

Synthesis of Novel Dinickel(II) and Nickel(II)–Copper(II) Bimetallic Complexes derived from an Acyclic Dinucleating Schiff Base–Pyridine Ligand

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Novel phenolic bridged dinickel(II) and nickel(II)–copper(II) complexes are synthesized by stepwise metallation of a dinucleating compartmental Schiff base–pyridine ligand.

Bimetallic complexes have continued to arouse interest since 1970^{1,2} due to their special roles in the fields of bioinorganic chemistry, homogeneous catalysis and magnetic exchange processes.^{3–5} Dinucleating ligands capable of binding two metal ions in close proximity serve as the essential precursors for the formation of homo- and hetero-bimetallic complexes.⁶ A vast array of symmetrical dinucleating macrocycles have been reported^{1,7} but examples of acyclic ligands incorporating non-equivalent binding sites are relatively scarce.¹ Schiff-base ligands are well-known to afford stable transition metal complexes⁸ and they have been extensively employed in their monometallic chemistry.⁹ Our aim was to synthesize homo- and hetero-bimetallic complexes from an acyclic side-off dinucleating system derived from a Schiff-base ligand. An example of this type of ligand is the Schiff base–carboxylic acid (L^1).¹⁰ The syntheses of the corresponding bimetallic complexes have been described and the metal ions were reported to be in close proximity (2.8–3.0 Å).¹¹ However, the free-base ligands and their bimetallic complexes exhibit low solubility in most organic solvents.¹²

While L^1 bears hard carboxylic groups as the donor set, we have recently synthesized a novel Schiff-base ligand (L^2) containing two relatively soft, redox-robust pyridyl groups as the binding ends.¹³ The dinucleating properties of L^2 arise from the presence of a salen type N_2O_2 cavity as the inner binding site and a O_2N_2 donor set derived from the pyridyl groups as the outer binding site. Here we report the successful synthesis of the homo- and hetero-bimetallic complexes derived from L^2 via stepwise metallation of the ligand (Scheme 1).[†]

Dropwise introduction of a hot ethanolic solution of $Ni(OAc)_2 \cdot 4H_2O$ (1 equiv.) to L^2 in ethanol afforded the diamagnetic mononickel(II) complex **1** in 95% yield. Reaction of **1** with $Ni(OAc)_2 \cdot 4H_2O$ and $Cu(OAc)_2 \cdot PH_2O$ in refluxing EtOH–MeCN mixture followed by anion exchange with ammonium hexafluorophosphate afforded the paramagnetic[‡] dinickel(II) complex **2** (74%) and the nickel(II)–copper(II) complex **3** (50%) as the hexafluorophosphate salt, respectively. The presence of nickel and copper ions in **2** and **3** was confirmed by X-ray fluorescence analysis.

It is noteworthy that the ligand and the complexes exhibit good solubility in common organic solvents such as dichloromethane, chloroform, acetone and acetonitrile. The enhanced solubility may arise from the incorporation of the lipophilic *tert*-butyl groups and tetramethylethylene bridge in the molecular skeleton and this property promotes the ease of characterization and reactivity study. In order to structurally characterize the bimetallic complexes, recrystallization of **2** and **3** from EtOH– CH_2Cl_2 yielded yellow parallelepiped and

yellowish green plates respectively suitable for X-ray crystallographic analysis.

Single-crystal X-ray analysis[§] shows that **2** and **3** are isomorphous with a C_2 symmetric axis passing through the two metal atoms and the midpoint of the ethylene bridge (Figs 1 and 2). In both complexes, the Ni^{II} ion is located in the salen type N_2O_2 cavity and exhibits a square-planar coordination

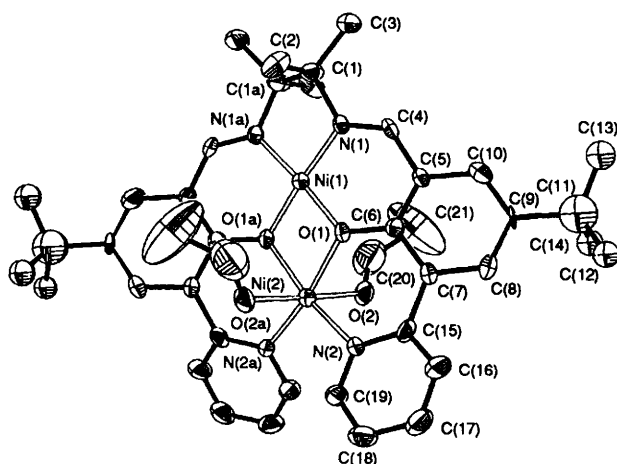
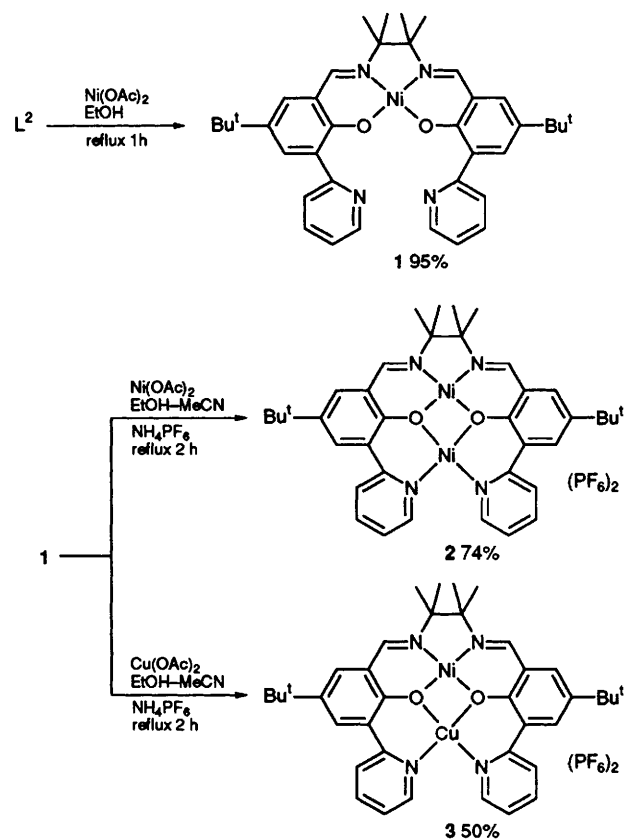
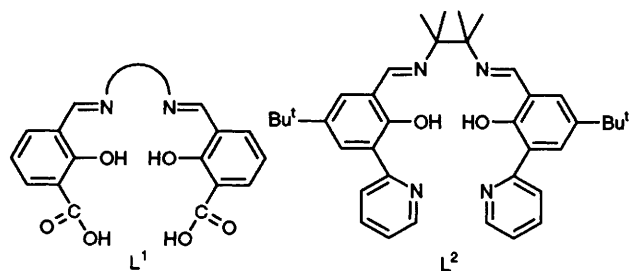


Fig. 1 Perspective view of the dinickel(II) complex **2** with thermal ellipsoids drawn at the 35% probability level. Selected interatomic distances (Å) and angles (°): $Ni(1) \cdots Ni(2)$ 2.950(3).



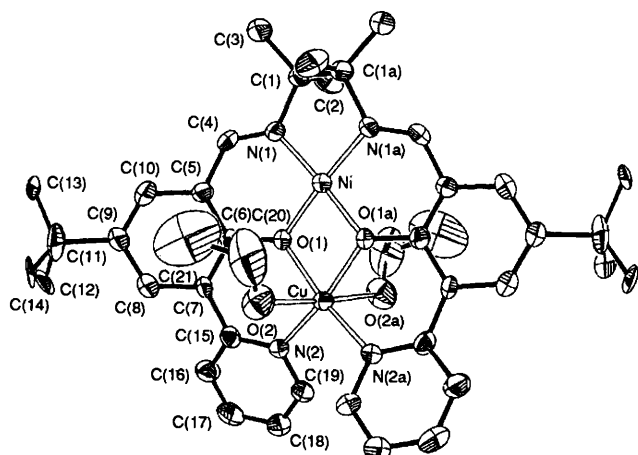


Fig 2 Perspective view of the nickel(II)-copper(II) complex **3** with thermal ellipsoids drawn at the 35% probability level. Selected interatomic distances (Å) and angles (°): Ni...Cu(1) 2.898(2).

geometry, while the second metal ion (Ni^{II} or Cu^{II}) occupies the outer O₂N₂ binding site with two ethanol molecules as the axial ligands in an octahedral coordination environment. The two metal ions are bridged by two phenolic oxygen atoms to show a planar Ni-O-M-O four-membered ring while the two aromatic spacers are close to coplanar.

In the dinickel(II) complex **2**, the equatorial Ni-O [1.879(9) Å] and Ni-N [1.84(1) Å] bonds in the four-coordinating site are significantly shorter than those in the six-coordinating site {Ni-O [2.008(9) Å] and Ni-N [2.02(1) Å]} and this observation is consistent with the fact that the effective ionic radius increases with coordination number.¹⁴ The nickel(II)-copper(II) complex **3** exhibits structural discrepancy in the coordination sphere around the copper(II) centre. The X-ray analysis indicates elongation of the axial M-O bonds [Cu(1)-O(2) 2.460(7) Å *cf.* Ni(2)-O(2) 2.13(1) Å]. As the difference in effective ionic radius of Ni^{II} and Cu^{II} in a six-coordinating environment was reported to be less than 0.1 Å,¹⁴ this observation can be attributed to the Jahn-Teller distortion which is characteristic of octahedral copper(II) complexes.¹⁵ Moreover, it is worthwhile to note that the nickel(II)-copper(II) complex **3** exhibits a smaller metal-metal separation in comparison to the dinickel(II) complex **2** [Ni(1)...Cu(1) 2.898(2) Å *cf.* Ni(1)...Ni(2) 2.950(3) Å].

In summary, we have successfully synthesized the novel dinucleating Schiff base-pyridine ligand L² and its dinickel(II) and nickel(II)-copper(II) bimetallic complexes. Further exploitation of the bimetallic chemistry of ligand L² is in progress.

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Footnotes

† All new compounds have satisfactory spectral and elemental analysis.

‡ Magnetic moments of **2** and **3** were found to be 3.57 and 2.03 μ_B respectively at 25 °C (Evans' method, SiMe₄ in [²H₆]acetone).

§ *Crystal data*: **2**, C₄₂H₅₆F₁₂N₄Ni₂O₄P₂, yellow parallelepiped, 0.20 × 0.20 × 0.30 mm, monoclinic, space group C2/c (no. 15), *a* = 19.693(3), *b* = 19.378(3), *c* = 19.044(3) Å, β = 135.59(1)°, *V* = 5086(1) Å³, *Z* = 4, *D_c* = 1.421 g cm⁻³, *R* (*R_w*) = 0.075 (0.078) for 1618 unique reflections with *F* > 3σ(*F*) and 310 variables. The *tert*-butyl

group exhibits two-fold orientational disorder about the C(9)-C(11) bond. The hydrogen atoms except those belonging to the *tert*-butyl group and ethanol ligand were generated geometrically (C-H bonds fixed at 0.96 Å) and allowed to ride on their respective parent C atoms. All hydrogen atoms were included in the structure-factor calculations. Refinement with isotropic thermal parameters for the hydrogen atoms and disordered carbon atoms, and anisotropic thermal parameters for the remaining non-hydrogen atoms, was carried out by full-matrix least squares. Computations were performed using the SHELXTL-PC program package.

3, C₄₂H₅₆CuF₁₂N₄NiO₄P₂, yellowish green plate, 0.15 × 0.30 × 0.40 mm, monoclinic, space group C2/c (no. 15), *a* = 19.946(2), *b* = 19.340(2), *c* = 18.906(2) Å, β = 135.64(1)°, *V* = 5098.5(9) Å³, *Z* = 4, *D_c* = 1.424 g cm⁻³, *R* (*R_w*) = 0.068 (0.076) for 2056 unique reflections with *F* > 3σ(*F*) and 326 variables. All hydrogen atoms except those attached to disordered carbon atoms and O(2) were generated geometrically (C-H bonds fixed at 0.96 Å) and allowed to ride on their respective parent C atoms. These hydrogen atoms were assigned the same isotropic thermal parameter (*U* = 0.08 Å²) and included in the structure-factor calculations. All non-hydrogen atoms except the disordered C atoms were subject to anisotropic full-matrix least-squares refinement. Computations were performed by using the SHELXTL-PC program package.¹⁶

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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