Synthesis, characterisation and activity in catalytic epoxidation of olefins of new dinuclear nickel(II) complexes

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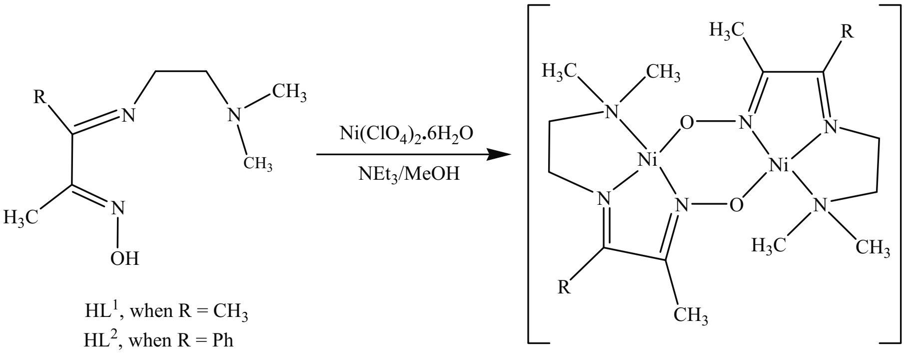
Two new dinuclear nickel(II) compounds of formula $[Ni^{II}_2(\mu\text{-}L^1)_2](ClO_4)_2\cdot MeCN$ (**1**·MeCN) and $[Ni^{II}_2(\mu\text{-}L^2)_2](ClO_4)_2$ (**2**) where HL^1 and HL^2 stand for 3-(2-(dimethylamino)ethylimino)butan-2-one oxime and 1-(2-(dimethylamino)ethylimino)-1-phenylpropan-2-one oxime respectively, have been synthesised. Single crystal X-ray analyses of the complexes reveal that the nickel(II) ions are in square-planar N_3O environments and form six-membered $(NiNO)_2$ metallacycles. Cyclic voltammetric measurements of **1**·MeCN and **2** in MeCN solution show quasirreversible one-electron oxidations at $E_{1/2}$ = 0.566 V and 0.603 V (*vs* Fc^+/Fc), respectively, attributed to $Ni^{III}Ni^{II}/Ni^{II}_2$ redox couples. Additional reversible $Ni^{III}_2/Ni^{III}Ni^{II}$ redox responses were observed at relatively higher potential near $E_{1/2}$ = 0.832 V and 0.850 V (*vs* Fc^+/Fc), respectively, for **1**·MeCN and **2**.Complexes **1**·MeCN and **2** display intense charge-transfer bands at ~390 and ~345 nm in the visible region. Chemical oxidation of complex **1**·MeCN by sodium hexachloroiridate(IV) hexahydrate generates red Ni_2^{III} species with characteristic new bands at ~520 and 427 nm in the visible region as well as the characteristic EPR signals at 77 K with $g_\perp > g_{\parallel}$. Similar phenomena were observed for complex **2** upon chemical oxidation. The dinickel(II) complexes are catalytically active for epoxidation of olefins using iodosylbenzene as the terminal oxidant.

Keywords: dinickel(II) complex, oxime ligand, X-ray crystal structure, NMR, olefin epoxidation

There are many nickel(II) complexes with ligands that incorporate oximate donors that have been shown to stabilise the nickel(III) and nickel(IV) oxidation states at low potential.[1-5] Such complexes in different oxidation states have a strong role in bioinorganic chemistry and redox enzyme systems,[6,7] and may provide the basis for models for active sites of biological systems[8,9] or act as catalysts.[10-12] Oximes represent a very important class of ligands in coordination chemistry.[13-16] Recent interest in oxime ligands is mostly due to the remarkable ability of the deprotonated oximato-groups to form bridges between metal ions giving rise to polynuclear complexes of different nuclearity with different types of oximate bridges.[17,18] Recently, Goldcamp *et al.* reported[19] that the ligand tris(2-hydroxyiminopropyl)amine binds to Ni(II) ion in multiple protonation states yielding mononuclear and oximate-bridged dinuclear complexes. The dinuclear complex of the fully deprotonated ligand in acetonitrile undergoes oxidation by O_2 and this system oxidises PPh_3 with incorporation of oxygen from O_2. With a similar system, they also reported substrate oxidation by the first Ni(II) + O_2 reaction that does not proceed *via* irreversible ligand oxidation.[20] The first example of olefin epoxidation by nickel(II) catalysts with iodosylbenzene was shown by Koola and Kochi.[21] Later, Burrows *et. al.*[22] also reported the syntheses and crystal structures of nickel(II) complexes and has used them as catalysts in the presence of iodosylbenzene for epoxidation of a wide variety of olefins. All the above examples have been studied with mononuclear nickel(II) systems. The application of dinuclear nickel(II) complexes in the epoxidation of olefins has received very limited attention.[23] So, in this paper, the synthesis, characterisations, electron transfer behaviour and catalytic activity of oximate-bridged, dinuclear nickel(II) complexes are reported in detail.

Results

The compounds **1**·MeCN and **2** were synthesised in ~90% yield from a methanolic medium under aerobic conditions at room temperature by stirring a reaction mixture consisting of $Ni(ClO_4)_2\cdot 6H_2O$, HL^1 (prepared by condensation of 1 mol of 2,3 butanedione monoxime and 1 mol of N,N-dimethyl ethylenediamine) and NEt_3 and $Ni(ClO_4)_2\cdot 6H_2O$, HL^2 (prepared by condensation of 1 mol of 1-phenyl-1,2-propanedione-2-oxime and 1 mol of N,N-dimethyl ethylenediamine) and NEt_3 respectively in a 1 : 1 : 1 molar ratio for 1 h. Thus, the reaction of the preformed tridentate imine-oxime ligands (HL^1 and HL^2) with nickel(II) ions in the presence of NEt_3 gave the square-planar dinuclear Ni^{II} compounds, containing a Ni_2 hexagon formed from bridging N–O group (Scheme 1).



HL^1, when R = CH_3
HL^2, when R = Ph

Complex **1**, when R = CH_3
Complex **2**, when R = Ph

Scheme 1 Synthetic procedure for the complexes.

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The complexes precipitate directly from the reaction mixture as dark orange-red solids. Copper(II) ions are known to bind with the similar tridenatate imine-oxime ligand to give distorted square pyramidal dinuclear complexes.[24,25] Three nitrogen atoms of one ligand bind the first nickel(II) ion in a tridentate N_3 mode and the oximate oxygen atom of the same ligand, binds the second nickel(II) ion. The whole ligand thereby binds two nickel(II) ions forming a six-membered metallacycle. During coordination to the nickel(II) ion, each ligand loses one proton from the oxime OH group and the resulting oximate ligand exhibits N_3O coordination to each nickel(II) ion. The crystalline cationic complexes are soluble in more polar solvents such as H_2O, MeCN, DMF and DMSO and are insoluble in less polar solvents such as $CHCl_3$, THF, Et_2O and C_6H_6. The complexes are highly stable in air both in solid state and in solution. The elemental analysis data fit the $[Ni^{II}_2(\mu\text{-}L^1)_2](ClO_4)_2\cdot MeCN$ and $[Ni^{II}_2(\mu\text{-}L^2)_2](ClO_4)_2$ formulations. The molar conductivity (Λ_M) values of the complexes in MeCN are in the range of 190–195 $\Omega^{-1}cm^2mol^{-1}$ indicating a behaviour attributable to 1 : 2 electrolytes.

Table 1 Crystallographic data for complexes **1**·MeCN and **2**

Molecular formula	$C_{18}H_{35}N_7O_{10}Cl_2Ni_2$	$C_{26}H_{36}N_6O_{10}Cl_2Ni_2$
Molecular weight	697.85	780.93
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	13.1320(3)	12.5432(5)
b (Å)	12.2045(3)	8.9714(4)
c (Å)	17.2959(5)	13.7277(5)
β (°)	91.6220(14)	93.745(2)
V (Å³)	2770.89(12)	1541.48(11)
D_c (g cm^{-3})	1.673	1.682
Z	4	2
F(000)	1448	808
Crystal size/mm	0.23 × 0.22 × 0.14	0.45 × 0.44 × 0.32
μ (mm^{-1})	1.615	1.461
θ Range (°)	1.92-31.50	2.13–47.26
R^1, wR^2 [$I > 2\sigma(I)$]	0.0349, 0.0894	0.0229, 0.0599
Goodness-of-fit on F^2	1.056	1.028
Final difference map max, min (e Å^{-3})	0.842, -0.479	0.714, -0.807

$R_1 = \Sigma(\,||F_o| - |F_c||\,)/\Sigma|F_o|$. $wR_2 = [\,\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$. $w = 0.75/(\sigma^2(F_o) + 0.0010F_o^2)$.

Table 2 Selected bond lengths (Å) and angles (°) in **1**·MeCN (a) and **2** (b)

Bond lengths (a)		Bond angles (a)	
Ni(1)–N(1)	1.8888(13)	N(2)–Ni(1)–O(2)	169.20(5)
Ni(1)–N(2)	1.8519(12)	N(2)–Ni(1)–N(1)	82.55(6)
Ni(1)–N(3)	1.9598(13)	O(2)–Ni(1)–N(1)	101.43(5)
Ni(1)–O(2)	1.8660(10)	N(2)–Ni(1)–N(3)	85.17(6)
Ni(2)–N(4)	1.8866(13)	O(2)–Ni(1)–N(3)	89.64(5)
Ni(2)–N(5)	1.8420(12)	N(1)–Ni(1)–N(3)	166.31(5)
Ni(2)–N(6)	1.9531(14)	N(5) –Ni(2)–O(1)	168.98(5)
Ni(2)–O(1)	1.8471(10)	N(5)–Ni(2)–N(4)	82.93(5)
		O(1)–Ni(2)–N(4)	101.81(5)
		N(5)–Ni(2)–N(6)	86.59(6)
		O(1)–Ni(2)–N(6)	88.85(5)
		N(4)–Ni(2)–N(6)	169.34(5)
Bond lengths (b)		**Bond angles (b)**	
Ni(1)–N(1)	1.8827(4)	O(1)–Ni(1)–N(2)	174.274(17)
Ni(1)–N(2)	1.8439(4)	O(1)–Ni(1)–N(1)	102.525(17)
Ni(1)–N(3)	1.9442(4)	N(2)–Ni(1)–N(1)	82.999(17)
Ni(1)–O(1)	1.8348(4)	O(1)–Ni(1)–N(3)	88.804(17)
		N(2)–Ni(1)–N(3)	85.674(17)
		N(1)–Ni(1)–N(3)	168.671(17)

Crystals of **1**·MeCN and **2** suitable for X-ray structure determination were obtained from acetonitrile-dichloromethane and chloroform-hexane solvent mixtures respectively. Thermal ellipsoid plots of the cationic part of **1**·MeCN and **2** are depicted in Fig. 1. Information concerning the X-ray data acquisition and refinement is given in Table 1. Selected bond lengths and bond angles are given in Table 2. Complex **1**·MeCN consists of a dinuclear $[Ni^{II}_2(\mu\text{-}L^1)_2]^{2+}$ cation, two perchlorate anions and one molecule of acetonitrile of crystallisation. Complex **2** consists of a dinuclear $[Ni^{II}_2(\mu\text{-}L^2)_2]^{2+}$ cation and two perchlorate anions. The coordination geometries around each nickel(II) ion in complex **1**·MeCN and **2** are best described by distorted square planar N_3O environments. One amine nitrogen, one imine nitrogen, one oxime nitrogen and one oximate oxygen satisfy the square-planar coordination geometry of each nickel(II) ion. The largest deviations from the plane of the four donor atoms are 0.020 (N2) and 0.090 Å (N6) with the metal ion 0.138 (Ni1) and 0.072 (Ni2) Å out of the mean basal plane for **1**·MeCN. In complex **2**, the largest deviation from the plane of the four donor atoms is 0.014 Å (N2) with the metal ion 0.012 Å out of the mean basal plane. Three nitrogen atoms of one ligand are coordinated to one metal centre forming two five-membered (N-Ni-N) chelate rings. The average chelate bite angles for the five-membered rings in **1**·MeCN and **2** are in the ranges 82.74(5)–85.88(6)° and 82.99(17)–85.67(17)° respectively. In complexes **1**·MeCN and **2**, one central six-membered dimetallic chelate ring Ni(1)N(1)O(1)Ni(2)N(4)O(2) and Ni(1)N(1)O(1)Ni(1A)N(1A)O(1A), respectively, is formed

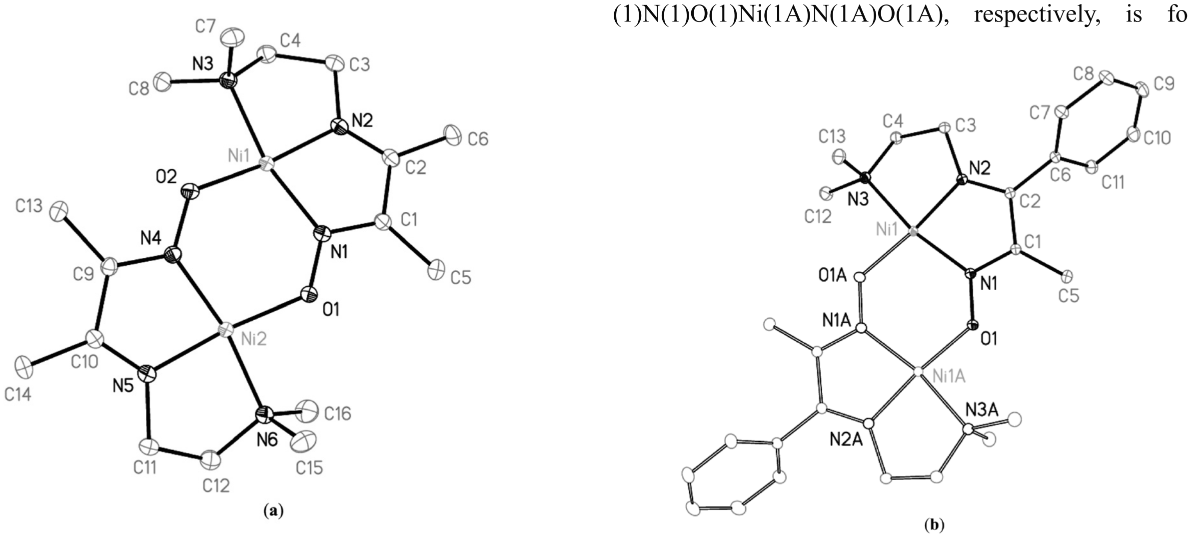

Fig. 1 Molecular structures and numbering schemes for complexes (a) $[Ni^{II}_2(\mu\text{-}L^1)_2](ClO_4)_2\cdot MeCN$ (**1**·MeCN) and (b) $[Ni^{II}_2(\mu\text{-}L^2)_2](ClO_4)_2$ (**2**).

through the coordination of oxime nitrogen and oximate oxygen to each nickel(II) ion in a *trans* arrangement. The average C–N and N–O distances of the oximate (–(CH$_3$)C=N–O$^-$) moieties in **1**·MeCN are 1.318(17) and 1.338(15) Å, respectively and in **2** are 1.313(6) and 1.326(5) Å, respectively. These distances are consistent with the deprotonated form of the oxime functionalities.[26-28] The C=N$_{\text{imine}}$ distances are significantly shorter than the C=N$_{\text{oximate}}$ distances in both complexes. The intradimer Ni–Ni distances are 3.602 Å in **1**·MeCN and 3.653 Å in **2** which are consistent with Goldcamp's octahedral dinickel(II) complex[19] but quite larger than distances in other square planar dinickel(II) systems.[23,29,30] The dihedral angle between the two basal planes is 22.2° in **1**·MeCN, whereas in complex **2** it is 0°.

An interesting feature of the crystal structure lies in the packing of complex **1**·MeCN (Fig. 2), in which the geometry of the perchlorate groups shows some typical disorders. The disordered perchlorate anion fills the channels that run parallel to the *b*-direction. The other perchlorate anion is in pockets surrounded by cations. Within these channels the uncoordinated acetonitrile molecule makes a 2.513 Å contact with the Ni(1) ion. The Ni–N–C contact angle is 172.75°. There is no evidence of channels in the packing of complex **2**.

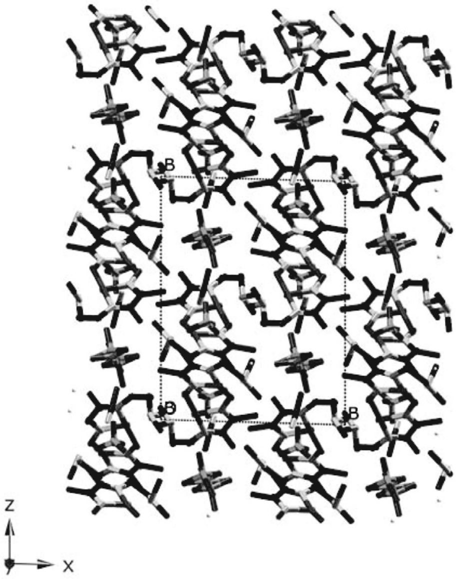

Fig. 2 Molecular packing view of [Ni$^{II}_2$(μ-L^1)$_2$](ClO$_4$)$_2$·MeCN (**1**·MeCN) along the *b*-axis.

The IR spectra of the complexes show strong C=N stretching of the imine function at ~1630 cm^{-1} which is shifted from the free ligand value of ~1639 cm^{-1}. The bands at ~1580 cm^{-1} and ~1235 cm^{-1} in the IR spectrum of the complexes may be assigned to the oxime C=N groups and NO groups respectively.[31,32] The strong unsplit band (ν_{ClO4^-}) at around 1090 cm^{-1} suggests absence of coordinated perchlorate ions.

The complexes are diamagnetic both in solution and in the solid state, as evidenced by sharp, unshifted ^{1}H NMR spectra and a magnetic susceptibility measurement consistent with a square planar geometry. The ^{1}H NMR spectra of **1**·MeCN and **2** show two multiplets corresponding to the two sets of ethylenic protons at δ ~3.47–3.65 ppm and 2.65–2.78 ppm. The sharp singlets corresponding to the amine-methyl protons and both imine- and oxime-methyl protons in ^{1}H NMR spectrum appear at δ ~1.90 ppm and 2.19 ppm respectively. The aromatic protons in complex **2** appear as multiplets in the ranges δ = 7.21–7.65 ppm. The absence of a broad signal due to the oxime proton (in free ligand, δ ~11.55 ppm) in the complex indicates that the ligands undergo complete deprotonation during complexation and in solution the dimeric structures exist. The sharpness of these NMR peaks as well as the small shift of approximately 0.35 ppm for the above proton signals relative to that of free ligand are indicative of the diamagnetic nickel(II) complex. That is to say, the Ni^{II} ions are in a square-planar coordination geometry (low-spin d^8-electronic configuration for Ni^{II}). These spectroscopic observations were further confirmed by the single crystal X-ray structure determination.

The electronic absorption spectra of the complexes **1**·MeCN and **2** in acetonitrile solution are dominated by two intense bands in the UV region centred at ~392 and ~340 nm, corresponding to charge-transfer transitions.[33,34] A third, less intense band appears in the visible region at ~550 nm, which corresponds to a d–d transition of a low-spin d^8–Ni^{II} ion.[30] Chemical oxidation of **1**·MeCN and **2** in MeCN by sodium hexachloroiridate(IV) hexahydrate in 1:2 molar ratio gives a red-coloured solution developing characteristic Ni$_2^{III}$ bands at approximately 520 nm and 427 nm.The Ni$_2^{III}$ species is reasonably stable at ambient temperature only under an argon atmosphere and the bands are assigned to d–d transition and charge-transfer transition respectively. In addition to the 427–520 nm bands, some further low intensity bands/shoulders are observed at longer wavelengths which are presumably due to axial solvent coordination to the two nickel centres.[34] Representative spectra for complex **1**·MeCN are shown in Fig. 3.

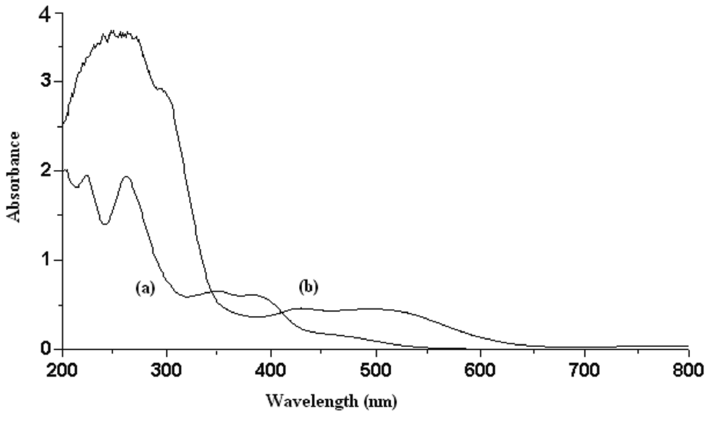

Fig. 3 Electronic absorption spectra in acetonitrile solution of (a) [Ni$^{II}_2$(μ-L^1)$_2$](ClO$_4$)$_2$·MeCN (**1**·MeCN) and (b) chemically oxidised Ni$_2^{III}$ species.

The EPR spectrum of the red solution is obtained after chemical oxidation of **2** by sodium hexachloroiridate(IV) hexahydrate in 1:2 molar ratio. The spectrum can be interpreted in terms of mononuclear Ni^{III} chromophores in an axial geometry, which is in line with the above observation that, at these temperatures, the ions within the complex are essentially uncoupled. This is consistent with a tetragonally distorted octahedral geometry at the metal centres, presumably with axial coordination of solvent molecules.[35,36] The value of $g_{\perp}$ and g_{II} are 2.11 and 1.99 respectively.

With the aim of investigating the extent of stabilisation of nickel(II) species towards both oxidation and reduction, and thereby the possibility of accessing variable oxidation states, cyclic voltammetry experiments were performed on **1**·MeCN and **2.** Both the complexes are electroactive with respect to the metal centres in acetonitrile solution (tetrabutylammonium perchlorate as supporting electrolyte, at 298 K). Both the complexes **1**·MeCN and **2** display a quasireversible cyclic voltammetric response with $E_{1/2}$ near 0.566 V(ΔE_p = 102 mV) and 0.836 V(ΔE_p = 125 mV) (*vs* Fc^+/Fc) respectively,. Additional quasireversible redox responses were observed at relatively higher potential near $E_{1/2}$ = 0.832 V(ΔE_p = 67 mV) and 0.850 V(ΔE_p = 77 mV) (*vs* Fc^+/Fc), respectively, for **1**·MeCN and **2**. The lower potential oxidative response observed is possibly due to the $Ni^{III}Ni^{II}/Ni^{II}_2$/couple. The relatively higher potential oxidative response observed is due to the $Ni^{III}_2/Ni^{III}Ni^{II}$ couple. The oxidation processes can be assigned as follows:

$$Ni^{II}Ni^{II} \rightleftharpoons Ni^{III}Ni^{II} \rightleftharpoons Ni^{III}Ni^{III}$$

Similar behaviour has been reported for other square-planar dinuclear nickel(II) complexes.[37]

The majority of successful catalytic epoxidations have been developed using mononuclear metal complexes.[21,38,39] A major breakthrough in this respect was the discovery by Jacobsen and co-workers of the enantioselective epoxidation of unfunctionalised alkenes by chiral manganese salen catalysts.[40] The catalytic efficiency of **1**·MeCN and **2** for the epoxidation of olefins using iodosylbenzene as the terminal oxidant has been examined. The products were analysed by GC–MS relative to the internal standard nitrobenzene. The products were isolated in medium to high yield and characterised by ^1H NMR. In all cases, the products of the epoxidation using **1**·MeCN and **2** were almost identical and produced in the same ratio. This led us to conclude that both the complexes catalyse the epoxidation of olefins in the presence of iodosylbenzene through the formation of a reactive transient intermediate, most likely, a dinickel(III)-oxo species, in an intermolecular fashion.[21] Thus activated oxygen and olefin are arranged in such a way that oxygen transfer to the olefin occurs in the vicinity of the ligand. Therefore, the overall shuttling of the metal complex between the two states formally corresponds to an oxidative–addition/reductive–elimination sequence. But the detailed insight into the possible cooperative effects of the two nickel centres in the dinuclear catalysts needs more mechanistic study. Here, the results of our study on the epoxidation of styrene, 1-hexene, cyclohexene, 1-octene and 5-hexen-1-ol are reported. The percentage yields and turn-overs from reactions with these olefins are shown in Table 3. These results indicate that both **1**·MeCN and **2** show almost identical catalytic efficiency using the same terminal oxidant, iodosylbenzene. The control experiments have also been performed using $Ni(ClO_4)_2·6H_2O$ as a catalyst. The experiment did not give rise to the epoxide formation, which indicates that for oxidation with iodosylbenzene as the terminal oxidant, nickel activation by the coordination of a suitable ligand, as in **1**·MeCN and **2**, is essential.

Table 3 Epoxidation of olefin compounds catalysed by **1**·MeCN and **2** using iodosylbenzene

Entry	Substrates	Catalyst	% Conversion[a]	Turnover number[b]
1	Styrene	**1**·MeCN	74	24
		2	71	21
2	1-Hexene	**1**·MeCN	81	35
		2	78	32
3	Cyclohexene	**1**·MeCN	44	14
		2	49	17
4	1-Octene	**1**·MeCN	70	37
		2	65	35
5	5-Hexen-1-ol	**1**·MeCN	53	19
		2	57	22

[a] Determined by GC analysis.

[b] Mol of epoxide/mol of catalyst used.

The kinetics of these systems to investigate the reactive transient intermediate formed during the catalysis has been studied. This experiment was done using the catalyst **1**·MeCN. A transient spectral band at ~325 nm suggests the formation of a reactive intermediate. These spectral changes demonstrate that the dicationic Ni^{II}_2 catalyst reacts readily with iodosylbenzene to afford a new transient species, which is most likely a dinickel(III)-oxo species.[41-43] Unfortunately, single crystals of this reactive intermediate could not be obtained despite great efforts, even at –40 °C. The decay of this absorption band in presence of added styrene follows approximately first-order kinetics at 25 °C as shown in Fig. 4.

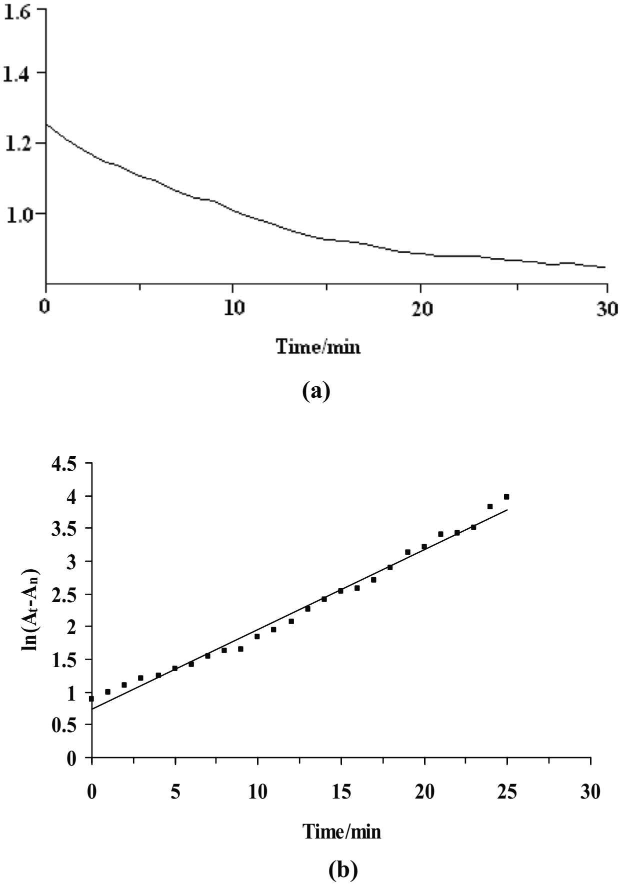

Fig. 4 (a) decay of the transient absorption band at 325 nm derived from $[Ni^{II}_2(\mu\text{-}L^1)_2](ClO_4)_2·MeCN$ (**1**·MeCN) (10^{-3}M) and excess iodosylbenzene in acetonitrile in presence of 0.03M styrene; (b) change in $\ln(A_t–A_n)$ with time at 25 °C followed at 325 nm.

Conclusions

Two new square-planar dinuclear nickel(II) complexes incorporating a six-membered dimetallic chelate ring have been synthesised and fully characterised. The spectral, electrochemical and catalytic properties of the complexes were studied. Both the complexes catalyse the epoxidation of olefins with almost similar efficiency. An extended work on manganese, iron and cobalt complexes probing the effects of structure on reactivities in small ligand binding and catalysis is on now progress.

Experimental

Materials and physical measurements:
$Ni(ClO_4)_2{\cdot}6H_2O$, N,N-dimethyl ethylenediamine, 2,3-butanedione monoxime and 1-phenyl-1,2-propanedione-2-oxime were purchased from Aldrich and used as received. HPLC-grade acetonitrile was used for electrochemical, conductivity and UV/Vis work and all other chemicals and solvents were of reagent grade and were used as received. Iodosylbenzene was prepared by the hydrolysis of the corresponding diacetate with aqueous sodium hydroxide and stored at –20 °C.[44] Elemental analyses (C, H, N) were performed with a Perkin–Elmer model 240 C elemental analyser. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 300 NMR spectrometer using TMS as the internal standard. Infrared spectra were recorded on a Nicolet Nexus 870 FT IR spectrophotometer. The solution electrical conductivity was obtained with a CDM 80 digital conductivity meter with a solute concentration of about 10^{-3} (M). UV-vis spectra and kinetics were run with a Varian Cary 9 UV-Visible spectrophotometer. Mass spectra were obtained with a Finnigan MAT 8200 (electron ionisation, EIMS) instrument. The room temperature magnetic susceptibilities in the solid state were carried out with a MPMS *XL* SQUID susceptometer (Quantum Design Inc). EPR spectra was recorded at the X-band on a BRUKER Win EPR spectrometer and calibrated with respect to diphenylpicrylhydrazyl (DPPH, g = 2.0037). Electrochemical measurements were made with an Autolab PGSTAT 30 electrochemical analyser with GPES 4.9 software. A platinum working-electrode, a platinum-wire auxiliary electrode, and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. The supporting electrolyte was tetrabutylammonium perchlorate (TBAP), and the potentials are referenced to the ferrocene-ferrocenium redox couple Fc^+/Fc as internal standard. Electrochemical measurements were made under an argon atmosphere.

Synthesis of the complexes:
$[Ni^{II}_2(\mu\text{-}L^1)_2](ClO_4)_2{\cdot}MeCN$ (**1·MeCN**): A methanolic solution (20 mL) of N,N-dimethyl ethylenediamine (0.40 mL, 3.8 mmol) and 2,3 butanedione monoxime (0.38 g, 3.8 mmol) was stirred at room temperature. After stirring for an hour, a methanolic solution (20 mL) of $Ni(ClO_4)_2{\cdot}6H_2O$ (1.38 g, 3.8 mmol) was added followed by the addition of NEt_3 (0.52 mL, 3.8 mmol). After complete addition a dark orange-red compound was seen separating in solution. The whole reaction mixture was stirred for another hour at room temperature. The solvent was evaporated in air. The orange-red precipitate was filtered through a glass frit and washed with ethanol and hexane. Recrystallisation from acetonitrile/dichloromethane mixture gave needle-shaped crystals, which were dried *in vacuo* over fused $CaCl_2$. Yield: 1.11 g (85%). Anal. Calcd for $C_{18}H_{35}N_7O_{10}Cl_2Ni_2$: C, 30.98; H, 5.05; N, 14.05; Ni, 16.75. Found: C, 30.67; H, 4.97; N, 14.27, Ni, 16.86%. ^1H NMR ([D$_6$]DMSO): δ = 3.53–3.65 (m, 4H, CH_2 attached to imine nitrogen), 2.65–2.69 (m, 4H, CH_2 attached to amine nitrogen), 2.19 (s, 6H, imine CH_3), 2.27 (s, 6H, oxime CH_3), 1.92 (s, 12H, amine CH_3). FT IR (cm^{-1}, KBr disk):ν = 3429(b), 2924(m), 1632(s), 1583(s), 1537(s), 1475(s), 1237(s),1091(s), 963(s), 714(s). Molar conductance, Λ_M: (MeCN solution) 190.34 $\Omega^{-1}cm^2mol^{-1}$. UV-vis spectra [λ_{max}, nm (ε, L mol^{-1}cm^{-1})]: (MeCN solution) 556 (290), 395 (8770), 341 (8565), 225 (18750).

$[Ni^{II}_2(\mu\text{-}L^2)_2](ClO_4)_2$ (**2**): This complex was prepared by similar method as for complex **1**·MeCN using 1-phenyl-1,2-propanedione-2-oxime instead of 2,3 butanedione monoxime. Yield: 1.38 g (92%). Anal. Calcd for $C_{26}H_{36}N_6O_{10}Cl_2Ni_2$: C, 39.98; H, 4.64; N, 10.76; Ni, 14.96. Found: C, 39.53; H, 4.77; N, 10.57, Ni, 14.75%.^1H NMR ([D$_6$]DMSO): δ = 7.21–7.65 (m, 10H, C_6H_5), 3.47–3.65 (m, 4H, CH_2 attached to imine nitrogen), 2.68–2.78 (m, 4H, CH_2 attached to amine nitrogen), 2.22 (s, 6H, oxime CH_3), 1.90 (s, 12H, amine CH_3). FT IR (cm^{-1}, KBr disk):ν = 3425(b), 2936(m), 1627(s), 1587(s), 1520(s), 1447(s), 1234(s),1094(s), 924(s), 722(s). Molar conductance, Λ_M: (MeCN solution) 194.46 $\Omega^{-1}cm^2mol^{-1}$. UV-vis spectra [λ_{max}, nm (ε, L mol^{-1}cm^{-1})]: (MeCN solution) 563 (225), 387(6240), 343 (7550), 231(20435)

Catalysis reactions: To a solution of olefin (5 mmol) and the catalyst (5 μmol) was added iodosylbenzene (0.5 mmol) in degassed acetonitrile (5 mL) under an argon atmosphere. The reaction mixture was stirred vigorously for 4 h. Products were analysed by GC relative to the internal standard nitrobenzene. A blank experiment was also performed in a similar way using $Ni(ClO_4)_2{\cdot}6H_2O$ instead of catalyst.

CAUTION: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared and handled with caution.

X-ray crystallography: Needle-shaped deep violet crystals of complex **1**·MeCN and parallelepiped red crystals of complex **2** suitable for XRD were obtained on recrystallisation from a acetonitrile/dichloromethane (1:1) and chloroform/hexane (1 : 1) mixtures respectively.The intensity data were collected on a Bruker ApexII CCD X-ray diffractometer with graphite-monochromated Mo-*K*a radiation (λ = 0.71073). Precise unit cell dimensions were determined by least-squares refinement of 25 strong reflections having 2θ values. The structures were solved by the use of direct methods, and refinement was performed by least-squares methods on F^2 with the SHELXL-97 package.[45,46]

Supplementary material: CCDC 292398 and 292399 contain the supplementary crystallographic data for complexes **1.**MeCN and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+ 44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

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