

Structure of Diaqua[tris(3-aminopropyl)amine]cobalt(III) Aquatetrakis(trifluoromethanesulfonato)sodate(I) Monohydrate

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Abstract. $[\text{Co}(\text{C}_9\text{H}_{24}\text{N}_4)(\text{H}_2\text{O})_2][\text{Na}(\text{CF}_3\text{O}_3\text{S})_4\text{H}_2\text{O}]\cdot\text{H}_2\text{O}$, $M_r = 938.6$, monoclinic, $P2_1/c$, $a = 13.2099$ (9), $b = 12.1272$ (12), $c = 21.847$ (2) Å, $\beta = 107.400$ (6)°, $V = 3339.7$ (5) Å³, $Z = 4$, $D_m = 1.87$, $D_x = 1.867$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 8.977$ cm⁻¹, $F(000) = 1904$, $T = 198$ K, $R = 0.0357$ for 5920 unique reflections. The cobalt(III) ion in the cation is surrounded by one tertiary and three primary N atoms from the tripodal tetraamine ligand [trpn: tris(3-aminopropyl)amine] and by two O atoms from the coordinated waters. The Co—N bond with the tertiary N atom is the longest of these. In the complex anion, the Na ion is coordinated to six O atoms: one each from a water molecule and three trifluoromethanesulfonate (triflate) groups, and chelated through two O atoms from a fourth one, resulting in a distorted octahedron [e.g. one O—Na—O angle is 53.47 (9)°].

Experimental. Crystals of $[\text{Co}(\text{C}_9\text{H}_{24}\text{N}_4)(\text{H}_2\text{O})_2][\text{Na}(\text{CF}_3\text{O}_3\text{S})_4\text{H}_2\text{O}]\cdot\text{H}_2\text{O}$ were prepared from the corresponding carbonate complex as described elsewhere for the perchlorate salt (Rawji & Milburn, 1988), with the exceptions that HO_3SCF_3 was used instead of HClO_4 and $\text{NaCF}_3\text{O}_3\text{S}$ was added to promote crystallization. Crystals were obtained as large violet plates by slow evaporation from aqueous solution. The data crystal was cut from a much larger crystal and had approximate dimensions 0.17 × 0.35 × 0.81 mm. Data were collected at 198 K using a Nicolet LT-2 low-temperature delivery system on a Nicolet R3 diffractometer that was equipped with a graphite monochromator and Mo $K\alpha$ radiation. The crystal system is monoclinic and the space group is $P2_1/c$ (No. 14), as uniquely determined from systematically absent reflections. The lattice parameters were obtained from least-squares refinement of 45 reflections with $20.1 < 2\theta < 24.6^\circ$. The data were collected using the φ -scan technique. A total of 7048 reflections were collected, of which 5920 were unique. The R value for averag-

ing the equivalent reflections was 0.0192. The 2θ range was 4.0–50.0°, with a 1.2° ω scan at 12° min⁻¹ ($h = 0 \rightarrow 15$, $k = 0 \rightarrow 14$, $l = -25 \rightarrow 25$). Four reflections ($\bar{5}, 2, 10$, $\bar{5}\bar{5}\bar{1}$, $5\bar{5}\bar{8}$ and 524) were remeasured every 196 reflections to monitor instrument and crystal stability. A smoothed curve of the intensities of these check reflections was used to scale the data. The scaling factor ranged from 0.991 to 1.12. The data were also corrected for Lp effects and absorption. The absorption correction was applied on the basis of carefully measured crystal dimensions. The transmission factors ranged from 0.7335 to 0.8707. Data reduction and decay correction were performed using the *SHELXTL-Plus* software package (Sheldrick, 1987). Reflections having $F_o < 4\sigma(F_o)$ were considered unobserved (1311 reflections). The structure was solved by direct methods and refined by full-matrix least-squares procedures (Sheldrick, 1987), with anisotropic thermal parameters for the non-H atoms. The H atoms were obtained from a ΔF map and were refined with isotropic thermal parameters. A total of 588 parameters were refined. The data were checked for secondary extinction but no correction was necessary. One reflection ($\bar{1}22$) had a very asymmetric background and was deleted during refinement. The function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/[\sigma(F_o)]^2$ and $\sigma(F_o) = 0.5kI^{-1/2} \times \{[\sigma(I)]^2 + (0.02I)^2\}^{1/2}$. The intensity, I , is given by $(I_{\text{peak}} - I_{\text{background}}) \times (\text{scan rate})$, 0.02 is a factor to downweight intense reflections and to account for instrument instability, and k is the correction for Lp effects and absorption decay. $\sigma(I)$ was estimated from counting statistics; $\sigma(I) = [(I_{\text{peak}} + I_{\text{background}})^{1/2} \times (\text{scan rate})]$. The final $R = 0.0357$ for 4609 reflections, $wR = 0.0401$ (R for all reflections = 0.0621, wR for all reflections = 0.0477) and goodness of fit = 1.297. Maximum $|\Delta/\sigma| < 0.1$ in the final refinement cycle and the minimum and maximum peaks in the final ΔF map were -0.41 and 0.38 e Å⁻³, respectively. Neutral-atom scattering factors for the non-H atoms were taken from Cromer & Mann (1968), with

Table 1. Fractional coordinates and equivalent isotropic thermal parameters (\AA^2) for the non-H atoms of [Co(trpn)(H₂O)₂][Na(CF₃O₃S)₄H₂O].H₂O

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* A_{ij}$$

where A_{ij} is the dot product of the i th and j th direct-space unit-cell vectors.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Co	0.25592 (3)	0.96959 (3)	0.18556 (2)	0.01704 (13)
O(1)	0.1224 (2)	1.0513 (2)	0.17486 (13)	0.0305 (9)
O(2)	0.2723 (2)	0.9715 (2)	0.27863 (11)	0.0245 (8)
N(1)	0.1706 (3)	0.8329 (3)	0.18011 (14)	0.0292 (10)
C(2)	0.0874 (3)	0.7939 (3)	0.1226 (2)	0.0371 (14)
C(3)	0.0785 (3)	0.8610 (3)	0.0637 (2)	0.0307 (12)
C(4)	0.1858 (3)	0.8825 (3)	0.0538 (2)	0.0281 (12)
N(5)	0.2482 (2)	0.9767 (2)	0.09256 (11)	0.0218 (8)
C(6)	0.1952 (3)	1.0837 (3)	0.0636 (2)	0.0307 (12)
C(7)	0.2558 (3)	1.1882 (3)	0.0892 (2)	0.0325 (13)
C(8)	0.2815 (3)	1.2065 (3)	0.1607 (2)	0.0277 (12)
N(9)	0.3326 (2)	1.1098 (2)	0.19909 (13)	0.0214 (10)
C(10)	0.3548 (3)	0.9740 (3)	0.0797 (2)	0.0273 (12)
C(11)	0.4278 (3)	0.8795 (3)	0.1088 (2)	0.0287 (12)
C(12)	0.4724 (3)	0.8900 (3)	0.1801 (2)	0.0269 (12)
N(13)	0.3883 (2)	0.8876 (3)	0.21249 (13)	0.0236 (10)
S(1a)	0.78894 (6)	0.74649 (7)	0.17167 (4)	0.0259 (3)
O(1a)	0.8535 (2)	0.8394 (2)	0.16772 (13)	0.0506 (11)
O(2a)	0.7048 (2)	0.7707 (2)	0.19810 (12)	0.0484 (10)
O(3a)	0.8482 (2)	0.6486 (2)	0.19812 (11)	0.0353 (9)
C(1a)	0.7238 (3)	0.7113 (4)	0.0884 (2)	0.049 (2)
F(1a)	0.6665 (2)	0.7958 (3)	0.05860 (11)	0.0795 (12)
F(2a)	0.7943 (3)	0.6909 (2)	0.05805 (11)	0.0851 (13)
F(3a)	0.6635 (3)	0.6249 (3)	0.08404 (14)	0.108 (2)
S(1b)	0.62431 (6)	1.05698 (6)	0.33296 (4)	0.0247 (3)
O(1b)	0.5115 (2)	1.0570 (2)	0.31199 (12)	0.0503 (10)
O(2b)	0.6729 (2)	1.1628 (2)	0.33332 (12)	0.0457 (10)
O(3b)	0.6722 (2)	0.9711 (2)	0.30595 (12)	0.0434 (10)
C(1b)	0.6585 (3)	1.0208 (3)	0.4171 (2)	0.0443 (15)
F(1b)	0.6258 (3)	1.0949 (2)	0.45015 (11)	0.0825 (13)
F(2b)	0.6187 (3)	0.9249 (2)	0.42525 (12)	0.0768 (13)
F(3b)	0.7631 (2)	1.0111 (3)	0.44155 (13)	0.0941 (14)
S(1c)	0.63069 (6)	1.17283 (6)	0.15734 (4)	0.0249 (3)
O(1c)	0.5286 (2)	1.1792 (2)	0.16762 (11)	0.0424 (10)
O(2c)	0.7033 (2)	1.2585 (2)	0.18855 (11)	0.0371 (9)
O(3c)	0.6770 (2)	1.0652 (2)	0.16322 (12)	0.0441 (10)
C(1c)	0.6024 (3)	1.2030 (3)	0.0726 (2)	0.0397 (14)
F(1c)	0.5332 (2)	1.1299 (3)	0.03796 (10)	0.0711 (11)
F(2c)	0.5636 (2)	1.3015 (2)	0.05867 (12)	0.0802 (13)
F(3c)	0.6894 (2)	1.1959 (2)	0.05417 (10)	0.0520 (9)
S(1d)	1.02686 (7)	0.84525 (7)	0.33031 (4)	0.0302 (3)
O(1d)	1.0661 (2)	0.7339 (2)	0.33766 (13)	0.0524 (11)
O(2d)	0.9157 (2)	0.8563 (2)	0.32172 (12)	0.0425 (10)
O(3d)	1.0664 (2)	0.9110 (2)	0.28719 (12)	0.0412 (9)
C(1d)	1.0884 (4)	0.9059 (3)	0.4086 (2)	0.052 (2)
F(1d)	1.0526 (2)	1.0058 (2)	0.41196 (13)	0.0745 (12)
F(2d)	1.1930 (2)	0.9147 (3)	0.41877 (14)	0.0888 (13)
F(3d)	1.0716 (3)	0.8461 (3)	0.45393 (12)	0.107 (2)
O(1f)	0.9190 (2)	0.0236 (3)	0.11221 (12)	0.0365 (9)
O(1g)	0.9050 (3)	1.1088 (3)	0.2659 (2)	0.0466 (12)
Na	0.78861 (11)	0.96375 (11)	0.24882 (7)	0.0390 (5)

Table 2. Bond lengths (\AA) and angles ($^\circ$) for the non-H atoms of [Co(trpn)(H₂O)₂][Na(CF₃O₃S)₄H₂O].H₂O

Co—O(1)	1.975 (3)	N(5)—C(10)	1.516 (5)
Co—O(2)	1.980 (2)	N(9)—C(8)	1.482 (4)
Co—N(1)	1.988 (3)	N(13)—C(12)	1.486 (5)
Co—N(5)	2.006 (3)	C(2)—C(3)	1.497 (5)
Co—N(9)	1.956 (3)	C(3)—C(4)	1.518 (5)
Co—N(13)	1.943 (3)	C(6)—C(7)	1.514 (5)
N(1)—C(2)	1.478 (4)	C(7)—C(8)	1.512 (5)
N(5)—C(4)	1.511 (4)	C(10)—C(11)	1.510 (5)
N(5)—C(6)	1.520 (4)	C(11)—C(12)	1.496 (5)
O(1)—Co—O(2)	86.29 (11)	C(4)—C(3)—C(2)	112.2 (3)
O(1)—Co—N(1)	86.63 (12)	N(5)—C(4)—C(3)	115.3 (3)
O(1)—Co—N(5)	94.92 (11)	C(6)—N(5)—C(10)	106.2 (3)
O(1)—Co—N(9)	89.18 (11)	C(6)—N(5)—Co	109.6 (2)
O(2)—Co—N(1)	87.55 (12)	C(6)—N(5)—C(4)	107.8 (2)
O(2)—Co—N(5)	175.51 (11)	C(10)—N(5)—Co	114.7 (2)
O(2)—Co—N(9)	86.68 (12)	C(10)—N(5)—C(4)	105.2 (3)
O(2)—Co—N(13)	83.27 (12)	Co—N(5)—C(4)	112.9 (2)

Table 2 (cont.)

N(1)—Co—N(5)	96.83 (11)	C(7)—C(6)—N(5)	115.8 (3)
N(1)—Co—N(9)	173.07 (14)	C(8)—C(7)—C(6)	115.7 (3)
N(1)—Co—N(13)	91.95 (13)	N(9)—C(8)—C(7)	113.1 (3)
N(5)—Co—N(9)	89.02 (11)	Co—N(9)—C(8)	118.3 (2)
N(5)—Co—N(13)	95.56 (12)	C(11)—C(10)—N(5)	116.7 (3)
N(9)—Co—N(13)	91.17 (12)	C(12)—C(11)—C(10)	112.1 (3)
N(13)—Co—O(1)	169.51 (12)	N(13)—C(12)—C(11)	112.1 (3)
C(2)—N(1)—Co	125.5 (2)	Co—N(13)—C(12)	125.4 (2)
C(3)—C(2)—N(1)	113.9 (3)		
O(1a)—S(1a)	1.431 (3)	O(1c)—S(1c)	1.434 (3)
O(2a)—S(1a)	1.428 (3)	O(2c)—S(1c)	1.440 (2)
O(3a)—S(1a)	1.444 (2)	O(3c)—S(1c)	1.431 (2)
Na—O(1a)	2.656 (3)	Na—O(3c)	2.353 (3)
Na—O(2a)	2.683 (3)	F(1c)—C(1c)	1.334 (4)
F(1a)—C(1a)	1.324 (5)	F(2c)—C(1c)	1.300 (5)
F(2a)—C(1a)	1.318 (6)	F(3c)—C(1c)	1.329 (5)
F(3a)—C(1a)	1.302 (6)	O(1d)—S(1d)	1.438 (3)
O(1b)—S(1b)	1.423 (3)	O(2d)—S(1d)	1.429 (3)
O(2b)—S(1b)	1.434 (3)	O(3d)—S(1d)	1.446 (3)
O(3b)—S(1b)	1.435 (3)	Na—O(2d)	2.336 (3)
Na—O(3b)	2.253 (4)	F(1d)—C(1d)	1.310 (5)
F(1b)—C(1b)	1.305 (5)	F(2d)—C(1d)	1.317 (5)
F(2b)—C(1b)	1.310 (5)	F(3d)—C(1d)	1.298 (6)
F(3b)—C(1b)	1.330 (5)	Na—O(1g)	2.293 (4)
O(1a)—S(1a)—O(2a)	114.3 (2)	O(1c)—S(1c)—O(2c)	114.3 (2)
O(2a)—S(1a)—O(3a)	113.7 (2)	O(2c)—S(1c)—O(3c)	114.18 (14)
O(3a)—S(1a)—O(1a)	114.22 (15)	O(3c)—S(1c)—O(1c)	115.6 (2)
Na—O(1a)—S(1a)	95.2 (2)	Na—O(3c)—S(1c)	134.3 (2)
Na—O(2a)—S(1a)	94.13 (13)	F(1c)—C(1c)—F(2c)	108.8 (3)
F(1a)—C(1a)—F(2a)	106.4 (3)	F(2c)—C(1c)—F(3c)	107.7 (3)
F(2a)—C(1a)—F(3a)	108.7 (4)	F(3c)—C(1c)—F(1c)	107.1 (3)
F(3a)—C(1a)—F(1a)	109.8 (3)	O(1d)—S(1d)—O(2d)	115.1 (2)
O(1b)—S(1b)—O(2b)	115.2 (2)	O(2d)—S(1d)—O(3d)	114.82 (15)
O(2b)—S(1b)—O(3b)	113.6 (2)	O(3d)—S(1d)—O(1d)	113.7 (2)
O(3b)—S(1b)—O(1b)	114.6 (2)	Na—O(2d)—S(1d)	130.0 (2)
Na—O(3b)—S(1b)	135.6 (2)	F(1d)—C(1d)—F(2d)	106.7 (4)
F(1b)—C(1b)—F(2b)	108.9 (4)	F(2d)—C(1d)—F(3d)	108.8 (3)
F(2b)—C(1b)—F(3b)	106.1 (3)	F(3d)—C(1d)—F(1d)	109.1 (4)
F(3b)—C(1b)—C(1b)	108.3 (3)		
O(1a)—Na—O(2a)	53.47 (9)	O(2a)—Na—O(1g)	155.58 (14)
O(1a)—Na—O(3a)	143.27 (10)	O(2c)—Na—O(3c)	92.90 (11)
O(1a)—Na—O(3c)	90.97 (10)	O(3b)—Na—O(2d)	96.59 (11)
O(1a)—Na—O(2d)	80.13 (10)	O(3b)—Na—O(1g)	114.54 (13)
O(1a)—Na—O(1g)	102.11 (13)	O(3c)—Na—O(2d)	170.27 (13)
O(2a)—Na—O(3b)	89.86 (10)	O(3c)—Na—O(1g)	87.61 (11)
O(2a)—Na—O(3c)	92.57 (9)	O(2d)—Na—O(1g)	90.39 (11)
O(2a)—Na—O(2d)	85.32 (9)		

the anomalous-dispersion corrections taken from the work of Cromer & Liberman (1970). The scattering factors for the H atoms were obtained from Stewart, Davidson & Simpson (1965). Values used to calculate the linear absorption coefficient are from *International Tables for X-ray Crystallography* (1974, Vol. IV, p. 55). Figs. 1 and 2, showing the Co and Na complexes, respectively, and Fig. 3 showing the unit-cell packing, were produced using *SHELXTL-Plus*. Other computer programs used in this work are listed elsewhere (Gadol & Davis, 1982). Table 1 lists positional parameters and Table 2 geometrical parameters.*

* Lists of anisotropic thermal parameters, H-atom positional parameters, bond distances and angles involving the H atoms, torsional angles and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55125 (33 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST0558]

Related literature. The triflate group has been reported coordinated to an Li ion as a monodentate ligand by O'Connor, Uhrhammer, Rheingold & Staley (1989) and by Shumann, Meese-Markscheffel & Loebel (1990). In both cases, one triflate acts as a bridge between two Li atoms. In contrast, in the structure in this report it is coordinated to the Na ion as a bidentate ligand. As for complexes with the

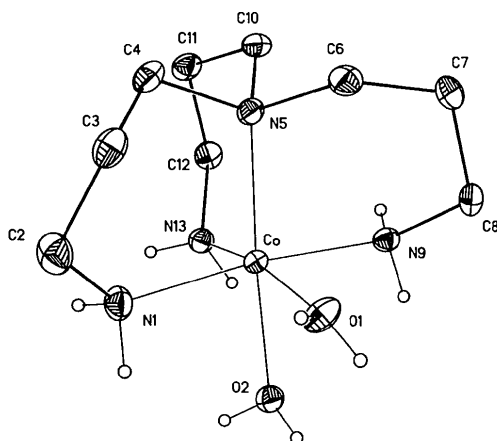


Fig. 1. View of $[\text{Co}(\text{trpn})(\text{H}_2\text{O})_2]^{3+}$ complex showing the atom-labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Methylene H atoms are omitted for clarity; other H atoms are represented as spheres of arbitrary size.

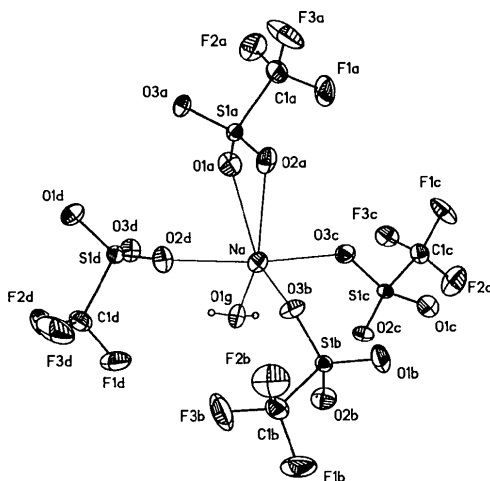


Fig. 2. View of $[\text{Na}(\text{CF}_3\text{O}_3\text{S})_2(\text{H}_2\text{O})]^{3-}$ anion complex showing the atom-labeling scheme. Thermal ellipsoids are scaled to the 30% probability level.

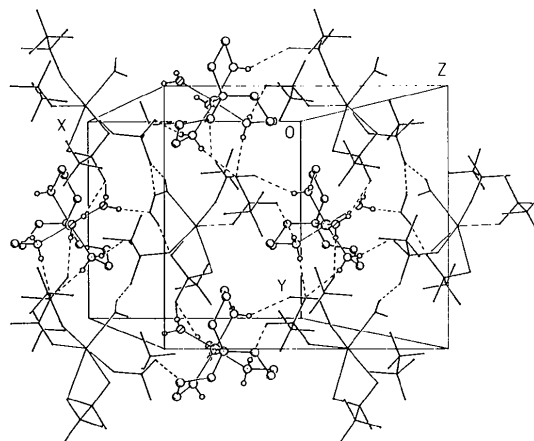


Fig. 3. View of unit-cell packing for $[\text{Co}(\text{trpn})(\text{H}_2\text{O})_2][\text{Na}(\text{CF}_3\text{OS})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$. The cobalt(III) complex ion is shown with spheres of arbitrary size while the Na triflate complex ion is shown by line drawing. The complex packs in layers perpendicular to c^* . The tertiary amine of the cation and the triflate group of the anion from the outer boundaries of each layer. Within each layer an extended H-bonding network exists as indicated by the dashed lines.

trpn ligand, only two structures have been reported (Shafer & Raymond, 1971; Banaszczyk, Lee & Menger, 1991).

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