Nickel(II) Compounds of Three Homologous Linear Tetra-amines, Especially Solvent Effects and Configuration

DONALD F. COOK and E. DONALD McKENZIE*

*Chemistry Department, The University, Sheffield, S3 7HF, U.K.*

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A comparative study has been made of the 1:1 nickel(II) compounds of three homologous linear tetraamines: 1,4,7,10-tetraazadecane(trien), 1,4,8,11-tetraazaundecane(2,3,2-tet), and 1,5,8,12-tetraazadodecane(3,2,3-tet). A range of solid compounds Ni-(tetraamine)X₂ (X = Cl, Br, I, NCS, NO₂, NO₃, ClO₄), a number of which are new, has been prepared from 2,3,2-tet and 3,2,3-tet. These include the structural isomers yellow low-spin [Ni(3,2,3-tet)]I₂ and lilac high-spin trans-[Ni(3,2,3-tet)I₂]. The high-spin species have a trans octahedral configuration, except for [Ni(2,3,2-tet)NO₃]NO₃, which appears to have a chelating nitrate. In solution in water, DMF, and DMSO two equilibria of these compounds have been studied under varying conditions: (a) the cis ⇌ trans equilibria of the high-spin [Ni(N₄)(S)₂]²⁺ species (S = solvent); and (b) high-spin octahedral ⇌ low-spin planar equilibria. It is shown for the first time that equilibria (a) occur in such solutions for both 2,3,2-tet and 3,2,3-tet. The trans isomers are preferred over cis in the orders: (i) (for solvent) H₂O > DMF > DMSO; and (ii) (for the amines) 3,2,3-tet > 2,3,2-tet ≫ trien. In concentrated LiNO₃ and LiClO₄, Ni-(trien)²⁺, but not the others, forms high spin cis-[Ni-(N₄)O₂] species which apparently have a chelating anion. For equilibria (b) (the singlet ⇌ triplet equil.) the planar low-spin species are preferred in the order 2,3,2-tet > 3,2,3-tet > trien – an order different from that observed in (a). Difficulties in defining εmax for these low-spin species, and hence in quantifying the equilibria are discussed with evidence for the complications. The observations on both equilibria can be rationalised by reference to the steric effects of the amines: 3,2,3-tet has a greater preference than 2,3,2-tet for trans high-spin isomers, but it can less easily accommodate to the shorter Ni–N bond lengths in the low-spin species.

Introduction

In 1966 we [1] showed that a general pattern could be discerned in the configurations adopted by two homologous tetraamines in their transition-metal compounds, and that this could be related to the steric constraints in each ligand. Whereas, 1,4,7,10-tetraazadecane(trien, I for x = y = 2) showed a

$$NH_2-(CH_2)_x-NH-(CH_2)_y-NH-(CH_2)_x-NH_2$$

I
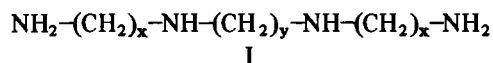
marked preference for cis-octahedral (or, more generally, non-planar) configurations (II or III),1,4,8,11-tetraazaundecane (2,3,2-tet, I for x = 2 and y = 3) appeared

cis-α   cis-β
II   III
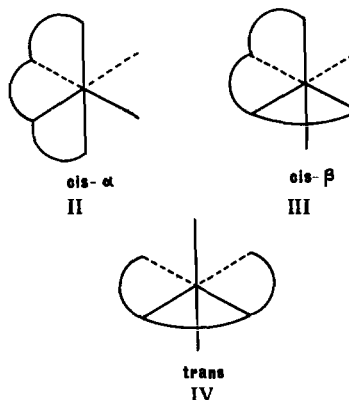
trans
IV

to prefer trans-octahedral (or planar N₄) configurations (IV). Subsequent work on these [2–5] and related systems [6–8], especially the thermodynamic studies [4–6] and some X-ray structural studies [9–11], have amply confirmed our view of the importance of the steric effects.

The 1966 paper [1] included data on nickel(II) compounds of 2,3,2-tet and trien, and subsequent papers have made further comments [4, 5], especially on the singlet ⇌ triplet equilibrium in aqueous solutions [12–15]. More recently Curtis and Milestone [16] reported an extensive preparative study of the 2,3,2-tet nickel(II) system, with both trans and cis-octahedral compounds.

Here we report the results of our further study of the Ni^II compounds of the three homologues – trien,

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*Author for correspondence. Present address: Chemistry Department, University of Queensland, Brisbane, Australia 4067

2,3,2-tet and 3,2,3-tet. These results refer especially to the equilibria in water, DMF and DMSO, and comment on the configurations adopted – evidence coming from the electronic absorption spectra.

The new data generally confirm the importance of the steric effects, but also demonstrate that solvation effects can be important in defining configuration in these labile systems.

Experimental

Preparation of Compounds

The various methods used are as follows (Table I contains the key for the method for each compound):

(a) The ligand (~2g) in ethanol (~10ml) was treated with 10% less than the calculated amount of the appropriate hydrated binary nickel(II) compound in ethanol (~20ml). We obtained an anhydrous chloride, whereas Curtis and Milestone [13] reported a slightly hygroscopic trihydrate. We also made the monochloroacetate, but it was deliquescent and hence not used.

(b) See ref. 13.

(c) A hot solution of NiI_2 in ethanol was added to an estimated excess of the ligand in hot ethanol. The product was recrystallised from ethanol.

(d) The general method involved adding an excess of the appropriate lithium salt to an aqueous solution of $[Ni(L)Cl_2]$. The –NCS compounds precipitated readily $\{[Ni(3,2,3-tet)(NCS)_2]$ is practically insoluble in water} as did $[Ni(2,3,2-tet)]X_2$ (X = I, ClO_4). For the nitro compound, small volumes were necessary: ~1g of the chloro spp. in water (5ml) was treated with solid $NaNO_2$ until precipitation occurred. The product was washed with saturated aqueous $NaNO_2$, aqueous ethanol and then acetone.

(e) See ref. 1.

(f) These were reported as anhydrous compounds in ref. 1 – the data there referring to samples that had been dehydrated at 110C.

(g) An aqueous solution of the calculated amounts of $[Ni_2(2,3,2-tet)_3](NO_3)_4$ and $[Ni(H_2O)_6]-(NO_3)_2$ was evaporated almost to dryness. The resulting yellow gum was triturated with 95% ethanol, giving a purple solid. This tended to deliquesce and was best kept covered with ethanol throughout the filtration and washing procedures – the last of the ethanol being removed in a vacuum desiccator. Once dry, the sample was air stable.

(h) The nickel(II) halide in ethanol was treated with the calculated amount of the ligand in ethanol. Yellow $[Ni(3,2,3-tet)]I_2$ is deliquescent and needs to be kept in a sealed container.

(i) The hot filtrate from method (c) was treated with an excess of NiI_2 in hot ethanol, and the solution was set aside to cool. Lilac crystals separated. They tended to deliquesce and were isolated in the manner described in (g).

(j) $[Ni(3,2,3-tet)Cl_2]$ in water was treated with the calculated amount of $AgNO_3$. After removal of the AgCl, the solution was evaporated until a yellow gum was obtained. This was triturated with ethanol. The product was recrystallised by dissolving in several mls of water and precipitating with ethanol.

(k) Several attempts to prepare $[Ni(3,2,3-tet)]-(ClO_4)_2$ were unsuccessful. Evaporation of an aqueous solution left a yellow gum, which on trituration with acetone gave the yellow acetone Schiff base compound V.

Electronic Spectra

All spectra were measured on a Unicam SP700 instrument, with the SP735 attachment for the diffuse reflectance spectra of the solids.

Results and Discussion

Solid Compounds

The compounds prepared are listed in Table I. The majority of these are high-spin octahedral nickel(II) species: as proven by the diffuse reflectance electronic spectra.

A larger range of compounds has been reported by Curtis and co-workers for both trien [17] and 2,3,2-tet [16], and their results and conclusions support those of the present paper.

Among the new compounds in Table I are nearly all those of the 3,2,3-tet ligand. Isomeric forms of $Ni(3,2,3-tet)I_2$ were obtained from ethanol. The lilac isomer is trans-$[Ni(3,2,3-tet)I_2]$ and the yellow, deliquescent one is the four-co-planar diamagnetic $[Ni(3,2,3-tet)]I_2$.

In an early preparation of $Ni(2,3,2-tet)(NO_3)_2$ in which the oily residue obtained by evaporating an aqueous solution was triturated with acetone, we once obtained several quite large crystals (~6mm³) of a yellow compound which must have been the isomeric $[Ni(2,3,2-tet)](NO_3)_2$. But this also was very deliquescent and the crystals were lost. We find no evidence here for reaction with the acetone [18]: attempts to prepare acetone condensates were not successful. By contrast, in the 3,2,3-tet system, V was easily prepared.
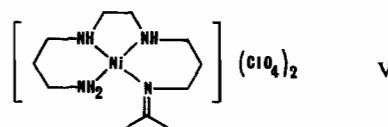
TABLE I. The Compounds Isolated and the Analytical Data.

Compound	Colour	Method of preparation	Analyses				Calculated			
			Found							
			C	H	N	Other	C	H	N	Other
$[Ni_2(2,3,2\text{-tet})_3](NO_3)_4 \cdot 6H_2O$	pink	a	28.4	6.4	25.7		28.6	7.5	25.4	
$[Ni_2(2,3,2\text{-tet})_3](ClO_4)_4$	pink	a, b	25.1	5.9	16.9	Cl, 14.1	25.3	6.1	16.9	Cl, 14.2
$[Ni_2(2,3,2\text{-tet})_3]Cl_4$	pink	a, b	33.5	8.2	23.0		34.1	8.2	22.7	
$[Ni_2(3,2,3\text{-tet})_3]I_4 \cdot 3H_2O$	lilac	c	23.9	5.6	13.6	I, 42.0; H$_2$O, 4.0	23.3	5.9	13.6	I, 41.0; H$_2$O, 4.4
$[Ni(2,3,2\text{-tet})(NCS)_2]H_2O$	pink	d, b	30.7	6.0	23.3	S, 17.9	30.6	6.3	23.8	S, 18.2
$[Ni(2,3,2\text{-tet})Cl_2]H_2O$	pink	e								
$[Ni(2,3,2\text{-tet})Br(H_2O)]Br$	pink	d, f	21.2	5.7	14.3	Br, 40.7	21.2	5.6	14.1	Br, 40.3
$[Ni(2,3,2\text{-tet})]I_2 \cdot H_2O$	pink-brown	d, f	17.6	4.3	11.1	I, 51.8	17.1	4.5	11.4	I, 51.7
$[Ni(2,3,2\text{-tet})](ClO_4)_2$	orange-yellow	e								
$[Ni(2,3,2\text{-tet})(NO_2)_2]$	brown-pink	d	26.7	6.6	27.0		27.0	6.5	27.0	
$[Ni(2,3,2\text{-tet})(NO_3)]NO_3$	pink	g	24.7	6.2	24.2		24.5	5.9	24.5	
$[Ni(3,2,3\text{-tet})(NCS)_2]$	lilac	d	34.7	6.7	24.9	S, 18.0	34.4	6.4	24.1	S, 18.4
$[Ni(3,2,3\text{-tet})Cl_2]$	lilac	h	31.1	7.5	18.2	Cl, 23.2	31.6	7.3	18.4	Cl, 23.3
$[Ni(3,2,3\text{-tet})Br_2]$	lilac	h	24.4	5.6	14.6	Br, 39.9	24.5	5.6	14.3	Br, 40.7
$[Ni(3,2,3\text{-tet})I_2]$	yellow	i	19.9	4.4	11.3	I, 52.5	19.8	4.6	11.5	I, 52.1
$[Ni(3,2,3\text{-tet})]I_2$	lilac	h	19.7	4.5	11.2	I, 52.3	19.8	4.6	11.5	I, 52.1
$[Ni(3,2,3\text{-tet})(NO_3)_2]$	yellow	j	27.3	6.3	24.0		26.9	6.2	23.6	
Compound V		k	27.8	5.5	12.1	Cl, 14.8	28.0	5.6	11.9	Cl, 15.0

Configuration

There is only one apparent exception to the general rule that the solid octahedral compounds $Ni(L)X_2 \cdot nH_2O$ of Table I are *trans* isomers (L = 2,3,2-tet or 3,2,3-tet and X is a monoanion).

The assignment of configuration is based confidently on the electronic spectra in the near i.r. region (Table II), and Figure 1 gives some representative spectra. For $[Ni(2,3,2-tet)Br(H_2O)]$ Br also there is an X-ray structural confirmation of the assignment [19].
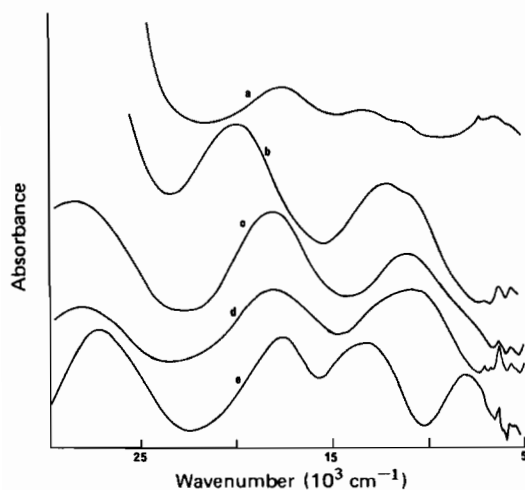

Figure 1. The diffuse reflectance electronic spectra of some representative solid compounds: (a) *trans*-Ni(3,2,3-tet)I$_2$], (b) $[Ni(2,3,2-tet)(NO_2)_2]$, (c) $[Ni(2,3,2-tet)(NO_3)]NO_3$, (d) $[Ni(3,2,3-tet)(NCS)_2]$, (e) *trans*-$[Ni(3,2,3-tet)Cl_2]$.

Curtis and Milestone [16] have already described a number of *cis* compounds* of 2,3,2-tet with bidentate ligands, including $[Ni(2,3,2-tet)(OAc)]BF_4$ and $[Ni(2,3,2-tet)NO_3]ClO_4$. The nitrate described here (Tables I and II and Figure 1) appears to belong to this same class: that is, it has the structure $[Ni(2,3,2-tet)NO_3]NO_3$ with a bidentate nitrate, and a non-planar (folded) amine. By contrast $[Ni(3,2,3-tet)(NO_3)_2]$ has a *trans*$[NiN_4O_2]$ structure, presumably with unidentate nitrates.

Of course, for anions adjacent to the amine nitrogens in the spectrochemical series, *viz.* isothiocyanato and nitro, the electronic spectra cannot be used to determine gross configuration. So we have no evidence about structure for these, except that the anions both appear to be N-bonded. [We do not follow others into meaningless speculations from the i.r. spectra of the anions].

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*Here we use the generic *cis* terminology to describe the mutual dispositions of the other two donor atoms. These may be unidentate anions, water (or other solvent molecules) or the two necessarily adjacent atoms of a chelating oxyanion. Curtis and co-workers [16] prefer to talk of 'folded' configurations in a terminology derived from their macrocyclic work.

Thus, in all definable cases where a "*cis*" configuration is observed for 2,3,2-tet or 3,2,3-tet, both here and in the work of Curtis and Milestone [16], there is a bidentate ligand which can be said at least partially to force the configuration.
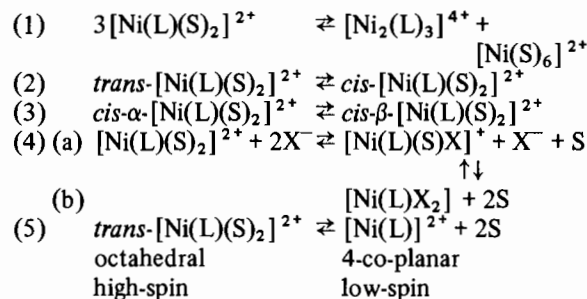
The majority of the $Ni(L)X_2 \cdot nH_2O$ compounds [L = 2,3,2-tet or 3,2,3-tet] of Table I, having a definable *trans* configuration, generally support the contentions of our 1966 paper [1].

I.r. Spectra

These were obtained on all solids and were considered to be consistent with proposed structures. One feature was the number of bands in the NH stretch region: at least ten are discernible at high resolution for $[Ni(2,3,2-tet)(NCS)_2]$. These i.r. spectra cannot be used in any meaningful way to determine structure.

Solution Equilibria

These are generally labile compounds, as expected for high-spin Ni^{II}. One interesting *exception*, which we have reported elsewhere [20], is a slow *trans* $\rightleftarrows$ *cis* isomerisation in DMSO of $[Ni(2,3,2-tet)(DMSO)_2]^{2+}$, but for the rest, reactions are fast, and for the solutions we need to consider a number of possible equilibria. Those important here appear to be (S = solvent):

(1) $3[Ni(L)(S)_2]^{2+}$ $\rightleftarrows$ $[Ni_2(L)_3]^{4+}$ + $[Ni(S)_6]^{2+}$

(2)   *trans*-$[Ni(L)(S)_2]^{2+}$ $\rightleftarrows$ *cis*-$[Ni(L)(S)_2]^{2+}$

(3)   *cis*-α-$[Ni(L)(S)_2]^{2+}$ $\rightleftarrows$ *cis*-β-$[Ni(L)(S)_2]^{2+}$

(4) (a) $[Ni(L)(S)_2]^{2+}$ + $2X^-$ $\rightleftarrows$ $[Ni(L)(S)X]^+$ + X^- + S

(b) $[Ni(L)X_2]$ + 2S

(5)   *trans*-$[Ni(L)(S)_2]^{2+}$ $\rightleftarrows$ $[Ni(L)]^{2+}$ + 2S
        octahedral   4-co-planar
        high-spin   low-spin

We have no data pertaining to equilibrium (3): the electronic spectra do not allow a distinction between *cis*-α(II) and *cis*-β(III) species. Thus, throughout this paper we use the generic terms *cis* to include both II and/or III.

The other equilibria are all significant for our interpretation of the solution data, and will be discussed in turn. However, we need to note immediately that most solutions appear to have the *ionisation equilibria* (4) fully to the left. So, unless we note specifically to the contrary, dissolution of $[Ni(L)X_2]$ or $[Ni(L)(H_2O)X]X$ species in our solvents at the concentrations studied, leads effectively to full ionisation to dicationic $[Ni(L)(S)_2]^{2+}$ species.

[For example, measured molecular conductivities in water at $10^{-3}M$ for some of the 2,3,2-tet species were found to be Cl, 200; I, 208; NCS, 85 (see later comments); NO$_3$, 187; ClO$_4$, 205 mho].

TABLE II. The Diffuse Reflectance Spectra of the Solid Compounds with Assigned Configurations.

Compound	Observed Bands (kK)[a]						Configuration[b]
[Ni₂(2,3,2-tet)₃](NO₃)₄·6H₂O	28.7		18.2		11.3[c]		[NiN₆]
[Ni₂(2,3,2-tet)₃](ClO₄)₄	28.4		18.1		11.1[c]		[NiN₆]
[Ni₂(3,2,3-tet)₃]I₄	(~28)		17.6		10.8[c]		[NiN₆]
Ni(2,3,2-tet)Cl₂·H₂O	28.1		18.3	13.5[d]		8.3	*trans*[NiN₄Cl₂] or [NiN₄ClO]
Ni(2,3,2-tet)Cl₂	27.4		18.0	13.6[d]		8.1	*trans*[NiN₄Cl₂]
[Ni(2,3,2-tet)(H₂O)Br]Br	27.9[d]		18.5[d]	13.55[d]		8.0	*trans*[NiN₄BrO][c,e]
[Ni(2,3,2-tet)]I₂·H₂O		20.5[f]					four co-planar [NiN₄]
[Ni(2,3,2-tet)]I₂							[NiN₄]
[Ni(2,3,2-tet)](ClO₄)₂		21.5[g]					[NiN₄]
Ni(2,3,2-tet)(NO₃)₂	28.3		18.1		11.1	(~8.5)	*cis*[NiN₄O₂]
Ni(2,3,2-tet)(NO₂)₂	29.0		19.9		12.3	(11.0)	[NiN₆]
Ni(2,3,2-tet)(NCS)₂·H₂O	28.6		18.4		11.2[c]		[NiN₆]
[Ni(3,2,3-tet)Cl₂]	27.3[d]		17.6	13.4[d]		8.0	*trans*[NiN₄Cl₂]
[Ni(3,2,3-tet)Br₂]	27.0		17.6	13.1[d]		7.4	*trans*[NiN₄Br₂]
[Ni(3,2,3-tet)I₂] (violet)			17.6	13.4		6.7	*trans*[NiN₄I₂]
[Ni(3,2,3-tet)]I₂(yellow)		21.0 (broad)			(11.3)		
[Ni(3,2,3-tet)(NO₃)₂]	28.4		18.4	13.75[d]		8.5	*trans*[NiN₄O₂]
[Ni(3,2,3-tet)(NCS)₂]	28.1		18.1[d]		11.0[c]		[NiN₆]
[Ni(cyclam)Cl₂][h]	28.5		19.0	14.7[d]		8.4	*trans*[NiN₄Cl₂]
[Ni(cyclam)Br₂][h]	(~29)		18.4[d]	15.0	(13.2)	7.5	*trans*[NiN₄Br₂]

[a]Shoulders are indicated by parentheses. [b]Configuration or structure assignable from the spectra. [c]Bands were asymmetric to high energy, indicating the weak absorption at ~12–13kK usually observed in such octahedral Ni[II] compounds. [d]Asymmetric. [e]Structure confirmed by an X-ray study (ref. 19). [f]A broad asymmetric peak with an ill-defined shoulder at ~18kK. [g]Broad, but nearly symmetrical. [h]See ref. 21.

Equilibrium (1) is a possible complication. If it lies significantly to the right, it may interfere with attempts to use the electronic spectra to deduce structure of the monochelate species in solution. However, qualitative checks of these equilibria for 2,3,2-tet and 3,2,3-tet in water show that they lie distinctly to the left and do not cause complications in the present work.
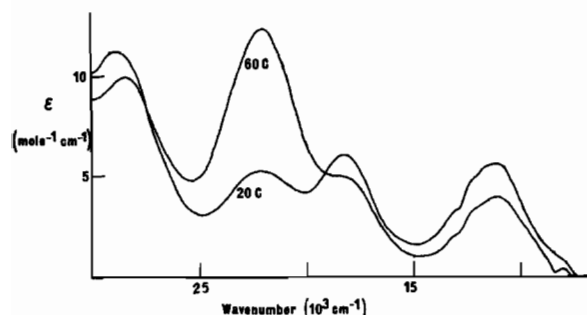

Figure 2. The electronic absorption spectra of $[Ni_2(2,3,2\text{-}tet)_3](NO_3)_4$ in water at 20 °C and 60 °C (c = 0.042M).

For example, Figure 2 shows the spectra of $[Ni_2\text{-}(2,3,2\text{-}tet)_3](NO_3)_4$ in water at 20 °C and 60 °C. Both spectra include bands at ~22000 cm^{-1} which typify the four co-planar mono-chelate compound $[Ni(L)]^{2+}$, and we analyse the broad envelope between 8000 and 14000 cm^{-1} as containing components of a single relatively sharp band from $[Ni_2(L)_3]^{4+}$ at ~11000 cm^{-1} and a broad envelope from some high-spin $[Ni(L)(H_2O)_2]^{2+}$ (see below). The proportion of the various mono-chelate species increases markedly with temperature: especially the amount of low-spin $[Ni(L)]^{2+}$ species.

Similar aqueous solution spectra are obtained for $[Ni_2(3,2,3\text{-}tet)_3]^{4+}$, but $[Ni_2(trien)_3]^{4+}$ maintains its integrity as largely the $[NiN_6]^{2+}$ species until near 90 °C when some low spin $[Ni(L)]^{2+}$ species are evidenced by the appearance of a brown colour in the solution.

From these observations we conclude that:
(a) equilibria (1) lie distinctly to the left and can be neglected for the 2,3,2-tet and 3,2,3-tet systems;
(b) both 2,3,2-tet and 3,2,3-tet show a much more marked tendency than trien to form four co-planar $[NiN_4]^{2+}$ species.

Equilibria (2) (*cis* $\rightleftarrows$ *trans*): we previously reported [1] that $[Ni(2,3,2\text{-}tet)(H_2O)_2]^{2+}$ in water had the *trans* configuration. However, our observation of the unusually slow *trans* $\rightleftarrows$ *cis* isomerisation in DMSO [20] now allows a better definition of these solutions, and shows that all aqueous solutions of the 2,3,2-tet species contain some *cis* isomer(s) of high-spin $[Ni(2,3,2\text{-}tet)(H_2O)_2]^{2+}$. Figure 3 shows a typical spectrum of $Ni(2,3,2\text{-}tet)X_2$ in water at ~0.05M. Comparing with the changing spectra in
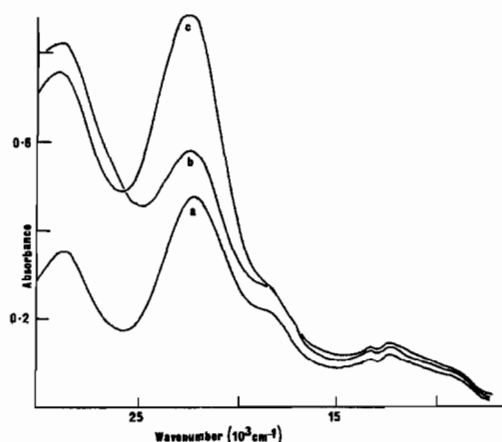

Figure 3. The electronic absorption spectra in water of: (a) $[Ni(2,3,2\text{-}tet)](ClO_4)_2$ (0.048M), (b) $[Ni(2,3,2\text{-}tet)Br_2]$ (0.052M), and (c) $[Ni(2,3,2\text{-}tet)]I_2$ (0.042M).

DMSO [20], we estimate that the high-spin species present are made up of 90% *trans* and 10% *cis* isomers. These high-spin species make up ~85% of the total nickel present at 25 °C, there being also present ~15% of the low-spin $[NiN_4]^{2+}$ species (see below). Note also from Fig. 3 that changes in the amount of low-spin species occur for the different salts, and this seems to be a direct result of ion-pairing. However, the shape of the low energy band envelope does not change. Thus the relative proportions of *cis* and *trans* high-spin isomers are unchanged. Indeed we have measured the spectra of all three tetraamines in solutions of different lithium salts up to 4M (see, *e.g.* Fig. 4), and can find no evidence that the ion-pairing, which must be quite extensive in these solutions, alters the proportions of *cis* and *trans* high-spin isomers.

In the same way, we have estimated the positions of the equilibria for the three homologues in water, DMF and DMSO. The results are gathered in Table
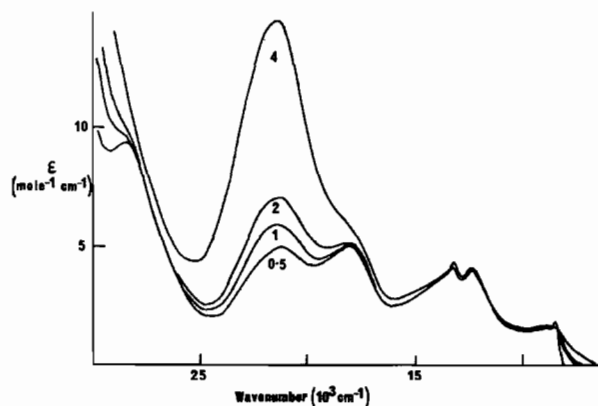

Figure 4. The electronic absorption spectra of $[Ni(3,2,3\text{-}tet)\text{-}Cl_2]$ (0.05M) in aqueous $NaNO_3$ solutions of the indicated molarities.

TABLE III. Configurations of the High-spin $[NiN_4(S)_2]^{2+}$ Species in the Different Solvents at $0.05M$.

Amine	Solvent[a]	Configuration of $[NiN_4(S)_2]^{2+}$		Comments
		cis (%)	*trans* (%)	
2,2,2-tet	H_2O	100		b
(trien)	DMF	100		b
	DMSO	100		b
2,3,2-tet	H_2O	10	90	c
	DMF	20	80	d
	DMSO	80	20	e
3,2,3-tet	H_2O	<5	95 → 100	f
	DMF	<10	>90	g
	DMSO	25	75	g

[a] DMF and DMSO solutions were dried over molecular sieve (4A), but addition of water to the solutions generally had little, if any, affect on the spectra. [b] No evidence was found for the *trans* high-spin isomer here. Although it could be present in amounts up to 20% and remain undetected in the electronic spectra, we are confident of its absence, because of the very small amounts of low spin $[NiN_4]^{2+}$ spp. present (<2%). [c] We found no reproducible variation with the counter-anion for Cl^-, Br^-, I^-, NO_2^-, NO_3^- and ClO_4^-. [d] No apparent variation (±5%) with counter-anion (ClO_4^-, Cl^-, Br^- and I^-). [e] These solutions are slow to reach equilibrium (see ref. 20). [f] No variation with counter-anion (NO_3^-, Cl^-, Br^-, I^-). [g] Variations in relative concentrations did occur for different counter-anions. These figures refer to the iodides, which give relatively more of the *cis* isomers.

III, and they allow us to make the following generalisations: *cis* isomers are preferred over *trans* isomers in the order

(i) (for solvent) H_2O < DMF < DMSO; and
(ii) (for amine) trien $\gg$ 2,3,2-tet > 3,2,3-tet.

Equilibria (4) (anation) appear also to be important in some cases in defining the positions of the *cis* $\rightleftarrows$ *trans* equilibria.

Figure 5 shows the different spectra of Ni(3,2,3-tet)X_2 (X = Cl, Br, I) in DMSO. Clearly, with increasing intensity at 11–12kK, there are increasing amounts of *cis* isomers in the order Cl < Br < I, ranging from ~5% *cis* for the chloride to ~25% *cis* for the iodide.

The addition of an excess of chloride to Ni(3,2,3-tet)Cl_2 in DMSO gives a solution for which the spectra indicate ~100% *trans* isomer.

But we are uncertain whether these variations in the positions of the *cis* $\rightleftarrows$ *trans* equilibria are the result of changes in the anation equilibria (4), or alternatively ion-pairing, or both. Certainly, ion-pairing alone is insufficient to explain the observations, for, by comparison with known [22] ion-pairing constants for cobalt(III) species in DMF and DMSO, we would expect it to favour *cis* isomers in DMF more than in DMSO, but observe the reverse.
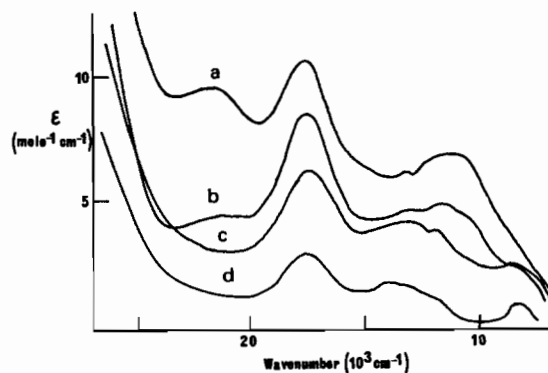

Figure 5. The electronic absorption spectra of $0.05M$ DMSO solutions (dried over 4Å molecular sieve) of: (a) [Ni(3,2,3-tet)I_2]; (b) [Ni(3,2,3-tet)Br_2]; (c) [Ni(3,2,3-tet)Cl_2] and (d) solution (C) with an excess of solid LiCl added (so the concentration for this solution is less than $0.05M$).

Similar but smaller effects were observed for Ni-(3,2,3-tet)X_2 (X = Cl, Br, I) in DMF, (*i.e. cis* preferred in the order Cl < Br < I) but for all other solutions studied any variations of this sort were within the limits of our experimental method (<5%).

Anation effects also were observed in aqueous solution. [Ni(2,3,2-tet)(NCS)$_2$] is far from completely ionised in water at 25 °C (molecular conductivity = 85 mho) and this is reflected in the spectra which are dominated by the $[NiN_6]$ chromophore of the bis-(and perhaps mono) isothiocyanato species. [Ni-(3,2,3-tet)NCS)$_2$] is effectively insoluble in water and could apparently be used for gravimetric determination of the metal.

In concentrated LiNO$_3$ and LiClO$_4$ solutions, Ni-(trien)$^{2+}$ forms octahedral high-spin [Ni(trien)NO$_3$]$^+$ and [Ni(trien)(ClO$_4$)]$^+$. This is in marked contrast to the other two homologues, neither of which show signs of forming such species, and must result partly from the stereochemical preferences of the two ligands. The effect is quite dramatic: instead of the normal (see below) displacement of equilibria (5) to the right as a salt is added to aqueous Ni(trien)$^{2+}$, we observe with LiNO$_3$ and LiClO$_4$, but not LiCl, LiBr or LiI, the formation of new high-spin *cis*-[NiN$_4$O$_2$] species in the electronic spectra. This is one of the few documented examples of perchlorate co-ordination in aqueous solution, but, since our first reports [23] of the phenomenon in 1961, the covalent bonding of perchlorate to a transition-metal has been described often enough.

Finally, we note the example of alkaline aqueous solutions. Ni(2,3,2-tet)$^{2+}$ in $2M$ NaOH exists almost totally in the high-spin *trans* dihydroxo (or aquahydroxo) form, whereas the 2,3,2-tet species has about the same mixture of *cis* and *trans* isomers as exists in neutral aqueous solution. However, when both solutions are exposed to the air, their spectra change to those typical of *cis*-[NiN$_4$O$_2$] species.

Undoubtedly, this is the result of CO_2 absorption and the formation of $[Ni(N_4)CO_3]$ species with bidentate carbonate.

Equilibria (5) are firmly established for NiN_4X_2 compounds in solution. They appear to have been first described by Lifschitz and co-workers [24], and were the subject of some interest in the decade following the application of crystal/ligand field theory to transition-metal chemistry. Much of this earlier published work is noted in papers by Farago [25] and Busch [26]. After early flirtations with other explanations of the diamagnetic $\rightleftarrows$ para-magnetic equilibria (such as invoking planar S = 1 species) there appears now to be little, if any, doubt that the equilibria here involve only four co-planar $[Ni(N_4)]^{2+}$ species with a spin singlet ground state, and octahedral NiN_4L_2 species (where L can be an anion or a neutral, usually solvent, molecule) with a spin triplet ground state.

Except in special cases, such as our 3,2,3-tet tetra-amine [27], where specific steric effects play a major role, there is no evidence that the five-co-ordinate intermediate exists in significant concentration.

Several recent papers have dealt with such equilibria for the tetraamines in aqueous solution. The reactions are very fast [12–14], but measurable by temperature jump [14] and photochemical perturbation [13] methods. More recently, Fabbrizzi et al. [15] have shown that the equilibrium constants (K_{eq} for eqn. (5), as written) vary for the nickel tetra-amine compounds in the order:

$$2,3,2\text{-tet} > 3,2,3\text{-tet} > \text{trien} > 3,3,3\text{-tet} \qquad (6)$$
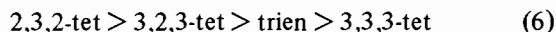
and we confirm this order. Hinz et al. [28] also present pertinent data and discussion.

The equilibria are displaced to the right by increasing the temperature and/or by adding salts of non-coordinating anions to the solutions [29] (see also Fig. 4).

The planar diamagnetic species are characterised by electronic absorption bands at ~450 nm, giving brown or yellow colours to solutions containing them. The band occurs in a region where there is little, if any, absorption from the high-spin species, and appears at first sight to be ideal for defining the position of the equilibrium. However, the planar species in water is only obtained effectively pure in strong salt solutions, and this raises difficulties when one wants to use the extinction coefficients so obtained for equilibria in more dilute solutions. For example, ion-pairing, giving $\{[Ni(N_4)]^{2+}...X^-\}$ spe-cies, can lead to charge-transfer processes which can add intensity to the electronic absorption at the lower end of the visible region. Further, in such ion-pairs, there is a strong possibility of electronic perturbations changing intensity (and position) of the 450 nm band(s). (Actually this band is a composite of several electronic processes [29, 30]).
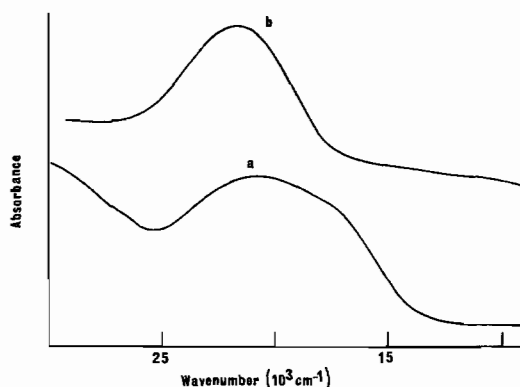

Figure 6. The diffuse reflectance electronic spectra of [Ni-(2,3,2-tet)]X_2, X = (a) I and (b) ClO_4.

Pertinent to the point are three observations:
(a) the diffuse reflectance spectra of the solids [Ni-(2,3,2-tet)]I_2 and [Ni(2,3,2-tet)]$(ClO_4)_2$ are noticeably different (Figure 6);
(b) the spectra of $0.05M$ aqueous solutions of Ni-(2,3,2-tet)X_2 (Figure 3) show that the propor-tion of low-spin species is significantly greater for X = I^-, Br^- than for X = ClO_4^- (the spectra for X = Cl^-, NO_3^- are very close to that of the latter);
(c) the marked increase in absorbance for the bromide and iodide (Fig. 3), in the high energy region, suggests that the proposed charge-transfer processes are already occurring in these compara-tively dilute solutions.
Both (b) and (c) are evidence for ion-pairing even in the absence of added salts.

Previous authors [12, 15, 28] have assumed that the equilibria are entirely to the right in saturated $NaClO_4$ at 25 °C, and have taken the measured extinction coefficients as appropriate to the more dilute solutions. However, the data of Table IV show that extinction coefficients up to 79 can be obtained in saturated lithium halide solutions of 2,3,2-tet and 3,2,3-tet. These higher values, nevertheless, are probably perturbations, as noted above, and we accept values near 60 (Table IV), but suggest that appropriate e.s.ds for the measurements, if they are to be applied to the cations in dilute solutions, are not less than 2.

Initially, we had hoped that a detailed study of these systems would help to clarify the various factors affecting equilibria (5). But these are many and complex: in all such solutions, there will be a complex interplay between solvation effects (in-cluding solvent structure in all of its manifestations [20]), ion-pairing [25], intramolecular ligand steric [25] and electronic effects {including possible Ni–X bonding, ligand field strengths of the amines [15], and secondary effects resulting from hydrogen-bonding of solvent to the amine ligand(s) [25]}. And, in general, these will all be interrelated.

TABLE IV. Maximum Extinction Coefficients for the [Ni-(N$_4$)]$^{2+}$ Species of the Different Tetraamines, Measured in Various Saturated Aqueous Salt Solutions at ~25 °C, and in Acetone.

Salt	ϵ_{max}		
	(trien)	(2,3,2-tet)	(3,2,3-tet)
LiCl (14.3M)	60	60	79
LiBr (20.1M)	43	66	78
LiI (10.1M)		78	
LiNO$_3$ (12.9M)	15	44	64
LiClO$_4$ (5.7M)	7	57	63
NaClO$_4$ (7.4M)		67 [ref. 12]	65 [ref. 15]
Acetone (dry)		54	
Suggested values to use[a]:	60(2)	60(2)	64(2)

[a]These are the figures that we think most appropriate to dilute solution: the figures in parentheses are suggested e.s.ds. for the measurements.

Yet, having detailed the problems, we note that the results do fit nicely into a rationalisation based on ligand steric effects [1]. Whereas 2,3,2-tet has more of the low-spin planar species in its solutions (*cf.* Figures 3 and 4), 3,2,3-tet has more *trans* isomers of the high-spin species [equil. (2)]. And this fits the steric effects, for the bulkier 3,2,3-tet will want to remain planar more than 2,3,2-tet [equil. (2), B-strain [31]) yet its 6,5,6 system of chelate rings can less easily adjust to the shorter Ni–N bond-lengths [9] of the low-spin species than the 5,6,5 system of chelate rings of 2,3,2-tet (C-strain [31]).

One point that we have established is that there is little, if any, variation of equilibria (2) whilst quite massive changes are occurring in equilibria (5). That is, the changes in the latter in concentrated salt solutions are real and not an indirect result of changes in equil. (2) [see Fig. 4 and discussion above].

Apropos solvation effects, we checked the effect of added water (up to ~5%) on the equilibria in DMSO and DMF. However, although there is a marked acceleration of the slow isomerisation [20] of [Ni(2,3,2-tet)(S)$_2$]$^{2+}$ in DMSO, we find very little effect on the positions of either equilibria (2) or (5).

Concluding Comments

The data presented here show that as well as the high-spin octahedral $\rightleftarrows$ low-spin planar equilibrium for Ni(tetraamine)X$_2$ compounds in solution, there is an equilibrium between *cis* and *trans* isomers of the high-spin octahedral species. The relative proportions of each depend on a variety of factors, but a major one seems to be the steric effects of the ligands: at least we can rationalise all of the general trends in these terms.

The situation is likely to be even more complicated than we have presented it, for the *trans* isomers can exist in R,R and R,S forms (in which R and S refer to the chirality of the coordinated secondary nitrogens), and the *cis* isomers can be in *cis-α* or *cis-β* forms, with each of these also subject to the same form of diastereoisomerism as the *trans* isomer [31]. Not all will be likely to co-exist, but it would be very surprising if only one each of the *trans* and *cis* isomers occurred in the various solutions.

Perhaps this is the reason why our analysis of the data for 2,3,2-tet appears to be at variance with some observations of Wilkins *et al.* [12]. They note that, when aqueous Ni(2,3,2-tet)$^{2+}$ (T = 25 °C, μ = 0.5M) reacts with edta and oxalate, approx. 40% reacts immediately and then the remainder by a slow process. One might expect this 40% to represent *cis* isomers, yet we can find only ~10% of *cis* isomers in such solutions. It seems necessary to postulate that the *trans* (including low-spin) species is present in both R,R and R,S forms, and that these react at very different rates.

This also highlights the problem of detailed comparisons of the thermodynamic data of the different amines and with different metals [4–6, 15, 28]: what is one comparing if the configurations of the different amines about the different metals are not the same? Hinz and Margerum [28] were aware of this problem and partially corrected their stability constants for Ni(2,3,2-tet)$^{2+}$ to refer to complete formation of the four co-planar species.

Perhaps a thorough n.m.r. study of these systems will help to clear up some of the uncertainties raised here.

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