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X-ray Structure of a Ni(II)-Tri-Phenoxy Radical Complex

X-ray Structure of a Ni(II)-Tri-Phenoxy Radical Complex

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The dimino-diphenolato neutral square-planar Ni(II) complex, NiL₂, is readily oxidised by 2 equiv. of Ag[SbF₆], to produce the unprecedented octahedral Ni(II) tris(phenoxy) radical complex, [Ni(L[•])₃][SbF₆]₂. This study reveals, for the first time, the X-ray structure of metal -tri-phenoxy radicals complex.

In the last two decades, inspired by the unique Cu(II)-tyrosyl radical moiety of the active site of Galactose oxidase (GO)¹ [a fungal enzyme that catalyses the aerobic two-electron oxidation of a wide range of primary alcohols to their corresponding aldehydes]; chemists have been successful in generating and characterising phenoxy radical complexes of Cu(II) and other transition metals such as Fe(III), Zn(II), Co(II/III), Ni(II).² However, to date, isolated persistent phenoxy radical complexes are still rare,³ and only a few X-ray structures have been reported.^{4–7} Thus, the isolation and exploration of transition metal compounds containing one (or more) phenoxy radical ligand(s) with desired catalytic or magnetic properties still remain a significant challenge. In particular, for compounds that possess two and/or three phenoxy radical ligands which are known to be highly unstable.^{2f, 8}

In a continuous search for a suitable ligand framework capable of sustaining a phenoxy radical state, we have recently designed^{5,9} a versatile *N,O*-phenol-imidazole/pyrazole pro-ligand family that incorporates: (a) *t*-Bu protections of the phenol *ortho*- and *para*- positions, preventing radical coupling decomposition pathways, and (b) no other oxidisable position than the phenol(ate) moiety itself. These ligand frameworks have allowed tetracoordinated M(II)– (M = Cu, Zn, and Co) and octahedral Co(III)– mono-phenoxy radical complexes to be isolated as air-stable crystalline powders.^{5,9a,b}

Herein, we report, using the phenol-pyrazole pro-ligand LH^{9c} (Scheme 1), the synthesis, characterisation and X-ray structure of an unprecedented octahedral Ni(II) tri-(phenoxy) radical complex, [Ni(L[•])₃]²⁺ (**2**²⁺); produced by an unusual two-electron chemical oxidation of the parent Ni^{II}L₂ phenolate complex (**1**) (Scheme 1).

The reaction of LH with [Ni(H₂O)₆][BF₄]₂ in methanol in a 2 : 1 ratio in the presence of triethylamine, affords the pale-green NiL₂ compound (**1**) (see ESI †). The X-ray structure of **1** (Fig. 1, Tables 1 and SI1-3) is isostructural to that of neutral CuL₂^{9c,d} displaying a neutral centrosymmetric *trans*-N₂O₂ square-planar geometry, resulting from the coordination of two N, O- ligands in their anionic forms.

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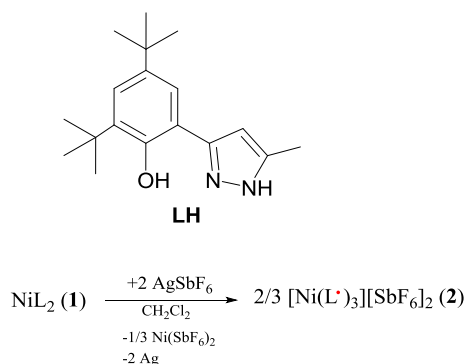
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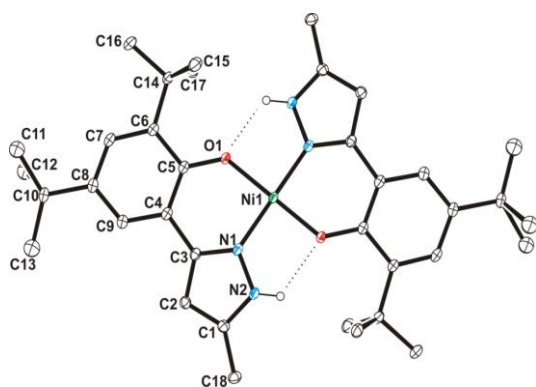
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Electronic Supplementary Information (ESI) available: Experimental, instrumental, crystallographic, together with supplementary results are presented in the Supporting Information. The structures of **1** and **2** are available at the Cambridge Crystallographic Data Centre as supplementary publications CCDC-1005503, 1005504. See DOI: 10.1039/x0xx00000x



Scheme 1

Fig. 1 ORTEP representation of the molecular structure of **1**.

The Ni–O and Ni–N bond distances (1.869(2) Å and 1.850(2) Å respectively) are as expected for Ni(II)-phenolato-imino complexes in an N_2O_2 environment.² The planar structure of **1** is reinforced by two intramolecular N–H \cdots O hydrogen bonds between the pyrazole N–H and phenolate-O atoms (N \cdots O distances of 2.717(2) Å, <N–H \cdots O> angle of 121 °; Fig. 1). As expected for low-spin, d^8 , square planar Ni(II) ions, complex **1** is diamagnetic and exhibits a well resolved ^1H NMR spectrum in CDCl_3 , displaying one set of resonance for the two magnetically equivalent ligands; and a concentration-independent broad N–H singlet at 10.95 ppm, suggesting that the intramolecular N–H \cdots O H-bonds are retained in solution. (Fig. S11) The UV/vis spectrum of **1** in CH_2Cl_2 displays absorption peaks at λ_{max} ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$): 400 (610), 484 (120) and 630 (170); Fig. 4). The band at *ca.* 400 nm is attributed to a phenolate-to-Ni(II) charge transfer transition, whereas the weak lower energy bands are assigned to ligand-field transitions.^{2f}

The chemical oxidation of **1** with two equiv. of AgSbF_6 in CH_2Cl_2 under dry inert atmosphere, produces a dark-brown crystalline powder of **2** in 46 % yield, after filtration of metallic silver and $\text{Ni}^{2+}[\text{SbF}_6]_2$ insoluble side-products (Scheme 1, see ESI[†]). The slow diffusion of hexane into a saturated CH_2Cl_2 solution of **2** at 4 °C for a two days under dry inert atmosphere, yields dark-brown cube-like single crystals suitable for X-ray crystallography (Fig. 2, Tables 1 and S11, 4, 5). The X-ray structure of **2** reveals a unique salt composed of a dicationic *tris*(phenoxy) nickel complex, $[\text{NiL}_3]^{2+}$, and two SbF_6^- counter anions (Fig. 2). Both the cations and anions in the structure of **2** are located in the special positions on the 3-fold axis. The nickel ion binds in an octahedral *fac*- N_3O_3 coordination environment of three C_3 -symmetry related N,O-ligands. This *fac*-arrangement contrasts with the *mer*-conformation observed for the neutral Co(III)-*tris*(phenolate) analogue complex, CoL_3 ^{9c}; and appears to be stabilised by the presence of close N–H \cdots F contacts between the three fluoro atoms of one SbF_6^- counter anion, and the three pyrazole N–H groups in the dicationic complex (N \cdots F 2.864 Å; see Fig. 2).

Since all three ligands are identical (symmetrically related), the overall + 2 charge of the nickel complex in **2** can only be satisfied for the two extreme cases: (a) a Ni(V) with three anionic phenolate ligands, $[\text{Ni}^{\text{V}}(\text{L}^-)_3]^{2+}$; or (b) a Ni(II) with three neutral radical phenoxy ligands ($[\text{Ni}^{\text{II}}(\text{L}^\bullet)_3]^{2+}$). The Ni–N and Ni–O bonds in **2** are long (2.047(3) Å and 2.025(3) Å, respectively), clearly excluding a putative Ni(V)-phenolate complex. Rather, these are typical of those in octahedral Ni(II) $S = 1$ complex bearing

neutral N/O ligands. The Ni–O bond length in **2** of 2.025(3) is unprecedentedly long for an M–O bond involving either a phenolate or a phenoxyl radical ligand, (generally not exceeding 1.95 Å). The long Ni–O bond length in **2** suggests a Ni(II) centre coordinated by three neutral phenoxyl radical ligands. Indeed, upon oxidation of a phenolate to a phenoxyl radical ligand, a significant lengthening of the M–O bond is generally observed (e.g. Cu–O: 1.948(3) Å (L[•]) vs. 1.850 Å (L⁻) in [Cu(L)(L[•])]⁺).⁵ Such an effect is expected to be largely enhanced for *bis*, or *tris*(phenoxyl) radical complexes, as the effective charge increases; thereby resulting in much longer M–O bonds over 2 Å as in **2**.

The three identical phenoxyl rings in **2** display a quinonoid bond pattern observed for true localised phenoxyl radical complexes, as reported in the literature.^{4–7} Thus, the length of the C_{iso}–O bond (1.258(5) Å) is significantly shorter than that in the phenolate complexes **1**, CuL₂, or CoL₃ (1.30–1.34 Å)^{8c} (Table 1); whereas those of the two adjacent C_{iso}–C_o bonds are significantly longer (av. 1.465(5) Å vs. 1.40–1.44 Å; Table 1), in accordance with the two resonance forms depicted in Scheme 2. Thus, these structural data strongly suggest that **2** contains the Ni(II)-*tris*(phenoxyl)radical dicationic complex, [Ni(L[•])₃]²⁺.

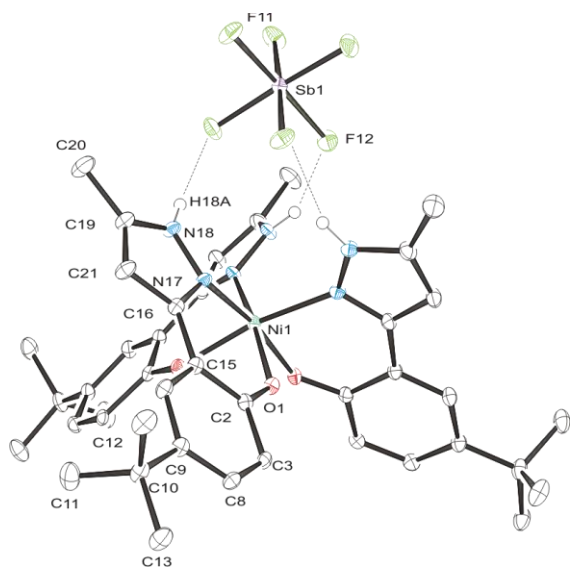


Fig. 2 ORTEP representation of the molecular structure of [NiL₃][SbF₆]₂ (**2**). Dashed lines represent H-bonds. The ortho- *t*-Bu groups of all ligands and one SbF₆⁻ counter ions have been omitted for clarity.

Table 1 Selected average bond lengths in crystal structures of **1** and **2**, and comparison with DFT-optimised structure for **2**.

	NiL ₂ (1)	[NiL ₃] ²⁺ (2) (Expt)	[Ni(L [•]) ₃] ²⁺ (2) (Calcd)
Ni–O	1.869(2)	2.025(3)	2.037
Ni–N	1.850(2)	2.047(3)	2.053
C _{iso} –O	1.333(2)	1.258(5)	1.269
C _{iso} –C _o	1.428(3)	1.465(5)	1.468
C _o –C _m	1.394(3)	1.372(6)	1.384
C _m –C _p	1.390(3)	1.409(6)	1.414

Scheme 2 Resonance forms of the neutral phenoxyl radical ligands in **2**.

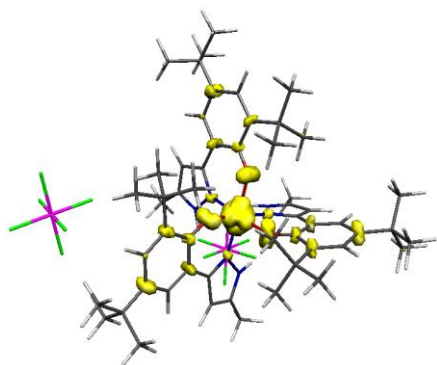


Fig. 3 Spin density plot of DFT-optimised **2**.

In order to support the structural data, DFT-calculations were performed on the high spin (HS) state of **2**, assuming a multiplicity of six ($S=5/2$) with five unpaired electrons distributed on four magnetic centers in a parallel alignment. The geometrically optimised structure of **2** matches remarkably well with the crystallographic data. First, the facial N_3O_3 geometry is preserved and the three $N-H\cdots F$ close contacts with one SbF_6 counter anion (av. $N\cdots F$ 2.82 Å) (Fig. S12) are reproduced. Second, the lengths of the Ni–O/N bonds, as well as the C–C and C–O bonds within each of the phenoxyl rings, are accurately reproduced by the calculation within 0.015 Å (Tables 1, S16). Thus, the calculation predicts long Ni–O/N bonds, and phenoxyl radical-like short C–O and long $C_{iso}-C_o$ bonds (Table 1); strongly suggesting that the Ni(II) *tris*(phenoxyl) radical is the relevant form of **2**. This assignment is further confirmed by the energetic analysis performed on all possible spin configurations of **2** (Fig S13). Comparison of the HS state energy with those of the $M_s=3/2$ and $M_s=1/2$ states evinced that the $S=5/2$ is the ground spin state of **2** which is best described as a $S=1$ Ni(II) ion ferromagnetically coupled to three radical ligands (Table S17). Analysis of the electronic structure of the HS state of **2** shows five singly occupied molecular orbitals (SOMO). Three of them are ligand-based orbitals, each localised mainly on the phenoxyl radical ring, and the two others are metal-based (Ni $3d_{x^2-y^2}$ and $3d_{z^2}$) as expected for such spin configuration (Fig. S14). The calculated spin density plot depicted in Figure 3 shows that the spin density is equally spread over the complex consistently with the distribution of the five unpaired electrons over the four magnetic centers of the system.

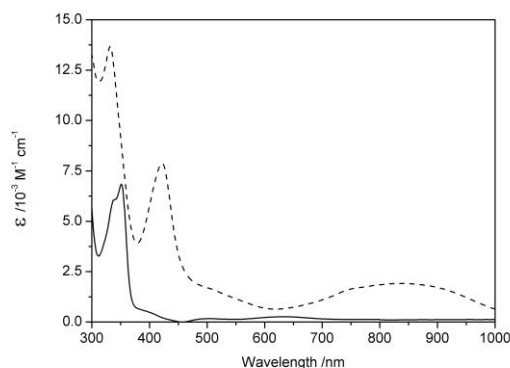


Fig. 4 UV/vis/NIR spectra of **1** (solid line) and **2** (dashed line) in CH_2Cl_2 at room temperature.

In the 200 – 1100 nm region, the absorption spectrum of **2** displays a UV-band at 332 nm ($12500 M^{-1} cm^{-1}$) and a strong visible band at 422 nm ($7500 M^{-1} cm^{-1}$) accompanied by a broad NIR band centred at ca. 840 nm ($2100 M^{-1} cm^{-1}$); Fig. 4. This absorption profile is characteristic of that of phenoxyl radicals, the band at ca. 400 nm being generally assigned to the $\pi-\pi^*$ transition in the phenoxyl ring.^{2e} Moreover, the 1:4 ratio between the intensities of the ca. 400 nm band and the NIR bands supports the presence of localised phenoxyl radical ligands. For delocalised phenoxyl radical π -systems, stronger NIR bands tend to be observed, reaching a similar intensity to the 400 nm band (e.g. with a 1:1 ratio in $[Cu(L^{OMe^*})(L^{OMe})]^+$).^{9b} Interestingly, in the 1000 – 3300 nm NIR region, the spectrum of **2** is silent, and contrasts with delocalised Class III Ni(II)salen radical complexes which exhibit an intense IVCT transition at 2100–2500 nm.^{2f} This observation further supports the presence of three localised phenoxyl radical ligands in **2**.

Herein, we have reported, using the suitably protected N,O-phenol-pyrazole pro-ligand, LH, the synthesis and characterisation of the neutral *bis*-Ni^{II}L₂ complex (**1**) together with that of the product of its two-electron oxidation with $Ag[SbF_6]$, **2**. Our combined crystallographic and theoretical studies reveal that **2** contains an unprecedented dicationic Ni(II) complex, $[Ni(L^*)_3]^{2+}$, bearing

three neutral phenoxy radical ligands. The latter represents the first example of an isolated and crystallographically characterised *tris*(phenoxy) radical complex. Further in-depth spectroscopic characterisations of **2** are in progress in our laboratory.

Notes and references

‡ Experimental, instrumental, crystallographic, together with supplementary results are presented in the Supporting Information. The structures of **1** and **2** are available at the Cambridge Crystallographic Data Centre as supplementary publications CCDC-1005503, 1005504.

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