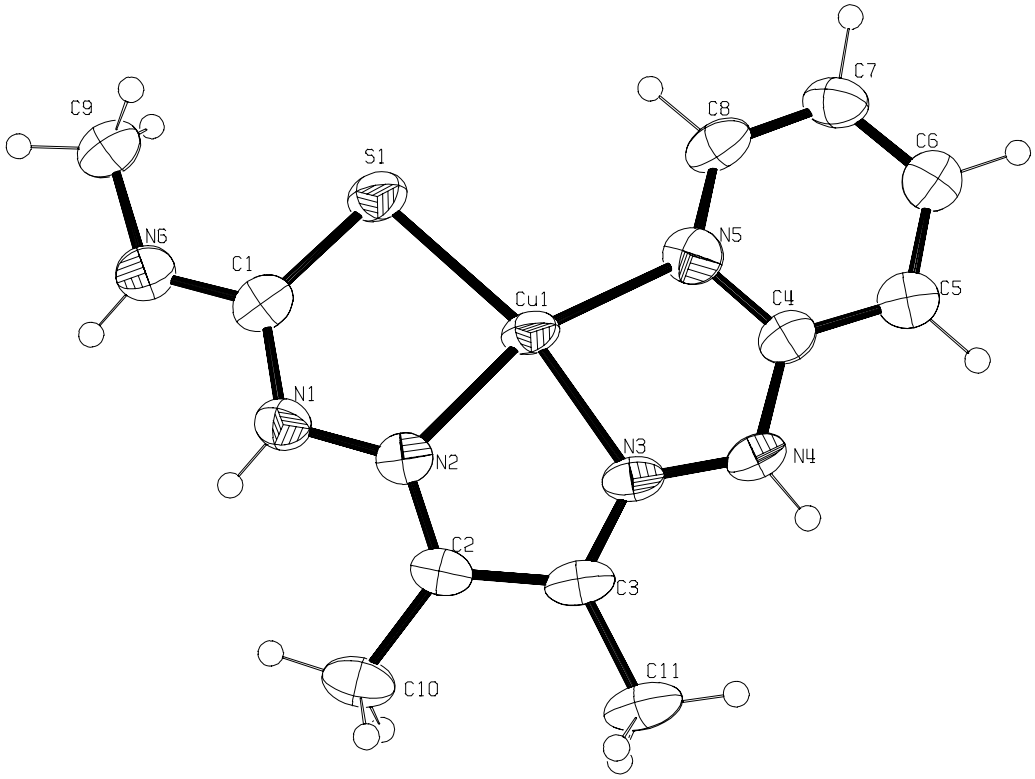
Inorganic Chemistry Crystallography Service

Single-crystal X-ray diffraction report for $[Cu(C_{11}H_{16}N_6S)][ClO_4]_2$ (ARC771)

Andrew R. Cowley
E-mail: a_r_cowley@hotmail.com
Tel. (2)70827



ClO_4^- ions not shown

Crystals of **ARC771** were grown by *. A single crystal having dimensions approximately 0.07 x 0.26 x 0.28 mm was mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150K in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated MoK_α radiation, λ = 0.71073 Å). Intensity data were processed using the DENZO-SMN package[1].

The structure was solved in the space group $P\ \bar{1}$ using the direct-methods program SIR92[2], which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite[3]. Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. It was clear from the resulting model that one of the ClO_4 ions was disordered. This was modelled as disordered over two orientations. The coordinates, isotropic thermal parameters and site occupancies of the Cl and O atoms were refined. Geometric restraints were applied: the Cl-O distances were restrained to 1.41(2) Å and the O-Cl-O angles to 109(2)°. The refined thermal parameters of the second anion were also observed to be relatively large, suggesting that this might also be disordered, but attempts to include this in the model did not lead to any improvement in the agreement with the X-ray data.

The NH hydrogen atoms were located in a difference Fourier map and their coordinates and isotropic thermal parameters subsequently refined, with N-H distances restrained to 0.90(3) Å. Other hydrogen atoms were positioned geometrically after each cycle of refinement. A 3-term Chebychev polynomial weighting scheme was applied. Refinement converged satisfactorily to give R = 0.0758, wR = 0.0919.

An attempt was made to refine the structure in the space group *P* 1 to verify that the disorder was not a consequence of incorrect choice of symmetry. The disorder was still clearly apparent and the refinement was not stable, suggesting the initial choice of space group to be correct.

Attached is a thermal ellipsoid plot (ORTEP-3[4]) at 40% probability. A summary of crystallographic data is given below, as are full lists of atomic coordinates, anisotropic thermal parameters and those bond lengths and angles not concerning geometrically-positioned H atoms.

Comments:

There are relatively short contacts between the Cu atom and O atoms of ClO_4^- ions above and below the plane of the thiosemicarbazone ligand (Cu(1)···O(1) 2.540(6) Å, Cu(1)···O(5) 2.799(13) Å, Cu(1)···O(15) 2.668(9) Å). The disorder of the anions suggests that these interactions have little directional character, and may be largely Coulombic in nature.

There are a number of relatively short distances between all three protonated N atoms and neighbouring O atoms. As a consequence of the disorder it is difficult to assign these as well-defined hydrogen bonds.

References:

1 Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods Enzymol.*, 1997, **276**, Eds C. W. Carter and R. M. Sweet, Academic Press.

2 A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi ,M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst*. 1994, **27**, 435.

3 CRYSTALS Issue 12, P. W. Betteridge, J. R. Cooper, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Cryst.*, 2003, **36**, 1487

4 ORTEP-3 v. 1.0.2, C. K. Johnson and M. K. Burnett, 1998.

Table 1: Crystal data and refinement details

Crystal identification	ARC771
Chemical formula	$C_{11}H_{16}Cl_2CuN_6O_8S$
Formula weight	526.80
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\ \bar{1}$
a (Å)	8.4190(3)
b (Å)	9.3588(3)
c (Å)	12.3341(5)
α (°)	79.2579(13)
β (°)	89.7935(14)
γ (°)	82.8946(15)
Cell volume (Å^3)	947.27(6)
Z	2
Calculated density (Mg/m^3)	1.847
Absorption coefficient (mm^{-1})	1.601
F_{000}	534
Crystal size (mm)	0.07 x 0.26 x 0.28
Description of crystal	Green-brown plate
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.64, 0.89
θ range for data collection (°)	$5.0 \leq \theta \leq 27.5$
Index ranges	$-10 \leq h \leq 10$, $-11 \leq k \leq 12$, $0 \leq l \leq 16$
Reflections measured	14544
Unique reflections	4315
R_{int}	0.043
Observed reflections ($I > 3\sigma(I)$)	2728
Refinement method	Full-matrix least-squares on *F*
Parameters refined	270
Weighting scheme	Chebychev 3-term polynomial
Goodness of fit	1.1596
R	0.0758
wR	0.0919
Residual electron density (min,max) (eÅ^{-3})	-1.12, 1.57

Table 2: Atomic coordinates and equivalent isotropic thermal parameters (Å^2) of non-hydrogen atoms

Atom	x	y	z	U_{equiv}
Cu(1)	0.26219(10)	0.34764(9)	0.25044(8)	0.0433
S(1)	0.0922(2)	0.1865(2)	0.31886(19)	0.0538
C(1)	-0.0489(9)	0.3160(8)	0.3550(6)	0.0465
N(1)	-0.0348(7)	0.4615(7)	0.3347(5)	0.0463
N(2)	0.1022(7)	0.5010(6)	0.2828(5)	0.0417
C(2)	0.1394(9)	0.6333(7)	0.2630(5)	0.0406
C(3)	0.2955(9)	0.6450(7)	0.2064(6)	0.0439
N(3)	0.3696(7)	0.5202(6)	0.1993(5)	0.0414
N(4)	0.5127(8)	0.4927(7)	0.1526(5)	0.0457
C(4)	0.5674(9)	0.3462(8)	0.1596(6)	0.0444
C(5)	0.7135(9)	0.2996(9)	0.1173(6)	0.0490
C(6)	0.7594(10)	0.1519(10)	0.1241(7)	0.0552
C(7)	0.6577(10)	0.0550(8)	0.1726(8)	0.0556
C(8)	0.5143(10)	0.1091(9)	0.2142(7)	0.0545
N(5)	0.4685(7)	0.2474(7)	0.2076(6)	0.0513
N(6)	-0.1836(8)	0.2807(7)	0.4047(5)	0.0496
C(9)	-0.2166(11)	0.1287(10)	0.4349(7)	0.0577
C(10)	0.0406(11)	0.7612(9)	0.2946(7)	0.0555
C(11)	0.3529(11)	0.7900(8)	0.1650(8)	0.0608
Cl(1)	0.1684(2)	0.27472(18)	-0.01726(15)	0.0448
O(1)	0.1771(8)	0.3816(6)	0.0490(5)	0.0670
O(2)	0.0044(9)	0.2701(9)	-0.0446(6)	0.0823
O(3)	0.2411(10)	0.3151(9)	-0.1249(6)	0.0833
O(4)	0.2291(12)	0.1349(7)	0.0407(7)	0.1017
Cl(2)*	0.4087(6)	0.3041(5)	0.5560(3)	0.0470(12)‡
O(5)*	0.3485(17)	0.3940(15)	0.4589(11)	0.077(3)‡
O(6)*	0.5731(12)	0.3050(13)	0.5718(10)	0.061(3)‡
O(7)*	0.3482(19)	0.3827(16)	0.6444(11)	0.082(3)‡
O(8)*	0.3472(17)	0.1692(14)	0.5674(13)	0.072(3)‡
Cl(12)†	0.3604(6)	0.3191(5)	0.5434(4)	0.0457(13)‡
O(15)†	0.4321(11)	0.3359(10)	0.4348(7)	0.040(2)‡
O(16)†	0.4322(19)	0.4026(16)	0.6127(13)	0.082(4)‡
O(17)†	0.1998(15)	0.3917(15)	0.5250(12)	0.076(3)‡
O(18)†	0.3754(18)	0.1735(14)	0.6021(12)	0.064(3)‡

*disordered atom, site occupancy 0.514(10)
†disordered atom, site occupancy 0.486(10)
‡directly-refined value of U_{iso} (Å^2)

Table 3: Atomic coordinates and isotropic thermal parameters (Å^2) of hydrogen atoms

Atom	x	y	z	U_{iso}
H(1)	-0.093(9)	0.530(7)	0.364(6)	0.05(2)
H(2)	0.577(8)	0.561(7)	0.140(7)	0.05(2)
H(3)	-0.249(6)	0.354(5)	0.425(5)	0.023(15)
H(51)	0.7846	0.3724	0.0823	0.0585
H(61)	0.8644	0.1156	0.0945	0.0661
H(71)	0.6871	-0.0529	0.1777	0.0664
H(81)	0.4428	0.0377	0.2510	0.0642
H(91)	-0.3231	0.1261	0.4710	0.0691
H(92)	-0.1314	0.0715	0.4874	0.0691
H(93)	-0.2181	0.0847	0.3671	0.0691
H(101)	-0.0586	0.7291	0.3312	0.0673
H(102)	0.1033	0.8036	0.3467	0.0673
H(103)	0.0103	0.8371	0.2270	0.0673
H(111)	0.4594	0.7743	0.1299	0.0717
H(112)	0.3637	0.8417	0.2282	0.0717
H(113)	0.2742	0.8509	0.1093	0.0717

Table 4: Anisotropic thermal parameters (Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	0.0415(5)	0.0273(4)	0.0589(6)	-0.0013(3)	-0.0116(4)	-0.0050(3)
S(1)	0.0446(10)	0.0354(9)	0.0781(14)	-0.0021(8)	-0.0091(9)	-0.0055(7)
C(1)	0.052(4)	0.049(4)	0.036(4)	0.000(3)	-0.011(3)	-0.012(3)
N(1)	0.048(3)	0.041(3)	0.048(4)	-0.007(3)	-0.003(3)	-0.002(3)
N(2)	0.047(3)	0.041(3)	0.036(3)	-0.005(2)	-0.007(2)	-0.005(2)
C(2)	0.052(4)	0.035(3)	0.035(3)	-0.008(3)	-0.015(3)	0.001(3)
C(3)	0.064(4)	0.032(3)	0.035(3)	-0.002(3)	-0.022(3)	-0.011(3)
N(3)	0.052(3)	0.033(3)	0.040(3)	-0.006(2)	-0.013(3)	-0.009(2)
N(4)	0.052(3)	0.038(3)	0.050(3)	-0.006(3)	-0.005(3)	-0.018(3)
C(4)	0.045(4)	0.047(4)	0.042(4)	-0.007(3)	-0.009(3)	-0.013(3)
C(5)	0.053(4)	0.051(4)	0.043(4)	-0.007(3)	-0.012(3)	-0.007(3)
C(6)	0.057(5)	0.059(5)	0.049(4)	-0.008(4)	-0.002(4)	-0.008(4)
C(7)	0.056(4)	0.041(4)	0.070(5)	-0.013(4)	-0.013(4)	0.001(3)
C(8)	0.052(4)	0.045(4)	0.064(5)	0.004(3)	-0.018(4)	-0.017(3)
N(5)	0.042(3)	0.055(4)	0.058(4)	-0.016(3)	-0.016(3)	-0.003(3)
N(6)	0.056(4)	0.047(4)	0.044(3)	-0.003(3)	-0.002(3)	-0.008(3)
C(9)	0.064(5)	0.052(5)	0.057(5)	-0.002(4)	-0.001(4)	-0.018(4)
C(10)	0.076(5)	0.041(4)	0.051(4)	-0.018(3)	-0.013(4)	0.001(4)
C(11)	0.078(6)	0.034(4)	0.067(5)	0.005(3)	-0.023(4)	-0.016(4)
Cl(1)	0.0476(9)	0.0415(9)	0.0457(9)	-0.0093(7)	0.0006(7)	-0.0062(7)
O(1)	0.098(5)	0.041(3)	0.061(4)	-0.017(3)	-0.035(3)	0.008(3)
O(2)	0.067(4)	0.107(6)	0.071(4)	-0.003(4)	-0.017(3)	-0.026(4)
O(3)	0.099(5)	0.099(5)	0.066(4)	-0.030(4)	0.026(4)	-0.047(4)
O(4)	0.154(8)	0.040(3)	0.104(6)	-0.021(4)	-0.054(5)	0.026(4)

Table 5: Bond lengths (Å)

Cu(1) - S(1)	2.255(2)	C(3) - C(11)	1.496(10)
Cu(1) - N(2)	1.941(6)	N(3) - N(4)	1.350(9)
Cu(1) - N(3)	1.950(6)	N(4) - C(4)	1.378(10)
Cu(1) - N(5)	1.988(7)	N(4) - H(2)	0.87(3)
S(1) - C(1)	1.709(8)	C(4) - C(5)	1.386(11)
C(1) - N(1)	1.358(10)	C(4) - N(5)	1.372(10)
C(1) - N(6)	1.335(10)	C(5) - C(6)	1.375(12)
N(1) - N(2)	1.374(9)	C(6) - C(7)	1.378(13)
N(1) - H(1)	0.89(3)	C(7) - C(8)	1.385(13)
N(2) - C(2)	1.293(9)	C(8) - N(5)	1.292(10)
C(2) - C(3)	1.492(12)	N(6) - C(9)	1.462(11)
C(2) - C(10)	1.484(10)	N(6) - H(3)	0.90(3)
C(3) - N(3)	1.272(9)		
Cl(1) - O(1)	1.413(6)	Cl(1) - O(3)	1.465(7)
Cl(1) - O(2)	1.430(7)	Cl(1) - O(4)	1.405(7)
Cl(2) - O(5)	1.386(13)	Cl(2) - O(7)	1.480(13)
Cl(2) - O(6)	1.400(11)	Cl(2) - O(8)	1.406(13)
Cl(12) - O(15)	1.457(10)	Cl(12) - O(17)	1.435(13)
Cl(12) - O(16)	1.441(13)	Cl(12) - O(18)	1.410(13)

Note – geometrically-positioned H atoms have been excluded

Table 6: Bond angles (°)

S(1) - Cu(1) - N(2)	87.32(19)	C(2) - C(3) - N(3)	112.3(6)
S(1) - Cu(1) - N(3)	166.73(19)	C(2) - C(3) - C(11)	121.8(7)
N(2) - Cu(1) - N(3)	79.4(3)	N(3) - C(3) - C(11)	125.9(8)
S(1) - Cu(1) - N(5)	111.8(2)	Cu(1) - N(3) - C(3)	118.0(6)
N(2) - Cu(1) - N(5)	160.6(3)	Cu(1) - N(3) - N(4)	114.7(4)
N(3) - Cu(1) - N(5)	81.4(3)	C(3) - N(3) - N(4)	127.1(6)
S(1) - Cu(1) - O(1)	97.16(17)	N(3) - N(4) - C(4)	114.8(6)
N(2) - Cu(1) - O(1)	94.4(2)	N(3) - N(4) - H(2)	120(6)
N(3) - Cu(1) - O(1)	83.8(2)	C(4) - N(4) - H(2)	122(6)
N(5) - Cu(1) - O(1)	86.5(2)	N(4) - C(4) - C(5)	122.0(7)
Cu(1) - S(1) - C(1)	94.7(3)	N(4) - C(4) - N(5)	117.0(7)
S(1) - C(1) - N(1)	123.3(6)	C(5) - C(4) - N(5)	121.0(7)
S(1) - C(1) - N(6)	121.9(6)	C(4) - C(5) - C(6)	119.2(8)
N(1) - C(1) - N(6)	114.9(7)	C(5) - C(6) - C(7)	118.6(8)
C(1) - N(1) - N(2)	116.1(6)	C(6) - C(7) - C(8)	119.1(7)
C(1) - N(1) - H(1)	127(6)	C(7) - C(8) - N(5)	123.1(8)
N(2) - N(1) - H(1)	116(6)	Cu(1) - N(5) - C(4)	111.5(5)
Cu(1) - N(2) - N(1)	118.5(4)	Cu(1) - N(5) - C(8)	129.4(6)
Cu(1) - N(2) - C(2)	116.9(5)	C(4) - N(5) - C(8)	118.9(7)
N(1) - N(2) - C(2)	124.3(6)	C(1) - N(6) - C(9)	122.1(7)
N(2) - C(2) - C(3)	113.0(6)	C(1) - N(6) - H(3)	117(4)
N(2) - C(2) - C(10)	124.3(7)	C(9) - N(6) - H(3)	121(4)
C(3) - C(2) - C(10)	122.7(7)		
O(1) - Cl(1) - O(2)	109.2(5)	O(1) - Cl(1) - O(4)	110.6(4)
O(1) - Cl(1) - O(3)	111.9(4)	O(2) - Cl(1) - O(4)	107.3(5)
O(2) - Cl(1) - O(3)	103.5(5)	O(3) - Cl(1) - O(4)	113.8(6)
O(5) - Cl(2) - O(6)	113.1(8)	O(5) - Cl(2) - O(8)	109.1(9)
O(5) - Cl(2) - O(7)	104.7(8)	O(6) - Cl(2) - O(8)	119.2(8)
O(6) - Cl(2) - O(7)	99.1(8)	O(7) - Cl(2) - O(8)	110.2(9)
O(15) - Cl(12) - O(16)	111.2(8)	O(15) - Cl(12) - O(18)	114.3(7)
O(15) - Cl(12) - O(17)	105.3(7)	O(16) - Cl(12) - O(18)	106.2(9)
O(16) - Cl(12) - O(17)	103.7(9)	O(17) - Cl(12) - O(18)	115.7(9)

Note – geometrically-positioned H atoms have been excluded