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 {Ni(Dien)}$_2$(μ_3-OH)$_2${Ni$_2$(Moda)$_4$}(ClO$_4$)$_2$·Solv (Solv = H$_2$O, **1a**; Solv = 2CH$_3$NO$_2$, **1b**; Solv = 2H$_2$O·2C$_4$H$_8$O$_2$, **1c**), {Ni(Sdien)}$_2$(μ_3-OH)$_2${Ni$_2$(Moda)$_4$}(ClO$_4$)$_2$·H$_2$O (**2**), {Ni(Odien)}$_2$(μ_3-OH)$_2${Ni$_2$(Moda)$_4$}(ClO$_4$)$_2$·0.6H$_2$O (**3**), {Ni(Dien)}$_2$(μ_3-OH)$_2${Ni$_2$(Inaf)$_4$}(ClO$_4$)$_2$·CH$_3$NO$_2$ (**4**) and {Ni(Odien)}$_2$(μ_3-OH)$_2${Ni$_2$(Inaf)$_4$}(ClO$_4$)$_2$·2NaClO$_4$·2H$_2$O (**5**) and the dinuclear complex (Ni{Odien})$_2$-(Moda)$_2$(ClO$_4$)$_2$ (**6**) have been prepared (Dien = 1,5-diamino-3-azapentane, Odien = 1,5-diamino-3-oxapentane, Sdien = 1,5-diamino-3-thiapentane, ModaH = butane-2,3-dione monooxime, InafH = phenylglyoxaldoxime). 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 magnetochemistry, 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[1–3] and as models for metal active sites in proteins, many of which contain polymetallic cores.[4,5] During the last few years, phenomena such as spin frustration[6] and single molecule magnetism[7,8] 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[9–12] topology for their polynuclear core, though several tetranuclear nickel(II) complexes possessing topologies without high symmetry have also been examined.[13–16] Only a few examples of rhombic tetranuclear nickel(II) complexes are known,[17–23] the majority of which were prepared by insertion of nickel(II) ions into polyoxotungstates[19–23] or contain trimethylacetates as bridging groups,[24–26] 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.[18,19] A μ_3-CO$_3^{2-}$-bridged example has also been reported.[17] Although several tetrameric cubane-type nickel(II) complexes have been examined and correlations have been found[9] between Ni–O–Ni angles and exchange integrals (J-values), the magnetochemical 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.[27] Previous work on Fe$_4$ and Mn$_4$ rhombic "butterflies" revealed phenomena of fundamental interest, such as different kinds of spin frustration,[28,29] 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, dimethylglyoxime 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.[30–33] Oximes containing additional nitrogen, phenolate 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 monooxime,[34–38] complexes with 2,6-diacylphenol dioximes[39–41] and with the dioxime of 4,7-dithiadecane-2,9-dione.[42] 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.[43,44] 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-diketomonooxime ligands 2,3-butanedione monooxime (ModaH) and phenylglyoxaldoxime (InafH) (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.

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† Electronic supplementary information (ESI) available: mass spectra, χT vs. T, response of magnetic properties, low-lying spin levels and UV-VIS data. See http://www.rsc.org/suppdata/dt/b3/b300539a/
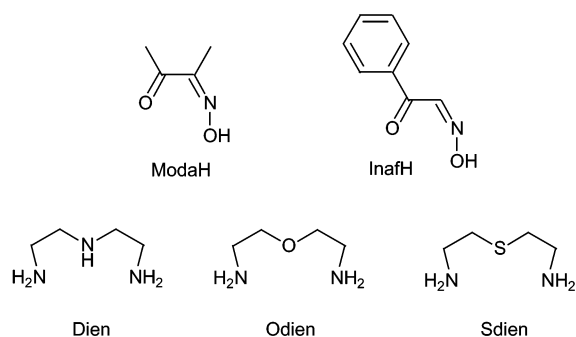
ModaH   InafH

Dien   Odien   Sdien

Fig. 1 Ligands treated in this work.

Experimental

Materials

The sodium salt of phenylglyoxaldoxime (2-isonitrosoaceto-phenone; 2-phenylethan-2-one-1-aldoxime; Inaf⁻Na⁺)[45] and the Odien[46] were prepared according to literature procedures. Other reagents were commercially available (Aldrich and Ukr-ReaChim) and were used without further purification. The dioxane used throughout was the 1,4-isomer. Acetonitrile for electrochemistry was distilled off P_4O_{10} under N_2 and N,N-di-methylformamide (DMF) off CaH_2 under a reduced pressure (10 Torr) of N_2, while ethers were treated with aqueous iron(II) and/or distilled off Na-metal.

Physical measurements

Fast-atom bombardment (FAB) mass spectra were run on a Micromass-VG 70SE instrument, while electrospray ionis-ation mass spectra (ESI-MS) were obtained from a Micro-mass Electrospray MS platform. Mass spectra are reported by denoting the complex cation as the species M. X-Ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometer (**1a′**, **1b** and **1c**) or Siemens P4S diffractometer (other complexes), using the ω–2θ scan technique. Structures were solved with the help of SIR-92[47] (**1a′** and **1b**), SIR-99[48] (**1c**), SHELXS-86[49] (**1a**, **2**, **3** and **6**) and refined by SHELXL-97[50] (**1a′**, **1b** and **1c**), or SHELXL-93[51] (**1a**, **2**, **3** and **6**) by full-matrix least-squares on F^2. H atoms were treated by a riding model. Disorder was a problem, particularly for the $MeNO_2$ molecules of **1b**: atom C10A/B is disordered over two positions with a side occupancy factor (sof) of 0.55/0.45. The atoms were refined with isotropic temperature factors using different but fixed sof until the U_{iso} converged, after which the structure was re-refined with anisotropic temper-ature factors. O3L (a disordered perchlorate-O) and N1L–O5L were refined isotropically. Variable-temperature magnetic susceptibility data were collected in the range 2–290 K using a Quantum Design SQUID magnetometer, employing an applied field of 1 T and a gradient field of 10 T m⁻¹. Susceptibility data were corrected for diamagnetism using Pas-cal's constants[52] and $Co[Hg(SCN)_4]$ was used as a calibration standard. Electrochemical measurements were made at 25 °C as described previously,[42] on deoxygenated CH_3CN or DMF solutions using a PI-50 potentiostat or a BAS 100A electro-chemical analyzer. The three-electrode assembly comprised the working electrode, a Pt auxiliary electrode and an Ag⁺/Ag reference electrode (0.01 M $AgNO_3$, 0.1 M NEt_4ClO_4, CH_3CN), which is at +298 mV vs. the SCE.[53] The work-ing electrodes were Pt disks or wires for voltammetry (at scan rates from 20 to 2000 mV s⁻¹) and an Hg/Au disk for rotating disc electrode polarography (wherein $E_{1/2}$ is defined[54] as $i = i_L/2$). The supporting electrolyte was 0.1–0.2 M NEt_4ClO_4 and solutions for voltammetry and polarography were ca. 1 mM in complex.

Syntheses

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

[{Ni(Dien)}₂(μ₃-OH)₂{Ni₂(Moda)₄}](ClO₄)₂·H₂O (1a)

1.46 g (4 mmol) of $Ni(ClO_4)_2·6H_2O$ 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 Dien in 10 mL ethanol. The solution was warmed to clarify it, after which 0.61 g (6 mmol) of Et_3N was added. The resulting crystalline purple–brown precipitate (**1**) was filtered off, recrystallized from a benzonitrile/MeCN/dioxane (2 : 1 : 1) mixture and air-dried, to give 0.93 g of black blocks. Yield 85%. Anal: Calcd. for $C_{24}H_{54}Cl_2N_{10}Ni_4O_{19}$ (Found): C, 26.4(26.3); H, 4.95(4.90); N, 12.8(12.8); Ni, 21.5(21.5)%. ES-MS: 975 ((M + ClO₄)⁺). IR (in KBr), cm⁻¹: 3385s (ν(NH)); 2930w (ν(CH)); 1630m, 1470s (ν(C=O) + δ(NH₂) + ν(C=N)); 1385s (δₐₛ(CH₂)); 1340w (δₛ(CH₂)); 1240m (ν(N–O)); 1120s (ν(ClO₄)); 980m, 655m, 625m (δ(ClO₄⁻)). Re-crystallization of **1** from mixture of nitromethane and dioxane (3 : 1) produced the $MeNO_2$ disolvate {Ni(Dien)}₂(μ₃-OH)₂{Ni₂-(Moda)₄}(ClO₄)₂·2CH₃NO₂ **1b** (yellow plates), while recrystal-lization from a 1 : 1 $MeNO_2$: dioxane mixture gave the dioxane/water solvate {Ni(Dien)}₂(μ₃-OH)₂{Ni₂(Moda)₄}(ClO₄)₂·2H₂O·2C₄H₈O₂ **1c** (black–brown blocks). Anal.: For **1b**: $C_{26}H_{58}Cl_2N_{12}Ni_4O_{22}$: Calc.(Found): C, 26.1(26.0); H, 4.85(4.85); N, 14.0(14.0); Ni, 19.6(19.6)%. For **1c**: $C_{32}H_{72}Cl_2N_{10}Ni_4O_{24}$: Calc.(Found): 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 **1b** and **1c** were identical with those for **1a**.

[{Ni(Sdien)}₂(μ₃-OH)₂{Ni₂(Moda)₄}](ClO₄)₂·H₂O (2)

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.: $C_{24}H_{52}Cl_2N_8Ni_4O_{19}S_2$: Calc.(Found): C, 25.6(25.2); H, 4.62(4.20); N, 9.95(9.51)%. ES-MS: 1007 ((M + ClO₄)⁺). IR (in KBr), cm⁻¹: 1393m, 1182s (ν(N–O)); 1100s (ν(ClO₄)); 900m; 800w; 720w; 690w; 630m (δ(ClO₄⁻)).

[{Ni(Odien)}₂(μ₃-OH)₂{Ni₂(Moda)₄}](ClO₄)₂·0.6H₂O (3)

To a solution of 0.145 g of **6** in 4 mL of MeCN was added 0.146 g (0.4 mmol) of $Ni(ClO_4)_2·6H_2O$ 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 overnight. The black crystalline (blocks) precipitate which formed was filtered off and air-dried. Yield 0.175 g (80%). Anal.: $C_{24}H_{51.2}Cl_2N_8Ni_4O_{20.6}$: Calc.(Found): C, 26.50(26.5); H, 4.71(4.70); N, 10.31(10.42); Ni, 21.6(21.0)%. ES-MS: 974 (M + ClO₄⁺). IR (in KBr), cm⁻¹: 3360s (ν(NH)); 2950w (ν(CH)); 1615s, 1475s, 1450s (ν(C=O) + δ(NH₂) + ν(C=N)); 1390m (δₐₛ(CH₂)); 1350w (δₛ(CH₂)); 1270m, 1250m (ν(N–O)); 1125s (ν(ClO₄)); 985m, 660m, 625m (δ(ClO₄⁻)).

[{Ni(Dien)}₂(μ₃-OH)₂{Ni₂(Inaf)₄}](ClO₄)₂·CH₃NO₂ (4)

$Ni(ClO_4)_2·6H_2O$ (1.46 g, 4 mmol) were added to 0.684 g (4 mmol) of InafNa and 0.206 g (2 mmol) of Dien in 15 mL of 96% ethanol at ambient temperature, followed by Et_3N (0.202 g, 2 mmol). The resulting green precipitate was filtered off, recrystallized from 1 : 1 $MeNO_2$: dioxane and air-dried,

giving 1.06 g (80% yield) of green microcrystals. Anal.: $C_{41}H_{55}Cl_2N_{11}Ni_4O_{20}$: Calc.(Found): C, 37.1(37.9); H, 4.15(4.20); N, 11.62(11.25); Ni, 17.7(17.8)%. ES-MS: 1165 ($(M + ClO_4)^+$). IR (in KBr), cm^{-1}: 3350s (ν(NH)); 2930w (ν(CH)); 1595m, 1575m, 1465s (ν(C=O) + δ(NH$_2$) + ν(C=N) + ν(NO$_2$)); 1430m (ν(C=C)); 1200m (ν(N–O)); 1150s (broad) (ν(ClO$_4^-$)); 895m; 710m; 685m; 625m (δ(ClO$_4^-$)).

[{Ni(Odien)}₂(μ₃-OH)₂{Ni₂(Inaf)₄}](ClO₄)₂·2NaClO₄·2H₂O (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.: $C_{40}H_{54}Cl_4N_8Ni_4Na_2O_{30}$: 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 (ν(N–O)); 1100s (ν(ClO$_4$)); 900m; 800w; 720w; 690w; 630m (δ(ClO$_4^-$))

[Ni₂(Moda)₂(Odien)₂](ClO₄)₂ (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$_2$O 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.: $C_{16}H_{36}N_6O_{14}Cl_2Ni_2$: Calc.(Found): C, 26.50(26.55); H, 4.97(5.50); N, 11.60(11.65); Ni, 16.2(16.2)%. ES-MS: 625 ($(M + ClO_4)^+$). IR (in KBr), cm^{-1}: 1620, 1450 (δ(NH$_2$) and ν(C=N)); 1260 (ν(N–O)); 1100 (ν(ClO$_4^-$)); 665, 625 (δ(ClO$_4^-$)).

CCDC reference numbers 155327 (**1c**), 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 Sdien (1 equiv.) with the monooxime of a 1,2-diketone (2 equiv.) and Ni(ClO$_4$)$_2$·6H$_2$O (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$^-$HNEt$_3^+$ or PhCH$_2$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[55–58] along with indications of the metal-induced hydrolysis of such compounds.[57,58]

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$_3$N (2, 2 and 4 equiv. per equiv. of **6**, respectively) in MeCN produced the tetranuclear complex **3**. Use of appropriately stoichiometric quantities of reagents gave **6** in better yield, as described in the experimental section.

Table 1 Crystallographic data for complexes 1–3 and 6

Complex	1a	1a'	1b	1c	2	3	6
Empirical formula	$C_{24}H_{54}Cl_2N_{10}Ni_4O_{19}$	$C_{24}H_{54}Cl_2N_{10}Ni_4O_{19}$	$C_{26}H_{54}Cl_2N_{12}Ni_4O_{22}$	$C_{32}H_{72}Cl_2N_{10}Ni_4O_{24}$	$C_{24}H_{54}Cl_2N_8Ni_4O_{20}S_2$	$C_{24}H_{51.2}Cl_2N_8Ni_4O_{20.6}$	$C_{16}H_{36}Cl_2N_6Ni_2O_{14}$
FW	1092.43	1092.43	1195.8	1286.7	1144.61	1087.27	724.83
Space group	$P2_1/c$	$P2_1/c$	$Cmca$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
$a/\text{Å}$	10.6517(3)	10.7475(6)	15.137(5)	10.4880(7)	9.6136(6)	9.7838(6)	8.5117(6)
$b/\text{Å}$	17.5058(6)	17.8722(16)	14.921(7)	16.1935(10)	13.7058(9)	20.327(2)	9.9561(8)
$c/\text{Å}$	22.544(1)	22.8691(17)	21.516(12)	16.2944(11)	16.8831(11)	11.1143(9)	10.3216(9)
$\beta/°$	92.53(1)	92.903(5)	90	106.9580(10)	95.52(1)	111.50(1)	75.05(2)^a
$V/\text{Å}^3$	4199.6(3)	4387.3(6)	4860(4)	2647.1(3)	2214.2(2)	2056.6(3)	708.67(10)
Z	4	4	8	2	2	2	1
μ/mm^{-1}	1.977	3.76	3.511	1.589	1.971	2.020	1.591
Reflections measured	34327	8878	7142	24155	20491	20067	7625
Unique reflections	12100	8878	2568	6524	6463	5995	4602
R_w^{2b}	0.1158	0.2389	0.3200	0.1103	0.1604	0.0927	0.0727
R^{2b}	0.0539	0.1478	0.1755	0.1495	0.0921	0.0563	0.0342

^{a} Triclinic, $\alpha = 62.35(2)°$, $\gamma = 66.71(2)°$. ^{b} Calculated from all data.

Complex	1a′ (295 K)	1a (100 K)	1b (295 K)	1c (295 K)	2 (100 K)	3 (100 K)
Ni_c–O	2.032; 2.053	2.016; 2.046	2.069; 2.069	2.038; 2.039	2.046; 2.049	2.047; 2.037
Ni_t–O	2.066	2.048	2.048	2.069	2.059	2.042
Ni_c–Ni_c	3.067	3.056	3.073	3.070	3.073	3.072
Ni_c–Ni_t	3.408; 3.392	3.389; 3.382	3.398; 3.398	3.412; 3.397	3.398; 3.389	3.384; 3.386
Ni_t–Ni_t	6.067	6.047	6.061	6.077	6.052	6.033
Ni–Ni[a]	7.210	7.066	7.485	7.807	8.243	8.193
Ni_c–O–Ni_c	97.34	97.61	95.90	97.73	97.24	97.55
Ni_c–O–Ni_t	112.51; 110.88	113.01; 111.38	111.21; 111.21	112.37; 111.61	111.72; 111.17	112.22; 111.70
Ni_t–Ni_2O_2	124.58	124.67	122.70	124.69	123.58	124.58

[a] The closest intermolecular Ni–Ni separation.

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 $[Ni_4(Moda)_4(Dien)_2(\mu_3\text{-}OH)_2(ClO_4)]^+$ and the deprotonated and perchlorate-stripped $[Ni_4(Moda)_4(Dien)_2\text{-}(\mu_3\text{-}OH)(\mu_3\text{-}O)]^+$ 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 $[Ni_4(Moda)_4(Sdien)_2(\mu_3\text{-}OH)_2(ClO_4)]^+$ ($m/e = 1007$) and $[Ni_4(Moda)_4(Sdien)_2(\mu_3\text{-}OH)_2]^+$ ($m/e = 908$) with approximately equal intensities. In the mass spectrum of **3**, a peak assigned to the deprotonated (oxo-) species $[Ni_4(Moda)_4(Odien)_2(\mu_3\text{-}O)_2]^+$ ($m/e = 873$) is approximately ten times more intense than the $[Ni_4(Moda)_4(Odien)_2(\mu_3\text{-}OH)(\mu_3\text{-}O)(ClO_4)]^+$ 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 $Ni_3O(Moda)_3^+$ 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 $[Ni_4(OH)_2(Dien)_2\text{-}(Inaf)_4(ClO_4)]^+$ and to $[Ni_4(O)_2(Dien)_2(Inaf)_4]^+$ 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 $[Ni_4(OH)_2(Odien)_2(Inaf)_4\text{-}(ClO_4)]^+$ 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 $[Ni_3O(Inaf)_3]^+$ core ion.

The dinuclear Moda⁻/Odien complex **6** displayed an intense peak at $m/e = 625$ corresponding to ClO_4^--adduced $Ni_2\text{-}(Odien)_2(Moda)_2^{2+}$. Peaks at $m/e = 519$ and 262 are attributed to $[Ni_2(Moda)_2(Odien)]^+$ and $[Ni(Odien)(Moda)]^+$.

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
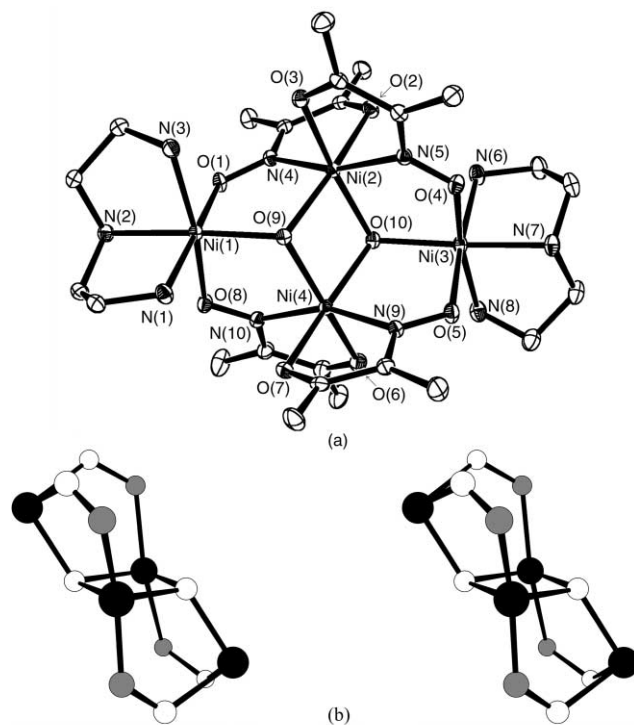
Fig. 2 (a) ORTEP plot of the $[\{Ni(Dien)\}_2(\mu_3\text{-}OH)_2\{Ni_2(Moda)_4\}]^{2+}$ cation of **1a**. H atoms omitted for clarity. Ni(3) and Ni(4) are the counterparts of Ni(1) and Ni(2). Selected bond lengths (Å): Ni(1)–O(9) 2.048(2); Ni(1)–O(8) 2.057(2); Ni(1)–O(1) 2.078(2); Ni(1)–N(2) 2.098(2); Ni(1)–N(3) 2.099(2); Ni(1)–N(1) 2.108(2); Ni(2)–O(9) 2.016(2); Ni(2)–N(5) 2.026(2); Ni(2)–N(4) 2.028(2); Ni(2)–O(10) 2.043(2); Ni(2)–O(2) 2.095(2); Ni(2)–O(3) 2.102(2); Ni(3)–O(10) 2.042(2); Ni(3)–O(5) 2.044(2); Ni(3)–N(7) 2.087(2); Ni(3)–O(4) 2.095(2); Ni(3)–N(6) 2.099(2); Ni(3)–N(8) 2.116(2); Ni(4)–N(9) 2.013(2); Ni(4)–N(10) 2.014(2); Ni(4)–O(10) 2.032(2); Ni(4)–O(9) 2.046(2); Ni(4)–O(7) 2.122(2); Ni(4)–O(6) 2.138(2). (b) Inverse stereoview of the $Ni_4N_4O_6$ "chair" core in **1** (black = Ni, grey = N, white = O).
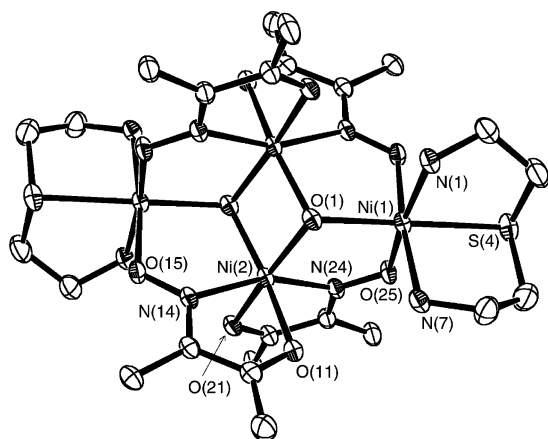
terminal atoms (Ni(1), Ni(3)). In a "butterfly" structural designation, the "c" are often denoted as "body" atoms and the "t" as "wing" atoms. In the complex dication $[Ni(Dien)\}_2\text{-}(\mu_3\text{-}OH)_2\{Ni_2(Moda)_4\}]^{2+}$, the four Ni atoms form a rhomb, planar within 0.001 Å. The Ni_4O_2 core, however, is based on a rhombic Ni_4O_2 "chair" (Fig. 2(b)), the two Ni_c with pseudo-octahedral N_2O_4 donor sets being bridged by hydroxyl ions to form a central $Ni_{c2}O_2$ rhombus. Two terminal nickel(II) atoms are in turn bonded to $\mu_3\text{-}OH^-$ groups on each side of this $Ni_{c2}O_2$ rhombus, so that each $\mu_3\text{-}OH^-$ group acts as the bridge amongst three nickel(II) atoms. The Moda⁻ anions are coordinated to the central nickel(II) atoms *via* their ketone oxygen and oximate nitrogen atoms. The Ni_c–O(ketone) bond lengths in **1a** (2.110 and 2.102 Å at 295 K) are essentially the same as another recently described[59] rare example of a Ni–O(ketone)

bond (2.13 Å). The Ni_ts are additionally anchored to the $Ni_{c2}O_2$ group by oxygens from oximate groups (Fig. 2(b)). The pseudo-octahedral N_3O_3 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).[60]
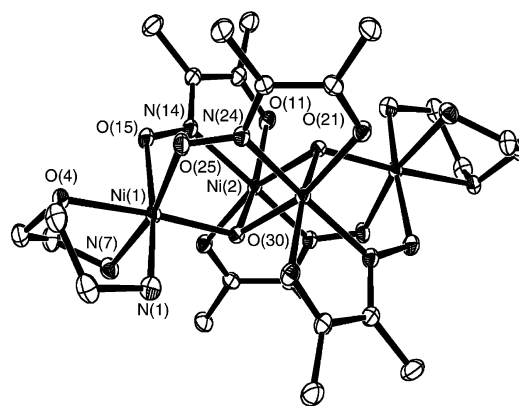
The different solvations have no significant influence on the molecular structure of the complex cation in **1**, but dramatically change the crystal packing. Monoclinic **1a** contains one H_2O molecule per complex cation of [Ni(Dien)}$_2$(μ_3-OH)$_2$-{Ni$_2$(Moda)$_4$}]$^{2+}$ (4 cations per unit cell). 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 H_2O 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 ClO_4^- ions and molecules of solvent, with no layering of cations being apparent, while **1a** possesses packing similar to **1c**, 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_t–Ni_t separation within the complex cation roughly by 1 Å.

Selected structural data for the tetranuclear cations [{Ni-(Sdien)}$_2$(μ_3-OH)$_2${Ni$_2$(Moda)$_4$}]$^{2+}$ in **2** (Fig. 3) and [{Ni-(Odien)}$_2$(μ_3-OH)$_2${Ni$_2$(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 Ni_t–O(ether) bonds are quite long (2.155 Å) – about 0.11 Å longer than the Ni_t–(μ_3-O) bond. The Ni-donor atom distances thus portray the nickel ion as being distorted along its pseudo-C_3 axis (through the centre of the O(25)–O(15)–O(30) triangle and the Ni atom). In the Odien complex **3**, Ni_t 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**.

Previous structurally characterized rhombic Ni_4 complexes with all four nickel(II) atoms in the high-spin $S = 1$ state include
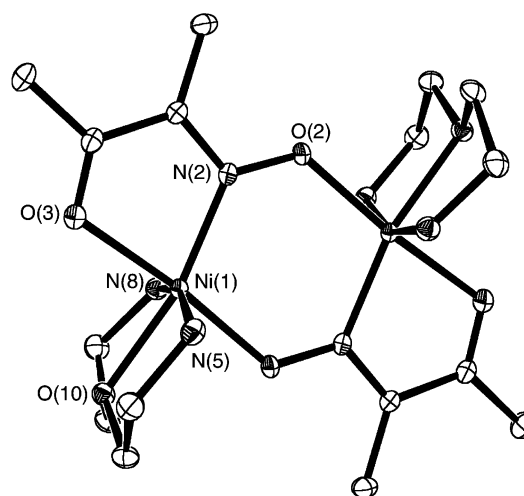

Fig. 4 ORTEP diagram of the [{Ni(Odien)}$_2$(μ_3-OH)$_2${Ni$_2$-(Moda)$_4$}]$^{2+}$ cation of **3**. H atoms are omitted for clarity. Selected bond lengths (Å): Ni(1)–O(30) 2.042(2); Ni(1)–O(25) 2.050(2); Ni(1)–O(15) 2.051(2); Ni(1)–O(4) 2.155(2); Ni(1)–N(7) 2.091(2); Ni(1)–N(1) 2.113(2); Ni(2)–N(14) 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 2.047(2).

[Ni$_4$(μ-CO$_3$)$_2$(Aetpy)$_8$](ClO$_4$)$_2$ (Aetpy = 2-aminoethylpyridine),[17] certain tetranickel units within polytungstate ions [21,22] and some trimethylacetato derivatives.[24–26] In [Ni$_4$(μ-CO$_3$)$_2$(Aetpy)$_8$]-(ClO$_4$)$_2$ the Ni_c–Ni_c and Ni_c–Ni_t 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 Ni$_4$-units in the Moda$^-$ complexes **1**, **2** and **3** might also be compared with the tetranickel cores in the β-Keggin polyoxotungstates.[21,22] These contain an Ni$_4$ "butterfly" bridged by μ_3-O atoms with a Ni_c–Ni_c distance of 3.01 Å, average Ni_c–Ni_t distances of 3.6 Å, Ni_c–(μ_3-O)–Ni_c angles of 94° and average Ni_c–(μ_3-O)–Ni_t angles of 123°.[22] This β-Keggin structure provides approximately the same Ni_c–Ni_c distance compared to **1**, **2** or **3**, but an Ni_c–(μ_3-O)–Ni_c angle reduced by about 3° and an Ni_c–Ni_t distance approximately 0.2 Å longer, which results in different magnetochemical properties, as will be discussed below. Recently reported trimethylacetato-complexes with Ni$_4$(μ_3-O)$_2$ cores have the nickel(II) atoms additionally bridged by (CH$_3$)$_3$CCO$_2^-$ groups.[24–26] The Ni_c–Ni_c distances are 3.1 Å, the Ni_c–Ni_t 3.5 Å, while the Ni_c–(μ_3-O)–Ni_t and Ni_t–(μ_3-O)–Ni_t angles average 97 and 115° respectively – structural features rather similar to those found in the Moda$^-$ complexes.

In the centrosymmetric dinuclear cation of Ni$_2$(Moda)$_2$-(Odien)$_2$$^{2+}$, **6** (Fig. 5), two nickel(II) atoms are bound by two

Fig. 3 ORTEP diagram of the [{Ni(Sdien)}$_2$(μ_3-OH)$_2${Ni$_2$(Moda)$_4$}]$^{2+}$ cation of **2**. H atoms are omitted for clarity. Selected bond lengths (Å): Ni(1)–O(15)#1 2.046(3); Ni(1)–O(25) 2.048(3); Ni(1)–O(1) 2.059(3); Ni(1)–N(1) 2.110(3); Ni(1)–N(7) 2.113(3); Ni(1)–S(4) 2.4361(12); Ni(2)–N(14) 2.036(3); Ni(2)–N(24) 2.041(3); Ni(2)–O(1)#1 2.046(3); Ni(2)–O(1) 2.048(3); Ni(2)–O(11) 2.093(3); Ni(2)–O(21) 2.104(3); O(1)–Ni(2)#1 2.047(3).


Fig. 5 ORTEP plot of the Ni$_2$(Moda)$_2$(Odien)$_2$$^{2+}$ cation of **6**. H atoms are omitted for clarity. Selected bond lengths (Å): Ni(1)–N(2) 2.0201(13); Ni(1)–N(5) 2.0789(13); Ni(1)–N(8) 2.0868(13); Ni(1)–O(10) 2.1008(11); Ni(1)–O(2) 2.0208(12); Ni(1)–O(3) 2.0846(13).

N,O-bridging oximate groups of Moda⁻, thus forming an Ni₂N₂O₂ metallocycle. Each nickel(II) atom possesses a distorted octahedral *mer*-N₃O₃ donor set. The oximate bridges between nickel(II) atoms in **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)₂Cl₂·H₂O[61] and *fac*-Dien in cations of Ni(Dien)₂(TCNQ)₂.[62] Meridionally and facially coordinated Odien were observed[63,64] in Ni(Odien)₂(ClO₄)₂ and Cd(Odien)(SCN)₂, 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(II) similar to that in **2**, has been reported[65,66] for Ni(Sdien)₂(PF₆)₂ and Ni(Sdien)₂(ClO₄)₂.

Magnetochemical properties

The magnetic behaviours of polycrystalline samples of the complexes were measured in the temperature range 2–300 K for **1c** and 2–290 K for the other complexes. For **1a**, the decrease in $\chi_m T$, from 3.74 (at 290 K) to 0.053 cm³ K mol⁻¹ (at 2 K) is representative of these complexes (Fig. 6). As the value of $\chi_m T$
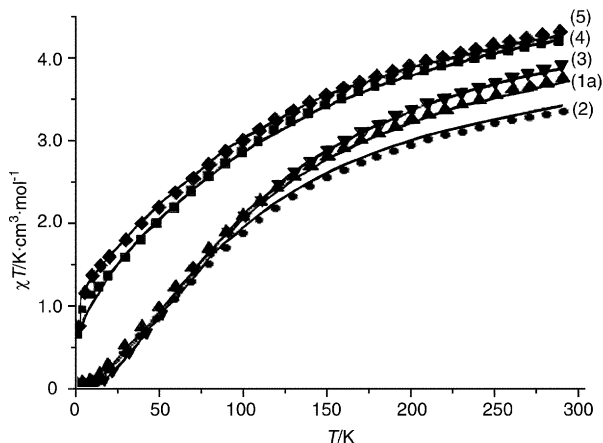
Fig. 6 χT *vs.* T plots for compounds **1a**, **2**, **3**, **4** and **5**. Solid lines represent fits to eqns. (3)–(5), with parameters from Table 3.

for a tetranuclear unit of four non-interacting $S = 1$ Ni(II) ions with $g = 2.0$ would be 4.0 cm³ K mol⁻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 χ *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$_c$ and Ni$_t$ may be represented by the isotropic exchange Hamiltonian [eqn. (1)] for a rhombic arrangement of four $S = 1$ metal centers:

$$\mathscr{H} = -2J_a(S_1 \cdot S_2 + S_1 \cdot S_4 + S_2 \cdot S_3 + S_3 \cdot S_4) - \\ 2J_b(S_1 \cdot S_3) - 2J_c(S_2 \cdot S_4) \quad (1)$$

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$_t$ renders J_c not sensibly different from zero. The spin states are designated as (S_T, S_{13}, S_{24}), where $S_{13} = S_1 + S_3$, $S_{24} = S_2 + S_4$. and $S_T = S_{13} + S_{24}$. The energies of the states corresponding to the various S_T are then[67]

$$E(S_T) = -J_a S_T(S_T + 1) - S_{13}(S_T + 1)(J_c - J_a) - \\ S_{24}(S_{24} + 1)(J_b - J_a) + 4J_b + 4J_c \quad (2)$$

The variable-temperature magnetic data were fitted according to expressions [eqn. (2)–(5)] based on application of the van Vleck equation[68] to Kambe's vector coupling scheme:[69]
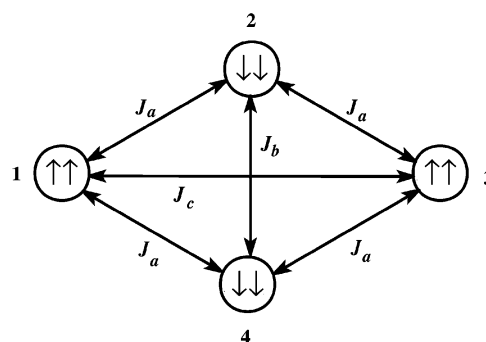
Fig. 7 Coupling scheme for the tetranuclear complexes **1**–**5**. The circles represent nickel(II) ions and the spin orientations illustrate a (0,2,2) state.

$$\chi_m' = \frac{Ng^2\beta^2 \cdot P}{3kT \cdot Q} \quad (3)$$

where $P = \Sigma S_T(S_T + 1)(2S_T + 1) \exp(-E_{(S_T)}/kT)$ (4)

and $Q = \Sigma(2S_T + 1) \exp(-E_{(S_T)}/kT)$ (5)

A similar analytical expression was also attributed to Dubicki,[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_c were negligably small, while for most of the Moda⁻ complexes (**1**–**3**) the $2J_a$ values are −30 to −40 cm⁻¹, with small positive J_b. Relatively weak dependence of χT on the value of a positive J in the presence of competing negative J-values is an expected numerological consequence in clusters of small nuclearity. However, this insensitivity of χT even extends to negative values of J_b in these tetranuclear systems: plots[27] of the dependence of $R^2(\chi T)$ on J_a and J_b for the Moda⁻ 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_b, most notably for **1a** and **1c**. The Dien/Moda⁻ tetramer **1c** (having the largest intermolecular Ni–Ni distance and thus the lowest potential intermolecular coupling) confirms that χT is much more weakly dependent on J_a or J_c than on J_b (see Supplementary Materials †).

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,[6] classical spin frustration cannot appear when $S_T = 0$, so it is more appropriate to consider the positive J_b as the consequence of spin ordering by the dominating J_as. The dominant antiferromagnetic Ni$_c$–Ni$_t$ interaction concomitantly dictates a parallel (pseudoferromagnetic) orientation for the spins of the central nickel atoms. Although the situation for the Moda⁻ chelates **1**–**3** is linked to the idea of *topological spin frustration*,[73] it is more straightforwardly viewable as one of *competing spin interactions*, one consequence being an indeterminability of J_b as previously noted for an Fe₄ "butterfly".[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 [Ni1, Ni2, Ni3, Ni4] = [↑↑, ↓↓, ↑↑, ↓↓], with the first excited spin state (1,2,2) about 40 cm⁻¹ higher, and the $S_T = 4$ state well-removed at *ca.* +400 cm⁻¹ (Fig. 8).

According to observed correlations of J *vs.* the Ni–O–Ni angle,[9,12,17,74] J_{Ni-Ni} decreases markedly with angle, a value of $J_b \approx 0$ cm⁻¹ being anticipated for the Ni–Ni interactions mediated by the Ni$_c$–O–Ni$_c$ bridge angles near 97° in **1**–**3**. ‡ In the same way, rather negative $2J_a$ values are expected for Ni$_c$–O–Ni$_t$

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

Ligand set	g^a	J_a/cm^{-1}	J_b/cm^{-1}	J_c/cm^{-1}	R^2
1a Dien/Moda^{-b}	2.14(1)	−19.8(2)	+4.8(22)	0	1.4×10^{-5}
1b Dien/Moda^{-c}	2.08(3)	−15.6(6)	0^c	0	3×10^{-3}
1c Dien/Moda$^-$	2.36(1)	−20.0(1)	+10(4)	0	6.0×10^{-6}
2 Sdien/Moda$^-$	2.02(2)	−18.3(4)	+9(2)	0	4.8×10^{-4}
3 Odien/Moda$^-$	2.20(1)	−20.2(3)	+4(1)	0	1.8×10^{-4}
4 Dien/Inaf$^-$	2.28(1)	−11.8(3)	−24.0(8)	−4.1(1)	1.0×10^{-4}
5 Odien/Inaf$^-$	2.23(2)	−10.6(7)	−20(2)	0	8.5×10^{-4}
6 Odien/Moda^{-d}	2.153(6)	−32.0(1)	–	–	3.4×10^{-7}

^{a} Value in parentheses is ESD in last significant figure. TIP set to 2×10^{-4} cm^3 mol^{-1} per Ni. ^{b} $\rho = 0.019(2)$. ^{c} $\rho = 0$; values for J_b oscillate about zero, with $\sigma J_b > |J_b|$. ^{d} $D = +4.5(3)$ cm^{-1}.
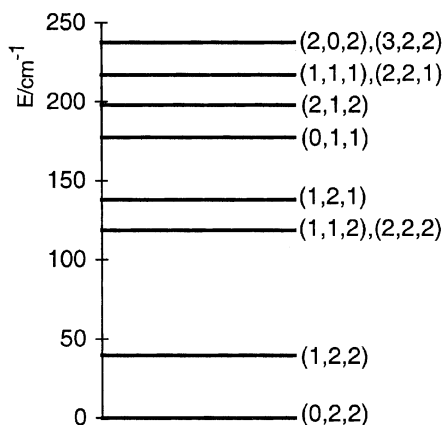
Fig. 8 Low-lying spin levels in complex **1a**.

angles near 110°. The large Ni$_c$–O–Ni$_t$ angles are thus the structural determinant rendering the dominant antiferromagnetic Ni$_c$–Ni$_t$ interactions in **1–3** as a significant driver for setting the Ni$_c$,Ni$_c$ 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 $S_T > 0$ state,[6] for instance, when $J_b/J_a = 2$,[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 Mn$_4$ "butterfly" in Mn$_4$O$_2$(O$_2$CCH$_3$)$_7$(bipy)$_2$(ClO$_4$)·3H$_2$O.[28,29] The $\chi_m T$ values decrease to *ca.* 0.7 cm^3 K mol^{-1} at 2 K for **4** and **5**, consistent with: (i) both the J_a and J_b values being negative in each case (the exchanges are all antiferromagnetic) and (ii) J_c playing a significant role in the Inaf$^-$/Dien compound **4**. The magnitudes of J_b in both **4** and **5** are greater than those of J_a, the Ni$_c$–Ni$_c$ 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 J_b/J_a is close to two[6]) 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 $\chi_m T$ values for complexes **4** and **5** at 2 K are both 0.7 cm^3 K mol^{-1}, which is quite consistent with the expected population of the higher multiplicity states accessible even at this temperature.

The ligand substituents (Moda$^-$–CH$_3$ *vs.* Inaf$^-$–C$_6$H$_5$) 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 J_a couplings in **4** and **5** is not sufficient to set the Ni$_c$ spins parallel as it was in **1–3**.

Compound **4** is comparable with the aforementioned [Ni$_4$-(μ-CO$_3$)$_2$(Aetpy)$_8$](ClO$_4$)$_2$, also characterised as having three negative J values, $|J_a| > |J_b|$ and a mixed ground state.[17] The tetranickel(II) cores in Na$_{16}$[Ni$_4$(H$_2$O)$_2$(P$_2$W$_{15}$O$_{56}$)$_2$]·52H$_2$O[20] and K$_6$Na$_4$[Ni$_4$(H$_2$O)$_2$(PW$_9$O$_{34}$)$_2$]·24H$_2$O[21] are ferromagnetic, while for K$_{12}$[{β-SiNi$_2$W$_{10}$O$_{36}$(OH)}(H$_2$O)}$_2$]·20H$_2$O,[22] the ferromagnetic Ni$_c$–Ni$_c$ component dominates over the antiferromagnetic Ni$_c$–Ni$_t$ one, the polyoxotungstate cores providing smaller Ni$_c$–O–Ni$_c$ angles. In the pivalate complexes, the sign of the dominant J-value is dependent on the co-ligand.[25]

The dinuclear compound **6** behaves as an antiferromagnet in the temperature range 2–290 K, with the moment decreasing from 2.8 μ_B per Ni at 290 K to 0.2 μ_B per Ni at 2 K. The variable-temperature magnetic data were fitted to an exchange expression derived from the appropriate isotropic exchange Hamiltonian:

$$\mathcal{H} = -2J(S_1 \cdot S_2) - D(S_{1z}^2 + S_{2z}^2) \qquad (6)$$

taking zero-field splitting into account.[41,75] This yielded $-2J = 64.1(2)$ cm^{-1}. with $D = +4.5(3)$ cm^{-1}. A similar result ($-2J = 79$ cm^{-1}) was reported for the nickel(II) dimer Ni$_2$L$_2$(ClO$_4$)$_2$·H$_2$O (LH is the 1 : 1 Schiff base from ModaH and tris[2-aminoethyl]amine).[76] Both complexes contain flat Ni$_2$N$_2$O$_2$ metallocycles with Ni–Ni distances of 3.705 ± 0.001 Å.

Electronic spectra

CT transitions dominate the spectra, the principal features indicating preservation of the tetranickel cores within a variety of solvent environments, though the MLCT nature of these bands make them responsive to minor external influences.[77] A band in the electronic spectra of **6** (MeCN, λ_{max} = 563 nm, ε = 50 L cm^{-1} mol^{-1}) is attributed to the $^3A_{2g} \longrightarrow {}^3T_{1g}$(F) transition.[77] The attendant 10 Dq value, slightly less than 11,000 cm^{-1}, matches reported data for Ni(II) with pseudooctahedral donor sets containing O atoms,[77,78] and supplies an affirmation for the assigned g and tip values.[71] The intense CT bands observed in the electronic spectra of the tetranuclear complexes are absent for dinuclear **6**, which has no μ$_3$-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 NEt$_4$ClO$_4$ in DMF showed a well-defined but irreversible reduction wave at $E_{1/2}$ = −1.23 V *vs.* the Ag$^+$/Ag reference electrode. The value for $D\eta$ (2.4 × 10^{-13} kg m s^{-2}) corresponds to a two-electron redox process (Table 4),[41,79] attributable to two simultaneous Ni^{2+} $\longrightarrow$ Ni$^+$ processes on two different nickel centers. For the Moda$^-$/Odien 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$^-$/Sdien compound **2**. Cyclic voltammetry (Pt electrode in acetonitrile) revealed reversible oxidations for **1** at $E_{1/2}$ = +0.408 and +0.599 V, assigned to the initial simultaneous

Table 4 Redox potentials for the nickel(II) chelates

Ligand set	Solvent	$E_{1/2}/V^{a}$	$\Delta E/mV^{b}$	$10^{13}\,D\eta/kg\,m\,s^{-2\,c}$	n^{c}
1 Dien/Moda⁻	MeCN	+0.408	80	3.2	2
	MeCN	+0.599	80	2.5	1
	DMF	−1.230	^{d}	2.4	2
2 Sdien/Moda⁻	MeCN	+0.527	70	3.4	2
	MeCN	+0.715	75	5.0	1
	DMF	−1.830	^{d}	4.8	1^{e}
3 Odien/Moda⁻	MeCN	+0.590	75	3.9	2
	MeCN	+0.807	85	2.6	1
	DMF	−1.13	^{d}	^{f}	
	DMF	−1.17	^{g}		
4 Dien/Inaf⁻	MeCN	+0.660	150	2.0	1
6 Odien/Moda⁻	MeCN	+0.869 ^{g}			

^{a} *Vs.* the Ag^{+} (0.01 M $AgNO_3$)/Ag(MeCN) electrode, which is at +298 mV *vs.* the SCE (ref. 48). ^{b} $\Delta E = E_{p,a} - E_{p,c}$. ^{c} $D\eta = RT/6\pi NR$ (see ref. 41 and footnote-29 of ref. 42). ^{d} Irreversible, $E_{1/2}$ in rotating (Hg on Hg/Au) disk electrode polarography. ^{e} $n = 2$, $D\eta = 1.7 \times 10^{-13}$ is also credible. ^{f} Poorly defined wave. ^{g} Irreversible, $E_{p,a}$.

$Ni^{2+} \longrightarrow Ni^{3+}$ process at two equivalent nickels, most probably terminal ones, followed by the corresponding $Ni^{2+} \longrightarrow Ni^{3+}$ 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(II) oxidation as a function of donor atom strength: aliphatic-N > thioether-S > ether-O: stronger σ-donors stabilize Ni(III) relative to Ni(II).[42,59,80] In addition, we note that the two pairs of $Ni^{2+} \longrightarrow Ni^{3+}$ oxidations are separated in each case by 0.20 ± 0.02 V. For the Inaf⁻–Dien tetramer **4**, one quasi-reversible $Ni^{2+} \longrightarrow Ni^{3+}$ oxidation wave was observed ($E_{1/2} = +0.660$ V), while the dinuclear Odien chelate **6** displayed an irreversible oxidation at $E_{p,a} = +0.869$ V, attributed to a single $Ni^{2+} \longrightarrow Ni^{3+}$ oxidation followed by rapid product decomposition.

Concluding remarks

Nickel(II) perchlorate reacts with Moda⁻ or Inaf⁻ and tridentate amines producing tetra- and dinuclear nickel(II) complexes. The tetranuclear complexes have similar topologies, with four high-spin nickel(II) ions at the corners of a rhombus, linked by by μ_3-OH⁻ and N,O-oximate bridges. The donor atoms capping the terminal nickel(II) ions have little influence on the structural features of the Moda⁻ complexes. Magnetic susceptometry of the tetranuclear Moda⁻ complexes showed a singlet ground state arising from antiferromagnetic exchange between the central and terminal nickel(II) atoms and concomitant spin forcing for the two central nickel(II) atoms. The tetranuclear Inaf⁻ complexes display all-antiferromagnetic exchanges, yielding triplet ground states for their tetrameric units.

Acknowledgements

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