Crystal Structure of Aqua(2,2′:6′,2″:6″,2‴-quaterpyridyl)sulphitocobalt(III) Nitrate Monohydrate

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The crystal structure of the title compound has been determined by the heavy-atom method from *X*-ray diffractometer data and refined by block-diagonal least-squares to *R* 0·056 for 1891 observed reflections. Crystals are monoclinic, space group $P2_1/n$, a = 19·005(4), b = 15·598(3), c = 6·913(1) Å, β = 92·34(1)°, Z = 4.

The quaterpyridyl ligand is planar and coplanar with the cobalt, the inner nitrogen atoms bonding to it at a shorter distance (1·855 ± 0·005) than the outer (1·97 ± 0·01 Å). Co–OH$_2$ is 2·067(5) and Co–S 2·244(2) Å. The nitrate ion is disordered.

As yet no structural data are available on complexes of the ligand 2,2′:6′,2″:6″,2‴-quaterpyridyl (quaterpy). During the course of a series of structure determinations on derivatives of 2,2′:6′,2″-terpyridyl (terpy), a derivative of quaterpy was fortuitously isolated; its structure has been determined and is now reported.

TABLE 1

Atomic fractional cell (x, y, z) and thermal parameters ($\times 10^3$) for non-hydrogen atoms, with least squares estimated standard deviations in parentheses; a decimal point precedes (x, y, z)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	28324(6)	49232(7)	4807(2)	30·9(8)	19·4(7)	30·8(8)	−2·1(5)	4·4(5)	−2·3(5)
(*a*) Ligand									
N(1)	2133(3)	5713(4)	5912(8)	29(4)	28(3)	31(4)	−4(3)	2(3)	−4(3)
N(2)	3324(3)	5950(4)	4483(8)	31(4)	26(3)	23(3)	−4(3)	2(3)	−2(3)
N(3)	3622(3)	4502(4)	3654(8)	28(3)	31(4)	27(3)	−4(3)	1(3)	5(3)
N(4)	2553(3)	3723(3)	4774(8)	35(4)	22(3)	21(3)	3(3)	5(3)	−1(3)
C(1)	1518(4)	5548(5)	664(1)	47(5)	34(5)	53(6)	−3(4)	7(4)	−8(4)
C(2)	1037(4)	6168(6)	712(1)	37(5)	54(6)	70(7)	1(4)	13(5)	−8(5)
C(3)	1213(4)	7006(5)	683(1)	48(6)	39(5)	58(6)	10(4)	15(4)	−12(4)
C(4)	1857(4)	7180(4)	612(1)	62(6)	21(4)	36(5)	10(4)	−4(4)	2(4)
C(5)	2330(4)	6549(4)	568(1)	39(5)	24(4)	23(4)	3(3)	−5(3)	−6(3)
C(6)	3028(4)	6675(5)	498(1)	31(4)	33(4)	30(4)	−8(4)	−3(3)	−2(4)
C(7)	3384(4)	7427(5)	475(1)	59(6)	35(5)	35(5)	−9(4)	−2(4)	−8(4)
C(8)	4056(4)	7401(5)	402(1)	56(6)	32(5)	39(5)	−22(4)	−12(4)	7(4)
C(9)	4341(4)	6641(5)	344(1)	52(5)	41(5)	41(5)	−17(4)	−1(4)	6(4)
C(10)	3956(4)	5905(5)	368(1)	27(4)	36(4)	30(4)	−8(4)	−4(3)	6(4)
C(11)	4147(4)	5035(5)	321(1)	29(4)	34(4)	27(4)	−4(3)	−2(3)	1(3)
O(12)	4743(4)	4743(5)	241(1)	33(5)	48(5)	40(5)	−4(4)	5(4)	9(4)
C(13)	4795(4)	3871(5)	210(1)	23(4)	57(6)	46(5)	9(4)	6(4)	3(4)
C(14)	4269(4)	3333(5)	257(1)	45(5)	37(5)	39(5)	5(4)	0(4)	−4(4)
C(15)	3676(4)	3660(5)	337(1)	28(4)	34(4)	30(4)	4(4)	2(3)	−2(4)
C(16)	3050(4)	3214(4)	401(1)	31(4)	26(4)	30(4)	5(4)	−1(4)	−1(3)
C(17)	2970(4)	2339(5)	392(1)	50(5)	25(4)	28(4)	11(4)	0(4)	−11(4)
C(18)	2365(4)	1991(5)	458(1)	56(5)	27(4)	29(4)	−4(4)	−13(4)	−2(4)
C(19)	1850(4)	2503(7)	529(1)	38(5)	23(4)	40(5)	−5(4)	3(4)	−1(4)
C(20)	1966(4)	3370(5)	537(1)	26(4)	28(4)	39(5)	−7(3)	13(4)	0(4)
(*b*) Sulphite									
S	3297(1)	4699(1)	7797(3)	37(1)	30(1)	34(1)	0(1)	0(1)	−2(1)
O(1)	2707(3)	4372(3)	8875(7)	42(3)	40(3)	42(3)	−7(3)	15(3)	1(3)
O(2)	3560(3)	5503(3)	8589(7)	51(4)	26(3)	47(3)	−5(3)	−8(3)	−8(3)
O(3)	3855(3)	4065(3)	7648(7)	36(3)	35(3)	36(3)	4(3)	−4(2)	2(3)
(*c*) Co-ordinated water									
O(4)	2281(3)	5097(3)	2193(7)	43(3)	30(3)	34(3)	−2(2)	2(3)	−3(2)
(*d*) Lattice water									
O(5)	0928(4)	4583(4)	215(1)	66(5)	73(5)	120(6)	7(4)	−5(4)	−26(5)
(*e*) Nitrate									
N(5)	0109(5)	3678(5)	718(2)	66(6)	48(5)	22(13)	−29(5)	38(7)	−15(7)
O(6)	−0433	3687(5)	798(1)	91(6)	63(5)	193(9)	−14(4)	62(6)	2(5)
O(7)	0293(4)	3120(5)	606(1)	81(6)	73(5)	185(9)	−3(5)	33(6)	−9(6)
O(81) *	0616(8)	4106(9)	808(2)	126(13)	115(12)	141(14)	−67(10)	23(10)	−4(10)
O(82) *	0186(11)	4428(10)	585(3)	159(19)	83(13)	124(16)	−57(12)	−17(13)	22(11)

* Populations: O(81) 0·63(2), O(82) 0·49(2).

EXPERIMENTAL

[Co(terpy)$_2$](NO$_3$)$_2$ (*ca.* 1 g) Was prepared by standard methods;[1] crystals obtained by cooling an aqueous solution were unsatisfactory for crystallographic work and the solution was diluted and allowed to evaporate slowly in air during several weeks. At first a very few well-formed small crystals were obtained, and were assumed to be representative of the bulk phase. In retrospect, it

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[1] J. S. Judge and W. A. Baker, *Inorg. Chim. Acta*, 1967, **1**, 68.

is evident that this was not so and that they were a very small quantity of a quite insoluble product, presumably generated by impurity traces in the reagents and by aerial oxidation. *X*-Ray structure determination has shown the product to be [Co(quaterpy)(SO_3)(H_2O)]NO_3,H_2O.

A single crystal 0·08 × 0·10 × 0·18 mm was used for *X*-ray work. Cell dimensions were obtained by 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 in the range $2\theta < 100°$ was collected by using a conventional $2\theta/\theta$ scan. 1891 Independent reflections having $I > \sigma(I)$ were considered observed and used in the structure solution and refinement with unit weights.

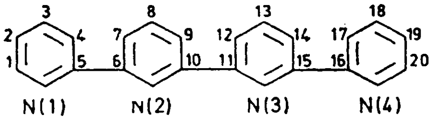
Crystal Data.—$C_{20}H_{18}CoN_5O_8S$, $M = 547{\cdot}4$, Monoclinic, $a = 19{\cdot}005(4)$, $b = 15{\cdot}598(3)$, $c = 6{\cdot}913(1)$ Å, $\beta = 92{\cdot}34(1)°$, $U = 2073{\cdot}8(6)$ Å^3, $Z = 4$, $D_c = 1{\cdot}753$ g cm^{-1}, $F(000) = 1120$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$; $\mu(\text{Cu-}K_\alpha) = 78{\cdot}2$ cm^{-1}. Space group $P2_1/n$ (C^5_{2h}, No. 14).

Scattering factors for neutral atoms were taken from ref. 2, values for cobalt and sulphur being corrected for the effects of anomalous dispersion ($\Delta f', \Delta f''$).[3] Data were corrected for absorption and the structure solved by the heavy-atom method and refined by 9 × 9 block-diagonal least-squares; during the latter stages of refinement, the CoN_4S molecular core with the five associated oxygen atoms O(1)—(5) were refined as a single block in order to approximate to a full matrix. All hydrogen atoms were located in difference maps and their positional parameters refined; thermal parameters of the pyridyl hydrogens were set at 0·05 Å^2 and those of the lattice water at 0·10 Å^2, thermal parameters being estimated from the size of the peak in the difference map. The nitrate group was found to be disordered; O(8) existed as a double peak in an electron-density map while N(5) was a seriously elongated ellipsoid, and O(6) and O(7) rather less so. O(8) Accordingly was refined as a pair O(81), O(82) with the population as a refinable parameter, while the disorder of the remaining atoms, being less, was accommodated by the thermal anisotropy. Anisotropic thermal parameters were of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. No parameter shift in the final cycle of refinement exceeded $0{\cdot}1\sigma$ and a final difference map showed no significant features. At convergence R was 0·056 and R' 0·056, $[R' = (\Sigma||F_o| - |F_c||^2/\Sigma|F_o|^2)^{\frac{1}{2}}]$.

Tables of structure factors and hydrogen atom parameters are given in Supplementary Publication No. SUP 21078 (12 pp., 1 microfiche).*

Computation was carried out by use of a local adaptation of the *X*-Ray '72 system, on a CDC 6200.[4]

The numbering used in the crystallographic analysis for the atoms in the quaterpyridyl ligand is shown in (I); hydrogen atoms are numbered according to the atom to which they are bonded. Final positional and thermal parameters are listed in Table 1, for non-hydrogen atoms, and bonds and angles are listed in Table 2. Unit-cell contents are illustrated in Figure 1 and a view of the cation



(I) Showing the crystallographic atom numbering

TABLE 2

Interatomic distances (Å) and angles (°) for non-hydrogen atoms, with least-squares estimated standard deviations in parentheses

(*a*) Co environment			
Co–N(1)	1·979(6)	N(1)–Co–N(2)	82·5(2)
Co–N(2)	1·860(6)	N(1)–Co–N(3)	163·1(2)
Co–N(3)	1·854(6)	N(1)–Co–N(4)	114·3(2)
Co–N(4)	1·960(6)	N(2)–Co–N(3)	80·6(3)
Co–O(4)	2·067(5)	N(2)–Co–N(4)	163·2(3)
Co–S	2·244(2)	N(3)–Co–N(4)	82·7(2)
		S–Co–N(1)	89·4(2)
O(4)–Co–N(1)	86·4(2)	S–Co–N(2)	93·9(2)
O(4)–Co–N(2)	91·6(2)	S–Co–N(3)	92·4(2)
O(4)–Co–N(3)	93·4(2)	S–Co–N(4)	87·2(2)
O(4)–Co–N(4)	89·0(2)	S–Co–O(4)	172·6(2)
(*b*) SO_3			
S–O(1)	1·463(6)	O(1)–S–O(2)	111·7(3)
S–O(2)	1·449(5)	O(1)–S–O(3)	111·9(3)
S–O(3)	1·457(5)	O(1)–S–O(4)	112·0(3)
		Co–S–O(1)	104·2(2)
		Co–S–O(2)	108·8(2)
		Co–S–O(3)	107·8(2)
(*c*) Quaterpyridyl ligand			
N(1)–C(1)	1·315(10)	Co–N(1)–C(1)	130·3(5)
N(1)–C(5)	1·366(9)	Co–N(1)–C(5)	110·6(4)
N(2)–C(6)	1·316(9)	Co–N(2)–C(6)	118·6(5)
N(2)–C(10)	1·345(9)	Co–N(2)–C(10)	117·9(5)
N(3)–C(11)	1·344(9)	Co–N(3)–C(11)	119·8(5)
N(3)–C(15)	1·322(9)	Co–N(3)–C(15)	119·2(5)
N(4)–C(16)	1·358(9)	Co–N(4)–C(16)	112·0(5)
N(4)–C(10)	1·325(9)	Co–N(4)–C(20)	128·9(5)
C(5)–C(6)	1·44(1)	N(1)–C(5)–C(6)	115·3(6)
C(10)–C(11)	1·45(1)	N(2)–C(6)–C(5)	112·3(6)
C(15)–C(16)	1·46(1)	N(2)–C(10)–C(11)	112·3(6)
C(1)–C(2)	1·38(1)	N(3)–C(11)–C(10)	109·4(6)
C(4)–C(5)	1·38(1)	N(3)–C(15)–C(16)	111·0(6)
C(6)–C(7)	1·37(1)	N(4)–C(16)–C(15)	115·3(6)
C(9)–C(10)	1·38(1)	N(1)–C(1)–C(2)	124·3(7)
C(11)–C(12)	1·36(1)	N(1)–C(5)–C(4)	118·3(7)
C(14)–C(15)	1·38(1)	N(2)–C(6)–C(7)	119·2(7)
C(16)–C(17)	1·38(1)	N(2)–C(10)–C(9)	119·7(7)
C(19)–C(20)	1·37(1)	N(3)–C(11)–C(12)	121·7(7)
C(2)–C(3)	1·37(1)	N(3)–C(15)–C(14)	119·6(7)
C(3)–C(4)	1·36(1)	N(4)–C(16)–C(17)	121·3(7)
C(7)–C(8)	1·39(1)	N(4)–C(20)–C(19)	122·3(7)
C(8)–C(9)	1·37(1)	C(4)–C(5)–C(6)	126·4(7)
C(12)–C(13)	1·38(1)	C(5)–C(6)–C(7)	128·4(7)
C(13)–C(14)	1·36(1)	C(9)–C(10)–C(11)	128·0(7)
C(17)–C(18)	1·37(1)	C(10)–C(11)–C(12)	128·9(7)
C(18)–C(19)	1·37(1)	C(14)–C(15)–C(16)	129·4(7)
		C(15)–C(16)–C(17)	123·3(7)
C(11)–C(12)–C(13)	117·4(7)	C(1)–C(2)–C(3)	117·6(8)
C(12)–C(13)–C(14)	120·9(7)	C(2)–C(3)–C(4)	118·2(8)
C(13)–C(14)–C(15)	119·5(7)	C(3)–C(4)–C(5)	122·7(7)
C(16)–C(17)–C(18)	118·2(7)	C(6)–C(7)–C(8)	118·8(7)
C(17)–C(18)–C(19)	120·8(7)	C(7)–C(8)–C(9)	120·7(7)
C(18)–C(19)–C(20)	118·2(7)	C(8)–C(9)–C(10)	118·0(8)
C(1)–N(1)–C(5)	118·8(6)	C(6)–N(2)–C(10)	123·5(6)
C(11)–N(3)–C(15)	120·9(6)	C(16)–N(4)–C(20)	119·1(6)
(*d*) NO_3			
N(5)–O(6)	1·19(1)	O(6)–N(5)–O(7)	125·2(9)
N(5)–O(7)	1·22(1)	O(6)–N(5)–O(81)	113·8(12)
N(5)–O(81)	1·31(2)	O(6)–N(5)–O(82)	112·6(11)
N(5)–O(82)	1·50(2)	O(7)–N(5)–O(81)	116·2(10)
O(81) · · · O(82)	1·79(2)	O(7)–N(5)–O(82)	97·6(11)
		O(81)–N(5)–O(82)	78·8(11)

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

[2] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[3] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[4] *X*-Ray system, version of June 1972, Computer Science Centre, Technical Report TR 192, University of Maryland, U.S.A.

in Figure 2. 50% Thermal ellipsoids are shown, hydrogen radii being arbitrarily set at 0·1 Å.

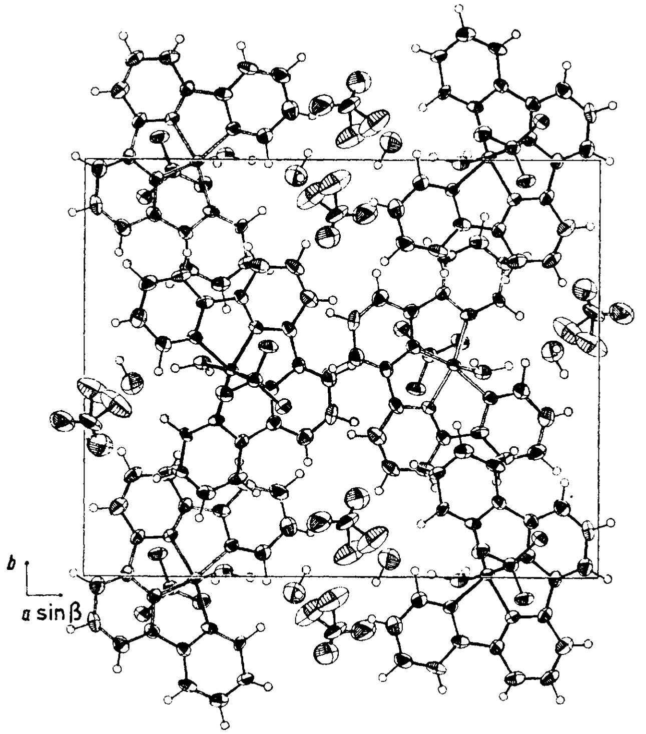

FIGURE 1 Unit-cell contents projected down *c*

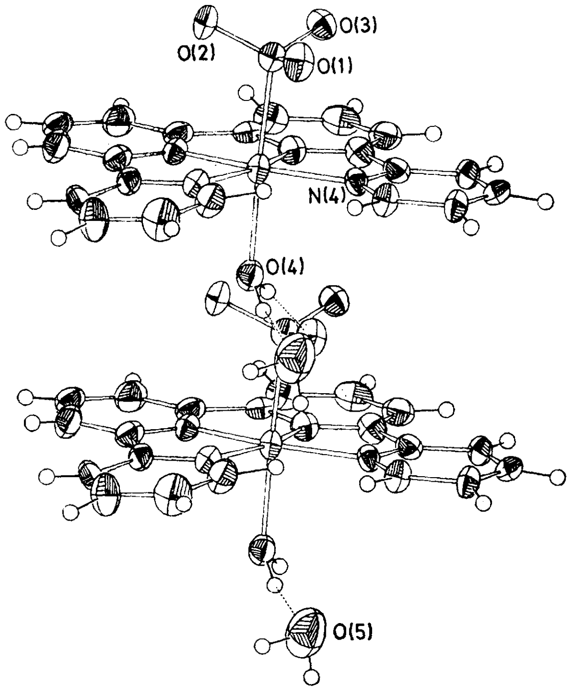

FIGURE 2 A view of the $[Co(H_2O)(SO_3)(quaterpy)]^+$ species, showing hydrogen bonding interactions of the water ligand

DISCUSSION

The probable composition of the complex obtained as a minor product of the reaction between terpy and cobalt(II) nitrate and possibly, atmospheric oxygen, has been shown by *X*-ray crystallography to be $[Co(quaterpy)(SO_3)(H_2O)]NO_3,H_2O$. It is formed as a consequence of traces of quaterpy and sulphate, these being the greatest impurities in the respective reagents. The valence state of the cobalt has not been unequivocally established because of the lack of the substance available, but it seems unlikely from general chemical considerations that the heavy atom in the ligand is other than sulphur. An attempt to observe an e.s.r. signal at liquid-nitrogen temperature was negative, as were attempts at a sulphur analysis; in view of the microscopic sample and possibly insufficient magnetic dilution, these results cannot be regarded as useful.

The cobalt environment is six-co-ordinate: the four quaterpy nitrogen atoms occupy positions in the equatorial plane with the water oxygen atom and the sulphite sulphur atom co-ordinated in axial *trans*-positions. Co–S is 2·244(2) Å. Only one other cobalt–sulphite derivative appears to have been crystallographically studied, *viz.*, *trans*-sulphitoisothiocyanatobis(ethylenediamine)cobalt(III) dihydrate.[5] Here too, co-ordination occurs *via* the sulphur atom, with Co–S 2·203(6) Å; the thermal motion in both structures is sufficiently low for us to be able to regard this as a significant difference in the absence of appropriate correction; the present value is close to the previously estimated Co^{III}–S covalent bond distance of 2·26 Å.[5] Similarly, in the present structure the cobalt–oxygen distance [2·067(5) Å] is quite different from that observed in the only previous determination of comparable accuracy, namely, *cis*-β-chloroaquatriethylenetetraminecobalt(III) perchlorate[6] [1·98(1) Å] and approaches the lower limit of values observed in Co^{II} systems; *e.g.* in the $[Co(H_2O)_6]^{2+}$ ion in the cobalt(II) Tutton salt, Co–O range from 2·070(4) to 2·107(4),[7] whereas in $[Co(CO_3)(OH_2)_2(imidazole)_2]$[8] the distance is 2·166(6) Å.[8] In both cases, the substituent *trans* to the bond concerned is quite different from that in the present complex and the differences are indicative of considerable *trans*-effects.

Within the sulphite group, the observed sulphur–oxygen distances [1·463(6), 1·449(5), and 1·457(5) Å] are in good agreement, and suggest that the ligand is, in fact, sulphite rather than chlorate, phosphate, or bisulphite. The mean is appreciably shorter than that (1·485 Å) observed in $[Co(en)_2(NCS)(SO_3)],2H_2O$, but the Co–S distance in the present complex is longer (see earlier), and the O–S–O angle is increased to 111·9° (*vs.* 110·3°). The geometries of these two *S*-co-ordinated sulphite species have appreciably shorter oxygen–sulphur distances and larger O–S–O angles than is usual in the 'free' sulphite ion, typically $>1·50$ Å and $<106°$.[9]

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[5] S. Baggio and L. N. Becka, *Acta Cryst.*, 1969, **B25**, 946.

[6] H. C. Freeman and I. E. Maxwell, *Inorg. Chem.*, 1969, **8**, 1293.

[7] H. Montgomery, R. V. Chastain, J. J. Natt, A. M. Whitkowska, and E. C. Lingafelter, *Acta Cryst.*, 1967, **22**, 775.

[8] E. Baraniak, H. C. Freeman, J. M. James, and C. E. Nockolds, *J. Chem. Soc.* (*A*), 1970, 2558.

[9] P. Kierkagaard, L. O. Larsson, and B. Nyberg, *Acta Chem. Scand.*, 1972, **26**, 218, and refs. therein.

TABLE 3

Equations of least-squares planes in the form $pX + qY + rZ = s$ where X, Y, and Z are orthogonal (Å) co-ordinates, defined by: $X = ax + cz \cos\beta$, $Y = by$, $Z = cz \sin\beta$. Deviations (Å) of atoms from the planes are given in square brackets; σ is the standard deviation of atoms defining the plane

	10^4p	10^4q	10^4r	s	σ/Å	
Plane (i): Quaterpy ligand, C(1)—(20), N(1)—(4)	3816	−0979	9191	4·246	0·07	[N(1) 0·12, N(2) 0·05, N(3) −0·03, N(4) 0·02, C(1) 0·14, C(2) 0·01, C(3) −0·18, C(4) −0·17, C(5) 0·00, C(6) 0·04, C(7) 0·04, C(8) 0·07, C(9) 0·03, C(10) 0·02, C(11) −0·01, C(12) −0·03 C(13) −0·05, C(14) −0·06, C(15) −0·03, C(16) −0·03, C(17) −0·01, C(18) 0·02, C(19) 0·02, C(20) 0·02, Co 0·05]
Plane (ii): C(1)—(5), N(1)	3648	0315	9306	5·515	0·01	[C(1) 0·00, C(2) 0·01, C(3) −0·01, C(4) 0·00, C(5) 0·02, N(1) −0·02, C(6) 0·06, N(2) −0·08, Co −0·27]
Plane (iii): C(6)—(10), N(2)	3834	−1068	9174	4·203	0·02	[C(6) 0·00, C(7) −0·02, C(8) 0·02, C(9) −0·01, C(10) −0·01, N(2) 0·02, C(5) −0·06, C(11) −0·02, N(1) 0·08, N(3) −0·04, Co 0·03]
Plane (iv): C(11)—(15), N(3)	3876	−1125	9149	4·156	0·01	[C(11) 0·01, C(12) 0·00, C(13) 0·00, C(14) 0·00, C(15) 0·01, N(3) −0·01, C(10) 0·01, C(16) 0·01, N(2) 0·03, N(4) 0·04, Co 0·05]
Plane (v): C(16)—(20), N(4)	3948	−0951	9138	4·309	0·01	[C(16) −0·01, C(17) 0·00, C(18) 0·01, C(19) −0·01, C(20) 0·00, N(4) 0·01, C(15) 0·00, N(3) 0.01, Co 0·07]

Angles between planes (°):

(i)–(ii)	7·5	(ii)–(iv)	8·4
(i)–(iii)	0·5	(ii)–(v)	7·5
(i)–(iv)	0·9	(iii)–(iv)	0·4
(i)–(v)	0·8	(iii)–(v)	1·0
(ii)–(iii)	8·0	(iv)–(v)	1·1

The quaterpyridyl ligand co-ordinates with the cobalt as a substantially planar entity (Table 3), the two inner nitrogen atoms being considerably closer [1·860(6), 1·854(6) Å] than the two outer [1·979(6), 1·960(6) Å] as a consequence of strain; similarly N(2)–Co–N(3) [80·6(3)°] is much smaller than N(1)–Co–N(2) and N(3)–Co–N(4) [81·5(2) and 82·3(2)°]. The Co–N distances in the present complex are considerably shorter than those observed in the [Co(terpy)$_2$]$^{2+}$ species [10] [Co–N 2·10 and 1·89(1) Å for the ' outer ' and ' inner ' bonds] and may reflect the proportion of high-spin complex with occupied $e_g(O_h)$ orbitals in the latter. The strain is also reflected in the differences between both the N–C–C and C–C–C angles (Table 2), where the latter (mean 127·4°) exceed the former (mean 112·6°) by some 15°; similar behaviour is found in terpyridyl derivatives.[10] A scale diagram shows that a considerable gap exists between the two ends of the quaterpy ligand in the equatorial plane, sufficient to accommodate a fifth aromatic ring; attempts are being made to prepare cycloquinquepyridyl and its complexes.

The co-ordinated water molecule is hydrogen bonded to the adjoining sulphite group of the next molecule down the c axis [O(1) · · · H(41$^{\text{I}}$) 1·93(7), O(1) · · · O(4$^{\text{I}}$) 2·711(7) Å] and to the lattice water [O(5) · · · H(42) 1·79(7), O(5) · · · O(4) 2·693(9) Å]. The lattice water in turn is hydrogen bonded to the disordered oxygen of the nitrate group [O(81) · · · H(52$^{\text{I}}$) 2·12(9), O(82) · · · H(51$^{\text{II}}$) 2·26(9), O(81) · · · O(5$^{\text{I}}$) 2·94(2), O(82) · · · O(5$^{\text{II}}$) 3·00(2) Å; superscript Roman numerals denote the following equivalent positions: I, $x, y, 1 + z$; II, $\bar{x}, 1 - y, 1 - z$].

The nitrate ion is accommodated in two overlapping orientations pivoting about the O(6) · · · O(7) axis, so that while O(6) and O(7) do not appear to be disordered, N(5) is an elongated ellipsoid and O(8) the pair of partly populated sites O(81) and O(82). Each of these sites is adjacent to a hydrogen atom from the lattice water molecule, and in each of these potential minima, hydrogen bonding appears to occur (see earlier). The populations of the two sites are 0·63 and 0·49 respectively; although the total (1·12) is significantly different from unity this is probably due to the inability of the thermal tensors used to provide a satisfactory model of the disorder, rather than to any physically significant cause.

It has been predicted elsewhere that quaterpy should be incapable of acting as a planar quadridentate ligand because of the stereochemical strain involved in co-ordination to a single central atom; [11] the present result shows that that is clearly not so.

[4/675 *Received, 2nd April*, 1974]

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[10] See *e.g.* E. N. Maslen, C. L. Raston, and A. H. White, *J.C.S. Dalton*, 1974, 1803 and refs. therein.

[11] W. W. Brandt, F. P. Dwyer, and E. C. Gyarfas, *Chem. Rev.*, 1954, **54**, 974.