

taken with regard to the KKM effect (Kroon, Kanters, Peerdeman & Vos, 1971). In addition, therefore, difference Fourier syntheses [Figs. 4(a-d)] were calculated (program *GENFOR*; Craven, Weber & Ruble, 1979). The splitting is evident in all these maps. The positions of the maxima are in good agreement with the positions obtained in the refinement. All calculations were carried out on a MicroVAX and on the PDP10 of the Rechenzentrum der Universität Kiel.

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Structure of (Ethylenediamine)(tetramethylenediamine)(trimethylenediamine)-cobalt(III) Hexacyanocobaltate(III) Monohydrate, $\Delta-(+)$ ₅₈₉[Co(en)(tn)(tmd)]-[Co(CN)₆].H₂O

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Abstract. [Co(C₂H₄N₂)(C₃H₆N₂)(C₄H₈N₂)]-[Co(CN)₆].H₂O, *M_r* = 514.5, triclinic, *P*1, *a* = 9.599 (2), *b* = 15.344 (3), *c* = 8.944 (2) Å, α = 100.47 (2), β = 113.93 (2), γ = 81.37 (2)° *V* = 1179.9 (4) Å³, *Z* = 2, *D_x* = 1.45 Mg m⁻³, λ (Mo *K* α) = 0.71073 Å, μ = 1.43 mm⁻¹, *F*(000) = 513.4, *T* = 120 (2) K, final *R* = 0.069 for 3935 reflections. The five-, six- and seven-membered chelate rings of the complex cation take *lel*, *lel*(skew-boat), *lel* configuration. The complex cations take two possible orientations around the approximate twofold axis

through the Co atom and the center of the C—C bond of the five-membered chelate ring with interchanging six- and seven-membered chelate rings. The disorder was analyzed by a split atom model. A conformational analysis has been performed to show that the *lel*₃ conformation observed in the crystal has the second lowest strain energy with a difference of only 2.2 kJ mol⁻¹ owing to the relatively small non-bonded interactions.

Introduction. Conformations of the five-, six- and seven-membered chelate rings in several tris-bidentate Co^{III} complexes have been investigated

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(Saito, 1979, 1985). The title complex cation synthesized by Kojima, Yamada, Ogino & Fujita (1977) is of fundamental interest for the steric interactions in the mixed chelate-ring systems. Unfortunately, there exists disorder in the crystal structure of $\Delta\text{-}(+)\text{_{589}}\text{-}[\text{Co}(\text{en})(\text{tn})(\text{tmd})][\text{Co}(\text{CN})_6]\cdot\text{H}_2\text{O}$ (en = ethylenediamine, tn = trimethylenediamine, tmd = tetramethylenediamine), and the structural study had been left for ten years. All the attempts failed to obtain suitable crystals by replacement of the counter anions. Thus, it was decided to take up this crystal again. The X-ray diffraction data have been remeasured at 120 K to improve the resolution of the electron density and the disorder was analyzed by a split atom model. A strain-energy minimization study has also been carried out to examine the structural model from the energetic point of view.

Experimental. A dark orange needle-like crystal of dimensions $0.35 \times 0.15 \times 0.14$ mm was kept at 120 K with a stream of cold nitrogen gas. Intensities were measured up to $2\theta = 55^\circ$ (h : $0 \rightarrow 12$; k : $-19 \rightarrow 19$; l : $-11 \rightarrow 11$) on a Rigaku AFC-5R automated four-circle diffractometer with graphite-monochromatized $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073$ Å). The ω -scan technique was employed with a scan speed of 6° min^{-1} in θ and scan width 2.2° to cover the broad peak profile. Variation of five standard reflections was within 1%. 5746 reflections were measured and 3935 reflections were observed with $|F_o| > 3\sigma(|F_o|)$. Lattice constants were determined based on 40 2θ values ($20 < 2\theta < 30^\circ$). Absorption was corrected, $0.78 < A < 0.84$. The space group was expected to be $P1$ since the crystal is constructed with the optically active complex cation $(+)\text{_{589}}\text{-}[\text{Co}(\text{en})(\text{tn})(\text{tmd})]^{3+}$, whose absolute configuration was assigned to be Δ based on the CD spectrum in the first absorption region (Kojima, Yamada, Ogino & Fujita, 1977). The structure was solved by the Patterson-Fourier method. There exist two crystallographically independent complex anions and cations. The atomic positions of $[\text{Co}(\text{CN})_6]^{3-}$ and the $\text{Co}(\text{en})$ moieties were located straightforwardly ($R = 0.12$). However, the six- and seven-membered chelate rings of the complex cations could not be interpreted uniquely. After a number of trials, it was revealed that the observed electron density can only be interpreted as a superposition of the six- and seven-membered chelate rings assuming orientational disorder of the complex. Then, a split atom model was adopted to construct six- and seven-membered chelate rings. The populations of the disordered C atoms were estimated with the condition that the isotropic thermal parameters should be nearly equal to each other. Seventeen H atoms among 40 could be located on a difference synthesis, $0.5 < \Delta\rho < 0.8 \text{ e \AA}^{-3}$. The H atoms bonded to the C atoms in the tn and tmd ligands were not introduced.

Anisotropic thermal parameters were introduced for non-H atoms except for disordered C atoms. The function $\sum w(|F_o| - |F_c|)^2$ was minimized by block-diagonal least-squares refinement with weight $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$. Final $R = 0.069$, $wR = 0.077$, $S = 2.5$ for 3935 observed unique reflections. Reflection/parameter ratio was 8.3, $\Delta/\sigma < 0.31$ for non-H atoms, and $-1.6 < \Delta\rho < 1.4 \text{ e \AA}^{-3}$. Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The calculations were carried out on a FACOM M-380R computer at Keio University with the program system UNICSIII (Sakurai & Kobayashi, 1979). Final atomic coordinates are listed in Table 1.* It was impossible to confirm the absolute structure by the anomalous-scattering technique because of the pseudo-centrosymmetric structure as seen in Fig. 1.

Discussion. The crystal structure is shown in Fig. 1. Each hydrate H atom participates in hydrogen bonding, $\text{O}\cdots\text{H}\cdots\text{N}$ with $[\text{Co}(\text{CN})_6]^{3-}$, the $\text{O}\cdots\text{N}$ distances being $2.69(2)\text{--}2.89(2)$ Å. There are two crystallographically independent complex cations with the absolute configuration Δ , having almost the same structure as illustrated in Fig. 1, in which some positions for disordered C atoms are omitted for clarity. The side-on views of the chelate rings in Fig. 2 show the disordered arrangement of six- and seven-membered chelate rings. This can be explained by the orientational disorder of the complex. One of the orientations of the complex cation is approximately related to the other by rotation around the twofold axis of the $\text{Co}(\text{en})$ moiety. As seen in Fig. 3, the six- and seven-membered chelate rings are interchanged

* Lists of structure factors, anisotropic thermal parameters, bond lengths, bond angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53166 (40 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

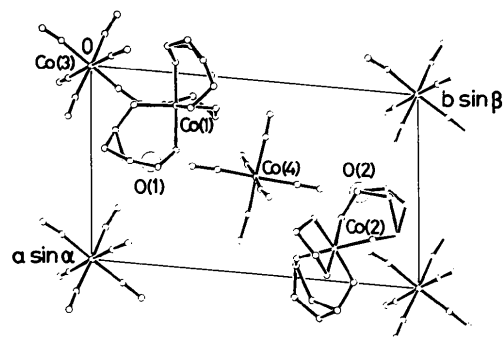


Fig. 1. A projection of the crystal structure along c . H atoms are omitted for clarity. All the atoms are represented by circles of radius 0.1 Å except for hydrate O atoms with radius 0.3 Å.

Table 1. Positional parameters ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10$; Hamilton, 1959)

	x	y	z	B/B _{eq}
Co(1)	1670 (2)	2589 (1)	6843 (2)	14
Co(2)	8321 (2)	7413 (1)	3066 (2)	17
Co(3)	0	0	0	15
Co(4)	4979 (5)	4977 (3)	4959 (5)	14
O(1)	4679 (10)	1806 (6)	10878 (10)	17
O(2)	5300 (13)	8190 (8)	-939 (14)	48
N(1)	3127 (12)	3210 (6)	8874 (12)	14
N(2)	266 (13)	2823 (7)	8021 (13)	19
N(3)	997 (12)	3739 (6)	5921 (12)	14
N(4)	27 (11)	2001 (6)	4842 (11)	13
N(5)	3271 (11)	2377 (7)	5917 (11)	12
N(6)	2308 (13)	1423 (6)	7636 (13)	17
N(7)	8371 (20)	6201 (10)	1891 (18)	52
N(8)	8315 (17)	7771 (9)	1077 (18)	41
N(9)	6017 (19)	7424 (13)	1964 (19)	58
N(10)	8181 (19)	8693 (10)	3992 (18)	47
N(11)	8283 (19)	6976 (10)	4989 (19)	51
N(12)	10573 (16)	7425 (10)	4068 (16)	42
N(13)	1693 (14)	1521 (7)	2428 (14)	23
N(14)	-1024 (13)	1001 (7)	-3000 (13)	21
N(15)	-2713 (15)	724 (8)	849 (15)	28
N(16)	-1747 (14)	-1504 (8)	-2549 (14)	26
N(17)	1016 (18)	-1111 (9)	2764 (17)	48
N(18)	2768 (17)	-807 (11)	-880 (22)	60
N(19)	4676 (11)	3016 (6)	3591 (11)	9
N(20)	8310 (13)	4516 (7)	7057 (12)	17
N(21)	4034 (16)	4563 (10)	7543 (16)	40
N(22)	5251 (17)	6941 (9)	6208 (19)	43
N(23)	1636 (14)	5496 (9)	2870 (17)	36
N(24)	6028 (13)	5413 (7)	2343 (14)	22
C(1)	2357 (16)	3745 (9)	9870 (17)	22
C(2)	1234 (19)	3163 (10)	9914 (19)	30
C(3)	6167 (17)	3763 (9)	4097 (17)	23
C(4)*	-1100 (34)	3272 (19)	3227 (35)	24
C(41)*	-1023 (27)	3816 (15)	3056 (28)	12
C(42)*	-2001 (39)	3054 (21)	2964 (39)	33
C(5)	-1519 (16)	2512 (9)	4043 (16)	20
C(6)	4714 (17)	1876 (9)	6760 (17)	24
C(7)*	4991 (32)	962 (17)	6370 (32)	20
C(71)*	4565 (32)	901 (17)	6758 (32)	20
C(8)*	4250 (30)	383 (16)	6948 (30)	16
C(9)	2616 (16)	648 (9)	6557 (17)	22
C(10)	7925 (17)	6216 (9)	100 (17)	24
C(11)	8873 (21)	6913 (12)	136 (17)	38
C(12)	5056 (20)	7980 (11)	2972 (20)	36
C(13)†	5413 (39)	9020 (22)	3535 (39)	63
C(131)‡	5264 (61)	8817 (34)	3846 (63)	30
C(132)‡	5797 (73)	9603 (39)	3451 (73)	43
C(14)	6782 (24)	9252 (13)	3167 (24)	49
C(15)†	9491 (24)	6263 (13)	5797 (24)	22
C(151)‡	10018 (63)	6338 (35)	5974 (64)	31
C(16)†	10810 (24)	6598 (13)	7245 (25)	24
C(161)‡	11469 (75)	6949 (40)	6847 (75)	44
C(17)†	11766 (27)	7056 (15)	7193 (28)	32
C(18)	11369 (20)	7663 (11)	5808 (20)	35
C(19)	1158 (19)	936 (11)	1563 (20)	36
C(20)	-762 (16)	708 (9)	-1986 (16)	20
C(21)	-1731 (16)	499 (9)	329 (16)	21
C(22)	-1053 (13)	-939 (7)	-1493 (13)	8
C(23)	620 (14)	-625 (8)	1647 (14)	13
C(24)	1703 (15)	-418 (8)	-686 (15)	17
C(25)	4796 (20)	3712 (10)	4090 (23)	38
C(26)	7117 (15)	4654 (8)	6343 (14)	15
C(27)	4362 (18)	4819 (10)	6524 (18)	28
C(28)	5192 (12)	6166 (6)	5858 (12)	3
C(29)	3025 (15)	5233 (8)	3723 (15)	16
C(30)	5589 (13)	5254 (7)	3241 (13)	8

The coordinates of Co(3) were used to define the origin of the unit cell and are listed without e.s.d.'s.

*0.5, †0.7 and ‡0.3 are the population parameters of disordered carbon atoms.

by the twofold rotation. The possibility of [Co(en)(tn)₂]³⁺ and [Co(en)(tmd)₂]³⁺ complexes was discounted by the complete separation of the products by column chromatography (Kojima, Yamada,

Ogino & Fujita, 1977). Bond lengths and bond angles for en rings are normal. For example, the C—C bond lengths and the N—Co—N bond angles are 1.49 (3)–1.52 (3) Å and 84.2 (7)–84.9 (5)°, respectively, almost the same as those of 1.50 (1)–1.52 (2) Å and 85.3 (3)–85.4 (3)° observed in [Co(en)₃]Cl₃.H₂O (Iwata, Nakatsu & Saito, 1969). At least it is evident that the complex cations take *lel*₃ configuration with the skew-boat form of the six-membered chelate ring. The conformation of en and tmd rings is the same as observed in the *lel*₃ conformations in [Co(en)₃]Cl₃.H₂O (Iwata *et al.*, 1969) and [Co(tmd)₃]Br₃ (Sato & Saito, 1975). However, the skew-boat form of the tn ring differs from that observed in the C₃ chair₃ [Co(tn)₃]Cl₃.H₂O (Nagao, Marumo & Saito, 1973). In the crystals of [Cr(tn)₃]-[Ni(CN)₅].2H₂O, the complex cation takes the *syn* chair₂, *lel*(skew-boat) conformation (Jurnak & Raymond, 1974). Strain-energy minimization for [Co(en)(tn)(tmd)]³⁺ has been carried out for sixteen different conformations with the six-membered chelate ring in skew-boat or chair form (Ohba &

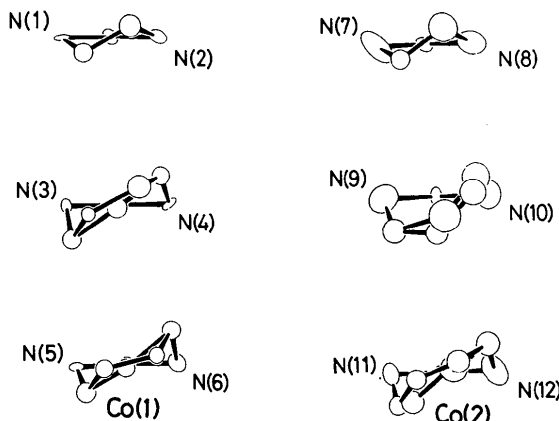


Fig. 2. ORTEPII drawings of side-on views of the chelate rings (Johnson, 1976) of the complex cations with thermal ellipsoids scaled at 50% probability level. There exists oriented disorder and the images for six- and seven-membered chelate rings are overlapped.

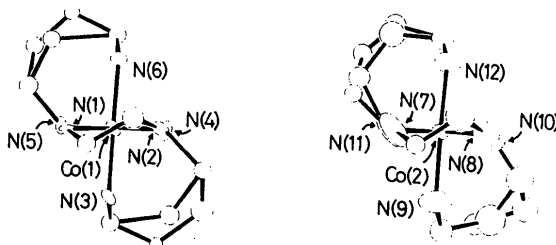


Fig. 3. Perspective views of the complex cations along the pseudo twofold axis through the Co atom and the midpoint of the C—C bond in the ethylenediamine chelate ring. The locations of six- and seven-membered chelate rings are interchanged by the pseudo-rotational symmetry.

Rasmussen, 1990). The calculations were made by the program *CFF* with the energy parameter set *NIKIPAR6* (Niketić & Rasmussen, 1977) on an AMDAHL *VP1100* computer. The lowest strain energy is found for the *en(lel)*, *tn(p-chair)*, *tmd(lel)* conformation. The observed conformation in the crystal is the second lowest on the energy scale with an energy difference of only 2.2 kJ mol^{-1} , which may be compensated by intermolecular interactions. The skew-boat form of the *tn* chelate ring has a strain energy which is larger than that of the chair form by *ca* 5 kJ mol^{-1} . However, the *lel₃* conformation has the second lowest strain energy because of relatively small non-bonded $\text{H}\cdots\text{H}$ repulsions between the chelate rings.

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Structure of *trans*-Bis[4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole-*N*¹,*N*']diaquamanganese(II) Dibromide

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Abstract. $[\text{Mn}(\text{C}_{12}\text{H}_{10}\text{N}_6)_2(\text{H}_2\text{O})_2]\text{Br}_2$, $M_r = 727.28$, orthorhombic, *Pbca*, $a = 10.734$ (6), $b = 17.084$ (0), $c = 15.182$ (6) Å, $V = 2784$ Å³, $Z = 4$, $D_x = 1.734 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 33.23 \text{ cm}^{-1}$, $F(000) = 1450$, $T = 295 \text{ K}$, final $R = 0.032$ for 1493 reflections [$I > 2\sigma(I)$]. The title compound is the first reported mononuclear compound with the ligand 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole. The manganese ions, situated on an inversion centre, are coordinated by four nitrogen atoms with an N—Mn—N angle of 74.1 (1)° and Mn—N distances of 2.188 (4) and 2.266 (4) Å. Two axial water molecules [$\text{Mn—O} = 2.200$ (4) Å] complete the coordination sphere of the metal, which is pseudo-octahedral. The two bromide ions are not

coordinated but are involved in an extended hydrogen-bridging network with the water ligands and the amino group of the triazole.

Introduction. In order to study magnetic exchange between first-row transition metals, the use of ligands derived from 1,2,4-triazole has proved to be of great value. Many studies have already been reported on polynuclear compounds (Engelfriet, Groeneveld & Nap, 1980, and references cited therein; Vos, Haasnoot, Verschoor, Reedijk & Schaminee, 1985, and references cited therein; Haasnoot & Groeneveld, 1979). In this respect, the ligand 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole (hereafter abbreviated to abpt) which was first synthesized by Dallacker (1960), has been shown to act as a tetradentate nitrogen-donor ligand. Up to now, only nickel and

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