the point group is of lower symmetry than $m\bar{3}m$. The octahedrally enforced dynamic structure is stabilized by this crystal field.

(*c*) With a noncentrosymmetric point symmetry for the Te atom the TeX_6^{2-} group will be statically distorted. According to Pearson (1976) the resulting symmetry must be $4mm$, $2mm$ or $3m$, displaying the three orientations of one component of the T_{1u} deformation vibration of the octahedron.

Symmetry rule (*c*) is obeyed resulting in a $2mm$ distortion in most cases known to date. An irregular distortion found in $[(MeHN)_2CS]_2TeCl_6$ (Rosso, Valle & Calogero, 1980) should be regarded with care because no significance test for the noncentrosymmetric space group is given for this structural refinement. At least for TeI_6^{2-} the known structures show a center of symmetry for the Te position exclusively, *e.g.*, Rb_2TeI_6 (Abriel, 1982). With a knowledge of the above symmetry rules, we shall find a suitable cation for building a salt with a statically distorted anion.

The rules given above should also be useful when considering compounds containing SeX_6^{2-} (X = Cl, Br). Most recently we found the first distorted species in $[H_3N(CH_2)_3NH_3]SeBr_6$ with approximate point symmetry $3m$ for the anion (Abriel, 1986).

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References

ABRIEL, W. (1982). *Mater. Res. Bull.* **17**, 1341-1346.

ABRIEL, W. (1986). To be published.

ABRIEL, W. & EHRHARDT, H. (1984). *Angew. Chem.* **96**, 965-967; *Angew. Chem. Int. Ed. Engl.* **23**, 963-965.

ABRIEL, W. & FRIEDRICH, C. (1985). *Z. Naturforsch. Teil B*, **40**, 1691-1697.

ABRIEL, W. & IHRINGER, J. (1984). *J. Solid State Chem.* **52**, 274-280.

ADAMS, D. M. & MORRIS, D. M. (1967). *J. Chem. Soc. A*, pp. 2067-2069.

BARTLETT, G. & LANGMUIR, I. (1921). *J. Am. Chem. Soc.* **43**, 84-91.

BRILL, T. B., GEARHART, R. C. & WELSH, W. A. (1974). *J. Magn. Reson.* **13**, 27-37.

BROWN, I. D. (1964). *Can. J. Chem.* **42**, 2758-2767.

BURBANK, R. D. & JONES, G. R. (1974). *J. Am. Chem. Soc.* **96**, 43-48.

CHRISTE, K. O. (1972). *Inorg. Chem.* **11**, 1215-1219.

COUCH, D. A., WILKINS, C. J., ROSSMAN, G. R. & GRAY, H. B. (1970). *J. Am. Chem. Soc.* **92**, 307-310.

DAHAN, F. & LEFÈBVRE-SOUBEYRAN, O. (1976*a*). *Acta Cryst.* B**32**, 2859-2862.

DAHAN, F. & LEFÈBVRE-SOUBEYRAN, O. (1976*b*). *Acta Cryst.* B**32**, 2863-2866.

GILLESPIE, R. J. (1972). *Molecular Geometry.* London: Van Nostrand-Rheinhold.

GILLESPIE, R. J. & NYHOLM, R. S. (1957). *Q. Rev. Chem. Soc.* **11**, 339-380.

GREENBERG, A. L. & WALDEN, G. H. (1940). *J. Chem. Phys.* **8**, 645-658.

GREENWOOD, N. N. (1970). *Nature et Propriétés des Liaisons de Coordination*, pp. 104-116. Paris: Editions du CNRS.

HAZELL, A. C. (1966). *Acta Chem. Scand.* **20**, 165-169.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D Reidel, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

PEARSON, R. G. (1976). *Symmetry Rules for Chemical Reactions*, p. 199 ff. New York: John Wiley.

ROBERTS, P. & SHELDRICK, G. M. (1979). *XANADU.* Program for crystallographic calculations. Univ. of Cambridge, England.

ROSSO, U., VALLE, G. & CALOGERO, S. (1980). *J. Chem. Soc. Dalton Trans.* pp. 2303-2305.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63-76.

STUFKENS, D. J. (1970). *Recl Trav. Chim. Pays-Bas*, **89**, 1185-1201.

WEIGLE, J. & SAINI, H. (1936). *Helv. Phys. Acta*, **9**, 515-519.

WELLS, A. F. (1984). *Structural Inorganic Chemistry*, p. 357. Oxford: Clarendon Press.

Acta Cryst. (1986). B**42**, 453-461

Structures of Diisothiocyanatotetrakis(1-phenyl-1-ethylamine)nickel(II): Enclathration of Organic Guests with Host Isomerization

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Abstract

Host complexes of $Ni(NCS)_2$(1-phenyl-1-ethylamine)$_4$, prepared from racemic and enantiomerically pure amine and its clathrates with *sec*-butylbenzene and *o*-xylene have been examined by X-ray diffraction: (*a*) $\frac{1}{2}\{[Ni(NCS)_2\{(R)$-1-phenyl-1-ethylamine$\}_2\{(S)$-1-phenyl-1-ethylamine$\}_2]$-$[Ni(NCS)_2$-$\{(R)$-1-phenyl-1-ethylamine$\}_4]\}$, $\frac{1}{2}\{[Ni(C_8H_{11}N)_4$-$(NCS)_2].[Ni(C_8H_{11}N)_4(NCS)_2]\}$, $M_r = 659{\cdot}59$, orthorhombic, $P2_12_12$, $a = 15{\cdot}543\ (2)$, $b = 15{\cdot}300\ (4)$, $c = 14{\cdot}75\ (3)$ Å, $U = 3507\ (7)$ Å^3, $Z = 4$, $D_x = 1{\cdot}25$

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$Mg\,m^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 6{\cdot}53\ mm^{-1}$, $F(000) = 1400$, $T = 294$ K, final $R = 0{\cdot}072$ ($wR = 0{\cdot}066$) for 2233 independent reflections; (*b*) $[Ni(NCS)_2\{(R)$-1-phenyl-1-ethylamine$\}_4]$, $[Ni(C_8H_{11}N)_4(NCS)_2]$, $M_r = 659{\cdot}59$, orthorhombic, $P2_12_12$, $a = 15{\cdot}587\,(3)$, $b = 15{\cdot}151\,(3)$, $c = 14{\cdot}773\,(2)$ Å, $U = 3489\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}26\ Mg\,m^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 6{\cdot}56\ mm^{-1}$, $F(000) = 1400$, $T = 294$ K, final $R = 0{\cdot}069$ ($wR = 0{\cdot}057$) for 2081 independent reflections; (*c*) $[Ni(NCS)_2\{(S)$-1-phenyl-1-ethylamine$\}_4]$, $[Ni(C_8H_{11}N)_4(NCS)_2]$, $M_r = 659{\cdot}59$, triclinic, $P1$, $a = 11{\cdot}641\,(4)$, $b = 11{\cdot}697\,(4)$, $c = 14{\cdot}868\,(9)$ Å, $\alpha = 71{\cdot}28\,(5)$, $\beta = 71{\cdot}74\,(4)$, $\gamma = 84{\cdot}61\,(3)°$, $U = 1820\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}20\ Mg\,m^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 5{\cdot}74\ mm^{-1}$, $F(000) = 700$, $T = 294$ K, final $R = 0{\cdot}084$ ($wR = 0{\cdot}077$) for 3703 independent reflections; (*d*) $[Ni(NCS)_2\{(R)$-1-phenyl-1-ethylamine$\}_2\{(S)$-1-phenyl-1-ethylamine$\}_2]$-*sec*-butylbenzene, $[Ni(C_8H_{11}N)_4(NCS)_2].C_{10}H_{14}$, $M_r = 793{\cdot}82$, monoclinic, $C2/c$, $a = 10{\cdot}72\,(1)$, $b = 30{\cdot}604\,(6)$, $c = 13.69\,(3)$ Å, $\beta = 97{\cdot}7\,(1)°$, $U = 4451\,(10)$ Å^3, $Z = 4$, $D_x = 1{\cdot}19\ Mg\,m^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 4{\cdot}73\ mm^{-1}$, $F(000) = 1696$, $T = 294$ K, final $R = 0{\cdot}095$ ($wR = 0{\cdot}079$) for 1395 independent reflections; (*e*) $[Ni(NCS)_2\{(R)$-1-phenyl-1-ethylamine$\}_2\{(S)$-1-phenyl-1-ethylamine$\}_2]$-*o*-xylene, $[Ni(C_8H_{11}N)_4(NCS)_2].C_8H_{10}$, $M_r = 765{\cdot}76$, orthorhombic, *Pbcn*, $a = 15{\cdot}597\,(4)$, $b = 18{\cdot}781\,(3)$, $c = 31{\cdot}293\,(4)$ Å, $U = 9167\,(3)$ Å^3, $Z = 8$, $D_x = 1{\cdot}11\ Mg\,m^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 5{\cdot}04\ mm^{-1}$, $F(000) = 3264$, $T = 294$ K, $R = 0{\cdot}26$ (partial solution for 3530 independent reflections). The coordinated –NCS groups are *cis* to each other in (*a*), (*b*) and (*c*) but are *trans* in the clathrate complexes (*d*) and (*e*). This is the first enclathration *via* isomerization observed for inclusion compounds of Werner complexes. An energy calculation of the *trans*-to-*cis* transformation of the nickel complex gave the energy barriers as 113 and 147 kJ mol^{-1} through a *gauche* conformation and 80 kJ mol^{-1} for the *cis*-to-*cis* transformation through an *anti* eclipsed form. In both the clathrate complexes the guest molecules are disordered. The crystallographic results allow interpretation of IR spectra of the compounds. A brief resumé of the results for structures (*a*), (*b*) and (*d*) has been published [*Nassimbeni, Niven & Zemke (1985). J. Chem. Soc. Chem. Commun.* pp. 1788–1791].

Introduction

Since the pioneering work (Schaeffer, Dorsey, Skinner & Christian, 1957) on Werner clathrate complexes of the type $[Ni(NCS)_2(subst.pyridine)_4]$, these compounds have attracted wide interest, and they have been used to separate xylenes, cymenes, methylnaphthalenes and other isomeric compounds. X-ray crystallography has revealed a variety of structures with guest cavities of the channel, layer and cage type; however, in all cases, the coordinated –NCS groups are *trans* to each other (Lipkowski, 1984).

The ability of complexes of the type $[Ni(NCS)_2(1$-arylalkylamine$)_4]$ (host) to form inclusion compounds with aromatic species (guest) is well known, and has recently been reviewed (Hanotier & de Radzitzky, 1984). Little structural work has been carried out on these compounds and X-ray studies are few and incomplete. As a result, the nature of the Ni^{II} coordination in the host and clathrate complexes is not understood.

Our initial interest in these compounds stems from the fact that certain 1-arylalkylamine ligands are chiral and the nickel(II) complexes they form may preferentially include one enantiomer from a racemic mixture of chiral guest molecules. Chiral discrimination by enclathration has previously been achieved with compounds of deoxycholic acid (Sobotka & Goldberg, 1932), cyclodextrin (Cramer & Dietsche, 1959), tri-*o*-thymotide (Arad-Yellin, Green, Knossow & Tsoucaris, 1983) and others.

We report here structures of the tetraamine Ni^{II} isothiocyanates obtained from enantiomerically pure and racemic 1-phenylethylamine alone, and in the presence of the potential guests *sec*-butylbenzene (racemic) and *o*-xylene.

Experimental

The host complexes (*a*) and (*b*) were prepared from racemic (±) and enantiomerically pure (*R*)-(+) [*Aldrichimica Acta* (1980), **13**(1), 13] amine respectively, according to the previously reported method (de Radzitzky & Hanotier, 1962*a*) and single crystals obtained by recrystallization from methanol. For (*d*) and (*e*) the racemic amine and for (*c*) the (*S*)-(−) amine were dissolved in excess guest compound and added to the Ni^{II} isothiocyanates: single crystals were grown by dissolving the complex in methanolic guest solutions. Microanalysis was used to ascertain C, H, N of each compound; the results are shown in Table 1. UV/visible and mass spectra were recorded in the hope that they would provide a rapid means of identifying whether a clathrate had formed. The results were such that in the light of the X-ray diffraction studies we can conclude that neither technique is suitable for this purpose.

For each structure, the single crystals were mounted in glass capillaries in the presence of saturated solutions of the complex (particularly necessary in the case of the clathrates).

Intensity data collection: CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω–2θ scans, final acceptance limit 20σ at $20°\,min^{-1}$ in ω and max. recording time 40 s. Intensities of 3 standard reference reflections checked every hour and recentring carried out every 100 measured reflections.

Table 1. *Crystal data, experimental and refinement parameters*

	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)
Microanalysis %C, %H, %N					
found	61·9, 6·7, 12·7	61·7, 6·6, 12·7	61·8, 6·7, 12·6	66·1, 7·1, 10·3	66·6, 7·1, 10·2
(expected)	(61·3, 6·6, 12·7)	(61·3, 6·6, 12·7)	(61·3, 6·6, 12·7)	(66·6, 7·4, 10·6)	(70·1, 6·1, 9·5)
Data collection					
Crystal dimensions (mm)	0·22×0·38×0·13	0·16×0·19×0·25	0·45×0·40×1·12	0·25×0·19×0·19	0·25×0·28×0·45
Range scanned (θ) (°)	1–20	1–20	1–20	1–25	1–23
Range of indices h, k, l,	0→14, 0→14, 0→15	0→14, 0→14, 0→15	−11→11, −11→11, 0→14	−12→12, 0→36, 0→16	0→17, 0→20, 0→34
Reflections for lattice parameters					
[number, θ range (°)]	25, 9–17	24, 12–14	20, 10–16	24, 10–12	24, 16–17
Stability of standard					
reflections (%)	2·4	1·4	3·7	1·7	1·9
Scan width in ω (°)	(0·93+0·35 tan θ)	(0·88+0·35 tan θ)	(1·44+0·35 tan θ)	(0·78+0·35 tan θ)	(0·54+0·35 tan θ)
Vertical aperture length (mm)	4	4	4	4	4
Aperture width (mm)	(1·32+1·05 tan θ)	(1·25+1·05 tan θ)	(1·37+1·05 tan θ)	(1·11+1·05 tan θ)	(1·12+1·05 tan θ)
Number of reflections					
collected	3231	3821	5945	4188	7042
Number of reflections					
observed with $I_{rel}>2\sigma I_{rel}$	2233	2081	3703	1395	3530
Final refinement					
Number of parameters	204	204	383	137	221
R	0·072	0·069	0·084	0·095	0·26*
wR	0·066	0·057	0·077	0·079	—
w	$(\sigma^2F)^{-1}$	$(\sigma^2F)^{-1}$	$(\sigma^2F)^{-1}$	$(\sigma^2F)^{-1}$	—
S	4·4	2·5	7·7	3·3	—
Max. shift/e.s.d.	0·02	0·02	0·17	0·09	2·68*
Max. height in difference Fourier					
map (e Å^{-3})	0·57	1·17	0·62	0·65	1·60*
Min. height in difference Fourier					
map (e Å^{-3})	−0·56	−1·12	−0·73	−0·33	−1·57*

* Large values because only partial solution; structure greatly disordered.

Intensities corrected for Lorentz and polarization factors, but not for absorption. Structure solution: heavy-atom method using *SHELX* (Sheldrick, 1978); final refinements using F magnitudes with Ni and S atoms anisotropic, all others isotropic; methyl hydrogens treated as rigid groups with a single temperature factor; phenyl and methine hydrogens placed in calculated positions again with single temperature factor; amino hydrogens omitted. Complex neutral-atom scattering factors for non-hydrogen atoms from Cromer & Mann (1968), for hydrogen atoms from Stewart, Davidson & Simpson (1965); dispersion corrections from Cromer & Liberman (1970). Molecular parameters obtained from *PARST* (Nardelli, 1983), drawings with *PLUTO* (Motherwell, 1974*a*) and energy calculations carried out using *EENY* (Motherwell, 1974*b*). All computations carried out on a Sperry 1100 computer. All further details given in Table 1. IR spectra were obtained as Nujol mulls on a Perkin–Elmer 983 IR spectrophotometer using CsI sample plates.

Results and discussion

Fractional atomic coordinates for all structures are shown in Tables 2–6.*

* H-atom coordinates, anisotropic thermal parameters, molecular parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42696 (96 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Solution of host structures (a), (b) and (c)

The solution of these structures was non-trivial and merits discussion. In (*a*) and (*b*) one of the two independent Ni atoms lies close to the origin and hence contributes little to the phasing of the structure factors. In addition, the observed intensities in the almost tetragonal cell are related by pseudo-symmetry which is thus retained in difference maps; it was only once nearly all atoms were located that the refinement converged.

(*c*) was prepared in the presence of *sec*-butylbenzene. Enclathration of the guest failed, but its presence in solution altered the structure considerably. The similarity of a and b and α and β made us treat the triclinic cell with suspicion. However, the monoclinic C-centred transformation indicated by the Niggli matrix values did not yield the required equivalences and the triclinic cell was hence retained. Solution of the structure was again difficult. Having located two Ni atoms in the Patterson map, no sensible phasing information was obtained in a difference Fourier map; seeking the sulfur atoms from the Patterson map was not straightforward as the centrosymmetric Ni–S vectors yielded eight S peaks, all approximately equidistant from both Ni positions. Only after much trial and error were all non-hydrogen atoms located and sensible refinement ensued. At this stage an intense peak in the Patterson such that $I_{Ni-S} < I_{peak} < I_{Ni-Ni}$ at $0, 0, \frac{1}{3}$; $0, 0, \frac{2}{3}$ (which had earlier caused confusion) could be assigned to a series of multiple S×C and C×C vectors, fortuitously additive.

Table 2. *Fractional atomic coordinates* ($\times 10^4$) *and thermal parameters* ($Å^2 \times 10^3$) *for structure* (*a*)

	x	y	z	U_{iso}
Molecule 1				
Ni(1)	5000	5000	5703 (2)	46 (1)*
N(11)	4380 (7)	4340 (8)	4711 (8)	63 (4)
C(11)	4036 (8)	4052 (8)	4099 (10)	47 (4)
S(11)	3469 (3)	3596 (3)	3244 (3)	83 (2)*
N(12)	4384 (6)	4307 (6)	6816 (8)	47 (3)
C(121)	3840 (9)	3545 (9)	6601 (11)	67 (5)
C(122)	3260 (10)	3365 (11)	7423 (12)	94 (6)
C(123)	4368 (9)	2719 (9)	6448 (10)	65 (5)
C(124)	4287 (9)	2267 (10)	5615 (11)	72 (5)
C(125)	4731 (8)	1491 (10)	5445 (11)	73 (5)
C(126)	5316 (10)	1236 (11)	6066 (12)	87 (6)
C(127)	5514 (10)	1648 (11)	6843 (13)	102 (6)
C(128)	4984 (10)	2391 (9)	7061 (9)	67 (4)
N(13)	4089 (7)	6038 (7)	5779 (8)	66 (4)
C(131)	3351 (10)	6128 (11)	5249 (13)	87 (6)
C(132)	3065 (10)	7032 (9)	4962 (12)	93 (6)
C(133)	2556 (9)	5672 (10)	5768 (12)	80 (5)
C(134)	2250 (9)	4842 (10)	5444 (11)	81 (5)
C(135)	1548 (11)	4487 (11)	5954 (13)	100 (6)
C(136)	1205 (10)	4868 (10)	6656 (13)	93 (5)
C(137)	1457 (12)	5642 (12)	6963 (13)	108 (7)
C(138)	2173 (11)	6071 (12)	6529 (12)	101 (6)
Molecule 2				
Ni(2)	5000	5000	928 (2)	45 (1)*
N(21)	5451 (7)	4183 (8)	−90 (9)	66 (4)
C(21)	5793 (9)	4099 (10)	−783 (10)	58 (4)
S(21)	6356 (3)	3968 (3)	−1711 (3)	73 (2)*
N(22)	4638 (6)	5872 (7)	2016 (7)	50 (3)
C(221)	4030 (8)	6621 (8)	1819 (10)	54 (4)
C(222)	4178 (10)	7374 (9)	2470 (11)	79 (5)
C(223)	3102 (8)	6321 (8)	1825 (10)	54 (4)
C(224)	2608 (9)	6377 (9)	1081 (11)	72 (5)
C(225)	1742 (10)	6033 (10)	1087 (12)	84 (5)
C(226)	1432 (10)	5688 (10)	1865 (12)	83 (5)
C(227)	1911 (11)	5614 (11)	2619 (13)	94 (6)
C(228)	2753 (9)	5904 (9)	2612 (11)	71 (5)
N(23)	6278 (6)	5526 (6)	982 (7)	46 (3)
C(231)	6536 (10)	6171 (10)	326 (12)	82 (6)
C(232)	6211 (11)	7070 (10)	617 (13)	104 (6)
C(233)	7517 (9)	6212 (9)	149 (10)	58 (4)
C(234)	7847 (9)	5681 (9)	−530 (11)	71 (5)
C(235)	8749 (10)	5652 (10)	−666 (13)	93 (6)
C(236)	9290 (9)	6145 (10)	−138 (11)	75 (5)
C(237)	8980 (9)	6680 (10)	503 (12)	80 (5)
C(238)	8077 (9)	6699 (10)	683 (11)	78 (5)

* $U_{eq} = \frac{1}{3}$ the trace of the orthogonalized matrix.

Table 3. *Fractional atomic coordinates* ($\times 10^4$) *and thermal parameters* ($Å^2 \times 10^3$) *for structure* (*b*)

	x	y	z	U_{iso}
Molecule 1				
Ni(1)	5000	5000	5764 (2)	39 (1)*
N(11)	4379 (7)	4339 (8)	4779 (9)	56 (5)
C(11)	4069 (9)	4037 (9)	4150 (11)	38 (5)
S(11)	3524 (3)	3608 (3)	3269 (4)	78 (2)*
N(12)	5635 (6)	5697 (7)	6842 (8)	31 (3)
C(121)	6166 (8)	6483 (8)	6640 (10)	31 (4)
C(122)	6776 (10)	6647 (11)	7447 (11)	83 (6)
C(123)	5647 (9)	7291 (9)	6466 (9)	40 (5)
C(124)	5051 (10)	7612 (8)	7053 (8)	42 (4)
C(125)	4553 (9)	8362 (10)	6863 (11)	70 (5)
C(126)	4684 (9)	8827 (11)	6064 (11)	68 (6)
C(127)	5293 (8)	8513 (10)	5466 (10)	54 (5)
C(128)	5742 (8)	7738 (9)	5660 (10)	48 (4)
N(13)	5896 (6)	3937 (7)	5801 (8)	43 (3)
C(131)	6676 (7)	3914 (9)	5199 (9)	27 (4)
C(132)	6915 (9)	2998 (9)	4878 (10)	63 (5)
C(133)	7454 (8)	4341 (9)	5707 (10)	43 (4)
C(134)	7835 (10)	3904 (10)	6425 (9)	62 (5)
C(135)	8525 (11)	4264 (11)	6918 (11)	82 (6)
C(136)	8797 (9)	5123 (11)	6669 (11)	75 (5)
C(137)	8470 (9)	5528 (10)	5968 (11)	64 (5)
C(138)	7772 (9)	5147 (10)	5451 (9)	59 (5)
Molecule 2				
Ni(2)	5000	5000	818 (2)	48 (2)*
N(21)	5401 (7)	4119 (9)	−217 (9)	64 (5)
C(21)	5829 (10)	4099 (11)	−892 (12)	59 (6)
S(21)	6423 (3)	3966 (3)	−1747 (3)	63 (2)*
N(22)	5335 (6)	4144 (8)	1932 (7)	39 (4)
C(221)	5949 (9)	3354 (9)	1745 (11)	54 (5)
C(222)	5770 (10)	2618 (10)	2406 (10)	80 (6)
C(223)	6875 (8)	3669 (8)	1741 (11)	40 (4)
C(224)	7390 (11)	3569 (10)	1020 (11)	71 (6)
C(225)	8256 (12)	3899 (11)	1059 (12)	90 (6)
C(226)	8549 (11)	4303 (11)	1820 (13)	79 (6)
C(227)	8047 (12)	4371 (11)	2521 (13)	95 (7)
C(228)	7197 (10)	4117 (11)	2545 (11)	63 (5)
N(23)	6263 (9)	5428 (9)	684 (10)	93 (5)
C(231)	6689 (15)	6167 (16)	711 (17)	159 (10)
C(232)	6325 (11)	7064 (10)	654 (12)	96 (7)
C(233)	7615 (10)	6230 (10)	279 (11)	55 (5)
C(234)	8218 (11)	6688 (10)	797 (12)	81 (6)
C(235)	9088 (11)	6634 (11)	504 (11)	80 (6)
C(236)	9347 (11)	6161 (11)	−177 (11)	77 (6)
C(237)	8739 (11)	5700 (11)	−673 (12)	86 (6)
C(238)	7859 (9)	5720 (10)	−442 (10)	61 (5)

* $U_{eq} = \frac{1}{3}$ the trace of the orthogonalized matrix.

Determination of absolute structure for (*a*), (*b*) *and* (*c*)

For (*a*), the absolute configuration was obtained according to the method of Marsh (1981), by refining the structure as solved with $f'' = 0{\cdot}0$ for all atoms giving rise to a coordinate set $+x_j$. Two sets of structure factors, F_c, were then calculated without any further refinement: one for the coordinate set $+x_j$ and one for the antipodal structure $-x_j$. Both sets used the same isotropic thermal parameters and scale factor and $+if''$ for each dispersive atom. Two different residuals were obtained: $R_G^- = 0{\cdot}0717$ and $R_G^+ = 0{\cdot}0677$. Using Hamilton's test (Hamilton, 1965), the hypothesis that the structure which had given the higher residual was a better model of the measured intensities could be rejected at a significance level of 0·005.

For (*b*) Bijvoet pairs of reflections were collected to enhance the determination of absolute structure. The refinement procedure described above was again employed, yielding residuals $R_G^+ = 0{\cdot}0881$ and $R_G^- = 0{\cdot}0909$; the hypothesis that the structure with the higher residual is a better model of the measured intensities could be rejected at a significance level of 0·005.

Complex (*c*) was prepared using the opposite enantiomer (amine) to that used in (*b*), from whose results its absolute configuration could be inferred.

Description of host structures (*a*), (*b*) *and* (*c*)

Perspective views of each host molecule in all three structures, together with atomic nomenclature, are shown in Fig. 1. In all three structures the coordinated –NCS groups are *cis* to each other and deviate from linearity.

Structures (*a*) and (*b*) each have one molecule with four (*R*)-1-phenylethylamine ligands, and the conformations of each of these molecules are very similar. More remarkable is the fact that the conformations of the second molecule in both (*a*) and (*b*) are similar despite the differences in chirality: for (*a*) the second molecule has two (*R*)-1-phenylethylamine ligands *trans* to the two isothiocyanate groups, while two

Table 4. *Fractional atomic coordinates* ($\times 10^4$) *and thermal parameters* ($Å^2 \times 10^3$) *for structure* (*c*)

	x	*y*	*z*	U_{iso}		*x*	*y*	*z*	U_{iso}
Molecule 1					Molecule 2				
Ni(1)	0	0	0	52 (1)*	Ni(2)	−118 (2)	−212 (2)	5036 (2)	51 (1)*
N(11)	61 (13)	1156 (12)	−1362 (11)	66 (5)	N(21)	1006 (13)	−384 (13)	3737 (12)	69 (5)
C(11)	357 (15)	1612 (16)	−2179 (14)	66 (5)	C(21)	1589 (16)	−335 (15)	2983 (15)	68 (5)
S(11)	745 (5)	2377 (5)	−3432 (5)	92 (2)	S(21)	2657 (5)	−308 (5)	1863 (4)	77 (2)
N(12)	−209 (13)	−1345 (13)	−539 (11)	70 (5)	N(22)	−1508 (15)	−183 (14)	4457 (13)	87 (6)
C(12)	−272 (14)	−1907 (14)	−1014 (12)	57 (5)	C(22)	−1946 (16)	143 (16)	3856 (15)	72 (6)
S(12)	−311 (5)	−2757 (5)	−1694 (4)	81 (2)	S(22)	−2544 (6)	696 (6)	2931 (5)	116 (2)
N(13)	−1915 (12)	−79 (11)	646 (10)	59 (4)	N(23)	1443 (13)	−108 (12)	5602 (10)	57 (4)
C(131)	−2731 (16)	555 (15)	11 (14)	74 (6)	C(231)	2601 (17)	−350 (17)	5015 (14)	79 (6)
C(132)	−3959 (18)	−72 (18)	459 (16)	104 (7)	C(232)	3646 (21)	58 (21)	5288 (18)	130 (9)
C(133)	−2807 (14)	1955 (13)	−132 (12)	50 (4)	C(233)	2806 (15)	−1701 (15)	5222 (13)	60 (5)
C(134)	−2429 (16)	2710 (17)	−1006 (14)	76 (6)	C(234)	2498 (15)	−2529 (16)	6236 (14)	75 (6)
C(135)	−2524 (22)	3966 (23)	−1039 (20)	127 (9)	C(235)	2592 (18)	−3800 (19)	6402 (16)	92 (7)
C(136)	−3013 (20)	4347 (21)	−284 (19)	117 (8)	C(236)	3071 (20)	−4130 (21)	5537 (18)	116 (8)
C(137)	−3415 (18)	3486 (19)	656 (16)	93 (7)	C(237)	3531 (20)	−3383 (21)	4525 (18)	110 (8)
C(138)	−3272 (16)	2281 (17)	701 (14)	74 (6)	C(238)	3303 (18)	−2141 (19)	4434 (17)	100 (7)
N(14)	122 (12)	1453 (11)	592 (10)	60 (4)	N(24)	−115 (12)	−2144 (11)	5621 (10)	53 (4)
C(141)	506 (17)	2740 (16)	−112 (14)	78 (6)	C(241)	−795 (15)	−2858 (15)	5312 (13)	66 (5)
C(142)	−20 (19)	3567 (18)	499 (15)	104 (7)	C(242)	−274 (17)	−4159 (16)	5403 (14)	84 (6)
C(143)	1815 (16)	2854 (15)	−597 (14)	66 (5)	C(243)	−2091 (15)	−2949 (14)	5936 (12)	54 (5)
C(144)	2284 (18)	3203 (17)	−1609 (15)	84 (6)	C(244)	−2593 (17)	−3143 (16)	6989 (14)	77 (6)
C(145)	3438 (20)	3389 (18)	−2104 (18)	101 (7)	C(245)	−3810 (19)	−3293 (17)	7499 (16)	89 (7)
C(146)	4276 (23)	3193 (20)	−1532 (19)	123 (9)	C(246)	−4569 (17)	−3182 (16)	6963 (14)	71 (6)
C(147)	3807 (20)	2831 (18)	−465 (17)	103 (7)	C(247)	−4263 (18)	−2943 (17)	6007 (15)	84 (6)
C(148)	2594 (17)	2688 (16)	−30 (15)	77 (6)	C(248)	−3066 (18)	−2774 (16)	5461 (15)	86 (6)
N(15)	1955 (12)	13 (12)	−547 (10)	63 (4)	N(25)	−1161 (13)	−67 (12)	6456 (10)	61 (4)
C(151)	2523 (16)	−676 (15)	−1242 (13)	69 (5)	C(251)	−2485 (17)	−31 (17)	6750 (15)	77 (6)
C(152)	3701 (19)	−24 (21)	−2018 (17)	121 (8)	C(252)	−2978 (20)	−436 (21)	7848 (16)	121 (8)
C(153)	2861 (17)	−1891 (18)	−644 (14)	78 (6)	C(253)	−2928 (17)	1160 (17)	6317 (14)	75 (6)
C(154)	2527 (19)	−2881 (19)	−783 (16)	100 (7)	C(254)	−3618 (20)	1400 (21)	5686 (17)	113 (8)
C(155)	2956 (21)	−4086 (22)	−240 (18)	117 (8)	C(255)	−4037 (23)	2577 (25)	5184 (20)	148 (10)
C(156)	3605 (26)	−4129 (27)	390 (22)	160 (12)	C(256)	−3690 (25)	3558 (26)	5417 (21)	146 (11)
C(157)	3958 (22)	−3265 (24)	514 (20)	132 (9)	C(257)	−3024 (19)	3441 (21)	6033 (17)	109 (8)
C(158)	3709 (21)	−1985 (22)	−100 (17)	121 (8)	C(258)	−2674 (18)	2186 (19)	6500 (16)	100 (7)
N(16)	75 (11)	−1169 (11)	1450 (10)	53 (4)	N(26)	−259 (13)	1759 (13)	4571 (12)	76 (5)
C(161)	61 (16)	−2479 (15)	1627 (13)	64 (5)	C(261)	361 (17)	2510 (16)	3520 (14)	77 (6)
C(162)	559 (22)	−3007 (22)	2500 (17)	136 (9)	C(262)	−475 (23)	3612 (21)	3191 (21)	166 (12)
C(163)	−1250 (18)	−2907 (17)	1919 (15)	78 (6)	C(263)	1578 (20)	2781 (18)	3396 (16)	90 (7)
C(164)	−2105 (21)	−2609 (19)	2657 (17)	109 (8)	C(264)	2571 (25)	2311 (22)	2828 (19)	132 (9)
C(165)	−3329 (25)	−3057 (23)	2902 (20)	148 (10)	C(265)	3745 (27)	2777 (24)	2709 (21)	141 (11)
C(166)	−3508 (33)	−3846 (30)	2362 (27)	202 (16)	C(266)	3880 (29)	3405 (26)	3191 (23)	155 (12)
C(167)	−2660 (24)	−4088 (23)	1596 (20)	132 (9)	C(267)	3108 (28)	3728 (24)	3783 (22)	147 (11)
C(168)	−1471 (22)	−3665 (20)	1387 (17)	119 (8)	C(268)	1767 (29)	3578 (26)	3898 (22)	172 (12)

* $U_{eq} = \frac{1}{3}$ the trace of the orthogonalized matrix.

(*S*)-amine ligands are situated *trans* to each other; in (*b*) the two *R* ligands *trans* to the –NCS groups are similar to those in (*a*) and the remaining two have their phenyls and methyls similarly orientated to those of the *S* ligands in (*a*), the change in chirality having been accommodated by a flip of the H, the smallest substituent.

For structure (*c*) the conformation of each of the independent molecules corresponds closely to the inverse of the four *R* molecules in (*a*) and (*b*). We believe that the similarities in all three structures may be an indication of the steric restrictions experienced by the nitrogen and adjacent carbon atoms in contrast to the freedom of the C atoms further from the NH_2 to accommodate either methyl or phenyl groups and probably any of the many other groups previously investigated (de Radzitzky & Hanotier, 1962*b*).

Molecular packing of (*a*), (*b*) *and* (*c*)

A packing diagram for (*a*) has previously been published (Nassimbeni, Niven & Zemke, 1985). The packing of (*b*) and (*c*) is shown in Fig. 2. Each structure consists of discrete acentric molecules which may be described as having an amine-ligand 'head' and a 'tail' of isothiocyanate groups. For (*a*) and (*b*) each of the two different molecules are alternately stacked head-to-tail along the twofold axes in the [001] direction ($x, y = 0{\cdot}0$); the same stacking but in the opposite direction is observed for the twofold axes at ($x, y = 0{\cdot}5$). It is important to note that a conformational difference between two chemically equivalent molecules in (*b*) allows them to pack in the same manner as two chemically different molecules in (*a*); this implies that intermolecular interactions play an important role during the crystallization of these complexes. Structure (*c*) differs from (*a*) and (*b*) in that its molecules are all orientated in the same way down [001]; *i.e.* the isothiocyanate groups of all the molecules are situated on the same side of the nickel atoms. The resulting structure is somewhat less efficiently packed than the orthorhombic host structures [volume per non-H atom for (*c*) 21·2 $Å^3$; for (*a*), (*b*) 20·3 $Å^3$].

Clathrate with sec-butylbenzene (*d*)

After the Ni atom had been located in the Patterson map, a difference Fourier synthesis revealed all non-

Table 5. *Fractional atomic coordinates* ($\times 10^4$) *and thermal parameters* ($Å^2 \times 10^3$) *for structure* (*d*)

	x	*y*	*z*	U_{iso}
Ni	2500	2500	5000	51 (1)*
N(1)	2182 (8)	2491 (4)	3489 (6)	59 (3)
C(1)	1967 (9)	2528 (5)	2652 (9)	52 (3)
S(1)	1670 (3)	2586 (1)	1458 (2)	70 (2)*
N(2)	3996 (9)	2982 (3)	5092 (8)	45 (3)
C(21)	4292 (12)	3246 (5)	4217 (11)	60 (5)
C(22)	5652 (12)	3410 (5)	4371 (11)	88 (5)
C(23)	3360 (12)	3619 (4)	3994 (10)	54 (4)
C(24)	2578 (12)	3648 (5)	3121 (10)	73 (5)
C(25)	1685 (15)	3980 (5)	2924 (12)	94 (5)
C(26)	1674 (14)	4286 (5)	3607 (12)	93 (5)
C(27)	2387 (14)	4289 (5)	4494 (11)	94 (5)
C(28)	3268 (13)	3950 (4)	4692 (11)	79 (5)
N(3)	3868 (9)	1964 (3)	5105 (8)	54 (4)
C(31)	4328 (13)	1787 (4)	4218 (11)	60 (5)
C(32)	5299 (12)	2093 (4)	3839 (10)	70 (4)
C(33)	4921 (13)	1334 (4)	4373 (10)	67 (4)
C(34)	4457 (15)	1007 (5)	3726 (12)	101 (6)
C(35)	5037 (17)	580 (6)	3895 (13)	119 (6)
C(36)	6010 (16)	526 (6)	4599 (12)	106 (6)
C(37)	6476 (16)	852 (6)	5217 (13)	114 (6)
C(38)	5903 (14)	1269 (5)	5100 (11)	92 (5)
Guest				
C(10)	0	1483 (8)	2500	106 (8)
C(20)	1035 (17)	1292 (6)	2141 (14)	131 (7)
C(30)	1062 (18)	827 (6)	2155 (15)	135 (7)
C(40)	0	606 (9)	2500	114 (9)
C(50)	0	64 (14)	2500	201 (15)
C(601)	542 (56)	−24 (26)	1640 (42)	114 (11)
C(602)	−749 (67)	−25 (45)	1059 (69)	114 (11)
C(603)	324 (77)	−358 (18)	3047 (48)	114 (11)
C(611)	1280 (47)	−32 (29)	3076 (50)	114 (11)
C(612)	358 (68)	−124 (44)	3839 (67)	114 (11)
C(613)	−887 (67)	−121 (33)	1619 (52)	114 (11)

* $U_{eq} = \frac{1}{3}$ the trace of the orthogonalized matrix.

Table 6. *Fractional atomic coordinates* ($\times 10^4$) *of the atoms located in the best model obtained and thermal parameters* ($Å^2 \times 10^3$) *for structure* (*e*)

	x	*y*	*z*	U_{iso}
Ni(1)	2464 (2)	1066 (3)	228 (2)	38 (1)*
N(11)	2492 (9)	−119 (18)	−305 (15)	46 (7)
C(11)	2443 (9)	−708 (18)	−658 (15)	23 (7)
S(11)	2401 (3)	−1480 (6)	−1192 (5)	46 (4)*
N(12)	2421 (8)	2220 (16)	732 (13)	29 (6)
C(12)	2438 (10)	2819 (19)	1100 (16)	26 (7)
S(12)	2549 (4)	3629 (7)	1661 (5)	53 (4)*
N(13)	1971 (9)	491 (20)	832 (17)	48 (9)
C(131)	1793 (9)	1020 (21)	1405 (17)	22 (8)
C(132)	2055 (17)	1086 (37)	2076 (28)	98 (17)
C(133)	1326 (16)	707 (33)	1611 (27)	74 (14)
C(134)	989 (15)	1237 (33)	1765 (26)	76 (15)
C(135)	568 (20)	751 (42)	1992 (32)	111 (21)
C(136)	405 (27)	−178 (59)	2472 (49)	226 (36)
C(137)	834 (22)	−287 (46)	2084 (36)	132 (25)
C(138)	1300 (13)	−106 (28)	1868 (22)	60 (11)
N(14)	1945 (11)	1613 (23)	−436 (20)	64 (11)
C(141)	1765 (12)	1247 (26)	−995 (21)	47 (10)
C(142)	1643 (20)	1801 (43)	−1686 (37)	120 (22)
C(143)	1465 (12)	804 (26)	−720 (22)	52 (11)
C(144)	1154 (13)	1281 (30)	−302 (24)	71 (13)
C(145)	781 (15)	887 (33)	46 (26)	74 (15)
C(146)	704 (18)	168 (40)	−45 (31)	98 (17)
C(147)	982 (22)	−269 (48)	−421 (37)	136 (26)
C(148)	1373 (14)	−49 (30)	−703 (24)	65 (12)
N(15)	2971 (8)	527 (17)	930 (14)	27 (7)
C(151)	3291 (16)	965 (32)	1532 (26)	72 (14)
C(152)	3320 (14)	540 (33)	2120 (27)	68 (14)
C(153)	3687 (16)	1311 (34)	1188 (28)	83 (15)
C(154)	3713 (14)	2283 (29)	1191 (24)	66 (12)
C(155)	4115 (20)	2862 (45)	831 (34)	112 (21)
C(156)	4355 (20)	2366 (40)	778 (32)	105 (19)
C(157)	4392 (20)	1222 (40)	826 (31)	107 (20)
C(158)	4017 (16)	823 (35)	1083 (28)	89 (16)
N(16)	2955 (10)	1648 (20)	−439 (17)	52 (9)
C(161)	3217 (13)	1031 (29)	−1029 (23)	52 (12)
C(162)	3012 (13)	1104 (27)	−1571 (22)	54 (11)
C(163)	3718 (13)	1630 (27)	−1116 (22)	54 (11)
C(164)	3732 (23)	2375 (46)	−1416 (37)	131 (25)
C(165)	4134 (23)	2929 (51)	−1678 (39)	143 (27)
C(166)	4534 (16)	2241 (34)	−1659 (28)	79 (15)
C(167)	4560 (23)	1707 (47)	−1265 (38)	134 (26)
C(168)	4109 (15)	1212 (31)	−1058 (25)	73 (14)
C(1*G*)	3574	1361	5588	†
C(2*G*)	3534	1223	4857	†
C(3*G*)	3889	1137	4436	†
C(4*G*)	4303	1190	4745	†
C(5*G*)	4343	1329	5476	†
C(6*G*)	3978	1414	5897	†

* $U_{eq} = \frac{1}{3}$ the trace of the orthogonalized matrix.

† Best refinement obtained with temperature factor fixed and atoms at corners of a regular hexagon.

hydrogen ligand atoms, and with subsequent refinement $R = 0{\cdot}17$ was achieved. There now remained seven peaks of electron density which were independent of the nickel complex. Three of these were located at the Wyckoff position (*e*), requiring twofold site symmetry. Although the *sec*-butylbenzene molecule does not have a twofold axis, the major portion of the molecule can be accommodated with this symmetry: we were able to achieve an acceptable model by invoking statistical disorder for the butyl substituent. Regrettably, the disorder makes it difficult to ascertain whether there has been selective enclathration of only one enantiomer; however, the shape of the area of disordered electron density cannot be explained by the presence of just one enantiomer in this guest site; we therefore believe that no chiral selectivity has occurred.

Description of the structure (*d*)

A perspective drawing of the *trans*-NCS Ni complex with atomic nomenclature is shown in Fig. 3. The structure consists of discrete centrosymmetric nickel-complex molecules and asymmetric guest molecules. Most significantly, the –NCS groups are now *trans* to each other. This *cis*/*trans* isomerism between the host and clathrate species is the first ever reported, and perhaps explains why these clathrates cannot be formed by addition of guest to previously prepared host complexes, as is the case for the better studied Werner clathrates $Ni(NCS)_2(subst.pyridine)_4.guest$ (Lipkowski, 1984).

A relevant packing diagram for (*d*) has been published (Nassimbeni *et al.*, 1985) and reveals that the phenyl planes of guest *sec*-butylbenzene molecules and host 1-phenylethylamine ligands are not parallel as previously expected (Hanotier & de Radzitzky, 1984). The hypothesis of charge-transfer guest–host interaction is therefore not supported by the crystal structure.

Clathrate with ortho-xylene (*e*)

The nickel atom was located in a Patterson map and subsequent difference Fourier syntheses revealed most of the remaining non-hydrogen atoms of the coordinated and guest species. However, extensive disorder of one of the amine ligands and the *o*-xylene

molecule were revealed; our best model of the situation yielded $R = 0{\cdot}26$. The structure cannot be considered refined; however, we have included it in this work because the results do permit an examination of the gross structure, which is interesting for the following reasons: the –NCS groups are again *trans* to each other, as in the *sec*-butylbenzene clathrate; the phenyl groups of the amine ligands are not parallel to the aromatic ring of the guest, again implying that there is no host–guest charge-transfer interaction. A perspective view with atomic nomenclature of the host molecule is given in Fig. 4, and the packing of the clathrate is shown in Fig. 5.

Energy study of the configurational change of $Ni(NCS)_2(1\text{-}phenylethylamine)_4$

The existence of the Ni^{II} complex in both *cis* and *trans* forms raised interest in the energy of configurational change. In a manner similar to the 'Berry pseudorotation' which models configurational change in trigonal-bipyramidal complexes (Berry, 1960), the *trans*-to-*cis* transformation without bond breaking of an octahedral complex may be modelled by rotating, with respect to each other, two opposite triangular faces of the octahedron. *EENY* (Motherwell, 1974*b*) was used to calculate non-bonded potential energies for the [$Ni(NCS)_2$(1-phenylethylamine)$_4$] molecule as it was twisted to change configuration.

The initial geometry of the nickel complex was taken from the crystal structure of its clathrate with *sec*-butylbenzene (*d*). In order to describe the rotation of the facing triangles of the octahedron, midpoints in two opposite N–N–N faces were found by simple vector averages in orthogonal space. Because dummy atoms in these N–N–N faces interfere with the calculations by forming close contacts with other atoms, two dummy atoms $D(1)$ and $D(2)$ were

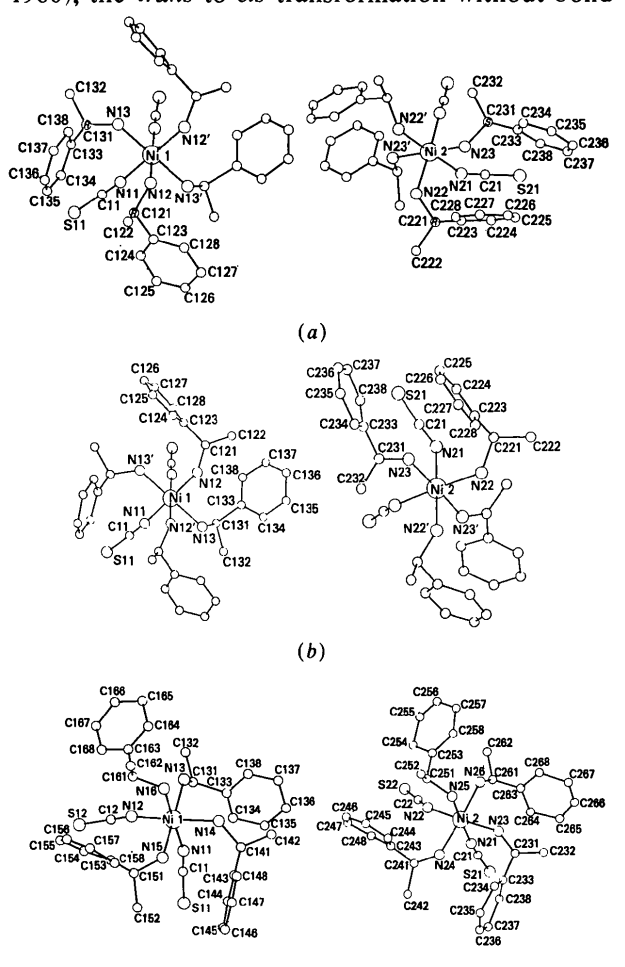

Fig. 1. Perspective views of each host molecule (*a*), (*b*) and (*c*), with atomic nomenclature.

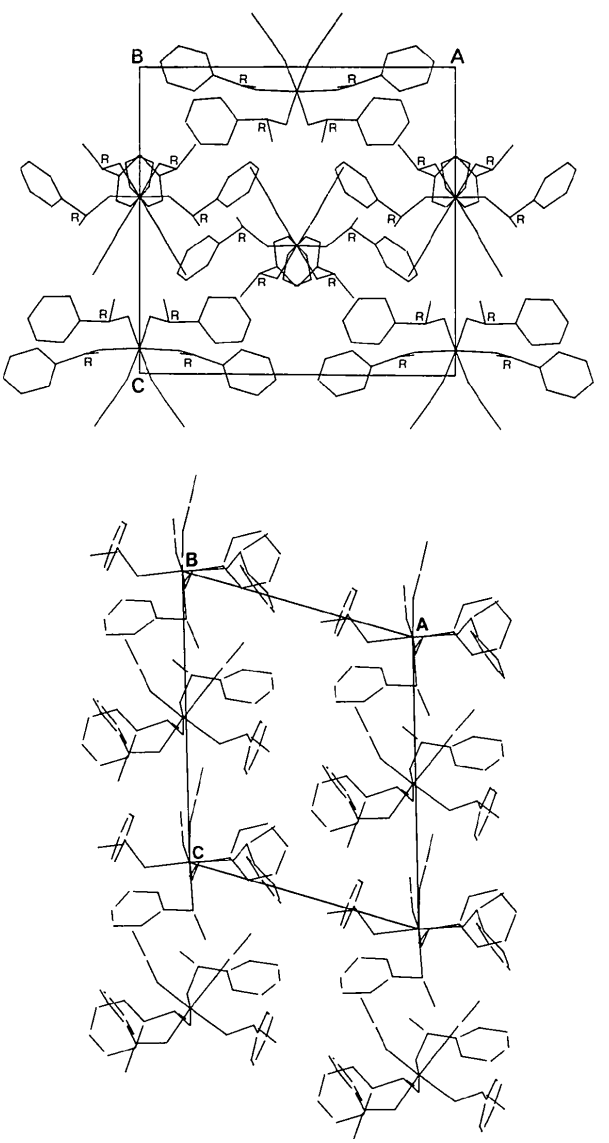

Fig. 2. Packing diagrams of structure (*b*) (top) and structure (*c*) (bottom).

defined on the vector midpoints between the nickel atom and the mid-points of the N–N–N faces, and for the purpose of program insertion were treated as hydrogen atoms.

A conformation-governing torsion angle τ_0 was then defined as N(11)–*D*(1)–*D*(2)–N(14) as shown in Fig. 6 [value in clathrate structure = 179 (1)°]. This angle was then varied in steps of 10° through 360°. After each 10° twist, 16 parameters (two angles and fourteen torsion angles defined in Fig. 6) were allowed to vary in order to achieve a minimum-energy structure. Energy barriers are expected when the two triangular faces are eclipsed ($\tau_0 = 0$, 120, 140°) and energy minima when they are staggered ($\tau_0 = 60$, 180, 300°).

The resulting energy curve (Nassimbeni *et al.*, 1985) is not entirely symmetrical which may result from one or both of the following: the N–N–N faces are not exactly parallel, and when twisted by τ_0 some of the N–N distances between opposite faces in eclipsed positions became shorter than others, depending on whether τ_0 is positive or negative; the prescribed variables may be insufficient to describe the molecule adequately. However, the calculated energy barriers for the *trans*-to-*cis* transformation through a *gauche* conformation are 113 and 147 kJ mol^{-1}, and for the *cis*-to-*cis* change through an '*anti*' eclipsed form it is 80 kJ mol^{-1}. We appreciate that the real physical meaning of these values may be limited because Ni–ligand electronic interactions have been ignored.

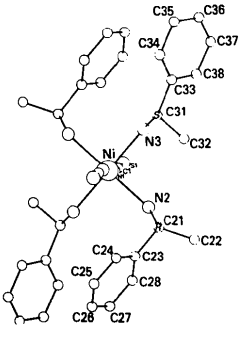

Fig. 3. Perspective view of the Ni complex of the *sec*-butylbenzene clathrate (*d*) indicating atomic nomenclature.

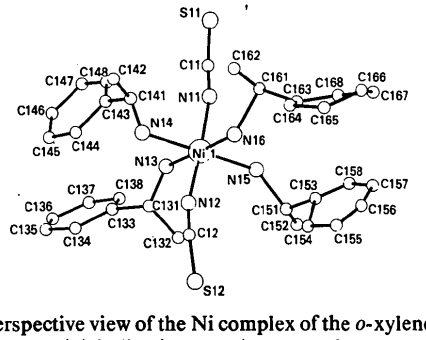

Fig. 4. Perspective view of the Ni complex of the *o*-xylene clathrate (*e*) indicating atomic nomenclature.

However, these energy barriers are of the same order of magnitude as that observed for the *M*-(−)- to *P*-(+)-tri-*o*-thymotide enantiomerization (*viz* 88 kJ mol^{-1}) which takes place rapidly at room temperature (Downing, Ollis & Sutherland, 1970). For our nickel complex, the energy difference between the *trans* and *cis* minima is 8–12 kJ mol^{-1}, the *cis* configuration having the lower energy. Although little significance may be attached to such a small calculated energy difference, it concurs with the fact that this nickel complex crystallizes in the *cis* rather than the *trans* form unless in the presence of some other compound with which it can crystallize.

IR spectra

It has previously been observed (de Radzitzky & Hanotier, 1962*b*; Hanotier, Brandli & de Radzitzky, 1966) that the IR spectra of these inclusion compounds are very different from the sum of the spectra of their components, this fact having been attributed

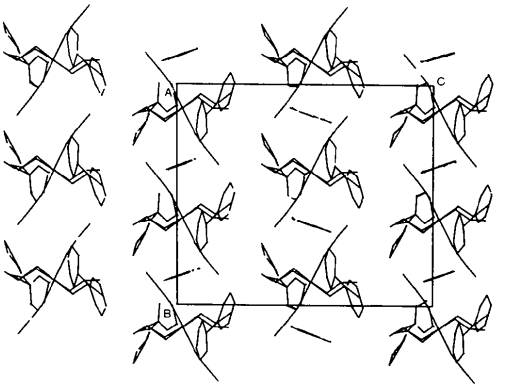

Fig. 5. Packing diagram of the *o*-xylene clathrate (*e*).

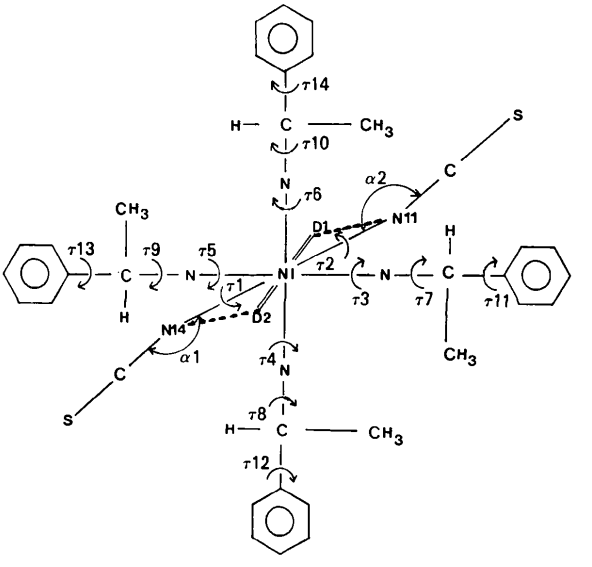

Fig. 6. Schematic representation of the Ni complex showing the variable parameters in the energy-minimization calculations (torsion angles designated τ, bond angles designated α).

Table 7. *IR spectra* (550-200 cm^{-1}) *of the host and clathrate complexes*

Compound	(a)*	(d)	(d)†	(e)	(e)‡	Assignment
	532	541	531	542	543	NH_2 rock
		524		526	532	
	486	497	487	494	486	
	479	475	480	475	478	δ_{NCS}
	459		459	437	459	
	408		407		408	
	388	400	386	400	388	
	365	393	368	387	368	$\nu_{Ni-N(amine)}$
	349		347		349	
		256		249		
	222	218	222	219	222	ν_{Ni-NCS}

* The spectra of (*b*) and (*c*) are essentially the same as the spectrum of (*a*).
† Compound (*d*) after 24 h as a Nujol mull.
‡ Compound (*e*) after 24 h as a Nujol mull.

to the occurrence of charge-transfer interactions. In the light of our structural findings we can interpret the differences in terms of a point-symmetry change around the Ni atom, C_2 in the host structures and D_{2h} in the clathrates. We have measured the IR spectrum of each complex in the range 3000-200 cm^{-1} and report in Table 7 the region which exhibits a differing band pattern for the hosts as compared to the clathrate compounds. Assignments have been made by comparison with previously reported spectra of related compounds (Engelter & Thornton, 1977; Lee-Thorp, Ruede & Thornton, 1978). Regrettably, group theoretical calculations (Cotton, 1971) only predict accurately the number of $\nu_{M-N\,(amino)}$ stretching frequencies and not the ν_{M-NCS} observed. However, the differences between the IR spectra of the host and clathrate compounds are such that assignments to *cis* and *trans* configurations respectively may be made. Interestingly, after storage as Nujol mulls for 24 h, the clathrates give rise to spectra resembling those of the host complexes implying that as Nujol mulls the clathrates revert to *cis* configuration.

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References

ARAD-YELLIN, R., GREEN, B. S., KNOSSOW, M. & TSOUCARIS, G. (1983). *J. Am. Chem. Soc.* **105**, 4561-4571.

BERRY, R. S. J. (1960). *J. Chem. Phys.* **32**, 933-938.

COTTON, F. A. (1971). *Chemical Applications of Group Theory*, 2nd ed., pp. 295-339. New York: Wiley-Interscience.

CRAMER, F. & DIETSCHE, W. (1959). *Chem. Ber.* **92**, 378-384.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891-1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321-324.

DOWNING, A. P., OLLIS, W. D. & SUTHERLAND, I. O. (1970). *J. Chem. Soc. B*, pp. 24-34.

ENGELTER, C. & THORNTON, D. A. (1977). *J. Mol. Struct.* **42**, 51-58.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502-510.

HANOTIER, J., BRANDLI, J. & DE RADZITZKY, P. (1966). *Bull. Soc. Chim. Belg.* **75**, 265-280.

HANOTIER, J. & DE RADZITZKY, P. (1984). In *Inclusion Compounds* I, edited by J. L. ATWOOD, J. E. D. DAVIES & D. D. MACNICOL, pp. 105-134. New York: Academic Press.

LEE-THORP, J. A., RUEDE, J. E. & THORNTON, D. A. (1978). *J. Mol. Struct.* **50**, 65-71.

LIPKOWSKI, J. (1984). In *Inclusion Compounds* I, edited by J. L. ATWOOD, J. E. D. DAVIES & D. D. MACNICOL, pp. 59-104. New York: Academic Press.

MARSH, R. E. (1981). *Acta Cryst.*, B**37**, 1985-1988.

MOTHERWELL, W. D. S. (1974*a*). *PLUTO.* Program for plotting molecular and crystal structures. Cambridge Univ., England. Unpublished.

MOTHERWELL, W. D. S. (1974*b*). *EENY. Potential Energy Program.* Cambridge Univ., England. Unpublished.

NARDELLI, M. (1983). *Comput. Chem.* **7**, 95-98.

NASSIMBENI, L. R., NIVEN, M. L. & ZEMKE, K. J. (1985). *J. Chem. Soc. Chem. Commun.* pp. 1788-1791.

RADZITZKY, P. DE & HANOTIER, J. (1962*a*). *Ind. Chim. Belg.* **27**, 125-136.

RADZITZKY, P. DE & HANOTIER, J. (1962*b*). *Ind. Eng. Chem. Process Des. Dev.* **1**(1), 10-14.

SCHAEFFER, W. D., DORSEY, W. S., SKINNER, D. A. & CHRISTIAN, C. G. (1957). *J. Am. Chem. Soc.* **79**, 5870-5876.

SHELDRICK, G. M. (1978). *SHELX.* In *Computing in Crystallography*, edited by H. SCHENK, R. OLTHOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 34-42. Delft Univ. Press.

SOBOTKA, H. & GOLDBERG, A. (1932). *Biochem. J.* **26**, 905-909.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175-3187.