The first thermally-stable singly oxo-bridged dinuclear Ni(III) complex

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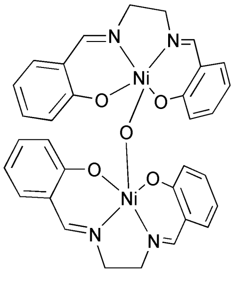
A new thermally stable oxo-bridged dinuclear nickel(III) complex has been synthesised and its crystal structure showed two nickel(III) ions with distorted square pyramidal coordination geometry.

Complexes of Ni(III) are very significant for their participation in the catalytic action of hydrogenases.[1] Generally Ni(III) complexes are obtained by electrochemical oxidation of the corresponding Ni(II) species.[2] Although many homo- and hetero-metallic oxo-bridged complexes have been reported,[3,4] there are a limited number of high valent metal oxo-species that have been extensively characterised. Recently, structures of doubly oxo bridged dinuclear nickel(III) complexes were published.[5,6] However, both these species are thermally unstable. Usually M–O–M type complexes, where M has a d^n electronic configuration with $n > 5$, are unstable due to the presence of electrons in the higher level antibonding orbitals.[7]

We have synthesised and structurally characterised the stable oxo-bridged nickel(III) complex $[Ni(salen)]_2O$ **1**. The present work provides the elemental analysis, X-ray structure analysis and magnetic studies of the complex and the results show that the two nickel ions in 3+ oxidation state are joined together by a bridging oxo group to form the dinuclear unit (Fig. 1).



1

The [Ni(salen)] complex was synthesised as reported earlier.[8] Pure oxygen gas was allowed to pass through a methanolic solution of [Ni(salen)], containing a few drops of NEt_3. On standing overnight, deep red crystals were obtained from the solution (yield 17%).† The crystals were thoroughly washed and air dried and one single crystal was selected for X-ray crystal structure analysis.‡

A perspective view of the molecule is shown in Fig. 1. As in most oxo-bridged complexes,[9] the Ni–O–Ni linkage is not linear [146.32(16)°]. Both the nickel(III) ions are five coordinate with distorted square pyramidal geometry. However, calculation of the geometrical factor τ shows that the degree of distortion in the two nickel centres is different [τ for Ni(1) is 0.15, for Ni(2), 0.33]. However the apical Ni–O(5) distance is 1.790(2) Å for both Ni centres.

The Ni–O distances are shorter here than in the doubly-bridged species [1.870(8), 1.841(7) Å]. The Ni–O distances found in closely related aqua species[6] are longer, typically by 0.1 Å and in the bridging hydroxo species,[5] longer still, by 0.2 Å.

The mean Ni–O and Ni–N salen distances are substantially longer [1.929(15) and 2.115(9) Å, respectively] than those found in a survey on Ni(II) salen species using the Cambridge Structural Database[10] where the mean Ni–N distance was found to be 1.858(32) Å and the mean Ni–O distance 1.849(15) Å. The standard deviations quoted are those of the population.

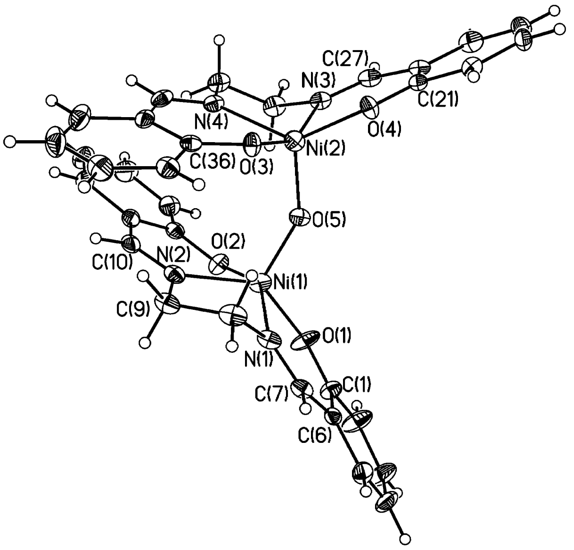


Fig. 1 Perspective view of **1** with displacement ellipsoids drawn at the 50% probability level. Selected distances (Å) and angles (°): Ni(2)–O(5) 1.790(2), Ni(2)–O(4) 1.918(2), Ni(2)–N(3) 2.108(3), Ni(2)–O(3) 1.949(2), Ni(2)–N(4) 2.116(3), Ni(1)–O(1) 1.912(2), Ni(1)–O(2) 1.938(2), Ni(1)–N(2) 2.130(3), Ni(1)–O(5) 1.790(2), Ni(1)–N(1) 2.108(3); O(2)–Ni(1)–O(1) 148.46(11), O(1)–Ni(1)–N(2) 139.37(12), Ni(1)–O(5)–Ni(2) 146.32(16).

The thermally stable complex decomposed at 41 °C. The solid reflectance electronic spectrum of the complex exhibited two intense absorption bands at 390 and 320 nm which are assigned as salen-based bands, but there are no characteristic absorption bands due to d–d transitions of the nickel ions. The IR spectrum shows bands at 882 and 430 cm^{-1} assigned as ν_{as}(NiONi) and δ(NiONi) respectively and there is no characteristic band for ν(OH). An electrochemical study of the complex shows a reversible process ($E_{1/2}$ = 1.05 V *vs.* SCE in methanol). The spectroscopic and CV results strongly support an oxo-bridged Ni(III) complex with square pyramidal geometry. The presence of strong donating groups in the Schiff base ligand stabilises the nickel ion in the higher oxidation state.

The observed room temperature magnetic moment value for **1** is 6.16 μ_B, fairly close to the expected value of 5.5 μ_B for two high spin d^7 ions.

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Notes and references

† *Analytical results* for **1**. Found C, 57.9; H, 4.3; N, 8.3. calc. for $C_{32}H_{28}N_4Ni_2O_5$: C, 57.7; H, 4.2; N, 8.4%.

‡ *Crystal data* for **1**, $C_{32}H_{28}N_4Ni_2O_5$, M_w = 666, triclinic, space group $P\bar{1}$, a = 10.7370(14), b = 10.8370(14), c = 13.7620(14) Å, α = 67.040(11), β = 85.710(10), γ = 73.110(11)°, V = 1409.5(2) Å^3, Z = 2, D_c = 1.569

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Mg m^{-3}, $\mu = 1.386$ mm^{-1}, $T = 160(2)$ K, Crystal size 0.28 × 0.48 × 0.30 mm, 4820 independent reflections 4820 ($R_{\mathrm{int}} = 0.0323$), $R_1 = 0.0443$, $wR_2 = 0.1296$. A single crystal was mounted with vacuum grease on a glass fibre and transferred to a Bruker AXS P4 diffractometer[11] and data were measured at 160 K, using an Oxford Cryosystems Cryostream. Solution and refinement were performed using the SHELXTL[12] suite of programs.

CCDC 182/1733. See http://www.rsc.org/suppdata/cc/b0/b004165n/ for crystallographic files in .cif format.

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