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From metal to ligand electroactivity in nickel(II) oxamato complexes†

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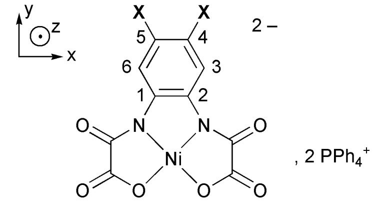
Received (in Cambridge, UK) 3rd October 2003, Accepted 30th October 2003
First published as an Advance Article on the web 11th December 2003

The locus of oxidation in square-planar nickel(II) oxamato complexes can be continuously shifted from the metal to the ligand by an appropriate choice of electron-donating substituents on the aromatic moiety of the ligand.

Numerous metalloenzymes use radical cofactors in their catalytic cycle as a means of storing oxidizing or reducing equivalents.[1] Similarly, non-innocent ligands participate in the redox properties of their metal complexes by being oxidized or reduced.[2–5] These ligands commonly possess an extensive delocalised π-system and can exist in different redox forms, both closed- and open-shell. Unique electronic properties are displayed by the ensuing metallo-radical species, whose electronic distribution relies on the respective energy and symmetry of the frontier orbitals of the metal ion and of the ligand. On one hand, when these orbitals overlap, the redox process takes place at both fragments (metal + ligand), the actual oxidation state of the metal having in this case to be determined by direct spectroscopic means.[4,6] On the other hand, orthogonal orbitals close in energy may induce valence tautomerism, *i.e.* an equilibrium between the species oxidized on the metal and the one oxidized on the ligand.[3] Here, we describe a series of mononuclear nickel(II) complexes with aromatic bisoxamato ligands symmetrically substituted with electron-donating groups (Scheme 1 and ESI†). In this series, the nature of the substituents modulates the nature of the oxidized species.



X	Name
H	**1**
Me	**2**
OMe	**3**
NMe_2	**4**

Scheme 1

The diamagnetic nature of the square-planar nickel(II) (d^8) complexes **1–4** was evidenced by sharp peaks in ^1H NMR and minor differences in chemical shifts when compared to the free ligands (Table 1).§ On going from **1** to **4**, the upfield shift of about 0.65 ppm for the protons in positions 3 and 6 reveals a higher electron density on the benzene ring with the more electron-donating groups in the order H < Me < OMe < NMe_2. UV–Vis solution spectra of **1–4** are typical of square-planar nickel(II) complexes, presenting primarily a charge transfer band in the range 356–365 nm and a weak d–d feature at *ca.* 450 nm (Fig. S3†).

A dramatic influence of the peripheral substituents in **1–4** is observed by cyclic voltammetry. All complexes present a reversible 1e^- oxidation wave whose potential is lower for complexes carrying the more electron-donating groups (Table 1). On going from **1** to **4**, the large potential decrease by over 450 mV resulting from the substitution on the aromatic ring suggests a progressive participation of the ligand in the location of oxidation.

The 1e^- oxidized species $\mathbf{1^{ox}}$–$\mathbf{4^{ox}}$ were produced by bulk electrolysis in dry CH_2Cl_2 under an inert atmosphere at −30 °C and were characterized in solution by EPR and UV–Vis–NIR spectroscopies. X-Band EPR on frozen solutions (100 K) provided the most straightforward way of assigning the nature of these paramagnetic (S = 1/2) oxidized species (Fig. 1, Table 1).[5] Complexes $\mathbf{1^{ox}}$ and $\mathbf{2^{ox}}$ (X = H and Me) exhibit anisotropic axial spectra typical for nickel(III) complexes in a square-planar geometry or an axially elongated octahedron.[7,8] Thus the metal is oxidized and, as $g_{\parallel} \approx$

Table 1 NMR data and oxidation potentials of **1–4**; EPR *g* parameters and main Vis-NIR absorptions of $\mathbf{1^{ox}}$–$\mathbf{4^{ox}}$

	δ [a]	$E_{1/2}$ [b,c]		$g_{\parallel}$ [b,d]	$g_{\perp}$ [b,d]	λ_{max}/nm (ε/ $mM^{-1}cm^{-1}$) [b,e]	
1	7.99	0.45	$\mathbf{1^{ox}}$	2.008	2.255		969 (6.3)
2	7.82	0.35	$\mathbf{2^{ox}}$	2.008	2.253		1014 (6.7)
3	7.77	0.19	$\mathbf{3^{ox}}$	2.040	2.005	863 (3.9)	993 (5.8)
4	7.34	−0.05	$\mathbf{4^{ox}}$	2.005 [f]		872 (6.1)	

[a] In ppm, ^1H-NMR on the NBu_4^+ salts in $CDCl_3$, H3 and H6. [b] 1 mM in CH_2Cl_2, 0.1 M NBu_4PF_6. [c] V vs. SCE, 20 °C, 100 mV s^{-1}. [d] 100 K. [e] −30 °C. [f] Isotropic signal.

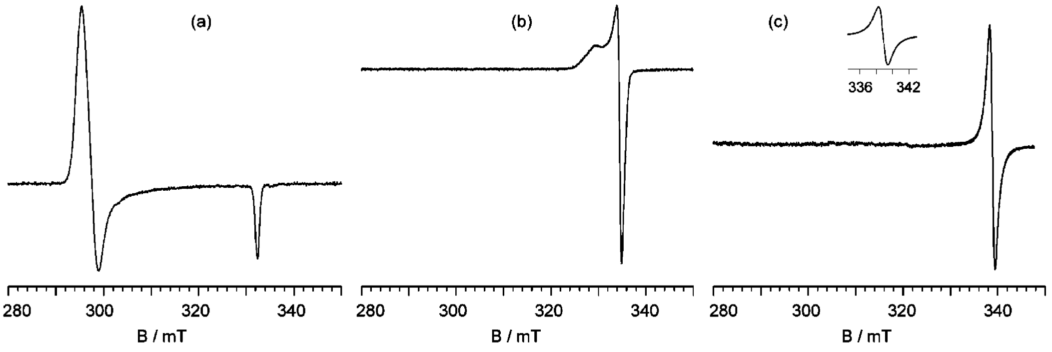


Fig. 1 X-Band EPR spectra of (a) $\mathbf{2^{ox}}$, (b) $\mathbf{3^{ox}}$ and (c) $\mathbf{4^{ox}}$; 1 mM in CH_2Cl_2, 0.1 M NBu_4PF_6, 100 K.

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† Electronic Supplementary Information (ESI) available: Syntheses, experimental details, optical spectra of **1–4** and $\mathbf{1^{ox}}$–$\mathbf{4^{ox}}$. See http://www.rsc.org/suppdata/cc/b3/b312295f/

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DOI: 10.1039/b312295f

$2.01 < g_\perp \approx 2.25$, d_{z^2} is the singly-occupied molecular orbital (SOMO), *i.e.* the orbital from which the electron has been abstracted. For the oxidized complex with the most electron-donating substituents, $\mathbf{4^{ox}}$, an isotropic spectrum is observed, characteristic for a radical entity, the unpaired electron being in that case confined on the π organic skeleton.¶ Interestingly, the spectrum of $\mathbf{3^{ox}}$ is of axial symmetry, but with $g_\parallel > g_\perp$. This anisotropy, inverse to that for $\mathbf{1^{ox}}$ and $\mathbf{2^{ox}}$, is characteristic for a nickel(III) with a $(d_\pi)^1$ configuration ($d_\pi = d_{xy}$, d_{xz} or d_{yz}). However, both $g_\parallel$ and $g_\perp$ values for $\mathbf{3^{ox}}$ are closer to g_e than those reported for nickel(III) complexes with the same anisotropy ($g_\parallel$ = 2.134 to 2.299, $g_\perp$ = 2.012 to 2.060).[7,9] This suggests that the SOMO of $\mathbf{3^{ox}}$ may significantly be developed on the ligand moiety, yet with a significant contribution on the metal center. This finding is indeed corroborated by preliminary DFT calculations at the B3LYP level that evaluate a non-negligible contribution of the Ni d_{yz} orbital into the SOMO of $\mathbf{3^{ox}}$ (Fig. 2) and an atomic spin density of 0.28 on Ni.‖ Hence, $\mathbf{3^{ox}}$ is best described as a nickel(II) complex with a semiquinone-type radical ligand.

Contrary to the optical spectra of the starting complexes, those of $\mathbf{1^{ox}}$–$\mathbf{4^{ox}}$ in CH_2Cl_2 at −30 °C all present remarkably intense bands in the Vis–NIR region at *ca.* 1000 nm (Table 1, Fig. 3 and Fig. S4†). With such intensities, these features must derive from charge transfer (CT) transitions, likely ligand-to-metal CT for the nickel(III) complexes $\mathbf{1^{ox}}$–$\mathbf{2^{ox}}$ and metal-to-ligand CT for the radical species $\mathbf{3^{ox}}$ and $\mathbf{4^{ox}}$. However, the low energy of these transitions is indicative of a small energy gap between the ground and excited states (MOs mainly developed on the ligand compared to those mainly located on the metal center), suggesting that orbital mixing may occur, as in $\mathbf{3^{ox}}$.**

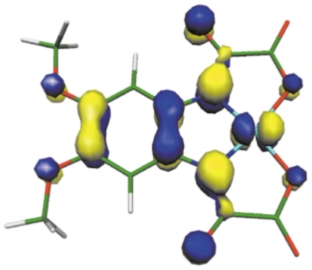

Fig. 2 Calculated SOMO of $\mathbf{3^{ox}}$.

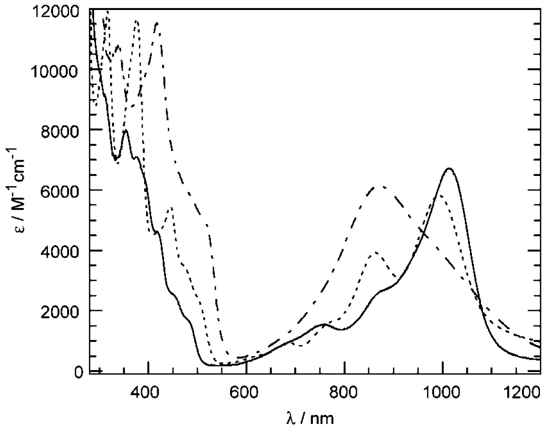

Fig. 3 Electronic spectra of $\mathbf{2^{ox}}$ (—), $\mathbf{3^{ox}}$ (---) and $\mathbf{4^{ox}}$ (-··-); 1 mM in CH_2Cl_2, −30 °C, 0.1 M NBu_4PF_6.

In conclusion, the locus of oxidation for a series of low-spin square-planar nickel(II) complexes with aromatic oxamato ligands is shifted from the metal center to the organic framework upon judicious substitution of the aromatic ligand. With H and Me groups, a nickel(III) complex forms upon oxidation ($\mathbf{1^{ox}}$, $\mathbf{2^{ox}}$). With the more electron-donating substituents OMe and NMe_2, the ligand instead is oxidized, yielding metallo-radical species ($\mathbf{3^{ox}}$, $\mathbf{4^{ox}}$). Altogether these results highlight the delicate energy and symmetry balance between the orbitals involved upon oxidation of complexes with non-innocent ligands, in the present case ligand π orbitals and metal d_{z^2} and d_π orbitals.

Notes and references

§ The X-ray structures of **1** and **3** (to be reported elsewhere) show the Ni^{II} ion in a square-planar environment.[10]

¶ The width at half-height of the signal, 2.8 mT, is somewhat broader than for a pure organic radical, likely due to hyperfine coupling with the amino and amidato nitrogen atoms.

‖ Computational details: we used the hybrid B3LYP method as implemented in GAUSSIAN98, with the all-electron double-basis proposed by Ahlrichs, except for the metal atom where we have used a triple-basis and two p polarization functions.[11]

** Additionally, the optical spectra of both $\mathbf{3^{ox}}$ and $\mathbf{4^{ox}}$ are temperature dependent (−80/+30 °C), indicating a valence tautomerism behavior (to be reported elsewhere).

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