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Redetermination of the Structure of (Isothiocyanato)(2,2′,2′′-triaminotriethylamine)-nickel(II), $[Ni(C_6H_{18}N_4)(NCS)_2]$

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Abstract. $M_r = 321·11$, $P2_12_12_1$, $a = 10·852$ (1), $b = 8·6460$ (6), $c = 14·724$ (2) Å, $V = 1381·5$ (2) Å^3, $Z = 4$, $D_x = 1·544$ (1) g cm^{-3}, Nb-filtered Mo $K\alpha$ radiation ($\lambda = 0·71069$ Å), $F(000) = 672$, $\mu = 16·8$ cm^{-1}, $T \approx 290$ K, $R = 0·060$, $S = 1·21$, 3235 reflections, 172 parameters. Quasi-octahedral coordination around Ni with average Ni—N(tren) and Ni—NCS bond lengths 2·12 and 2·09 Å. All bond lengths normal, including the N—C bond lengths of the tertiary N atom of tren, in contrast to earlier reports [Cradwick & Hall (1970). *Acta Cryst.* B**26**, 1384–1385, and references therein]. Both NCS groups essentially linear, 178 [1]°, but slightly bent at N, Ni—N—C 161 [3]°; average N—C and C—S bond lengths 1·153 [3] and 1·638 [1] Å.

Introduction. On comparing our recent structural results on Co^{III}–tren complexes with the reports on other tren complexes, we noticed that the most recent results for Ni(tren)(NCS)$_2$ [Cradwick & Hall (1970), C&H hereafter] were obviously still inaccurate and also, by present standards, rather imprecise.

Experimental. Dark blue 0·3 × 0·5 × 0·3 mm crystal from a hot aqueous stoichiometric solution of $NiCl_2$, tren, and KSCN, upon standing. Space group $P2_12_12_1$ (confirming the previous reports) by oscillation and Weissenberg photographs ($h00$ absent for h odd, $0k0$ absent for k odd, $00l$ absent for l odd). Diffractometry: Picker FACS-1, Nb-filtered Mo $K\alpha$ radiation, crystal mounted roughly along **b**. Lattice constants by least-squares refinement of average 2θ values from four settings on a Syntex $P2_1$ diffractometer (Mo $K\alpha$, graphite monochromator), '$\pm 2\theta$' hkl and '$\pm 2\theta$' $\bar{h}\bar{k}\bar{l}$, 15 reflections. Intensity measurements: 3530 reflections $hk\pm l$, $2\theta \leq 55°$, by 1° min^{-1} θ–2θ scans of 2θ width 1·2° plus the α_1–α_2 angular dispersion; 20-s post-scan stationary-counter–stationary-crystal background counts fore and aft. Six check reflections, every 150 reflections – no decomposition and $g = 0·006$, used in $\sigma_I^2 = S + r^2B + (gI)^2$, for scan count S, total background count B, scan-to-total-background time ratio $r = t_s/t_b$, and net intensity $I = S - rB$. Reduction: $F_o = \sqrt{I/\mathrm{Lp}}$, $w_{F_o} = 4(\mathrm{Lp}F_o/\sigma_I)^2$, no absorption corrections applied (ratio of extreme absorption factors, A_{min}/A_{max}, roughly 0·8). Form factors from *International Tables for X-ray Crystallography* (1962), and for H from *International Tables* (1974), including f' and f'' for Ni and S.

Initial non-H coordinates from C&H with $U = 0·032$ Å^2 estimated by *NORMSF* (the XRAY76 system, Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), and H-atom coordinates by *BONDAT* (the XRAY76 system) for idealized bond angles, 0·99 Å C–H and N–H bond lengths, and $U = 0·050$ Å^2. Least-squares minimization of $\sum w(F_o - |F_c|)^2$ on all parameters but H-atom coordinates, 172 parameters and 3235 reflections in the final cycle, 204 F's with both F_o and $|F_c|$ less than $2\sigma_{F_o}$ and 44 with $|\Delta F|/\sigma_{F_o} > 3·9$ rejected, the 44 still included in R and R_w. Final R 0·060, R_w 0·046, and S 1·21 (enantiomer: R 0·069, R_w 0·054 and S 1·38); max. and average

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shift/error = 0·2, <0·01; max. $|\Delta\rho|$, final map, 0·6 e Å^{-3}.*

Discussion. In all general features the structure (Table 1; Fig. 1 for labels) agrees with the earlier determinations (Rasmussen, 1958, 1959; Hall & Woulfe, 1958; C&H), but it now has normal ligand bond lengths and reasonably good precision, as shown in Table 2.

The coordination octahedron, with tertiary N[N(1)] and a *trans* isothiocyanate [N(21)] axial and three primary N atoms [N(2), N(3) *trans* N(4)] and the second isothiocyanate [N(11)] equatorial, is distorted: the N(1)—Ni—N(tren) angles are notably acute (82·4 [4]°),*† the N(1)···N contact distances being 2·77–2·79 Å. The average Ni—N(tren) and Ni—NCS bond lengths are about equal: 2·118 [13] and 2·086 [27] Å.

The bond lengths and angles (Table 2) are all normal. In particular, the N(1)—C distances, average 1·473 [3] Å, are unexceptional, unaffected by the strain imposed at N(1) by the ligand-to-Ni coordination, in contrast to the earlier reports [*cf.* N—C = 1·68 Å (Rasmussen, 1959), 1·58 Å, C&H). The N—C—C—N dihedral angles range from 43·1 (5) to 50·8 (5)° and are normal for octahedral tren complexes (Santarsiero, 1980).

Like the bond angles, the NCS bond lengths are reasonable, N—C 1·153 [3] Å and C—S 1·638 [1] Å, *cf.* 1·216 (10) and 1·561 (5) Å in HNCS (*Landolt–Börnstein*, 1976), 1·180 and 1·648 Å in NaSCN (Bats, Coppens & Kvick, 1977), and 1·180 and 1·650 Å in NH_4SCN (Bats & Coppens, 1977). If S is assumed to ride on C, then C—S increases by about 0·02 Å.

Table 1. *Coordinates* (×10^4) *and* $U_{\rm eq}$*'s* (Å^2, ×10^4)

	x	*y*	*z*	$U_{\rm eq}$
Ni	1218·3 (5)	1642·6 (7)	1667·6 (4)	265
N(11)	1153 (4)	2026 (4)	3085 (2)	398
N(21)	−672 (3)	1471 (5)	1607 (3)	380
N(1)	3148 (3)	1730 (5)	1545 (2)	282
N(2)	1305 (4)	1190 (4)	275 (2)	305
N(3)	1613 (3)	−731 (5)	1975 (3)	352
N(4)	1384 (4)	4088 (4)	1522 (3)	400
C(21)	3498 (4)	1435 (6)	592 (3)	325
C(31)	3609 (4)	543 (6)	2182 (3)	385
C(41)	3507 (4)	3289 (6)	1836 (3)	388
C(22)	2526 (4)	555 (6)	58 (3)	335
C(32)	2960 (5)	−993 (6)	2019 (3)	426
C(42)	2683 (5)	4503 (6)	1387 (3)	445
C(1)	735 (4)	2186 (5)	3795 (3)	303
C(2)	−1667 (4)	1145 (6)	1400 (3)	332
S(1)	88·0 (14)	2399·9 (18)	4792·1 (8)	534
S(2)	−3082·1 (12)	685·7 (18)	1125·4 (9)	469

Table 2. *Bond lengths* (Å) *and angles* (°)

tren	*i* = 2	*i* = 3	*i* = 4	Average*
N(1)—C(*i*1)	1·475 (6)	1·477 (6)	1·467 (7)	1·473 [3]
C(*i*1)—C(*i*2)	1·520 (6)	1·522 (7)	1·529 (7)	1·524 [3]
N(*i*)—C(*i*2)	1·469 (6)	1·480 (7)	1·468 (7)	1·472 [4]
Ni—N(*i*)†	2·090 (4)	2·145 (4)	2·132 (4)	2·118 [13]
Ni—N(*i*)—C(*i*2)	108·9 (3)	110·7 (3)	109·7 (3)	109·8 [5]
N(1)—C(*i*1)—C(*i*2)	113·5 (3)	110·5 (4)	110·4 (4)	111·5 [10]
N(*i*)—C(*i*2)—C(*i*1)	109·1 (4)	109·3 (4)	109·6 (4)	109·3 [1]
C(*i*1)—N(1)—C	113·4 (4)	111·3 (3)	111·6 (4)	112·1 [7]
Ni—N(1)—C(*i*1)	109·4 (2)	104·9 (3)	105·8 (3)	106·7 [14]
N(1)—C(*i*1)—C(*i*2)—N	43·1 (5)	−48·6 (5)	50·8 (5)	

SCN	*i* = 1	*i* = 2	Average
N(*i*1)—C(*i*)	1·150 (6)	1·156 (6)	1·153 [3]
C(*i*)—S(*i*)	1·638 (5)	1·637 (5)	1·638 [1]
Ni—N(*i*1)	2·112 (4)	2·059 (4)	2·086 [27]
Ni—N(*i*1)—C(*i*)	158·6 (4)	163·6 (4)	161·1 [25]
S(*i*)—C(*i*)—N(*i*1)	177·8 (4)	179·0 (4)	178·4 [6]

* Standard deviation of average estimated as $[\sum_{k=1}^{n}(d_k-\bar{d})^2/n(n-1)]^{1/2}$.

† Ni—N(1) 2·104 (3), included in average.

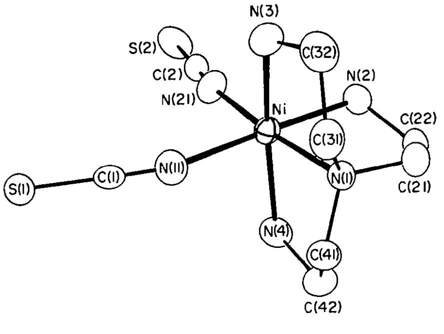

Fig. 1. The atom numbering scheme.

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* Anisotropic Gaussian amplitudes for non-hydrogen atoms, atom coordinates for hydrogen atoms, and a listing of structure factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38628 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Standard deviation of average, in square brackets, defined in Table 2.

† The rows of the upper half of the matrix of N—Ni—N bond angles, N-order N(11), N(21), N(1), N(2), N(3), N(4) read 91·2 (2), 96·5 (2), 178·1 (2), 87·1 (1), 87·0 (2); 172·3 (2), 89·3 (2), 98·0 (2), 98·7 (2); 83·0 (1), 81·6 (1), 82·6 (2); 91·1 (1), 94·8 (1); 162·4 (2)°.

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