Crystal Structure of *trans*-Aquabis(ethylenediamine)sulphitocobalt(III) Perchlorate Monohydrate

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The crystal structure of the title compound, previously reported as having one less molecule of water, has been determined from *X*-ray diffractometer data and refined by least squares to *R* 0·080 for 1455 observed reflections. Crystals are monoclinic, space group $P2_1/n$, $a = 11{\cdot}210(3)$, $b = 13{\cdot}626(2)$, $c = 9{\cdot}727(3)$ Å, $\beta = 105{\cdot}17(2)°$, $Z = 4$. Interatomic distances are: mean Co–N 1·94, Co–S 2·181(3), Co–O 2·037(7), mean Cl–O 1·41, and mean S–O 1·46 Å. The Co–OH_2 distance is long, presumably as a consequence of the *trans*-effect of the sulphite ligand.

THE present structure determination was carried out for two reasons. (i) Examination of the reactions of the complex formulated [1] by Werner as $[Co(en)_2SO_3]Cl,H_2O$ (en = ethylenediamine) has provoked the suggestion that a more correct description of the complex and its properties may be made in terms of the formula $[Co(en)_2(SO_3)(H_2O)]Cl$.[2] Kinetic studies have shown that the sulphite ligand exerts a very large *trans*-effect in cobalt(III) complexes; [3] for example, there is at least a 10^6 increase in the water exchange rate in $[Co(en)_2(SO_3)(H_2O)]^+$ compared to $[Co(en)_2(H_2O)_2]^{3+}$.[3,4] The origin of this enormous *trans*-effect is unclear. It has been proposed [4] that the dominant factor resulting in *trans*-labilization is stabilization of the transition state, although there is evidence of an unusually weak Co–OH_2 bond in the ground state, *e.g.* both $[Co(en)_2(SO_3)(H_2O)]Cl$ and its perchlorate analogue lose water readily, the latter simply when pumped under vacuum at room temperature. We expected that a ground-state effect would be reflected in a long cobalt–oxygen bond, and hence a crystal-structure determination might help distinguish between ground- and transition-state effects.

(ii) The recent determination of the crystal structure of aquasulphitoquaterpyridylcobalt(III) nitrate monohydrate [5] has shown the presence of a cobalt–sulphur bond [2·244(2) Å] appreciably longer than that found in *trans*-bis(ethylenediamine)isothiocyanatosulphitocobalt(III) dihydrate [2·203(6) Å].[6] In order to determine the relative importance of the *trans*-substituent and the presence or absence of a π-bonding ligand in determining this distance, it was considered of interest to determine the structure of the present system, since it appeared likely from the evidence in (i) that it might provide an extreme example.

EXPERIMENTAL

The complex was prepared as described in the literature. A single crystal 0·07 × 0·12 × 0·13 mm was selected for the crystallographic work. Cell dimensions were obtained from a least-squares fit of the angular parameters of 15 reflections centred in the counter aperture of a Syntex $P\bar{1}$ diffractometer. A unique data set was collected in the range $2\theta < 100°$ by a conventional 2θ—θ scan yielding 1478 reflections of which 1455 having $I > \sigma(I)$ were considered observed and used in the subsequent solution and refinement after absorption correction.

Crystal Data.—$C_4ClCoH_{20}N_4O_9S$, $M = 394{\cdot}7$, Monoclinic, $a = 11{\cdot}210(3)$, $b = 13{\cdot}626(2)$, $c = 9{\cdot}727(3)$ Å, $\beta = 105{\cdot}17(2)°$, $U = 1434{\cdot}0(6)$ Å^3, $D_m = 1{\cdot}82(1)$, $Z = 4$, $D_c = 1{\cdot}83$ g cm^{-3}, $F(000) = 820$, Cu-K_α radiation (Ni filtered), $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 125·8 cm^{-1}. Space group $P2_1/n$ (C^5_{2h}, No. 14).

The structure was solved by the heavy-atom method and refined by block-diagonal least-squares, the parameters of the cation and those of the remainder of the structure being refined as separate blocks in the final stages to approximate to a full-matrix process. Scattering factors employed were for the neutral atoms,[7] those for cobalt and sulphur being corrected for anomalous dispersion effects ($\Delta f',\Delta f''$).[8] Hydrogen atoms were located from difference maps; attempts to refine them meaningfully failed and they were included in the structure as invariants with fixed isotropic thermal parameters. Anisotropic thermal parameters for the remainder of the structure were of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. A weighting scheme of the form $w = (\sigma^2(F_o) + n \times 10^{-4}(F_o)^2)^{-1}$ was used, a value of $n = 3$ being found appropriate. No parameter shift in the final least-squares cycle exceeded $0{\cdot}03\sigma$ and refinement converged at R 0·080 and R' 0·081, $[R' = \Sigma w(||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]$.

Structure factors and hydrogen atom positional parameters are deposited as Supplementary Publication No. SUP 21169 (8 pp., 1 microfiche).† Computation was carried out on an adaptation of the *X*-RAY '72 system on the CDC 6200 machine at this University.[9] Final positional and thermal parameters are listed in Table 1, bond lengths and angles in Table 2. Unit-cell contents are illustrated in Figure 1. Details of the CoN_4 plane are in Table 3.

DISCUSSION

X-Ray structure determination shows that the complex reported in the literature as *trans*-$[Co(en)_2(SO_3)(H_2O)](ClO_4)$ is the monohydrate, *trans*-$[Co(en)_2(SO_3)(H_2O)]ClO_4,H_2O$, although the conclusion that the cation is *trans*-$[Co(en)_2(SO_3)(H_2O)]^+$ rather than $[Co(en)_2SO_3]^+$ (or some polymeric variety) is correct.

† For details, see Notice to Authors, No. 7, in *J.C.S. Dalton*, 1973, Index issue.

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TABLE 1

Atomic fractional cell ($\times 10^4$) and thermal parameters ($\times 10^3$ Å^2), with estimated standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	3290(1)	2021(1)	2828(2)	16(1)	19(1)	25(1)	1(1)	−6(1)	−2(1)
S	1619(2)	2865(2)	1908(3)	24(2)	25(2)	31(2)	5(1)	−6(1)	1(1)
O(1)	0902(7)	2279(6)	0708(8)	37(5)	63(6)	47(5)	30(5)	−40(4)	−21(5)
O(2)	0928(6)	3007(5)	2957(8)	19(4)	34(5)	55(5)	12(4)	10(4)	13(4)
O(3)	1931(7)	3817(6)	1376(8)	47(5)	28(5)	67(6)	8(4)	8(4)	24(4)
O(4)	4808(6)	1180(5)	3670(7)	23(4)	35(5)	37(5)	16(4)	−16(4)	−12(4)
N(11)	2270(8)	0882(6)	2965(9)	23(5)	20(6)	31(6)	−2(4)	−7(5)	−1(4)
C(11)	1892(11)	0908(8)	4311(13)	38(8)	26(8)	66(10)	−2(6)	15(7)	0(6)
C(12)	2898(10)	1417(9)	5395(12)	31(7)	55(9)	42(8)	8(7)	1(6)	5(7)
N(12)	3246(7)	2305(6)	4747(8)	11(5)	23(6)	35(5)	−1(4)	−8(4)	7(4)
N(21)	3418(8)	1691(6)	0921(9)	25(5)	37(6)	29(5)	0(5)	0(4)	2(5)
C(21)	4053(13)	2488(10)	0342(13)	77(10)	48(9)	45(8)	−7(8)	22(8)	−7(7)
C(22)	4966(12)	2965(10)	1574(14)	57(9)	63(10)	69(9)	−25(8)	36(8)	−7(8)
N(22)	4374(7)	3123(6)	2742(9)	20(5)	23(5)	37(6)	−6(4)	−1(4)	0(4)
Cl	3249(3)	4658(2)	6485(3)	41(2)	36(2)	60(2)	8(2)	−1(2)	−5(2)
O(11)	2559(11)	3862(8)	6753(13)	132(11)	77(8)	133(10)	−32(8)	68(9)	2(7)
O(12)	3303(12)	4599(7)	5043(12)	167(12)	66(7)	93(8)	6(8)	78(9)	−12(6)
O(13)	4416(12)	4653(9)	7414(17)	106(10)	98(11)	247(17)	51(9)	−97(11)	−23(10)
O(14)	2657(9)	5562(7)	6678(9)	95(8)	64(7)	53(6)	47(6)	−3(5)	−6(5)
O(5)	5005(7)	−0131(5)	1725(8)	45(5)	28(5)	53(5)	0(4)	11(4)	−9(4)

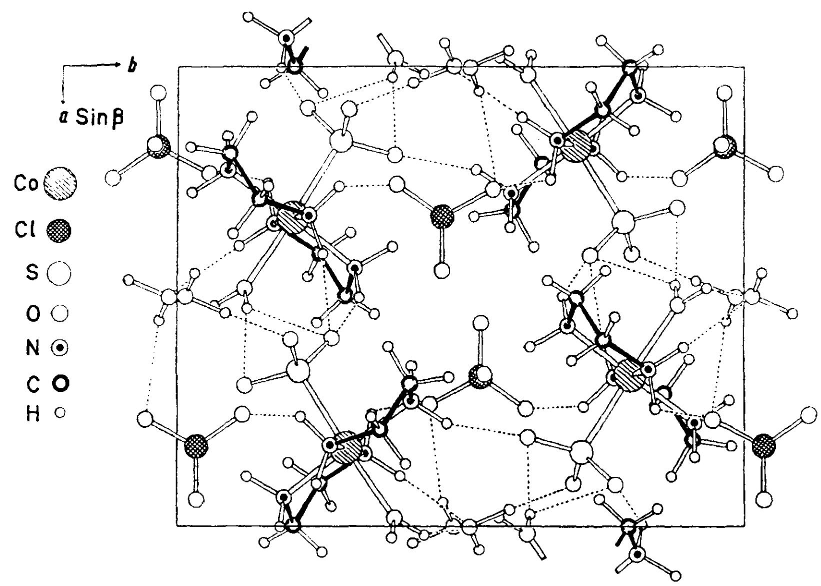

FIGURE 1 Unit-cell contents, projected down c; dotted lines indicate hydrogen bonding within the lattice

In the cation, the two ethylenediamine ligands are bound to the cobalt with Co–N distances not significantly different from the usual values, the ligands

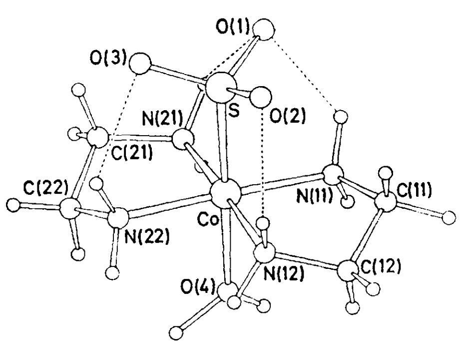

FIGURE 2 The cation geometry; dotted lines indicate hydrogen-bonding within the cation. Atomic numbering is given

adopting the usual *meso*-configuration. The disposition with respect to the sulphite group also agrees with that observed previously in *trans*-[Co(en)$_2$(SO$_3$)(SCN)],3H$_2$O,[6] and is presumably a consequence of the requirements of intra-cation hydrogen bonding (Figure 2, Table 2). O(2) and O(3) are disposed towards N(12) and N(22) respectively *via* a single hydrogen bond, whereas O(1) is disposed between N(11) and N(21) and is hydrogen bonded to both. As a consequence, the distances S–N(11) and S–N(21) [2·92 and 2·93(1) Å] are shorter than S–N(12) and S–N(22) [2·98 and 3·00(1) Å], while the ethylenediamine rings are distorted so that the deviations of C(12) and C(22) on one side of the CoN$_4$ plane are considerably greater than those of C(11) and C(21) on the other. The cobalt atom lies slightly above the plane of the co-ordinating nitrogen atoms and towards the sulphur atom.

As expected the high lability of the aqua-ligand in the sulphito-complex is accompanied by an appreciable increase in the cobalt–oxygen bond length [2·037(7) Å] compared to the only other well authenticated Co^{III}–OH$_2$

TABLE 2

Interatomic distances (Å) and angles (°), with least squares estimated standard deviations in parentheses

(*a*) The cation

(i) Co environment

Co–S	2·181(3)	S–Co–O(4)	177·6(2)
Co–O(4)	2·037(7)	S–Co–N(11)	89·5(2)
Co–N(11)	1·953(9)	S–Co–N(12)	93·1(2)
Co–N(12)	1·920(9)	S–Co–N(21)	90·0(3)
Co–N(21)	1·950(9)	S–Co–N(22)	93·1(2)
Co–N(22)	1·947(9)	O(4)–Co–N(11)	88·2(3)
		O(4)–Co–N(12)	87·4(3)
N(11)–Co–N(12)	85·9(4)	O(4)–Co–N(21)	88·5(3)
N(11)–Co–N(21)	94·1(4)	O(4)–Co–N(22)	89·2(3)
N(11)–Co–N(22)	177·4(3)	N(12)–Co–N(21)	176·8(3)
N(21)–Co–N(22)	86·3(4)	N(12)–Co–N(22)	93·5(4)

(ii) Ligands

S–O(1)	1·467(8)	O(1)–S–O(2)	110·6(5)
S–O(2)	1·446(9)	O(1)–S–O(3)	109·3(5)
S–O(3)	1·473(8)	O(2)–S–O(3)	110·5(5)
		O(1)–S–Co	105·8(3)
O(3)–S–Co	110·6(3)	O(2)–S–Co	110·0(3)
N(11)–C(11)	1·48(2)	Co–N(11)–C(11)	110·5(6)
C(11)–C(12)	1·50(2)	N(11)–C(11)–C(12)	107·3(10)
C(12)–N(12)	1·46(2)	C(11)–C(12)–N(12)	108·4(9)
		C(12)–N(12)–Co	109·2(7)
N(21)–C(21)	1·49(2)	Co–N(21)–C(21)	110·7(7)
C(21)–C(22)	1·51(2)	N(21)–C(21)–C(22)	107·8(10)
C(22)–N(22)	1·47(2)	C(21)–C(22)–N(22)	109·1(11)
		C(22)–N(22)–Co	109·4(7)

(*b*) The anion

Cl–O(11)	1·40(1)	O(11)–Cl O(12)	108·0(7)
Cl–O(12)	1·42(1)	O(11)–Cl–O(13)	110·5(8)
Cl–O(13)	1·38(1)	O(11)–Cl–O(14)	110·2(7)
Cl–O(14)	1·44(1)	O(12)–Cl–O(13)	111·6(9)
		O(12)–Cl–O(14)	108·5(6)
		O(13)–Cl–O(14)	108·0(7)

(*c*) Interspecies hydrogen bonded contacts

N(11)[H(11a)] $\cdots$ O(1)	3·01(1) (2·36)
N(12)[H(12a)] $\cdots$ O(11)	3·11(2) (2·41)
N(12) [H(12b)] $\cdots$ O(2)	2·89(1) (2·23)
N(21)[H(21b)] $\cdots$ O(14^{I})	2·94(1) (2·31)
N(22)[H(22a)] $\cdots$ O(1^{II})	3·00(1) (2·07)
O(4)[H(4a)] $\cdots$ O(5)	2·65(1) (1·80)
O(4)[H(4b)] $\cdots$ O(3)	3·05(1) (2·06)
O(5)[H5b)] $\cdots$ O(14^{III})	3·04(1) (2·36)
N(11)[H(11b)] $\cdots$ O(3^{I})	2·97(1) (2·08)
N(12)[H(12b)] $\cdots$ O(1^{II})	2·93(1) (2·00)
N(21)[H(21a)] $\cdots$ O(5)	3·04(1) (2·07)
N(21)[H(21b)] $\cdots$ O(1)	2·89(1) (2·23)
N(22)[H(22b)] $\cdots$ O(3)	2·87(1) (2·20)
O(4)[H(4b)] $\cdots$ O(1^{II})	2·93(1) (2·25)
O(5)[H(5a)] $\cdots$ O(2^{I})	2·79(1) (1·72)

Transformation of the asymmetric unit (x, y, z)

I ($\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$) II ($1 + x, \frac{1}{2} - y, \frac{1}{2} + z$)
III ($\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$)

TABLE 3

Details of the CoN_4 plane

Equation of plane, in orthogonal (Å) co-ordinates X, Y, Z where $X = ax + cz\cos\beta$, $Y = by$, $Z = cz\sin\beta$:

$$0{\cdot}7406X - 0{\cdot}5600Y + 0{\cdot}3713Z = 1{\cdot}6810 \ (\sigma = 0{\cdot}02 \text{ Å})$$

Deviations (Å) of (i) Defining atoms: N(11) 0·00, N(12) N(21), N(22) 0·01

(ii) Other atoms: Co −0·04, C(11) −0·11, C(12) 0·51, C(21) −0·16, C(22) 0·43

value [1·98(1) Å] in the more inert complex *cis*-aqua-β-chlorotrisethylenetetraminecobalt(III) perchlorate.[10] The increased bond length implies that, at least in part, the *trans*-effect of the sulphito-ligand must be assigned a ground-state origin. This conclusion is supported by the recently reported crystal structure of $[Co(NH_3)_5(SO_3)]NO_3$ in which the *trans*-cobalt–nitrogen distance (2·055 Å) is much longer than *cis*-cobalt–nitrogen distance (mean 1·966 Å).[11] It is curious, therefore, that in the complex *trans*-$[Co(en)_2(SO_3)(NCS)]$, the cobalt–thiocyanato-bond length was not found to be abnormally long.

Since the well studied *trans*-effect in cobalt(III) corrinoids [12] is paralleled by a smaller *cis*-effect, which is reflected in increased cobalt–corrin nitrogen distances (1·86 Å in vitamin B_{12} up to 1·94 Å in DBC coenzyme [13]), a similar, although smaller, increase might have been expected in the sulphito-complexes. However, the data do not support this expectation; if anything, the *cis*-cobalt–nitrogen bond lengths in both $[Co(en)_2(SO_3)(H_2O)]^+$ (mean 1·94 Å) and $[Co(NH_3)_5(SO_3)]^+$ (1·966 Å) are shorter than in similar complexes without sulphite.[14]

Considerable variation has been found in the cobalt(III)–sulphite distances in the crystal structures of the three sulphito-complexes with saturated ancillary ligands {*trans*-$[Co(en)_2(SO_3)(H_2O)]^+$ 2·181(3), *trans*-$[Co(en)_2(SO_3)(SCN)]$ 2·203(6), and $[Co(NH_3)_5SO_3]$ 2·218 Å}, but the cation with the strongly π bonding quaterpyridyl ligand *trans*-$[Co(quaterpy)(SO_3)(H_2O)]^+$ has an extraordinarily long cobalt–sulphur bond length [2·244(4) Å] lying outside the range in the other three complexes.

The sulphite geometry is comparable with that observed in the other examples (Table 4), showing the

TABLE 4

Sulphite geometry in Co^{III}–SO_3 complexes

	Mean S–O/ Å	Mean O–S–O/ (°)
$[Co(quaterpy)(SO_3)(H_2O)]NO_3,H_2O$	1·456	111·9
$[Co(en)_2(SO_3)(SCN)],2H_2O$	1·485	110·3
$[Co(en)_2(SO_3)(H_2O)]ClO_4,H_2O$	1·462	110·1
$[Co(NH_3)_5(SO_3)]_2SO_3$	1·483	

usual S–O contraction and O–S–O expansion when compared with the free ion (typically >1·50 Å, <106°); the accuracy is not great enough to allow any meaningful conclusion to be drawn about any possible correlation with the Co–S distance, except perhaps in the case of the quaterpyridyl complex.

The perchlorate anion is well ordered, although its thermal motion is rather higher than that of the remainder of the structure; the geometry is normal and not significantly distorted from tetrahedral. It is hydrogen bonded through two of the oxygen atoms to ethylenediamine (nitrogen) hydrogen atoms on adjacent molecules and to the lattice water (Figure 1, Table 2).

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