Structure of *cis*-Bis(isothiocyanato)(1,4,7,10-tetraazacyclotetradecane)nickel(II). Electronically Controlled *cis* Coordination

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Abstract. *cis*-[Ni($C_{10}H_{24}N_4$)(NCS)$_2$], orthorhombic, $Pbn2_1$, $a = 11.399$ (1), $b = 16.231$ (2), $c = 9.503$ (2) Å, $U = 1758.1$ (4) Å^3, $Z = 4$, $D_x = 1.42$, $D_m = 1.41$ Mg m^{-3}, μ(Mo $K\alpha$) = 1.31 mm^{-1}, $R = 0.042$, $R_w = 0.059$ for 2033 independent reflections ($2\theta < 70°$). The complex is of *cis*(NCS) type with the tetraaza fourteen-membered macrocyclic ligand folded. The seven-membered chelate ring adopts a *skew*(h)-like conformation.

Introduction. In a series of structural studies on *trans*-NiX_2N_4-type complexes (X = halide or pseudo halide ion; N_4 = tetraazacycloalkane), we found a correlation between Ni—N and Ni—X distances: the Ni—X distance decreases as the Ni—N distance increases (Sugimoto, Fujita, Ito, Toriumi & Ito, 1982). On the other hand, Martin, Sperati & Busch (1977) reported a similar correlation, which they called a *cis* effect, between ligand-field parameters, Dq^z(axial) and Dq^{xy} (in-plane), in electronic spectra of *trans*-diacido-(tetraazamacrocycle)nickel(II) complexes: the Dq^z value decreases linearly as the Dq^{xy} value increases. It seems that these two phenomena are caused by the same electronic origin. The present study was undertaken to investigate the electronic *cis* effect from the viewpoint of the relation between hole size of a tetraazamacrocyclic ligand and ligand-field strength.

The tetraaza fourteen-membered macrocycle (here-

N_47
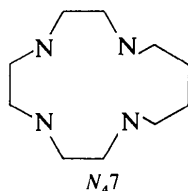
after abbreviated as N_47) forms a Ni^{II} complex with a 5,5,5,7 sequence of chelate rings. The hole size of the N_47 ligand is just suitable or possibly slightly small to accommodate a high-spin Ni^{II} ion in a planar fashion. The four-coordinate complex |Ni(N_47)|(ClO$_4$)$_2$ with singlet ground state and the six-coordinate dichloro complex |NiCl$_2$(N_47)| with triplet ground state have been isolated and characterized (Sugimoto, Nonoyama,

Ito & Fujita, 1982). In general, a Ni—N distance in this type of complex is longer by approximately 0.1 Å in the high-spin form than in the low-spin form (Ito & Toriumi, 1981, and references therein). Coordination of two Cl$^-$ ions to the axial sites of [Ni(N_47)]$^{2+}$ should cause elongation of the Ni—N distance. The crystal-structure analysis of [NiCl$_2$(N_47)] revealed that the N_47 ligand adopts a square-planar geometry about the Ni to give the *trans* dichloro complex (Sugimoto, Fujita, Ito, Toriumi & Ito, 1982). This observation prompted us to investigate a coordination geometry of [NiX_2(N_47)] in which the unidentate ligand X has a much stronger ligand field than Cl$^-$. From the electronic *cis* effect and the cavity size of N_47, it was anticipated that the ligand N_47 in the [NiX_2(N_47)] complex with the strong ligands X may not adopt a square-planar geometry about the Ni but might be folded to yield a *cis* complex, *cis*-

Table 1. *Fractional positional parameters* ($\times 10^4$) *and equivalent isotropic temperature factors for non-hydrogen atoms with e.s.d.'s in parentheses*

The equivalent isotropic temperature factor is calculated using the expression $B_{eq} = \frac{4}{3} \sum_i \sum_j a_i \cdot a_j \beta_{ij}$, where the a_i's are unit-cell edges in direct space.

	x	y	z	B_{eq} (Å^2)
Ni	973 (1)	1087 (1)	0	3.3
S(1)	−3091 (1)	777 (1)	−1319 (3)	7.2
S(2)	1041 (1)	−1847 (1)	96 (3)	5.4
N(1)	2643 (4)	848 (3)	942 (5)	3.9
N(2)	590 (5)	1574 (3)	2019 (5)	4.4
N(3)	1175 (4)	2350 (3)	−441 (5)	4.1
N(4)	1423 (4)	982 (3)	−2158 (6)	5.0
N(5)	−791 (4)	1151 (3)	−622 (7)	5.0
N(6)	693 (4)	−162 (3)	371 (6)	5.0
C(1)	2696 (6)	1347 (4)	2245 (8)	5.1
C(2)	1525 (7)	1310 (4)	2970 (8)	5.4
C(3)	505 (7)	2487 (4)	1907 (8)	5.8
C(4)	326 (6)	2775 (4)	459 (8)	5.6
C(5)	1030 (6)	2460 (5)	−1959 (8)	5.7
C(6)	1749 (6)	1809 (5)	−2675 (7)	6.1
C(7)	2123 (7)	311 (5)	−2764 (9)	6.4
C(8)	3441 (6)	329 (5)	−2386 (9)	6.6
C(9)	3804 (5)	132 (4)	−893 (11)	5.9
C(10)	3737 (4)	830 (4)	162 (11)	4.8
C(11)	−1744 (5)	1015 (3)	−901 (8)	4.5
C(12)	852 (4)	−858 (3)	251 (6)	3.3

[NiX_2($N_4$7)]. For this purpose, we chose a thiocyanato derivative [Ni(NCS)$_2$($N_4$7)]. It has been reported that Dq^z values for $trans$-[NiX_2(cyclam)] (cyclam = 1,4,8,11-tetraazacyclotetradecane) was 876 cm^{-1} for X = NCS$^-$ and 379 cm^{-1} for X = Cl$^-$ (Martin, Sperati & Busch, 1977).

The compound was prepared as described elsewhere (Sugimoto, Nonoyama, Ito & Fujita, 1982). Blue prismatic crystals were obtained by slow recrystallization from acetonitrile. X-ray diffraction data were measured, using a specimen with dimensions 0.38 × 0.35 × 0.34 mm, on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Within the range 2θ < 70°, 2033 independent reflections with $|F_o| > 3\sigma(|F_o|)$ were obtained. The intensities were corrected for Lorentz and polarization factors and for absorption.

The structure was solved by the heavy-atom method and refined by a block-diagonal least-squares method. The weighting scheme employed was $w = [\sigma^2_{count} + (0.015|F_o|^2)]^{-1}$. All H atoms were located by difference Fourier syntheses, and included in the final refinement with isotropic temperature factors. Atomic parameters for nonhydrogen atoms are given in Table 1.*

Discussion. Fig. 1 shows a perspective drawing of the [Ni(NCS)$_2$($N_4$7)] complex. Some bond lengths and angles of interest are listed in Table 2.

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* Lists of structure factors, anisotropic thermal parameters for non-H atoms and positional and thermal parameters for H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36847 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
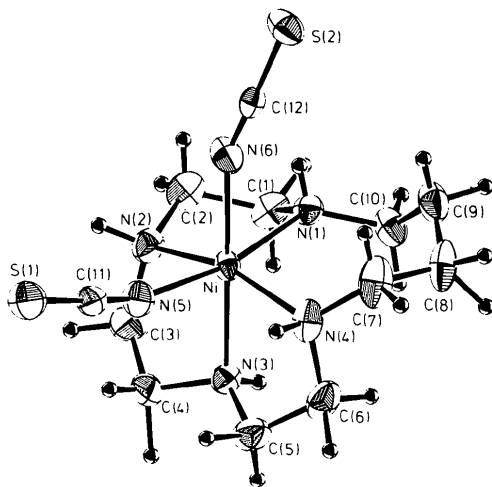
Table 2. *Selected bond distances* (Å) *and angles* (°) *for cis*-[Ni(NCS)$_2$($N_4$7)]

Ni—N(1)	2.138 (4)		Ni—N(6)	2.081 (5)
Ni—N(2)	2.121 (5)		S(1)—C(11)	1.632 (6)
Ni—N(3)	2.106 (5)		S(2)—C(12)	1.626 (6)
Ni—N(4)	2.121 (6)		N(5)—C(11)	1.140 (8)
Ni—N(5)	2.099 (5)		N(6)—C(12)	1.150 (7)
N(1)—Ni—N(2)	82.7 (2)		N(3)—Ni—N(5)	90.0 (2)
N(1)—Ni—N(3)	99.4 (2)		N(3)—Ni—N(6)	176.9 (2)
N(1)—Ni—N(4)	100.1 (2)		N(4)—Ni—N(5)	87.9 (2)
N(1)—Ni—N(5)	168.5 (2)		N(4)—Ni—N(6)	97.1 (2)
N(1)—Ni—N(6)	83.7 (2)		N(5)—Ni—N(6)	87.1 (2)
N(2)—Ni—N(3)	80.8 (2)		Ni—N(5)—C(11)	165.7 (5)
N(2)—Ni—N(4)	162.7 (2)		Ni—N(6)—C(12)	156.3 (5)
N(2)—Ni—N(5)	92.2 (2)		S(1)—C(11)—N(5)	177.5 (6)
N(2)—Ni—N(6)	100.3 (2)		S(2)—C(12)—N(6)	178.4 (5)
N(3)—Ni—N(4)	81.9 (2)			

The Ni^{II} ion is surrounded octahedrally by six N atoms, with two NCS$^-$ ligands occupying the cis positions. The $N_4$7 ligand is folded in contrast to the $trans$-dichloro analog, $trans$-[NiCl$_2$($N_4$7)] (Sugimoto, Fujita, Ito, Toriumi & Ito, 1982). Coordination bond distances between the Ni and nitrogens of the $N_4$7 ligand (Table 2) are distinctly longer than corresponding Ni—N distances in $trans$-[NiCl$_2$($N_4$7)] [2.056 (3), 2.060 (3), 2.062 (3), and 2.093 (3) Å]. Poraj-Košic, Jukhno, Anciškina & Dikareva (1957) reported the crystal structure of $trans$-[Ni(NCS)$_2$(NH$_3$)$_4$]. The mean Ni—N(NH$_3$) length in $trans$-[Ni(NCS)$_2$(NH$_3$)$_4$] [2.15 (2) Å] is longer than the Ni—N($N_4$7) of cis-[Ni(NCS)$_2$($N_4$7)], while Ni—N(NCS$^-$) distances in $trans$-[Ni(NCS)$_2$(NH$_3$)$_4$] [2.07 (3) Å] and cis-[Ni(NCS)$_2$($N_4$7)] are close to each other. In view of coordination geometries and Ni—N distances of the $N_4$7 and related complexes, it seems that the $N_4$7 ligand in a metal complex cannot adopt a square-planar nitrogen geometry when a mean metal–nitrogen distance exceeds ca 2.10 Å. There are no obvious intramolecular steric interactions between the $N_4$7 ligand and acido ligands in either $trans$-[NiCl$_2$-($N_4$7)] or cis-[Ni(NCS)$_2$($N_4$7)].

It is most reasonable to consider the cis coordination of the $N_4$7 ligand observed for [Ni(NCS)$_2$($N_4$7)] to be determined by the cavity size of the $N_4$7 ligand and the electronic cis effect provided by the strong ligand field of NCS$^-$ groups.

The seven-membered chelate ring in cis-[Ni(NCS)$_2$($N_4$7)] takes a $skew(h)$-like conformation (Kashiwabara, Hanaki & Fujita, 1980) as found for $trans$-[NiCl$_2$($N_4$7)] and tris(1,4-butanediamine)cobalt(III) bromide (Sato & Saito, 1975).

Calculations were carried out on the HITAC-M200H computer at the Computer Center of the Institute for Molecular Science with the Universal Crystallographic Computation Program System, UNICS III (Sakurai & Kobayashi, 1979).

Fig. 1. A perspective drawing of cis-[Ni(NCS)$_2$($N_4$7)], showing the atom-numbering scheme.

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Benzoyl(2,7,12,17-tetraethyl-3,8,13,18-tetramethyl-21H,23H-porphinato)rhodium(III)

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Abstract. C$_{39}$H$_{41}$N$_4$ORh, M_r = 684·4, triclinic, C$\bar{1}$, a = 12·300 (1), b = 21·621 (3), c = 13·185 (2) Å, α = 90·79 (2), β = 111·13 (1), γ = 91·39 (2)°, U = 3268·9 Å^3, D_c = 1·390 g cm^{-3}, Z = 4, μ(Mo Kα) = 5·5 cm^{-1}, $F(000)$ = 1424. The final R and R_w values are 0·053 and 0·052 respectively for 3164 observed reflections. The Rh atom lies 0·096 Å out of the plane of the four pyrrole N atoms, away from the benzoyl residue.

Introduction. Oxidative addition of benzaldehyde to the bis[rhodium(I)] complex, [etio-I{Rh(CO)$_2$}$_2$] (etio-I = 2,7,12,17-tetraethyl-3,8,13,18-tetramethyl-21H,23H-porphine), was shown to give the title compound benzoyl(etio-I)rhodium(III) [(PhCO)Rh(etio-I)] (Abeysekera, Grigg, Trocha-Grimshaw & Viswanatha, 1977). This benzoyl complex showed two ν_{CO} stretching frequencies at 1685 and 1727 cm^{-1} both as a KBr disc and in solution. The crystal structure was investigated to establish whether a conformational process involving two possible orientations of the phenyl ring with respect to the position of the carbonyl group and the macrocycle could be responsible for the observed IR spectrum.

Intensity measurements were made from a crystal of dimensions 0·08 × 0·06 × 0·06 mm with a Nonius CAD-4 diffractometer, graphite monochromator, Mo Kα radiation using $\omega/2\theta$ scans (ω-axis/θ-axis scan-speed ratio of 1·333:1). 5722 reflections were measured within the range 3 ≤ θ ≤ 25° of which 3164

were considered to be observed [$I \geq 3\sigma(I)$]. Lorentz and polarization corrections were made. No absorption correction was applied. The sample appeared to be homogeneous and unit cells for several crystals were found and all gave the same P$\bar{1}$ cell. The abnormally low values of the P$\bar{1}$ unit-cell angles used in the data collection (a = 12·300, b = 12·293, c = 13·185 Å, α = 68·87, β = 78·89, γ = 61·43°, U = 1631 Å^3, Z = 2) were expected to lead to problems with correlation factors in refinement and consequently the data were transformed to the C$\bar{1}$ cell and the coordinates listed in Table 1 refer to this cell (transformation matrix: 100/ $\bar{1}$20/00$\bar{1}$). The structure was solved by the Patterson method and refined by full-matrix least squares with SHELX (Sheldrick, 1976). The H-atom positions were estimated geometrically (C–H = 1·08 Å). Atomic scattering factors were taken from International Tables for X-ray Crystallography (1974). In the final cycles of refinement the Rh, N and O atoms were assigned anisotropic thermal parameters. The final R and R_w values were 0·053 and 0·052 with $w = 1/\sigma^2 F$. The maximum residual peak of electron density was 0·31 e Å^{-3}, approximately 0·5 Å from the Rh atom. The refined atomic parameters are given in Table 1.*

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* Lists of structure factors, H-atom coordinates, anisotropic thermal parameters and least-squares-planes data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36900 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.