Synthesis, Magnetic Properties, Redox Behaviour, and Crystal Structure of the Bridged Binuclear Nickel(II) Complex $[Ni_2(\mu\text{-}OH)(\mu\text{-}CH_3CO_2)_2L_2]ClO_4\cdot H_2O$†

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Reaction of $Ni(CH_3CO_2)_2\cdot 4H_2O$ with *N,N',N''*-trimethyl-1,4,7-triazacyclononane(L) in methanol and addition of solid $NaClO_4\cdot H_2O$ yielded a blue-green binuclear nickel(II) complex containing a hydroxo and two acetate groups as bridging ligands. The crystal and molecular structure of the compound has been established by *X*-ray diffraction. It consists of binuclear cations $[LNi(\mu\text{-}OH)(\mu\text{-}CH_3CO_2)_2NiL]^+$, unco-ordinated perchlorate anions, and water of crystallization. Variable temperature (4—300 K) magnetic susceptibility measurements show a weak antiferromagnetic exchange coupling (J = −4.5 cm^{-1}, $\langle g \rangle$ = 2.17) between nickel centres with $T_N \approx 7.1$ K. The electronic spectra, measured both in the solid state and in solution, yielded the Racah parameter B (873 cm^{-1}) and the spin–orbit coupling constant λ(−208 cm^{-1}). The cyclic voltammogram of the compound in acetonitrile revealed a quasi reversible one-electron transfer ($E_{\frac{1}{2}}$ = +0.38 V *vs.* ferrocenium–ferrocene) corresponding to the couple $Ni^{III}Ni^{II}$–$Ni^{II}Ni^{II}$ and an irreversible oxidation wave at $E_p^{ox} \approx +1.04$ *vs.* ferrocenium–ferrocene.

During recent years much interest has arisen in the chemistry of acetates of first-transition-series metal ions, because of their relevance to biological systems. A general high-yield synthesis of binuclear complexes containing the $M_AM_B(\mu\text{-}OH)(\mu\text{-}CH_3CO_2)_2$ moiety, where M_A and M_B may be similar or dissimilar metal atoms, has been found.[1] The inherent stability of this core is indicated by its ready formation in solution. In the last few years we have been investigating the ligating properties of the small tridentate cyclic amine *N,N',N''*-trimethyl-1,4,7-triazacyclononane(L)[2] towards substitution-labile first-transition-series bivalent metal ions. In the presence of bridging ligands, stable complexes containing a dimetal core are readily obtainable. These materials are ideally suited for the study of intramolecular magnetic exchange interactions. Furthermore, a μ-hydroxo-di-μ-acetato-di-iron(II) complex has been prepared[3,4] to model the redox and magnetic behaviour of the oxygen-transfer protein deoxyhaemerythrin.

In the present paper we report results of similar redox, magnetic and spectroscopic studies of a compound with the same molecular structure, but with a different electronic structure of the paramagnetic centre, *i.e.* $[Ni_2(\mu\text{-}OH)(\mu\text{-}CH_3CO_2)_2L_2]ClO_4\cdot H_2O$.

Experimental

The ligand *N,N',N''*-trimethyl-1,4,7-triazacyclononane(L) was prepared as previously described.[5] All other starting materials were commercially available and of reagent grade.

Microchemical carbon, hydrogen, and nitrogen analyses were performed by Beller Microanalytical Laboratory, Göttingen, West Germany. Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer, i.r. spectra on a Beckmann Acculab 10 instrument (KBr disks). The magnetic susceptibility of the powdered sample was measured by using the Faraday method between 4 and 300 K. Diamagnetic corrections were applied using Pascal's constants.[6]

The apparatus used for cyclic voltammetric measurements has been described previously.[7] Fast voltammograms (0.5—5 V s^{-1}) were recorded on a Gould OS 4200 digital storage oscilloscope. Cyclic voltammograms of $[LNi(\mu\text{-}OH)(\mu\text{-}CH_3CO_2)_2NiL]ClO_4\cdot H_2O$ were measured in acetonitrile with 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate as supporting electrolyte at a platinum electrode at 25 °C. Measurements were made under an argon atmosphere using an Ag–AgCl reference electrode. At the beginning of each experiment a cyclic voltammogram of the solution containing only the supporting electrolyte was measured. To this solution, solid samples were added and dissolved with stirring to yield a concentration of *ca.* 1.5 × 10^{-3} mol dm^{-3} of the binuclear complex.

The compound $[LNi(\mu\text{-}OH)(\mu\text{-}CH_3CO_2)_2NiL]ClO_4\cdot H_2O$ was prepared by treating a solution of the cyclic amine (0.34 g, 2 mmol) in methanol (30 cm^3) with a sample of $Ni(CH_3CO_2)_2\cdot 4H_2O$ (0.37 g, 1.5 mmol). The resulting blue solution was refluxed with stirring for 0.5 h, after which a solid $NaClO_4\cdot H_2O$ (0.4 g) was added. The volume of the solution was reduced by passing argon over its surface, until blue crystals separated out. The crystals were filtered off and air-dried. Yield: 0.27 g (77%) (Found: C, 38.0; H, 7.1; N, 11.8; Ni, 16.8; ClO_4, 14.1. Calc. for $C_{22}H_{51}ClN_6Ni_2O_{10}$: C, 37.1; H, 7.2; N, 11.8; Ni, 16.5; ClO_4, 13.95%). The perchlorate anion was determined gravimetrically as tetraphenylarsonium(V) perchlorate.[8] **CAUTION**: Although we have experienced no difficulties with the compound isolated as its perchlorate salt, the unpredictable behaviour of perchlorate salts necessitates extreme caution in their handling.

Crystal Structure Determination and Refinement.—The blue-green tabular shaped crystal used for data collection had dimensions 0.2 × 0.2 × 0.25 mm. The unit-cell parameters were obtained at 23 °C by a least-squares refinement of the angular settings (9 < 2θ < 23°) of 20 reflections (Table 1). The

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† Di-μ-acetato-μ-hydroxo-bis[(*NN'N''*-trimethyl-1,4,7-triazacyclononane)nickel(II)] perchlorate hydrate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Summary of crystal data and intensity measurements

Molecular formula	$C_{22}H_{49}ClN_6Ni_2O_9{\cdot}H_2O$
M	712.57
Crystal system	Tetragonal
a/Å	10.841(6)
c/Å	27.790(3)
U/Å^3	3 266(2)
Z	4 (Dimers)
F(000)	1 500
Space group	$P4_12_12(D_4^4)$
D_c/g cm^{-3}	1.45
Diffractometer	AED II Siemens
Radiation	Mo-K_α (λ = 0.710 69 Å) graphite monochromatized
2θ Limits/°	2.5—60
Scan type	ω
μ/cm^{-1}	12.2
Total no. of reflections	1 984
Reflections used	1 138 [$I \geqslant 2.0\sigma(I)$]
No. of refined parameters	184
Transmission factors (min., max.)	0.555, 0.698
Shift/error (mean, max.)	0.17, 0.78
Residual peaks (eÅ^{-3}) (max., min.)	1.0, −0.5
R^a	0.063
R'^b	0.049
Weighting factor, w_i	$1/\sigma(F)^2$

[a] $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [b] $R' = [\Sigma w_i(\|F_o| - |F_c\|)^2/\Sigma w_i|F_o|^2]^{\frac{1}{2}}$.

Table 2. Atomic co-ordinates of $[Ni_2(OH)(CH_3CO_2)_2L_2]ClO_4{\cdot}H_2O$

Atom	x	y	z
Ni(1)	0.485 9(1)	0.333 0(2)	0.214 7(1)
Cl(1)	0.441 2(4)	0.441 2(4)	0.500 0(0)
O(1)	0.646 9(7)	0.353 1(7)	0.250 0(0)
O(2)	0.471 1(8)	0.512 1(8)	0.194 5(3)
O(3)	0.384 5(7)	0.363 5(8)	0.275 3(3)
N(1)	0.569 9(10)	0.275 8(10)	0.147 6(3)
N(2)	0.318 5(11)	0.304 4(10)	0.173 4(4)
N(3)	0.471 5(9)	0.137 9(9)	0.223 8(3)
C(1)	0.539 0(15)	0.071 2(13)	0.185 1(5)
C(2)	0.625 5(14)	0.163 4(15)	0.158 5(5)
C(3)	0.471 9(14)	0.265 3(13)	0.110 9(4)
C(4)	0.355 8(12)	0.333 3(14)	0.123 8(5)
C(5)	0.279 6(13)	0.174 8(14)	0.179 1(5)
C(6)	0.332 8(13)	0.116 3(12)	0.220 1(5)
C(7)	0.527 5(13)	0.709 1(15)	0.157 8(5)
C(8)	0.544 2(12)	0.596 9(13)	0.196 4(4)
C(9)	0.515 6(13)	0.093 7(11)	0.271 5(4)
C(10)	0.215 8(11)	0.389 0(15)	0.188 0(5)
C(11)	0.665 6(12)	0.369 7(12)	0.130 9(4)
O(11)	0.413 4(5)	0.317 8(5)	0.499 1(3)
O(12)	0.476 3(3)	0.512 2(3)	0.459 4(11)
O(13)	0.535 9(3)	0.535 9(3)	0.500 0(0)
O(14)	0.478 6(3)	0.653 5(3)	−0.016 1(9)
O(15)	0.568 0(3)	0.626 2(4)	0.047 0(12)
O_w	0.238 7(2)	0.238 7(2)	0.000 0(0)

data were corrected for Lorentz and polarization effects. An empirical X-ray absorption correction was carried out (ψ scans). Computations were carried out on an ECLIPSE computer using the program STRUCSY.[9] The structure was solved by standard Patterson and Fourier difference methods and refined with anisotropic thermal parameters for all non-hydrogen atoms, with the exception of the oxygen atoms of disordered perchlorate anions, which were refined isotropically. Idealized positions of H atoms bound to carbon atoms were calculated on the basis of d(C–H) = 0.96 Å and regular tetrahedral geometry around the carbon atoms. Scattering factors were from ref. 10.

Table 3. Selected bond distances (Å) and angles (°) for $[Ni_2(\mu\text{-}OH)(\mu\text{-}CH_3CO_2)_2L_2]ClO_4{\cdot}H_2O$

Ni(1) ··· Ni(1′)	3.400(3)		
Ni(1)–O(1)	2.014(7)	Ni(1)–N(1)	2.166(10)
Ni(1)–O(2)	2.028(9)	Ni(1)–N(2)	2.169(11)
Ni(1)–O(3)	2.038(8)	Ni(1)–N(3)	2.136(9)
N(1)–Ni(1)–N(2)	81.7(6)	N(2)–Ni(1)–N(3)	82.0(5)
N(1)–Ni(1)–N(3)	81.3(5)	N(2)–Ni(1)–O(3)	90.6(5)
N(1)–Ni(1)–O(2)	93.9(5)	N(2)–Ni(1)–O(1)	176.9(10)
N(1)–Ni(1)–O(3)	169.9(4)	N(2)–Ni(1)–O(2)	85.7(5)
N(1)–Ni(1)–O(1)	94.9(4)		
N(3)–Ni(1)–O(3)	91.3(5)	O(3)–Ni(1)–O(1)	92.7(4)
N(3)–Ni(1)–O(1)	96.5(6)	O(3)–Ni(1)–O(2)	91.8(5)
N(3)–Ni(1)–O(2)	167.2(3)	O(1)–Ni(1)–O(2)	95.7(4)
Ni(1)–O(1)–Ni(1′)	115.2(1)		

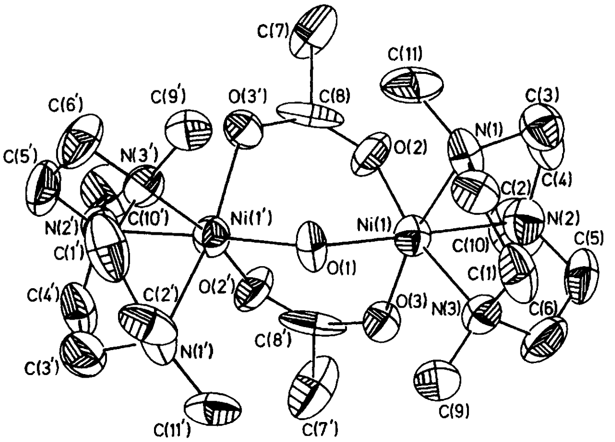

Figure 1. Structure of the $[Ni_2(OH)(CH_3CO_2)_2L_2]^+$ cation and the atom labelling scheme

Final positional parameters for all non-hydrogen atoms are given in Table 2. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The binuclear nickel complex containing μ-hydroxo-di-μ-acetato bridging groups was synthesized in good yield by the reaction of the tridentate cyclic amine with $Ni(CH_3CO_2)_2{\cdot}4H_2O$ in methanol.

The molecular geometry and the atom labelling scheme for the cation $[Ni_2(\mu\text{-}OH)(\mu\text{-}CH_3CO_2)_2L_2]^+$ are shown in Figure 1. A confacial bioctahedral geometry containing two Ni^{II} atoms is present. Each nickel atom has a distorted octahedral co-ordination sphere comprising two bridging acetates, a bridging hydroxo group, and a facially co-ordinating tridentate nitrogen ligand. Selected bond distances and bond angles are listed in Table 3. The structure consists of four distinct $[Ni_2(\mu\text{-}OH)(\mu\text{-}CH_3CO_2)_2L_2]^+$ cations, non-co-ordinatively bound to four statistically disordered perchlorate anions and four molecules of water of crystallization. The structure is thus quite similar to that reported previously for $[Fe_2(\mu\text{-}OH)(\mu\text{-}CH_3CO_2)_2L_2]^+$.[3] A deviation from the idealized orthogonal geometry is found within the five-membered N–Ni–N chelate rings, the N–Ni–N angles ranging between 81.3 and 82.0°, whereas the O–Ni–O angles fall between 91.8 and 95.7°. The Ni–O (av. 2.03 Å) and Ni–N (av. 2.16 Å) bond lengths are shorter than those found for

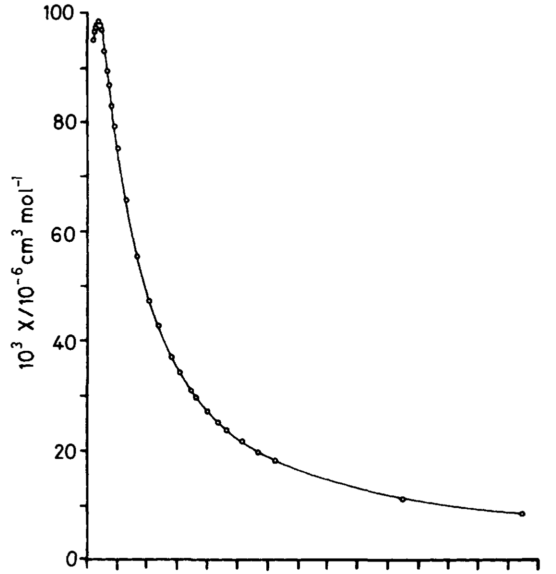

Figure 2. Plot of magnetic susceptibility *vs.* temperature. The solid line represents the best least-squares fit of the experimental susceptibility data to the theoretical equation (see text)

the model compound[3] for the di-iron centres in deoxyhaemerythrin (Fe–O, av. 2.083; Fe–N, av. 2.29 Å).

A comparison of the present structure with that of the binuclear unit of the μ-aqua-di-μ-acetato-dinickel[11] compound and with the $[Fe_2(\mu\text{-}OH)(\mu\text{-}CH_3CO_2)_2L_2]^+$ cation[3,4] shows that the metal–metal distances are significantly different (Table 4). Protonation of the μ-hydroxo bridge to yield a μ-aqua bridge results in a significant lengthening of the Ni–O distance [Δ(Ni–O) = 0.074 Å]. It is interesting to compare this with the lengthening of the corresponding Fe–O distances of a μ-oxo-di-μ-acetato bridged iron(III) dimer and its protonated μ-hydroxo bridged analogue where a Fe–O bond-distance difference of 0.17 Å has been observed.[12]

The absorption spectrum of the binuclear complex has been measured both in solution and in the solid state. The diffuse reflectance spectrum of a KBr disk is in good agreement with the solution spectra, showing that practically no dissociation of the binuclear units occurs in solution. As is expected for a d^8 configuration in a near-octahedral ligand field, three spin-allowed transitions from $^3A_{2g}$ to $^3T_{2g}$, $^3T_{1g}$, and $^3T_{1g}\,(P)$ are observed at 9 800 (ν_1), 15 600 (ν_2), and 26 600 (ν_3) cm^{-1}, respectively, with the following absorption coefficients 22 (ν_1), 14 (ν_2), and 30 (ν_3) dm^3 mol^{-1} cm^{-1}. The similarity of these absorptions to those of simple mononuclear nickel(II) complexes confirms that the ground state is a spin-triplet with no orbital degeneracy. The band at 9 800 cm^{-1} yields the octahedral splitting parameter $\Delta_{oct} \approx 9\,800$ cm^{-1}, which lies between those of pure $Ni^{II}O_6$ and $Ni^{II}N_6$ chromophores. For the octahedral case, by calculation in the strong-field coupling scheme with a d^8 configuration, the Racah parameter B is found to be 873 cm^{-1} which leads to a nephelauxetic ratio β of 0.827 [considering $15\,B = 15\,840$ cm^{-1} for the gaseous ion (^3P) for Ni^{2+}]. With $\langle g \rangle = 2.17$, obtained from the magnetic susceptibility measurements (see below), from the equation $g = 2 - 8\lambda/10Dq$ we calculated the spin–orbit coupling constant λ to be −208 cm^{-1} for the present compound. Compared with the free-ion value of −315 cm^{-1},[13] there is a marked reduction of about 35%. This is not uncommon for nickel complexes in distorted cubic crystal fields.

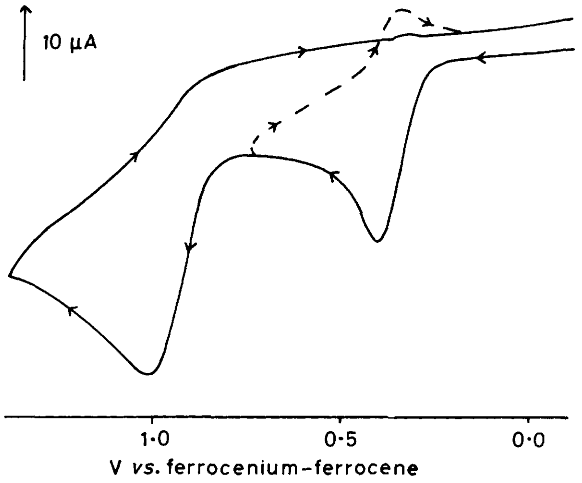

Figure 3. Cyclic voltammogram of $[Ni_2(OH)(CH_3CO_2)_2L_2]ClO_4\cdot H_2O$ in acetonitrile containing 0.1 mol dm^{-3} $[NBu_4][PF_6]$ at scan speed 100 mV s^{-1}, 25 °C, platinum bead electrode. Scan range 0 to +2.0 V(——) and 0 to +1.2 V (– – –)

For Ni^{II} in a trigonally distorted cubic crystal field, *e.g.* $CsNiBr_3$, λ has been reported[14] to be −175 cm^{-1}; λ for $[Ni(NH_3)_6]Br_2$ is known[14] to be −200 cm^{-1}.

To see whether or not magnetic exchange is present, the magnetic susceptibility of the compound was studied in the range of 4—300 K. The temperature dependence of the molar susceptibility χ_M is shown in Figure 2. The experimental magnetic susceptibility increases as the temperature is lowered until a maximum is reached at ≈7 K, after which there is a rapid decrease in χ_M. The $\mu_{eff.}$ per Ni values over their temperature range vary from 3.11 μ_B at 289.5 K to 1.26 μ_B at 4.2 K. The observed plot of χ_M *vs.* T is characteristic of an antiferromagnetic coupling. The data were fitted by means of least squares to the formula[15] (using a Weiss constant θ) for the paramagnetic susceptibility, which results from the spin Hamiltonian ($\mathcal{H} = 2JS_1S_2$) for an isotropic magnetic exchange with $S_1 = S_2 = 1$ without zero-field splitting. Although powder measurement is not ideal for a thorough analysis of $S = 1$ binuclear systems, the intradimer exchange term J is the dominant term in the spin Hamiltonian and hence is not influenced markedly by the value of either the zero-field splitting parameter D or the interdimer interaction $z'J'$.[16]

The least-squares fit of very good quality resulting in the following values, $J = -4.5(1)$ cm^{-1}, $\langle g \rangle = 2.17(1)$, and $\theta = 2.7(1)$ K, is also shown in Figure 2. The J value for the μ-aqua-di-μ-acetato-dinickel compound has not been reported,[11] but the maximum in the susceptibility plot ($T_N < 2$ K) definitely indicates a weaker coupling than that in the μ-hydroxo-di-acetato-dinickel unit. Thus protonation of the μ-hydroxo bridge results in a significant reduction of the exchange interactions. Apparently, there is a correlation between the exchange interactions, the bridging angles, and the metal–metal separations.

No polycrystalline powder e.s.r. spectrum (*X*-band) could be detected at 100 K for $[Ni_2(OH)(CH_3CO_2)_2L_2]ClO_4\cdot H_2O$.

The homodinuclear Ni^{II}–Ni^{II} couple has been studied by cyclic voltammetry in the potential range −1.80 to +2.0 V (*vs.* Ag–AgCl, saturated LiCl in ethanol) at a platinum-bead electrode in CH_3CN. The complex shows an irreversible reduction wave at *ca.* −0.85 V. No other electrochemical response in the range −1.80 to +0.40 V is observed. At more positive potentials the complex shows two oxidation waves (Figure 3) corresponding presumably to the sequential formation of $Ni^{III}Ni^{II}$ and $Ni^{III}Ni^{III}$ species. Both oxidation waves remain irreversible in the scan rate range 20—100 mV s^{-1}. The

Table 4. Selected structural information for compounds with the $M_2O(CH_3CO_2)_2$ unit (M = Ni^{II} or Fe^{II})

Compound	M–M/Å	M–O–M/°	M–OH or M–OH_2/Å	Ref.
$[Fe_2(OH)(CH_3CO_2)_2L_2]^+$	3.32(1)	113.2(2)	1.987(8)	3,4
$[Ni_2(OH)(CH_3CO_2)_2L_2]^+$	3.40(3)	115.2(1)	2.014(7)	This work
$[Ni_2(OH_2)(CH_3CO_2)_4(tmen)_2]$*	3.56	117.2	2.088	10

* tmen = *NNN′N′*-tetramethyl-1,2-diaminoethane.

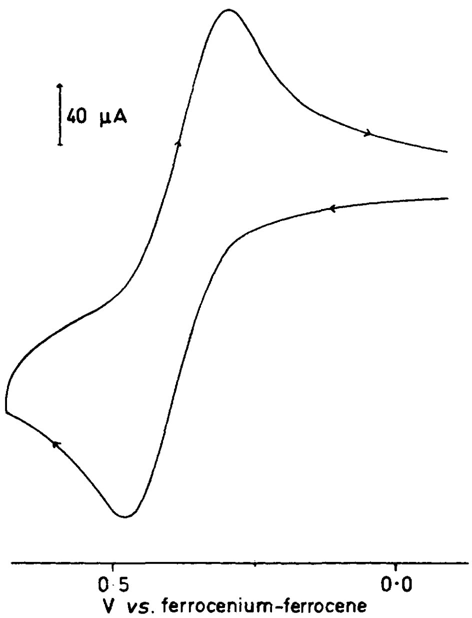

Figure 4. Cyclic voltammogram of $[Ni_2(OH)(CH_3CO_2)_2L_2]ClO_4 \cdot H_2O$ in acetonitrile containing 0.1 mol dm^{-3} $[NBu_4][PF_6]$ at scan speed 5 V s^{-1}, 25 °C, platinum-bead electrode

first wave changes its nature with increasing scan rates; in the scan rate range 0.5 to 5 V s^{-1} the first wave becomes quasi-reversible showing the transient nature of the $Ni^{III}Ni^{II}$ mixed-valence species. The second oxidation wave at $E_p^{ox} \approx +1.04$ V (*vs*. ferrocenium–ferrocene), associated with the oxidation of the mixed-valence species, remains irreversible even at fast scan rates. A cyclic voltammogram in the range +0.40 to +1.2 V at a fast scan rate of 5 V s^{-1} is shown in Figure 4. The single one-electron transfer occurs quasi-reversibly for the first wave as is evident from the adherence to the following criteria: (i) the $E_{\frac{1}{2}}$ values $[E_{\frac{1}{2}} = 0.5\,(E_{p,a} + E_{p,c})]$ are independent of scan rates, (*ii*) the separation of peak potentials ($\Delta E = E_{p,c} - E_{p,a}$) increases with scan rate and is always greater than 60 mV, and (*iii*) the ratio of the peak currents due to cathodic ($I_{p,c}$) and anodic ($I_{p,a}$) sweeps is close to unity at different scan rates. Thus a quasi-reversible one-electron transfer process at $E_{\frac{1}{2}} = +0.38$ V *vs*. ferrocenium–ferrocene is observed for the equilibrium $[LNi^{II}(OH)(CH_3CO_2)_2Ni^{II}L]^+ \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [LNi^{III}(OH)(CH_3CO_2)_2Ni^{II}L]^{2+}$. The lifetime of the mixed-valence species at the electrode surface can be estimated to be at least 140 ms.

Acknowledgements

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