Structural, magnetic and related attributes of some oximate-bridged tetranuclear nickel(II) rhombs and a dinuclear congener

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New oximate-bridged tetranuclear nickel(II) complexes of compositions \[\text{[Ni(Dien)]_4(µ-OH)_4(Ni_{\text{Moda}})_4(ClO}_4)_4\] Solv (Solv = H_2O, 1a; Solv = 2CH_3NO_2, 1b; Solv = 2H_2O-2CH_3NO_2, 1c). (Ni(Sdien))_4(µ-OH)_4(Ni_{\text{Moda}})_4(ClO}_4)_4, H_2O (2), (Ni(Odien))_4(µ-OH)_4(Ni_{\text{Moda}})_4(ClO}_4)_4, 0.6H_2O (3). (Ni(Dien))_4(µ-OH)_4(Ni_{\text{Inaf}})_4(ClO}_4)_4, 2NaClO_4, 2H_2O (5) and the dinuclear complex [Ni(Odien)]_2(µ-OH)_2Ni_{\text{Moda}}_2(ClO}_4)_3, 2H_2O (6) have been prepared (Dien = 1,5-diamino-3-azapentane, Odien = 1,5-diamino-3-thiazapentane, Sdien = 1,5-diamino-3-thiapentane, Moda = butane-2,3-dione oxime, Inaf = phenylglyoxalidoxime). X-ray examination revealed similar structures for 1a, 1b, 1c, 2 and 3, with a rhombic “chair” (out-of-phase “butterfly”) arrangement of the four nickel(II) atoms and two hydroxo-bridges. The complexes were examined by magnetocrymetry, UV-VIS spectroscopy and voltammetry. 1–3 display antiferromagnetic coupling of the central with the terminal nickel(II) atoms and ferromagnetic spin alignment between the central nickel(II) atoms. In contrast, all the spin exchanges in 4 and 5 were found to be antiferromagnetic, as is the coupling in dinuclear 6.

Introduction

Polynuclear complexes of 3d-metals containing unpaired electrons are considered promising compounds for the design of new magnetic materials and as models for metal active sites in proteins, many of which contain polymetallic cores. During the last few years, phenomena such as spin frustration and single molecule magnetism have been found in complexes with moderate to high nuclearity. The development of methods for the preparation of polynuclear complexes of targeted topology and predefined number of metal atoms is an important and necessary step for investigation of these phenomena. The majority of reported tetranuclear nickel(II) complexes possess a cubic topology for their polynuclear core, though several tetranuclear nickel(II) complexes possessing topologies without high symmetry have also been examined. Only a few examples of rhombic tetranuclear nickel(II) complexes are known, the majority of which were prepared by inclusion of nickel(II) ions into polynoxotungstates or contain trimethylacetates as bridging groups. While two of the rhombic complexes contain the two central nickel(II) pair in the high-spin state, but the terminal ions as low-spin, A µ_3-OCO_2^−-bridged example has also been reported. Although several tetrameric cubane-type nickel(II) complexes have been examined and correlations have been found between Ni-O-Ni angles and exchange integrals (J-values), the magnetocrymetrical properties of only a very few rhombic nickel(II) tetranuclear complexes have been delineated, the most recent tetranuclear (all S = 1) system (1c) having been reported by our laboratories. Previous work on Fe_4 and Mn_4 rhombic “butterflies” revealed phenomena of fundamental interest, such as different kinds of spin frustration, so the question arises, as to what types of magnetic phenomena may arise in association with other metal spin-states; nickel(II) “butterflies” thus become an intriguing example.

Oximate ligands exhibit a notable ability to bridge between metal ions. For example, dimethylglyoximato has been widely used as starting material for preparation of linear homo- and heterometallic oligonuclear complexes containing nickel(II), via the “complex as ligand” strategy. Oximes containing additional nitrogen, phenolato oxygen or thioether donors have also found application in the preparation of complexes following this strategy, such as those with Schiff bases formed by condensation of diamines with diacetyl monoximes complexes with 2,6-diacylphenol dioximes and with the dioxime of 4,7-dithiadecane-2,9-dione. The exact composition and coordination topology of polynuclear complexes with oxime ligands bearing additional donor atoms is basically unpredictable as yet, though complexes with high nuclearity have often been isolated. To investigate the role of additional donor atoms in the control of the composition and structure of polynuclear compounds, we have examined ternary complexes derived from the α-diketomonooximate ligands 2,3-butanedione monoxime (ModaH) and phenylglyoxalidoxime (InaH) (Fig. 1). Nickel(II) complexes were prepared by the reaction of these oximes with nickel(II) perchlorate and 1,5-diamino-3-azapentane (Dien), 1,5-diamino-3-thiapentane (Sdien) or 1,5-diamino-3-oxapentane (Odien) in the presence of bases (to deprotonate the oxime group). We report here the properties of the resulting di- and tetranuclear compounds, including some variations of these properties with differing crystal solvation.
Experimental

Materials

The sodium salt of phenylglyoxaldehyde (2-isonitrosoacetophenone; 2-phenylanil-2-one-1-aldoxime; Inaf Na") and the Odien were prepared according to literature procedures. Other reagents were commercially available (Aldrich and Ukrek-Chim) and were used without further purification. The dioxane used throughout was the 1,4-isomer. Acetonitrile for the chemical analyzer. The three-electrode assembly comprised platinum working, platinum auxiliary, and a silver/silver chloride reference electrode (0.01 M AgNO3, 0.1 M Na2SO4, CH3CN), which is at +298 mV vs the SCE. The working electrodes were Pt disks or wires for voltammetry (at scan rates from 20 to 2000 mV s⁻¹) and an Hg/Ag disk for rotating disc electrode polarography (wherein Ei is defined as i = i/2). The supporting electrolyte was 0.1 M Na2SO4, and solutions for voltammetry and polarography were ca. 1 mM in complex.

Syntheses

Caution: although none of the compounds described here has yet proven to be mechanically sensitive, perchlorates are potentially explosive and should be prepared only in small amounts and handled with due caution.

\[\text{[Ni(Diien)]_2(\mu-\text{OH})_2[Ni(\text{Moda})_2](\text{ClO}_4)_2][\text{H}_2\text{O}}\]

1.46 g (4 mmol) of Ni(ClO4)2·6H2O in 5 mL of ethanol (96%) were added to a solution of 0.41 g (4 mmol) of ModaH and 0.20 g (2 mmol) of Diien in 10 mL of ethanol. The solution was warmed to clarify it, after which 0.61 g (6 mmol) of Et3N was added. The resulting crystalline purple–brown precipitate (1a) was filtered off, recrystallized from a benzene/MeCN/dioxane (2 : 1 : 1) mixture and air-dried, to give 0.93 g of black blocks. Yield 85%. Anal. Calcd. for C26H26Cl2N4O10Ni4: C, 29.9(29.8); H, 5.60(5.55); N, 10.9(10.9); Ni, 18.3(18.3)%. Positions of the principal bands in the IR spectrum for 0.5 h. 2-Chloroethylamine

\[\text{[Ni(Sdien)]_2(\mu-\text{OH})_2[Ni(\text{Moda})_2](\text{ClO}_4)_2][\text{H}_2\text{O}}\]

Na metal (0.14 g, 6 mmol) was dissolved in ethanol (25 mL), followed by cysteamine hydrochloride (0.22 g, 2 mmol) and the mixture was stirred under reflux for 0.5 h. 2-Chloroethylamine (0.23 g, 2 mmol) was then added and reaction mixture was stirred under reflux for 2 h, after which it was cooled to room temperature and used directly as the source of 2 mmol of Sdien for the preparation of 2. The remainder of the procedure was as described for 1. The brown precipitate was recrystallized from MeCN and air-dried, giving 0.93 g of green–red dichroic blocks. Yield 83%. Anal. Calcd. for C26H26Cl2N4O10Ni4S2: C, 25.6(25.5); H, 4.71(4.70); N, 10.31(10.42); Ni, 21.6(21.0)%.

\[\text{[Ni(ODien)]_2(\mu-\text{OH})_2[Ni(\text{Moda})_2](\text{ClO}_4)_2]}\]

To a solution of 0.145 g of 6 (0.2 mmol) in 4 mL of MeCN was added 0.146 g (0.4 mmol) of Ni(ClO4)2·6H2O and 0.041 g (0.4 mmol) of ModaH. Triethylamine (0.085 mL, 0.6 mmol) was then added and the reaction mixture was allowed to stand for 0.5 h. 2-Chloroethylamine (0.202 g, 2 mmol). The resulting green precipitate was filtered off, recrystallized from 1 : 1 MeNO2/dioxane and air-dried, to give 0.93 g of black blocks. Yield 85%. Anal. Calcd. for C26H26Cl2N4O10Ni4: C, 29.9(29.8); H, 5.60(5.55); N, 10.9(10.9); Ni, 18.3(18.3)%.
giving 1.06 g (80% yield) of green microcrystals. Anal.: C_{22}H_{26}Cl_{12}N_{16}O_{12}; Calc. (Found): C, 37.3(37.9); H, 4.15(4.20); N, 11.62(11.25); Ni, 17.17(17.8). ES-MS: 1165 ((M + ClO_4)^+). IR (in KBr), cm^{-1}: 3550 (v(NH)); 2930 (v(CH)); 1595m, 1575m, 1465s (v(C-O) + v(=N) + v(=C)); 1430m (v(C-C)); 1200m (v(N-O)); 1150s (v(ClO_4)); 895m; 710m; 685m; 625m (v(ClO_4)^+).

\[
\left[\text{Ni(Odien)}\right]_2\left[\text{µ-ClO}_4\right]\left[\text{Ni(2AAF)}\right]_2\left[\text{ClO}_4\right]_2\cdot 2\text{NaClO}_4\cdot 2\text{H}_2\text{O} (5)
\]

This was prepared analogously to 4, but by using 0.606 g (2 mmol) of Odien-2HClO_4 instead of Dien. The resulting green precipitate was filtered off and recrystallized from 2 : 1 MeCN : dioxane and air-dried, which gave 1.16 g of green microcrystals (yield 75%). Anal.: C_{22}H_{26}Cl_{12}N_{16}O_{12}Na; Calc. (Found): C, 30.99(30.86); H, 3.49(3.93); N, 7.23(7.68); Ni, 15.2(15.1). ES-MS: 1166 ((M + ClO_4)^+). IR (in KBr), cm^{-1}: 1390m, 1180s (v(N-O)); 1100s (v(ClO_4)); 900m; 800m; 720w; 690w; 635m (v(ClO_4)^+).

\[
\left[\text{Ni(2AAF)}\right]\left[\text{ClO}_4\right]_3 (6)
\]

To a stirred solution of 0.642 g (2 mmol) of Odien-2HClO_4 and 0.404 g (4 mmol) of NEt_3 in 10 mL 96% ethanol was added 0.202 g (2 mmol) of ModaH, followed by a solution of 0.731 g (2 mmol) of Ni(ClO_4)_2·6H_2O in 5 mL of 96% ethanol. After the addition of NEt_3 (0.202 g, 2 mmol), the red precipitate which formed was filtered off and recrystallized from 1 : 1 MeNO_2 : dioxane to give 0.65 g of red crystals of 6 (yield 90%). Single crystals for X-ray study were prepared from a solution of 2 in 1 : 1 MeNO_2 : dioxane by vapor diffusion of diethyl ether. Anal.: C_{22}H_{26}N_{16}O_{12}Cl_2Ni_2; Calc. (Found): C, 26.50(26.55); H, 4.97(5.00); N, 11.60(11.65); Ni, 16.2(16.2%). ES-MS: 625 ((M + ClO_4)^+). IR (in KBr), cm^{-1}: 1620, 1450 (v(N=NIH) and v(C=N)); 1260 (v(N-O)); 1100 (v(ClO_4)); 665, 625 (v(ClO_4)^+).

CCDC reference numbers 155327 (1e), 190465 (1a'), 190466 (1b), 192596–192598 (6, 3 and 2, respectively), and 193550 (1a).

See http://www.rsc.org/suppdata/dt/b3/b300539a/ for crystallographic data in CIF or other electronic format.

Crystal data for the various compounds are summarized in Table 1.

Results and discussion

Syntheses of nickel(II) complexes

Reaction of the tridentate amines Dien or Odien (1 equiv.) with the monooxime of a 1,2-diketone (2 equiv.) and Ni(ClO_4)_2·6H_2O (2 equiv.) in the presence of base (6 equiv.) in 96% ethanol resulted in formation of tetranuclear nickel(II) complexes.

The nature of the products was not affected by the order of reagent addition or use of the sodium salt of the oxime instead of the oxime-NEt_3 sequence. Excess of base (beyond a 1 : 1 ratio to oxime) was used to generate the bridging OH^-. Remarkably, use of PhO'Na^+, PhS'HNCH_2'or PhCH=N'S'Na^+ as bases did not incorporate any of these as bridging anions in place of OH^-, but instead gave 1. Nor was Schiff base formation between amine and ketone observed, although several examples of Schiff bases derived from ModaH and diamines have been reported along with indications of the metal-induced hydrolysis of such compounds.

The combination of nickel(II) with ModaH and Odien at the same ratios and conditions as for preparation of all other tetranuclear compounds, initially yielded a dinuclear complex (6) instead of a tetranuclear one. However, further treatment of 6 with nickel(II) perchlorate, ModaH and Et_3N (2, 2 and 4 equiv. per equiv. of 6, respectively) in MeCN produced the tetranuclear complex 3.

![Table 1 Crystallographic data for complexes 1–3 and 6](image-url)

- **α**: 62.35(2)
- Z: 3
- μ: 0.0539
- µ: 0.1475
- R^2: 0.0539
- R: 0.1475
- R_2: 62.35(2) = 66.71(2)^a

^a Calculated from all data.
Mass spectra

The details of the mass spectra, in terms of the degree of (de)protonation, are somewhat dependent on the ionization conditions (i.e., FAB vs. ESI, nature of matrix). However, a consistent overall pattern of molecular and fragment ions was observed, and the various tetranuclear molecules were clearly evident. For the Dien/Moda-complex 1, peaks due to the molecular ion \([\text{Ni}_4(\text{Moda})_4(\text{Dien})_2(\mu_3-\text{OH})(\text{ClO}_4)_4]^-\) and the deprotonated and perchlorate-stripped \([\text{Ni}_4(\text{Moda})_4(\text{Dien})_2(\mu_3-\text{OH})(\mu_4-\text{O})]^-\) were observed in the FAB mass spectrum at \(m/e = 973\) and 873, respectively (975, 875 in ESI). Further fragmentation included removal of the Dien ligands, though without destruction of the tetranuclear skeleton. The mass spectra of 1a, 1b and 1c are identical (as well as all their solution properties). The mass spectra of 2 and 3, the other tetranuclear complexes with Moda, are analogous in their main features with that of 1. The mass spectrum of 2 contains peaks assigned to \([\text{Ni}_4(\text{Moda})_4(\text{Sdien})_2(\mu_3-\text{OH})(\text{ClO}_4)_4]^-\) (\(m/e = 1007\)) and \([\text{Ni}_4(\text{Moda})_4(\text{Sdien})_2(\mu_3-\text{OH})]^-\) (\(m/e = 908\)) with approximately equal intensities. In the mass spectrum of 3, a peak assigned to the deprotonated (oxo-) species \([\text{Ni}_4(\text{Moda})_4(\text{O}^\text{in})_4(\mu_3-\text{OH})(\mu_4-\text{O})]^-\) (\(m/e = 974\)) is approximately ten times more intense than the \([\text{Ni}_4(\text{Moda})_4(\text{O}^\text{in})_4(\mu_3-\text{OH})(\mu_4-\text{O})]^{\text{ClO}_4^-}\) one (\(m/e = 974\)). Each mass spectrum of complexes 1–3 contains a peak at \(m/e = 491\), the position of which is independent of the nature of the amine, evidencing its assignment to the Ni\(_2\)O(Moda)\(_2\) core ion. Clearly, neutral ligands are removed more easily than anionic ones.

In the mass spectrum of the Inaf/Dien product 4, peaks corresponding to the parent molecular ion \([\text{Ni}_4(\text{OH})_2(\text{Dien})_2(\text{Inaf})]^{\text{(ClO}_4^-)}\) and to \([\text{Ni}_4(\text{OH})_2(\text{Dien})^{\text{Inaf}}]^-\) were observed at \(m/e = 1165\) and 1064, respectively. For the Odien/Inaf product 5, the main distinguishing feature is the relatively low intensity of any molecular ion peak \([\text{Ni}_2(\text{OH})_2(\text{Odien})_2(\text{Inaf})]^{\text{(ClO}_4^-)}\) near \(m/e = 1166\) and the absence of any corresponding ion without perchlorate. Similarly to the Moda-containing complexes, the mass-spectra of 4 and 5 contain peaks at \(m/e = 636\), assigned to the \([\text{Ni}_2(\text{Odien})^{\text{Inaf}}]^-\) core ion.

The dinuclear Moda/Odien complex 6 displayed an intense peak at \(m/e = 625\) corresponding to \(\text{ClO}_4^-\)-adduced Ni\(_2\)- (Odien)\(_2\) (Moda)\(_2\). Peaks at \(m/e = 595\) and 562 are attributed to \([\text{Ni}_4(\text{Moda})_4(\text{O}^\text{in})_4]^-\) and \([\text{Ni}_4(\text{Odien})_4(\text{Moda})_4]^-\).

Molecular and crystal structures

The principal features of the structures of the complex cations in the different solvate lattices 1a, 1b and the previously described\(^{27}\) 1c are similar, so those will be described only for the tetranuclear cation in 1a. Diffraction data for 1a were collected at both 100 K (1a) and 295 K (1a'). Selected structural metrics of cations in 1a, 1b and 1c are listed in Table 2. The ORTEP presentation of the complex cation of 1a with its atom labeling scheme is displayed in Fig. 2(a). Subscripts “c” and “t” refer respectively to central nickel(II) atoms (Ni(2), Ni(4)) and terminal atoms (Ni(1), Ni(3)). In a “butterfly” structural designation, the “c” are often denoted as “body” atoms and the “t” as “wing” atoms. In the complex dication \([\text{Ni}_4(\text{Dien})_4(\mu_3-\text{OH})_4(\text{ClO}_4)_4]^{2+}\), the four Ni atoms form a rhomb, planar within 0.001 Å. The Ni\(_2\)O\(_2\) core, however, is based on a rhombic Ni\(_2\)O\(_2\) “chair” (Fig. 2(b)), the two Ni with pseudo-orthohedral Ni\(_2\)O\(_2\) donor sets being bridged by hydroxyl ions to form a central Ni\(_2\)O\(_2\) rhombus. Two terminal nickel(II) atoms are in turn bonded to μ\(_3\)-OH- groups on each side of this Ni\(_2\)O\(_2\) rhombus, so that each μ\(_3\)-OH- group acts as the bridge amongst three nickel(II) atoms. The Moda anions are coordinated to the central nickel(II) atoms via their keto oxygen and oximate nitrogen atoms. The Ni–O(ketone) bond lengths in 1a (2.110 and 2.102 Å at 295 K) are essentially the same as another recently described\(^{28}\) rare example of a Ni–O(ketone)…
bond (2.13 Å). The Ni₆s are additionally anchored to the Ni₆O₂ group by oxygens from oximate groups (Fig. 2(b)). The pseudo-octahedral Ni₆O₆ coordination around each terminal nickel(II) atom is completed by nitrogen atoms of facially coordinated Dien molecules. The Ni–N(oxime), Ni–N(amine) and Ni–O(hydroxide) bond lengths in 1 are within the usual ranges reported for high-spin octahedral nickel(II).³⁰

The different solvations have only minor influences on the molecular structure of the complex cation in 1, but dramatically change the crystal packing. Monoclinic 1a contains one H₂O molecule per complex cation of [Ni(Dien)](µ₂-OH)₂[Ni₆(Moda)₄]²⁺ (4 cations per unit cell). In rhombic 1b, there are two nitromethane molecules per cation (8 cations per unit cell), while for monoclinic 1c (2 cations per unit cell), there are two disordered H₂O molecules and two dioxane molecules per cation. The compound 1b displays layers composed of tetranuclear cations with an average Ni–Ni separation of c/2 = 10.8 Å. Perchlorate ions and nitromethane molecules intervene between these layers in 1b. In contrast, the tetranuclear cations in 1c are shielded by ClO₄⁻ ions and molecules of solvent, with no layering of cations being apparent, while 1a possesses packing similar to 1b, but without dioxane molecules between the tetranuclear cations. The shortest intermolecular Ni–Ni separations in these solvates are presented in Table 2. For 1a it changes somewhat with temperature (in contrast to the intramolecular features), as illustrated by comparison of the crystal data for this complex at 295 and 100 K. This intermolecular distance exceeds the Ni–Ni separation within the complex cation roughly by 1 Å.

Selected structural data for the tetranuclear cations [(Ni(Sdien)].(µ₂-OH)₂Ni₆(Moda)₄]²⁺ in 2 (Fig. 3) and [(Ni(Dien)].(µ₂-OH)₂Ni₆(Moda)₄]²⁺ in 3 (Fig. 4) are listed in Table 2. Replacement of the secondary amine donor atoms in the coordination spheres of the terminal nickels by thioether or ether donors has only minor effects on the common structural details of the cations; the main difference is that in 3 the Ni₆–O(ether) bonds are quite long (2.155 Å) – about 0.11 Å longer than the Ni₆–(µ₂-O) bond. The Ni-donor atom distances thus portray the nickel ion as being distorted along its pseudo-C₃ axis (through the centre of the O(25)–O(15)–O(30) triangle and the Ni atom). In the Oiden complex 3, Ni₆ is 0.02 Å from the least-squares plane passing through the donor atoms N(1)–N(7)–O(15)–O(25) (Fig. 4) – about double the excursion observed for 1 and 2.

Previously structurally characterized rhombic Ni₆ complexes with all four nickel(II) atoms in the high-spin S = 1 state include [Ni₆(µ₂-CO₂)(Aetpy)₆][ClO₄] (Aetpy = 2-aminoethylpyridine)¹⁷ certain tetranickel units within polytungstate ions²¹,²² and some trimethylacetato derivatives.²⁴–²⁶ In [Ni₆(µ₂-CO₂)(Aetpy)](ClO₄)²⁻ the Ni₆–Ni₆ and Ni₆–Ni₆ distances are respectively about 0.40 and 1.98 Å longer than in 1, due to the different nature of the anion bridge. The molecular structures of the Ni₆ units in the Moda complexes 1, 2 and 3 might also be compared with the tetranickel cores in the β-Keggin polyoxo-}

**Fig. 3** ORTEP diagram of the [(Ni(Sdien)].(µ₂-OH)₂Ni₆(Moda)₄]²⁺ cation of 2. H atoms are omitted for clarity. Selected bond lengths (Å): Ni(1)–O(15) 2.046(3); Ni(1)–O(25) 2.048(3); Ni(1)–O(1) 2.059(3); Ni(1)–O(1) 2.051(2); Ni(1)–O(2) 2.155(2); Ni(1)–N(7) 2.091(2); Ni(1)–N(1) 2.113(2); Ni(2)–N(14) 2.028(2); Ni(2)–N(24) 2.032(2); Ni(2)–O(30) 2.037(2); Ni(2)–O(11) 2.120(2); Ni(2)–O(21) 2.106(2); Ni(2)–O(30) 2.047(2).

**Fig. 4** ORTEP diagram of the [(Ni(Oden)].(µ₂-OH)₂Ni₆(Moda)₄]²⁺ cation of 3. H atoms are omitted for clarity. Selected bond lengths (Å): Ni(1)–O(30) 2.042(2); Ni(1)–O(25) 2.050(2); Ni(1)–O(15) 2.051(2); Ni(1)–O(4) 2.155(2); Ni(1)–N(7) 2.091(2); Ni(1)–N(1) 2.113(2); Ni(2)–N(14) 2.028(2); Ni(2)–N(24) 2.032(2); Ni(2)–O(30) 2.037(2); Ni(2)–O(11) 2.120(2); Ni(2)–O(21) 2.106(2); Ni(2)–O(30) 2.047(2).
N,O-bridging oximate groups of Moda\textsuperscript{−}, thus forming an Ni\textsubscript{3}N\textsubscript{2}O\textsubscript{6} metalloccycle. Each nickel(ii) atom possesses a distorted octahedral mer-N\textsubscript{2}O donor set. The oximate bridges between nickel(ii) atoms in \textit{6}, which lacks the oxo-bridges of 1-3, yield a Ni–Ni separation (3.704 Å) longer by about 0.3 Å than in 1-3.

Complexes 3 and 6 differ in Odien coordination type (fac- and mer-, respectively). Both coordination types are known for Dien and Odien: mer-Dien in Ni(Dien)\textsubscript{2}Cl\textsubscript{2}H\textsubscript{2}O\textsuperscript{−} and fac-Dien in cations of Ni(Dien)\textsubscript{2}(TNCQ)\textsubscript{2}\textsuperscript{−}. Meridionally and facially coordinated Odien were observed\textsuperscript{63,64,65} in Ni(Odien)\textsubscript{2}(ClO\textsubscript{4})\textsubscript{2} and Cd(Odien)(SCN)\textsubscript{2}\textsuperscript{−}, respectively.

The nature of the tridentate “cap” coordination is thus not an important factor controlling complex nuclearity in 3 or 6. For Sdien, fac-coordination to nickel(t) similar to that in 2, has been reported\textsuperscript{63,66} for Ni(Sdien)\textsubscript{2}(PF\textsubscript{6})\textsubscript{2} and Ni(Sdien)\textsubscript{3}(ClO\textsubscript{4})\textsubscript{2}.

### Magnetochemical properties

The magnetic behaviours of polycrystalline samples of the complexes were measured in the temperature range 2-300 K for 1\textit{c} and 2-290 K for the other complexes. For 1\textit{a}, the decrease in $\chi\textsubscript{M}$ from 3.74 (at 290 K) to 0.053 cm\textsuperscript{3}mol\textsuperscript{−1} (at 2 K) is representative of these complexes (Fig. 6). As the value of $\chi\textsubscript{M}$

![Fig. 6 $\gamma$T vs. T plots for compounds 1a, 2, 3, 4 and 5. Solid lines represent fits to eqns. (3)-(5), with parameters from Table 3.](image)

for a tetranuclear unit of four non-interacting $S = 1$ Ni(ii) ions with $g = 2.0$ would be 4.0 cm\textsuperscript{3}mol\textsuperscript{−1}, it is evident that the dominant interaction in complexes 1-3 is antiferromagnetic in nature: it is not critically dependent on the tridentate capping ligand. Plots of $\gamma$ vs. $T$ for 1, 2 and 3 show broad maxima around 80 K (absent from such plots for 4 and 5). The different Ni-Ni exchange interactions among the Ni\textsubscript{i} and Ni\textsubscript{j} may be represented by the isotropic exchange Hamiltonian [eqn. (1)] for a rhombic arrangement of four $S = 1$ metal centers:

$$\mathcal{H} = -2J_a(S_aS_b + S_bS_c + S_cS_d + S_dS_a) - 2J_b(S_bS_c - 2J_f(S_fS_g)$$

The exchange integrals $J_a$, $J_b$ and $J_c$ are defined as in Fig. 7, though in nearly all the present cases, the relative isolation of the Ni\textsubscript{i} renders $J_a$ not sensibly different from zero. The spin states are designated as $(S_aS_bS_cS_d)$, where $S_{11} = S_1 + S_2$, $S_{22} = S_2 + S_3$, $S_{33} = S_3 + S_4$, and $S_{44} = S_4 + S_5$. The energies of the states corresponding to the various $S$ are then

$$E(S_f) = -J_a(S_a + 1) - S_d(S_d + 1)(J_f - J_b) + S_a(S_b + 1)(J_b - J_c) + J_f + J_b + J_c$$

The variable-temperature magnetic data were fitted according to expressions [eqn. (2)-(5)] based on application of the van Vleck equation\textsuperscript{69} to Kambe’s vector coupling scheme.\textsuperscript{69}

![Fig. 7 Coupling scheme for the tetranuclear complexes 1-5. The circles represent nickel(t) ions and the spin orientations illustrate a (0,2,2) state.](image)

A similar analytical expression was also attributed to Dubicki,\textsuperscript{70} with three $J$-values for a rhombic tetranuclear complex of $S = 1$ ions. Results are summarized in Table 3 and displayed in Fig. 6. For all but 4, the values of $J_a$ were negligibly small, while for most of the Moda\textsuperscript{−} complexes (1-3) the 2$J_c$ values are $\sim 30$ to $\sim 40$ cm\textsuperscript{−1}, with small positive $J_b$. Relatively weak dependence of $\gamma T$ on the value of a positive $J$ in the presence of competing negative $J$-values is an expected numerical consequence in clusters of small nuclearity. However, this insensitivity of $\gamma T$ even extends to negative values of $J_a$ in these tetranuclear systems: plots\textsuperscript{72} of the dependence of $\mathcal{R}(\gamma T)$ on $J_a$ and $J_b$ for the Moda\textsuperscript{−} complexes 1-3 showed the presence of extended minima (as sloping troughs) at the appropriate $J_a$, indicating the onset of indeterminacy in the estimation of $J_a$, most notably for 1\textit{a} and 1\textit{e}. The Dien/Moda\textsuperscript{−} tetramer 1\textit{c} (having the largest intermolecular Ni-Ni distance and thus the lowest potential intermolecular coupling) confirms that $\gamma T$ is much more weakly dependent on $J_a$ or $J_b$ than on $J_b$ (see Supplementary Materials).\textsuperscript{†}

The task of differentiating amongst the various possible modes of coupling or frustration in such situations is not a trivial one. According to Kahn’s definition,\textsuperscript{4} classical spin frustration cannot appear when $S_1 = 0$, so it is more appropriate to consider the positive $J_a$ as the consequence of spin ordering by the dominating $J_b$. The dominant antiferromagnetic Ni$_i$-Ni$_j$ interaction concomitantly dictates a parallel (pseudoferromagnetic) orientation for the spins of the central nickel atoms. Although the situation for the Moda\textsuperscript{−} chelates 1-3 is linked to the idea of topological spin frustration,\textsuperscript{73} it is more straightforwardly viewable as one of competing spin interactions, one consequence being an indeterminacy of $J_b$ as previously noted for an Fe\textsuperscript{3+} “butterfly.”\textsuperscript{28}

Calculation of the energy levels using the $J$-values from Table 3 illustrates the spin state (0,2,2) as the ground state in the complexes 1-3, as [Ni\textit{i}, Ni\textit{j}, Ni\textit{k}, Ni\textit{l}] = [↑↑, ↓↓, ↑↑, ↓↓], with the first excited spin state (1,2,2) about 40 cm\textsuperscript{−1} higher, and the $S_f = 4$ state well-removed at ca. $+400$ cm\textsuperscript{−1} (Fig. 8).

According to observed correlations of $\gamma$ vs. the Ni-O-Ni angle,\textsuperscript{74} $J_{\text{Ni-Ni}}$ decreases markedly with angle, a value of $J_{\text{Ni-Ni}} = 0$ cm\textsuperscript{−1} being anticipated for the Ni-Ni interactions mediated by the Ni-O-Ni bridges near 97° in 1-3.\textsuperscript{‡} In the same way, rather negative 2$J_c$ values are expected for Ni$_i$-O-Ni$_j$.

\begin{align}
\text{Z}_n^\ast &= \frac{N g^2 \beta^2 P}{3kT Q} \quad \text{(3)} \\
\text{where } P &= \Sigma S_f(S_f + 1)(2S_f + 1) \exp(-E_{\text{vib}}/kT) \quad \text{(4)} \\
\text{and } Q &= \Sigma(2S_f + 1) \exp(-E_{\text{vib}}/kT) \quad \text{(5)}
\end{align}

\textsuperscript{†} For appropriate comparison, $J$-values are based on the form of the Hamiltonian in eqn. (4), some literature $J$-values based on an alternative spin-Hamiltonian thus being redesignated here as 2$J$-values.

\textsuperscript{‡} In Table 3, the $J$-values for the Moda\textsuperscript{−} complexes 1-3 (Table 3) are given only for $J_a$, $J_b$, and $J_c$.
angles near 110°. The large Ni₃-O-Ni₃ angles are thus the structural determinant rendering the dominant antiferromagnetic Ni₃–Ni₃ interactions in 1–3 as a significant driver for setting the Ni₃-Ni₃ spins parallel,6,17 via the competing spin interaction.

Consideration of a degenerate frustrated state, which occurs if the ground state is (or is at a crossing with) an Sₚ > 0 state,6 for instance, when Jₐ/Jₙ = 2,17 is more appropriate for the Inaf complexes. The rather different situation for the Inaf complexes 4 and 5 is similar to that for the Mn₃ “butterfly” in Mn₃O₄(C₂H₅OH)₂(bipy)₃ClO₄·3H₂O.28,29 The EₐT values decrease to ca. 0.7 cm⁻¹ K mol⁻¹ at 2 K for 4 and 5, consistent with: (i) both the Jₐ and Jₙ values being negative in each case (the exchanges are all antiferromagnetic) and (ii) Jₐ playing a significant role in the Inaf/Dien compound 4. The magnitudes of Jₐ in both 4 and 5 are greater than those of Jₙ, the Ni₃–Ni₃ exchange interactions dominating in these complexes, presumably in association with larger Ni–O–Ni bridge angles than in the Moda chelates. Although the ground state is again (0,0,0) in the Inaf/Dien complex 4, the (1,2,1) state is very close-lying (1.8 cm⁻¹), and the triplet state (1,1,0) is only 8 cm⁻¹ above ground. On the other hand, the spin ordering in 5 (in which Jₐ/Jₙ is close to two) is essentially the inverse of that for 1–3, and the associated energy levels for 5 include a triplet ground state (1,2,1), followed by a set of quintet, triplet and singlet states forming a manifold at 24 cm⁻¹. In both cases, there are thus numerous spin-multiplet states which become occupied even at relatively low temperatures. The observed JₐT values for complexes 4 and 5 at 2 K are both 0.7 cm⁻¹ K mol⁻¹, which is quite consistent with the expected population of the higher multiplicity states accessible even at this temperature.

The ligand substituents (NiO₂–CH₂ vs Inaf–CH₂H₄) may also be a factor in the difference between complexes 1–3 and 4 and 5. If inductive effects can reduce the electronic density on the oximate bridge and thus affect the NiONi angle. In any case, the magnitude of the Jₐ couplings in 4 and 5 is not sufficient to set the Ni₃ spins parallel as it was in 1–3.

Table 3 Magnetic properties of the nickel(ttt) complexes 1–6

<table>
<thead>
<tr>
<th>Ligand set</th>
<th>g</th>
<th>Jₛ/cm⁻¹</th>
<th>Jₐ/cm⁻¹</th>
<th>Jₐ/Jₘ</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a Dien/Moda⁺⁺</td>
<td>2.14(1)</td>
<td>−19.8(2)</td>
<td>+4.8(22)</td>
<td>0</td>
<td>1.4 × 10⁻⁶</td>
</tr>
<tr>
<td>1b Dien/Moda⁺⁺</td>
<td>2.08(3)</td>
<td>−15.6(6)</td>
<td>0</td>
<td>0</td>
<td>3 × 10⁻¹</td>
</tr>
<tr>
<td>1c Dien/Moda⁺⁺</td>
<td>2.36(1)</td>
<td>−20.0(1)</td>
<td>+10(4)</td>
<td>0</td>
<td>6.0 × 10⁻⁶</td>
</tr>
<tr>
<td>2 Dien/Moda⁺⁺</td>
<td>2.02(2)</td>
<td>−18.3(4)</td>
<td>+9(2)</td>
<td>0</td>
<td>4.8 × 10⁻⁴</td>
</tr>
<tr>
<td>3 Odien/Moda⁺⁺</td>
<td>2.29(1)</td>
<td>−20.2(3)</td>
<td>+4(1)</td>
<td>0</td>
<td>1.8 × 10⁻⁴</td>
</tr>
<tr>
<td>4 Dien/Inaf⁺⁺</td>
<td>2.23(1)</td>
<td>−11.6(3)</td>
<td>−24.0(8)</td>
<td>−4.3(1)</td>
<td>1.0 × 10⁻⁰</td>
</tr>
<tr>
<td>5 Odien/Inaf⁺⁺</td>
<td>2.153(6)</td>
<td>−10.6(7)</td>
<td>−20(2)</td>
<td>0</td>
<td>8.5 × 10⁻¹</td>
</tr>
</tbody>
</table>

* Value in parentheses is ESD in last significant figure. TIP set to 2 × 10⁻⁴ cm⁻¹ mol⁻¹ per Ni. †:p = 0.019(2), ‡:p = 0; values for Jₐ oscillate about zero, with σJₐ/Jₙ.<ref>Fig. 8</ref> Low-lying spin levels in complex 1a.

Compound 4 is comparable with the aforementioned [Ni₄-(μ₃-CO)₆(Acetylene)]ClO₄₂⁻, also characterised as having three negative J values, |Jₐ| > |Jₙ| and a mixed ground state.17 The tetrancelk(ttt) cores in Na₃[Ni₃(H₂O)₂(P(W₆O₁₉)₈)·52H₂O•30 and K₂Na₄[Ni₃(H₂O)₆(P(W₆O₁₉)₈)·24H₂O]•27 are ferromagnetic, while for K₃[β-Si₃Ni₃W₆O₁₉(OH)₆(H₂O)]•20H₂O,22 the ferromagnetic Ni₃–Ni₃ component dominates over the anti-ferromagnetic Ni₃–Ni₃ one, the polyoxotungstate cores providing smaller Ni₃–O–Ni₃ angles. In the pivalate complexes, the sign of the dominant J-value is dependent on the co-ligand.29

The dinuclear compound 6 behaves as an antiferromagnet in the temperature range 2–290 K, with the moment decreasing from 55.8 µµ₅ per Ni at 290 K to 0.2 µµ₅ per Ni at 2 K. The variable-temperature magnetic data were fitted to an exchange expression derived from the appropriate isotropic exchange Hamiltonian:

\[
\mathcal{H} = -2J(S₁S₂ - D(S₁² + S₂²))
\]

taking zero-field splitting into account.46,25 This yielded −2 J = 64.1(2) cm⁻¹, with D = +4.5(3) cm⁻¹. A similar result (−2 J = 79 cm⁻¹) was reported for the nickel(ttt) dimer Ni₃L₄(ClO₄)₄·H₂O (LH is the 1:1 Schiff base from ModaH and tri(2-aminoethyl)amine).26 Both complexes contain flat Ni₃O₄ metalloycles with Ni–Ni distances of 3.705 ± 0.001 Å.

Electronic spectra

CT transitions dominate the spectra, the principal features indicating preservation of the tetrancelk(ttt) cores within a variety of solvent environments, though the MLCT nature of these bands makes them responsive to minor external influences.27 A band in the electronic spectra of 6 (MeCN, λmax = 563 nm, ε = 50 L cm⁻¹ mol⁻¹) is attributed to the A₀g → T₁g(F) transition.77 The attendant 10 Dq value, slightly less than 11,000 cm⁻¹, matches reported data for Ni(ttt) with pseudooctahedral donor sets containing O atoms,78,79 and supplies an affirmation for the assigned g and tip values.75 The intense CT bands observed in the electronic spectra of the tetrancelk(ttt) complexes are absent for dinuclear 6, which has no µ4-OH bridges. Electronic spectroscopic data are in Table S1.†

Electrochemistry

Rotating mercury disk electrode polarography of the Moda/Dien chelate 1 in 0.1 M Na₂EDTA·3H₂O in DMF showed a well-defined but irreversible reduction wave at E₁/₂ = −1.23 V vs. the Ag⁺/Ag reference electrode. The value for Dq (2.4 × 10⁻¹⁰ m² s⁻¹) corresponds to a two-electron redox process (Table 4),41,29 attributable to two simultaneous Ni₃²⁺ → Ni₃³⁺ processes on two different nickel centers. For the Moda/Dien chelate 3, a poorly-defined reduction wave is seen at ca. −1.13 V, while a clear but again irreversible reduction appears at −1.830 V for the Moda/Dien compound 2. Cyclic voltammetry (Pt electrode in acetonitrile) revealed reversible oxidations for 1 at Eo = +0.408 and +0.599 V, assigned to the initial simultaneous
Table 4: Redox potentials for the nickel(ttt) chelates

<table>
<thead>
<tr>
<th>Ligand set</th>
<th>Solvent</th>
<th>E/V</th>
<th>ΔEmV</th>
<th>10^13 Dp/kg m s^-2</th>
<th>n'</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Dien/Moda</td>
<td>MeCN</td>
<td>+0.408</td>
<td>80</td>
<td>3.2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>+0.599</td>
<td>80</td>
<td>2.5</td>
<td>2</td>
</tr>
<tr>
<td>2 Sdien/Moda</td>
<td>MeCN</td>
<td>+0.527</td>
<td>70</td>
<td>3.4</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>+0.715</td>
<td>75</td>
<td>5.0</td>
<td>1</td>
</tr>
<tr>
<td>3 Odien/Moda</td>
<td>MeCN</td>
<td>+0.590</td>
<td>75</td>
<td>3.9</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>+0.807</td>
<td>85</td>
<td>2.6</td>
<td>1</td>
</tr>
<tr>
<td>4 Dien/Inaf</td>
<td>MeCN</td>
<td>+0.660</td>
<td>150</td>
<td>2.0</td>
<td>1</td>
</tr>
<tr>
<td>6 Odien/Inaf</td>
<td>MeCN</td>
<td>+0.869</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* E vs the Ag⁺/Ag (0.01 M AgNO₃/Ag(MeCN) electrode, which is at +298 mV vs the SCE (ref. 48). ΔE = Eₐ - Eₚ,a. Dp = RT f πN, see ref. 41 and footnote-29 of ref. 42. Irreversible, Eₚ,a in rotating (Hg on Hg/Au) disk electrode polarography. n' = 2, Dp = 1.7 × 10^-12 is also credible. Poorly defined wave. Irreversible, Eₚ,a.

Ni²⁺ → Ni³⁺ process at two equivalent nickelos, most probably terminal ones, followed by the corresponding Ni²⁺ → Ni³⁺ at a third nickel ion. For the Sdien/Moda complex 2 in MeCN, the n = 2 oxidation is seen at +0.527 V, with the second oxidation wave at +0.715 V. In the Odien complex 3, the corresponding oxidations are observed at +0.590 and +0.807 V. The potentials of both oxidations are shifted anodically by about 200 mV compared to 1, which is in accord with the previously observed ease of Ni(ttt) oxidation as a function of donor atom strength: aliphatic-N > thioether-S > ether-O: stronger σ-donors stabilize Ni(ttt) relative to Ni(ttt). In addition, we note that the two pairs of Ni²⁺ → Ni³⁺ oxidations are separated in each case by 0.20 ± 0.02 V. For the Inaf–Dien tetramer 4, one quasi-reversible Ni²⁺ → Ni³⁺ oxidation wave was observed (Eₚ,a = +0.660 V), while the dinuclear Odien chelate 6 displayed an irreversible oxidation at Eₚ,a = +0.869 V, attributed to a single Ni²⁺ → Ni³⁺ oxidation followed by rapid product decomposition.

Concluding remarks

Nickel(ttt) perchlorate reacts with Moda or Inaf and tridentate amines to form tetra- and dinuclear nickel(ttt) complexes. The tetranuclear complexes have similar topologies, with four high-spin nickel(ttt) ions at the corners of a rhombus, linked by μ₁-OH and N,O-oximate bridges. The donor atoms capping the terminal nickel(ttt) ions have little influence on the structural features of the Moda complexes. Magnetic susceptibility data indicate that the tetranuclear complexes are antiferromagnetic, with a single ground state arising from antiferromagnetic exchange between the central and terminal nickel(ttt) ions and concomitant spin forcing for the two central nickel(ttt) atoms. The tetranuclear Inaf complexes exhibit all-antiferromagnetic exchanges, yielding triplet ground states for their tetrameric units.

Acknowledgements

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References and notes


31 E. Sinn, *Coord. Chem. Rev.*, 1970, 5, 313. For tetranickel(n), \(S_2\) and \(S_4\) may take values of \(-2, -1, 0, 1\) and \(S_4\) ranges from 0 to 4. For instance, triplet states of \(S_4\) are associated with \([S_1, S_4]=\{0,1\}\) or \([1,0]\), yielding \((1,0,1)\) and \((1,1,0)\), the latter depictable as \(\downarrow\uparrow\uparrow\downarrow\).

30 J. H. van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford University Press, Oxford, 1932. With the other symbols having their usual meanings, the temperature-independent paramagnetism and the metal mole fraction as paramagnetic impurity are denoted tip and \(\rho\), respectively, and 

\[
\chi(T) = \chi_{\text{tip}} + \chi_{\rho} = \chi_{\text{tip}} + \frac{N\chi_{\text{tip}}^\text{eff}}{\chi_{\rho}^\text{eff}}
\]

with \(\chi_{\text{tip}}^\text{eff} = \chi_{\text{tip}}(T)\), \(\chi_{\rho}^\text{eff} = \chi_{\rho}(T)\), and \(N\) the number of paramagnetic impurities.


18 J. E. Greedan, *J. Phys. Soc. Jpn.*, 1970, 5, 313. For tetranickel(n), \(S_2\) and \(S_4\) may take values of \(-2, -1, 0, 1\) or \(S_4\) ranges from 0 to 4. For instance, triplet states of \(S_4\) are associated with \([S_1, S_4]=\{0,1\}\) or \([1,0]\), yielding \((1,0,1)\) and \((1,1,0)\), the latter depictable as \(\downarrow\uparrow\uparrow\downarrow\).

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\[
\chi(T) = \chi_{\text{tip}} + \chi_{\rho} = \chi_{\text{tip}} + \frac{N\chi_{\text{tip}}^\text{eff}}{\chi_{\rho}^\text{eff}}
\]

with \(\chi_{\text{tip}}^\text{eff} = \chi_{\text{tip}}(T)\), \(\chi_{\rho}^\text{eff} = \chi_{\rho}(T)\), and \(N\) the number of paramagnetic impurities.


