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Synthesis and characterisation of κ^2-*N*,*O*-oxazoline-enolate complexes of nickel(II): explorations in coordination chemistry and metal-mediated polymerisation†‡

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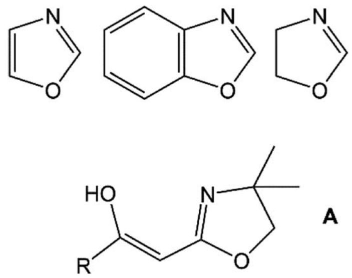
The synthesis and characterisation (UV-Vis, IR, X-ray diffraction, *etc.*) of a series of Ni(II) complexes derived from both known and novel 2-acylmethyl-2-oxazolines (**2a–g**: *i.e.*, (*Z*)-1-R-2-(4,4′-dimethyl-2′-oxazolin-2′-yl)eth-1-en-1-ol; R = –Ph, –2-furanyl, –*p*-NO_2-Ph, –*t*-Bu, –2-thiofuranyl, *p*-NC-Ph, –CF_3) is reported. These Ni materials (**3a–g**) represent the first group 10 metal complexes of this ligand class. All derivatives reported are paramagnetic ($S = 1$) compounds of formulae Ni(κ^2-*N*,*O*-L)$_2$ where **L** represents an enolate of structure (*Z*)-1-R-2-(4′,4′-dimethyl-2′-oxazolin-2′-yl)eth-1-en-1-ate formed *via* proton loss from **2**. The air- and moisture-stable metal complexes feature a less typical distorted seesaw-shaped disposition of binding atoms around the metal centre for six structurally characterised (X-ray) examples. Preliminary investigations indicate that **3a** (R = –Ph) is a useful catalysts for olefin polymerisation in the presence of alkylaluminum reagents.

Introduction

Polymerisation chemistry, specifically involving the use of transition metal (TM) catalysts, has been an arena of academic and industrial importance for many decades.[1] The application of first row transition metals, such as Ni, has enabled the development of cheaper protocols for the formation of not only atactic polymers but also stereo-regular macromolecules.[1] Nickel-based mediators represent an interesting avenue in modern catalyst design as the metal itself is relatively inexpensive (*cf.* Zr, Pd, *etc.*) and the ambient stability hallmarks a system that is inherently easy-to-handle. Nickel(II) complexes exhibit rich coordination chemistry and redox behaviour, facets that are often exploited in catalyst and property directed systems.[1] Ligands are the linchpin of controlling and modifying reactivity at the active metal centre and with this in mind, we have been inclined to use bi- or multi-dentate ligand scaffolds that can be easily fine-tuned and ideally are air-stable. Azole heterocycles typically meet all of these pre-requisites (Scheme 1). Our use of azole ligands is directed towards a number of applications in coordination[2] and medicinal chemistry,[3] ligand design strategies[4] and catalysis.[5] In terms of metal-mediated polymerisation, our investigations of Ni-based trinuclear coordination complexes has revealed active catalytic systems for the synthesis of polymers such as *syndio*-tactic polystyrene.[6] Sometime ago, we began a parallel investigation into a sub-class of azoles, the 2-acylmethyl-2-oxazolines (**A**; Scheme 1).[7] These materials, and their analogues, have been primarily studied as sources of reactive enols in organic syntheses and/or as potential medicinal agents.[7–15]

Oxazolines of general structure **A** (Scheme 1), referred to by us as *Tohda's ligands*, had few scattered examples[8] until the pioneering synthetic work on this class of organics by Yasao



Scheme 1 Azole heterocycles: 1,3-oxazole (top, left); 1,3-benzoxazole (top, middle); 4,5-dihydro-1,3-oxazole (*i.e.*, 2-oxazoline: top, right); 2-acylmethyl-2-oxazoline (**A**: bottom; enol tautomer shown).

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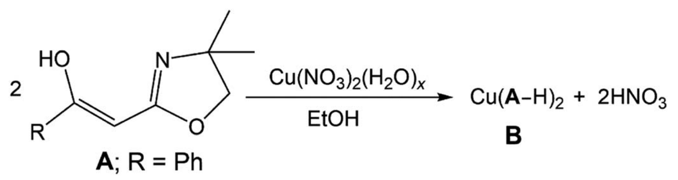
‡ Electronic supplementary information (ESI) available. CCDC 1884791–1884796 have been assigned to the structural data for **3a–c** and **3e–g**, other crystallographic data, .cif files; μ_{eff} calculations, DFT calculations, polymer characterisation data. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8ra10304f

§ Contact for queries on crystallography.

Tohda and co-workers beginning in the mid-1980s.[9–12] Since that time, other studies have explored the tautomeric nature of compounds **A** (Scheme 1: R = aryl or alkyl group)[7–14] and a number of alternative synthetic methodologies to these and related species have been probed.[13–15] In 2013, we reported the first TM coordination compound derived from these materials; a formally Cu(II) complex **B** (eqn (1)).



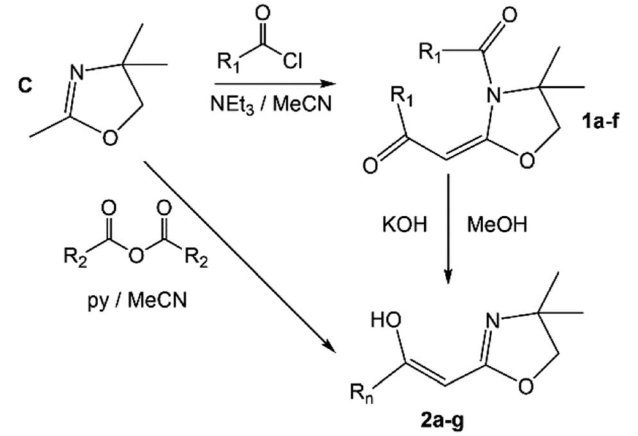
(1)

This compound results from the de-protonation of **A** (R = Ph) and κ^2-*N*,*O*-coordination of the resulting enolate. Herein, we expand the coordination chemistry of these ligands into the realm of Ni(II) chemistry. This work reveals aspects of the rich bonding potential of these enolate sources. In addition, one of the resulting air-stable Ni(II) complexes is shown to be useful catalytic precursors for olefin polymerisation in the presence of MAO (MAO = methyl-alumoxane).

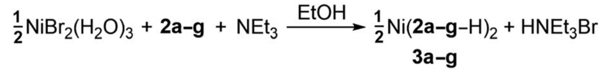
Results and discussion

The synthesis of the 2-acylmethyl-2-oxazolines described herein is directly based on known methodologies (Scheme 2) previously developed by Tohda *et al.*[9–12] This involves the reaction of commercial 2,4,4-trimethyl-2-oxazoline (**C**) and acid chlorides (NEt_3/MeCN) forming the key intermediate amides **1a–f**.[9] Treatment of these materials with KOH (MeOH) gives **2a–f**. Good yields are obtained for all materials with the exception of **1f** which could not be isolated in pure form; hence it was formed *in situ* and thereafter treated with KOH (MeOH) to yield **2f** (see Experimental section).[9,11,12] Alternatively, **C** can be reacted with trifluoromethylacetic anhydride (pyridine/MeCN: 0 °C) to give **2g** (Scheme 2).[10,12] The synthesis of **1e**, **2e** and **2f** has not been previously reported and hence these are novel compounds. The materials are, however, obtained using the Tohda protocols with little modification.

The desired Ni complexes (**3**: eqn (2)) were obtained by the reaction of $NiBr_2 \cdot 3(H_2O)$ with two equivalents of **2** in a solution consisting of NEt_3 and 95% EtOH (see Experimental section).¶ The addition of base was required to give suitable yields; this is in contrast to the Cu(II) derivative **B** (eqn (1)) which forms directly in the absence of external nucleophiles.[7] Metal chelation is thus presumed to occur once **2** is converted into a more reactive enolate form. Complexes **3a**, **b**, **3d** and **3f** are green coloured crystalline solids while **3c** and **3e** are brown in colour. Complex **3g** is a shade of lavender in the solid-state; however, when **3g** is dissolved in a variety of solvents, the colour of the solution is distinctly green. All Ni complexes are novel and are air- and moisture-stable. Elemental analyses, IR and UV-Vis spectroscopies are all consistent with materials of general formulae Ni(**2**–H)$_2$ (see Experimental section). Measurement of μ_{eff} for **3a** confirmed the presumed paramagnetic $S = 1$ spin state suggested by UV-Vis spectroscopy ($\mu_{\text{eff}} = 3.31$ B.M.).‡[16] Complexes **3a–g** represent the first group 10 TM examples of this ligand class.



Scheme 2 The general synthetic scheme for **2a–g**; R_1 = –Ph (**a**), 2-furanyl (**b**), –Ph-*p*-NO$_2$ (**c**), –*t*-Bu (**d**), 2-thiofuranyl (**e**), –Ph-*p*-CN (**f**); R_2 = –CF$_3$ (**g**).



$$\tfrac{1}{2}\mathrm{NiBr_2(H_2O)_3} + \mathbf{2a\text{–}g} + \mathrm{NEt_3} \xrightarrow{\mathrm{EtOH}} \underset{\mathbf{3a\text{–}g}}{\tfrac{1}{2}\mathrm{Ni}(\mathbf{2a\text{–}g}\text{–H})_2} + \mathrm{HNEt_3Br} \qquad (2)$$

X-ray crystallography

Crystals of complexes **3a–c** and **3e**, **f**, suitable for X-ray diffraction study, were obtained by slow crystallisation after dissolving the compounds in 95% EtOH and layering the solvent with hexanes followed by slow evaporation in open air. The crystals of **3g** were grown by recrystallization from acetone solution. All attempts to obtain suitable quality crystals of **3d** were unsuccessful. Crystallographic parameters and a list of selected bond lengths and angles for **3a–c** and **3e–g** can be found in Tables 1 and 2, respectively.‡

In all cases, these data confirm that the materials are four-coordinate Ni complexes with a high degree of tetrahedral distortion around the metal centre (Scheme 3). Two deprotonated ligands **2**, in the enolate configuration, are chelated to the formal Ni^{2+} ion.[17] Bond lengths between Ni and N or O are typical for Ni(κ^2-*N*,*O*-**L**)$_2$ complexes and are thus unsurprising.[18,19] In all materials studied, the O–Ni–N bond angles ranged from 91.5 to 94.3° (chelate) and 102.81 to 113.07°. The N–Ni–N and O–Ni–O bond angles range from 114.5 to 127.1° and 109.8 to 142.0°, respectively (Table 2). In the vast majority of cases, complexes with a Ni(κ^2-*N*,*O*-**L**)$_2$ composition have

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¶ Reduced yields were noted employing $[Ni(OH_2)_6](NO_3)_2$ or $[Ni(OH_2)_6]Cl_2$.

Table 1 Crystal and refinement data for complexes **3a–3c** and **3e–3g**

Complex	**3a**	**3b**	**3c**	**3e**	**3f**	**3g**
Formula	$C_{26}H_{28}N_2NiO_4$	$C_{22}H_{24}N_2NiO_6$	$C_{26}H_{26}N_4NiO_8$	$C_{22}H_{24}N_2NiO_4S_2$	$C_{28}H_{26}N_4NiO_4$	$C_{16}H_{18}F_6N_2NiO_4$
Molar mass (g mol^{-1})	491.21	471.14	581.22	503.26	541.24	475.03
Cryst. syst.	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$Pbca$
T/K	150	150	150	150	150	150
a (Å)	12.0764(17)	10.2574(8)	9.5476(10)	9.8995(5)	6.9179(6)	11.1193(4)
b (Å)	9.6715(15)	11.7648(9)	10.5561(12)	14.7668(8)	9.6038(10)	18.3316(8)
c (Å)	20.657(4)	23.418(2)	14.4705(16)	16.2988(9)	20.210(2)	19.0410(8)
α (°)	90	90	74.720(3)	90	103.140(3)	90
β (°)	92.155(5)	95.190(3)	70.961(3)	104.652(2)	94.606(3)	90
γ (°)	90	90	70.689(3)	90	98.490(3)	90
V (Å^3)	2411.0(7)	2127.9(3)	1281.1(2)	2305.1(2)	1284.2(2)	3881.2(3)
Z	4	4	2	4	2	8
Density (calc.; Mg m^{-3})	1.353	1.471	1.507	1.450	1.400	1.626
Absorption coefficient (mm^{-1})	0.839	0.953	0.815	1.054	0.797	1.081
Crystal size (mm^3)	0.150 × 0.150 × 0.040	0.180 × 0.160 × 0.050	0.200 × 0.180 × 0.110	0.280 × 0.240 × 0.220	0.250 × 0.080 × 0.050	0.300 × 0.150 × 0.050
λ (MoKα: Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Goodness-of-fit-on F^2	1.001	1.001	1.024	1.052	1.024	0.993
Max. 2θ (°)	24.999	27.559	27.698	27.519	27.673	27.524
Reflections	35 050	33 572	31 731	31 003	52 010	26 354
$R_{(\mathrm{int})}$	0.1140	0.0562	0.0333	0.0282	0.0449	0.0721
Param.	302	284	356	321	338	294
$R_1[I > 2\sigma(I)]$	0.0438	0.0324	0.0301	0.0264	0.0305	0.0386
wR_2 (all data)	0.08686	0.0714	0.0733	0.0667	0.0692	0.0789

Table 2 Selected bond angles (°) and bond lengths (Å) for **3a–3c**, and **3e**, **3f**; estimated standard deviations are in parentheses

Descriptor	**3a**	**3b**	**3c**	**3e**	**3f**	**3g**
O(3)–Ni(1)–O(1)	131.15(9)	140.61(6)	141.83(5)	137.71(5)	138.36(5)	123.24(7)
O(3)–Ni(1)–N(2)	92.44(10)	92.89(6)	93.04(5)	93.18(5)	92.11(5)	92.62(8)
O(1)–Ni(1)–N(2)	112.04(10)	102.81(6)	104.36(5)	110.04(5)	106.42(5)	111.40(8)
O(3)–Ni(1)–N(1)	113.07(10)	110.44(6)	107.53(5)	106.88(5)	109.82(5)	113.00(8)
O(1)–Ni(1)–N(1)	92.62(10)	94.29(6)	92.16(5)	93.58(5)	91.51(5)	92.58(*XX*)
N(2)–Ni(1)–N(1)	117.71(11)	117.02(7)	121.31(6)	117.17(6)	122.31(6)	127.11(8)
Ni(1)–O(3)	1.912(2)	1.9272(13)[a]	1.9377(11)[b]	1.9253(11)	1.9282(11)	1.9284(16)
Ni(1)–O(1)	1.917(2)	1.9325(13)	1.9362(11)[b]	1.9214(11)	1.9276(11)	1.9185(17)
Ni(1)–N(2)	1.937(3)	1.9531(16)	1.9597(14)	1.9479(14)	1.9338(14)[c]	1.940(2)
Ni(1)–N(1)	1.937(3)	1.9560(16)	1.9547(14)	1.9437(14)	1.9381(13)	1.941(2)

[a] Bonds are labelled Ni(1)–O(4); additional O atom originates from the furan functionality. [b] Bonds are labelled Ni(1)–O(5) and Ni(1)–N(3); additional O atoms originate from the nitro group. [c] Bonds are labelled Ni(1)–N(3); additional N atom originates from the cyano group.

a square planar arrangement of donor atoms around the Ni centre and are diamagnetic ($S = 0$).[20] Some of these materials also subsequently bind opportunistic solvent molecules (water, acetone, *etc.*) leading to the formation of high spin octahedral or square pyramidal Ni complexes.[21–23] With the materials herein, we observe none of these typical characteristics. Despite the wide variety of substituents on the enolate skeleton (steric, EDG, EWG), these groups appear to have little influence on the resulting solid-state structures of these Ni compounds. This is true in both an intramolecular sense (bond lengths/angles around Ni) and in the lack of propensity for formation of noticeable long-range intermolecular character (*e.g.*, μ *O*/*S* furan/thiophene binding: **3b** and **3e**; Ni⋯NC interactions: **3f**). As deviation from square planar is an atypical bonding motif for complexes such as these, we have further modelled the materials by calculating their τ_4 values.‖[24] This parameter gives a quantitative measure of the degree of distortion from idealised square planar ($\tau_4 = 0.00$) to truly tetrahedral ($\tau_4 = 1.00$) by examining the larger bond angles between the ligating atoms

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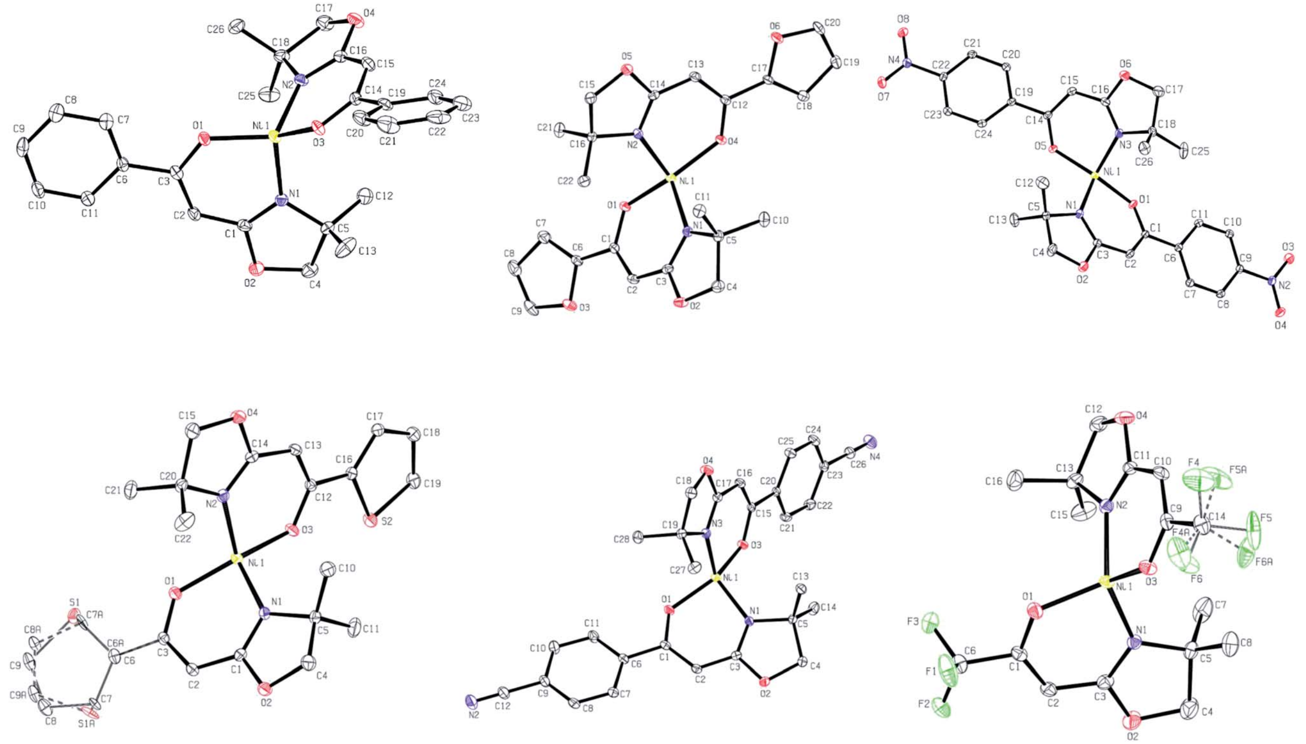
‖ *N.b.*, the structural characterisation of the apparent distorted tetrahedral complex bis(5-bromo-*N*-cyclohexylsalicylideneaminato)-nickel(II), in the *orthorhombic* crystal system (Y.-X. Sun, G. Yang, G. Chen, M. Sun and H.-L. Zhang, *Acta Cryst.*, 2005, **E61**, m1103–m1104), has been challenged (C. M. Wandtke, M. Weil, J. Simpson and B. Dittrich, *Acta Cryst.*, 2017, **B73**, 794–804). A related complex (X.-F. Zhao, *Acta Cryst.*, 2007, **E63**, m704–m705) has since been withdrawn from the literature (*Acta Cryst.*, 2017, **E73**, 926).



Scheme 3 ORTEP representations of unit cell molecules of **3a** (top, left), **3b** (top, middle), **3c** (top, right), **3e** (bottom, left), **3f** (bottom, middle) and **3g** (bottom, right).

Table 3 Calculated τ_4 values of **3a–c** and **3e–g**

Complex	$\tau_4{}^a$
3a	0.79
3b	0.73
3c	0.69
3e	0.74
3f	0.70
3g	0.77

[a] Calculated using $\tau_4 = [360° - (\alpha + \beta)°]/141°$; where α and β are the two largest L–Ni–L bond angles.[24]

and the metal. The calculated values are displayed in Table 3. All six complexes give similar τ_4 values in the range of 0.70–0.79. Although often simply referred to using the generic term *distorted tetrahedral* in nature,[18,19] these complexes are best described as having a distorted *seesaw* coordination disposition of ligating atoms around Ni. This latter descriptor is found in idealised systems with $\tau_4 = 0.64$.[24] Scheme 3 contains ORTEP representations of a unit cell molecule of each complex.

Catalytic activity of 3a

We first tested Ni complex **3a** for possible activity in C–C bond formation under standard *Suzuki* cross-coupling conditions using PhI and $PhB(OH)_2$.[25,26] Unfortunately, **3a** shows no activity for biphenyl formation in this regard. However, structurally related Ni materials are known to mediate olefin polymerisation in the presence of alkyl-Al reagents such as MAO.[27] Therefore, **3a** was tested as catalyst for the polymerisation of styrene under such conditions. As expected, a large excess of MAO was required for catalytic activity; no polymerisation was observed in the absence of the Ni promoter. Although not vigorously active, **3a** does gives reasonable conversions to narrow dispersed polystyrene products at 60 °C in toluene solution (Table 4). Examination of this material revels it is *atactic* in nature.‡ This preliminary examination was designed to show the proof-of-principle activity of these complexes for olefin activation. A more detailed study of the polymerisation characteristics of these Ni systems will be the subject of a subsequent submission.

Experimental

General considerations

All reactions were carried out under ambient atmosphere conditions unless otherwise stated. Chemical reagents were purchased commercially and used as received. Reaction

Table 4 Aspects of the polymerisation of styrene by **3a**^{a}

Run	Al : Ni (mol ratio)	Polymer yield (%)	Activity (TON h^{-1})	Molecular weight (Da)	PDI
1	0	0	0	n/a	n/a
2	500 : 1	97	1.3×10^3	1.5×10^4	1.1
3	800 : 1	93	1.2×10^3	2.8×10^4	1.1
4	1000 : 1	65	8.4×10^2	1.0×10^4	1.2

[a] Polymerisation conditions: 1 h at 60 °C; 20 μmol of **3a** in 2 mL of C_7H_8; 3 mL (2.7 g; 0.026 mol) of styrene in 7 mL C_7H_8.

solvents were further purified by an mBraun Solvent Purification System (SPS) or as received. NMR spectra were recorded on a Bruker AV400 spectrometer using $CDCl_3$ as solvent (chloroform-*d*) at 400 MHz (^1H), 100 MHz (^{13}C) and 376 MHz (^{19}F) at room temperature (RT). In all the spectra, chemical shifts were adjusted to the solvent peak (7.26 ppm for $CHCl_3$ for ^1H and 77.16 ppm for $CDCl_3$ for ^{13}C). Elemental analysis was performed by Atlantic Microlab, Inc. of Norcross, GA (USA). Time-of-flight mass spectrometry analyses were performed using a JMS-T1000LC mass spectrometer (JEOL Inc., Peabody, MA [USA]) equipped with a direct analysis in real time (DART) ionization source (DART-SVP, Ionsense Inc., Saugus, MA, USA) located at the University of Toronto. The DART source was operated with He (g), and the temperature was adjusted in the range 100–400 °C. Isotopic distributions for the observed ionic species were calculated using the Mass Center utility (JEOL) and were in good agreement with the measured spectra. Melting points were determined using a Fisher Scientific melting point apparatus (max. temperature of 300 °C) and are uncorrected. IR spectra were obtained on Agilent Technologies Cary 630 Fourier Transform Infrared (FTIR)-Diamond Attenuated Total Reflectance (ATR). Ultraviolet-visible (UV-Vis) spectra were obtained on Agilent Technologies Cary Series UV-Vis-NIR Spectrophotometer. THF (tetrahydrofuran) and DCM (dichloromethane), having the onset peaks at 215 nm and 230 nm respectively, were used as solvents. The average molecular weights and properties of the polystyrene produced was determined by gel permeation chromatography (GPC) using a Viscotek Triple Model 302 Detector system equipped with a Refractive Index Detector (RI), a four-capillary differential viscometer (VISC), a right angle (90°) laser light scattering detector. GPC columns were calibrated *versus* polystyrene standards (American Polymer Standards). A flow rate of 1.0 mL min^{-1} was used with ACS grade THF as eluent. GPC samples were prepared using 5 mg of polymer per mL THF and filtered using a 0.45 μm filter. The University of Toronto X-ray Crystallographic facility was used to obtain the X-ray structural information as previously described.[28,29] Data was collected on a Bruker Kappa APEX DUO diffractometer using monochromated Mo-Kα radiation (Bruker Triumph) and were measured using a combination of ϕ scans and ω scans. The data was processed using APEX2 and SAINT1. Absorption corrections were carried out using SADABS software 1. The structures were solved using SHELXT2 and refined using SHELXL-20132 for full matrix least-squares refinement that was based on F^2. For all structures, H atoms were included in calculated positions and allowed to refine in a riding-motion approximation with $U\sim$iso tied to the carrier atom as described previously. Molecular modelling calculations were carried out using the *Spartan 16.0* suite of programs as described earlier.‡[30] Compounds **1a–1d**, **2a–2d**, and **2g** were synthesised using literature methods.[9–12] Spectroscopic data of these products were consistent within experimental error to those previously reported.

Compound 1e. A sample of 2,4,4-trimethyl-2-oxazoline (**C**: 15 mmol) was treated with 2-theonyl chloride (30 mmol) and NEt_3 (37.5 mmol) in MeCN solution (30 mL). The solution turned orange in colour and yellow-coloured precipitates formed. The mixture was then heated to reflux temperature for 3 h. The solution was cooled and solvents removed by rotary evaporation. To the resulting residue as added 50 mL of water and this aqueous mixture extracted with DCM (3 × 20 mL). The organic layer was then isolated, washed with 10% aq. Na_2CO_3 and then dried over $MgSO_4$. Evaporation of the solvents revealed an orange-coloured oil. This crude material was recrystallized using 1 : 1 (v : v) hexanes–toluene as solvent affording a white coloured *product*. The yield of this solid was 4.1 g (82%). Mp: 171–174 °C. ^1H NMR: $\delta_H = 7.71$ (d, $^3J = 4$ Hz, 1H), 7.68 (d, $^3J = 4$ Hz, 1H), 7.42 (d, $^3J = 4$ Hz, 1H), 7.11 (t, $^3J = 4$ Hz, 1H), 7.07 (d, $^3J = 4$ Hz, 1H), 6.94 (t, $^3J = 2$ Hz, 1H), 5.35 (s, 1H), 4.32 (s, 2H), 1.61 (s, 6H). ^{13}C {^1H} NMR: $\delta_C = 179.3$, 162.0, 161.4, 147.5, 137.1, 133.7, 133.5, 131.4, 128.7, 128.0, 127.7, 84.7, 79.8, 63.4, 22.8. Selected IR (cm^{-1}): 1671 (m, C=O), 1625 (m, C=C). HRMS-DART (*m/z*): calculated for $^{12}C_{16}{}^1H_{16}{}^{14}N_1{}^{16}O_3{}^{32}S_2$: 334.05716 ($[M + H]^+$); found 334.05577.

Compound 2e. This material was prepared by treating a sample of **1e** (2.0 g; 6.0 mmol) with 2.0 M solution of methanolic KOH. The initial solution was clear and turned to a yellow and then orange solution with the formation of white precipitate over time. After stirring the solution overnight, the precipitates were filtered off and water (50 mL) was added to the filtrate. The mixture was then extracted with 50 mL of DCM. The organic layer was washed with water and then dried over $MgSO_4$. After removal of the solvent (rotary evaporation), the residue was recrystallized from hexanes : toluene (4 : 1; v : v) yielding a pale-yellow solid (0.84 g; 63%). Mp = 100.5–103.5 °C. ^1H NMR: $\delta_H = 9.67$ (s, 1H), 7.50 (m, 2H), 7.41 (d, $^3J = 4$ Hz, 2H), 7.05 (t, $^3J = 4$ Hz, 1H), 5.45 (s, 2H), 4.14 (s, 2H), 1.42 (s, 6H). ^{13}C {^1H} NMR: $\delta_C = 180.90$, 169.29, 147.17, 129.62, 127.13, 127.15, 79.11, 73.67, 58.60, 27.17. Selected IR (cm^{-1}): 3254 (w, O–H), 1610 (m). Anal. calc. for $C_{11}H_{13}NO_2S$: C 59.17, H 5.87, N 6.27; found: C 59.22, H 5.90, N 6.29.

Compound 2f. The intermediate **1f** was prepared *in situ* but not isolated by the following method. A sample of **C** (10 mmol) in MeCN (30 mL) was treated with 4-cyanobenzoyl chloride (30 mmol) and NEt_3 (37.5 mmol). Isolation was initiated as per **1e** above and the resulting solids (crude **1f**) treated directly with 2.0 M methanolic KOH. A pale-yellow coloured solid was isolated as detailed above for **2e** (yield 0.11 g: 14%). Mp = 179–180 °C. ^1H NMR: $\delta_H = 9.99$ (s, 1H), 7.89 (d, $^3J = 8$ Hz, 2H), 7.63 (d, $^3J = 8$ Hz, 2H), 5.49 (s, 1H), 4.17 (s, 2H), 1.43 (s, 6H). ^{13}C {^1H} NMR: $\delta_C = 184.9$, 169.9, 143.9, 132.1, 127.3, 118.7, 113.7, 79.2, 74.6, 58.8, 27.1. Selected IR (cm^{-1}): 3235, 2230 (C≡N), 1618 (m). HRMS-DART (*m/z*): calculated for $^{12}C_{14}{}^1H_{15}{}^{14}N_2{}^{16}O_2$ ($[M + H]^+$): 243.11335; found 243.11383.

Synthesis of complex 3a

Nickel(II) bromide trihydrate (0.45 g, 2.04 mmol) was dissolved in 30 mL of EtOH. This was followed by the addition of **2a** (0.89 g, 4.08 mmol) and NEt_3 (1.25 mL, 8.98 mmol). The initial green coloured solution turned into darker green in colour with precipitate(s) being formed. The solution was stirred overnight at RT. Volatile components of this mixture were then removed (*vacuo*) yielding a green coloured oil. A volume of Et_2O was then used to precipitate the assumed $HNEt_3Br$ salt that had formed; this material was filtered off using vacuum filtration. The filtrate was then collected and the solvent was again evaporated *in vacuo*. The resulting green coloured oil was solidified by tituration with aq. EtOH and the resulting green coloured solids were washed with further aq. EtOH. This afforded a green coloured crystalline *product* (0.77 g, 77%). Mp: 210–212 °C. Selected IR (cm^{-1}): 1526 (s). UV-Vis: 242 nm ($\varepsilon = 4.65 \times 10^4$), 319 nm ($\varepsilon = 3.79 \times 10^4$), 421 nm ($\varepsilon = 1.37 \times 10^3$). Anal. calc. for $C_{26}H_{28}N_2O_4Ni$: C, 63.57; H, 5.75; N, 5.70. Found: C, 63.42; H, 5.85; N, 5.79.

Synthesis of complex 3b

The compound was prepared and purified as for **3a** using **2b** (0.25 g, 1.20 mmol) and $NiBr_2 \cdot 3H_2O$ (0.16 g, 0.60 mmol). The product was isolated as green coloured crystalline solid (0.17 g, 61%). Mp: 208–211 °C. Selected IR (cm^{-1}): 1522 (s). UV-Vis: 266 nm ($\varepsilon = 3.91 \times 10^4$), 322 nm ($\varepsilon = 4.72 \times 10^4$), 435 nm ($\varepsilon = 1.22 \times 10^3$). Anal. calc. for $C_{22}H_{24}N_2O_6Ni$: C, 56.09; H, 5.13; N, 5.95. Found: C, 56.20; H, 5.23; N, 6.08.

Synthesis of complex 3c

The compound was prepared and purified as for **3a** using **2c** (0.25 g, 1.20 mmol) and $NiBr_2 \cdot 3H_2O$ (0.16 g, 0.60 mmol). The product was isolated as green coloured crystalline solid (0.15 g, 54%). Mp: 261 °C (decomp.). Selected IR (cm^{-1}): 1514 (s), 1300 (s). UV-Vis: 263 nm ($\varepsilon = 5.16 \times 10^4$), 368 nm ($\varepsilon = 2.89 \times 10^4$). Anal. calc. for $C_{26}H_{26}N_4O_8Ni$: C, 53.73; H, 4.51; N, 9.81. Found: C, 54.00; H, 4.60; N, 9.81.

Synthesis of complex 3d

The compound was prepared and purified as for **3a** using **2d** (0.25 g, 1.2 mmol) and $NiBr_2 \cdot 3H_2O$ (0.17 g, 0.62 mmol). The product was isolated as green coloured crystalline solid (0.24 g, 86%). Mp: 215–221 °C. Selected IR (cm^{-1}): 2959, 1522 (s). UV-Vis: 280 nm ($\varepsilon = 2.11 \times 10^4$), 383 nm ($\varepsilon = 1.24 \times 10^3$). Anal. calc. for $C_{22}H_{36}N_2O_4Ni$ (*n.b.*, a reproducible combustion analysis for this compound could not be obtained). HRMS-DART (*m*/*z*): calculated for $^{12}C_{22}{}^{1}H_{37}{}^{14}N_2{}^{16}O_4{}^{58}Ni$ ($[M + H]^+$): 451.21156; found 451.21068.

Synthesis of complex 3e

The compound was prepared and purified as for **3a** using **2e** (0.25 g, 1.20 mmol) and $NiBr_2 \cdot 3H_2O$ (0.15 g, 0.60 mmol). The product was isolated as green coloured crystalline solid (0.21 g, 75%). Mp: 203–206 °C. Selected IR (cm^{-1}): 1511 (s). UV-Vis: 251 nm ($\varepsilon = 3.16 \times 10^4$), 336 nm ($\varepsilon = 3.96 \times 10^4$), 435 nm ($\varepsilon = 1.02 \times 10^3$). Anal. calc. for $C_{22}H_{26}N_2O_4S_2Ni$: C, 52.51; H, 4.89; N, 5.57. Found: C, 51.88; H, 4.84; N, 5.58.

Synthesis of complex 3f

The compound was prepared and purified as for **3a** using **2f** (0.25 g, 1.0 mmol) and $NiBr_2 \cdot 3H_2O$ (0.11 g, 0.52 mmol). The product was isolated as green coloured crystalline solid (0.14 g, 50%). Mp: 160–161 °C (decomp.). Selected IR (cm^{-1}): 2227, 1522 (s). UV-Vis: 248 nm ($\varepsilon = 4.83 \times 10^4$), 337 nm ($\varepsilon = 2.73 \times 10^4$), 423 nm ($\varepsilon = 3.43 \times 10^3$). Anal. calc. for $C_{28}H_{26}N_4O_4Ni$: C, 62.24; H, 4.84; N, 10.35. Found: C, 62.09; H, 4.91; N, 10.35.

Synthesis of complex 3g

The compound was prepared and purified as for **3a** using **2g** (0.25 g, 1.2 mmol) and $NiBr_2 \cdot 3H_2O$ (0.16 g, 0.60 mmol). The product was isolated as green coloured crystalline solid (0.77 g, 77%). Mp: 160–162 °C (decomp.). Selected IR (cm^{-1}): 1531 (s). UV-Vis: 274 nm ($\varepsilon = 1.69 \times 10^4$). Anal. calc. for $C_{16}H_{18}N_2O_4F_6Ni$: C, 40.46; H, 3.82; N, 5.90. Found: C, 40.72; H, 3.82; N, 5.94.

Styrene polymerisation

Under an N_2 atmosphere, a 20 μmol sample of the nickel(II) complex **3a** (dissolved in 2.0 mL C_7H_8), 3 mL of styrene and 7 mL of toluene were added to a 50 mL three-neck round bottom flask. The mixture was then degassed for 15 min (N_2 purge) and the temperature subsequently raised to 60 °C for 5 min. A 5.80 mL sample (10% in weight toluene) of MAO was charged into the system *via* syringe and stirring was continued. After 1 h, acidic MeOH ($V_{MeOH}/V_{conc.\ HCl} = 20/1$) was added to terminate the reaction. The resulting PS mixture was then dissolved in $CHCl_3$ and extracted with water. The organic layer was dried ($MgSO_4$) and evaporated to give the crude product. This material was dissolved in minimal THF and was added dropwise to a stirring solution of cold MeOH in a 100 mL Erlenmeyer flask. White precipitates were thus formed and the MeOH was decanted off. The resulting white coloured solids were transferred to a 50 mL round bottom flask and then dried under vacuum. The above purification step was repeated two more times and the PS obtained was then analysed.

Conclusions

The synthesis and characterisation of the first group 10 complexes, specifically Ni(II), of the enolates derived from 2-acylmethyl-2-oxazolines (*Tohda's ligands*) has been described. Examination by spectroscopy and X-ray diffraction methods have shown these materials to be of the less common paramagnetic $Ni(\kappa^2\text{-}N,O\text{-}\mathbf{L})_2$ formulation with a distorted seesaw arrangement of bonding atoms around the metal centres. A preliminary examination of one derivative has shown that it is an active catalyst, in the presence of excess MAO, for the formation of low dispersity atactic polystyrene from the monomer at elevated temperatures.

Conflicts of interest

The authors declare no conflict of interest.

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