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Structures of *cis*- and *trans*-Bis(ethylenediamine)(isothiocyanato)(thiosulfato)cobalt(III)

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Abstract. *cis*-Bis(ethylenediamine)(isothiocyanato)-(thiosulfato)cobalt(III) monohydrate, *cis*-[Co(NCS)-$(S_2O_3)(C_2H_8N_2)_2].H_2O$, $M_r = 367.4$, orthorhombic, $Pca2_1$, $a = 12.369$ (9), $b = 7.958$ (8), $c = 13.818$ (9) Å, $V = 1360$ (2) Å^3, $Z = 4$, $D_m = 1.78$, $D_x = 1.79$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 1.75$ mm^{-1}, $F(000) = 760$, $T = 294$ K, $R = 0.037$ for 1293 observed [$F > 6\sigma(F)$] reflections. *trans*-Bis-(ethylenediamine)(isothiocyanato)(thiosulfato)cobalt-(III) sesquihydrate, *trans*-[Co(NCS)$(S_2O_3)(C_2H_8$-$N_2)_2].1.5H_2O$, $M_r = 376.4$, monoclinic, Pc, $a = 9.941$ (8), $b = 8.884$ (5), $c = 16.42$ (2) Å, $\beta = 94.03$ (8)°, $V = 1446$ (2) Å^3, $Z = 4$, $D_m = 1.71$, $D_x = 1.73$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 1.64$ mm^{-1}, $F(000) = 780$, $T = 294$ K, $R = 0.0457$ for 3148 observed [$F > 6\sigma(F)$] reflections. The structural *trans* effect, STE, the difference between the Co—N(en) bond lengths *trans* to a ligand and the average of the two Co—N(en) bond lengths that are both *cis* to that ligand and *trans* to each other, is 0.03 (1) Å for SSO_3^{2-} and 0.00 (1) Å for $^-$NCS in *cis*-$[Co(NCS)(S_2O_3)(en)_2].H_2O$.

Experimental. In a simplification of the procedure reported previously (Cooper, McCoy, Katz & Deutsch, 1980) for the preparation of the *trans* isomer, 1.0 g Na *trans*-$[(en)_2Co(S_2O_3)_2]$ and 1.36 g NaSCN were dissolved in 45 ml H_2O, heated at 333 K for 9 min, and then cooled in an ice bath for 9 min. The neutral products in the mixture were separated from the anions and cations by water elution on a Sephadex QAE-Q25 (Cl^-) anion-exchange column, and the pink *cis* and burgundy *trans* bands were each collected separately. These solutions were concentrated by rotary evaporation, to 6 ml for the *cis*, and to 12 ml for the *trans* and left to stand overnight at 278 K in glass test tubes. The crystals were filtered but not rinsed. (Typical crude yields: *cis*, 31 mg; *trans*, 236 mg). Crystal densities were measured by neutral bouyancy in CH_2BrCH_2Br/CCl_4.

Table 1. *Summary of structure determination*

	cis Isomer	*trans* Isomer
Color	Red–orange	Dark red
Crystal size (mm)	1.05 × 0.18 × 0.02	0.70 × 0.32 × 0.21
Diffractometer used	Siemens *R3m/V*	Siemens *R3m/V*
Scan type	2θ–θ	2θ–θ
Reflections collected	3711	3756
Independent reflections	1639 (R_{int} = 0.0265)	3533 (R_{int} = 0.0752)
Observed reflections	1293 [$F > 6.0\sigma(F)$]	3148 [$F > 6.0\sigma(F)$]
Monochromator	Highly oriented graphite crystal	
2θ range (°)	3–55	3–55
Index ranges h	−16 to 16	0 to 12
k	0 to 10	0 to 11
l	−17 to 0	−21 to 21
Standard reflections, interval	3, 50 reflections	3, 50 reflections
System used	Siemens *SHELXTL-Plus* (VMS) (Sheldrick, 1990)	
Solution	Direct methods	Direct Methods
Refinement method	Full-matrix least-squares based on F	
Final R indices (obs. data) R	3.70%	4.57%
wR	3.88%	6.92%
No. of parameters refined	163	333
No. of reflections used	1293	3148
Goodness-of-fit	0.94	0.78
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0017F^2$	$w^{-1} = \sigma^2(F) + 0.0073F^2$
Largest and mean Δ/σ	0.001, 0.000	0.001, 0.000
Largest difference peak (e Å^{-3})	0.47	0.90
Largest difference hole (e Å^{-3})	−0.51	−1.00
Extinction correction	$x = 0.0002$ (2), where $F^* = F[1 + 0.002xF^2/\sin(2\theta)]^{-1/4}$	

Spectra and elemental analysis for the *trans* isomer have been reported previously (Cooper, McCoy, Katz & Deutsch, 1980). Elemental analysis for Co, S, C, N and H was performed by Galbraith Labs, Knoxville, Tennessee, and gives experimental (and calculated) percent composition as follows: *trans* (anhydrous) C 17.10 (17.19), H 4.32 (4.62), N 19.92 (20.05), S 27.51 (27.53) and Co 16.10 (16.87); *cis* (monohydrate) C 16.53 (16.35), H 4.98 (4.95), N 19.11 (19.07), S 26.19 (26.18) and Co 16.01 (16.04). For the *cis* isomer UV/vis., $\lambda_{max}(\varepsilon/M^{-1}cm^{-1})$: 510 (234), 292 (12644). IR in KBr disk (cm^{-1}): SCN^- 2127; $S_2O_3^{2-}$ 1180, 1147, 1131, 1006, 645.

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Table 2. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* ($Å^2 \times 10^2$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

cis Isomer	*x*	*y*	*z*	U_{eq}
Co	617 (1)	1142 (1)	0	17 (1)
S(1)	−319 (1)	−816 (2)	861 (2)	26 (1)
S(2)	−666 (1)	−2858 (2)	11 (2)	25 (1)
S(3)	1941 (2)	−2393 (3)	−2414 (2)	40 (1)
O(1)	−1464 (5)	−3747 (6)	595 (5)	42 (2)
O(2)	312 (4)	−3872 (5)	−111 (6)	41 (2)
O(3)	−1123 (4)	−2266 (7)	−896 (4)	38 (2)
O(4)	−2401 (5)	−6952 (6)	279 (4)	38 (2)
N(1)	−598 (4)	1510 (7)	−881 (4)	22 (2)
N(2)	1345 (4)	2929 (7)	−765 (5)	25 (2)
N(3)	79 (4)	2808 (7)	933 (5)	25 (2)
N(4)	1828 (4)	857 (8)	904 (5)	29 (2)
N(5)	1217 (5)	−421 (7)	−879 (5)	27 (2)
C(1)	−382 (5)	2900 (9)	−1580 (5)	27 (2)
C(2)	844 (6)	2996 (12)	−1729 (7)	34 (3)
C(3)	923 (7)	3174 (11)	1662 (6)	34 (3)
C(4)	1529 (7)	1547 (10)	1854 (6)	34 (2)
C(5)	1502 (5)	−1261 (8)	−1522 (5)	22 (2)
trans Isomer Molecule *A*				
Co(1)	2895	3939 (1)	6199	24 (1)
S(1)	1707 (2)	5701 (2)	5479 (1)	30 (1)
S(2)	2878 (2)	7154 (2)	4863 (1)	28 (1)
S(3)	4767 (3)	−84 (2)	7782 (2)	53 (1)
O(1)	1832 (7)	8121 (7)	4472 (4)	46 (2)
O(2)	3760 (6)	7967 (6)	5459 (4)	38 (2)
O(3)	3670 (7)	6311 (8)	4305 (4)	44 (2)
N(1)	4015 (7)	3423 (7)	5309 (4)	35 (2)
N(2)	1573 (6)	2488 (7)	5706 (5)	37 (2)
N(3)	4172 (6)	5394 (7)	6722 (3)	31 (2)
N(4)	1775 (7)	4382 (8)	7113 (4)	39 (2)
N(5)	3808 (6)	2365 (7)	6845 (4)	34 (2)
C(1)	3501 (11)	2011 (11)	4903 (7)	54 (3)
C(2)	1967 (12)	2054 (11)	4886 (7)	55 (3)
C(3)	3814 (9)	5641 (11)	7571 (5)	42 (2)
C(4)	2332 (9)	5721 (11)	7559 (5)	47 (3)
C(5)	4212 (7)	1350 (9)	7248 (5)	34 (2)
Molecule *B*				
Co(1*b*)	−2253 (1)	−2167 (1)	4765 (1)	22 (1)
S(1*b*)	−3300 (2)	−3920 (2)	5476 (1)	27 (1)
S(2*b*)	−2022 (2)	−5501 (2)	6014 (1)	25 (1)
S(3*b*)	−886 (4)	1819 (3)	3112 (2)	60 (1)
O(1*b*)	−1340 (6)	−6294 (6)	5372 (4)	40 (2)
O(2*b*)	−1045 (6)	−4737 (7)	6582 (3)	39 (2)
O(3*b*)	−2981 (6)	−6465 (6)	6404 (3)	38 (2)
N(1*b*)	−986 (6)	−1638 (7)	5694 (4)	32 (2)
N(2*b*)	−3510 (6)	−710 (7)	5202 (5)	37 (2)
N(3*b*)	−1001 (6)	−3552 (7)	4287 (3)	29 (2)
N(4*b*)	−3506 (7)	−2702 (8)	3829 (4)	40 (2)
N(5*b*)	−1514 (7)	−587 (8)	4116 (4)	37 (2)
C(1*b*)	−1455 (9)	−164 (10)	6022 (6)	47 (3)
C(2*b*)	−2966 (10)	−240 (9)	6032 (6)	48 (3)
C(3*b*)	−1480 (10)	−3864 (10)	3430 (5)	42 (2)
C(4*b*)	−2983 (10)	−4001 (10)	3401 (5)	46 (3)
C(5*b*)	−1244 (8)	416 (9)	3716 (5)	35 (2)
Water of hydration				
O(4)	1163 (9)	1277 (10)	7799 (5)	69 (3)
O(5)	1752 (7)	567 (8)	1416 (4)	54 (2)
O(6)	6461 (8)	2356 (8)	4350 (5)	58 (3)

The *trans*-$[Co(en)_2(NCS)(S_2O_3)].1.5H_2O$ forms macroscopically twinned crystals which turn to powder in air in a couple of days, presumably due to the loss of water of hydration. One large twinned crystal was cut and a single (untwinned) fragment, well coated with cyanoacrylate, was used for data collection. Systematic absences were observed for the reflections *h*0*l*, *l* = odd, indicating either a *Pc* or a *P*2/*c* space group. All attempts to solve the structure in the space group *P*2/*c* failed. Successful solution and refinement in the space group *Pc*, with two crystallographically unique cobalt complex molecules and three water molecules in the asymmetric unit, confirmed *Pc* to be the correct space group.

For *cis*-$[Co(en)_2(NCS)(S_2O_3)].H_2O$, systematic absences were observed for the reflections 0*kl*, *l* = odd and *h*0*l*, *h* = odd, indicating either a $Pca2_1$ or a *Pcam* space group. With four molecules in the unit cell, and no molecular point-group symmetry consistent with the special positions in the space group *Pcam*, the space group was assumed to be $Pca2_1$. Successful refinement of the structure confirmed this assumption. No absorption corrections were applied.

H-atom positions were calculated for all but those of water, and were included using a riding model with fixed isotropic thermal parameters. All non-H atoms were refined using anisotropic thermal parameters. Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol.

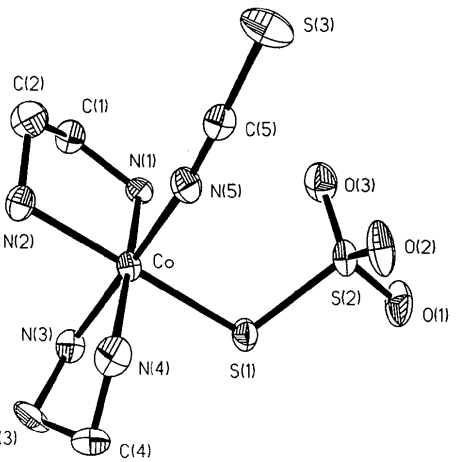

Fig. 1. Thermal ellipsoid plot of *cis*-$[Co(en)_2(S_2O_3)(NCS)]$ drawn at the 50% probability level.

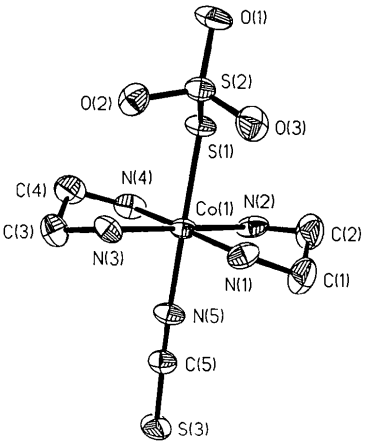

Fig. 2. Thermal ellipsoid plot of *trans*-$[Co(en)_2(S_2O_3)(NCS)]$, molecule *A*, drawn at the 50% probability level. Molecule *B* is essentially identical to molecule *A* and is shown in the supplementary material.

Table 3. *Bond lengths* (Å), *bond angles* (°) *and possible hydrogen-bond distances* (Å) *in the two isomers of* $Co(en)_2(S_2O_3)(NCS)$

		trans Isomer	
	cis Isomer	Molecule *A*	Molecule *B*
Co—S(1)	2.277 (3)	2.246 (3)	2.246 (3)
Co—N(1)	1.956 (6)	1.953 (7)	1.965 (7)
Co—N(2)	1.988 (6)	1.973 (7)	1.969 (7)
Co—N(3)	1.965 (6)	1.966 (7)	1.953 (7)
Co—N(4)	1.963 (6)	1.970 (7)	1.967 (7)
Co—N(5)	1.890 (6)	1.941 (7)	1.938 (8)
S(1)—S(2)	2.051 (3)	2.052 (4)	2.052 (3)
S(2)—O(1)	1.458 (6)	1.463 (7)	1.471 (7)
S(2)—O(2)	1.465 (5)	1.459 (6)	1.465 (6)
S(2)—O(3)	1.453 (6)	1.455 (7)	1.462 (6)
S(3)—C(5)	1.621 (7)	1.621 (8)	1.647 (8)
N(1)—C(1)	1.492 (9)	1.493 (12)	1.503 (11)
N(2)—C(2)	1.470 (11)	1.480 (14)	1.490 (12)
N(3)—C(3)	1.479 (11)	1.479 (10)	1.479 (9)
N(4)—C(4)	1.470 (10)	1.484 (12)	1.466 (12)
N(5)—C(5)	1.166 (9)	1.173 (10)	1.150 (10)
C(1)—C(2)	1.532 (10)	1.523 (17)	1.504 (14)
C(3)—C(4)	1.520 (12)	1.474 (13)	1.497 (14)
S(1)—Co—N(1)	92.1 (2)	94.4 (2)	93.3 (2)
S(1) Co N(2)	176.3 (2)	85.9 (2)	86.4 (2)
N(1)—Co—N(2)	84.8 (2)	86.5 (3)	87.1 (3)
S(1)—Co—N(3)	87.0 (2)	94.1 (2)	95.9 (2)
N(1)—Co—N(3)	92.7 (2)	95.5 (3)	94.1 (3)
N(2)—Co—N(3)	91.1 (2)	178.0 (3)	177.3 (3)
S(1)—Co—N(4)	88.7 (2)	87.5 (2)	86.9 (2)
N(1)—Co—N(4)	177.9 (2)	177.9 (3)	179.4 (3)
N(2)—Co—N(4)	94.3 (2)	92.7 (3)	93.4 (3)
N(3)—Co—N(4)	85.3 (2)	85.3 (3)	85.4 (3)
S(1)—Co—N(5)	94.9 (2)	176.2 (2)	174.7 (2)
N(1)—Co—N(5)	90.0 (3)	88.3 (3)	90.4 (3)
N(2)—Co—N(5)	87.2 (3)	91.5 (3)	89.9 (3)
N(3)—Co—N(5)	176.7 (2)	88.4 (3)	87.6 (3)
N(4)—Co—N(5)	91.9 (3)	89.8 (3)	89.4 (3)
Co—S(1)—S(2)	110.5 (1)	113.7 (1)	113.7 (1)
S(1)—S(2)—O(1)	102.0 (3)	100.1 (3)	108.8 (3)
S(1)—S(2)—O(2)	109.2 (3)	108.4 (3)	108.6 (3)
O(1)—S(2)—O(2)	110.8 (3)	112.2 (3)	111.1 (4)
S(1)—S(2)—O(3)	108.6 (2)	109.7 (3)	100.7 (3)
O(1)—S(2)—O(3)	111.8 (3)	115.1 (4)	112.4 (3)
O(2)—S(2)—O(3)	113.7 (4)	110.6 (4)	114.6 (3)
Co—N(1)—C(1)	112.1 (4)	109.6 (6)	106.8 (5)
Co—N(2)—C(2)	108.5 (5)	109.4 (6)	108.5 (5)
Co—N(3)—C(3)	109.9 (5)	108.5 (5)	109.2 (5)
Co—N(4)—C(4)	109.5 (4)	109.0 (5)	109.8 (5)
Co—N(5)—C(5)	170.1 (6)	172.1 (6)	171.1 (7)
N(1)—C(1)—C(2)	107.5 (6)	107.4 (8)	107.5 (7)
N(2)—C(2)—C(1)	107.1 (6)	108.5 (8)	107.6 (8)
N(3)—C(3)—C(4)	107.4 (7)	107.6 (7)	107.4 (7)
N(4)—C(4)—C(3)	106.6 (6)	107.8 (8)	107.9 (7)
S(3)—C(5)—N(5)	177.9 (6)	178.3 (7)	177.8 (7)
cis Isomer			
O(4)···O(1)	2.836 (8)	O(4)···O(2)^{i}	2.953 (8)
trans Isomer			
O(4)···O(1)^{ii}	2.830 (11)	O(5)···O(2)^{iv}	2.931 (12)
O(4)···O(5)^{iii}	2.892 (12)	O(6)···O(1*b*)^{v}	2.918 (10)

Symmetry code: (i) $-0+x, -1-y, z$; (ii) $x, 1-y, 0.5+z$; (iii) $x, -y, 0.5+z$; (iv) $x, 1-y, -0.5+z$; (v) $1+x, 1+y, z$.

IV). The other experimental data are listed in Table 1.* Bond lengths and angles are in Table 2. Thermal ellipsoid plots of the *cis* and *trans* isomers are shown in Figs. 1 and 2, respectively.

Related literature. The structures and the structural *trans* effect of seven bis(ethylenediamine)cobalt(III) complexes having monodentate oxalato, azido, nitro, sulfito and thiosulfato ligands have been reported (Kastner, Smith, Kuzmission, Cooper, Tyree & Yearick, 1989). The kinetic *trans* effect of (thiosulfato)(pentaammine)cobalt(III) has been documented (Cooper, McCoy, Katz & Deutsch, 1980) and the crystal structure has been reported (Restivo, Ferguson & Balahura, 1977). The absence of a structural *trans* effect by the thiocyanato ligand has also been reported for *cis*-bis(isothiocyanato)bis(ethylenediamine)cobalt(III) (Schubert, Zimmer-Gasser, Dash & Chaudhury, 1981).

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and an additional figure have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55967 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1005]

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