DALTON

Azooximates of bi- and tri-valent nickel†

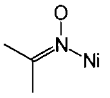
Soma Karmakar, Suranjan Bhanja Choudhury, Sanjib Ganguly and Animesh Chakravorty*

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science,
Calcutta 700 032, India

The reaction of arylazooximes, RC(NOH)NNPh (HL^R, R = Me or Ph), with nickel(II) acetate tetrahydrate in methanol under anaerobic conditions afforded $[NiL^R_3]^-$ isolated as the NEt_4^+ salt. One $(L^{Ph})^-$ ligand in $[NiL^{Ph}_3]^-$ underwent facile displacement by L–L ligands like 2,2′-bipyridine (bipy) furnishing $[NiL^{Ph}_2(bipy)]$. The Ni^{III}–Ni^{II} reduction potential of $[NiL^R_3]^-$ in acetonitrile is ≈ 0.1 V *vs.* saturated calomel electrode. The trivalent complex $[NiL^R_3]$ was quantitatively isolated *via* constant-potential electrolysis at 0.3 V. The Ni^{IV}–Ni^{III} couple of the tris chelate was observed near 0.9 V, but the nickel(IV) complex could not be isolated in the solid state. The relatively low metal reduction potential allowing facile preparation of the stable $[NiL^R_3]$ system is attributed to the strong-field nature of the oximato-*N* atom. In going from $[NiL^{Ph}_3]^-$ to $[NiL^{Ph}_2(bipy)]$ the Ni^{III}–Ni^{II} reduction potential increases by ≈ 0.3 V showing that $(L^{Ph})^-$ is a much better stabiliser of Ni^{III} than is bipy. The crystal structures of $[NEt_4][NiL^{Ph}_3]$ and $[NiL^{Ph}_2(bipy)]$ have been determined. The geometry of $[NiL^R_3]$ ($S = \frac{1}{2}$) was studied with the help of its EPR spectrum (d_{z^2} ground state) in the $[CoL^R_3]$ lattice. Both $[NiL^R_3]^-$ and $[NiL^R_3]$ have exclusive meridional geometry consistent with steric and angular-overlap considerations. In $[NiL^{Ph}_2(bipy)]$ the two anionic oximato functions are placed in mutually *trans* positions. The oximato-*N* ligand displays substantial *trans* influence. Thus in $[NiL^{Ph}_3]^-$ the Ni–N (azo) bond lying *trans* to Ni–N (oxime) is ≈ 0.05 Å longer than the other two mutually *trans* Ni–N (azo) bonds. The average Ni–N (azo) distance in $[NiL^{Ph}_2(bipy)]$ is ≈ 0.04 Å shorter than that in $[NiL^{Ph}_3]^-$ because none of the Ni–N (azo) bonds in the former complex is subject to the *trans* influence of Ni–N (oxime). In both complexes the Ni–N (oxime) lengths are significantly shorter than the Ni–N (azo) lengths, consistent with stronger Ni–N (oxime) σ bonding which is also a reason behind the strong-field nature of the oximate ligand.

The oxime function ligated as in motif **1** is a remarkable tool for redox activation of pseudo-octahedral nickel especially over the valence states 2–4.[1–3] The function is generally employed in conjunction with other donors ensuring chelate formation. Notable examples of bidentate chelators of this type, **2**, are dioximes (X = NOH),[1a,4] imine oximes (X = N)[2b] and ketoximes (X = O).[5] In the present work we explore the new situation where the codonor is an azo function as in **3**, abbreviated as HL^R. Unlike the cases of palladium and platinum,[6] very little is known about the nickel chemistry[7] of HL^R.

Herein we report the synthesis of tris chelates of type $[NEt_4][Ni^{II}L^R_3]$ and of certain species derived from them *via* metal oxidation or ligand substitution such as $[Ni^{III}L^R_3]$ and $[Ni^{II}L^R_2(bipy)]$ (bipy = 2,2′-bipyridine). The features scrutinised include structure, isomer preference and metal redox.



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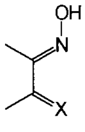

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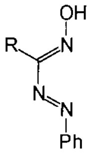

HL^R

3

Results and Discussion

Bivalent complexes

Two HL^R compounds (R = Me or Ph) have been used in the present work. The stoichiometric (3:1) reaction of HL^R with nickel(II) acetate tetrahydrate in dry methanol containing sodium acetate trihydrate and tetraethylammonium chloride affords a 1:1 electrolyte $[NEt_4][NiL^R_3]$ as a brown solid in excellent yield, equation (1). It is necessary to carry out the synthesis

$$Ni^{2+} + 3(L^R)^- + NEt_4^+ \longrightarrow [NEt_4][NiL^R_3] \qquad (1)$$

in an oxygen-free atmosphere, otherwise intractable radical species contaminate the product. Once isolated in pure form, the $[NEt_4][NiL^R_3]$ salts are stable in air, both in the solid state and in solution.

Solutions of $[NiL^{Ph}_3]^-$ in methanol are, however, susceptible to facile substitution of a $(L^{Ph})^-$ ligand by *N*,*N*′-co-ordinating ligands such as ethane-1,2-diamine (en), bipy and 1,10-phenanthroline (phen), equation (2). The $[NiL^{Ph}_2(L–L)]$ complexes are

$$[NiL^{Ph}_3]^- + L–L \longrightarrow [NiL^{Ph}_2(L–L)] + (L^{Ph})^- \qquad (2)$$

isolated from the reaction mixture as dark solids in very good yields. The $[NiL^{Me}_2(L–L)]$ type species can also be similarly prepared but have not been studied in detail.

Magnetic and spectral data for the two families are collected in Table 1. The complexes uniformly contain two unpaired electrons ($t_2^6e^2$). Owing to the presence of strong allowed absorptions in the visible region, ligand-field bands could not be resolved for $[NiL^R_3]^-$. In the case of $[NiL^{Ph}_2(L–L)]$, however, a weak band is observed near 1100 nm which is believed to be the octahedral ν_1 band or a component thereof.

Structures

The crystal structures of $[NEt_4][NiL^{Ph}_3]$ and $[NiL^{Ph}_2(bipy)]$ have been determined. Molecular views are shown in Figs. 1 and 2 and selected bond parameters in Tables 2 and 3.

In $[NEt_4][NiL^{Ph}_3]$ two crystallographically distinct but metrically very similar molecules making an enantiomeric pair constitute the asymmetric unit in which both metal atoms are tris chelated in meridional geometry, **4**. The other possible

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† *Non-SI units employed*: G = 10^{-4} T, $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

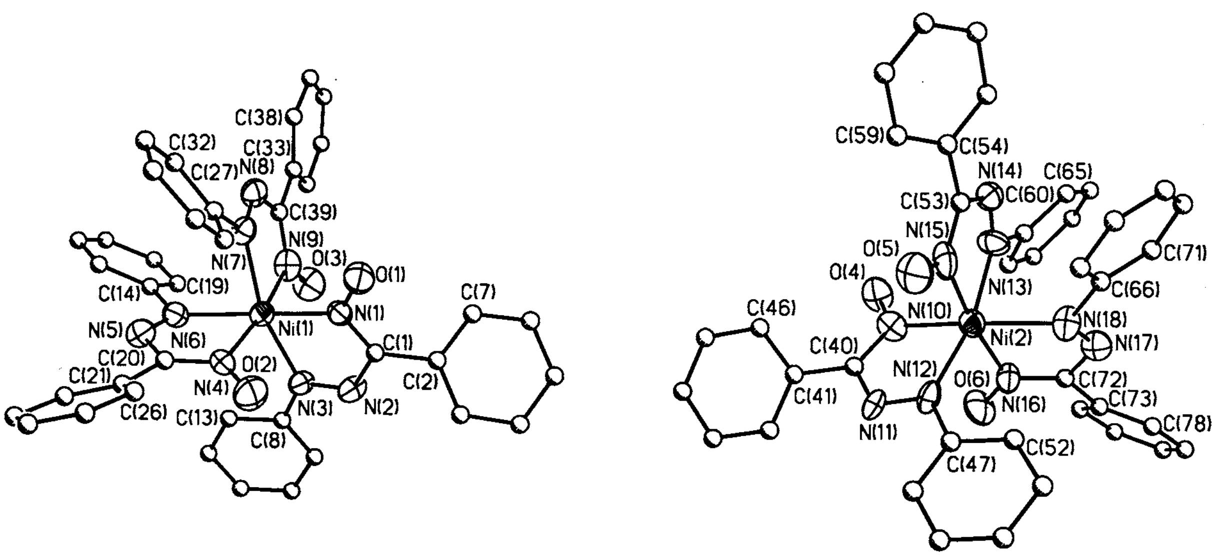


Fig. 1 Perspective view of the anion of $[NEt_4][NiL^{Ph}_3]$ showing 40% thermal probability ellipsoids for Ni, N and O atoms; H atoms are omitted for clarity

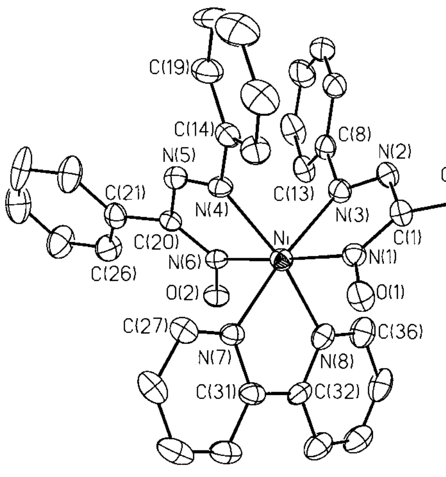


Fig. 2 An ORTEP[8] plot and the atom labelling scheme for $[NiL^{Ph}_2(bipy)]$. All atoms are represented by 40% thermal probability ellipsoids; H atoms are omitted for clarity

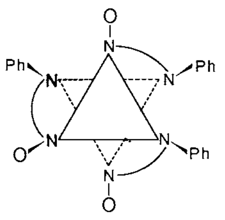
Table 1 Magnetic moment[a] and electronic spectral data for $[NEt_4][NiL^R_3]$,[b] $[NiL^R_3]$[b] and $[NiL^{Ph}_2(L–L)]$[c]

Compound	μ_{eff}/μ_B	UV/VIS λ/nm (ε/dm³ mol⁻¹ cm⁻¹)
$[NEt_4][NiL^{Me}_3]$	3.15	700[d] (2810), 400 (13 820)
$[NEt_4][NiL^{Ph}_3]$	3.18	700[d] (2120), 440 (14 760)
$[NiL^{Me}_3]$	1.99	1600 (100), 650[d] (1910), 400[d] (11 460)
$[NiL^{Ph}_3]$	2.01	1500 (280), 690 (3380), 475[d] (10 080)
$[NiL^{Ph}_2(en)]$	2.88	1125 (50), 460 (17 000)
$[NiL^{Ph}_2(bipy)]$	2.85	1150 (50), 625[d] (1225), 465 (16 440)
$[NiL^{Ph}_2(phen)]$	3.25	1150 (70), 625[d] (1185), 465 (18 210)

[a] In the solid state (298 K). [b] Solvent is acetonitrile. [c] Solvent is dichloromethane. [d] Shoulder.

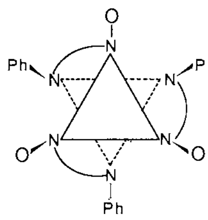
geometrical isomer (facial, **5**) has not been observed either in the solid state or in solution (see below). The NiN_6 co-ordination spheres are severely distorted from octahedral geometry as can be seen from the angles at the metal centre (Table 2).

The Ni–N (oxime) distances, 2.011(10)–2.060(11) Å, are generally shorter than the Ni–N (azo) lengths, 2.073(12)–2.150(10) Å. The Ni–N (oxime) bond displays a significant *trans* influence. In each molecule the Ni–N (azo) bond lying *trans* to Ni–N (oxime) is ≈ 0.05 Å longer than the other two mutually *trans* Ni–N (azo) bonds. The relevant lengths in molecule **1** are: Ni(1)–N(6) 2.150(10) *versus* Ni(1)–N(3) 2.108(10) and Ni(1)–N(7) 2.100 (11) Å. All the five-membered azooxime chelate rings are satisfactory planes. The bond lengths within the chelate rings are generally similar to those observed in HL^R complexes of other metal ions.[6b–d,9]



meridional

4



facial

5

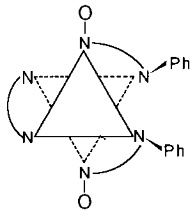
Table 2 Selected bond lengths (Å) and angles (°) for $[NEt_4][NiL^{Ph}_3]$

Ni(1)–N(1)	2.016(10)	Ni(2)–N(10)	2.011(10)
Ni(1)–N(3)	2.108(10)	Ni(2)–N(12)	2.096(10)
Ni(1)–N(4)	2.035(11)	Ni(2)–N(13)	2.073(12)
Ni(1)–N(6)	2.150(10)	Ni(2)–N(15)	2.024(12)
Ni(1)–N(7)	2.100(11)	Ni(2)–N(16)	2.060(11)
Ni(1)–N(9)	2.034(11)	Ni(2)–N(18)	2.137(11)
N(1)–Ni(1)–N(3)	77.3(4)	N(10)–Ni(2)–N(12)	76.3(4)
N(1)–Ni(1)–N(4)	94.5(4)	N(10)–Ni(2)–N(13)	94.7(4)
N(1)–Ni(1)–N(6)	167.9(4)	N(10)–Ni(2)–N(15)	92.9(4)
N(1)–Ni(1)–N(7)	91.5(4)	N(10)–Ni(2)–N(16)	93.8(4)
N(1)–Ni(1)–N(9)	92.7(4)	N(10)–Ni(2)–N(18)	167.5(4)
N(3)–Ni(1)–N(4)	93.7(4)	N(12)–Ni(2)–N(13)	166.0(4)
N(3)–Ni(1)–N(6)	109.5(4)	N(12)–Ni(2)–N(15)	93.1(4)
N(3)–Ni(1)–N(7)	163.0(4)	N(12)–Ni(2)–N(16)	91.5(4)
N(3)–Ni(1)–N(9)	91.2(4)	N(12)–Ni(2)–N(18)	109.7(4)
N(4)–Ni(1)–N(6)	75.4(4)	N(13)–Ni(2)–N(15)	76.5(5)
N(4)–Ni(1)–N(7)	99.9(4)	N(13)–Ni(2)–N(16)	99.8(5)
N(4)–Ni(1)–N(9)	172.0(4)	N(13)–Ni(2)–N(18)	81.4(4)
N(6)–Ni(1)–N(7)	83.9(4)	N(15)–Ni(2)–N(16)	172.6(4)
N(6)–Ni(1)–N(9)	97.0(4)	N(15)–Ni(2)–N(18)	97.7(4)
N(7)–Ni(1)–N(9)	76.4(4)	N(16)–Ni(2)–N(18)	75.3(4)

In $[NiL^{Ph}_2(bipy)]$ the asymmetric unit consists of a single severely distorted octahedral molecule (Fig. 2) in which the negatively charged oximato functions lie farthest from each other, *i.e.* in *trans* positions, **6**. Two other isomers in both of

Table 3 Selected bond lengths (Å) and angles (°) for $[NiL^{Ph}{}_2(bipy)]$

Ni–N(1)	2.036(5)	Ni–N(6)	2.035(5)
Ni–N(3)	2.062(6)	Ni–N(7)	2.073(6)
Ni–N(4)	2.070(5)	Ni–N(8)	2.066(6)
N(1)–Ni–N(3)	75.8(2)	N(3)–Ni–N(8)	100.3(2)
N(1)–Ni–N(4)	102.6(2)	N(4)–Ni–N(6)	76.3(2)
N(1)–Ni–N(6)	176.6(2)	N(4)–Ni–N(7)	96.3(2)
N(1)–Ni–N(7)	93.7(2)	N(4)–Ni–N(8)	166.8(2)
N(1)–Ni–N(8)	90.0(2)	N(6)–Ni–N(7)	89.6(2)
N(3)–Ni–N(4)	86.6(2)	N(6)–Ni–N(8)	91.4(2)
N(3)–Ni–N(6)	100.9(2)	N(7)–Ni–N(8)	78.9(2)
N(3)–Ni–N(7)	169.5(2)		



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which the oximato functions lie in *cis* positions are possible but these have not been observed. All the chelate rings are excellently planar. The Ni–N (azo) and Ni–N (bipy) distances are nearly equal lying within the range 2.062(6)–2.073(6) Å (Table 3). However, the Ni–N (oxime) lengths are shorter [average 2.036(5) Å] being nearly equal to those in $[NiL^{Ph}{}_3]^-$. The average Ni–N (azo) distance, 2.07 Å , in $[NiL^{Ph}{}_2(bipy)]$ is significantly shorter than that, 2.11 Å , in $[NiL^{Ph}{}_3]^-$ because none of the Ni–N (azo) bonds in the former complex is subject to the *trans* influence of an Ni–N (oxime) bond.

Metal redox

The $[NEt_4][NiL^R{}_3]$ complexes are electroactive in acetonitrile solution displaying two one-electron cyclic voltammetric responses with $E_{\frac{1}{2}}$ near 0.1 and 0.9 V *vs.* the saturated calomel electrode (SCE) (Table 4). The two responses are assigned to the $[Ni^{III}L^R{}_3]$–$[Ni^{II}L^R{}_3]^-$ (≈ 0.1 V) and $[Ni^{IV}L^R{}_3]^+$–$[Ni^{III}L^R{}_3]$ (≈ 0.9 V) couples respectively. The absence of any satellite response[5] is consistent with the exclusive population of one isomer only in the solution phase. In order to exclude the possibility of averaging *via* rapid isomerisation, voltammograms were run at low temperatures. Even at 263 K a single clean Ni^{III}–Ni^{II} response is observed. On the basis of the X-ray structural results and other considerations (see below), the observed solution isomer is identified as meridional. The near reversibility of the $[Ni^{III}L^R{}_3]$–$[Ni^{II}L^R{}_3]^-$ couple suggests that the redox process is stereoretentive. In other words, $[NiL^R{}_3]$ has meridional geometry like $[NiL^R{}_3]^-$. This is confirmed by solution and solid-state EPR results, see below.

All the three $[NiL^{Ph}{}_2(L–L)]$ complexes show a quasi-reversible Ni^{III}–Ni^{II} response (peak-to-peak separation ≈100 mV) in dichloromethane with $E_{\frac{1}{2}}$ of 0.44 V. Here $E_{\frac{1}{2}}$ is considerably higher than that of $[NiL^{Ph}{}_3]^-$ as expected. The $E_{\frac{1}{2}}$ of the $[Ni(bipy)_3]^{3+}$–$[Ni(bipy)_3]^{2+}$ couple is ≈1.6 V higher[10] than that of the $[NiL^R{}_3]$–$[NiL^R{}_3]^-$ couple. Thus the nickel(III) state is destabilised roughly by 0.5 V for every substitution of $(L^{Ph})^-$ by bipy.

Electrosynthesis of $[NiL^R{}_3]$: stabilisation of Ni^{III}

Exhaustive constant-potential electrolysis of $[NEt_4][NiL^R{}_3]$ in acetonitrile solution at 0.3 V causes the transfer of one electron and reddish brown $[NiL^R{}_3]$ is isolated from the oxidised solution in nearly quantitative yields. The cyclic voltammogram of $[NiL^R{}_3]$ (initial scan cathodic) is virtually the same as that of $[NiL^R{}_3]^-$ (initial scan anodic). Attempted electrosynthesis of $[Ni^{IV}L^R{}_3]^+$ and $[Ni^{III}L^{Ph}{}_2(L–L)]^+$ did not succeed due to instability of the species.

Table 4 Electrochemical data for $[NEt_4][NiL^R{}_3]$ in acetonitrile

	$E_{\frac{1}{2}}$/V($\triangle E_p{}^a$/mV), n^b	
Compound	Ni^{III}–Ni^{II} couple	Ni^{IV}–Ni^{III} couple
$[NEt_4][NiL^{Me}{}_3]$	0.06(80), 1.00	0.90(100)
$[NEt_4][NiL^{Ph}{}_3]$	0.07(70), 1.02	0.86(90)

[a] $\triangle E_p$ = Peak-to-peak separation. [b] $n = Q/Q'$, where Q is the observed Coulomb count and Q' the calculated count for one-electron transfer.

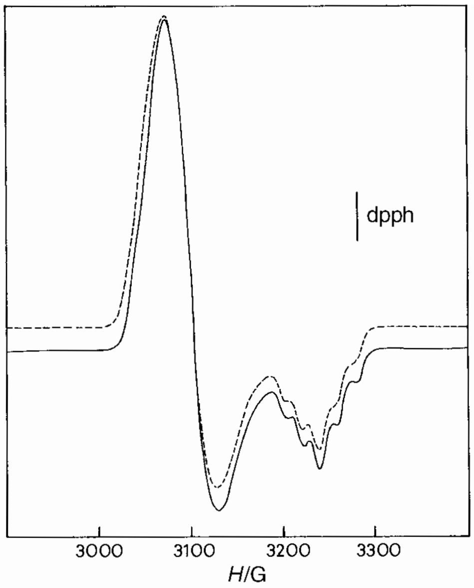

Fig. 3 X-Band EPR spectra of $[NiL^{Ph}{}_3]$ doped into $[CoL^{Ph}{}_3]$ (—) in polycrystalline form at 298 K and $[NiL^{Ph}{}_3]$ in acetonitrile–toluene (1:1) glass at 77 K(- - -). Instrument settings : power, 30 dB; modulation, 100 kHz; sweep centre, 3200 G; sweep width, 1000 G; sweep time, 240 s; receiver gain, 2×10^3 for (—) and 3.2×10^2 for (- - -). dpph = Diphenylpicrylhydrazyl

The EPR data for $[NiL^R{}_3]$ are collected in Table 5. Only a few oximato complexes of trivalent nickel have so far been isolated[1,2b,3b,5] in the pure state and $[NiL^R{}_3]$ augment this short list. The complexes have low-spin ($t_2{}^6e^1$) configuration (Table 1). In spite of our best efforts we have not succeeded in growing X-ray-quality single crystals of $[NiL^R{}_3]$ but its geometrical structure has been unequivocally established with the help of EPR spectra, see below.

The $(L^R)^-$ ligand exerts a remarkably strong crystal field. Thus when tris chelated it enforces a low-spin configuration even in Mn^{II} which has the highest spin-pairing energy among bivalent 3d ions.[11] In the case of $Ni^{II}(t_2{}^6e^2)$ the strong field of $(L^R)^-$ destabilises the antibonding e shell leading to facile ionisation (low Ni^{III}–Ni^{II} reduction potential). The strong metal–oximato σ bonding [we recall the shortness of Ni–N (oxime) bonds] is believed to be a crucial factor that makes $(L^R)^-$ as well as other type 2 species[2b,5] such strong-field ligands.

EPR spectra : meridional geometry

The $[NiL^R{}_3]$ chelates freely form solid solutions with $[CoL^R{}_3]$ which have exclusive meridional geometry.[12] The polycrystalline EPR spectra of the doped lattice is virtually invariant in the temperature range 298–77 K. The spectrum is axial (Fig. 3) with $g_{\parallel}$ and $g_{\perp}$ near 2.03 and 2.12 respectively (Table 5). The $g_{\parallel}$ signal has a symmetrical five-line superhyperfine structure (Fig. 3) with $a_{\parallel} \approx 18$ G due to coupling with two ^{14}N nuclei (see

Table 5 The EPR data for [NiL$^{R}{}_3$]

Compound	$g_\perp$	$g_\parallel$	$a_\parallel$/G
[NiL$^{Me}{}_3$]^a	2.120	2.027	18
[Co(Ni)L$^{Me}{}_3$]^b	2.120	2.028	19
[NiL$^{Ph}{}_3$]^a	2.120	2.029	18
[Co(Ni)L$^{Ph}{}_3$]^b	2.120	2.028	19

^{a} In acetonitrile–toluene (1:1) glass at 77 K. ^{b} 1% [NiL$^{R}{}_3$] in the corresponding [CoL$^{R}{}_3$] matrix (at 298 K).

below). The spectra of [NiL$^{R}{}_3$] in frozen (77 K) acetonitrile–toluene (1:1) glass are closely similar to those in the [CoL$^{R}{}_3$] lattice. Thus [NiL$^{R}{}_3$] has the same gross geometry in the solid and solution phases. In the [CoL$^{R}{}_3$] lattice, [NiL$^{R}{}_3$] must be meridional like the host. The meridional geometry has no symmetry and a rhombic EPR spectrum can be expected. The observed axial spectra show that the rhombic component in [NiL$^{R}{}_3$] is relatively weak.

The bond length order Ni–N (oxime) < Ni–N (azo) in meridional [NiL$^{Ph}{}_3$]$^-$ implies that oximato-*N* binds the 3d^8(Ni^{II}) ion more strongly than azo-*N*. The same applies to the low-spin 3d^6 case, [FeL$^{R}{}_3$]$^-$.[9g,h] We logically assume that this holds in the case of [NiL$^{R}{}_3$] (3d^7) as well. The N (azo)–Ni–N (azo) axis of the meridional complex can thus be approximately identified as the elongated *z* axis. The energy order of the split e components is then $d_{x^2-y^2} > d_{z^2}$. The unpaired electron will thus be in the d_{z^2} orbital in the ground state. This is consistent with the observed *g* inequality $g_\perp > g_\parallel$.[1a,13] The five-line ^{14}N structure of $g_\parallel$ is attributed to σ coupling with the two ^{14}N (azo) atoms co-ordinated on the *z* axis. Interestingly, [NiL$^{R}{}_3$] exhibits a relatively weak band in the near-IR region at ≈1500 nm (Table 1). This band is believed to correspond to the ligand-field transition $d_{z^2} \longrightarrow d_{x^2-y^2}$ within the split e shell.

Isomer preference

The tris chelates have exclusive meridional geometry for both bi- and tri-valent nickel. Angular-overlap considerations strongly favour meridional geometry for the low-spin d^7 case (Ni^{III}) but for d^8 (Ni^{II}) the two geometries are little discriminated energetically.[14] Sterically the meridional geometry is generally more favoured because the pendant azo Ph groups and oximato oxygen atoms are more spread out than in the facial form (compare **4** and **5**). The observed geometries of [NiL$^{R}{}_3$]$^-$ and [NiL$^{R}{}_3$] are thus consistent with collective consideration of angular-overlap and steric factors.

Interestingly, low-spin [MnL$^{R}{}_3$]$^-$ (3d^5) and [FeL$^{R}{}_3$]$^-$ (3d^6) are both facial due to strong metal to azooxime back bonding.[15,16] In [CoL$^{R}{}_3$] (low spin, 3d^6), back bonding, if any, is weak because of the higher oxidation state of the metal and its small radius (0.69 Å; compare Ni^{II}, 0.83 Å, and Ni^{III}, 0.70 Å)[17] augments steric crowding. It therefore assumes meridional geometry.

Conclusion

Arylazooximes display good affinity for both bi- and tri-valent nickel. The [NEt$_4$][Ni^{II}L$^{R}{}_3$], [Ni^{III}L$^{R}{}_3$] and [Ni^{II}L$^{Ph}{}_2$(L–L)] complexes are the first examples of simultaneous azo and oximato binding to nickel oxidation states. Crucial to the stabilisation of the trivalent state is the high ligand-field strength of oximato-*N* binding which also exerts a sizeable *trans* influence. Consistent with steric and electronic factors, both [NiL$^{R}{}_3$]$^-$ and [NiL$^{R}{}_3$] adopt meridional geometry exclusively while in [NiL$^{Ph}{}_2$(bipy)] the negatively charged oximato functions occupy mutually *trans* positions. The Ni^{III}–Ni^{II} reduction potential increases sharply upon replacing (L^{R})$^-$ by bipy.

Experimental

Materials

Electrochemical grade dry methanol, acetonitrile, dichloromethane and tetraethylammonium perchlorate were obtained as before.[18,19] All other chemicals and solvents were of analytical grade and used as received.

Physical measurements

A Hitachi 330 spectrophotometer was used to record UV/VIS spectra. The EPR spectra were obtained with a Varian E-109C spectrometer fitted with a quartz Dewar. Room-temperature magnetic susceptibilities were measured with a model 155 PAR vibrating-sample magnetometer fitted with a Walker Scientific L75FBAL magnet. A Perkin-Elmer 240C elemental analyser was used to collect microanalytical data (C,H,N). Electrochemical measurements were performed under a nitrogen atmosphere on a PAR 370-4 electrochemistry system as before:[19] working electrode, platinum disc; reference electrode, SCE; supporting electrolyte, NEt$_4$ClO$_4$ (0.1 mol dm^{-3}); scan rate, 50 mV s^{-1}; solute concentration, 10^{-3} mol dm^{-3}. Solution electrical conductivities were measured with a Philips PR 9500 bridge, the solute concentration being ≈10^{-3} mol dm^{-3}.

Syntheses

The pro-ligands were synthesized as before.[20] All the complexes were synthesized by general methods. Details are given below. Malatesta and Pizzotti[7] reported diamagnetic bis complexes of type [NiL$^{R}{}_2$] by the reaction of nickel(II) salts with HL^{R} in aqueous ammoniacal media. We have not been able to reproduce this preparation well, our products always being contaminated with paramagnetic impurities.

Tetraethylammonium tris(phenyldiazenylbenzaldoximato)nickel(II), [NEt$_4$][NiL$^{Ph}{}_3$]. The synthesis was carried out under a pure argon atmosphere. To a solution (10 cm^3) of Ni(O$_2$CMe)$_2$·4H$_2$O (0.05 g, 0.20 mmol), Na(O$_2$CMe)·3H$_2$O (0.084 g, 0.62 mmol) and NEt$_4$Cl (0.034 g, 0.20 mmol) in dry methanol was added a solution (15 cm^3) of HL^{Ph} (0.14 g, 0.62 mmol) in dry methanol through a syringe. A brown colour developed and it darkened quickly. The mixture was stirred at room temperature for 2 h and the solvent was then evaporated *in vacuo* to obtain a brown solid which was filtered off and washed several times with aqueous methanol (1:1) and dried over fused CaCl$_2$. It was then recrystallised from dichloromethane–hexane to give pure crystalline [NEt$_4$][NiL$^{Ph}{}_3$] (0.13 g, 75%) (Found: C, 65.4; H, 5.9; N, 16.35. Calc. for $C_{47}H_{50}N_{10}NiO_3$: C, 65.55; H, 5.8; N, 16.25%).

The complex [NEt$_4$][NiL$^{Me}{}_3$] was synthesized similarly in 72% yield (Found: C, 57.0; H, 6.5; N, 20.7. Calc. for $C_{32}H_{44}N_{10}NiO_3$: C, 56.9; H, 6.5; N, 20.75%).

Tris(phenyldiazenylbenzaldoximato)nickel(III), [NiL$^{Ph}{}_3$]. This complex was prepared electrochemically. The salt [NEt$_4$]-[NiL$^{Ph}{}_3$] (0.07 g, 0.08 mmol) was dissolved in acetonitrile (25 cm^3) and NEt$_4$ClO$_4$ was added as supporting electrolyte. The brown mixture was stirred at room temperature for 0.25 h and then subjected to exhaustive coulometric oxidation at 0.3 V *vs.* SCE under nitrogen. The oxidation was stopped when the Coulomb count corresponded to one-electron oxidation and the solution became reddish brown. The solvent was then evaporated *in vacuo* to obtain a brown solid, which was dissolved in benzene and filtered to remove the NEt$_4$ClO$_4$. The filtrate was collected and the solvent evaporated *in vacuo* to give [NiL$^{Ph}{}_3$] as a dark solid in pure form (0.05 g, 83%) (Found: C, 64.0; H, 4.2; N, 17.3. Calc. for $C_{39}H_{30}N_9NiO_3$: C, 64.05; H, 4.1; N, 17.25%).

The complex [NiL$^{Me}{}_3$] was synthesized similarly in a 78%

Table 6 Crystal data for [NEt$_4$][NiL$^{Ph}{}_3$] and [NiL$^{Ph}{}_2$(bipy)]

Complex	[NEt$_4$][NiL$^{Ph}{}_3$]	[NiL$^{Ph}{}_2$(bipy)]
Formula	$C_{47}H_{50}N_{10}NiO_3$	$C_{36}H_{28}N_8NiO_2$
M	861.7	663.4
Crystal size/mm	0.46 × 0.38 × 0.06	0.36 × 0.26 × 0.20
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a/Å	22.569(10)	14.931(9)
b/Å	13.391(7)	14.160(7)
c/Å	31.00(2)	33.88(2)
β/°	93.54(4)	99.35(5)
U/Å^3	9352(8)	7067(7)
Z	8	8
D_c/g cm^{-3}	1.224	1.247
μ(Mo-Kα)/cm^{-1}	4.65	5.91
F(000)	3632	2752
Total number of reflections	15 070	6757
Number of unique reflections	13 954	6214
Number of observed reflections	5052 [$I > 2\,\sigma(I)$]	2623 [$I > 3\,\sigma(I)$]
g in $w = 1/[\sigma^2(\|F\|) + g\|F\|^2]$	0.0007	0.0001
Number of refined parameters	637	424
R^a	8.91	5.37
R'^b	9.37	5.66
Goodness of fit	1.24	1.26
Maximum and mean Δ/σ	0.018, 0.000	0.019, 0.006
Data-to-parameter ratio	7.9:1	6.2:1
Maximum, minimum difference peaks/e Å^{-3}	0.66, −0.47	0.38, −0.32

$^aR = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$. $^bR' = [\Sigma\,w(|F_o| - |F_c|)^2/\Sigma\,w|F_o|^2]^{\frac{1}{2}}$.

yield (Found: C, 52.95; H, 4.35; N, 23.1. Calc. for $C_{24}H_{24}N_9NiO_3$: C, 52.85; H, 4.4; N, 23.15%).

(2,2′-Bipyridine)bis(phenyldiazenylbenzaldoximato)nickel(II), [NiL$^{Ph}{}_2$(bipy)]. To a solution of [NEt$_4$][NiL$^{Ph}{}_3$] (0.18 g, 0.20 mmol) in methanol (15 cm^3) was added a solution of 2,2′-bipyridine (0.032 g, 0.20 mmol) in methanol (10 cm^3). The mixture was stirred at room temperature for 1.5 h. The solvent was then evaporated to obtain a dark brown solid which was filtered off and washed several times with aqueous methanol (1:1) and then dried over fused $CaCl_2$. The solid was recrystallised from dichloromethane–hexane to obtain pure crystalline [NiL$^{Ph}{}_2$(bipy)] (0.14 g, 84%) (Found: C, 65.2; H, 4.3; N, 16.85. Calc. for $C_{36}H_{28}N_8NiO_2$: C, 65.2; H, 4.2; N, 16.9%).

The complexes [NiL$^{Ph}{}_2$(phen)] and [NiL$^{Ph}{}_2$(en)] were synthesized similarly in 80 and 78% yields respectively (Found: C, 66.3; H, 4.15; N, 16.4. Calc. for $C_{38}H_{28}N_8NiO_2$: C, 66.4; H, 4.1; N, 16.3. Found: C, 59.25; H, 4.9; N, 19.85. Calc. for $C_{28}H_{28}N_8NiO_2$: C, 59.3; H, 4.95; N, 19.75%).

Doped complex, [Co(Ni)L$^{Ph}{}_3$]. A dichloromethane solution (5 cm^3) containing [NiL$^{Ph}{}_3$] (0.001 g) and [CoL$^{Ph}{}_3$] (0.10 g) was gently rubbed with a pestle in a mortar till all the solvent evaporated. The solid so obtained was used for EPR studies.

Crystallography

Single crystals of both the compounds were grown by slow diffusion of hexane into dichloromethane solutions. Crystals of [NEt$_4$][NiL$^{Ph}{}_3$] were relatively weakly diffracting. The cell parameters were determined by least-squares fit of 30 machine-centred reflections having 2θ values in the range 15–25° in each case. Data were collected by the ω-scan method for [NEt$_4$][NiL$^{Ph}{}_3$] ($2 \leqslant 2\theta \leqslant 47°$) and [NiL$^{Ph}{}_2$(bipy)] ($2 \leqslant 2\theta \leqslant 50°$) on a Nicolet R3m/V diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Two standard reflections, monitored in each case, showed no significant variations. In both the cases the data were corrected for Lorentz-polarisation effects. Absorption was small in both cases and no correction was considered necessary.

The structures were solved by direct methods and refined by full-matrix least-squares procedures. All non-hydrogen atoms for [NiL$^{Ph}{}_2$(bipy)] were refined anisotropically. In the case of [NEt$_4$][NiL$^{Ph}{}_3$] only atoms other than carbon, Ni(1), Ni(2), all N and all O were made anisotropic. Hydrogen atoms were added at calculated positions with $U = 0.08$ Å^2 in the last cycle of refinement. Significant crystal data are listed in Table 6. Computations were carried out on a MicroVAX II computer using the SHELXTL PLUS program package[21] and crystal structure plots were drawn using ORTEP.[8]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/292.

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