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Structure of *trans*-Bis(aminoethylaminoethanol-*N*,*N'*)bis(isothiocyanato)nickel(II)

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Abstract. $[Ni(NCS)_2(C_4H_{12}N_2O)_2]$, $M_r = 383 \cdot 2$, orthorhombic, *Pbca*, $a = 8 \cdot 8954$ (11), $b = 14 \cdot 3450$ (12), $c = 13 \cdot 6824$ (16) Å, $V = 1745 \cdot 9$ (3) Å^3, $Z = 4$, $D_x = 1 \cdot 458$ Mg m^{-3}, Cu $K\alpha$ radiation (graphite-crystal monochromator, $\lambda = 1 \cdot 54178$ Å), μ(Cu$K\alpha$) = $3 \cdot 907$ mm^{-1}, $F(000) = 808$, $T = 290$ K. Final $R = 0 \cdot 032$, $wR = 0 \cdot 034$ for 1337 'observed' reflections and 133 variables. The structure is centrosymmetric with Ni^{2+} octahedrally coordinated by the N atoms of the NCS$^-$ ions, and the N atoms of the bidentate *N*-(2-hydroxyethyl)-ethylenediamine ligands. The five-membered ring Ni—N(1)—C(1)—C(2)—N(2) in the Ni coordination adopts a twist (*T*) conformation with C_2 symmetry. There is an OH···S internal hydrogen bond of $3 \cdot 332$ Å with O—H···S angle of 171°.

Introduction. In continuation of our studies of metal complexes of amino alcohols, we have determined the X-ray structure of the title compound as part of the series. The X-ray crystal structure will complement our spectroscopic studies which indicate a five-membered ring in the Ni coordination as well as reveal the possibility of any hydrogen bonding in the complex. The title compound was prepared by adding 10 cm^3 of aminoethylaminoethanol to 10 g of hydrated nickel(II) perchlorate dissolved in 50 cm^3 of methanol. To the resulting blue solution a solution of 10 g sodium thiocyanate in 30 cm^3 of methanol was added. Mauve crystals of the title compound separated out overnight. Crystallization was from hot methanol. Elemental analysis confirmed the identity of the complex {found: Ni 15·38, C 31·45, H 6·31, S 16·80, N 22·20%; calculated for $[Ni(NCS)_2(C_8H_{24}N_4O_2)]$: Ni 15·34, C 31·36, H 6·27, S 16·72, N 22·18%}.

Experimental. A mauve crystal of dimensions approximately $0 \cdot 15 \times 0 \cdot 25 \times 0 \cdot 29$ mm was used during the measurements. Throughout the experiment Cu $K\alpha$ radiation was used with a graphite-crystal monochromator on a Nonius CAD-4 single-crystal diffractometer ($\lambda = 1 \cdot 54178$ Å). The unit-cell dimensions were determined from the angular settings of 25 high-order reflections. The space group was inferred as *Pbca* (No. 61) from systematic absences (0*kl* with $k = 2n + 1$; *h0l* with $l = 2n + 1$ and *hk*0 with $h = 2n + 1$) and from the structure determination. The intensity data of 3692 reflections up to $\theta = 70°$ in the range $0 \le h \le 10$, $-17 \le k \le 17$, $0 \le l \le 16$ were measured, using the ω–2θ scan technique with a scan angle of $1 \cdot 00°$ and a variable scan rate with a maximum scan time of 20 s per reflection. The intensity of the primary beam was checked throughout the data collection by monitoring three standard reflections every 30 minutes. The final drift correction factors were between 1·00 and 1·04. On all reflections profile analysis was performed (Lehmann & Larsen, 1974; Grant & Gabe, 1978); an empirical absorption correction was applied, using ψ scans (North, Phillips & Mathews, 1968) (correction factors were in the range 0·88 to 1·00). Symmetry-equivalent

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reflections were averaged, $R_{int} = 0.034$, resulting in 1655 unique reflections of which 1337 were observed with $I > 3\sigma(I)$. Lorentz and polarization corrections were applied and the data were reduced to $|F_o|$ values.

With the use of *PATSYS* (Behm & Beurskens, 1985) the position of the Ni atom was located from the Patterson map, and automatically input into *DIRDIF* (Beurskens *et al.*, 1982). The positions of the non-hydrogen atoms were located in one *DIRDIF* run. Isotropic least-squares refinement with *SHELX* (Sheldrick, 1976) converged at $R = 0.103$. At this stage an additional empirical absorption correction was applied (Walker & Stuart, 1983), leading to a further reduction of R to 0.096 (relative correction factors were in the range 0.863 to 1.290 with an average of 1.005). All hydrogen atoms were located from a difference Fourier calculation.

During the final stages of the refinement all positional parameters and the temperature factors of all non-hydrogen atoms were refined. The hydrogen atoms had fixed isotropic temperature factors of 0.060 Å². The final conventional agreement factors were $R = 0.032$ and $wR = 0.034$, $S = 0.924$ for the 1337 'observed' reflections and 133 variables. The function minimized was $\sum w(F_o - F_c)^2$ with $w = 1/[\sigma^2(F_o) + 0.0004F_o^2]$, $\sigma(F_o)$ from counting statistics. The maximum shift-to-e.s.d. ratio in the final full-matrix least-squares cycle was less than 0.03 for all atoms. The final difference Fourier map showed no peak higher than 0.20 e Å⁻³. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Plots were made with *PLUTO* (Motherwell, 1976). Geometrical calculations were performed with *PARST* (Nardelli, 1983).

Discussion. Final positional and thermal parameters are given in Table 1,* while molecular geometry data are collected in Table 2. A view of the molecule showing the molecular configuration is given in Fig. 1. The crystallographic numbering scheme is given in Fig. 2. The structure is centrosymmetric with the Ni²⁺ ion at a crystallographic inversion centre. The Ni atom is octahedrally coordinated by the N atoms of the NCS⁻ ions and the N atoms of the aminoethylaminoethanol molecules acting as bidentate ligands. The five-membered ring Ni—N(1)—C(1)—C(2)—N(2) has a twist (*T*) conformation (pseudo-C_2 form) with the (pseudo-) twofold axis passing through the Ni atom and the middle of the C(1)—C(2) bond. The atoms C(1), C(2) lie on opposite sides of the plane N(1)—Ni—N(2), their

deviations from this plane being 0.300 (2) and −0.422 (3) Å respectively. The Cremer & Pople (1975) parameters are $q_2 = 0.463$ (2) Å, $\varphi = 94.4$ (2)°. The endocyclic torsion angles are given in Table 2. The N(3)—Ni bond of the linearly coordinated NCS⁻ ion is almost perpendicular to the Ni—N(1)—N(2) plane [89.53 (6)°], while the plane through O(1), C(4), C(3)

Table 1. *Fractional positional and thermal parameters (with e.s.d.'s in parentheses)*

All anisotropic thermal parameters were physically acceptable.
$$U_{eq} = \tfrac{1}{3}\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	$U_{eq}(\text{Å}^2 \times 10^2)$
Ni	0.00000	0.00000	0.00000	3.23 (2)
S	−0.47675 (6)	0.15004 (5)	0.07186 (5)	5.12 (2)
O	−0.0164 (2)	−0.1193 (2)	0.3305 (1)	7.11 (8)
N(1)	0.0554 (2)	−0.0271 (1)	0.1509 (1)	3.55 (5)
N(2)	0.1189 (2)	0.1242 (1)	0.0278 (1)	4.28 (6)
N(3)	−0.1992 (2)	0.0632 (1)	0.0438 (1)	4.47 (6)
C(1)	0.1688 (3)	0.0434 (2)	0.1790 (2)	4.27 (7)
C(2)	0.1284 (3)	0.1361 (2)	0.1348 (2)	4.74 (7)
C(3)	0.1009 (3)	−0.1224 (2)	0.1771 (2)	4.36 (7)
C(4)	0.1219 (3)	−0.1389 (2)	0.2854 (2)	4.74 (7)
C(5)	−0.3144 (2)	0.0992 (1)	0.0548 (1)	3.49 (6)

Table 2. *Selected distances (Å), bond angles (°) and torsion angles (°) in the title compound with e.s.d.'s in parentheses*

Ni—N(1)	2.158 (2)	N(1)—Ni—N(2)	82.2 (1)
Ni—N(2)	2.107 (2)	N(1)—Ni—N(3)	89.9 (1)
Ni—N(3)	2.079 (2)	N(2)—Ni—N(3)	90.4 (1)
C(5)—S	1.635 (2)	S—C(5)—N(3)	179.3 (2)
N(3)—C(5)	1.157 (3)	Ni—N(3)—C(5)	170.8 (2)
N(1)—C(1)	1.479 (3)	N(1)—C(1)—C(2)	109.7 (2)
N(1)—C(3)	1.470 (3)	N(2)—C(2)—C(1)	108.1 (2)
N(2)—C(2)	1.477 (3)	C(1)—N(1)—C(3)	112.6 (2)
C(1)—C(2)	1.505 (3)	N(1)—C(3)—C(4)	114.7 (2)
C(3)—C(4)	1.511 (3)	C(3)—C(4)—O	106.9 (2)
C(4)—O	1.405 (3)	Ni—N(1)—C(3)	117.6 (1)
		Ni—N(1)—C(1)	106.3 (1)
		Ni—N(2)—C(2)	107.8 (1)
Ni—N(1)—C(1)—C(2)	40.0 (2)	C(2)—N(2)—Ni—N(1)	−17.5 (1)
N(1)—C(1)—C(2)—N(2)	−57.6 (2)	N(2)—Ni—N(1)—C(1)	−12.2 (1)
C(1)—C(2)—N(2)—Ni	44.1 (2)		

* Lists of structure factors, hydrogen parameters, anisotropic thermal parameters and bond distances and angles involving hydrogen atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43437 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
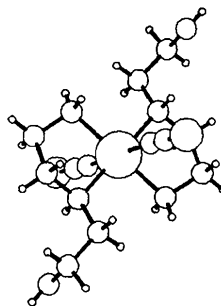

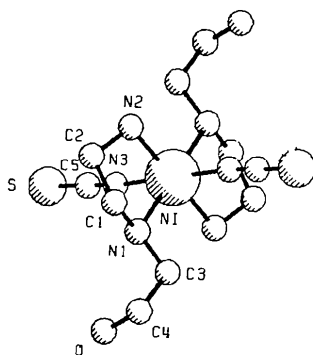Fig. 1. Perspective view of the molecule.

Fig. 2. Crystallographic atomic numbering scheme.

makes an angle of 77·7 (3)° with that bond line. The Ni—N bond distances [2·158 (2) and 2·107 (2) Å] and the N—Ni—N angle of 82·2 (1)° for the diamine agree reasonably well with the values of 2·095 (4) Å and 83·0 (2)° for *trans*-diaquabis(ethylenediamine)-nickel(II) bis(trichloroacetate) (Garcia-Granda & Gómez-Beltran, 1984). The influence of the N-substitution is clearly shown by the difference in Ni—N(diamine) coordination distances. The distance of 2·079 (2) Å found for the Ni—N(isothiocyanate) matches with the value of 2·062 (1) Å reported for the *trans* complex, bis(3-aminopropanol-*O,N*)bis(isothiocyanato)nickel(II) (Sanni, Lenstra & Patel, 1985). The OH distance is 0·81 (3) Å, while the average NH distance is 0·87 (3) Å. The CH distances in the complex lie in the range 0·93 (3) to 1·02 (3) Å [average 0·97 (4) Å]. There is an internal hydrogen bond OH···S with an O···S distance of 3·332 (3) Å, an

H···S distance of 2·530 (4) Å and an O—H···S angle of 171· (2)°.

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Tetra(methylthio)tetrathiafulvalenium Tetrachloroferrate(III)

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Abstract. $C_{10}H_{12}S_8^+.FeCl_4^-$, $M_r = 586·39$, monoclinic, $P2_1/c$, $a = 12·271$ (4), $b = 14·725$ (5), $c = 13·973$ (3) Å, $\beta = 115·35$ (2)°, $V = 2286$ Å^3, $Z = 4$, $D_x = 1·70$ g cm^{-3}, $\lambda(Mo\,K\alpha) = 0·7107$ Å, $\mu = 18·3$ cm^{-1}, $F(000) = 1176$, room temperature, final $R = 0·056$ for 2044 observed $[I/\sigma(I) \geq 2·5]$ independent reflections and 208 variables. The structure consists of isolated π-dimers of the organic radical

cations and of tetrahedral $[FeCl_4]^-$ anions. The methyl groups are forced out of the molecular planes and the TTF skeleton is slightly bent. The arrangement of the radical cations makes electrical conductivity unlikely.

Introduction. We are investigating the possibility of oxidizing the donor tetra(methylthio)tetrathiafulvalene (TTM-TTF) by metal cations in order to obtain cation