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Isolation and crystal structure of a novel dinuclear nickel(II) O-bound sulfinate from the oxidation of 2,2′-bipyridine-1,2-benzenedithiolatonickel(II)

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The first example of an O-bound sulfinate diimine nickel(II) complex has been isolated from the partial oxidation of Ni(bpy)(bdt) 1 (bpy = 2,2′-bipyridine, bdt = 1,2-benzenedithiolate), and characterized by X-ray crystallography and ESI-MS.

Since the first report by Miller and Dance in 1973, mixed dithiolene-α-diimine complexes of group 10 metals have received considerable attention because of their many unique physical properties, which include multiple accessible redox states, intense colors and non-linear optical behavior.[1] While complexes of this type have been reported for all three metals, particular attention has been focused on the heaviest (Pt^{II}) and the lightest (Ni^{II}) members of the group. In the former case this attention is the result of the unique optoelectronic properties of the systems.[2] In the latter case, the interest has been focused on the potential of these complexes to act as models for biological systems such as nickel-containing CO-dehydrogenase.[3,4] Investigations into the oxidation chemistry of nickel(II) diamine dithiolates have produced several compounds including monosulfenates [RS–M–SOR], disulfenates [M–$(SOR)_2$], monosulfinates [RS–M–SO_2R], disulfinates [M–$(SO_2R)_2$], and mixed sulfinate–sulfenate [ROS–M–SO_2R] complexes.[5] Recently, Henderson *et al.* reported the first process in which a Ni–S bond is oxidatively cleaved to yield an O-bound disulfonate [M–$(SO_3R)_2$].[6] However, to date no examples of O-bound sulfinates have been reported. We report herein the isolation and X-ray structure of an unusual dinuclear nickel(II) complex which contains the first example of an O-bound sulfinate diimine nickel(II) complex (**2**), as well as an additional example of a disulfonate diimine nickel(II) complex **3**.

During a UV–VIS study of Ni(bpy)(bdt) **1** (bpy = 2,2′-bipyridine, bdt = 1,2-benzenedithiolate) in DMF, we observed that solutions of **1** slowly changed color from purple to orange. While the initial spectrum contains a broad absorption between 500 and 600 nm, characteristic of complexes such as **1**, this band disappears and is replaced by a new absorption peak at 874 nm. Slow evaporation of this solution yielded a small amount of orange X-ray quality crystals. The X-ray crystal structure of these crystals was determined and is shown in Fig. 1.†

The solid material was found to be a co-crystal of both the monosulfinate $(bpy)_2Ni(bdtO_2)Ni(bdt)$ **2a** and the disulfinate $(bpy)_2Ni(bdtO_4)Ni(bdt)$ **2b** in an approximate 60:40 ratio. ESI-MS of the crystalline material yielded molecular ions for both **2a** and **2b** with appropriate relative intensities.[7] All attempts to prepare **2** in a rational fashion using a chemical oxidant, such as H_2O_2, produced only **3** (Fig. 2) regardless of the stoichiometry.†

The Ni–N distances in **2** and **3** (2.05–2.08 Å) are both similar to those observed for the related compound $(bpy)_2(PhS)_2Ni^{II}\cdot D_2O$ (2.08–2.10 Å).[8] As expected, the Ni(1)–O bond distance in **2** (2.104(5) Å) is longer than the Ni–O bonds in complex **3** (2.05-2.06 Å) and is also longer than the Ni–O bonds in [(3-thia-1,5-diaminopentane *S*-oxide)$_2$Ni]$^{2+}$ (2.07–2.09 Å)[9] and the Ni–OH_2 bond [2.084(1) Å] in $[Ni(dsodm)(H_2O)_2]\cdot 2H_2O$ (dsodm = $[(O_3SCH_2CH_2)MeNCH_2CH_2NMe(CH_2CH_2SO_3)]$).[6] This difference is most likely the result of the stronger donor ability of the bpy ligands in **2**. The Ni–O bonds in **3** [2.060(3) Å and 2.054(3) Å]) are also slightly longer than the Ni–sulfonato bonds in $[Ni(dsodm)(H_2O)_2]\cdot 2H_2O$ [2.044(1) Å], again probably due to the more electron-rich nickel in **3**.[6] The Ni–S bond lengths observed for **2** are 2.13–2.17 Å for the square planar Ni(2) and 2.499(3) Å for the octahedral Ni(1). The former are similar to those observed for other four-coordinate systems such as **1** (2.14–2.15 Å) and $Ni(bdt)_2^{2-}$ (2.17–2.18 Å).[10,11] Interestingly the Ni–S bond length in **2** and other four-coordinate Ni-sulfinates are not significantly affected by the oxidation state of the sulfur.[5] The Ni–S bond length for the octahedral Ni in **2** is similar to that in $(bpy)_2(PhS)_2Ni^{II}\cdot D_2O$ [2.445(2) Å].[8]

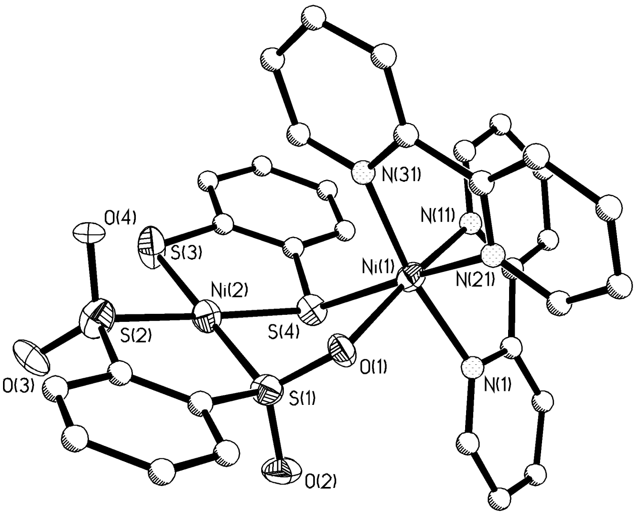

Fig. 1 Diagram showing the sulfinate complex **2a,b** with the significant atoms shown with displacement ellipsoids at 50% probability and the remaining atoms shown as spheres of arbitrary radius. The hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni(1)-N 2.05-2.07, Ni(1)-O(1) 2.104(5), Ni(1)-S(4) 2.499(3), Ni(2)-S(1) 2.127(3), Ni(2)-S(2) 2.156(3), Ni(2)-S(3) 2.166(3), Ni(2)-S(4) 2.154(3), S(1)-O(1) 1.490(6), S(1)-O(2) 1.472(6); O(1)-S(1)-Ni(2) 111.8(3), Ni(2)-S(4)-Ni(1) 101.85(10), S(1)-O(1)-Ni(1) 122.8(4).

While the exact origin of **2** is still uncertain, it can be seen from **3** that the complete oxidation of **1** to **3** involves both rupture of the Ni–S bonds and the exchange of ligands. While the fate of the other nickel thiolate fragment in conversion of **1** to **3** remains unknown, the observed ligand disproportionation allows for a rationalization for the formation of **2** (Scheme 1).

$$\underset{\mathbf{1}}{(bpy)Ni^{II}(bdt)} \xrightarrow{h\nu,\ O_2} (bpy)Ni^{II}(bdt^{ox}) \xrightarrow{(bpy)Ni^{II}(bdt)} \underset{\mathbf{2}}{(bpy)_2Ni^{II}(bdt^{ox})Ni^{II}(bdt)}$$

Scheme 1 A rationalization of the formation of **2** from **1** *via* a ‘partial’ disproportionation.

Under the ambient conditions present in the spectrometer, a small amount of **1** was converted into the mono or disulfinate form (**1^ox^**) which then begins to undergo a disproportionation process with an unoxidized molecule of **1**. The decreased solubility of **2**, in relation to **1** or **1^ox^**, leads to this ‘intermediate’

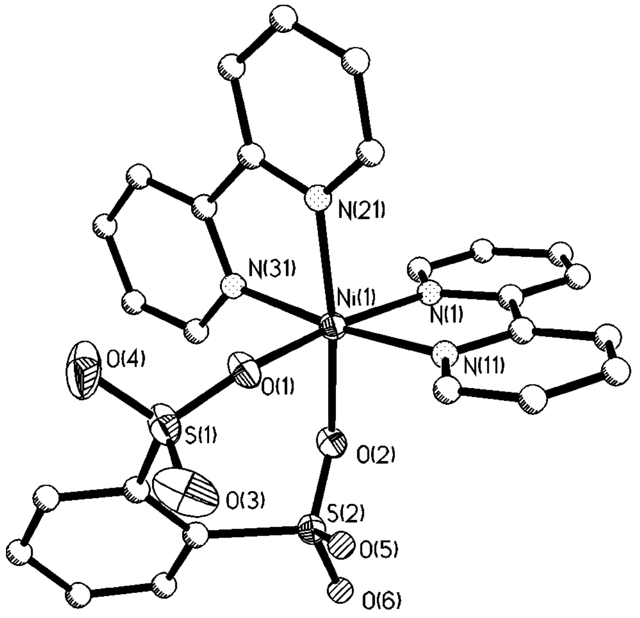

Fig. 2 Diagram showing the sulfonate complex **3**·0.5dmf with the significant atoms shown with displacement ellipsoids at 50% probability and the remaining atoms shown as spheres of arbitrary radius. The DMF molecule and the hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni(1)–O(1) 2.060(3), Ni(1)–O(2) 2.054(3), Ni(1)–N 2.06–2.08, S(1)–O(1) 1.452(3), S(1)–O(3) 1.452(4), S(1)–O(4) 1.420(4), S(2)–O(2) 1.485(3), S(2)–O(5) 1.436(3), S(2)–O(6) 1.446(3); O(2)–Ni(1)–O(1) 90.97(12), S(1)–O(1)–Ni(1) 151.98(19), S(2)–O(2)–Ni(1) 128.38(16).

in the disproportionation process being 'trapped' by precipitation, producing the observed result. We are currently pursuing a rationale synthesis of **2a,b** and attempting to resolve the outstanding mechanistic questions related to the formation of both **2** and **3**.

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Notes and references

† *Crystal data*: **2**: crystals of **2** were obtained by evaporation of a DMF solution used in a UV–VIS study at room temperature. $C_{32}H_{24}N_4Ni_2O_{2.83}S_4$, $M = 755.45$; monoclinic, $P2_1/n$, $a = 11.5407(3)$, $b = 16.9821(4)$, $c = 16.7013(4)$ Å, $\beta = 106.9880(10)°$, $V = 3130.39(13)$ Å^3, $Z = 4$, $D_c = 1.603$ g cm^{-3}, $\mu = 1.511$ mm^{-1}. All data were collected on a Bruker-AXS SMART CCD system at -100 °C. A small orange plate of **2** ($0.04 \times 0.16 \times 0.16$ mm) was mounted on a glass fiber using epoxy. The data were collected as described elsewhere[12] to provide a complete sphere of data to 0.75 Å ($2\theta_{max} = 56.62°$) yielding 25633 data. Final unit cell parameters were calculated using 5720 reflections culled from the entire data set. The data were corrected for Lorentz and polarization effects and an absorption correction was applied on the basis of equivalent reflection measurements using Blessing's method as incorporated into the program SADABS.[13]

Owing to their poor quality, the data were truncated on the basis of intensity statistics at a resolution of 0.85 Å ($2\theta_{max} = 49.42°$) to yield a final data set of 19526 reflections (5340 unique, $R_{int} = 0.2091$). The structure was solved using direct methods and refined against F^2 by full-matrix least-squares methods using the programs in SHELXTL and SHELX-97.[14] All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were refined isotropically. The oxygen atoms O(3) and O(4) were refined to 40% site occupancy and then held fixed at this value. The final refinement converged with residuals of $wR_2 = 0.2125$ (all data), $R_1(F) = 0.0785$ [$I > 2\sigma(I)$], and GOF = 0.998. Significant bond lengths and angles are given in Fig 1.

3·0.5 dmf; crystals of **3**·0.5 dmf were obtained by treatment of **1** with H_2O_2 in DMF followed by slow evaporation of the solution at room temperature. $C_{27.50}H_{20}N_{4.50}NiO_{6.50}S_2$, $M = 640.31$; triclinic, $P1$, $a = 9.31350(10)$, $b = 12.5526(2)$, $c = 12.7451(2)$ Å, $\alpha = 96.0170(10)$, $\beta = 101.8868(3)$, $\gamma = 110.0760(10)°$, $V = 1344.26(3)$ Å^3, $Z = 2$, $D_c = 1.582$ g cm^{-3}, $\mu = 0.932$ mm^{-1}. A small colorless plate of **3**·0.5 dmf ($0.02 \times 0.10 \times 0.16$ mm) was mounted on a glass fiber using epoxy and the data were collected as above to yield 11300 reflections (6302 unique, $R_{int} = 0.0599$). Final unit cell parameters were calculated using 5378 reflections culled from the entire data set. The dmf molecule was found to be disordered over the inversion center and was modeled as three separately oriented molecules with a total combined occupancy of 0.5. The final refinement converged with residuals of $wR_2 = 0.1340$ (all data), $R_1(F) = 0.0691$ [$I > 2\sigma(I)$], and GOF = 1.066. Significant bond lengths and angles are given in Fig 2.

CCDC 182/1210. See http://www.rsc.org/suppdata/cc/1999/875/ for crystallographic files in .cif format.

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