Tris(ethylenediamine)cobalt(III) Tetrakis(isothiocyanato)cobaltate(II) Nitrate

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Abstract. $Co^{III}(en)_3Co^{II}(NCS)_4NO_3$, orthorhombic, $P2_12_12_1$, $a = 10\cdot633$ (3), $b = 25\cdot712$ (6), $c = 8\cdot625$ (2) Å, $Z = 4$, $D_x = 1\cdot67$ g cm^{-3}. The structure was refined to a final conventional discrepancy factor of $R = 0\cdot062$ for 1638 observed reflections ($|F_o| > 2\sigma_{F_o}$). Slight distortions from the idealized octahedral and tetrahedral geometries of the Co^{III} and Co^{II} moieties are observed and the orientation of the $Co(NCS)_4^{2-}$ species relative to the crystal faces is described.

Introduction. A crystal of dimensions $0\cdot4 \times 0\cdot4 \times 0\cdot3$ mm was mounted on the end of a glass fiber with Duco cement. The reduced cell and associated reduced cell scalars obtained from our automatic indexing program (Jacobson, 1976) indicated an orthorhombic crystal system. The *mmm* symmetry was confirmed by three axial ω-oscillation photographs.

Data were collected at 25 °C on an automated four-circle diffractometer designed and built in the Ames laboratory. Graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0\cdot70954$ Å) was used for data collection. All data (4548 reflections) within a 2θ sphere of 50° [(sin θ)/$\lambda = 0\cdot596$] in the hkl and $hk\bar{l}$ octants were measured with an ω-scan technique and a take-off angle of $4\cdot5°$.

As a general check on electronic and crystal stability, the intensities of three standard reflections were remeasured every 50 reflections. These standards were not observed to vary significantly throughout the entire data collection period. Examination of the data revealed systematic absences of $h00$, $0k0$, and $00l$ reflections for $h = 2n + 1$, $k = 2n + 1$, and $l = 2n + 1$, respectively, thus defining the space group as $P2_12_12_1$.

The measured intensities were corrected for Lorentz and polarization effects and for absorption (Scott, 1971; de Meulenaer & Tompa, 1965) with minimum and maximum transmission factors of 0·48 and 0·58 ($\mu = 18\cdot25$ cm^{-1}). The estimated variance in each intensity was calculated by

$$\sigma^2(I) = C_T + K_t C_B + (0\cdot03C_T)^2$$
$$+ (0\cdot03C_B)^2 + (0\cdot06C_N/A)^2$$

where C_T, C_B, C_N, K_t, and A represent the total count, background count, net count, a counting time factor, and the absorption coefficient respectively. Reflections for which $|F_o| > 2\sigma_{F_o}$ (3009 reflections) were used in the refinement of the two enantiomorphs.

Initial atomic positions were obtained from analysis of the three-dimensional Patterson function and from successive structure factor (Busing, Martin & Levy, 1962) and electron density map calculations (Hubbard, Quicksall & Jacobson, 1971). In addition to positional parameters for all atoms, the anisotropic thermal parameters for all non-hydrogen atoms were refined by a full-matrix least-squares procedure (Busing *et al.*, 1962), minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma_F^2$, to a conventional discrepancy index of $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o| = 0\cdot085$ for both enantiomorphs. At this point in the refinement it was observed that 21 strong, low-angle reflections appeared to exhibit secondary extinction effects. A plot of I_o/I_o *versus* I_c for these reflections yielded a straight line with slope

Table 1. *Positional parameters* ($\times 10^4$) *for* $Co^{III}(en)_3$ $Co^{II}(NCS)_4NO_3$ *with e.s.d.'s in parentheses*

H atom parameters are given in the supplementary material.

	x	y	z
Co(A)	8781 (2)	6217 (1)	4262 (2)
Co(B)	3647 (2)	6360 (1)	9257 (2)
S(1B)	7638 (4)	7120 (2)	8470 (5)
S(2B)	746 (4)	7595 (2)	7350 (5)
S(3B)	3010 (4)	6644 (2)	14563 (5)
S(4B)	3719 (6)	4886 (2)	6073 (8)
O(1)	8928 (13)	5920 (4)	9443 (15)
O(2)	7908 (13)	5315 (4)	8250 (11)
O(3)	7885 (14)	5329 (5)	10748 (13)
N	8262 (14)	5523 (5)	9481 (15)
N(1A)	8637 (12)	6968 (4)	4458 (13)
N(2A)	9957 (12)	6333 (5)	2562 (15)
N(3A)	7518 (11)	6106 (5)	5850 (15)
N(4A)	7383 (11)	6177 (5)	2791 (15)
N(5A)	9091 (10)	5463 (4)	4036 (15)
N(6A)	10108 (11)	6183 (5)	5854 (16)
N(1B)	5346 (13)	6635 (6)	8944 (15)
N(2B)	2373 (15)	6823 (5)	8351 (15)
N(3B)	3312 (13)	6354 (5)	11484 (16)
N(4B)	3613 (13)	5712 (4)	8134 (17)
C(1A)	9659 (16)	7232 (5)	3459 (18)
C(2A)	9791 (16)	6906 (6)	2036 (20)
C(3A)	6230 (15)	6181 (6)	5259 (19)
C(4A)	6221 (13)	5967 (6)	3660 (21)
C(5A)	9907 (19)	5283 (7)	5322 (23)
C(6A)	10750 (16)	5671 (6)	5832 (25)
C(1B)	6319 (15)	6843 (6)	8773 (17)
C(2B)	1704 (14)	7154 (6)	7949 (17)
C(3B)	3177 (13)	6478 (6)	12740 (20)
C(4B)	3655 (16)	5358 (6)	7299 (22)

(2g) of 3.23×10^{-6}. All data were then corrected for secondary extinction by I_o(corrected) $\simeq I_o(1 + 2gI_c)$. Refinement using the unaveraged data set indicated that the contribution from the imaginary part of the anomalous dispersion correction was completely negligible. Therefore, for the final refinement, reflections in the hkl and hk$\bar{l}$ octants were then averaged, and the related $(F)_{ave}$ was calculated as $[\Sigma_{i=1}^{N} \sigma_i^2(F)]^{1/2}/N$, where N is the number of observed reflections for a 'unique' reflection to be averaged. There were consequently 1638 independent reflections used in subsequent calculations. The scattering factors used for non-hydrogen atoms were those of Hanson, Herman, Lea & Skillman (1960), modified for the real part of the anomalous dispersion (Templeton, 1962). The H scattering factors used were those of Stewart, Davidson & Simpson (1965). Final convergence was obtained with $R = 0.062$.

The final positional parameters are listed in Table 1.* The standard deviations were calculated from the inverse matrix of the final least-squares cycle.

Discussion. A stereographic view of Co^{III}(en)$_3$-Co^{II}(NCS)$_4$NO$_3$ depicting 50% probability ellipsoids (Johnson, 1971) is provided in Fig. 1. Interatomic bond distances and angles (Busing, Martin & Levy,

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* Lists of structure factors and thermal parameters and additional tables have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32787 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
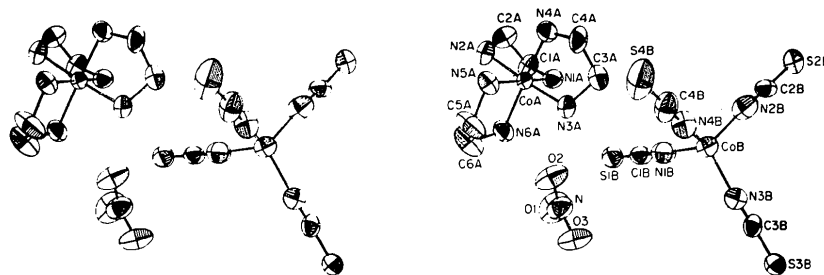
1964), listed as supplementary material,* are in good agreement with those reported previously in the literature (Mathieu & Weiss, 1973; Balahura, Ferguson & Schneider, 1975). However, slight distortions from the idealized octahedral and tetrahedral geometries of the Co^{III} and Co^{II} moieties are observed.

The Co(A)–N(A) distances of the octahedral moiety range from 1.939 (12) to 1.975 (11) Å, averaging 1.956 (14) Å, and the N(A)–Co(A)–N(A) angles range from 84.6 (4) to 94.1 (3)°. It is apparent that the H atoms bound to N(4A) and N(5A) are involved in hydrogen bonding with the O atoms of the nitrate group, i.e. the H(16)$\cdots$O(3) distance is 1.56 (1) Å and the H(18)$\cdots$O(2) distance is 1.89 (1) Å. In addition, H(17) of N(5A) interacts with S(4B) of the Co^{II} moiety, i.e. the H(17)$\cdots$S(4B) distance is 2.280 (6) Å. Similarly, the H(1)$\cdots$S(2B) distance is 2.446 (4) Å, while all other H$\cdots$S distances exceed 2.65 Å. Consequently, the distortions of the octahedral Co^{III} and tetrahedral Co^{II} groups are manifestations of these hydrogen-bond-like interactions.

The distortions of the tetrahedral Co^{II} moiety are evidenced by Co(B)–N(B) distances from 1.928 (12) to 1.966 (15) Å, averaging 1.952 (16) Å, and by the N(B)–Co(B)–N(B) angles which range from 105.1 (6) to 118.9 (6)°. In addition, Co(B)–N(B)–C(B)-type angles deviate from linearity by as much as 17°.

A unit-cell stereograph of the compound is provided in Fig. 2, and a stereographic view of the Co^{II} species in the unit cell as viewed down **b** is provided in Fig. 3. From inspection of the dihedral angles between various planes in the Co(NCS)$_4^{2-}$ moiety and the unit-cell faces

Fig. 1. A stereographic view of Co^{III}(en)$_3$Co^{II}(NCS)$_4$NO$_3$. In this and succeeding drawings 50% probability ellipsoids are depicted.
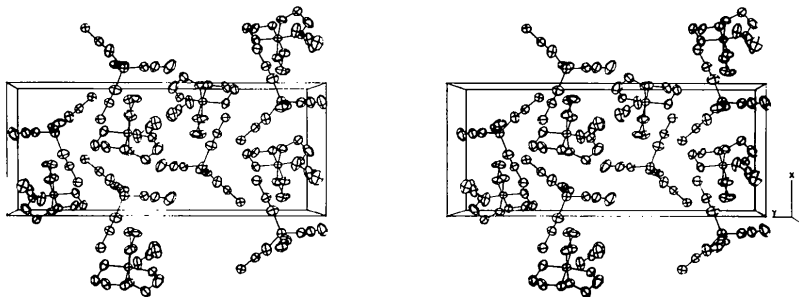

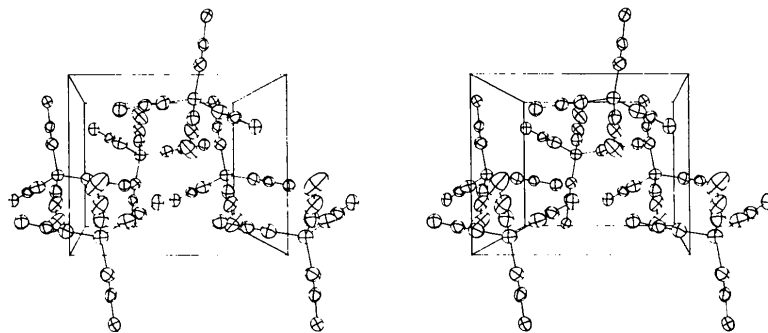Fig. 2. Unit-cell stereograph of Co^{III}(en)$_3$Co^{II}(NCS)$_4$NO$_3$.

Fig. 3. Arrangement of the $Co(NCS)_4^{2-}$ moieties as viewed down **b**. In this illustration **c** is vertical.

(*cf.* supplementary material),* it can be seen that one of the molecular pseudomirror planes is roughly parallel to the *bc* face; the plane defined by N(3*B*)—Co(*B*)—N(4*B*) subtends an angle of 11·94° with this face.

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* See deposition footnote.

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