Trunov & Pokrovskaya, 1978) and 1·936 (1) Å in $(Ph_3SbO_3SCH_2CH_2OH)_2O$ (Preut, Rüther & Huber, 1985) with linear bridges. We suppose that bond lengths in the Sb—O—Sb bridges are mainly influenced by the nature of the ligand *trans* to the bridging oxygen. It also appears to us that differences between the Sb—O—Sb and the Sb—O—S angles of the two title compounds and the compound $(Ph_3SbO_3SCH_2CH_2OH)_2O$ are probably caused by packing effects. Differences in Sb—O(sulfonate) distances can be related with the stronger $-I$ effect of CF_3 and a higher ionic character can be inferred for the Sb—O(sulfonate) bond in (II) than in (I).

Financial support by Fonds der Chemischen Industrie is gratefully acknowledged.

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Structural Investigations of Ni^{II} Complexes. VI. Two Isomers of Tetrakis(3-ethylpyridine)-bis(isothiocyanato)nickel(II)

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(*Received* 5 *July* 1985; *accepted* 3 *April* 1986)

Abstract. $[Ni(NCS)_2(C_7H_9N)_4]$. Complex (I): $M_r = 603{\cdot}6$, triclinic, $P\bar{1}$, $a = 10{\cdot}302\ (3)$, $b = 9{\cdot}265\ (3)$, $c = 8{\cdot}806\ (3)$ Å, $\alpha = 108{\cdot}43\ (5)$, $\beta = 97{\cdot}46\ (5)$, $\gamma = 90{\cdot}48\ (5)^\circ$, $V = 789{\cdot}6\ (5)$ Å^3, $Z = 1$, $D_x = 1{\cdot}27$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 7{\cdot}7$ cm^{-1}, $F(000) = 318$, room temperature, $R = 0{\cdot}042$ for 3270 diffractions. Complex (II): $M_r = 603{\cdot}6$, monoclinic, $P2/c$, $a = 10{\cdot}197\ (3)$, $b = 12{\cdot}164\ (4)$, $c = 16{\cdot}172\ (5)$ Å, $\beta = 123{\cdot}88\ (5)^\circ$, $V = 1665\ (1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}20$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 7{\cdot}3$ cm^{-1}, $F(000) = 636$, room temperature, $R = 0{\cdot}056$ for 2208 diffractions. The coordination polyhedra around Ni are distorted octahedra with an NiN_6 coordination sphere, NCS ligands being in *trans* positions in both complexes. The *trans*-coordinated pyridine rings in complex (I) are parallel, while for complex (II) these rings are almost perpendicular.

Introduction. Ni^{II} complexes with 3-*R*py (*R* is any bulky substituent on the pyridine ligand) form two isomers of composition $[Ni(NCS)_2(3\text{-}R\text{py})_4]$ depending on the preparation mode and the solvent properties used for the syntheses: blue (I) and violet (II) (Jamnický & Jóna,, 1982). Crystal-structure analysis of (I) and (II), $[Ni(NCS)_2(3\text{-Etpy})_4]$, showed the nature of their structural differences causing the actual phenomenon.

Experimental. Blue plates of (I) elongated in *z* direction [from ethanolic solution of $Ni(NCS)_2$ and 3-ethylpyridine], crystal dimensions adapted to 0·03 × 0·035 × 0·04 cm; violet prisms of (II) [from aqueous solution of $Ni(NO_3)_2$ and 3-ethylpyridine to which KSCN was added], 0·042 × 0·04 × 0·032 cm; Syntex $P2_1$ diffractometer, ten diffractions for lattice-parameter measurements with $4 \leq \theta \leq 15^\circ$ (I) and $6 \leq \theta \leq 15^\circ$ (II), 3270 (for I) and 2208 (for II) independent diffractions with $I > 1{\cdot}96\sigma(I)$, $2\theta \leq 55^\circ$, θ–2θ scan mode, scan speed 2·0–29·3° min^{-1}, *hkl* range 0, −12, −12 to 14, 12, 11 (for I) and 0, 0, −20 to 13, 15, 20 (for II), two check diffractions at intervals of 50, no significant intensity deterioration, Lp correction, absorption ignored; Patterson and Fourier methods, Et-group H atoms of complex (I) and two H of complex

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters with e.s.d's in parentheses*

$$B_{eq} = \tfrac{1}{3}\textstyle\sum_i B_{ii}.$$

	Complex (I)				Complex (II)			
	x	y	z	B_{eq}(Å^2)	x	y	z	B_{eq}(Å^2)
Ni	0	0	0	2·63 (2)	0	2233 (1)	2500	4·34 (6)
S	1727 (1)	5065 (9)	2723 (13)	6·50 (2)	4269 (2)	2861 (1)	5868 (1)	6·57 (12)
N	370 (2)	2268 (2)	1271 (2)	3·37 (1)	1741 (4)	2238 (3)	3993 (3)	5·28 (30)
N(11)	774 (2)	346 (2)	−2049 (2)	3·13 (13)	1206 (4)	3515 (3)	2271 (3)	5·11 (31)
N(21)	−1968 (2)	431 (2)	−837 (2)	3·03 (13)	1234 (4)	1022 (3)	2255 (2)	5·03 (30)
C	912 (2)	3448 (3)	1886 (3)	3·03 (13)	2794 (5)	2492 (3)	4779 (3)	4·67 (35)
C(12)	1012 (3)	1726 (3)	−2173 (3)	3·92 (19)	395 (6)	4344 (4)	1660 (3)	5·86 (41)
C(13)	1583 (3)	1980 (3)	−3414 (3)	4·66 (22)	1086 (7)	5310 (4)	1586 (4)	7·42 (53)
C(14)	1917 (3)	715 (4)	−4603 (3)	4·96 (24)	2707 (8)	5363 (5)	2209 (5)	8·49 (63)
C(15)	1675 (3)	−717 (4)	−4502 (3)	4·40 (22)	3561 (7)	4523 (6)	2838 (5)	8·29 (62)
C(16)	1115 (3)	−860 (3)	−3229 (3)	3·73 (18)	2780 (6)	3625 (4)	2847 (4)	6·28 (45)
C(17)	1826 (5)	3584 (5)	−3422 (6)	8·43 (42)	75 (10)	6247 (6)	879 (6)	10·20 (81)
C(18)*	2778 (8)	4501 (5)	−2163 (7)	12·19 (74)	−1629 (21)	6148 (12)	400 (12)	12·47 (197)
C(181)*	—	—	—	—	−520 (32)	6958 (13)	1474 (17)	15·26 (292)
C(22)	−2945 (2)	−649 (3)	−1187 (3)	3·27 (16)	1382 (5)	1109 (3)	1483 (3)	5·27 (37)
C(23)	−4211 (2)	−497 (3)	−1826 (3)	3·53 (17)	2149 (5)	336 (4)	1260 (3)	5·71 (39)
C(24)	−4497 (3)	880 (3)	−2081 (4)	4·49 (2)	2760 (6)	−586 (4)	1869 (4)	6·92 (49)
C(25)	−3515 (3)	2005 (3)	−1707 (4)	4·56 (22)	2601 (7)	−683 (4)	2664 (4)	7·48 (52)
C(26)	−2277 (2)	1747 (3)	−1091 (3)	3·59 (17)	1856 (6)	139 (4)	2832 (3)	6·06 (43)
C(27)	−5220 (3)	−1814 (3)	−2286 (4)	4·49 (22)	2368 (7)	523 (5)	426 (4)	8·71 (56)
C(28)	−5240 (4)	−2783 (4)	−4016 (5)	6·25 (32)	3846 (7)	1162 (7)	745 (5)	12·04 (88)

* These methyl groups are disordered in complex (II); site-occupation factors are 0·55 and 0·45 for C(18) and C(181), respectively.

(II) from difference map, remainder in calculated positions, anisotropic full-matrix refinement (except H atoms) based on F, $w = 1/\sigma^2(F)$, $R = 0{\cdot}042$, $wR = 0{\cdot}052$ (I), $R = 0{\cdot}056$, $wR = 0{\cdot}062$ (II), LS shift $= 0{\cdot}03$/e.s.d. (I) and $0{\cdot}04$/e.s.d. (II), $\Delta\rho$ excursions $+0{\cdot}45$ to $-0{\cdot}50$ e Å^{-3} (I) and $|0{\cdot}65|$ e Å^{-3} (II). *XTL* program system (Syntex, 1973) on a Nova 1200 computer, scattering factors from *International Tables for X-ray Crystallography* (1962). All calculations performed in the Department of Crystal Structures, Institute of Chemistry, University of Wrocław.

Discussion. Positional and equivalent isotropic thermal parameters are given in Table 1.* Complexes (I) and (II) form monomeric molecules with NCS groups in *trans* positions (Figs. 1 and 2) at equal Ni—N distances in both complexes (Table 2). The differences concern the Ni—N(11) and Ni—N(21) distances involving the 3-Etpy groups and in particular their orientation as well as the orientation of the NCS groups (Figs. 1 and 2). The *trans*-coordinated pyridine rings in complex (I) are parallel, while for complex (II) these rings are almost perpendicular [the dihedral angle being 75·3 (1)°]. The further differences concern the angles formed by the equatorial plane (1) [atoms Ni, N(11) and N(21)] with the 3-Etpy ligand planes (2 and 3, respectively) (pyridine-ring atoms) for both complexes: the 1,2 and

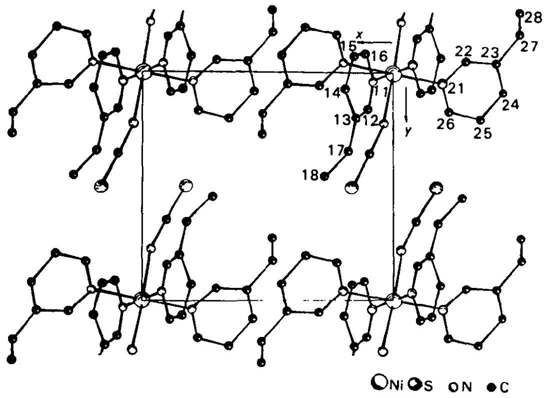

Fig. 1. Packing of the molecules of complex (I) projected along **c** (the sides are $a\sin\beta$ and $b\sin\alpha$).

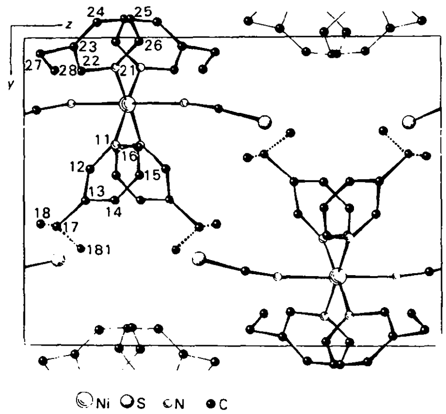

Fig. 2. Packing of the molecules of complex (II) projected along **a** (the sides are b and $c\sin\beta$).

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths involving H, least-squares-planes' details and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42979 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

	Complex (I)	Complex (II)		Complex (I)	Complex (II)		Complex (I)	Complex (II)
Ni–N	2·050 (2)	2·050 (4)	C(13)–C(14)	1·383 (4)	1·376 (11)	N(21)–C(26)	1·342 (3)	1·330 (6)
Ni–N(11)	2·174 (2)	2·142 (4)	C(13)–C(17)	1·507 (6)	1·535 (9)	C(22)–C(23)	1·379 (3)	1·394 (7)
Ni–N(21)	2·151 (2)	2·113 (4)	C(17)–C(18)	1·421 (8)	1·460 (25)	C(23)–C(24)	1·391 (4)	1·390 (7)
N–C	1·157 (3)	1·158 (6)	C(17)–C(181)	—	1·640 (30)	C(23)–C(27)	1·514 (4)	1·502 (9)
C–S	1·616 (3)	1·616 (5)	C(14)–C(15)	1·383 (4)	1·360 (10)	C(27)–C(28)	1·501 (5)	1·508 (11)
N(11)–C(12)	1·341 (4)	1·330 (6)	C(15)–C(16)	1·366 (4)	1·356 (9)	C(24)–C(25)	1·376 (4)	1·389 (9)
N(11)–C(16)	1·349 (3)	1·340 (8)	N(21)–C(22)	1·347 (3)	1·342 (6)	C(25)–C(26)	1·373 (4)	1·371 (9)
C(12)–C(13)	1·387 (4)	1·408 (8)						
N–Ni–N	180·0 (1)	179·7 (2)	N(11)–C(12)–C(13)	124·4 (3)	124·2 (5)	N(21)–C(22)–C(23)	124·2 (2)	124·0 (5)
Ni–N–C	161·5 (2)	163·2 (4)	C(12)–C(13)–C(14)	117·3 (3)	115·5 (6)	C(22)–C(23)–C(24)	117·4 (2)	117·0 (5)
N–C–S	177·6 (2)	179·1 (5)	C(12)–C(13)–C(17)	120·0 (3)	121·5 (6)	C(22)–C(23)–C(27)	120·4 (2)	121·1 (5)
Ni–N(11)–C(12)	123·4 (2)	120·1 (3)	C(13)–C(17)–C(18)	115·8 (4)	116·1 (10)	C(23)–C(27)–C(28)	111·1 (3)	113·0 (6)
Ni–N(11)–C(16)	119·9 (2)	122·2 (3)	C(13)–C(17)–C(181)	—	105·6 (11)	C(24)–C(23)–C(27)	122·2 (2)	121·8 (5)
Ni–N(21)–C(22)	120·8 (2)	120·5 (3)	C(13)–C(14)–C(15)	119·3 (3)	121·3 (7)	C(23)–C(24)–C(25)	119·1 (3)	119·2 (6)
Ni–N(21)–C(26)	122·3 (2)	122·2 (3)	C(14)–C(13)–C(17)	122·7 (3)	123·0 (7)	C(24)–C(25)–C(26)	119·5 (3)	119·0 (6)
N–Ni–N(11)	90·0 (1)	89·9 (2)	C(14)–C(15)–C(16)	119·5 (3)	118·5 (7)	C(25)–C(26)–N(21)	122·8 (2)	123·4 (5)
N–Ni–N(21)	90·6 (1)	90·5 (2)	C(15)–C(16)–N(11)	122·9 (3)	123·8 (5)	C(26)–N(21)–C(22)	116·9 (2)	117·3 (4)
N(21)–Ni–N(11)	93·1 (1)	90·9 (2)	C(16)–N(11)–C(12)	116·6 (2)	116·7 (4)			

1,3 angles in (I) are 75·8 (1) and 60·0 (1)°, while in (II) they are 55·0 (1) and 44·6 (1)°, respectively; 2,3 angles are 80·3 (1) (I) or 75·3 (1)° (II). The torsion angles (atoms defining the torsion angles are Ni, N, C and S) are 3·4 (1) and 15·2 (7)° for (I) and (II), respectively. The different arrangement of 3-Etpy and NCS ligands for complexes (I) and (II) can be assumed to be a consequence of the different mode of complex-molecule formation [*i.e.* of the different sequence of ligand bonding upon the formation of the complex molecules (I) and (II)]: as the bulky 3-Etpy ligands are bonding to the N^{II} atom in the presence of NCS groups in ethanolic solution (see *Experimental*) forming complex (I), they can occupy only the positions and Ni–N distances allowed by the NCS groups. On the other hand, upon formation of complex (II) the 3-Etpy formerly added to the aqueous Ni^{II} solution {$[Ni(H_2O)_6]^{2+}$ cations} can occupy the advantageous orientation in the presence of small H_2O ligands, forming the $[Ni(H_2O)_2(3\text{-Etpy})_4]^{2+}$ cation with the shorter Ni–N distances in comparison with those found for complex (I) (Table 2). The additional NCS^- bonding to this cation (KSCN added) allows only forced orientation of these groups (Fig. 2). The differences in the molecular structure lead to the different packing of the complex molecules [the higher density of complex (I)].

The structural differences of complexes (I) and (II) correspond to their spectral properties, *e.g.* the 10 D_q values of 10 200 cm^{-1} for complex (I) (blue) and 10 650 cm^{-1} for complex (II) (violet) (obtained from the electronic spectra) are in agreement with the differences in Ni—N(3-Etpy) interatomic distances of both complexes.

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Acta Cryst. (1986). C**42**, 1159–1161

Structure of Diacetato(*m*-tolyl)iodine(III)

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(*Received* 6 *January* 1986; *accepted* 21 *February* 1986)

Abstract. $[I(C_2H_3O_2)_2(C_7H_7)]$, $M_r = 336·1$, orthorhombic, *Pbca*, $a = 9·254$ (2), $b = 14·109$ (3), $c = 19·400$ (3) Å, $V = 2532·9$ Å^3, $Z = 8$, $D_x = 1·763$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2·56$ mm^{-1}, $F(000) = 1312$, $T = 294$ K. Final $R = 0·050$ for 1663 unique observed reflections. The characteristic T-shaped coordination geometry of dsp^3-hybridized trivalent iodine compounds [I–O, 2·13 (1), 2·15 (1) Å; I–C, 2·11 (1) Å] is the main conformational feature of the molecule. This is complemented by two equal intramolecular I···O contacts of 2·86 (1) Å which may be considered as secondary bonds so that

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0108-2701/86/091159-03$01.50