Crystal Structure of Aquo-2-benzothiazolin-2-ylideneaminomethylpyridine(picolinato)copper(II) Perchlorate

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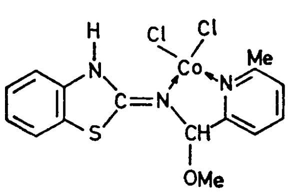
The crystal structure of the title compound has been determined from diffractometer data by the heavy-atom method and refined by block-diagonal least-squares techniques to R 5·9% for 3515 observed reflections. Crystals are triclinic, space group $P\bar{1}$, with unit-cell dimensions: a = 15·001(6), b = 8·803(4), c = 9·099(6) Å, α = 108·3(1), β = 111·8(1), γ = 84·3(1)°, Z = 2. The copper is five-co-ordinated by an oxygen and a nitrogen atom from the picolinic ligand [Cu–O 1·957(4), Cu–N 2·021(5) Å] and two nitrogen atoms (pyridine and imine) from 2-benzothiazolin-2-ylideneaminomethylpyridine [Cu–N 1·998(4), 1·981(5) Å], all at the base of the co-ordination pyramid, the water molecule [Cu–O 2·256(5) Å] being at the apex. Spectral and magnetic properties are in accord with this structure.

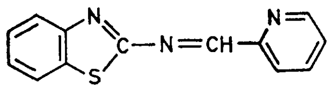
THE condensation product of pyridine-2-carbaldehyde (or 6-methylpyridine-2-carbaldehyde) with 2-aminobenzothiazole has been used as a ligand with Co^{II}, Cu^{II}, and Ni^{II}. For Co^{II} and the 6-methylpyridine-2-carbaldehyde product, it was found that the methanol solvent had reacted with the organic ligand to give a complex shown by X-ray investigation [1] to be (I).

(I)

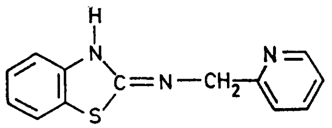


With the pyridine-2-carbaldehyde product, Ni^{II} and Co^{II} complexes were obtained in which the ligand was shown to be (II), from spectroscopic data.[2] With Cu^{II} a mixed-ligand complex was obtained in which a bidentate picolinic ion and a bidentate 2-benzothiazolin-2-ylideneaminomethylpyridine (III) molecule were present. This structure is confirmed by the present X-ray analysis which we now report.

(II)



(III)



It seems that the picolinic acid could be derived from hydrolysis of the ligand followed by oxidation of the pyridine-2-carbaldehyde product at the expense of the ligand itself. These processes are probably catalysed by the copper complex.

EXPERIMENTAL

Preparation.— N-Benzothiazol-2-yl-2-pyridylmethyleneamine, prepared as described in ref. 2, was dissolved in methanol and added slowly to a solution of $Cu(ClO_4)_2,7H_2O$

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[1] A. Mangia, M. Nardelli, C. Pelizzi, and G. Pelizzi, *J.C.S. Dalton*, 1972, 996.

[2] A. Montenero and C. Pelizzi, *Inorg. Chim. Acta*, 1972, **6**, 88.

TABLE 1

Final atomic fractional co-ordinates ($\times 10^4$) and thermal parameters * ($\times 10^2$ Å^2), with estimated standard deviations, for non-hydrogen atoms

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	2070(1)	4609(1)	4827(1)	250(2)	387(3)	447(3)	−13(2)	54(2)	223(2)
Cl	3872(1)	8326(2)	1087(2)	266(5)	483(6)	402(6)	9(4)	40(4)	245(5)
S	971(1)	7619(1)	1141(2)	271(5)	294(5)	356(5)	−11(4)	28(4)	186(4)
O(1)	738(2)	3847(4)	3968(4)	203(12)	343(14)	419(16)	−29(10)	12(11)	209(13)
O(2)	−192(2)	1982(5)	3846(5)	216(13)	430(17)	651(22)	−62(12)	44(14)	263(16)
O(3)	1753(3)	6132(5)	7078(5)	296(15)	512(19)	370(16)	40(13)	76(13)	116(14)
O(4)	3117(5)	7185(11)	267(8)	911(40)	1903(67)	588(31)	−822(43)	151(28)	26(36)
O(5)	3777(4)	9348(6)	2574(6)	879(32)	605(25)	591(25)	80(23)	252(23)	262(21)
O(6)	3891(6)	9200(8)	69(9)	1547(56)	961(38)	1026(41)	406(37)	814(41)	677(34)
O(7)	4672(4)	7397(9)	1400(8)	725(33)	1212(45)	921(39)	531(32)	133(29)	437(35)
N(1)	164(3)	6014(5)	2251(5)	214(14)	314(16)	320(17)	15(12)	30(12)	162(14)
N(2)	1846(3)	5927(4)	3318(5)	191(14)	283(15)	334(17)	−11(11)	26(12)	158(13)
N(3)	3392(3)	5551(5)	5714(5)	181(14)	308(16)	331(17)	−7(12)	26(12)	153(13)
N(4)	2318(3)	2534(4)	5409(5)	241(15)	266(15)	381(18)	17(12)	82(13)	164(14)
C(1)	−1562(4)	6545(7)	954(7)	248(19)	463(25)	359(23)	38(17)	63(17)	111(19)
C(2)	−2199(4)	7392(8)	−69(7)	274(21)	572(30)	393(25)	114(20)	47(18)	149(22)
C(3)	−1897(4)	8315(7)	−763(7)	351(24)	422(25)	445(27)	101(19)	−30(20)	155(21)
C(4)	−929(4)	8451(6)	−489(7)	397(23)	298(20)	358(23)	40(17)	12(18)	140(18)
C(5)	−287(3)	7642(5)	555(6)	278(19)	240(18)	333(21)	22(14)	17(16)	95(16)
C(6)	−595(3)	6715(5)	1243(6)	242(17)	291(19)	254(18)	35(14)	21(14)	84(15)
C(7)	1047(3)	6394(5)	2376(5)	257(17)	233(17)	263(18)	5(13)	36(14)	99(14)
C(8)	2735(3)	6447(6)	3292(6)	235(18)	385(21)	363(22)	−66(16)	36(16)	191(18)
C(9)	3555(3)	6354(5)	4829(6)	205(16)	256(17)	336(20)	2(13)	53(14)	117(15)
C(10)	4428(3)	7121(6)	5306(7)	244(19)	368(22)	439(25)	−25(16)	76(17)	179(19)
C(11)	5143(3)	7057(7)	6792(7)	211(18)	416(24)	497(27)	−59(16)	14(18)	174(21)
C(12)	4968(3)	6266(7)	7725(7)	218(19)	494(27)	422(25)	−25(18)	−27(17)	189(21)
C(13)	4086(3)	5518(6)	7186(6)	253(19)	432(23)	356(22)	−10(17)	27(16)	200(19)
C(14)	3146(4)	1878(6)	6162(7)	246(19)	359(22)	529(28)	46(16)	69(18)	210(20)
C(15)	3168(4)	549(6)	6660(8)	332(22)	345(23)	598(31)	89(18)	84(21)	235(22)
C(16)	2318(4)	−191(6)	6337(8)	427(25)	307(21)	527(28)	51(18)	144(21)	221(20)
C(17)	1468(4)	436(6)	5506(7)	331(21)	298(20)	473(26)	−20(16)	123(19)	151(19)
C(18)	1490(3)	1781(5)	5093(6)	214(16)	272(18)	310(19)	−7(13)	60(14)	105(15)
C(19)	594(3)	2586(6)	4214(6)	231(17)	302(19)	331(20)	−16(14)	62(15)	122(16)

* The anisotropic temperature factor is expressed in the form: $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

in methanol (molar ratio 2 : 1). After warming (70—80 °C) for 1 h the mixture was set aside. The green microcrystalline precipitate was recrystallized from hot methanol as green flattened prisms, slightly pleochroic (Found: C, 42·3; H, 3·5; Cu, 11·8; N, 10·3. $C_{19}H_{17}ClCuN_4O_7S$ requires C, 41·9; H, 3·2; Cu, 11·7; N, 10·3%).

Physical Measurements.—I.r. spectra were determined (4000—250 cm^{-1}) by use of KBr discs, on a Perkin-Elmer 457 double-beam spectrophotometer. Electronic spectra for methanol solution and the solid were measured on a Perkin-Elmer 402. Room-temperature magnetic susceptibility data were obtained, on a solid powdered sample, with a Gouy magnetic balance (Newport Instruments); μ_{eff} for copper was calculated from $\mu_{eff} = 2\cdot83\sqrt{\chi'_M T}$, where χ'_M is the molar susceptibility, corrected by use of Pascal's constants.[3]

X-Ray intensity data were collected on a Siemens single-crystal computer-controlled automated diffractometer by use of the ω—2θ scan technique. Unit cell parameters were determined from the least-squares fit to the $(\theta,\chi,\phi)_{hkl}$ values of 22 reflections measured on the diffractometer.

Crystal Data.—$C_{19}H_{17}ClCuN_4O_7S$, $M = 544\cdot4$, Triclinic, $a = 15\cdot001(6)$, $b = 8\cdot803(4)$, $c = 9\cdot099(6)$ Å, $\alpha = 108\cdot3(1)$, $\beta = 111\cdot8(1)$, $\gamma = 84\cdot3(1)°$, $U = 1060$ Å^3, $D_m = 1\cdot75$, $Z = 2$, $D_c = 1\cdot71$ g cm^{-3}, $F(000) = 554$. Cu-K_α radiation, $\lambda = 1\cdot5418$ Å; $\mu(\text{Cu-}K_\alpha) = 39\cdot8$ cm^{-1}. Space group $P\bar{1}$, from structural analysis.

Data Collection.—Intensity data were collected by use of Cu-K_α radiation up to $\theta = 70°$. 4014 Independent reflections were measured, of which 3515 were used in the analysis; reflections with intensities $< 2\sigma$ were considered unobserved. Lorentz and polarization corrections were applied, but no correction was made for absorption (mean linear dimension 0·10 mm; $\mu r = 0\cdot40$). The absolute scale was determined first by Wilson's method and later by correlation of observed and calculated values.

TABLE 2

Final atomic fractional co-ordinates ($\times 10^3$) and isotropic thermal parameters (Å^2) for hydrogen atoms

	x/a	y/b	z/c	B
H(1)	7(4)	534(6)	260(6)	3·2(1·0)
H(2)	−178(4)	579(6)	139(7)	4·0(1·2)
H(3)	−281(4)	753(6)	−16(7)	4·8(1·2)
H(4)	−233(4)	902(7)	−152(7)	4·9(1·4)
H(5)	−72(4)	911(7)	−110(7)	4·5(1·3)
H(6)	268(4)	755(6)	338(6)	3·1(1·1)
H(7)	283(4)	585(7)	233(7)	4·6(1·3)
H(8)	451(4)	782(7)	470(7)	4·5(1·3)
H(9)	567(4)	766(7)	712(7)	4·7(1·3)
H(10)	534(4)	623(7)	883(7)	5·4(1·4)
H(11)	394(4)	490(6)	773(6)	3·5(1·1)
H(12)	366(4)	248(6)	617(7)	4·4(1·2)
H(13)	369(5)	19(7)	712(8)	6·0(1·5)
H(14)	227(4)	−120(7)	666(8)	5·7(1·5)
H(15)	94(4)	−13(7)	519(7)	5·3(1·4)
H(16)	135(4)	664(6)	710(7)	4·8(1·2)
H(17)	208(4)	678(6)	785(7)	4·6(1·2)

Structure Analysis.—The structure was solved by the heavy-atom technique assuming the space group $P\bar{1}$ and the initial set of co-ordinates for Cu, Cl, and S deduced from the Patterson map. Refinement was by block-diagonal least-squares with anisotropic thermal parameters for

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[3] J. Lewis and R. G. Wilkins, 'Modern Co-ordination Chemistry,' Interscience, New York, 1964, p. 403.

non-hydrogen atoms, and isotropic parameters for hydrogen. The quantity minimized was $\Sigma w(\Delta F)^2$, the weighting function being $w = 1/(A + B|F_o|)^2$, with $A = 3{\cdot}850$ and $B = 0{\cdot}0754$); this led to a final R of 5·9%.

The final positional and thermal parameters with their estimated standard deviations are listed in Tables 1 and 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20442 (18 pp., 1 microfiche).* Atomic scattering factors were taken from ref. 4 for non-hydrogen atoms and from ref. 5 for hydrogen atoms.

Calculations were carried out on the CDC 6600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Bologna), using the programmes of Immirzi.[6]

RESULTS AND DISCUSSION

I.R. Spectrum.—The i.r. spectrum of the complex shows two strong and broad bands at *ca.* 3460 and 3120 cm^{-1}, which can be assigned to the stretching modes of OH and NH bonds respectively. The two strong bands at 1668 and 1360 cm^{-1} are attributed to the antisymmetric and symmetric stretching vibrations of the ionized carboxy-group respectively. The bands at *ca.* 1610, 1567, 1470, and 1448 cm^{-1}, due to the C=C and C=N vibrations of the aromatic rings, are not single owing to the presence of three non-equivalent rings and their frequencies indicate that the pyridine nitrogen atoms are involved in co-ordination to the metal. The strong and broad absorption at 1120—1050 cm^{-1} and the medium band at 620 cm^{-1} can be attributed to the vibrations of unco-ordinated perchlorate group.

Electronic Spectra.—The electronic spectrum shows a broad and almost symmetrical band which occurs at lower wavelengths in the solid state (625 nm) than in methanol solution (690 nm); this last value corresponds very closely to that usually found for five-co-ordinate copper(II),[7] so it can be inferred that co-ordination is not influenced by solvent effects.

Magnetic Data.—The magnetic moment of the complex (μ_{eff} 2·14 B.M. at 25 °C) is in good agreement with the values generally observed for Cu^{II} complexes, with no spin coupling interactions.

X-*Ray Structure.*—The structure (Figure 1) consists of separated $[Cu^{II}(C_6H_4NO_2)(C_{13}H_{11}N_3S)(OH_2)]^+$ cations and ClO_4^- anions, held together by a hydrogen bond of the type O–H · · · O involving the water molecule.

In the cation the three ligands, the picolinic anion, the ligand (III), and water, are arranged in a distorted tetragonal pyramid around the metal atom. The basal corners of the pyramid are occupied by the imine and pyridine nitrogen atoms from (III) and by the pyridine nitrogen and a carboxy-oxygen atom from the picolinate moiety; the oxygen atom of the water molecule is at the apex of the pyramid. The atoms forming the base of the co-ordination polyhedron do not lie in a plane, but there is a strong tetrahedral distortion as indicated by the deviations from the mean plane running through them: O(1) −0·22, N(2) +0·25, N(3) −0·27, N(4) +0·25 Å; copper is displaced from the base plane, toward the apex, by 0·20 Å. Figure 2 shows a clinographic projection of two cations related by a centre of symmetry and Table 3 lists all the main bond distances and angles in the structure. The Cu–N (1·981, 1·998, and 2·021) and Cu–O (1·957 Å) basal distances agree fairly well with the corresponding ones found in other five-co-ordinate copper(II) complexes.[8] The apical Cu–O bond (2·256 Å) is longer than usual Cu^{II}–O distances, but lies at the lower limit of the range usually observed for apical distances involving oxygen atoms in Cu^{II} complexes [*e.g.* 2·24 (ref. 9), 2·26 (ref. 10), 2·352 (ref. 11), and 2·439 Å (ref. 12)].

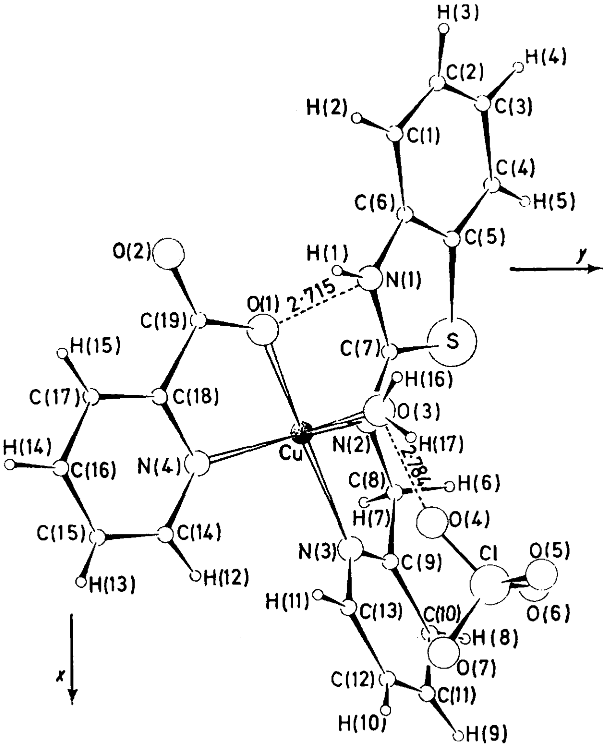

FIGURE 1 Projection of the structure along [001]

The ligand (III) is quite similar to the *N*-benzothiazolin-2-ylidene(methoxy)-6-methyl-2-pyridylmethylamine molecule as found in the cobalt(II) complex (I).[1] The benzothiazole system is practically planar, the maximum deviation from the least-squares plane being for C(7) (0·03 Å). The C–C distances in the benzene ring are not significantly different from the expected values and the C–S distances correspond very closely to

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

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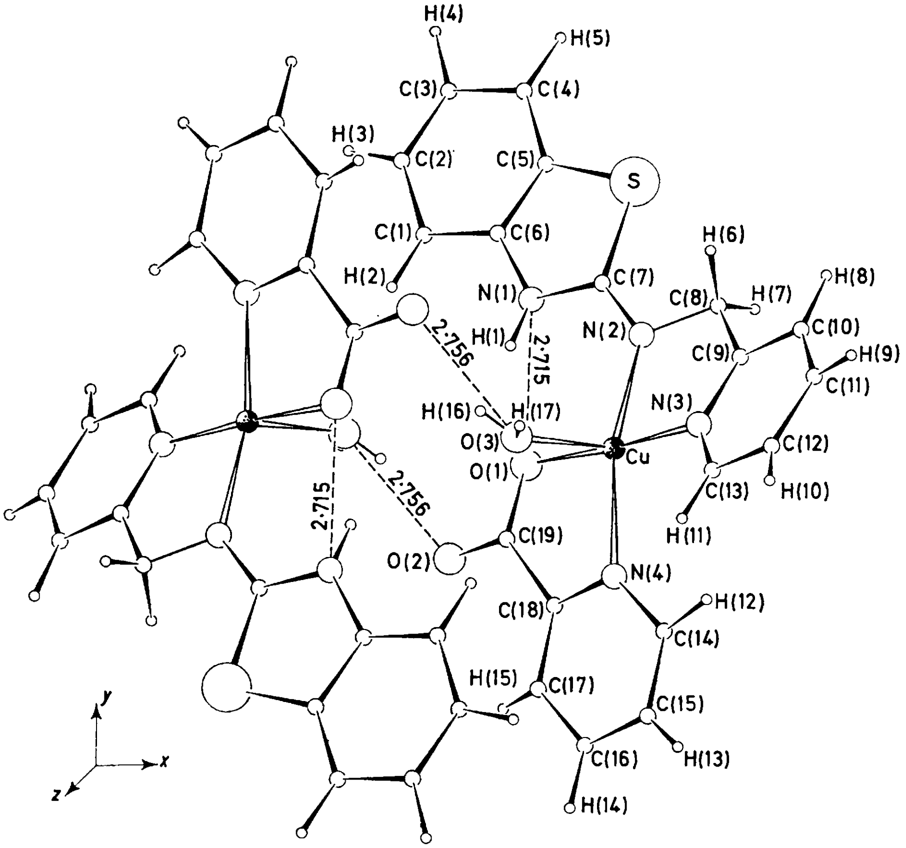

FIGURE 2 Clinographic projection of two cations related by a centre of symmetry

pure single bonds. The C–S–C angle (90·3°) is in agreement with those quoted for sulphur in five-membered rings: 88·5 (ref. 13), 90·0 and 92·4 (ref. 14), 90·9 and 91·2 (ref. 14), 90·7 in (I),[1] and 92·3° (ref. 15).

The values of the distances N(1)–C(7) (1·353) and N(2)–C(7) (1·305 Å) suggest some π-delocalization along the system N(1),C(7),N(2) with a preference for localization of the double bond between N(2)–C(7) and this is in agreement with the slightly pyramidal configuration of the bonds involving N(1) which is out of the C(6),-H(1),C(7) plane by 0·05 Å. This situation is significantly different from that observed in (I),[1] in which the double bond is completely delocalized along the system N(1),-C(7),N(2) [N(1)–C(7) 1·32, N(2)–C(7) 1·32 Å] and the C–N–H–C group is strictly planar. The distances N(2)–C(8) (1·463) and C(8)–C(9) (1·501 Å) are practically equal to the corresponding ones in (I), and are typical of single-bond contacts. The pyridine ring shows the expected planarity with the C–N and C–C bond lengths very close to those [1·3402(10) and 1·3945(10) Å] found from microwave spectroscopy for free pyridine.[16] The dihedral angle formed by the benzothiazole and pyridine planes is 153·0° [164·0° for (I)] and the internal rotation angle around the bond N(2)–C(8) in the bridging group is 20·7° [8·9° for (I)].

The picolinic ligand behaves as a chelating agent as usual, with bond distances and angles in agreement with those quoted in other similar complexes.[17,18] The two

TABLE 3

Bond distances (Å) and angles (°) with standard deviations in parentheses

(*a*) In the co-ordination polyhedron			
Cu–O(1)	1·957(4)	Cu–N(4)	2·021(5)
Cu–N(2)	1·981(5)	Cu–O(3)	2·256(5)
Cu–N(3)	1·998(4)		
O(1)–Cu–O(3)	85·4(1)	O(3)–Cu–N(3)	92·4(2)
O(1)–Cu–N(2)	95·3(2)	O(3)–Cu–N(4)	98·1(2)
O(1)–Cu–N(3)	175·7(2)	N(2)–Cu–N(3)	81·9(2)
O(1)–Cu–N(4)	81·8(2)	N(2)–Cu–N(4)	153·8(2)
O(3)–Cu–N(2)	107·6(2)	N(3)–Cu–N(4)	102·2(2)
(*b*) In the ligand (III)			
C(1)–C(2)	1·404(9)	S–C(5)	1·761(5)
C(2)–C(3)	1·37(1)	C(7)–N(2)	1·305(6)
C(3)–C(4)	1·390(9)	N(2)–C(8)	1·463(7)
C(4)–C(5)	1·396(7)	C(8)–C(9)	1·501(7)
C(5)–C(6)	1·372(9)	C(9)–C(10)	1·389(7)
C(6)–C(1)	1·390(7)	C(10)–C(11)	1·394(7)
C(6)–N(1)	1·400(6)	C(11)–C(12)	1·36(1)
N(1)–C(7)	1·353(7)	C(12)–C(13)	1·383(8)
C(7)–S	1·755(6)	C(13)–N(3)	1·365(6)

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TABLE 3 (*Continued*)

C(6)–C(1)–C(2)	115·9(5)	C(7)–N(2)–Cu	130·5(3)
C(1)–C(2)–C(3)	122·6(6)	C(7)–N(2)–C(8)	116·5(4)
C(2)–C(3)–C(4)	120·9(6)	Cu–N(2)–C(8)	113·0(3)
C(3)–C(4)–C(5)	116·9(5)	N(2)–C(8)–C(9)	109·5(4)
C(4)–C(5)–C(6)	121·8(5)	C(8)–C(9)–C(10)	121·0(5)
C(4)–C(5)–S	126·9(4)	C(8)–C(9)–N(3)	116·7(4)
S–C(5)–C(6)	111·3(4)	N(3)–C(9)–C(10)	122·3(5)
C(5)–C(6)–C(1)	121·8(5)	C(9)–C(10)–C(11)	118·0(5)
C(5)–C(6)–N(1)	112·6(4)	C(10)–C(11)–C(12)	119·7(5)
C(1)–C(6)–N(1)	125·6(5)	C(11)–C(12)–C(13)	119·8(5)
C(6)–N(1)–C(7)	114·7(4)	C(12)–C(13)–N(3)	120·6(5)
N(1)–C(7)–N(2)	124·0(4)	C(13)–N(3)–C(9)	119·5(4)
N(1)–C(7)–S	111·1(3)	C(13)–N(3)–Cu	125·0(3)
N(2)–C(7)–S	124·9(4)	Cu–N(3)–C(9)	115·3(3)
C(5)–S–C(7)	90·3(2)		

(*c*) In the picolinic ligand

N(4)–C(14)	1·350(6)	C(18)–N(4)	1·358(7)
C(14)–C(15)	1·37(1)	C(18)–C(19)	1·523(6)
C(15)–C(16)	1·379(9)	C(19)–O(1)	1·252(7)
C(16)–C(17)	1·382(8)	C(19)–O(2)	1·227(6)
C(17)–C(18)	1·357(8)		

N(4)–C(14)–C(15)	122·6(5)	C(18)–N(4)–C(14)	116·9(4)
C(14)–C(15)–C(16)	119·5(6)	C(18)–N(4)–Cu	111·9(3)
C(15)–C(16)–C(17)	118·2(5)	Cu–N(4)–C(14)	130·9(4)
C(16)–C(17)–C(18)	119·6(5)	C(18)–C(19)–O(1)	115·6(4)
C(17)–C(18)–N(4)	123·1(5)	C(18)–C(19)–O(2)	118·4(5)
C(17)–C(18)–C(19)	123·6(5)	O(1)–C(19)–O(2)	126·0(5)
N(4)–C(18)–C(19)	113·3(4)	C(19)–O(1)–Cu	117·0(3)

(*d*) In the perchlorate group

Cl–O(4)	1·406(8)	Cl–O(6)	1·386(9)
Cl–O(5)	1·419(6)	Cl–O(7)	1·375(7)

O(4)–Cl–O(5)	109·7(4)	O(5)–Cl–O(6)	110·9(4)
O(4)–Cl–O(6)	110·9(5)	O(5)–Cl–O(7)	111·8(4)
O(4)–Cl–O(7)	102·8(5)	O(6)–Cl–O(7)	110·5(5)

C–O distances (1·252 and 1·227 Å) are not significantly different, even though the longer involves co-ordinated oxygen. The picolinic ion is planar except for the oxygen atoms, as the carboxy-group is rotated by only 2·8° with respect to the pyridine moiety. An intramolecular N–H ··· O hydrogen bond connects picolinic ion with (III) [O(1) ··· N(1) 2·715(7) Å, H(1)–N(1) ··· O(1) 27°].

The water molecule is directly concerned in co-ordination around the metal through the Cu–O apical bond, this contact being directed just between the two intermolecular hydrogen bonds (Figures 1 and 2) the water molecule forms with the unco-ordinated picolinic oxygen atom [O(3) ··· O(2$^{\mathrm{IV}}$) 2·756(6) Å; H(16)–O(3) ··· O(2) 19°] and with an oxygen atom from the perchlorate group [O(3) ··· O(4$^{\mathrm{V}}$) 2·784(8) Å; H(17)–O(3) ··· O(4) 26°]. The orientation of the water molecule with respect to the metal atom is defined by the angle (29·6°) between the Cu–O(3) bond and the plane of the water molecule.

The oxygen atoms of the perchlorate ion show particularly high thermal parameters, possibly corresponding to a slightly disordered situation. This may account for the values of the Cl–O distances which are slightly shorter than those usually observed for well localized ClO_4^- tetrahedra.

The non-hydrogen bond packing contacts are consistent with van der Waals interactions; those $<3·40$ Å are quoted in Table 4.

TABLE 4

Intermolecular contacts $<3·4$ Å

O(1) ··· C(4$^{\mathrm{I}}$)	3·276(8)	O(7) ··· C(14$^{\mathrm{III}}$)	3·191(8)
O(2) ··· C(17$^{\mathrm{II}}$)	3·312(9)	C(1) ··· C(18$^{\mathrm{IV}}$)	3·396(8)
O(4) ··· C(8)	3·27(1)	C(12) ··· O(7$^{\mathrm{V}}$)	3·36(1)
O(7) ··· C(13$^{\mathrm{III}}$)	3·33(1)		

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $\bar{x}, \bar{y}+1, \bar{z}$
II $\bar{x}, \bar{y}, \bar{z}+1$
III $\bar{x}+1, \bar{y}+1, \bar{z}+1$
IV $\bar{x}, \bar{y}+1, \bar{z}+1$
V $x, y, z+1$

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