Synthesis, Spectroscopy, and Electrochemistry of Heterocyclic Thionato Complexes of Divalent Nickel: Crystal Structure of Tetraethylammonium *fac*-[tris(benzothiazoline-2-thionato)nickelate(II)]†

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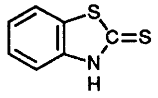
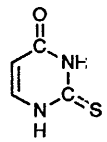
The deprotonated anions derived from benzothiazoline-2-thione ($C_7H_5NS_2$), thiouracil ($C_4H_4N_2OS$) and 6-amino-2,3-dihydro-2-thioxo-(1*H*)-pyrimidin-4-one ($C_4H_5N_3OS$) react with $[NEt_4]_2[NiCl_4]$ in acetonitrile to give $[NEt_4][Ni(C_7H_4NS_2)_3]$, (**1**), $[NEt_4][Ni(C_4H_3N_2OS)_3]$, (**2**), and $[NEt_4][Ni(C_4H_4N_3OS)_3]$, (**3**). Crystal structure analysis shows that (**1**) crystallises in the monoclinic space group $P2_1/n$ with $a = 10.290(1)$, $b = 19.137(2)$, $c = 16.814(2)$ Å, $\beta = 101.95(1)°$, $Z = 4$, $R = 0.082$ from 5 336 unique reflections with $F > 4\sigma(F)$. The $[Ni(C_7H_4NS_2)_3]^-$ anion adopts the confacial isomeric form with the metal in a distorted-octahedral environment formed from three, four-membered, S,N-chelating ligands. Average Ni^{II}–N and Ni^{II}–$S_{thionate}$ distances are 2.070 and 2.555 Å, respectively, and the mean N–Ni^{II}–S angle is 67.8°. Solid-state electronic spectra and room-temperature magnetic moments show that Ni^{II} is octahedrally co-ordinated in complexes (**1**)—(**3**). They also suggest that the anions have the same isomeric form. Electrochemical measurements show the complexes to be irreversibly oxidised in acetonitrile.

The chemistry of nickel with sulphur-containing ligands has attracted considerable attention in recent years with the increased awareness of the significance of nickel–sulphur interactions in biological systems.[1] Attempts to model the active sites in nickel enzymes[2] have been mostly directed towards mononuclear complexes and have generally involved relatively simple alkyl-[3] and arene-thiolates[4] as well as more complicated 'thiolic' ligands designed to produce specific co-ordination geometries and often with the additional advantage of incorporating nitrogen as well as sulphur donor atoms.[5] Heterocyclic thioamides are also S- and/or N-donating, are inherently bioactive, and a useful source of potentially biomimetic ligands especially with nickel and copper.[5] Imidazolethione derivatives (HL) are typical of this group of ligands which we have used in the production of a variety of nickel(II) complexes including paramagnetic tetragonally distorted octahedral species, $[Ni(HL)_4X_2]$ (X = Cl, HL = 1-methylimidazoline-2-thione,[6] X = Cl, Br, I, NCS, NO_3, BF_4, or ClO_4, HL = imidazoline-2-thione[7]), as well as diamagnetic, distorted, square-planar species, $[Ni(HL)_4]X_2$ (X = BF_4,[6] ClO_4,[8] or Br;[9] HL = 1-methylimidazoline-2-thione) and pseudo-tetrahedral species, $[Ni(HL)_2X_2]$ (X = Cl or Br, HL = 1,3-dimethylimidazoline-2-thione).[10] All of the above complexes are mononuclear with monodentate-S donating ligands. Anionic tris chelates obtained by *in situ* deprotonation of pyridine-2-thione (Hpyt) and pyrimidine-2-thione (Hpymt)[11] are the only examples of mononuclear, heterocyclic-thionato, S,N-chelated octahedral complexes of divalent nickel so far reported.

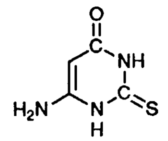
In this paper we extend the range of S,N-chelated complexes of divalent nickel with new complexes derived from benzothiazoline-2-thione, thiouracil [2,3-dihydro-2-thioxo-(1*H*)-pyrimidin-4-one], and 6-amino-2,3-dihydro-2-thioxo-(1*H*)-pyrimidin-4-one.



benzothiazoline - 2 - thione



thiouracil



6 - aminothiouracil

Experimental

Synthesis.—The ligands were obtained from the Aldrich Chemical Co. and, with the exception of the 6-amino derivative which was recrystallised from hot distilled water as the monohydrate, they were used as supplied. The salt $[NEt_4]_2$-$[NiCl_4]$ was synthesised by a standard method[12] and thoroughly dried before use. All preparations were carried out in pure dry N_2 and all solvents were degassed before use.

$[NEt_4][Ni(C_7H_4NS_2)_3]$ (**1**). A suspension of benzothiazoline-2-thione (6 mmol, 1.002 g) in MeCN (10 cm^3) was added, with constant stirring, to a solution of $[NEt]_2[NiCl_4]$ (2 mmol, 0.92 g) in MeCN (10 cm^3) at room temperature. On addition of the ligand the colour of the reaction mixture changed from bright blue to pale green. A solution of triethylamine (3 cm^3 in 5 cm^3 of MeCN) was then added, also with continuous stirring. After several minutes a pale green solid was produced. The reaction mixture was then stirred for 1 h. The solid product was removed by filtration, washed with cold MeCN, and dried over $CaCl_2$. Yield 0.486 g (70.7%) (Found: C, 50.75; H, 4.50; N, 7.95; Ni, 9.4. $C_{29}H_{32}N_4NiS_6$ requires C, 50.65; H, 4.65; N, 8.15; Ni, 8.6%). Electronic spectrum; 330, 695, 1 180, and 1 150(sh) nm;

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Dq = 848 cm^{-1}: μ_B (22 °C) = 3.25. Diffraction-quality crystals were obtained by dissolving (**1**) (0.200 g) in MeCN (15 cm^3) at room temperature. After several days bright-green crystals formed and were removed, washed, dried, and stored.

$[NEt_4][Ni(C_4H_3N_2OS)_3]$ (**2**). The procedure was as for complex (**1**) but with thiouracil (6 mmol, 0.7680 g) in MeCN (10 cm^3). The pale green product was obtained from a pale green reaction mixture, washed, dried, and stored as for (**1**). Yield 0.3600 g (63.2%) (Found: C, 48.0; H, 5.20; N, 16.85; Ni, 11.8. $C_{20}H_{29}N_7NiO_3S_3$ requires C, 42.10; H, 5.10; N, 17.20; Ni, 10.4%). Electronic spectrum: 320, 660, 1 200, and 1 500(sh) nm; Dq = 848 cm^{-1}. μ_B (22 °C) = 3.21.

$[NEt_4][Ni(C_4H_4N_3OS)_3]$ (**3**). The preparative procedure was as for complex (**1**) but with 6-amino-2,3-dihydro-2-thioxo-(1*H*)-pyrimidin-4-one (6 mmol, 0.8580 g) in MeCN (10 cm^3). The pale green solid was obtained from a pale green reaction mixture and isolated, washed, and dried as for (**1**). Yield 0.3970 g (64.6%) (Found: C, 38.80; H, 6.20; N, 20.35; Ni, 7.0. $C_{20}H_{32}N_{10}NiO_3S_3$ requires C, 39.00; H, 5.85; N, 22.75; Ni, 9.6%). Electronic spectrum: 325, 670, 1 190, and 1 500 nm; Dq = 855 cm^{-1}. μ_B (22 °C) = 2.92.

Elemental (C, H, N) analysis made at the Department of Chemistry, University of Leeds. Metal analysis, as NiO, obtained by thermogravimetric analysis using a Stanton-Redcroft TG 770 thermal analyser, column-dried air, platinum crucibles, heating rate 20 °C min^{-1}, and sample masses 5—8 g.

Physical Methods.—Infrared spectra (4 000—200 cm^{-1}) obtained as CsI discs from a Perkin-Elmer 684 grating spectrophotometer. Room-temperature magnetic measurements were made on a Newport Instruments Gouy balance with $Hg[Co(NCS)_4]$ as calibrant. Solid-state diffuse-reflectance electronic spectra (200—2 400 nm) were obtained from a Beckmann DK-2A spectrophotometer with MgO as standard. Cyclic voltammetry was undertaken with a Sycopel Scientific potentiostat and data-acquisition system together with a single-compartment three-electrode cell with platinum working and secondary electrodes and a saturated calomel reference electrode, (s.c.e.). Measurements were taken at room temperature with the complexes in dry dioxygen-free acetonitrile, at 1×10^{-3} mol dm^{-3} concentration and with tetrabutylammonium tetrafluoroborate (1×10^{-3} mol dm^{-3}) as supporting electrolyte.

Crystal Structure Analysis of $[NEt_4][Ni(C_7H_4NS_2)_3]$ (**1**).—*Crystal data.* $C_{29}H_{32}N_4NiS_6$, M = 687.7, monoclinic at 22 °C, space group $P2_1/n$, a = 10.290(1), b = 19.137(2), c = 16.814(2) Å, β = 101.95(1)°, U = 3 239.3 Å^3, D_m = 1.42(1), Z = 4, D_c = 1.410 g cm^{-3}, $F(000)$ = 1 432, μ = 4.62 mm^{-1} for Cu-K_α radiation λ = 1.541 84 Å. Cell parameters from 32 accurately centred reflections in the range 2θ 30—40°.

Data collection and processing. A representative green crystal of dimensions 0.25 × 0.27 × 0.30 mm and a Stoe-Siemens AED-2 diffractometer were used for the intensity measurements with ω—θ scans, on-line profile fitting,[13] variable scanning range and time in the range 2θ 3—130°, and index ranges h −12 to 12, k 0 to 22, l 0 to 19 and some equivalents with h −12 to −6 and $k < 0$. Three standard reflections recorded a decay of about 2% which was incorporated into the data processing, together with standard corrections, including monochromator effects and a semiempirical absorption correction; transmission factors ranged from 0.172 to 0.334. A total of 5 336 unique data were collected with 4 129 observed $[F > 4\sigma_c(F)]$ and σ_c from counting statistics only, R_{int} = 0.042.

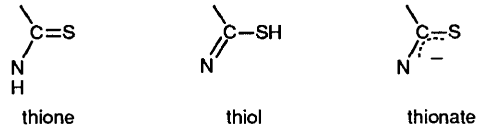
Structure solution and refinement.[14] The non-H atoms were located by a combination of direct methods and difference Fourier calculations and refined by blocked-cascade least-squares methods on F to a minimum of $\Sigma w\Delta^2$ with anisotropic thermal parameters. The H atoms of the anion were allocated positions on the ring-angle external bisectors with C–H 0.96 Å and U(H) = $1.2U_{eq}$(C); H atoms were not included for the cation, which shows high thermal motion and may be somewhat disordered. Final conventional $R = \Sigma|\Delta|/\Sigma|F_o|$ = 0.082 and $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$, = 0.076 with $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 243 - 415G - 465G^2 - 654S + 421S^2 + 676GS$ where $G = F_o/F_{max.}$ and $S = \sin\theta/\sin\theta_{max.}$.[15] Mean Δ/σ = 0.03, maximum 0.15, largest peak in final difference synthesis +1.12 e Å^{-3} and largest hole −0.70 e Å^{-3}; S = 1.38, 362 parameters. Isotropic extinction parameter, x = 1.7(6) 10^{-6}, $[F_c' = F_c/(1 + xF_c^2/\sin2\theta)^{\frac{1}{4}}]$. Scattering factors for neutral atoms from ref. 16.

Final atomic co-ordinates are in Table 1, selected bond lengths and angles in Table 2. A perspective view of the complex anion is shown in the Figure with all of the atoms in ligand 1 numbered, hetero-S, hetero-N, and thionato-S atoms numbered for ligands 2 and 3; remaining atoms follow the scheme for ligand 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Results and Discussion

All of the ligands, in principle, exhibit thione–thiol tautomerism, adopt the thione form in the solid, and are readily deprotonated to the corresponding thionate anion in solution.[17] Deprotonation of the ligands is accompanied by substantial modification of their i.r. spectra with ν(NH) absent from the spectrum of complex (**1**) and significant perturbation of the 'Thioamide' spectra in all cases (1 500—750 cm^{-1}).[17] Additional ν(Ni–S) bands occur at 385, 310, and 300 cm^{-1} as well as ν(Ni–N) at 260, 260, and 265 cm^{-1} for (**1**) (**2**), and (**3**) respectively. Such vibrational activity is clearly indicative of ligand S,N-co-ordination.[17]



Crystal Structure of $[NEt_4][Ni(C_7H_4NS_2)_3]$ (**1**).—With four formula units in a monoclinic cell the structure contains one crystallographically independent cation and one anion. The cation is unexceptional although significantly distorted, selected bond lengths and angles are in Table 2. The anion (Figure) contains Ni^{II} in a highly distorted octahedrally co-ordinated environment formed from three four-membered S,N chelating ligands which adopt a *fac* configuration about the metal. In the corresponding tris chelates formed from pyt and pymt the ligands adopt the less-symmetrical *mer* isomeric form.[11] The symmetrical arrangement of the relatively bulky ligands in (**1**) minimises the intraligand interactions which would undoubtedly arise in the *mer* form of this complex. The N–Ni–$S_{thionate}$ angles, which directly connect each ligand to the metal in (**1**), 67.3(1)—68.1(1)°, are similar to the values reported in $[Ni(pyt)_3]^-$ and $[Ni(pymt)_3]^-$, 67.4(1)—67.8(1)°,[11] and are a result of the formation of four-membered S,N-chelates.

Some representative Ni^{II}–S distances are summarised in Table 3. The Ni–$S_{thionate}$ distances in the three reported heterocyclic thionato chelates form a reasonably compact group with values in the range 2.460(2)—2.588(2) Å. Comparable distances are reported for benzenethiolate in $[Ni(bipy)_2(PhS)_2]$ (bipy = 2,2′-bipyridine)[18] and also for Hmimt in $[Ni(Hmimt)_4Cl_2]$ (Hmimt = 1-methylimidazoline-2-thione);[6] both of these ligands are monodentate-S donating and generate distorted-

Table 1. Atomic co-ordinates (10^4) with standard deviations for complex (**1**)

Atom	*x*	*y*	*z*
Ni	4 524(1)	6 210(1)	7 313(1)
S(11)	6 338(1)	6 108(1)	8 627(1)
S(12)	8 833(1)	6 124(1)	7 869(1)
N(1)	6 407(3)	6 133(2)	7 083(2)
C(11)	7 103(4)	6 118(2)	7 826(2)
C(12)	7 182(3)	6 132(2)	6 499(2)
C(13)	6 702(4)	6 134(2)	5 659(2)
C(14)	7 603(5)	6 135(2)	5 152(3)
C(15)	8 976(5)	6 133(3)	5 482(3)
C(16)	9 453(4)	6 135(3)	6 296(3)
C(17)	8 531(4)	6 135(2)	6 813(3)
S(21)	2 501(1)	5 988(1)	7 916(1)
S(22)	2 201(1)	4 386(1)	7 684(1)
N(2)	3 962(3)	5 173(2)	7 224(2)
C(21)	2 937(4)	5 207(3)	7 587(2)
C(22)	4 217(4)	4 493(2)	7 011(2)
C(23)	5 233(5)	4 294(2)	6 619(3)
C(24)	5 393(6)	3 594(3)	6 476(4)
C(25)	4 574(8)	3 100(3)	6 719(4)
C(26)	3 545(7)	3 285(3)	7 079(4)
C(27)	3 365(5)	3 983(3)	7 218(3)
S(31)	4 428(1)	7 538(1)	7 264(1)
S(32)	2 608(2)	7 762(1)	5 586(1)
N(3)	3 450(3)	6 576(2)	6 200(2)
C(31)	3 518(4)	7 239(2)	6 364(3)
C(32)	2 717(3)	6 423(2)	5 450(2)
C(33)	2 467(4)	5 765(2)	5 094(2)
C(34)	1 705(5)	5 716(2)	4 324(3)
C(35)	1 166(5)	6 294(3)	3 891(3)
C(36)	1 410(5)	6 955(3)	4 221(3)
C(37)	2 166(4)	7 016(2)	5 005(2)
N(4)	2 373(8)	1 300(5)	4 421(4)
C(41)	2 364(11)	1 394(4)	3 563(5)
C(42)	3 189(13)	744(8)	3 370(10)
C(43)	3 624(9)	1 285(14)	5 006(6)
C(44)	4 506(17)	2 024(10)	4 953(10)
C(45)	1 560(10)	2 058(4)	4 585(7)
C(46)	1 381(11)	2 156(5)	5 436(6)
C(47)	1 563(13)	751(6)	4 689(9)
C(48)	101(13)	704(8)	4 280(9)

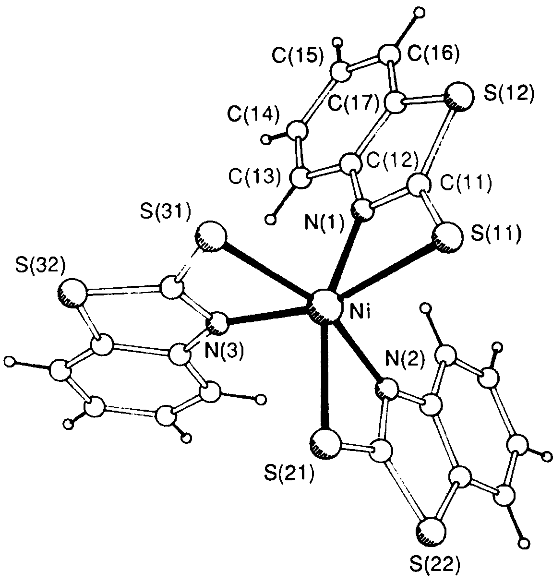


Figure. Perspective diagram of the $[Ni(C_7H_4NS_2)_3]^-$ anion with complete atomic labelling of ligand 1 and partial labelling of ligands 2 and 3

tetragonal environments in the complexes. In contrast, shorter Ni^{II}–S distances occur in the tetrahedral complexes $[Ni(RS)_4]^{2-}$ (R = aryl),[4] as well as in the diamagnetic, square-planar complexes $[Ni(Hmimt)_4]X_2$.[6–9] The wide-ranging distances in Table 3 emphasise the inherent flexibility of S-donating thionate, thione, and thiolate ligands towards divalent nickel.

The Ni^{II}–N distances in complex (**1**) fall in the narrow range 2.058(4)—2.087(3) Å. The reported distances for the corresponding tris chelates $[NiL_3]^-$ (L = pyt or pymt) are in the range 2.081(4)—2.202(5) Å.[11] In *trans*-$[Ni(py)_4Cl_2]$ (py = pyridine)[19] and in $[Ni(NO_2)_2(H_2O)_2(py)_2]$[20] the average Ni–N distances are 2.133 and 2.095 Å, respectively.

In contrast to most heterocyclic thionates, benzothiazoline-2-thione has a relatively well studied co-ordination chemistry.[17] Other complexes which are relevant to the present study include $[Zn(C_7H_4NS_2)_3(H_2O)]^-$ which has a combination of two monodentate S-donating ligands (mean Zn–S 2.338 Å) and one which is primarily monodentate-N [Zn–N 2.019(4) Å] but which also forms an additional weak Zn–S contact at 3.125 Å.[21] In $[Cd(C_7H_4NS_2)_3]^-$ the ligands are S,N-chelating with Cd–S at 2.667(6) Å and Cd–N at 2.474(1) Å.[22]

The average Ni–N and Ni–S distances in complex (**1**) are 2.070 and 2.555 Å respectively. In comparison with related distances summarised above and in Table 3 it would seem that the Ni–N and Ni–S distances in (**1**) are, respectively, relatively shorter and longer than expected. Consequently the sterically induced strain inherent in the formation of four-membered chelates is mediated largely at the thionate-S atoms in (**1**). The relatively narrow Ni–S–C angles [72.1(1)—73.8(2)°] also support this argument since corresponding angles for monodentate-S donating heterocyclic thiones are, on average, closer to the tetrahedral angle.[17]

The ligands are essentially planar in complex (**1**) with maximum mean-plane deviations observed for the hetero-N atom [N(1) +0.016 Å] and the thionato-S atom [S(21) +0.058 Å]. The mean exocyclic $C–S_{thionate}$ distance, 1.695 Å, contrasts with the value in the free ligand, 1.662(2) Å,[23] and confirms the increased thionate character of the ligands in (**1**).

Magnetism and Electronic Spectra.—The room-temperature magnetic moments (μ_B) for complexes (**1**)—(**3**) are in the range (2.90—3.40)[24] expected for octahedral complexes of divalent nickel. The three spin-allowed electronic transitions for such complexes from $^3A_{2g}$ to $^3T_{2g}$, $^3T_{1g}(F)$, and $^3T_{1g}(P)$ usually occur in the ranges 1 430—770, 910—500, and 530—370 nm[25a] respectively. Solid-state diffuse-reflectance data for (**1**)—(**3**) occur in the expected ranges with the *Dq* values (ν_1 = 10*Dq* = 8 480—8 700 cm^{-1}) indicative of relatively weak S,N-chelation.[25b] Although the crystal field around the nickel atom is distorted this is not reflected in the electronic spectra of the complexes to any significant extent. In each instance the $^3A_{2g} \longrightarrow {}^3T_{2g}$ transition is smooth except for the presence of a low-energy shoulder. This contrasts with the double-humped profile of the corresponding transitions in the *mer* isomers of the $[Ni(pyt)_3]^-$ and $[Ni(pymt)_3]^-$ anions[11] and suggests a common *fac*-isomeric form for (**1**)—(**3**).

Redox Properties.—The redox behaviour of complexes (**1**)—(**3**) has been studied electrochemically; results from cyclic voltammetric (c.v.) studies are summarised in Table 4. All of

Table 2. Selected bond lengths (Å) and angles (°) with standard deviations for complex (**1**)

Ni–S(11)	2.588(2)	S(22)–C(21)	1.765(5)	N(4)–C(47)	1.469(16)	S(22)–C(27)	1.742(6)
Ni–S(21)	2.533(2)	N(2)–C(21)	1.326(6)	Ni–N(1)	2.058(4)	N(2)–C(22)	1.390(6)
Ni–S(31)	2.544(2)	S(31)–C(31)	1.705(4)	Ni–N(2)	2.064(4)	C(22)–C(27)	1.404(7)
S(11)–C(11)	1.694(5)	S(32)–C(37)	1.737(4)	Ni–N(3)	2.087(3)	S(32)–C(31)	1.757(4)
S(12)–C(17)	1.739(5)	N(3)–C(32)	1.360(4)	S(12)–C(11)	1.766(4)	N(3)–C(31)	1.297(6)
N(1)–C(12)	1.387(6)	C(32)–C(37)	1.412(5)	N(1)–C(11)	1.306(5)	N(4)–C(41)	1.451(11)
C(12)–C(17)	1.379(5)	N(4)–C(43)	1.450(11)	S(21)–C(21)	1.687(5)	N(4)–C(45)	1.724(13)
S(11)–Ni–N(1)	67.3(1)	C(12)–C(17)–C(16)	121.0(4)	S(32)–C(37)–C(32)	109.4(3)	S(12)–C(17)–C(16)	128.9(3)
N(1)–Ni–S(21)	161.2(1)	C(21)–S(22)–C(27)	90.3(2)	S(11)–Ni–S(21)	98.8(1)	Ni–S(21)–C(21)	73.8(2)
Ni(1)–Ni–N(2)	100.2(1)	Ni–N(2)–C(22)	148.7(3)	S(11)–Ni–N(2)	97.5(1)	Ni–N(2)–C(21)	99.0(3)
S(11)–Ni–S(31)	96.9(1)	S(21)–C(21)–S(22)	127.6(3)	S(21)–Ni–N(2)	68.1(1)	C(21)–N(2)–C(22)	112.1(4)
S(21)–Ni–S(31)	98.7(1)	S(22)–C(21)–N(2)	113.4(4)	N(1)–Ni–S(31)	95.6(1)	S(21)–C(21)–N(2)	119.0(4)
S(11)–Ni–N(3)	161.0(1)	N(2)–C(22)–C(27)	115.2(4)	N(2)–Ni–S(31)	161.8(1)	N(2)–C(22)–C(23)	125.2(4)
S(21)–Ni–N(3)	95.1(1)	S(22)–C(27)–C(22)	109.0(4)	N(1)–Ni–N(3)	101.5(1)	S(22)–C(27)–C(26)	129.6(5)
S(31)–Ni–N(3)	68.1(1)	C(22)–C(27)–C(26)	121.3(5)	N(2)–Ni–N(3)	99.7(1)	Ni–S(31)–C(31)	72.7(2)
C(11)–S(12)–C(17)	89.6(2)	C(31)–S(32)–C(37)	89.3(2)	Ni–S(11)–C(11)	72.1(1)	Ni–N(3)–C(31)	98.1(2)
Ni–N(1)–C(12)	146.6(2)	Ni–N(3)–C(32)	148.0(3)	Ni–N(1)–C(11)	100.0(3)	C(31)–N(3)–C(32)	113.7(3)
S(11)–C(11)–S(12)	126.7(2)	S(31)–C(31)–S(32)	125.4(3)	C(11)–N(1)–C(12)	113.3(3)	S(31)–C(31)–N(3)	120.9(3)
S(12)–C(11)–N(1)	112.8(3)	S(32)–C(31)–N(3)	113.7(3)	S(11)–C(11)–N(1)	120.5(3)	N(3)–C(32)–C(33)	127.5(3)
N(1)–C(12)–C(17)	114.3(4)	N(3)–C(32)–C(37)	113.8(3)	N(1)–C(12)–C(13)	125.5(3)	S(32)–C(37)–C(36)	129.3(3)
S(12)–C(17)–C(12)	110.0(3)						

Table 3. Some representative Ni^{II}–S distances (Å)

Compound	
(*a*) Thionate	
$[Ni(pyt)_3]^-$	2.460(2)—2.545(2)[11]
$[Ni(pymt)_3]^-$	
$[Ni_2(tzt)_4Cl]^-$	2.217(1), 2.233(2)[26]
(*b*) Thiolate	
$[Ni(RS)_4]^{2-}$ (R = aryl)	2.269(2)—2.288(2)[4]
$[Ni(bipy)_2(PhS)_2]$	2.445(2)[18]
(*c*) Thione	
$[Ni(Hmimt)_4]X_2$ (X = ClO_4,[8] Br,[9] or BF_4[6])	2.207(2)—2.322(2)
$[Ni(Hmimt)_4Cl_2]$	2.537(1)[6]

Table 4. Electrochemical data *

Complex	E_p^{ox}/V
(**1**)	+0.90
	+1.33
(**2**)	−0.5
	+1.6
(**3**)	−0.4
	+0.90
	+1.40

* All values quoted *vs.* ferrocene–ferrocenium couple (+0.34 *vs.* s.c.e.) and a scan rate of 100 mV s^{-1}.

the complexes are irreversibly oxidised in acetonitrile but the respective c.v. curves do show some differences in the electrochemical behaviour of each of the complexes. The magnitude of the initial peak potential (+0.90V) for (**1**) suggests the complex to be relatively stable to oxidation. The initial peak potentials for (**2**) and (**3**) suggest that the pyrimidine-based ligands are more readily oxidised than benzothiazoline-2-thione. The presence of more than one peak in the oxidation cycle in each instance represents progressive ligand-centred oxidation of (**1**)—(**3**). The absence of significant detail on the reduction cycle of each of the complexes suggests that they decompose near the working electrode.

The involvement of redox-sensitive ligands effectively compromises the production of redox-stable Ni^{III}–Ni^{II} centres in these complexes. The ability of thiolates and thionates to be oxidised to the corresponding disulphides, $2RS^- \longrightarrow RSSR + 2e^-$, is probably the major cause of the ligand-centred redox instability in (**1**)—(**3**).

Conclusion

This work supports the original proposal by Mascharack and co-workers[11] that the successful synthesis of tris-chelated heterocyclic thionato complexes of Ni^{II} is dependent on the use of aprotic solvents, the correct order of addition of the reactants, as well as the *in situ* deprotonation of the parent heterocycle. While this synthetic strategy successfully avoids the production of polymeric thionates, which is the primary objective, it does not necessarily produce the appropriate tris chelate either. As this work demonstrates, with benzothiazoline-2-thione the resultant complex is $[Ni(C_7H_4NS_2)_3]^-$, however, with thiazoline-2-thione (Htzt) the product is a binuclear, paramagnetic (μ_B = 3.84), complex $[Ni_2(tzt)_4Cl]^-$ [26] and with thiazolidine-2-thione (Htzdt) the product is a diamagnetic complex of empirical formula $[Ni(tzdt)_2]$.[27] Three derivatives of the same heterocyclic base, thiazole, produce radically different complexes from the same synthetic strategy and thereby demonstrate the inherent potential which this synthetic strategy promises for nickel(II) complexes with the thione derivatives of other heterocyclic bases.[17]

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Received 23*rd February* 1990; *Paper* 0/00833H