DALTON
FULL PAPER

Nickel(II) complexes with dithiadiiminoamine and dithiabis(thiosemicarbazone) ligands†

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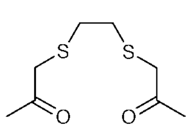
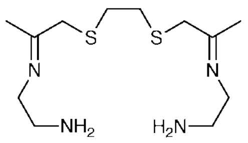
4,7-Dithiadecane-2,9-dione (Dtdk) serves as a starting point for generation of multidentate nitrogen/sulfur chelating agents. Condensation with ethylenediamine or diethylenetriamine yields the neutral hexadentate ligands 1,14-diamino-4,11-dimethyl-6,9-dithia-3,12-diazatetradeca-3,11-diene (Dtdida) and 15-amino-9-methyl-4,7-dithia-10,13-diazapentadec-9-en-2-one (Dtidak) respectively, while the diketone's bis(thiosemicarbazone), itself a neutral ligand, may be deprotonated to form the hexadentate dianion Dtdtz^{2-}. Blue/violet nickel(II) complexes with these ligands have been prepared, *viz.* $\mathrm{Ni(Dtdida)(ClO_4)_2{\cdot}0.5H_2O}$ **1**, $\mathrm{Ni(Dtidak)(ClO_4)_2{\cdot}0.5CH_3CN}$ **4**, $\mathrm{Ni(DtdtzH_2)(ClO_4)_2}$ **2**, and Ni(Dtdtz) **3**; they are all $S = 1$ pseudo-octahedral systems. Although diamines such as ethylenediamine or diethylenetriamine are in principle capable of forming macrocyclic ligands with Dtdk, the products obtained were acyclic. In the case of $\mathrm{Ni(Dtidak)}^{2+}$, a keto-group and a primary amine residue co-exist within the cation, entailing an unusual example of a complex with a non-conjugated ketone coordinated to nickel(II). The coordination spheres of all four complexes have parallel $\mathrm{N_2S_2X_2}$ donor sets, with the ligands similarly folded. The properties of Ni(Dtdtz) evidence significant contribution from the imino-thiolate resonance form of the thioamide moiety. One consequence of this is the relative facility of oxidation of Ni(Dtdtz) to the nickel(III) form, at +0.24 V *vs.* SCE.

Introduction

The factors governing the stabilization/destabilization of nickel(III) and nickel(I) species in various coordination environments are of interest not only for inorganic chemistry,[1,2] but also for biochemistry as nickel in these oxidation states occurs in the active sites of certain hydrogenases and dehydrogenases,[3] and may play a role in the supposed mutagenicity of nickel compounds.[4] EXAFS has shown that redox enzyme nickel ions are bound in S/N-donor environments. Whereas the factors affecting the redox characteristics of the neighboring elements (Fe and Cu) have been elucidated to quite some extent,[5–9] the corresponding aspect of nickel chemistry has been delineated to a much lesser degree. We recently reported the redox characteristics of some nickel complexes with thioether/imine/oxime ligands with quasi-macrocyclic and macrocyclic natures[10–12] and found[10] that, with $\mathrm{DtoxH_2}$, the dioxime of the dithiadiketone Dtdk, $\mathrm{Ni^{II}}$ forms a partially deprotonated trimeric complex. Such ketone precursors thus provide building blocks for a variety of oligonuclear structures based on nickel moieties, and so we have continued to prepare complexes with derivatives of the dithiadiketone Dtdk. We report here the synthesis of new nickel(II) N,S-ligated complexes with its derivatives 1,14-diamino-4,1-dimethyl-6,9-dithia-3,12-diazatetradeca-3,11-diene (Dtdida), 4,7-dithiadecane-2,9-dione bis(thiosemicarbazone) ($\mathrm{DtdtzH_2}$) and 15-amino-9-methyl-4,7-dithia-10,13-diazapentadec-9-en-2-one (Dtidak) as ligands. One specific aim of this study was to attempt to contextualize the redox behaviour of these complexes in regard to the factors influencing the relative stabilization of the various nickel oxidation states.


Dtdk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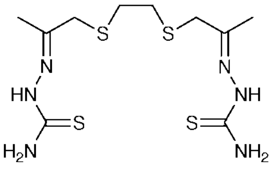
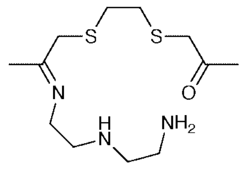

$\mathrm{DtdtzH_2}$


Dtidak

Experimental

Materials

Commercially available reagents (from UkrReaChim and Aldrich Chemical Co.) were used without further purification. 4,7-Dithiadecane-2,9-dione was prepared as described previously.[10] For electrochemistry, $\mathrm{CH_3CN}$ was distilled off $\mathrm{P_4O_{10}}$ under $\mathrm{N_2}$, while dimethylformamide (DMF) was vacuum-distilled (10 Torr) off $\mathrm{CaH_2}$.

Physical measurements

IR spectra were recorded on a Carl Zeiss-Jena Specord-75, electronic spectra on a Carl Zeiss-Jena Specord M40 spectrophotometer, diffuse reflectance spectra in the solid state being obtained from $\mathrm{BaSO_4}$ matrices, and ^{1}H NMR spectra on a Bruker WP250 spectrometer at 20 °C in DMSO-d_6. Mass

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† Electronic supplementary information (ESI) available: IR data and redox potentials. See http://www.rsc.org/suppdata/dt/a9/a906294g/

spectra were obtained from a VG-ZABHF instrument; 2-nitrobenzyl alcohol was used as the matrix for FAB mode. Elemental microanalyses were from a Carlo Erba 1106 C/H/N-microanalyzer. Electrochemical data were obtained using a Bioanalytical Systems BAS-100 electrochemical system, with potentials measured *vs.* the non-aqueous reference electrode Ag^+(0.01 M, 0.1 M NEt_4ClO_4, MeCN)–Ag; this electrode is at +0.296 V *vs.* the SCE; the $E_{1/2}$ for Fc^+–Fc in CH_3CN–NEt_4ClO_4 occurs at +82 mV *vs.* this electrode.[13] All potentials in this paper are reported *vs.* the SCE, using the conversions described recently.[13] The three-electrode cell utilized a platinum wire or rotating platinum disk working electrode, and solutions were deoxygenated by bubbling N_2. Ambient-temperature magnetic susceptibilities were determined using a Johnson Matthey Mk-I benchtop susceptometer.

Structure analyses

X-Ray diffraction procedures were as described previously for application to Ni(Dtdida)$(ClO_4)_2$·$0.5H_2O$,[14] Ni(DtdtzH$_2$)$(ClO_4)_2$,[14] Ni(Dtdtz)[14] and Ni(Dtidak)$(ClO_4)_2$.[15–19] Crystal data are given in Table 1. In the figures, thermal ellipsoids are drawn at the 20% probability level for clarity and H atoms are shown as spheres of arbitrary size.

CCDC reference number 186/1752.

See http://www.rsc.org/suppdata/dt/a9/a906294g/ for crystallographic files in .cif format.

Syntheses

CAUTION: although neither Ni(Dtdida)$(ClO_4)_2$·$0.5H_2O$, Ni(DtdtzH$_2$)$(ClO_4)_2$ nor Ni(Dtidak)$(ClO_4)_2$·$0.5CH_3CN$ has yet proved to be mechanically sensitive, such perchlorates are potentially explosive and should be handled with due caution.

Ni(Dtdida)$(ClO_4)_2$·$0.5H_2O$, 1. 4,7-Dithiadecane-2,9-dione (0.206 g, 1.0 mmol) was added to a solution of $Ni(ClO_4)_2$·$6H_2O$ (0.366 g, 1.0 mmol) and 1,2-diaminoethane (0.120 g, 2.0 mmol) in 70% ethanol (50 cm^3). The resulting solution was heated to 70 °C for 15 min and then allowed to stand for 3 d. The violet crystals formed were filtered off, washed with 70% ethanol, recrystallised from water and dried in air, affording **1** (0.466 g, 85%) (Found: C, 26.1; H, 4.80; N, 10.1; Ni, 10.7. $C_{12}H_{27}Cl_2N_4NiO_{8.5}S_2$ requires C, 25.9; H, 4.86; N, 10.1; Ni, 10.6%). Magnetic moment: μ_{eff}(Ni) = 3.10 μ_B (23 °C). The complex is soluble in acetonitrile or in hot water.

DtdtzH$_2$. A solution of 4,7-dithiadecane-2,9-dione (2.5 g, 12.1 mmol) in 96% ethanol (9 cm^3) was added to a solution of thiosemicarbazide (2.2 g, 24.2 mmol) in 96% ethanol (25 cm^3) at 70 °C. The mixture was stirred under reflux for 0.5 h and then left overnight for crystallization. The white bis(thiosemicarbazone) was filtered off, recrystallized from ethanol–water (2:3) and dried *in vacuo* to give DtdtzH$_2$ (4.1 g, 96%), mp 197–198 °C (decomp.) (Found: C, 33.9; H, 5.90; N, 24.0. $C_5H_{10}N_3S_2$ requires C, 34.1; H, 5.68; N, 23.9%); δ_H(100 MHz; solvent $(CD_3)_2SO$; standard $SiMe_4$) 1.99 (6 H, s, CH_3), 2.60 (4 H, s, CH_2 between C=N and S), 3.31 (4 H, s, SCH_2CH_2S, ^1H coupling unresolved), 7.60 (2 H, NH from former NH_2 due to the tautomerism of thioamides), 8.11 (2 H, NH), 10.06 (2 H, SH from the tautomeric form of C=S).

Ni(DtdtzH$_2$)$(ClO_4)_2$, 2. DtdtzH$_2$ (0.352 g, 1.0 mmol) was added to a solution of $Ni(ClO_4)_2$·$6H_2O$ (0.366 g, 1.0 mmol) in water (15 cm^3) and the mixture stirred at 95 °C. After dissolution of ligand, the dark blue solution was filtered and cooled to 20 °C; filtering off the resulting blue crystals and drying them over $CaCl_2$ resulted in **2** (0.520 g, 85%) (Found: C, 19.4; H, 3.75; N, 13.5; Ni, 9.50. $C_{10}H_{20}Cl_2N_6NiO_8S_4$ requires C, 19.7; H, 3.28; N, 13.8; Ni, 9.63%). μ_{eff}(Ni) = 3.00 μ_B (23 °C) The complex is soluble in acetonitrile and in hot water.

Ni(Dtdtz), 3. An excess of 20% aqueous NH_3 was added to a solution of Ni(DtdtzH$_2$)$(ClO_4)_2$ (0.100 g, 0.16 mmol) in water–CH_3CN (5 cm^3, 1:1 v/v) at 50 °C. Precipitation of blue-grey product began immediately; this was filtered off after 10 min, washed with water and dried over P_2O_5 to afford **3** (0.065 g, 97%) (Found: C, 29.4; H, 4.40; N, 20.6. $C_{10}H_{18}N_6NiS_4$ requires C, 29.6; H, 4.53; N, 20.4%). μ_{eff}(Ni) = 3.01 μ_B (23 °C). The compound is but sparingly soluble in common solvents. Dark blue crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a solution of Ni(Dtdtz) in DMSO (dimethyl sulfoxide).

Ni(Dtidak)$(ClO_4)_2$·$0.5CH_3CN$, 4. To $Ni(ClO_4)_2$·$6H_2O$ (1.77 g, 4.85 mmol) in 70% aqueous ethanol (25 cm^3) was added 4,7-dithiadecane-2,9-dione (1.00 g, 4.85 mmol), followed by slow addition of 0.50 g (4.85 mmol, 0.52 cm^3) of diethylenetriamine. There formed a lilac precipitate, which redissolved after 15 min at reflux. After the reaction mixture was allowed to cool overnight, the lilac crystalline product was filtered off and recrystallized from water. Crystals suitable for X-ray analysis were obtained by diffusion of ether into a solution of this product in a (2:2:1 v–v) PhCN–MeCN/1,4-dioxane mixture, to give deep violet **4** (Found: C, 27.4; H, 4.40; N, 8.40. $C_{13}H_{26.5}Cl_2N_{3.5}NiO_9S_2$ requires C, 27.4; H, 4.69; N, 8.61%). μ_{eff}(Ni) = 3.01 μ_B (23 °C).

Results and discussion

Syntheses

Under the above specific reaction conditions, the condensation of 4,7-dithiadecane-2,9-dione with two equivalents of 1,2-diaminoethane in the presence of nickel(II) leads to the formation of the violet octahedral nickel complex **1**, Ni(Dtdida)$(ClO_4)_2$·$0.5H_2O$. A ^1H NMR examination showed that, in the absence of Ni^{2+} ions, a mixture of condensation products forms, with overall identifiable yield *ca.* 60% in Dtdida, the 1:1 macrocycle and oligomeric products. The net yield of Dtdida in this system did not exceed 10%, as evidenced from the intensities of the CH_3 groups in the integrated ^1H NMR spectra for dithiadiketone reactant and resulting products. This indicates a template role for Ni^{2+} ions in the process of formation and isolation of Ni(Dtdida)$(ClO_4)_2$·$0.5H_2O$.

Reaction of the potentially diprotic ligand DtdtzH$_2$ with nickel(II) perchlorate in water in the absence of base proceeds without deprotonation and the blue perchlorate salt Ni(DtdtzH$_2$)$(ClO_4)_2$ forms. The addition of base to the reaction mixture leads to isolation of the neutral blue-grey complex Ni(Dtdtz).

Condensation of dien with the reactant dithiadiketone in 1:1 molar ratio leads to the formation of the lilac non-macrocyclic complex Ni(Dtidak)$(ClO_4)_2$·$0.5CH_3CN$, in which one keto-group remains free from condensation with the remaining primary amino group of the diethylenetriamine.

The magnetic moments (all corresponding to $S = 1$ states) are consistent with the four chelates entailing six-coordinate Ni^{II}.

Mass spectra

In their FAB mass spectra (Fig. 1) the complexes Ni(Dtdida)$(ClO_4)_2$·$0.5H_2O$, Ni(DtdtzH$_2$)$(ClO_4)_2$ and Ni(Dtdtz) reveal intense peaks for the parent cations: at $m/z = 409$ for ^{58}Ni(DtdtzH)$^+$, and for ^{58}Ni(Dtdida)($^{35}ClO_4$)$^+$ at $m/z = 447$. For Ni(Dtdida)$(ClO_4)_2$·$0.5H_2O$, a peak corresponding to ^{58}Ni(Dtdida − H)$^+$ at $m/z = 347$ was also observed. Peaks attributed to ligand fragmentation *via* C–S bond cleavage were apparent, such as $m/z = 249$ for Ni(Dtdida)$(ClO_4)_2$·$0.5H_2O$ (Ni–ligand fragment from N1(B) to S1(A), bond S1(A)–C4(A) being broken). Analogous fragmentation was observed before in the mass spectra of [Ni(Dtox·2CH_3CNH)][ClO_4]$_2$ (where Dtox·CH_3CNH is the covalent adduct of DtoxH$_2$ with CH_3CN) and Ni_3(Dtox)(DtoxH)$_2$[ClO_4]$_2$.[10]

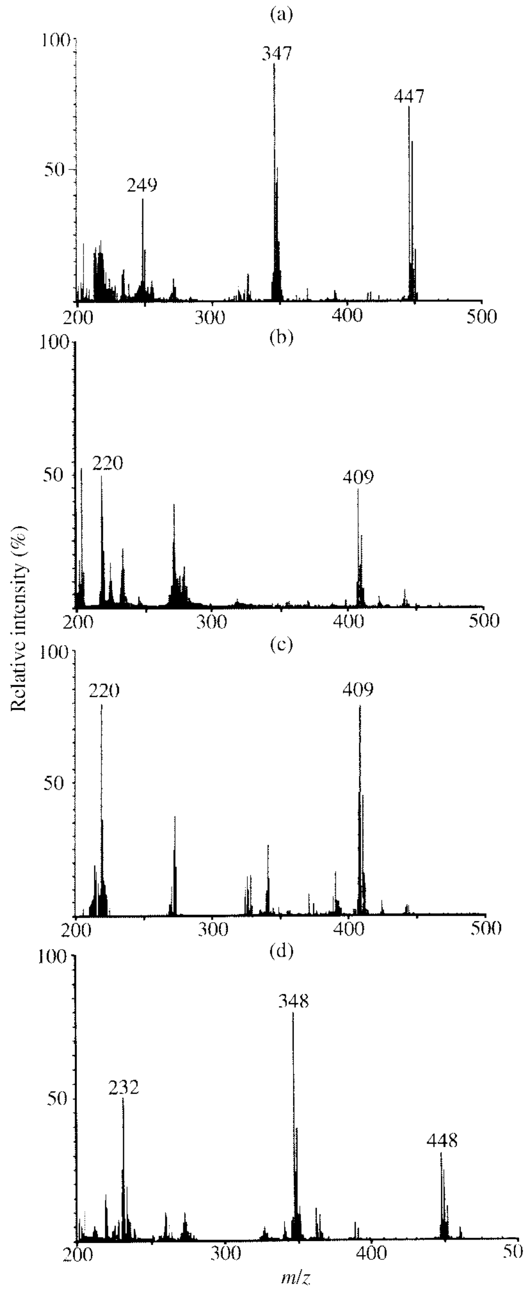

Fig. 1 FAB mass spectra of complexes: (a), Ni(Dtdida)$(ClO_4)_2$·$0.5H_2O$; (b), Ni$(DtdtzH_2)(ClO_4)_2$; (c), Ni(Dtdtz); (d), Ni(Dtidak)·$0.5CH_3CN$.

The Ni(Dtidak)$(ClO_4)_2$·$0.5CH_3CN$ FAB-MS reveals an intense parent peak for ^{58}Ni(Dtidak)$(ClO_4)^+$ at 448 *m*/*z* and a ^{58}Ni(DtidakH)$^+$ signal at 348 *m*/*z*.

Descriptions of the structures

Ni(Dtdida)$(ClO_4)_2$·$0.5H_2O$, 1. In the Ni(Dtdida)$^{2+}$ cation, Ni^{II} displays pseudo-octahedral co-ordination with a *cis*-S_2, *trans*-N_2 (imine) and *cis*-N_2 (amine) arrangement of donor pairs (Fig. 2). The Ni–N (amine) distances are 0.06 Å longer than the Ni–N(imine) ones. These and the Ni–S bond lengths are typical of pseudo-octahedral high-spin nickel(II) complexes,[2,21–27] and at 2.43 and 2.46 Å, are close to the sum (2.44 Å) of the octahedral nickel(II) ionic and the thioether sulfur covalent radii.[24] The bond angles centred at Ni^{II} are somewhat distorted from those for an ideal octahedron, the largest deviations being observed for N(2B)–Ni–N(1A) (99.8°) and N(2A)–Ni–N(1B) (101.8°), *i.e.* the angles formed by only nitrogen atoms. A determinative factor here is the presence of a sequence of only five-membered chelate rings, *i.e.* Dtdida is a 5,5,5,5,5-N_4S_2 chelating agent, and a consequence is that *cis* folding at thioether (and likely also at nitrogen) is thus expected.[28] There are two kinds of NH_2 groups present in the unit cell, one of which hydrogen bonds to the water molecules also present.

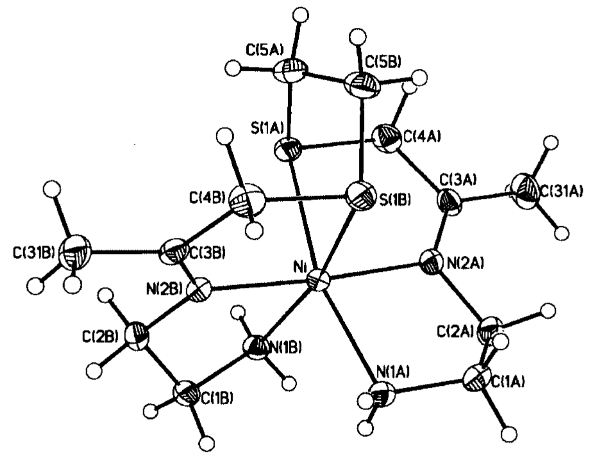

Fig. 2 An ORTEP[20] projection of the complex dication in Ni(Dtdida)$(ClO_4)_2$·$0.5H_2O$, **1**. Some bond lengths (Å) are: Ni–N(2A) 2.039(4); Ni–N(2B) 2.044(4); Ni–N(1B) 2.096(5); Ni–N(1A) 2.107(5); Ni–S(1B) 2.432(2); Ni–S(1A) 2.460(2).

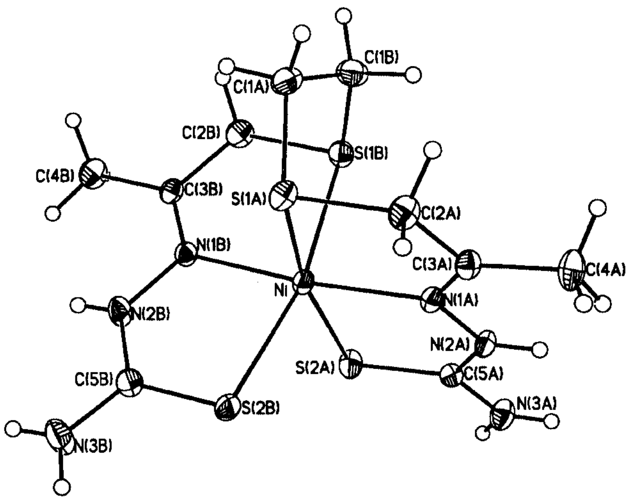

Fig. 3 An ORTEP projection of the dication in Ni$(DtdtzH_2)(ClO_4)_2$, **2**. Some bond lengths (Å) and angles (°) are: Ni–N(1B) 2.045(4); Ni–N(1A) 2.054(4); Ni–S(2A) 2.377(2); Ni–S(2B) 2.383(2); Ni–S(1A) 2.411(2); Ni–S(1B) 2.425(2); S(1A)–C(1A) 1.807(2); S(1A)–C(2A) 1.815(6); S(2A)–C(5A) 1.698(6); S(1B)–C(2B) 1.812(6); S(1B)–C(1B) 1.824(7); S(2B)–C(5B) 1.686(6); N(3A)–C(5A) 1.312(8); N(1A)–N(2A) 1.381(6); N(1B)–Ni–N(1A) 174.4(2); C(2A)–S(1A)–Ni 96.5(2); C(5A)–S(2A)–Ni 96.2(2); C(5B)–S(2B)–Ni 96.1(2); C(3A)–N(1A)–Ni 124.2(4); C(5A)–N(2A)–N(1A) 120.2(5).

Ni$(DtdtzH_2)(ClO_4)_2$, 2. This complex crystallizes as the diperchlorate salt (without ligand deprotonation). In the complex cation (Fig. 3) the nickel atom has a slightly distorted pseudo-octahedral donor set with a *cis*-S_2 (thioether), *cis*-S_2 (thione) and *trans*-N_2 arrangement of donor atoms, with Ni–S (thioether) bonds of 2.41 and 2.43 Å. The thiosemicarbazone moieties coordinate in a didentate manner through their imine nitrogens and thione sulfur atoms. The Ni–N distances (2.05 Å) are closer to those (2.01–2.02 Å) reported[29] for an $NiN_2S_2O_2$ coordination core in which there is significant R_2N^+=C–S^- character in the ligand, than to those (2.10–2.14 Å) for a nickel(II) thiosemicarbazone complex with more thione character in the ligand.[30] The Ni–S (thione) bonds (2.38 Å) are shorter than the Ni–S (thioether) bonds by 0.04 Å (on average) and again are within the range (2.36–2.39 Å) observed recently[29] in the nickel(II) thiosemicarbazone complex with

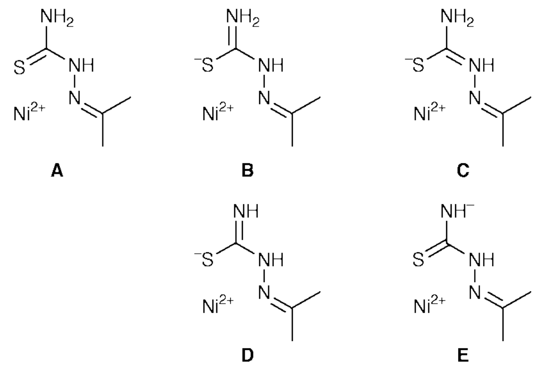

Fig. 4 Alternative resonance structures for Ni(DtdtzH$_2$)$^{2+}$ (**A**–**C**) and Ni(Dtdtz) (**D** and **E**).

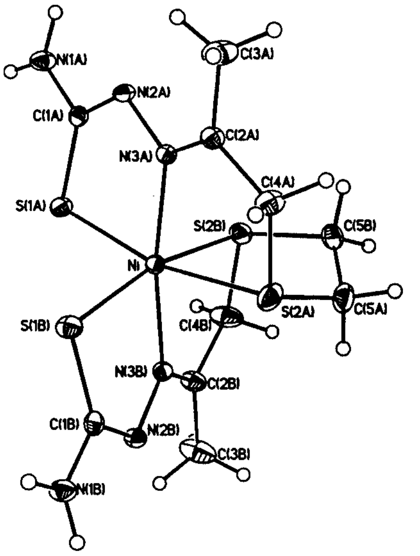

Fig. 5 An ORTEP projection of Ni(Dtdtz), **3**. Some bond lengths (Å) and angles (°) are: Ni–N(3A) 2.027(3); Ni–N(3B) 2.028(3); Ni–S(1B) 2.3414(13); Ni–S(1A) 2.3644(12); Ni–S(2B) 2.4117(14); Ni–S(2A) 2.4299(14); S(1A)–C(1A) 1.735(4); S(2A)–C(4A) 1.788(5); N(1A)–C(1A) 1.344(5); N(2A)–C(1A) 1.322(5); N(2A)–N(3A) 1.391(4); S(1A)–Ni–S(2A) 166.98(5); C(1A)–S(1A)–Ni 93.35(14); C(1B)–S(1B)–Ni 93.88(16).

considerable thiolate contribution. These bond lengths are markedly shorter than those (2.45–2.55 Å) in octahedral nickel(II) complexes with neutral substituted thioureas and thiosemicarbazones.[2,31] One reason for this shortening of the Ni–S(2B) bond in this complex is the impact of the thiolate resonance forms **B** and **C** (Fig. 4). The C=S bond lengths in Ni(DtdtzH$_2$)(ClO$_4$)$_2$ (1.686 and 1.698Å) are actually in the range typical of C=S bonds in non-coordinated thiosemicarbazones (1.68–1.74 Å).[32–35] However, upon thione coordination to Ni^{II}, the C=S distance generally increases (by 0.3–0.4 Å)[30] from the "free" ligand value, manifesting the thiolate resonance contribution. We thus may conclude that in Ni(DtdtzH$_2$)(ClO$_4$)$_2$ the C=S (thione) bonds have some contribution from the thiolate resonance form.

Ni(Dtdtz), 3. In the neutral Ni(Dtdtz) molecule the nickel(II) ion is again situated in an moderately distorted pseudo-octahedral environment, with *cis*-S (thioether) and *cis*-S (thione) donors arranged in a common plane, while the nitrogen donors are in correspondingly apical positions (Fig. 5). The Ni–S (thioether) distances (2.41 and 2.43 Å) are similar to those in Ni(DtdtzH$_2$)(ClO$_4$)$_2$, but the Ni–N bonds (2.03 and 2.03 Å) are shorter by 0.02 Å on average. The Ni–S (thione) bond lengths in Ni(Dtdtz) (2.34 and 2.36 Å) are also shorter than the same bonds in Ni(DtdtzH$_2$)(ClO$_4$)$_2$ (on average by 0.03 Å). As might be anticipated, deprotonation of DtdtzH$_2$ in Ni(Dtdtz) has resulted in an augmentation in the thiolate character, with an average C–S (thione) bond length increase of 0.04 Å, and a decrease in the average N–N bond length by 0.03 Å. DtdtzH$_2$ deprotonation also leads to an increase (by 0.04 Å) in the C–NH$_2$ distance (between the thioamide C atom and non-coordinated N atom of the NH$_2$ group) in Ni(Dtdtz). This change is associated with ascendance of the **D** resonance form relative to the **E** form (Fig. 4), as is supported also by the IR data (see below).

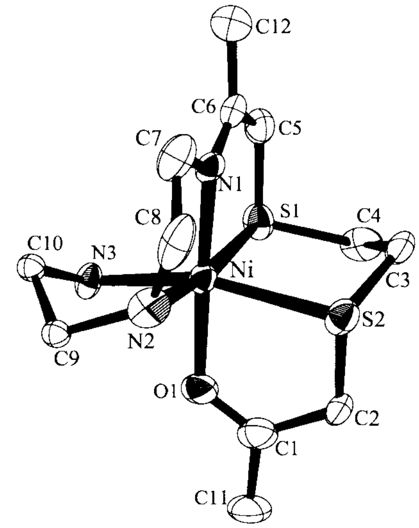

Fig. 6 An ORTEP projection of the complex cation in Ni(Dtidak)(ClO$_4$)$_2$·0.5CH$_3$CN, **4**. The hydrogen atoms are not shown. Some bond lengths (Å) and angles (°) are: Ni–O(1) 2.13(1); Ni–S(1) 2.422(5); Ni–S(2) 2.382(5); Ni–N(1) 2.06(1); Ni–N(2) 2.06(1); Ni–N(3) 2.05(1); S(1)–C(4) 1.74(2); O(1)–C(1) 1.18(2); N(1)–C(6) 1.27(2); N(1)–C(7) 1.47(2); N(3)–Ni–S(2) 163.6(4).

Ni(Dtidak)(ClO$_4$)$_2$·0.5CH$_3$CN, 4. In the Ni(Dtidak)$^{2+}$ cation, nickel(II) possesses a *fac*-N$_3$, *fac*-OS$_2$ distorted octahedral environment with a quite unusual Ni–O (ketone) coordination (Fig. 6). The constraints in the coordination core are likely connected to the keto and amine groups remaining uncondensed in the product complex, in the sense that the alternative macrocycle would presumably be even more strained. Note also the reduction of Ni–N bond lengths in comparison with those commonly observed for unconstrained structures.[34] The Ni–S(2) and Ni–O distances are also rather short.

For the family of complexes with the various ligands derived from 4,7-dithiadecane-2,9-dione, [Ni{(Dtox)(CH$_3$CNH)$_2$}][ClO$_4$]$_2$, Ni$_3$(Dtox)(DtoxH)$_2$(ClO$_4$)$_2$·CH$_3$CN,[10] Ni(Dtdida)(ClO$_4$)$_2$·0.5H$_2$O **1**, Ni(DtdtzH$_2$)(ClO$_4$)$_2$ **2**, Ni(Dtdtz) **3**, and Ni(Dtidak)(ClO$_4$)$_2$·0.5CH$_3$CN **4** (Fig. 1), the arrangements of the various types of donors around Ni^{II} all parallel one another: *cis*-S$_2$ (thioether); *trans*-N$_2$ (imine); *cis*-D$_2$, where D = S (thione), N (amine), O (oxime), N (imine), or N (amine) and C=O (in Ni(Dtidak)$^{2+}$) respectively. Again, this is presumably a consequence of the folding imposed by the five-membered chelate ring sets. All the Ni–S (thioether) bond lengths in these complexes lie in the range of 2.41–2.47 Å, and the Ni–N (imine) distances fall into a 2.00–2.05 Å interval. However it should be noted that in the Ni(DtdtzH$_2$)$^{2+}$ cation the Ni–S (thioether) bonds are slightly shorter than those in Ni(Dtdida)$^{2+}$. Thus, variation of the two donor atoms D in the S$_2$N$_2$D$_2$ donor set for those nickel(II) complexes does have some influence on the other distances.

IR spectra

Bands observed in the IR spectrum (see ESI data) for Ni(Dtdida)(ClO$_4$)$_2$·0.5H$_2$O are consonant with those that have been reported for other nickel(II) complexes with amine,

Table 1 Crystal data for the compounds[a]

	Ni(Dtida)$(ClO_4)_2$·$0.5H_2O$ **1**	Ni($DtdtzH_2$)$(ClO_4)_2$ **2**	Ni(Dtdz) **3**	Ni(Dtidak)$(ClO_4)_2$·$0.5CH_3CN$ **4**
Emp. formula	$C_{12}H_{27}Cl_2N_4NiO_{8.5}S_2$	$C_{10}H_{20}Cl_2N_6NiO_8S_4$	$C_{10}H_{18}N_6NiS_4$	$C_{12}H_{26.5}Cl_2N_{3.5}NiO_9S_2$
Formula weight	547.1	626.17	409.25	568.1
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pccn*	$P2_1/n$	$P2_1/n$	*C*2/*c*
a/Å	6.888(2)	7.649(2)	8.7734(8)	22.046(9)
b/Å	19.831(3)	14.789(3)	7.7896(9)	11.339(4)
c/Å	13.286(2)	21.618(5)	25.061(3)	21.32(1)
β/°		97.40(2)	99.209(5)	117.36(2)
V/Å^3	4449.7(10)	2425.1(9)	690.6(3)	4733(6)3
Z	8	4	4	8
Total reflections	5507	3894	4607	5063
independent	5507	3646	4267	4928
T/K	295(2)	295(2)	295(2)	294(2)
μ(Mo-Kα)/cm^{-1}	12.90	12.90	12.90	12.7
R_{int}	0.000	0.033	0.039	0.118
Rw^b	0.109	0.116	0.089	0.065

[a] The standard deviations are reported in parentheses. [b] On F^2.

Table 2 Electronic characteristics for the compounds[a]

Compound	Medium	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	10 *Dq*[b]	*β*[c]
1 Ni(Dtdida)$(ClO_4)_2$[d]	CH_3CN	276 (sh) (1200), 333 (70), 532 (20), 836 (40)	12.0	0.79
	CH_3NO_2	532 (21), 838 (45)	11.9	0.80
	DMF	328 (86), 529 (21), 833 (39)	12.0	0.80
	Solid	344, 541, 840	11.9	0.73
2 Ni($DtdtzH_2$)$(ClO_4)_2$	CH_3CN	279 (17600), 358 (sh) (1140), 557 (65), 825 (101)	12.1	0.59
	CH_3NO_2	559 (71), 829 (111)	12.1	0.59
	DMF	290 (16100), 323 (sh) (1140), 357 (sh) (798), 557 (61), 825 (95)	12.1	0.59
	Solid	357, 563, 828	12.0	0.56
3 Ni(Dtdtz)	DMF	293 (17200), 314 (14900), 388 (sh) (355), 566 (62), 828 (90)	12.1	0.55
	DMSO	294 (18000), 408 (sh) (386), 563 (62), 828 (105)	12.1	0.56
	Solid	400 (sh), 575, 833	12.0	0.52
4 Ni(Dtidak)$(ClO_4)_2$[e]	CH_3CN	275 (543), 333 (sh) (52), 542 (17), 847 (21)	11.8	0.75
	CH_3NO_2	545 (27), 842 (28)	11.9	0.71
	DMF	345 (sh) (49), 543 (16), 856 (22)	11.7	0.78
	Solid	340, 545, 847	11.8	0.74

[a] At ambient temperature; sh = shoulder. [b] In units of 10^3 cm^{-1}. [c] β = B/B_0, where B_0 is the free Ni^{2+} ion value, 1082 cm^{-1}.[55] [d] The hemihydrate. [e] The CH_3CN hemisolvate.

thiosemicarbazone and azomethine donors.[29–42] A band at 1674 cm^{-1} is attributed to $\nu_{C=N}$. In Ni($DtdtzH_2$)$(ClO_4)_2$ the frequency of the $\nu_{C=S}$ vibration of the "free" ligand at 840 cm^{-1} is lowered by 75 cm^{-1}, clearly indicating the coordination of the thioamide group to the nickel(II) ion. In the neutral complex Ni(Dtdtz) this $\nu_{C=S}$ appears at 740 cm^{-1}, which is 25 cm^{-1} lower in turn than the same vibration in Ni($DtdtzH_2$)$(ClO_4)_2$. Parallel shifts are seen for the δ_{N-H} vibration of the thiosemicarbazone moiety, the "free" ligand band at 1587 cm^{-1} shifting to 1556 cm^{-1} for Ni($DtdtzH_2$)$(ClO_4)_2$ and 1470 cm^{-1} for Ni(Dtdtz). The IR spectra thus evidence that the C=S bond order decreases in the sequence $DtdtzH_2$ > Ni($DtdtzH_2$)$(ClO_4)_2$ > Ni(Dtdtz), in agreement with the X-ray interpretations for the two complexes.

The $\nu_{C=O}$ and $\nu_{C=N}$ absorptions are not well separated for Ni(Dtidak)$(ClO_4)_2$·$0.5CH_3CN$, appearing as overlapping bands at 1695 and 1680 cm^{-1} (sh).[37] We note that the IR spectrum of crude Ni(Dtidak)$(ClO_4)_2$ was not affected by its recrystallization from water.

Electronic spectra

The electronic spectra of all the complexes (Table 2) are typical of pseudo-octahedral high-spin nickel(II) complexes. Three absorptions were observed in the UV-visible region in the electronic spectra of Ni(Dtdida)$(ClO_4)_2$·$0.5H_2O$, Ni($DtdtzH_2$)$(ClO_4)_2$, Ni(Dtidak)$(ClO_4)_2$·$0.5CH_3CN$, (CH_3CN solution) and Ni(Dtdtz) in DMSO. The transitions in the 275–280 nm region are most probably due to S→Ni LMCT,[40,42] while the two bands in the visible region are assigned as d–d transitions. In general, three d–d bands ($^3A_2 \longrightarrow {}^3T_2$; $^3A_2 \longrightarrow {}^3T_{1(F)}$; $^3A_2 \longrightarrow {}^3T_{1(P)}$) are expected in the electronic spectra of octahedral nickel(II) chromophores.[43,44] For many thioether nickel(II) complexes the third d–d band is less intense and usually obscured by S→Ni LMCT transitions. Values of 10*Dq* and *β* extracted from the spectra[44] exhibit the anticipated reduction in the nephelauxetic ratio *β*, as the coordination sphere is enriched in S-donors. It has been suggested that a low *β* in complexes may be connected with the possibility of stabilizing their low oxidation states,[45] as the significant mixing of ligand and metal orbitals implies that any added electron charge could be more efficaciously delocalized.

Redox chemistry

Ni(Dtdida)$(ClO_4)_2$·$0.5H_2O$ displays two redox processes in acetonitrile solution in the −1.0 to +1.5 V potential range. Broad, non-Nernstian cathodic and anodic peaks around the −200 mV region (*vs.* SCE) are attributed to a $Ni^{2+/+}$ redox process. The calculated values for the diffusion coefficients (*D*) and for the Walden product $D\eta^6$ (Table 3) are consistent only with an $n = 1$ redox assignment. Also, both the position of this process at an only moderately negative potential as well as the absence of a $Ni^0(s) \longrightarrow Ni^{2+}$ stripping peak favour its assignment as $Ni^{2+/+}$. However, this same complex undergoes an electrochemically reversible one-electron oxidation process at $E_{1/2} = +1170$ mV. Such an $E_{1/2}$ value is typical of $Ni^{3+/2+}$ redox couples in complexes where nickel is in a mixed sulfur–nitrogen environment. The reversibility of the redox couple is

Table 3 Redox properties of the compounds

Compound	Medium	$E_{1/2}{}^a$/V	$i_c/i_a{}^b$	$\Delta E_p{}^c$/mV	$10^{12}D\eta^d$/m^2 s^{-1}
1 Ni(Dtdida)$(ClO_4)_2\cdot0.5H_2O$	CH_3CN	+1.170	1.0	70	3.8
2 Ni$(DtdtzH_2)(ClO_4)_2$	CH_3CN	+1.235	1.09	95	3.6
3 Ni(Dtdtz)	DMF	+0.236	1.1	67	1.8
4 Ni(Dtidak)$(ClO_4)_2\cdot0.5CH_3CN$	CH_3CN	+1.061	1.08	108^e	3.6

^{a} Estimated as $(E_{p,c} + E_{p,a})/2$, and referred to the SCE. ^{b} Measured from cathodic and anodic peak currents at $v = 100$ mV s^{-1}. ^{c} $E_{p,a} - E_{p,c}$. ^{d} D is the diffusion coefficient and η the absolute viscosity; estimated for $n = 1$ after refs. 46 (voltammetry) and 47 (rotating disk electrode (rde) polarography). ^{e} At $v = 50$ mV s^{-1}.

presumably a result of the maintenance of the same six-coordination in both oxidation states. Comparison of the $E_{1/2}$ value for Ni(Dtdida)$^{3+/2+}$ with other selected redox potentials (see ESI data) indicates that this value is between those for $NiS_6{}^{3+/2+}$ (more positive) and $NiN_6{}^{3+/2+}$ (less positive: aliphatic amine donors) coordination cores. However, $E_{1/2}$ values for $NiN_6{}^{3+/2+}$ couples (heterocyclic nitrogens) are even more positive than those for homoleptic thioether NiS_6 complexes.

The redox behaviour of Ni$(DtdtzH_2)(ClO_4)_2$ is more complicated. This complex displays a one-electron reversible redox process at quite positive potential (>+1 V). The electrochemical characteristics support a one-electron Ni$(DtdtzH_2)^{3+/2+}$ assignment for this process. Substitution of two amine donor atoms in the Dtdida molecule for two thione sulfurs in $DtdtzH_2$ thus destabilizes Ni^{3+} relative to Ni^{2+}, in accord with prior observations.[48,49] At negative potentials, the complex shows an exaggerated, sharp cathodic peak at −1537 mV with an anodic stripping counter-peak at +54 mV, indicating a two-electron reduction with deposition of metallic Ni.[50] It is noteworthy that, by contrast, nickel salicylaldehyde thiosemicarbazone displays a reversible reduction[29] in this potential region.

Mainly because of solubility problems, the electrochemical behavior of Ni(Dtdtz) was examined in DMF rather than MeCN solution. As the complex is coordinatively saturated and the two solvents are of essentially the same polarity, any solvent effect on $E_{1/2}$ is expected to be minor.[51] Ni(Dtdtz) exhibits only one reversible redox process in the potential range −2.0 to +0.5 V. The results (including the rde limiting anodic current) evidence a one-electron Ni(Dtdtz)$^{+/0}$ ($Ni^{3+/2+}$) process. The considerable shift (by 1.0 V) of the $E_{1/2}$ value toward negative potential in comparison with the $E_{1/2}$ observed for Ni$(DtdtzH_2)^{3+/2+}$ accentuates the relative stabilization of Ni^{III} as a result of ligand deprotonation; on average, each anionic charge introduced into the NiN_2S_4 coordination core has lowered the $E_{1/2}$ by *ca.* 500 mV.

Ni(Dtidak)$(ClO_4)_2\cdot0.5CH_3CN$ in acetonitrile showed one quasireversible redox process for which the electrochemical characteristics (Table 3) are again consistent with an $Ni^{3+/2+}$ process: the substitution of one imino donor group in Ni(Dtdida)$(ClO_4)_2\cdot0.5H_2O$ for the keto group in Ni(Dtidak)$(ClO_4)_2\cdot0.5CH_3CN$ leads to the relative stabilization of Ni^{III} by *ca.* 0.10 V.

It is clear that anionic ligands stabilize Ni^{III} relative to Ni^{II}.[10] The exchange of a mercaptide donor group by a thioether one, for instance, results in relative destabilization of Ni^{III} and thus in a positive shift of $E_f(Ni^{2+/3+})$, while six-coordination is also a factor favouring Ni^{III} in contrast to Ni^{I}.[2,52–54]

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