Supplementary information

for the manuscript

Synthesis, structure, spectroscopy and redox chemistry of square-planar nickel(II) complexes with tetradentate *o*-phenylenedioxamidates and related ligands

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Table S1 Proton NMR spectroscopic data for **4–6**[a,b]

Complex	NMe	*m*-H	*o*-H
4	2.51 (6H, s)	6.56 (2H, dd) (5.9, 3.5)	8.03 (2H, dd) (6.0, 3.5)
5	2.50 (3H, s)	6.61 (2H, dd) (5.9, 3.5)	7.91 (2H, dd) (6.0, 3.5)
6		6.65 (2H, dd) (5.8, 3.4)	7.90 (2H, dd) (6.0, 3.5)

[a] δ (ppm) values in acetonitrile. J (Hz) values are given in parentheses. [b] Other signals from Me_4N^+ countercations at 3.10 (24 H, s).

Table S2 Electronic absorption spectroscopic data for **4–6**[a]

Complex	λ_{max}/nm (ε/M^{-1} cm^{-1})
4	256 (23000), 317 (sh), 357 (6500), 410 (sh)
5	254 (23000), 309 (sh), 352 (5500), 380 (sh), 410 (sh)
6	250 (23000), 274 (sh), 350 (7200), 465 (240)

[a] In acetonitrile.

Table S3 X-Ray absorption spectroscopic data for **4** and nickel(II) sulfate aqueous solution[a,b]

Complex	Preedge	Edge
4	8331.6 (0.04) (sh)	8339.2 (0.4) (sh), 8346.4 (0.7) (sh), 8351.5 (1.3), 8352.7 (1.3)
$[Ni(H_2O)_6]^{2+}$	8331.5 (0.03)	8348.6 (1.3)

[a] E (eV) values. Normalized absorbance values (relative to the atomic absorption) are given in parentheses. [b] Structure-contributing peaks on and above the broad absorption band of the rising edge have been precisely located from the absorption spectrum and its second derivative.

Table S4 X-Ray absorption structural data for **4**[a]

	N[b]	R[c]/Å	σ[d]/Å	Γ[e]	E_0[f]/eV
Ni−N(arylamidate)	2.0	1.85(2)	0.03	1.7	8331.0
Ni−N(alkylamidate)	2.0	1.93(2)	0.04	1.7	8331.0

[a] The fit was done using the theoretical amplitudes and phases of McKale (A. G. McKale, B. W. Veal and A. P. Paulikas, *J. Am. Chem. Soc.,* 1988, **110**, 3763). The residual factor defined as $\Sigma(k\chi_{exp} - k\chi_{th})^2/\Sigma\chi_{exp}^2$ was 8.7 x 10^{-3}. [b] The number of neighboring atoms N was allowed to vary during the fitting procedure. [c] R is the distance from the nickel absorber. Estimated errors are given in parentheses. [d] σ is the Debye-Waller coefficient. [e] The mean-electron-free path λ was chosen as $\lambda(k) = (1/\Gamma)[(\eta/k)^4 + k]$ with $\eta = 3.1$, and Γ was allowed to vary during the fitting procedure. [f] E_0 is the ionization energy.

Table S5 X-band EPR spectroscopic data for the singly oxidized species of **7–9**[a,b]

Complex	g_x	g_y	g_z
[NiL^1]$^-$	2.006	2.080	2.193
	(2.006)[c]	(2.081)[c]	(2.192)[c]
[NiL^2]$^-$	2.290	2.290	2.000
[NiL^3]$^-$	2.265	2.265	2.003

[a] Best fit g values corresponding to the x, y and z components of the allowed $M_s = +1/2 \rightarrow M_s = -1/2$ transition. [b] In acetonitrile at 110 K. [c] In dichloromethane at 110 K.