Preparation and characterization of copper(II) and nickel(II) complexes of a new chiral salen ligand derived from (+)-usnic acid[†]

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Chiral copper(II) and nickel(II) complexes were obtained after reaction of diacetate salts with a new chiral salen ligand derived from (+)-usnic acid.

Complexes of diimino functionalized ligands are often used as catalysts for a wide variety of reactions. Salen ligands are prepared by the condensation of two equivalents of a salicylaldehyde derivatives with diamines. Chiral versions of such ligands are usually accessed using chiral 1,2-diamines.¹ However it could be possible to prepare chiral salen ligands from enantiopure salicylaldehyde derivatives. As a continuation of our ongoing work on enhancing the use of lichen substances,² we recently developed an efficient and rapid parallel synthesis of polyamine usnic acid derivatives.³ Due to their structures, this class of products possesses all the characteristics of salen ligands.

(+)-Usnic acid **1**, a polyfunctionalized compound, exhibited several biological activities⁴ and also metal binding properties. The preparation of copper(II) and palladium(II) complexes from (+)-usnic acid, acetyl and enamine derivatives has been already reported.⁵ The metal coordination abilities of this abundant lichen substance indicate that lichens could be considered as biomonitors of environmental metal ions. On the basis of the above observation we decided to explore for the first time the metal binding capacity of chiral salen ligand derived from (+)-usnic acid **1**. Thus this communication deals with the synthesis of a new chiral salen ligand and its use for the preparation of copper(II) and nickel(II) complexes.

The chiral salen ligand **2** was prepared by condensation of one equivalent of ethylene diamine with two equivalents of **1** in refluxing EtOH-THF (Scheme 1). After removing of unreacted diamine by washing with water, the excess of **1**, tedious to eliminate using conventional column chromatography, was finally scavenged by aminomethyl resin. Such **2** was isolated as pure form after recrystallization in high yield (84%). NMR spectroscopic analysis (Table 1) and X-ray crystal structure analysis[‡] (Fig. 1 and 3) show that **2** was obtained in its ketoenamine form rather than enolimine tautomer. This observation is in accordance with previous works reported by us³ and others.^{5,6} This is supported by a short C10–O6 bond with a length of 1.244 Å and a N1–H1



Scheme 1 Synthesis of complexes 3, 4, 7 and 8.

bond length of 0.861 Å, in agreement with Albrecht *et al.*^{6b} The C10–O6 bond length and the value of the C17N1C19 bond angle (128.48°) are also in accordance with calculated bond lengths (about 1.246 Å) and interplanar angles (124.554–128.64°) in *N*-salicylidene anilines in their ketoenamine forms.⁷

We here report the complexation of **2** with copper(II) and nickel(II). Metal complexes were quickly formed by adding to a solution of **2** in dichloromethane one equivalent of diacetate salt dissolved in a little amount of methanol. Slow evaporation of solvents gave violet and orange microcrystalline solids of copper(II) **3** and nickel(II) **4**[†] respectively in almost quantitative yields. All attempts to obtain a single-crystal suitable for X-ray structure analysis have failed so far. We however confirmed the formation of complexes **3** and **4** by HRMS. The Ni(II) complex **4** is diamagnetic and its structure was determined by ¹H and ¹³C NMR (Table 1). Signals of the methylene and the CH₃-12 groups

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Table 1	Selected ¹ H and	1 ¹³ C NMR	data of 2, 4,	6 and 8 in	CDCl ₃ ^a
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Nucleus	¹ H NMR	¹ H NMR				¹³ C NMR			
	2	4	6	8	2	4	6	8	
CH ₃ -12 CH ₂ CO-3	2.66 3.86	2.45 3.26	2.40 3.70	2.21 3.18	18.16 42.58 191.03	21.37 54.01 183.46	16.30 42.67 190.18	20.00 53.99 179.13	

^{*a*}δ in ppm.



Fig. 1 ORTEP drawing of the molecular structure of 2.

have respectively an upfield and a downfield shift in the ¹H and ¹³C NMR spectra, in comparison to the salen ligand **2**. On the other hand, the CO-3 signal is shifted to lower value with respect to that of **2** (Table 1). Finally, no signal of the amine proton (NH) of the keto-enamine tautomer was found in the ¹H spectrum of **4**. Moreover the IR spectra of **4** showed the disappearance of NH bands and the shift of the CO-3 band from 1550 cm⁻¹ to 1450 and 1410 cm⁻¹. All these observations support the coordination of Ni ion to the nitrogen and oxygen atoms of the enolimine form.

To obtain crystals suitable for X-ray structure analysis, we prepared (+)-7,9-di-*O*-benzylusnic acid **5**. Thus, (+)-usnic acid **1** was treated with tetramethylammonium hydroxide in hexamethylphosphoramide (HMPA) at 0 °C, and the resulting phenoxide ion alkylated with benzylbromide to provide the dialkylated derivative **5** in 26% yield.⁸ A new ligand **6** was synthesized after condensation of **5** with diaminoethane. The lack of selectivity of carbonyl groups C13 and C11 gave a complex mixture of compounds from which **6** was isolated in low yield (15%). The



Fig. 2 ORTEP drawing of the molecular structure of the complex 8.

Cu(II) and Ni(II) complexes 7 and 8 were prepared from 6 following the above method (Scheme 1). IR data of 8 are similar to those reported for 4 with the disappearance of NH band at 3368 cm⁻¹, the appearance of C=N band at 1546 cm⁻¹ and the shift of the CO-3 band from 1569 cm⁻¹ to 1451 and 1400 cm⁻¹. NMR studies of 8 also show similar shifts for CH₃-12, methylene and CO-3 groups than those observed for 4 (Table 1) indicating the similar structure of these Ni(II) complexes. Recrystallisation from CH₂Cl₂-methanol of 8 results in crystals suitable for single X-ray structure analysis (Fig. 2). The selected bond lengths and angles are summarized in Fig. 3. The elongation and the shortening of certain bonds, and the decrease of the value of the C-N-C angle suggests the transition from a ketoenamine in 2 (C17-N1-C19 128.4(2)°) towards an enolimine form in 8 (C15-N2-C16 119.1(4)°). To our knowledge, the nature of complex 8 is scarce^{6c,9} and no crystal structure of Ni(II) complex has been reported. However, the Ni-N and Ni-O bond lengths in the complex 8 are comparable with those reported for Ni(II)-N,N'-bis(3',5'-di-tertbutylsalicylidene ethylene diamine) (Ni–N = 1.843(4) and 1.846(2) Å, Ni–O = 1.841(4) and 1.846(2) Å, respectively).¹⁰ In addition the value of C–N–C angle $(119.1(4)^{\circ})$ in 8 compares well with that described by Shimazaki (119.88°).¹⁰ Ni(II) ion coordinates thus two imine nitrogen atoms and two oxygen atoms in a square planar geometry as classical metal salen complexes with a pseudo C₂-symmetry. The structures of complexes 3, 4 and 7 were supposed by analogy with complex 8.

1.476(7) 1.309(6) 1.440(3) 1.424(7) 128.4(2) ,119.1(4) Me Me 1.230(6)-€CH₂· CH₂ 1.463(3) - 0.860(0) 1.430(7) - 1.843(4) 3 1.801 1.841(4) 2 8 1.260(6) 1.244(3)

Fig. 3 Selected bond lengths (Å) and angles (°) of 2 and 8.

In conclusion, we have developed the preparation of copper(II) and nickel(II) complexes based on a new chiral salen ligand derived from (+)-usnic acid. Formation of the metal complexes enhances the enolimine character of the salen-type ligand 2 significantly.

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Notes and references

‡ Crystal data for **2**: $C_{38}H_{36}N_2O_{12}$, M = 712.69, triclinic, P-1, a = 7.5006(6), b = 10.1555(7), c = 11.3793(9) Å, $\alpha = 72.374(6), \beta = 88.638(6), \gamma =$ 90.841(5)°, V = 825.64(11) Å³, Z = 1, D_x = 1.433 Mg.m⁻³, λ (MoK α) = $0.71069 \text{ Å}, \mu = 0.108 \text{ mm}^{-1}, F(000) = 374, T = 295(2) \text{ K}, Z = 1, 7721$ refelections collected, 5566 independent reflections ($R_{int} = 0.06221$) which were used in all calculations. The final wR_2 was 0.1245 (all data). Crystal data for 8: $C_{134}H_{118}Cl_6N_4Ni_2O_{24}$, M = 2498.44, monoclinic, P21, a =15.912(2), b = 23.792(4), c = 17.535(2) Å, $\alpha = 90$, $\beta = 113.5190(1)$, $\gamma = 113.5190(1)$ 90° , V = 6087.0(15) Å³, Z = 2, D_x = 1.363 Mg.m⁻³, λ (MoK α) = 0.71069 Å, $\mu = 0.515 \text{ mm}^{-1}$, F(000) = 2600, T = 110(2) K. Z = 1, 96611 reflections collected, 36765 independent reflections ($R_{int} = 0.0361$) which were used in all calculations. The final wR was 0.081 (all data). The CIF files have been deposit at Cambridge Crystallographic Deposit Center with registry number for 2 CCDC 627762 and for 8 CCDC 670706. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b811589c

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