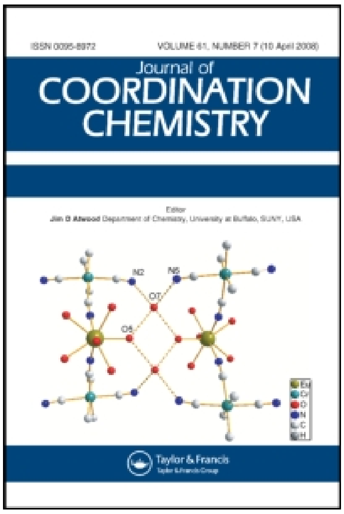

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BIS(DITHIOSQUARAMIDE) LIGANDS AND THEIR COMPLEXES WITH DIVALENT NICKEL: THERMOCHROMIC BEHAVIOUR AND UNANTICIPATED FORMATION OF 2:2 SPECIES

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BIS(DITHIOSQUARAMIDE) LIGANDS AND THEIR COMPLEXES WITH DIVALENT NICKEL: THERMOCHROMIC BEHAVIOUR AND UNANTICIPATED FORMATION OF 2:2 SPECIES

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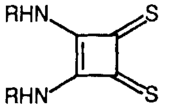
Reaction of two equivalents of *N*-mono- or di-substituted 3-amino-4-(*n*-butoxy)-3-cyclobutene-1,2-diones with a 1,2-diaminoethane gave *N*-mono- or di-substituted 1,2-bis((2-amino-1-cyclobutene-3,4-dione)amino)-ethane derivatives (bis(squaramides)). Reaction of the bis(squaramides) with excess P_4S_{10} gave the analogous tetrathio derivatives (bis(dithiosquaramides), LH_2) of formula $(NR^1R^2)C_4S_2(NHCH_2CH_2NH)$-$C_4S_2(NR^1R^2)$ ($R^1=n$-Bu, $R^2=H$; $R^1=R^2=$Et, *n*-Bu). The new bis(dithiosquaramide) ligands were characterized by elemental analysis, IR, ^{1}H NMR, ^{13}C NMR, electronic, and mass spectroscopic methods. The complexes of these ligands with nickel(II) were prepared, isolated and characterized. The isolated complexes are neutral 2:2 species of formula Ni_2L_2, as evidenced by results from mass spectrometry, and they exhibit thermochromic behaviour in pyridine solution. Additional spectroscopic data (IR, NMR) are consistent with the ligands being coordinated only through sulfur donor atoms and a structure for the complexes is proposed.

KEY WORDS: Nickel complexes, thermochromism, dinuclear, squaramides, dithiosquaramides, sulfur ligands.

INTRODUCTION

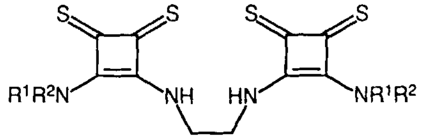
The coordination chemistry of 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid, $H_2C_4O_4$), its conjugate base ($C_4O_4^{2-}$), and its dithio- and tetrathio-derivatives ($C_4O_2S_2^{2-}$ and $C_4S_4^{2-}$) has been investigated in some detail by Beck, Castan, Coucouvanis and others.[1] Recently, we demonstrated that *N,N'*-disubstituted 3,4-dihydroxy-3-cyclobutene-1,2-dithione derivatives (*cis*-dithiosquaramides, $L'H_2$, structure I) chelate to transition metal ions such as nickel(II), copper(II), and palladium(II), giving neutral complexes of the formula $M(L'H)_2$ in which the ligands are bound in a symmetric bidentate S_2 fashion.[2]

In principle, *cis*-dithiosquaramide ligands should be able to bind to metal ions through nitrogen and such a change in the chelation mode might have a significant effect on the spectroscopic properties of the complexes. An obvious approach toward altering the coordination environment from MS_4, as observed for the bidentate *cis*-dithiosquaramide complexes, to MN_2S_2 is to link two dithiosquaramide moieties together into a potentially tetradentate ligand (structure II). By taking advantage of the chelate effect, coordination of such a ligand in an N_2S_2 fashion might occur



cis-Dithiosquaramide

I



Bis(Dithiosquaramide)

II

despite the obvious preference of nickel(II) for the available sulfur over nitrogen donor atoms. Such a strategy has been successful, for example, with dithiooxamide complexes of nickel(II).[3]

In this paper we report the synthesis of several bis(dithiosquaramide) ligands (LH_2) and their complexes with nickel(II). Surprisingly, rather than species of formula NiL, dark red neutral 2:2 complexes of formula Ni_2L_2 result. Evidence is presented that the ligands in the 2:2 complexes are coordinated only through sulfur atoms.

EXPERIMENTAL

General Methods

Mass spectra were recorded by staff at the Univerity of Kansas using a Ribermag R10-10 spectrometer for electron (EI) or chemical (CI) ionization, and a VG Analytical Ltd. ZAB HS mass spectrometer for fast atom bombardment (FAB). Infrared spectra were obtained by using a Perkin Elmer 1600 series Fourier transform spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a GE QE-300 Plus operating at 300 MHz for ^1H and 75 MHz for ^{13}C, and were referenced to residual solvent resonances. Electronic spectra were recorded using either a Varian Cary 2300 or a Hewlett-Packard 8452A Diode Array spectrophotometer. Elemental analyses were performed by staff at the University of Kansas. Dichloromethane was distilled from P_4O_{10}. All amines and pyridine were distilled from KOH. Dimethylformamide (DMF), dimethylsulfoxide (DMSO), other solvents, 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid, Aldrich, 98%), and P_4S_{10} (Aldrich, 99%) were reagent grade or better and were used as received. Electrochemical data were obtained using a Princeton Applied Research Model 173 Potentiostat/Galvanostat, Model 175 Universal programmer, and a Houston Instruments 2000 XY recorder. Cyclic voltammograms were obtained in a 0.1 M tetrabutylammonium tetrafluoroborate dichloromethane solution using a glassy carbon working electrode *versus* Ag/AgCl (in 0.1 M tetrabutylammonium tetrafluoroborate dichloromethane solution) and a platinum net secondary electrode with ferrocene as internal standard.

Syntheses

Bu_2H_2-enH_2-BSQ, Et_4-enH_2-BSQ, and Bu_4-enH_2-BSQ

Squaric acid (typically 4–5 g) suspended in *n*-butanol/benzene (100 cm^3 and 50 cm^3, respectively) was converted to its di-*n*-butyl ester by azeotropic removal of water as described by Maahs.[4] After the conversion was complete, the benzene was removed by distillation. The remaining solution of the di-ester was then cooled and a solution of one equivalent of the appropriate amine in *n*-butanol was added dropwise. The reaction solution was briefly heated at reflux. A solution of 0.5 equivalents of 1,2-diaminoethane in *n*-butanol was then added dropwise. The formation of a white precipitate was evident before this addition was complete. After the addition was complete, the reaction mixture was briefly heated at reflux. After cooling the mixture, the white precipitate of the bis(squaramide) was collected, washed with ethanol and diethyl ether, and dried *in vacuo* to give either crude Bu_2H_2-enH_2-BSQ (79% yield from squaric acid) or Et_4-enH_2-BSQ (57% yield from squaric acid).

Bu_4-enH_2-BSQ, which was soluble in the reaction medium, was isolated as follows. After filtering the reaction solution to remove a white solid, the filtrate was concentrated to an oil by rotary evaporation. The oil was extracted with diethyl ether in two portions (65 and 35 cm^3, respectively) and the ether was removed from the extract by rotary evaporation. The residue from the extract was recrystallized from tetrahydrofuran, washed with diethyl ether, and dried *in vacuo* to give Bu_4-enH_2-BSQ as a white solid (mp = 133–135°C, uncorrected).

The bis(squaramides) were used without further purification in preparing the bis(dithiosquaramides) described below.

Bu_2H_2-enH_2-BSQ (MW = 362.43). Anal.: calcd. for $C_{18}H_{26}N_4O_4$. $0.5H_2O$ (hemihydrate after recrystallation from DMSO): C, 58.21; H, 7.33; N, 15.08%. Found: C, 58.27; H, 7.30; N, 15.00%. Mass Spectrum (EI, DMSO solvent, daltons): *m/z* 362 (M^+), 289 ($(M\text{-}C_4H_{11}N)^+$), 277, 249 and other lower mass ions.

Bu_4-enH_2-BSQ (MW = 474.65). Anal.: calcd. for $C_{26}H_{42}N_4O_4$: C, 65.79; H, 8.92; N, 11.80%. Found: C, 65.80; H, 9.00; N, 12.00%. Mass Spectrum (EI, emthanol solvent, daltons): *m/z* 474 (M^+), 431 ($(M\text{-}C_3H_7)^+$), 417 ($(M\text{-}C_4H_9)^+$), 361 ($(M\text{-}C_8H_{17})^+$) and other lower mass ions.

Bu_2-H_2-enH_2-BDTSQ

The squaramide Bu_2H_2-enH_2-BSQ (0.65 g, 1.8 mmol) and excess P_4S_{10} (0.7 g) were suspended in dry pyridine (45 cm^3) under nitrogen. The mixture was heated at reflux for 45 min resulting in a dark brown solution. Ethanol (10 cm^3) was then added to destroy unreacted P_4S_{10}, and after cooling to room temperature, the solution was filtered. Upon the addition of water (50 cm^3) to the filtrate, crude Bu_2H_2-enH_2-BDTSQ precipitated as a yellow solid. The crude product was collected by filtration and washed with water, ethanol and diethyl ether. Purification was effected by reprecipitation from DMSO solution by the addition of water followed by recrystalization from ethanol/DMSO. Yield Bu_2H_2-enH_2-BDTSQ: 0.43 g, 1.0 mmol, 56%.

Bu_2H_2-enH_2-BDTSQ (MW = 426.67). Anal.: calcd. for $C_{18}H_{26}N_4S_4$: C, 50.67; H, 6.14; N, 13.13%. Found: C, 50.34; H, 6.21; N, 12.80%. Mass Spectrum (CI with NH_3, DMSO solvent, daltons): *m/z* 427 ($(M+H)^+$), 355, 342 and other lower mass ions. IR (KBr disc, bands of medium of greater intensity between 4400 and 450 cm^{-1} and additional selected bands, cm^{-1}): 3230 (w), 3170 (m), 3130 (m), 2992 (w), 2960 (w), 1712 (vs), 1600 (s), 1504 (m), 1324 (s), 1296 (m), 1239 (s), 1166 (m). Electronic spectrum (DMF, nm): λ_{max} (ε) 398 (38,100), 364 (shoulder), 278 (21,500); ε units M^{-1} cm^{-1}.

Et_4-enH_2-BDTSQ

The squaramide Et_4-enH_2-BSQ (1.24 g, 3.42 mmol) and excess P_4S_{10} (1.0 g) were suspended in dry dichloromethane and the mixture stirred for 23 h. Ethanol (10 cm^3)

was then added to destroy unreacted P_4S_{10}, and crude Et_4-enH_2-BDTSQ was isolated as a yellow solid upon filtration. The crude product was extracted into warm DMSO, precipitated by the addition of water, washed with ethanol and diethyl ether, and dried *in vacuo* to give analytically pure (Et_4-enH_2-BDTSQ. Yield: 0.471 g, 1.10 mmol, 32%.

Et_4-enH_2-BDTSQ (MW = 426.67). Anal.: calcd. for $C_{18}H_{26}N_4S_4$: C, 50.67; H, 6.14; N, 1.313%. Found: C, 50.50; H, 6.17; N, 13.28%. Mass Spectrum (EI, DMSO solvent, daltons): *m/z* 426 (M^+), 397 and other lower mass ions. IR (KBr disc, bands of medium or greater intensity btween 4400 and 450 cm^{-1} and additional selected bands, cm^{-1}): 3209 (m), 3178 (m), 2977 (w), 2932 (w), 1693 (s), 1575 (s), 1559 (s), 1439 (m), 1322 (s), 1290 (m), 1264 (m), 1229 (s), 1196 (s), 1176 (m). Electronic spectrum (DMF, nm): λ_{max} (ε) 402 (21,800), 390 (sh), 370 (sh), 282 (14,400). ^{1}H NMR (DMSO-d^6): δ 1.149 (m, 12H), 3.417 (q, 4H), 4.200 (q, 4H), 4.261 (s, 4H), 8.711 (s, broad, 2H).

Bu_4-enH_2-BDTSQ

The squaramide Bu_4-enH_2-BSQ (0.457 g, 0.963 mmol) and excess P_4S_{10} (0.5 g) were suspended in dry dichloromethane and the mixture stirred for 16 h. Ethanol (10 cm^3) was then added to destroy unreacted P_4S_{10}. The reaction solution was concentrated to *ca* 5 cm^3 and water (50 cm^3) was added to precipitate crude Bu_4-enH_2-BDTSQ. The crude product was washed with water, recrystallized from ethanol/DMSO and dried *in vacuo* to give purified Bu_4-enH_2-BDTSQ. Yield: 0.176 g, 0.327 mmol, 34%.

Bu_4-enH_2-BDTSQ (MW = 538.89). Anal.: calcd. for $C_{26}H_{42}N_4S_4$: C, 57.95; H, 7.86; N, 10.40%. Found: C, 57.48; H, 8.38; N, 10.10%. Mass Spectrum (EI, DMF solvent, daltons): *m/z* 538 (M^+), 505 (M-SH)$^+$), 481 ((M-C_4H_9)$^+$) and other lower mass ions. IR (KBr disc, bands of medium or greater intensity between 4400 and 450 cm^{-1} and additional selected bands, cm^{-1}): 3199 (m), 3168 (m), 2957 (m), 2929 (m), 2870 (w), 1691 (vs), 1555 (vs), 1425 (m), 1323 (s), 1296 (m), 1254 (m), 1230 (s), 1177 (m). Electronic spectrum (chloroform, nm): λ_{max} (ε) 408 (shoulder), 382 (46,800), 368 (shoulder), 278 (31,400). ^{1}H NMR (chloroform-*d*): δ 8.433 (s, br, 2H), 4.460 (s, br, 4H), 4.226 (t, 4H), 3.654 (t, 4H), 1.644 (m, 8H), 1.355 (m, 8H), 0.910 (m, 12H). ^{13}C NMR (chloroform-*d*): δ 205.80, 202.53, 170.68, 170.38, 52.20, 50.05, 43.80, 31.94, 31.92, 20.28, 19.88, 14.49, 14.27.

Ni_2L_2 Complexes

Method A

A solution of nickel(II) acetate tetrahydrate (62.2 mg, 0.250 mmol) in DMF (40 cm^3) and a solution of Et_4-enH_2-BDTSQ (106.8 mg, 0.250 mmol) in DMF (40 cm^3) were added simultaneously to a stirred bath of DMF (100 cm^3) at a rate of about 8 cm^3/hr using a syringe pump. The dark red precipitate that formed was then collected, washed with DMF, ethanol and diethyl ester, and dried *in vacuo*. Yield of $Ni_2(Et_4$-en-BDTSQ$)_2$ as a dark red microcrystalline solid: 86 mg, 0.089 mmol, 71%. The product thus isolated is either insoluble or very slightly soluble in tetrahydrofuran, dichloromethane, chloroform, DMF, DMSO, ethanol and methanol. It is soluble in pyridine giving a yellow solution.

Method A was also used to prepare $Ni_2(Bu_2H_2$-en-BDTSQ$)_2$ $4H_2O$ from nickel(II) acetate tetrahydrate (62.0 mg, 0.249 mmol) and Bu_2H_2-enH_2-BDTSQ (105.6 mg, 0.247 mmol). Yield as an red-brown powder: 85 mg, 0.082 mmol, 66%.

Method B

To a solution of nickel(II) acetate tetrahydrate (36.8 mg, 0.148 mmol) in warm DMF (5 cm^3) was added a solution of Bu_4-enH_2-BDTSQ (69.0 mg, 0.128 mmol) in warm DMF (5 cm^3) with stirring. A dark red solution immediately resulted. The reaction mixture was then stored at $-15°C$ for about 30 min. A small amount of product (13.8 mg) precipitated as a dark red solid and was removed by filtration. The greater portion of the desired product (48.4 mg), $Ni_2(Bu_4$-en-BDTSQ$)_2$, was isolated from the filtrate by the addition of water (10 cm^3). The product isolated in this manner was washed with water and ethanol, and dried *in vacuo*. Yield of $Ni_2(Bu_4$-en-BDTSQ$)_2$ as a dark red solid: 62.2 mg, 0.0522 mmol, 82%. The isolated complex is soluble in tetrahydrofuran and dichloromethane yielding red coloured solutions and in pyridine to give a yellow coloured solution. It is either insoluble or very slightly soluble in ethanol, DMF, DMSO and acetonitrile.

This method was also used to prepare $Ni_2(Et_4$-en-BDTSQ$)_2$ from nickel(II) acetate tetrahydrate (17.2 mg, 0.0691 mmol) and Et_4-enH_2-BDTSQ (29.6 mg, 0.0694 mmol). The product precipitated from the reaction medium upon standing without the addition of water as a dark red-violet microcrystalline solid. Yield: 20.4 mg, 0.0211 mmol, 61%. DMSO can also be used as a solvent for the complex forming reaction.

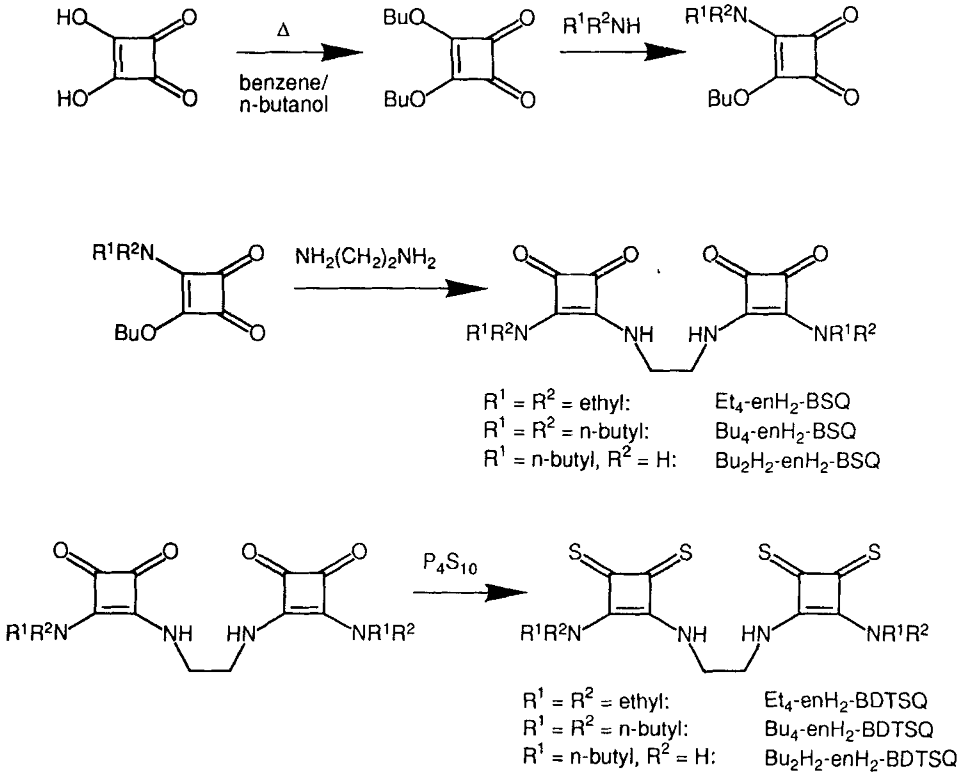
$Ni_2(Bu_4$-en-BDTSQ$)_2$ (MW = 1191.15). Anal.: calcd. for $Ni_2C_{52}H_{80}N_8S_8$: C, 52.43; H, 6.77; N, 9.41%. Found: C, 52.17; H, 7.00; N, 9.05%. Mass Spectrum (FAB, dithioerythritol/dithiothreitol matrix, positive ion, daltons): *m/z* (relative intensity) 1191 ($(M+H)^+$, 56%), 1133 ($(M-Ni)^+$, 16%), 595 (40%), 535 (100%). Mass Spectrum (FAB, *m*-nitrobenzyl alcohol matrix, positive ion, daltons): *m/z* (relative intensity) 1250 (13%), 1191 (100%), 595 (14%). IR (KBr disc, bands of medium or greater intensity between 4400 and 450 cm^{-1} and additional selcted bands, cm^{-1}): 2955 (m), 2928 (m), 2869 (w), 1707 (s), 1627 (s), 1461 (w), 1417 (vs), 1310 (m), 1275 (m), 1174 (w). Electronic spectrum (chloroform, nm): λ_{max} (ε) 520 (29,800), 474 (shoulder), 390 (shoulder), 348 (92,500), 314 (80,900), 276 (83,500). ^1H NMR (chloroform-*d*): δ 4.076 (t, 8H), 3.742 (s, 8H), 3.556 (t, 8H), 1.793 (m, 8H), 1.675 (m, 8H), 1.349 (m, 16H), 0.944 (t, 24H).

$Ni_2(Bu_2H_2$-en-BDTSQ$)_2$ $4H_2O$. (MW = 1038.78). Anal.: calcd. for $Ni_2C_{36}H_{56}N_8O_4S_8$: C, 41.63; H, 5.43; N, 10.79%. Found: C, 41.80; H, 5.28; N, 10.60%. IR (KBr disc, bands of medium or greater intensity between 4400 and 450 cm^{-1} and additional selcted bands, cm^{-1}): 3248 (vw), 3190 (vw), 3081 (vw), 2958 (m), 2931 (m), 2866 (w), 1713 (vs), 1644 (s), 1392 (vs), 1342 (s), 1218 (m). Electronic spectrum (DMF, nm): λ_{max} 512, 400 (shoulder), 360 (shoulder), 324, 274.

$Ni_2(Et_4$-en-BDTSQ$)_2$ (MW = 966.72). Anal.: calcd. for $Ni_2C_{36}H_{48}N_8S_8$: C, 44.73; H, 5.00; N, 11.59%. Found: C, 44.60; H, 4.99; N, 11.68%. Mass Spectrum (FAB, *m*-nitrobenzyl alcohol/pyridine matrix, positive ion, daltons): *m/z* 967 (M^+). IR (KBr disc, bands of medium or greater intensity between 4400 and 450 cm^{-1} and additional selected bands, cm^{-1}): 2972 (w), 2933 (w), 1704 (s), 1629 (s), 1414 (vs), 1300 (s), 1251 (m), 1170 (m). Electronic Spectrum (pyridine, nm): λ_{max} (ε) 432 (54.700), 388 (67,800).

RESULTS

Bis(squaramide) compounds have been prepared from squaric acid and then thionated using P_4S_{10} to give bis(dithiosquaramide) ligands (LH_2) of general formula



$R^1 = R^2 =$ ethyl: Et_4-enH_2-BSQ
$R^1 = R^2 =$ n-butyl: Bu_4-enH_2-BSQ
$R^1 =$ n-butyl, $R^2 =$ H: Bu_2H_2-enH_2-BSQ

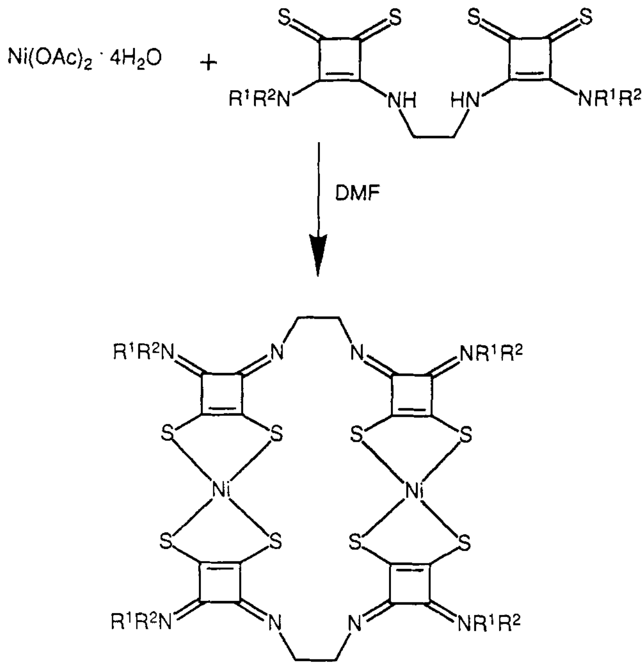
$R^1 = R^2 =$ ethyl: Et_4-enH_2-BDTSQ
$R^1 = R^2 =$ n-butyl: Bu_4-enH_2-BDTSQ
$R^1 =$ n-butyl, $R^2 =$ H: Bu_2H_2-enH_2-BDTSQ

$(NR^1R^2)C_4S_2(NHCH_2CH_2NH)C_4S_2(NR^1R^2)$ ($R^1 = n$-Bu, $R^2 = H$; $R^1 = R^2 = Et$, n-Bu). The synthetic procedure is outlined in Scheme 1. Reaction of the new ligands with nickel(II) acetate tetrahydrate in DMF gave dark red neutral 2:2 complexes of formula Ni_2L_2. A proposed structure for the new complexes is shown in Scheme 2. The ligands and complexes were characterized by a variety of spectroscopic techniques (Figures 1–3). Electronic spectra of the Ni_2L_2 complexes show an intense band in the visible region at 512–526 nm in non-coordinating solvents that is presumably charge transfer in origin. In the weakly coordinating solvent pyridine this band shows thermochromic behaviour, being nearly absent at 25°C but growing in intensity upon heating (Figure 3).

DISCUSSION

Bis-Dithiosquaramide Ligands

The formulations of the bis(dithiosquaramide) ligands, prepared as outlined in Scheme 1, were supported by the observation of appropriate parent ions by mass spectrometry, elemental analyses, and NMR spectroscopy. The infrared spectra of the ligands (see Figure 2) exhibit NH bands around 3150 cm^{-1} and CH bands around 2900 cm^{-1}. Both Bu_2H_2-enH_2-BDTSQ and Bu_4-enH_2-BDTSQ show two strong bands in the



$R^1 = R^2 =$ ethyl: $Ni_2(Et_4\text{-en-BDTSQ})_2$
$R^1 = R^2 =$ n-butyl: $Ni_2(Bu_4\text{-en-BDTSQ})_2$
$R^1 =$ n-butyl, $R^2 = H$: $Ni_2(Bu_2H_2\text{-en-BDTSQ})_2 \cdot 4H_2O$

region from 1750 to 1500 cm^{-1}. They occur at 1712 and 1600 cm^{-1} in Bu_2H_2-enH_2-BDTSQ, and 1691 and 1555 cm^{-1} in Bu_4-enH_2-BDTSQ. Strong bands near these wave number values are characteristic of *cis*-dithiosquaramide moieties, and bands between 1600 and 1550 cm^{-1} have been assigned as ν_{CN}.[3] Et_4-enH_2-BDTSQ shows a band at 1693 cm^{-1}, but the ν_{CN} band is split into two bands (1575 and 1559 cm^{-1}). The ligands are yellow coloured and their electronic spectra show intense bands with maxima near 390 and 280 nm. Such transitions are characteristic of the *cis*-dithiosquaramide group.[2,5]

Restricted rotation about the C-NR^1R^2 bond is evidenced by two inequivalent types of ethyl groups in Et_4-enH_2-BDTSQ and *n*-butyl groups in Bu_4-enH_2-BDTSQ. For example, the ^1H NMR spectrum of Et_4-enH_2-BDTSQ shows two quartets (δ 3.417 and 4.200, respectively) that are assigned to the inequivalent methylenes of a diethylamine moiety. Similarly, the methylenes adjacent to the nitrogen of a dibutylamine moiety in Bu_4-enH_2-BDTSQ are inequivalent and occur as two triplets (δ 3.654 and 4.226, respectively). Also, the ^{13}C NMR spectrum of Bu_4-enH_2-BDTSQ shows 8 lines for the *n*-butyl carbons rather than 4. Such a rotational barrier is consistent with there being significant double bond character in the CN bond.

The hydrogens of the bridging ethane group appear as singlets in the ^1H NMR spectra of both Et_4-enH_2-BDTSQ and Bu_4-enH_2-BDTSQ (δ 4.261 and 4.460, respectively). This suggests that either intramolecular hydrogen bonding or steric crowding fixes this group into one preferred conformation.

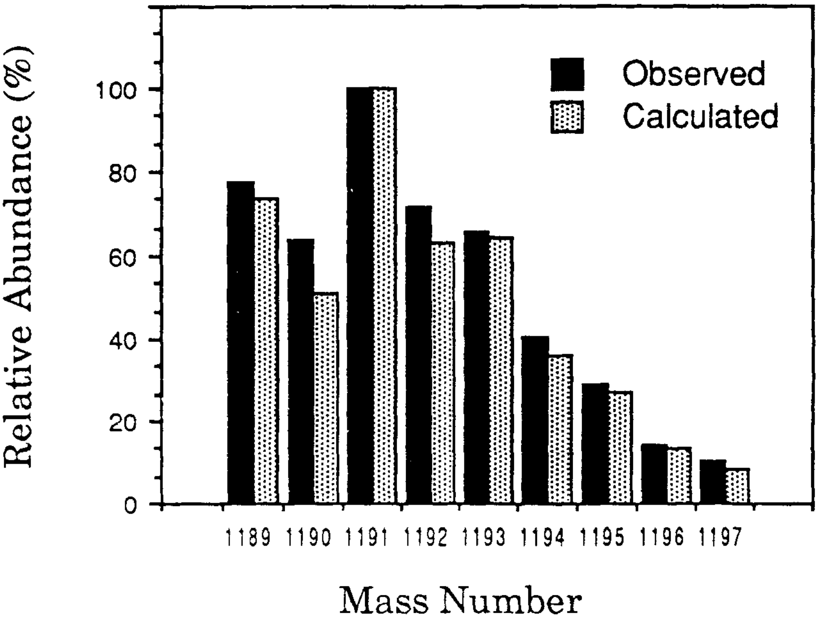


Figure 1 Comparison of the observed and calculated isotopic abundances for the $(Ni_2L_2+H)^+$ ion of $Ni_2(Bu_4\text{-en-BDTSQ})_2$ as obtained by positive ion fast atom bombardment mass spectrometry.

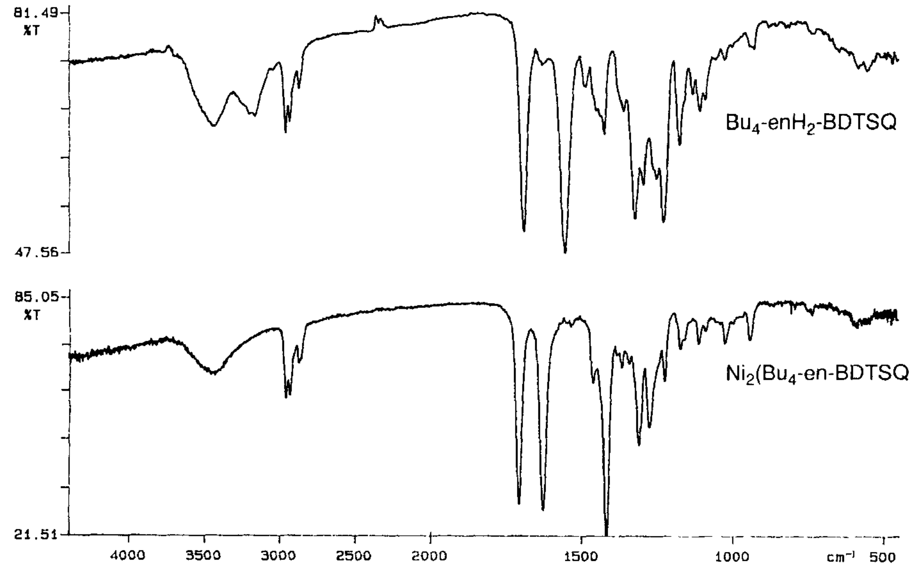


Figure 2 IR spectra of $Bu_4\text{-enH}_2\text{-BDTSQ}$ (top) and $Ni_2(Bu_4\text{-en-BDTSQ})_2$ (bottom) dispersed in KBr.

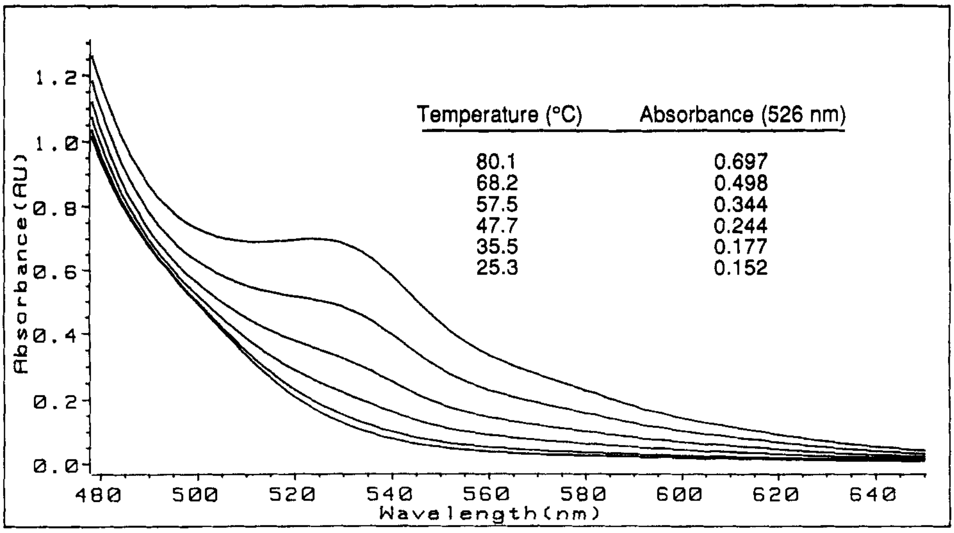


Figure 3 Temperature dependent electronic spectra of $Ni_2(Et_4\text{-en-BDTSQ})_2$ in pyridine.

Ni_2L_2 Complexes

Reactions in a 1:1 stoichiometry of bis(dithiosquaramide) ligands with nickel(II) acetate tetrahydrate proceed rapidly in DMF or DMSO to give dark red solutions from which the products precipitate directly or upon the addition of water (Scheme 2). The complexes $Ni_2(Bu_2H_2\text{-en-BDTSQ})_2{\cdot}4H_2O$ and $Ni_2(Et_4\text{-en-BDTSQ})_2$ have very poor solubility properties in most common organic solvents, though the latter complex is soluble in pyridine. $Ni_2(Bu_4\text{-en-BDTSQ})_2$ is soluble in dichloromethane, chloroform, tetrahydrofuran and pyridine, but has little or no solubility in DMF, DMSO, methanol, ethanol, hexane and acetonitrile.

Rather than forming 1:1 species, Ni_2L_2 complexes are formed as evidenced by the observation of $(Ni_2L_2+H)^+$ ions by FAB mass spectrometry for both $Ni_2(Bu_4\text{-en-BDTSQ})_2$ and $Ni_2(Et_4\text{-en-BDTSQ})_2$. Comparison of the observed isotopic abundances for the $(Ni_2L_2+H)^+$ ions shows close agreement with the calculated values (see Figure 1). Performing the complexation reactions under conditions of high dilution gave the same 2:2 species.

The mass spectra are matrix dependent. For $Ni_2(Bu_4\text{-en-BDTSQ})_2$ in *m*-nitrobenzyl alcohol an intense $(Ni_2L_2+H)^+$ ion is observed together with very weak $(Ni_2L_2+H+Ni)^+$ and NiL^+ ions, but in the more demetallating matrix of dithioerythritol/dithiothreitol the NiL^+ ion is more intense and ions corresponding to NiL_2^+ and the free ligand (most intense ion) are also seen. For $Ni_2(Et_4\text{-en-BDTSQ})_2$, only the $(Ni_2L_2+H)^+$ ion was observed using *m*-nitrobenzyl alcohol as the matrix. The apparent ease of demetallation in dithioerythritol/dithiothreitol suggests that ligand-metal bonding is not especially strong.

Upon coordination, several changes occur in the IR spectra. First, consistent with deprotonation of the ligands, the NH vibrations are absent in the spectra of both $Ni_2(Bu_4\text{-en-BDTSQ})_2$ and $Ni_2(Et_4\text{-en-BDTSQ})_2$. Such vibrations are present, but of diminished intensity, in the spectrum of $Ni_2(Bu_2H_2\text{-en-BDTSQ})_2$ since only two of the four amide hydrogens are removed from each ligand upon forming the neutral complex. Second, the ν_{CN} band, observed in the free ligands in the range 1555–1600 cm^{-1}; shifts to considerably higher energy upon coordination (44 to 72 cm^{-1}). Previously, it was established that coordination of *cis*-dithiosquaramide ligands in a bidentate S_2 arrangement causes the ν_{CN} band to shift 20–68 cm^{-1} to higher energy.[2] Third, each of the complexes shows a very strong band in the range 1392–1417 cm^{-1}, which is assigned as ν_{CCS}, though it is perhaps mostly ν_{CC} in character. This band has shifted to higher energy from its position in the free ligands.[6] Such a shift is consistent with an increase in the CC double bond character of the SCCS group as would be expected if the group becomes less dithione-like (S=C—C=S) and more dithiolene-like (S—C=C—S) upon coordination. Similarly, a ν_{CCS} band in tetrathiosquarate, around 1235 cm^{-1} in the free ligand, shifts about 70 cm^{-1} to higher energy upon coordination.[1a] Thus, it is apparent from the IR changes that the bis(dithiosquaramide) ligands are coordinated in an S_4 rather than an N_2S_2 fashion.

Changes in the ^1H NMR spectrum of $Ni_2(Bu_4\text{-en-BDTSQ})_2$ as compared with the free ligand are also consistent with deprotonated NH groups and coordination of the ligand *via* sulfur only, rather than nitrogen and sulfur. First, the NH resonance observed at δ 8.433 in the free ligand is absent in the complex. Second, the resonance for the bridging dimethylene group is shifted from δ 4.460 in the free ligand to δ 3.742 in the complex. Such an upfield shift for this resonance is expected on inductive grounds if the electronegativity of the amide nitrogen is reduced, as would occur if the amide group were deprotonated but not coordinated. In contrast, the resonance for the bridging dimethylene group in tetradentate dithiooxamide ligands shifts only slightly upfield (0.16–0.21 ppm) upon complexation to nickel(II) because the inductive effect of deprotonating the amide group is offset somewhat by coordination of the amide nitrogen to nickel.[3] Restricted rotation about the C-NR_2 bond is still evident as indicated by resonances for two different types of butyl groups in $Ni_2(Bu_4\text{-en-BDTSQ})_2$.

On the basis of the spectroscopic data discussed above, a proposed structure for the complexes is shown in Scheme 2. Each of the ligands is bound to two nickel(II) ions resulting in a diamagnetic 2:2 species having adjacent square planar nickel(II) ions with NiS_4 coordination environments. Electrochemical measurements show two closely overlapping redox processes at $E = 0.63$ V and 0.78 V (*versus* SHE), suggesting that oxidation of the two nickel(II) centres occurs in a stepwise fashion with the oxidation potential of the second nickel(II) centre being slightly more difficult than the first. Such behaviour is in accord with a dinuclear complex having adjacent metal centres.

The electronic spectra of the complexes in solvents with low coordinating abilities (e.g., dichloromethane and tetrahydrofuran) show an intense charge transfer band in the visible region at 512–526 nm ($\varepsilon \approx 30{,}000$) that accounts for their red colour. The nickel(II) complexes of didentate *cis*-dithiosquaramide ligands show a similar band at 492 nm ($\varepsilon \approx 10{,}000$).[2] In contrast, pyridine solutions of the complexes are brownish-yellow at 25°C and show essentially no band around 520 nm. Upon heating, however, the solutions become dark red, and the spectrum, of $Ni_2(Et_4\text{-en-BDTSQ})_2$ for example, clearly shows a band at 526 nm growing in intensity with increasing temperature. This thermochromic behaviour is reversible and equilibria such as those shown in Scheme 3 are probably responsible for the phenomenon.

$$\mathrm{Ni_2L_2} \rightleftharpoons \mathrm{Ni_2L_2py} \rightleftharpoons \mathrm{Ni_2L_2py_2} \rightleftharpoons \mathrm{Ni_2L_2py_3} \rightleftharpoons \mathrm{Ni_2L_2py_4}$$

In a related tetrathiosquarate complex of nickel(II), which also has a square planar NiS_4 core, axial coordination of pyridine occurs to give the bis-pyridine adduct $[Ph_4As]_2[Ni(C_4S_4)_2Py_2]\cdot 2py$.[7]

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References and Notes

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