Inorganica Chimica Acta, 25 (1977) 247–254
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Coordination Complexes Containing Multidentate Ligands. Part XIII [1]. Nickel(II) and Rhodium(III) Complexes of Tetradentate Diamine–Dithioether Ligands

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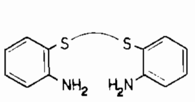
Received May 4, 1977

The preparation of four open-chain diamine–dithioether ligands is described: o-$H_2NC_6H_4S\frown SC_6H_4NH_2$-o $(\frown = -CH_2CH_2-, -CH_2CH_2CH_2-, -CH_2CH_2CH_2CH_2-$, *and* cis-CHCH–). *These form six-coordinate pseudo-octahedral* trans-$[NiLX_2]$ *(X = Cl, Br, I, NCS) complexes, which exhibit varying degrees of tetragonal distortion but which is least for the ligand with the* $C_2C_3C_2$ *carbon backbone sequence between the four donors. The parameters* D_q^{xy}, D_q^z *and Dt are evaluated and discussed in relation to changes in L and X. Rhodium(III) salts do not form simple monomeric adducts, but* $Rh_4L_3Cl_{12}$ *can be readily isolated; this phenomenon is discussed.*

Introduction

During the past decade many studies of tripod tetradentate ligands have been described [2]. The trigonal symmetry of these ligands often results in the formation of trigonal bipyramidal complexes. In contrast open-chain linear tetradentates are much more flexible and are more responsive to the properties of the metal ion. Only recently have open-chain ligands with heavy donor atoms become available [3]. We are currently examining a range of these tetradentates with the aims of elucidating the effects of mixed donor atoms and varying inter-donor linkages upon the spectroscopic properties of the complexes.

We have previously shown that tetrathioether (S_4) ligands form pseudooctahedral *trans*-$[Ni(S_4)X_2]$ and planar $[Pd_2(S_4)X_4]$ [4, 5]. The diarsine–dithioether $Me_2As(CH_2)_3S(CH_2)_3S(CH_2)_3AsMe_2$ exhibits more diverse behaviour, yielding four- $[NiL](ClO_4)_2$, five- $[NiLX]ClO_4$, and six-coordinate $[NiLX_2]$, nickel(II) complexes, whilst the five-coordinate [PdLX]X become *trans* planar $[PdLX_2]$ (As_2X_2 donor set) in halocarbon solvents [6]. Here we report an extension of our studies to a series of diamine–dithioether chelates (I).



$\frown$ = $-CH_2CH_2-$ (eS_2N_2)
$-CH_2CH_2CH_2-$ (pS_2N_2)
$-CH_2CH_2CH_2CH_2-$ (bS_2N_2)
cis-CH=CH (VS_2N_2)

The synthesis of 1,2-bis(*o*-aminophenylthio)ethane (eS_2N_2) has been reported by Cannon *et al.* [7] who showed that it formed six-coordinate nickel(II) and cobalt(III) complexes, and that the planar $[Pd(eS_2N_2)X_2]$ complexes contained eS_2N_2 behaving as a bidentate S_2 donor.

Experimental

Absolute ethanol was dried over magnesium ethoxide. *o*-Aminothiophenol was fractionated before use [B.P. 98 °C (3 mm)]. The ligand preparations were carried out under an atmosphere of dry nitrogen. Physical measurements were made as described previously [8].

1,2-Bis(o-aminophenylthio)ethane (eS_2N_2)

Sodium (7 g, 0.3 gatom) was dissolved in ethanol (250 cm^3) and *o*-aminothiophenol (37.5 g, 0.3 mol) added. After stirring for 1 hr, the mixture was treated with 1,2-dibromoethane (28.2 g, 0.15 mol) and then refluxed for 1 hr. The solution was treated with deoxygenated water (200 cm^3) and extracted with ether (3 × 100 cm^3). The ether extract was evaporated, the residual oil dissolved in methanol (100 cm^3) and the ligand precipitated by the addition of ice-cold water. The white crystalline product was dried *in vacuo*. Yield 30 g, ~75%; Fd. C = 60.8%, H = 5.8%, N = 9.9%. $C_{14}H_{16}N_2S_2$ requires C = 60.8%, H = 5.8%, N = 10.1%, MP 75 °C.

1,3-bis(*o*-aminophenylthio)propane and 1,4-bis(*o*-aminophenylthio)butane were prepared similarly.

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TABLE I. Diamine–Dithioether Ligands.

	MP (°C)	^{1}H nmr (τ)^a	IR cm^{-1} ^{b}
eS_2N_2	78.5	3.25(m) |8H|, 5.8(s) |4H|(NH_2) 7.25(t) |4H|(CH_2)	3300 3380
pS_2N_2	|BP 240°/1 mm|	3.0(m) |8H|, 5.75(s) |4H|(NH_2) 7.2(t) |4H|(SCH_2) 8.3(q) |2H| ($SCH_2\mathit{CH}_2$)	3300 3440
bS_2N_2	56	3.1(m) |8H|, 5.8(s) |4H|(NH_2) 7.35(t) |4H|(SCH_2) 8.25(q) |4H| ($SCH_2\mathit{CH}_2$)	3320 3460
VS_2N_2	63	3.0(m) |8H|, 3.84 |2H|(CH=CH) 5.75 (s) |4H|(NH_2)	3300 3400

^{a}CDCl$_3$ relative internal TMS. $^b\nu$(NH).

pS_2N_2: Fd. C = 62.3%, H = 6.3%, N = 9.3%. $C_{15}H_{18}N_2S_2$ requires C = 62.0%, H = 6.3%, N = 9.7%. This ligand is a colourless liquid, BP 240 °C/1 mm.

bS_2N_2 Fd. C = 62.8%, H = 6.6%, N = 9.4%. $C_{16}H_{20}N_2S_2$ requires C = 63.1%, H = 6.6%, N = 9.2%. MP 65 °C.

Cis-1,2-bis(*o*-aminophenylthio)ethylene VS_2N_2 was prepared similarly except that the mixture of the sodium salt of *o*-aminothiophenol and *cis*-1,2-dichloroethylene was refluxed for 48 hrs.

Fd. C = 61.2%, H = 5.0%, N = 10.0%. $C_{14}H_{14}N_2S_2$ requires C = 61.3%, H = 5.1%, N = 10.2%, MP 63 °C.

Dichloro{1,2-bis(o-aminophenylthio)ethane}nickel(II)

Nickel(II) chloride hexahydrate (1.72 g) in hot ethanol (30 cm^3) was filtered into a stirred solution of eS_2N_2 (2.0 g) in ethanol (10 cm^3). Immediate precipitation of a pale blue solid occurred. The mixture was refluxed for 15 minutes, the product filtered off, rinsed with ethanol and ether, and dried *in vacuo* (yield 80%).

The other nickel(II) complexes were made analogously using the appropriate nickel(II) halide, or nickel(II) thiocyanate made *in situ* from sodium thiocyanate and nickel(II) nitrate in ethanol. The nickel(II) perchlorate complexes were isolated only by concentrating the solutions to small volumes and precipitating with ether.

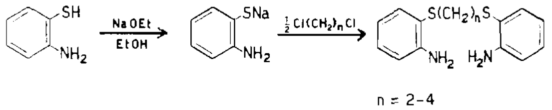
Dodecachlorotris{1,2-bis(o-aminophenylthio)ethane}-tetrarhodium(III)

Rhodium trichloride trihydrate (0.26 g) in ethanol (15 cm^3) was added slowly to a vigorously stirred solution of eS_2N_2 (0.25 g) in ethanol (20 cm^3). The mixture was stirred for 10 minutes, and the precipitate filtered off, washed with ethanol and dried *in vacuo*. Yield 90% (on $RhCl_3{\cdot}3H_2O$).

Results and Discussion

Ligands

The three, α,ω-bis(*o*-aminophenylthio)alkanes eS_2N_2, pS_2N_2, and bS_2N_2 were prepared by the general route:



The same route yields VS_2N_2, but the greater reluctance of RS$^-$ nucleophiles to attack vinyl C–Cl bonds [9] necessitates prolonged reflux of the mixture. Use of excess ethoxide is also advantageous. The properties of the ligands are given in Table I.

The mass spectra of these ligands also confirmed their identity. The fragmentation modes are similar to those of the corresponding tetrathioethers [10].

Nickel(II) Complexes

The reaction of nickel(II) halides and thiocyanate with eS_2N_2, pS_2N_2, bS_2N_2 and VS_2N_2 in ethanol produced [$NiLX_2$] complexes (X = Cl, Br, I, NCS), several of which were obtained as ethanol solvates on the evidence of analytical data and their IR spectra (Table II). The complexes are essentially insoluble in alcohols, acetone and halocarbons, and dissolve in NN-dimethylformamide with partial displacement of the coordinated halides since the solutions exhibit considerable conductivities, and their electronic spectra are markedly different from the solid state. In view of the insolubility of these complexes in any solvent with which they did not react, measurements were of necessity confined to the solid state. The complexes are paramagnetic with μ_{eff} 2.8–3.4 BM, corresponding to high-spin d^8 Ni(II) in a six-coordinate environment [11]. It is notable that the complexes

TABLE II. Analytical and Other Data.

Compound	Colour	C%[a]	H%[a]	N%[a]	X%[a,b]	μ_{eff} B.M.[c]	IR Data, cm^{-1} [d]		Others
							ν(N–H)	ν(M–X)	
$[Ni(eS_2N_2)Cl_2]$	Pale Blue	41.7(41.4)	4.2(4.0)	6.7(6.9)	17.8(17.5)	3.02	3270, 3265	250	–
$[Ni(eS_2N_2)Br_2]$	Pale Blue	33.9(33.9)	3.5(3.3)	5.3(5.7)	32.0(32.3)	3.36	3275, 3260	–	
$[Ni(eS_2N_2)I_2]$	Green	28.8(28.6)	2.8(2.7)	4.5(4.8)	43.0(43.1)	3.04	3265, 3250	–	
$[Ni(eS_2N_2)(NCS)_2]$	Mauve	41.2(42.6)	3.6(3.6)	12.7(12.4)	–	3.00	3275, 3265	243 (Ni–NCS)	2065 ν(CN)
$[Ni(eS_2N_2)(H_2O)_2](ClO_4)_2 \cdot EtOH$	Pale Purple	31.2(31.1)	4.4(4.4)	4.8(4.6)	11.9(11.7)	3.05	3255 br		1090, 620 (ClO_4) ~3500, ~1610 (OH)
$[Ni(VS_2N_2)Cl_2]$	Yellow–Green	39.6(41.4)	3.9(3.8)	6.0(6.9)	17.6(17.8)	3.04	3280, 3275	245	–
$[Ni(VS_2N_2)Br_2]$	Blue–Green	34.1(34.0)	2.9(2.9)	5.7(5.6)	32.4(32.7)	3.03	3295, 3280	–	
$[Ni(VS_2N_2)I_2]$	Yellow–Green	29.5(28.6)	2.6(2.4)	4.6(4.8)	42.0(43.2)	2.92	3290, 3275	–	
$[Ni(VS_2N_2)(NCS)_2]$	Pale–Green	42.0(42.8)	2.8(3.1)	12.5(12.5)	–	2.90	3300, 3285	240 sh, 210 (Ni–NCS)	2090 ν(CN)
$[Ni(pS_2N_2)Cl_2] \cdot EtOH$	Pale–Green	44.2(43.8)	4.8(5.1)	6.6(6.0)	14.7(15.2)	3.02	Not observed	250	3500, 4605 (OH)
$[Ni(pS_2N_2)Br_2]$	Blue–Green	35.1(35.4)	3.7(3.6)	5.2(5.3)	31.5(31.4)	2.81	3290, 3278	–	
$[Ni(pS_2N_2)I_2]$	Green	30.1(29.9)	3.1(3.0)	4.8(3.0)	41.8(42.1)	2.84	3280, 3275	–	
$[Ni(pS_2N_2)(NCS)_2]$	Purple–Pink	43.8(43.8)	4.0(3.9)	12.0(12.0)	–	2.80	3245, 3240	260 (Ni–NCS)	2060 ν(CN)
$[Ni(bS_2N_2)Cl_2]$	Pale Green	44.4(44.3)	4.8(4.6)	6.6(6.5)	16.8(16.3)	2.84	3245, 3238	230	
$[Ni(bS_2N_2)Br_2]EtOH$	Pale Blue	37.6(38.1)	4.2(4.6)	5.2(4.9)	28.2(28.2)	2.90	3250, 3240	–	3500, 1605 (OH)
$[Ni(bS_2N_2)I_2] \cdot EtOH$	Green	32.5(32.6)	3.6(3.9)	4.5(3.9)	38.6(38.3)	2.86	3260, 3255	–	3500, 1610 (OH)
$[Ni(bS_2N_2)(NCS)_2]$	Light Purple	45.0(45.1)	4.7(4.2)	11.1(11.7)	–	2.82	Not observed	260, 235 (Ni–NCS)?	2080 ν(CN)
$[Ni(bS_2N_2)(H_2O)_2](ClO_4)_2$	Grey	33.5(32.6)	4.4(4.0)	4.5(4.7)	12.4(12.0)	2.89	Not observed	–	1090, 618 (ClO_4) 3300, 1630 (H_2O)
$[Rh_4(eS_2N_2)_3Cl_{12}] \cdot EtOH$	Red Yellow	30.3(30.3)	4.5(3.0)	4.8(4.9)	23.5(24.8)	–[e]	–	330 br	
$[Rh_4(VS_2N_2)_3Cl_{12}] \cdot EtOH$	Brown	30.8(30.9)	3.1(3.0)	4.9(4.9)	24.9(24.8)	–[f]	–	335, 290 sh	
$[Rh_4(pS_2N_2)_3Cl_{12}] \cdot EtOH$	Brown	33.2(32.0)	3.6(3.4)	5.0(4.7)	24.4(24.2)	–[g]	–	340 sh, 315, 305 sh	
$[Rh_4(bS_2N_2)_3Cl_{12}] \cdot EtOH$	Yellow–Brown	33.7(33.7)	4.1(3.6)	4.6(4.2)	22.6(23.7)	–[h]	–	320 br	

[a] Fd (calc). [b] Halogen. [c] ±0.05 BM. [d] Nujol and HCB mulls. [e] Electronic spectrum: $\epsilon_{max} = 23{,}500\ cm^{-1}$. [f] $\epsilon_{max} = 22{,}700\ cm^{-1}$. [g] $\epsilon_{max} = 23{,}300\ cm^{-1}$. [h] $\epsilon_{max} = 24{,}400\ cm^{-1}$.

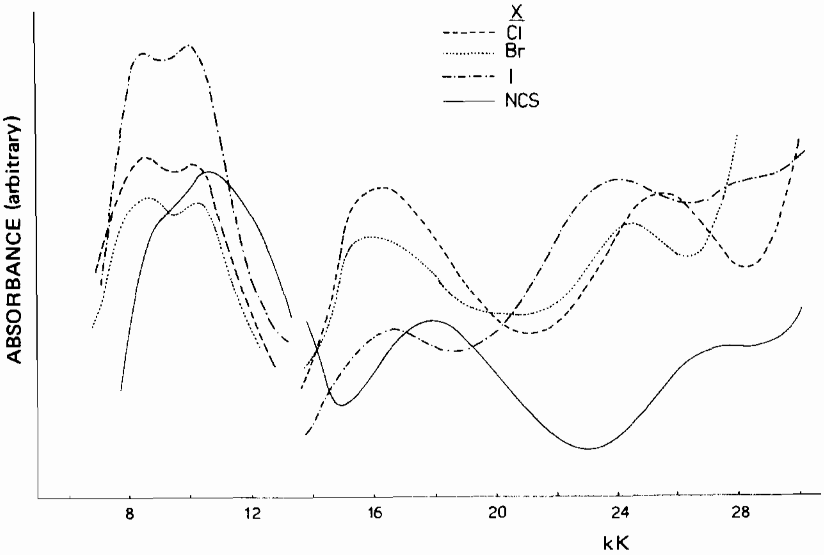


Figure 1. Reflectance spectra of [Ni(eS$_2$N$_2$)X$_2$].

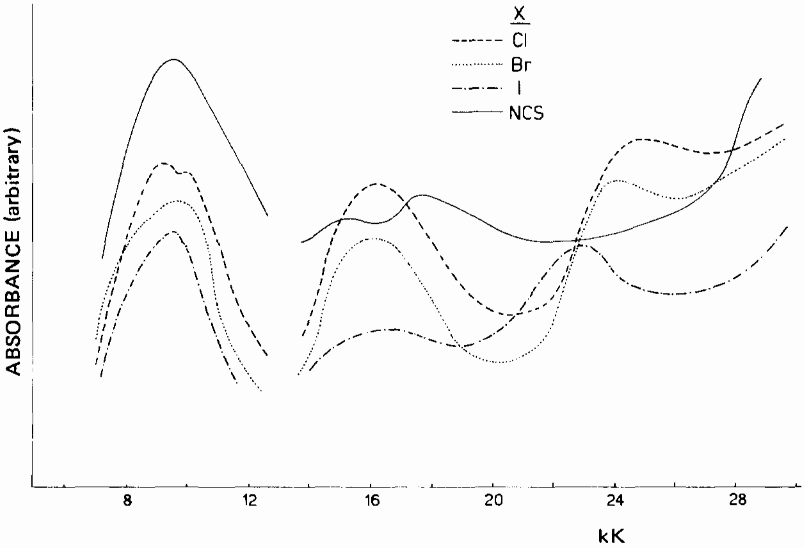


Figure 2. Reflectance spectra of [Ni(pS$_2$N$_2$)X$_2$].

which do not appear to be significantly tetragonally distorted (below) had lower μ_{eff} values than those for which marked distortion was found.

The IR spectra of the coordinated amine groups show a shift of ν(NH) to <3300 cm^{-1} compared with the values in the free ligands (3300–3500 cm^{-1}) (Tables I, II), consistent with coordination [7]. The far IR spectra of the bromo and iodo complexes are practically identical for each ligand, whilst the chlorocomplexes exhibit one strong band at 230–260 cm^{-1} tentatively assigned to ν(Ni–Cl). These values are very low for terminal Ni–Cl stretching vibrations [12], but may be due to the tetragonal distortion present, and hence longer than usual Ni–Cl bonds. The presence of a single ν(NiCl) vibration points to a *trans* pseudooctahedral structure. The thiocyanate complexes contain single strong ν(CN) vibrations at 2060–2090 cm^{-1} indicative of *trans* NiNCS linkages [13], but strong ligand absorptions prevented the assignment of ν(CS) or δ(NCS).

Despite a number of attempts, nickel(II) perchlorate complexes of VS$_2$N$_2$ and pS$_2$N$_2$ could not be obtained. However both eS$_2$N$_2$ and bS$_2$N$_2$ yielded complexes of stoichiometry NiL(ClO$_4$)$_2$·2H$_2$O. Neither complex showed any sign of perchlorate coordination [14] – both ν_3 and ν_4 (ClO$_4$) vibrations were unsplit, although it is apparent from the electronic spectra (below) that the complexes contain

TABLE III. Electronic Spectral Data on [$NiLX_2$] Complexes (cm^{-1}).

Compound	$^3B_{1g} \rightarrow {}^3E_g$		$^3B_{1g} \rightarrow {}^3B_{2g}$	$^3B_{1g} \rightarrow {}^1A_{1g}, {}^1B_{1g}$	$^3B_{1g} \rightarrow {}^3A_{2g}(F)$[a]	$^3B_{1g} \rightarrow {}^3A_{2g}(P)$	$^3B_{1g} \rightarrow {}^3E_g(P)$	D_q^{xy}	D_q^z	Dt
[$Ni(eS_2N_2)Cl_2$]	8350		10100	–	16250	25600	–	1010	660	200
[$Ni(eS_2N_2)Br_2$]	8400		10300	–	16000	24500	–	1030	650	217
[$Ni(eS_2N_2)I_2$]	8700		10200	–	16500	23800	28200 sh	1020	720	170
[$Ni(eS_2N_2)(NCS)_2$]	9100		10800	11800	18000	26200	–	1080	740	194
[$Ni(eS_2N_2)(H_2O)_2$]$(ClO_4)_2$	8930		10640	12200	17800	26320	–	1064	722	194
[$Ni(VS_2N_2)Cl_2$]	8100		10300	13300	16600	23000 sh	–	1030	590	251
[$Ni(VS_2N_2)Br_2$]	8350		10250	–	16300	23800	–	1025	645	217
[$Ni(VS_2N_2)I_2$]	8350		10100	–	17100	23800	–	1010	660	200
[$Ni(VS_2N_2)(NCS)_2$]	8600		10200	–	16000	27800 sh	–	1020	760	183
[$Ni(pS_2N_2)Cl_2$]	9200		10200	–	16500	25000	–	1020	820	114
[$Ni(pS_2N_2)Br_2$]		10200		–	16300	24400	–			
[$Ni(pS_2N_2)I_2$]		9800		–	16250	23200	–			
[$Ni(pS_2N_2)(NCS)_2$]		10200		14600 (w)	18000	26200 sh	–			
[$Ni(bS_2N_2)Cl_2$]	9000 sh		10000	14000 sh	16100	24600	–	1000	800	114
[$Ni(bS_2N_2)Br_2$]	8300		11200	15800 sh	16700	25300 sh	–	1120	540	312
[$Ni(bS_2N_2)I_2$]	8500		11000	–	16600	24300	–	1100	700	286
[$Ni(bS_2N_2)(NCS)_2$]		10500		–	18500	26200 sh	–			
[$Ni(bS_2N_2)(H_2O)_2$]$(ClO_4)_2$		11100		12300 sh	17240	26400 sh				

[a] This band also contains the absorption due to $^3B_{1g} \rightarrow {}^3E_g(F)$ transitions.

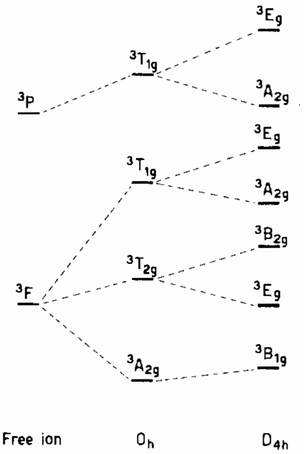


Figure 3. Correlation diagram.

pseudooctahedral nickel(II). In view of this they are formulated $[NiL(H_2O)_2](ClO_4)_2$ with coordinated aquo groups in the axial positions.

Electronic Spectra

The reflectance of these nickel(II) complexes are listed in Table III and several examples are shown in Figures 1 and 2. A number of studies [15–19] have discussed the assignment of the spectra of octahedral or tetragonal nickel(II) complexes. The information obtainable from the spectra depends to a great extent on the number of bands which can be identified [17]; in favourable cases D_q^{xy}, D_q^z, Dt, Ds, B, C and the McClure $\delta\pi$ and $\delta\sigma$ parameters have been calculated, but usually the number of absorbtions observed is smaller and correspondingly less information can be extracted. In the present case the symmetry of the complexes approximates to C_{2v}, but considering the tetradentate as the equatorial ligand and the X groups axial (as indicated by the IR spectra), the spectra may be treated to a first approximation on the basis of D_{4h} symmetry. The correlation diagram for the triplet states of a d^8 ion is shown in Figure 3, and based upon this the absorbtions may be assigned (in order of increasing energy) to $^3B_{1g} \rightarrow {}^3E_g$, $^3B_{2g}$, $^3A_{2g}(F)$, $^3A_{2g}(P)$ (Table III). Other weak bands observed may be due to spin-forbidden transitions. Based upon the treatment of Brubaker and Busch [15] and Rowley and Drago [16, 17] the transition $^3B_{1g} \rightarrow {}^3B_{2g}$ corresponds to the in plane ligand field splitting parameter D_q^{xy}, the separation in energy between the $^3B_{1g} \rightarrow {}^3E_g$, and $^3B_{1g} \rightarrow {}^3B_{2g}$ transitions [= 35/4 Dt] affords the tetragonal splitting parameter Dt, whilst the out of plane (axial) ligand field contribution D_q^z is given by

$$D_q^z = \frac{2\nu_1 - \nu_2}{10}$$

where ν_1 and ν_2 correspond to the transitions $^3B_{1g} \rightarrow {}^3E_g$, $^3B_{1g} \rightarrow {}^3B_{2g}$ respectively. The results are summarised in Table III. Attempts to extract further data from the spectra were unsuccessful since insufficient absorptions were usually present. Attempts to estimate DS or B produced unrealistic values probably due to the breakdown of the model.

From Table III it can be seen that all the $[Ni(eS_2N_2)X_2]$ and $[Ni(VS_2N_2)X_2]$ are markedly distorted, as are $[Ni(bS_2N_2)X_2]$ (X = Cl, Br, I) and $[Ni(pS_2N_2)Cl_2]$, but the $[Ni(pS_2N_2)X_2]$ (X = Br, I, NCS) and $[Ni(bS_2N_2)(NCS)_2]$ showed no splitting of the low energy band, and are thus not appreciably distorted. Comparison of the D_q^{xy} values show that they vary for the same ligand with changes in X-groups, whilst the D_q^z values of particular X groups vary more widely with changes in ligands. This is further proof that D_q^{xy} and D_q^z values are not transferable from complex to complex [4, 5, 16, 17]. Although too much reliance should not be placed upon the absolute numerical values, it is clear that the overall trends in D_q^{xy} are in keeping with expectation – thus these N_2S_2 donors have larger values of D_q^{xy} than the open chain diarsinedithioether [6] and tetrathioether ligands [4, 5] but smaller than N_4 donors such as $(py)_4$ or $(diamine)_2$ [16, 17], or macrocyclic N_4 or S_4 ligands [18, 19]. The D_q^z values of the X groups lie in the order NCS > I > Br > Cl, whereas one would expect NCS > Cl > Br > I. This illustrates the subtle effect of the in plane ligand upon the axial ligands, but in the absence of X-ray data on the metal–donor bond lengths speculation on the cause is not justified.

It is interesting that changing the central linkage $-(CH_2)_2- \rightarrow -(CH_2)_3-$ reduces the tetragonal distortion, whilst further increase to $-(CH_2)_4-$ again produces markedly tetragonal complexes. This effect is not simply steric hindrance along the z-axis by the $-(CH_2)_n-$ chains since the ligand with the planar CH=CH linkage also produces tetragonal complexes.

More likely the explanation is to be found in chelate ring strain [3, 21] which for planar coordination of a linear tetradentate is expected to be less for a 2,3,2 interdonor linkage than for either 2,2,2 or 2,4,2 [3]. Attempts to relieve this strain and the resulting steric and/or electronic effects is no doubt responsible for the variations along the series.

Rhodium(III) Complexes

Irrespective of the Rh:ligand ratio, the only complexes isolated with these ligands were of the type $Rh_4L_3Cl_{12}$, analogous to the tetrathioethers [4, 5] and thus all 24 donors $(Cl_{12}S_6N_6)$ are accommodated on octahedrally coordinated rhodium(III). This phenomenon is related to the inability of the S_2N_2 ligands to compete for coordination positions with chlorine; thus $[RhLCl_2]^+$ cannot be formed, but octahedral coordination is acceptable with

$Rh_4L_3Cl_{12}$ stoichiometry. Insolubility prevented further studies.

Conclusion

These S_2N_2 ligands form similar complexes to the S_4 ligands with Ni(II), although the former yield much more stable complexes as expected with the presence of hard N donors. The only type of complex formed are the six coordinate $[NiLX_2]$ and neither the diverse coordination modes nor the facile dealkylation [22]* found with diarsine–dithioethers were observed.

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*The complexes do not dealkylate on boiling in DMF, instead displacement of the diamine–dithioether occurs and $Ni(DMF)_6^{2+}$ is formed.