First Macrocycle to Incorporate Phenol and Thiophenol Head Units: the X-Ray Crystal Structure of $[Ni_2L(MeCN)_2](ClO_4)_2$ reveals Bridged Square-planar and Octahedral Nickel(II) Ions

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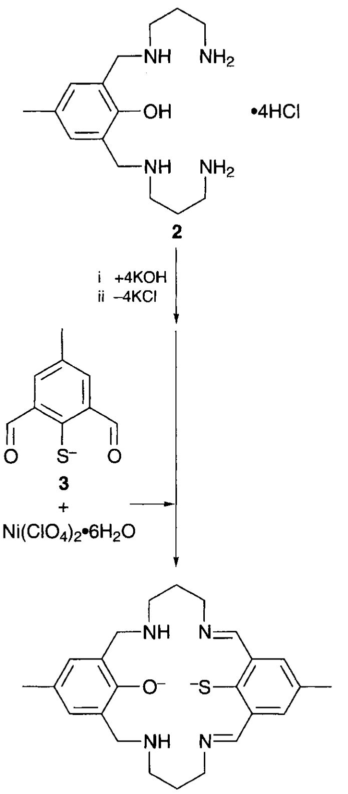
Nickel(II) ions template the formation of the first macrocycle to incorporate both phenol and thiophenol head units; the structure of $[Ni_2L(MeCN)_2](ClO_4)_2$ **1**, with adjacent square-planar and octahedral nickel(II) ions, is described.

Robson *et al.* have described a range of acyclic ligands and complexes derived from deprotonated 2-sulfanyl-5-methylisophthaldehyde **3** (Scheme 1),[1] yet, surprisingly, this exciting dicarbonyl component has only recently been incorporated into macrocycles.[2,3] We have prepared a range of macrocycles from **3** as part of our programme to introduce new dicarbonyl head units into Schiff-base macrocyclic chemistry.[2,4] This paper concerns the dinickel(II) complex of the unsymmetrical[5] macrocycle H_2L which, for the first time, incorporates both phenol and thiophenol head units, and which provides two potentially equivalent N_2OS binding sites.

The complex $[Ni_2L(MeCN)_2](ClO_4)_2$ **1** was prepared in 27% yield, using Schlenk techniques, from the two-arm precursor **2**[5] and deprotonated 2-sulfanyl-5-methylisophthaldehyde **3**,[2] as shown in Scheme 1. Red-brown crystals of **1** suitable for X-ray crystal structure analysis† were grown from the concentrated acetonitrile reaction solution by diethyl ether diffusion. The IR spectrum of the crystals‡ was consistent with macrocycle formation: a C=N stretch was present at 1630 cm^{-1} and no peaks corresponding to unreacted primary amine or carbonyl were present.

The structure determination reveals that the two nickel(II) ions have differing environments despite the fact that the macrocycle is potentially capable of providing identical N_2OS binding sites (Fig. 1). Ni(1) is square planar whereas Ni(2) is octahedral with two acetonitrile solvent molecules completing the coordination sphere. Bonds between the macrocycle donors and the square-planar nickel atom are shorter, by 0.07–0.15 Å, than those to the octahedral nickel atom. This is consistent with the observed difference in geometry.[2,8–10] Thiolate-bound nickel(II) ions are often square planar whereas octahedral geometries are relatively rare. The dinuclear macrocycle L^{2-} provides an intermediate ligand field strength which results in both geometries being present in **1**. The mean plane of the N_2OS donors to Ni(1) intersects the corresponding mean plane at Ni(2) with an angle of 148.2(5)°. In addition, the macrocycle is bent such that the two aromatic rings are inclined at 112.0(4)° to each other. These features are due in part to the tetrahedrally distorted sulfur donor [Ni(1)–S(1)–Ni(2) 87.78(11), Ni(1)–



L^{2-} as $[Ni_2L(MeCN)_2](ClO_4)_2$ **1**

Scheme 1 Synthesis of $[Ni_2L(MeCN)_2](ClO_4)_2$ **1**

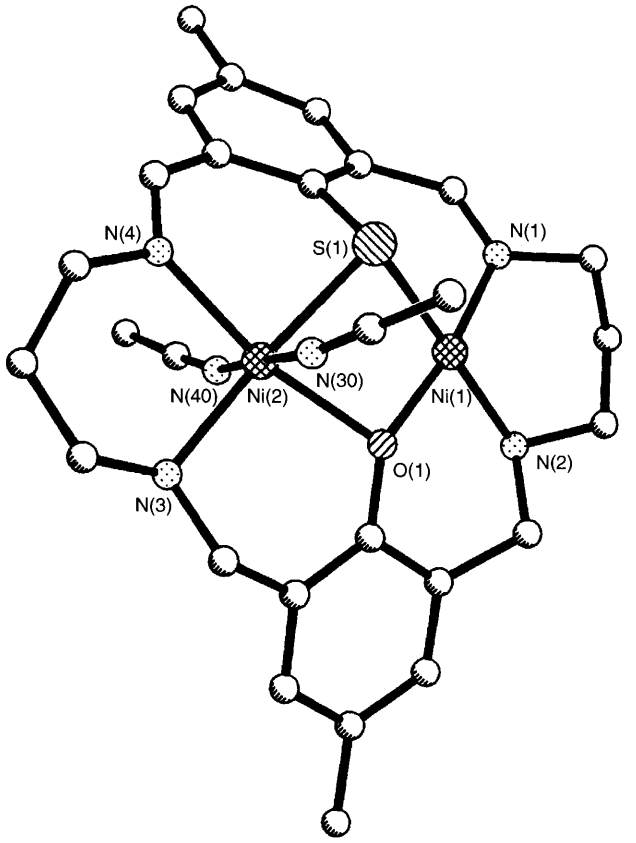


Fig. 1 Perspective view of the $[Ni_2L(MeCN)_2]^{2+}$ cation. Selected interatomic distances (Å) and angles (°): Ni(1)–N(1) 1.915(11), Ni(1)–N(2) 1.963(10), Ni(1)–O(1) 1.952(8), Ni(1)–S(1) 2.164(3), Ni(2)–N(3) 2.035(8), Ni(2)–N(4) 2.054(9), Ni(2)–O(1) 2.090(7), Ni(2)–S(1) 2.312(3), Ni(2)–N(30) 2.116(12), Ni(2)–N(40) 2.113(13), Ni(1)···O(11) 3.085(14), Ni(1)···O(21) 3.564(14), Ni(1)···Ni(2) 3.105(3), N(1)–Ni(1)–O(1) 171.0(4), N(1)–Ni(1)–N(2) 93.0(4), O(1)–Ni(1)–N(2) 98.4(4), N(1)–Ni(1)–S(1) 87.4(3), O(1)–Ni(1)–S(1) 85.2(2), N(2)–Ni(1)–S(1) 179.6(3), N(3)–Ni(2)–N(4) 96.3(4), N(3)–Ni(2)–O(1) 97.1(3), N(4)–Ni(2)–O(1) 166.0(3), N(3)–Ni(2)–N(40) 86.9(4), N(4)–Ni(2)–N(40) 88.0(4), O(1)–Ni(2)–N(40) 88.9(4), N(3)–Ni(2)–N(30) 93.1(4), N(4)–Ni(2)–N(30) 93.3(4), O(1)–Ni(2)–N(30) 89.8(3), N(40)–Ni(2)–N(30) 178.7(4), N(3)–Ni(2)–S(1) 175.6(3), N(4)–Ni(2)–S(1) 88.1(3), O(1)–Ni(2)–S(1) 78.5(2), N(40)–Ni(2)–S(1) 93.6(3), N(30)–Ni(2)–S(1) 86.4(3).

S(1)–C(1) 104.0(4), Ni(2)–S(1)–C(1) 100.5(4)°]. In contrast, the oxygen atom is much closer to a trigonal planar geometry [Ni(1)–O(1)–Ni(2) 100.3(3), Ni(1)–O(1)–C(13) 127.0(7), Ni(2)–O(1)–C(13) 119.3(6)°]. These observations are as expected for bridging phenolate oxygen and thiophenolate sulfur donors,[1,2,3,11] despite this being the first example in which phenolate and thiophenolate head units have been present simultaneously in a macrocycle. To our knowledge this is also the first macrocycle providing two potentially equivalent binding sites, yet facilitating the formation of bridged square-planar and octahedral nickel(II) centres.[8,10] We expect the combination of these unusual features to lead to **1** displaying quite different properties to those observed before for dinickel macrocyclic complexes. Our initial studies support this suggestion. Cyclic voltammetry has revealed one-electron oxidation processes at 0.9 and 1.3 V *vs.* SCE [Pt electrode, MeCN, 0.1 mol dm^{-3} $NEt_4(ClO_4)$]; the first oxidation is chemically irreversible whilst the second is chemically quasi-reversible (peak separation = 65 mV at 100 mV s^{-1}). In order to identify whether these are metal or ligand centred processes further work is underway.[2] Binding and X-ray absorption studies on this unique complex have also been initiated.[2,12]

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Footnotes

† *Crystal data* for: **1** $C_{28}H_{36}Cl_2N_6O_9SNi_2$, red-brown plate, 0.2 × 0.4 × 0.4 mm, monoclinic, space group *C2/c*, $a = 30.707(9)$, $b = 11.092(5)$, $c = 22.940(10)$ Å, $\beta = 120.96(3)°$, $U = 6700(4)$ Å^3, $Z = 8$, $\mu = 1.41$ mm^{-1}. Data were collected at 130 K on a Siemens P4 four-circle diffractometer using graphite-monochromated Mo-Kα radiation. 4517 Reflections were collected in the range $4 < 2\theta < 50°$ and the 4354 independent reflections were used in the structural analysis after a semi-empirical absorption correction had been applied. The structure was solved by direct methods (SHELXS-86)[6] and refined against all F^2 data (SHELXL-92 gamma release)[7] to $R_1 = 0.079$ [for 2379 $F > 4\sigma(F)$; $wR_2 = 0.219$ and goodness of fit = 1.06 for all 4354 F^2; 260 parameters; nickel, sulfur and perchlorate anisotropic]. 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.

‡ Satisfactory C, H, N, S, Cl elemental analysis was obtained for **1**.

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