Notes

Isolation and Crystal Structure of the *trans* Isomer of (6,7,13,14,15,16,17,18,24,25,31,32,33,34,35,36-Hexadecahydrotetrabenzo-[*e,m,s,a*][1,14,15,18,8,11,22,25]tetraoxatetra-azacyclo-octacosine)di-isothiocyanatonickel(II) †

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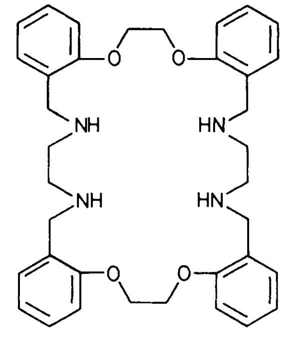
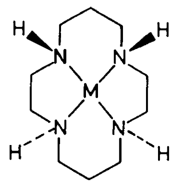
The first structure containing the *trans*-IV configurational isomer of a 1,4,8,11-tetra-azacyclotetradecane-like macrocycle is reported *via* the isolation and structural characterisation of the *trans* isomer of the di-isothiocyanatonickel(II) complex of the oxa-azamacrocycle 6,7,13,14,15,16,17,18,24,25,31,32,33,34,35,36-hexadecahydrotetrabenzo[*e,m,s.a*]-[1,14,15,18,8,11,22,25]tetraoxatetra-azacyclo-octacosine.

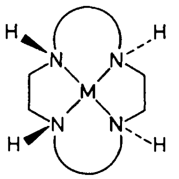
The octadentate, potentially dinucleating oxa-azamacrocycle (L) has been shown to form a *cis*-pseudo-octahedral mononuclear complex with nickel(II) in which only the tetra-aza (N_4) donor set co-ordinates to the metal ion.[1] When simple analogy is made with nickel(II) complexes of tetra-azamacrocycles such as 1,4,8,11-tetra-azacyclotetradecane (cyclam) it is noted that whereas the *cis*-octahedral configurational isomer has been identified[2,3] and characterised[4] it is the *trans*-III (or *RRSS*) configuration that generally provides the thermodynamically most stable diastereoisomer for both four- and six-co-ordinated Ni^{II}–cyclam complexes.[5,6] Molecular mechanics calculations on cyclam complexes have indicated that a six-co-ordinate *cis-RRRR* isomer should be comparable in stability to that of a six-co-ordinate *trans-RRSS* isomer when M–N distances are greater than 2.09 Å. It would therefore be anticipated that a *trans*-nickel(II) complex of L should be accessible. We report herein the solvent-dependent isolation of *trans*-$[NiL(NCS)_2]$, together with the crystal structure of the complex.



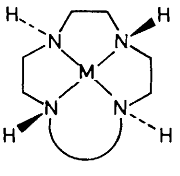
L



+ + *R* *S*
− − *R* *S*
trans-III
(cyclam 'stable' form)



+ − *R* *R*
+ − *S* *S*
trans-IV
(this work)



− + *S* *S*
+ − *R* *R*
trans-V
(ref. 7)

Experimental

The synthesis and characterisation of bulk samples of $[NiL(NCS)_2]$ was carried out as reported in the literature[1] as was the recrystallisation of the *cis* isomer. The *trans* isomer was obtained by the following procedure. A portion of the bulk sample was dissolved in hot $CHCl_3$; the solution was cooled and filtered and diethyl ether was layered on to the solution in order to effect crystallisation of the product.

Structure Determination.—Crystal data and parameters for the data collection are given in Table 1. Three-dimensional, room-temperature *X*-ray data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 diffractometer by the ω-scan method. The 2 083 independent reflections for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of azimuthal scans. The structure was solved by conventional Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. The carbon chain of the diamine was found to be disordered with equal

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

Table 1. Crystal data for [NiL(NCS)$_2$]·4CHCl$_3$

M	1 249.15
Crystal dimensions/mm	0.19 × 0.60 × 0.42
Space group	$P2_1/n$ (non-standard setting, $P2_1/c$, C_{2h}^5 no. 14)
Temperature of data collection/K	298
Cell constants	
a/Å	8.485(6)
b/Å	15.995(11)
c/Å	20.084(12)
β/°	95.99(5)
U/Å^3	2 711(3)
D_c/g cm^{-3}	1.530
Z	2
λ(Mo-K_α)/Å	0.710 69
μ(Mo-K_α)/cm^{-1}	10.74
F(000)	1 275.84
R	0.1146

Table 2. Atom co-ordinates (× 10^4)

Atom	x	y	z
Ni	0	0	0
S(1)	−458(8)	−1 727(4)	1 884(3)
O(1)	3 494(13)	1 882(7)	1 156 (5)
O(2)	460(12)	2 135(7)	1 670(5)
N(1)	2 308(14)	175(7)	485(6)
N(2)	−981(13)	1 073(7)	430(6)
N(3)	−650(17)	−680(8)	780(6)
C(1)	2 520(21)	251(11)	1 238(7)
C(2)	4 154(21)	516(9)	1 508(7)
C(3)	5 268(22)	−38(13)	1 768(8)
C(4)	6 736(24)	221(11)	2 035(8)
C(5)	7 106(23)	1 055(14)	2 031(8)
C(6)	6 025(19)	1 623(12)	1 753(8)
C(7)	4 585(17)	1 344(10)	1 489(7)
C(8)	3 092(18)	2 639(8)	1 470(7)
C(9)	1 963(18)	2 445(11)	1 971(7)
C(10)	−568(17)	2 714(10)	1 374(8)
C(11)	−1 220(23)	3 327(11)	1 737(9)
C(12)	−2 342(26)	3 819(12)	1 439(9)
C(13)	−2 802(22)	3 750(10)	765(11)
C(14)	−2 159(22)	3 167(11)	392(9)
C(15)	−1 022(19)	2 613(10)	691(8)
C(16)	−320(20)	1 897(9)	320(7)
C(17)	−2 737(16)	967(15)	312(10)
C(18)	−3 111(26)	658(11)	−417(10)
C(17a)	−2 609(23)	1 184(12)	69(16)
C(18a)	−3 380(21)	322(16)	−86(16)
C(19)	−638(19)	−1 091(9)	1 235(7)
Cl(1)	3 610(12)	4 034(4)	−972(4)
Cl(2)	5 200(10)	2 650(5)	−1 449(3)
Cl(3)	3 635(8)	2 485(5)	−292(3)
C(20)	3 565(26)	2 997(11)	−1 059(9)
Cl(4)	3 018(11)	4 873(5)	2 011(3)
Cl(5)	942(10)	6 185(5)	1 497(4)
Cl(6)	1 691(15)	4 814(5)	675(4)
C(21)	1 402(41)	5 186(16)	1 461(14)

Atoms Cl(1)–Cl(3), C(20) and Cl(4)–Cl(6), C(21) comprise the two chloroform molecules of solvation in the asymmetric unit.

Atoms C(17), C(18) and C(17a), C(18a) are the two disorder components of the dimethylene chain of the diamine fragment.

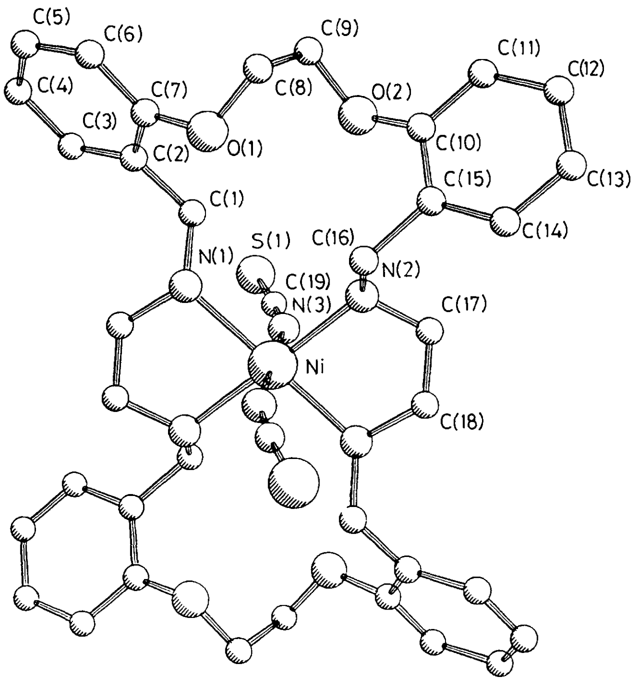


Figure. The molecular structure of [NiL(NCS)$_2$]

occupancies and constraints were applied to the fragment during refinement. Hydrogen atoms were placed in calculated positions with isotropic thermal parameters related to those of the supporting atoms. Refinement converged at a final R 0.1146 with allowance for the thermal anisotropy of all ordered non-hydrogen atoms. Complex scattering factors were taken from the program package SHELXTL[8] which was used throughout the refinement. Unit weights were used throughout. Atomic co-ordinates are listed in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Discussion

The free macrocycle (L) was synthesised by the method of Adam *et al.*[1] and reaction with Ni(NCS)$_2$·xH$_2$O in methanol gave only the mononuclear complex [NiL(NCS)$_2$]. This compound was of low solubility in common organic solvents and recrystallisation from MeOH–dimethylformamide (dmf) gave the light blue *cis*-octahedral isomer [i.r. (KBr disc), 2 080 and 2 060 cm^{-1} (anion)]. The i.r. spectrum of the bulk sample from MeOH gave two anion stretches at 2 080 and 2 060 cm^{-1}; the intensity of the broadened higher band is much enhanced over that of the lower band whereas in the spectrum of the *cis* isomer the intensities of the two stretches are equivalent. This suggests that the bulk sample is a mixture of the two isomers. When recrystallisation of the bulk sample was effected using chloroform–diethyl ether, a medium of both lower dielectric and lower donicity, lilac-mauve crystals were obtained. The positive-ion fast atom bombardment mass spectrum showed peaks at m/z 712 [NiL(NCS)]$^+$ and 654 [NiL]$^+$ but no peaks of higher mass as would be expected from a dinuclear complex and the i.r. spectrum showed some modifications in the ligand region and a single anion stretch at 2 075 cm^{-1} (KBr disc). This suggested that a different isomer of [NiL(NCS)$_2$] had been isolated and so an X-ray structural analysis was undertaken.

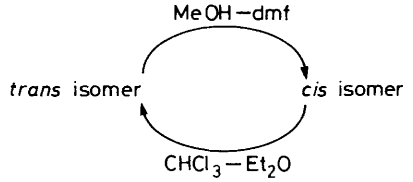
The molecule is a centrosymmetric complex between L and a nickel(II) ion (Figure). The unit cell also contains four chloroform solvent molecules per nickel, two per asymmetric unit. The structure confirms that the nickel(II) is co-ordinated solely to the N$_4$-donor set of the macrocycle as the *trans*-IV (*RRSS*) diastereoisomer and that the metal ion completes its closely octahedral geometry with two *trans*-N-bonded thiocyanate anions. The macrocycle defines two five- and two

Table 3. Bond lengths (Å) and angles (°)

Ni–N(1)	2.112(12)	Ni–N(2)	2.130(11)
Ni–N(3)	2.031(12)	S(1)–C(19)	1.647(16)
O(1)–C(7)	1.383(18)	O(1)–C(8)	1.423(18)
O(2)–C(9)	1.442(18)	O(2)–C(10)	1.365(18)
N(1^{I})–C(18)	1.509(22)	N(1^{I})–C(18a)	1.502(28)
N(2)–C(16)	1.459(18)	N(2)–C(17)	1.493(18)
N(2)–C(17a)	1.501(24)	N(3)–C(19)	1.125(19)
C(1)–C(2)	1.497(23)	C(1)–N(1)	1.509(18)
C(2)–C(3)	1.359(24)	C(2)–C(7)	1.376(21)
C(3)–C(4)	1.368(26)	C(4)–C(5)	1.372(29)
C(5)–C(6)	1.367(26)	C(6)–C(7)	1.357(21)
C(8)–C(9)	1.493(22)	C(10)–C(11)	1.373(24)
C(10)–C(15)	1.396(22)	C(11)–C(12)	1.329(27)
C(12)–C(13)	1.372(27)	C(13)–C(14)	1.347(27)
C(14)–C(15)	1.398(24)	C(15)–C(16)	1.521(22)
C(17)–C(18)	1.547(27)	C(17a)–C(18a)	1.543(31)
Cl(1)–C(20)	1.668(20)	Cl(2)–C(20)	1.752(23)
Cl(3)–C(20)	1.741(20)	Cl(4)–C(21)	1.742(32)
Cl(5)–C(21)	1.647(28)	Cl(6)–C(21)	1.728(29)
N(1^{I})–Ni–N(2)	84.9(4)	N(1^{I})–No–N(3)	88.4(5)
N(2)–Ni–N(3)	88.2(5)	N(2)–Ni–N(1)	95.1(4)
N(3)–Ni–N(1)	91.6(5)	N(3)–Ni–N(2^{I})	91.8(5)
C(7)–O(1)–C(8)	119.6(11)	C(9)–O(2)–C(10)	116.5(12)
Ni–N(1)–C(18^{I})	104.3(9)	Ni–N(1)–C(18a^{I})	105.6(11)
Ni–N(1)–C(1)	118.7(10)	C(18^{I})–N(1)–C(1)	98.8(12)
C(18a^{I})–N(1)–C(1)	124.1(14)	Ni–N(2)–C(16)	119.6(9)
Ni–N(2)–C(17)	105.6(10)	C(16)–N(2)–C(17)	118.2(13)
Ni–N(2)–C(17a)	106.1(11)	C(16)–N(2)–C(17a)	99.7(12)
Ni–N(3)–C(19)	163.7(14)	C(2)–C(1)–N(1)	113.3(13)
C(1)–C(2)–C(3)	122.4(14)	C(1)–C(2)–C(7)	120.1(14)
C(3)–C(2)–C(7)	117.6(16)	C(2)–C(3)–C(4)	121.4(18)
C(3)–C(4)–C(5)	119.4(18)	C(4)–C(5)–C(6)	120.3(17)
C(5)–C(6)–C(7)	118.6(17)	O(1)–C(7)–C(2)	116.5(13)
O(1)–C(7)–C(6)	121.0(15)	C(2)–C(7)–C(6)	122.5(15)
O(1)–C(8)–C(9)	108.8(12)	O(2)–C(9)–C(8)	113.0(12)
O(2)–C(10)–C(11)	121.9(14)	O(2)–C(10)–C(15)	116.6(14)
C(11)–C(10)–C(15)	121.3(15)	C(10)–C(11)–C(12)	119.5(16)
C(11)–C(12)–C(13)	120.9(18)	C(12)–C(13)–C(14)	120.9(17)
C(13)–C(14)–C(15)	120.1(16)	C(10)–C(15)–C(14)	117.2(15)
C(10)–C(15)–C(16)	119.1(13)	C(14)–C(15)–C(16)	123.7(14)
N(2)–C(16)–C(15)	115.5(13)	N(2)–C(17)–C(18)	106.8(14)
N(1^{I})–C(18)–C(17)	108.5(15)	N(2)–C(17a)–C(18a)	110.0(15)
N(1^{I})–C(18a)–C(17a)	108.2(17)	S(1)–C(19)–N(3)	174.6(16)
Cl(1)–C(20)–Cl(2)	110.5(12)	Cl(1)–C(20)–Cl(3)	112.1(11)
Cl(2)–C(20)–Cl(3)	106.9(11)	Cl(4)–C(21)–Cl(5)	115.2(17)
Cl(4)–C(21)–Cl(6)	107.6(18)	Cl(5)–C(21)–Cl(6)	115.5(16)

Symmetry operation: I $-x$, $-y$, $-z$.

thirteen-membered chelate rings, as in the *cis* isomer. In the present case the larger rings terminate in a +,− arrangement, in contrast to the +,+ arrangement found in the smaller tetra-azamacrocycles, so leading to a unique example of the *trans*-IV configuration. It is likely that this is a consequence of strain in the thirteen-membered rings being much reduced in the *trans*-IV isomer. A similar observation has been made for nickel(II) complexes of non-symmetric tetra-azamacrocycles in which there is present a nine-membered chelate ring leading to a *trans*-V diastereoisomer.[7] The two phenylene rings of the macrocycle are planar [root mean square (r.m.s.) deviations 0.013 and 0.012 Å]; the nickel–thiocyanate linkage is bent by 16° at the nitrogen, but essentially linear at carbon. The torsion angle at C(8)–C(9) is −65°, and those at the disordered C(17)–C(18) are +62 and −57° for the two components. A similar disorder was noted in the *cis* isomer and may be indicative of the inherent flexibility of the ligand framework. Within the estimated standard deviations (e.s.d.s), all bond lengths and angles are acceptable (Table 3). The Ni–N_{mac} distances lie within the range reported[1] for co-ordinate bonds from sp^3 N atoms in high-spin nickel(II) complexes of tetra-azamacrocycles; the Ni–N_{anion} distances are slightly shorter than the Ni–N_{mac} distances leading to a compressed rhombic octahedral co-ordination geometry. The hole size in cyclam and closely related 14-membered tetra-azamacrocycles appears slightly too small to provide a perfect fit for high-spin nickel(II), constraining Ni–N bond lengths to lie in the range 2.06—2.09 Å compared with a mean length of 2.11(2) Å for 69 high-spin nickel(II) to secondary amine bonds in unconstrained structures.[9] The flexible 28-membered ring in this macrocycle allows a planar N_4-donor set with nearly ideal bond lengths (Table 3) to be presented to the nickel.



The poor solubility of the complexes limits access to information concerning the species present in solution. The *cis* and *trans* isomers give similar electronic spectra in dmso, 364 (23.3) and 588 (13.3) and 364 (18.8) and 582 (10.7 dm^3 mol^{-1} cm^{-1}) nm respectively, and the *trans* isomer shows bands at 357 (12.4) and 564 (7.7 dm^3 mol^{-1} cm^{-1}) nm in chloroform solution. These are indicative of octahedral co-ordination. No evidence was found for the low-spin *RRRR* isomer. The *cis* and *trans* isomers of $[NiL(NCS)_2]$ may be readily interconverted by recrystallisation from the appropriate solvent.

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