $^1H$  NMR ( $\delta$ , 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),  $\lambda \sim 570$  (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).

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