Terdentate Co-ordination by a Cysteine Derivative: Crystal and Molecular Structure of Bis(S-Methyl-L-cysteinato)cobalt(III) Perchlorate Monohydrate

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The crystal and molecular structure of the title complex has been determined from three-dimensional X-ray diffracto-meter data by Patterson and Fourier methods. The compound crystallizes in the orthorhombic space group $P2_12_12_1$, with $Z = 4$ in a cell of dimensions $a = 16{\cdot}196(3)$, $b = 8.393(2)$, and $c = 11.944(2)$ Å. Full-matrix least-squares refinement using 1 436 independent reflections has reached R 0.043.

The structure contains one independent $[(S\text{-methyl-L-cysteinato})_2\text{cobalt(III)}]^+$ cation, a perchlorate anion, and a molecule of water of solvation. The metal, which is slightly distorted octahedral, makes two Co–S, two Co–O, and two Co–N bonds with the ligands [mean distances 2.271(2), 1.906(5), 1.946(6) Å]; bond angles at Co 83.8(3)—98.9(3)°. The two carboxy-oxygen and the amino nitrogen atoms are mutually *cis* while the two sulphur atoms are *trans*.

THE nature and extent of the binding of cysteine, methionine, and their derivatives to transition-metal ions have been the subjects of considerable recent research activity,[1-15] largely because of the importance of these factors in metal-chelation therapy [2] and in catalysis.[1] The recent report by Hidaka and his co-workers [16] of the synthesis, separation, and characterization of three isomers of formulation $[Co(smc)_2][ClO_4]{\cdot}H_2O$, where smc is S-methyl-L-cysteinato, was of considerable significance because it suggested that these complexes may contain octahedral chromophores in which all six sites were occupied by donor atoms from two cysteine derivatives. While terdentate co-ordination of cysteine derivatives has been observed,[4,5] it is sometimes found that one of the metal–ligand bonds is considerably weaker than the other two,[4] and in no previously documented case are there two terdentate cysteine residues interacting with a single metal ion.

Hence, in order to examine in detail this apparently new structural type in cysteine chemistry, and in order to further our knowledge of the binding properties of this important amino-acid, we have undertaken a complete

three-dimensional crystallographic study of one isomer of $[Co(smc)_2][ClO_4]{\cdot}H_2O$.

EXPERIMENTAL

Crystals of the title compound are brown elongated prisms. Preliminary diffraction photographs of a number of these crystals showed that all were twinned. Consequently, the crystals used in this study were fragments obtained by cleavage. Weissenberg and precession photographs were used to establish space group, and accurate unit-cell dimensions were obtained by least-squares procedures described previously [17] from the 2θ values of 12 reflections centred on a diffractometer (Mo-$K_{\alpha1}$).

Crystal Data.—$C_8H_{18}ClCoN_2O_9S_2$, $M = 444.8$, Ortho-rhombic, $a = 16.196(3)$, $b = 8.393(2)$, and $c = 11.944(2)$ Å, $U = 1\,623.6$ Å^3, $D_m = 1.85$ (by flotation), $Z = 4$, $D_c = 1.827$ g cm^{-3}, $F(000) = 912$. $\mu(Cu\text{-}K_\alpha) = 124.5$ cm^{-1}, $\mu(Mo\text{-}K_\alpha) = 15.7$ cm^{-1}. Space group $P2_12_12_1$ (No. 19) from systematic absences.

Data Collection.—Two sets of data were collected. *Set* (I). A crystal of dimensions $0.36 \times 0.08 \times 0.35$ mm was mounted on an automatic Picker four-circle diffractometer with its b axis parallel to the ϕ axis. A total of 1 599 independent reflections was measured (to 2θ 126°), by use of

[1] A. Tomita, H. Hirai, and S. Makishima, *Inorg. Chem.*, 1968, **7**, 760.

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[8] C. K. Prout, G. B. Allison, L. T. J. Delbaere, and E. Gore, *Acta Cryst.*, 1972, **B28**, 3043.

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[10] N. J. Taylor, Y. S. Wong, P. C. Chieh, and A. J. Carty, *J.C.S. Dalton*, 1975, 438.

[11] M. G. B. Drew and A. Kay, *J. Chem. Soc. (A)*, 1971, 1846.

[12] M. G. B. Drew and A. Kay, *J. Chem. Soc. (A)*, 1971, 1851.

[13] M. V. Veidis and G. J. Palenik, *Chem. Comm.*, 1969, 1277.

[14] N. C. Stephenson, J. F. McConnell, and R. Warren, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 553.

[15] L. M. Volshtein, L. F. Krylova, and M. F. Mogilevkina, *Doklady Akad. Nauk S.S.S.R.*, 1968, **178**, 595.

[16] J. Hidaka and Y. Shimura, presented at the XVI I.C.C.C., Dublin, Ireland, August 1974, Paper 1.7a.

[17] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1967, **22**, 457.

Cu-K_α radiation (Ni β filter), with a scan rate of 1° min⁻¹, a scan range of 1.2°, a time of 20 s for each background and a take-off angle of 2.0°. Of 1 599 reflections, 1 172 had intensities $I > 3\sigma(I)$.

Set (II). After the loss of the first crystal, a second crystal of dimensions $0.44 \times 0.06 \times 0.28$ mm, also mounted roughly parallel to its *b* axis, was used to collect a set of data with Mo-K_α radiation (graphite monochromator). Of 1 723 independent intensities [2θ(Mo) < 53°] obtained, 1 436 had $I > 2.6\sigma(I)$. Data were collected at a take-off angle of 1.4°; at this tube angle, the intensity of a typical peak was *ca.* 88% of the maximum value as a function of the take-off angle. Data were collected by the θ—2θ scan technique at a scan rate of 0.5° min⁻¹. Allowance was made for the presence of both K_{α_1} and K_{α_2} radiations, the scan range being from 0.6° below the calculated K_{α_1} peak position to 0.6° above the calculated K_{α_2} peak position. Stationary-crystal–stationary-counter background counts of 20 s were taken at each end of the scans.

Both sets of data were processed by the procedure of Ibers.[18] The intensities were assigned standard deviations according to the formula [19] and the value of *p* was chosen as

$$\sigma(I) = [C + 0.25(t_s/t_b)^2(B_H + B_L) + (pI)^2]^{1/2}$$

0.04 for both crystals. Data were corrected for Lorentz and polarization effects, and for absorption. For the set (I), transmission coefficients ranged from 0.047 to 0.43, and for set (II) data from 0.55 to 0.93.[20]

Solution and Refinement of the Structure.—The structure was initially solved by use of the Cu-K_α data [set (I)]. The locations of the cobalt atom and one sulphur atom were derived from a three-dimensional Patterson function, and these positions were refined by least-squares techniques. All least-squares refinements in this analysis were on *F*, the function minimized being $\Sigma w(F_o - F_c)^2$ where the weights *w* were taken as $4F_o^2/\sigma^2(F_o^2)$. Neutral atom scattering factors for cobalt, sulphur, and chlorine were from ref. 21, those for carbon, nitrogen, and oxygen from ref. 22, and for hydrogen from ref. 23. The effects of the anomalous dispersion of cobalt, chlorine, and sulphur were included in F_c,[24] values of $\Delta f'$ and $\Delta f''$ being taken from ref. 25.

The remaining non-hydrogen atoms were located in a subsequent difference-Fourier synthesis, and isotropic least-squares refinement of these twenty-three independent atoms gave R 0.149 and R' 0.189 {$R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$}. Anisotropic refinement of this model led to several non-positive-definite thermal ellipsoids and no substantial improvement in R'. At this stage, the co-ordinates (x,y,z) of all atoms were replaced by $(-x,-y,-z)$; anisotropic refinement of this model gave R 0.093, R' 0.118. This reversed arrangement is consistent with the formulation of the ligand as the L-isomer. Refinement with the Cu-K_α data set was terminated at this stage, because the large value of the linear absorption coefficient, μ, and the subsequently broad range of transmission coefficients (see above) suggested that much better agreement could be obtained by use of Mo-K_α radiation.

Atomic scattering factors and anomalous dispersion terms used for the Mo-K_α data were taken from the same sources as before. Three cycles of anisotropic least-squares calculation using as a starting point the parameters derived from the Cu-K_α data yielded R 0.059 and R' 0.078, and application of the absorption correction reduced these to R 0.054 and R' 0.072. The positions of sixteen of the eighteen hydrogen atoms were deduced from a difference Fourier map; the positions of the two remaining methyl hydrogen atoms were

TABLE 1

Fractional co-ordinates of non-hydrogen atoms with estimated standard deviations in parentheses

Atom	x	y	z
Co	0.812 28(7)	0.727 30(11)	0.882 90(7)
S(1)	0.700 4(1)	0.787 5(3)	0.776 5(2)
S(2)	0.926 7(1)	0.657 5(3)	0.981 7(2)
N(1)	0.874 0(4)	0.770 1(8)	0.746 2(5)
N(2)	0.795 2(5)	0.499 7(7)	0.863 7(5)
O(1)	0.829 5(4)	0.947 9(6)	0.991 3(4)
O(3)	0.747 1(4)	0.697 9(6)	1.014 3(4)
C(1)	0.640 7(8)	0.923 6(16)	0.862 2(10)
C(2)	0.756 3(7)	0.916 7(12)	0.678 4(7)
C(3)	0.845 2(6)	0.932 3(10)	0.716 0(6)
C(4)	0.846 4(6)	1.029 4(10)	0.825 4(5)
O(2)	0.856 9(5)	1.172 0(7)	0.825 9(5)
C(5)	0.918 0(6)	0.762 6(13)	1.110 0(7)
C(6)	0.891 4(7)	0.455 9(11)	1.018 1(6)
C(7)	0.801 2(6)	0.441 5(9)	0.982 7(6)
C(8)	0.748 4(6)	0.551 2(10)	1.051 6(6)
O(4)	0.714 2(4)	0.506 5(8)	1.135 3(4)
W	0.958 4(5)	0.387 2(10)	0.716 4(7)
Cl	0.562 0(2)	0.370 4(3)	0.929 8(2)
O(11)	0.494 4(6)	0.333 8(11)	0.863 3(6)
O(12)	0.628 4(10)	0.392 2(28)	0.855 5(13)
O(13)	0.586 7(11)	0.251 7(17)	0.991 8(11)
O(14)	0.555 0(11)	0.516 0(17)	0.979 2(10)

TABLE 2

Fractional co-ordinates of hydrogen atoms

Atom	Attached to	x	y	z
H(1)	C(3)	0.866	1.002	0.654
H(2)	C(2)	0.734	1.018	0.648
H(3)	C(2)	0.729	0.883	0.607
H(4)	C(1)	0.620	0.863	0.924
H(5) *	C(1)	0.672	1.012	0.886
H(6)	C(1)	0.589	0.969	0.809
H(7)	N(1)	0.929	0.762	0.764
H(8)	N(1)	0.859	0.696	0.688
H(9)	C(5)	0.871	0.749	1.133
H(10)	C(5)	0.951	0.714	1.175
H(11) *	C(5)	0.935	0.867	1.100
H(12)	C(6)	0.895	0.441	1.096
H(13)	C(6)	0.923	0.380	0.979
H(14)	C(7)	0.793	0.306	0.982
H(15)	N(2)	0.740	0.495	0.852
H(16)	N(2)	0.846	0.455	0.798
H(17)	W	0.958	0.457	0.640
H(18)	W	0.907	0.357	0.750

* Calculated positions. Isotropic thermal parameters set at 4.0 Å².

calculated geometrically assuming C–H 0.95 Å.[26,27] Refinement with these eighteen hydrogen atoms included (but not

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[20] For a description of the programs used, see E. D. Estes, W. E. Estes, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 1975, **14**, 106.

[21] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[22] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, Table 3.3.1A.

[23] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[24] J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, 1964, **17**, 781.

[25] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

[26] M. R. Churchill, *Inorg. Chem.*, 1973, **12**, 1213.

[27] J. J. Halgson, P. K. Hale, and W. E. Hatfield, *Inorg. Chem.*, 1971, **10**, 1061.

varied) gave R 0.043 and R' 0.056. In the final least-squares cycle, no atomic parameter exhibited a shift of $>0.48\sigma$. Examination of the values of F_o and F_c suggested to us that no correction for secondary extinction was necessary. A final difference-Fourier map was featureless, with no peak >0.5 eÅ^{-3}. The value of R' showed no dependence on $\sin \theta$ or on $|F_c|$.

The atom positional parameters are listed in Tables 1 and 2. Thermal parameters, and root-mean-square amplitudes of vibration derived from the final cycle of least-squares refinement, and observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 21603 (10 pp., 1 microfiche).*

DISCUSSION

The structure consists of $[Co(smc)_2]^+$ cations which are hydrogen bonded to perchlorate anions and water molecules. The geometry of the cation is shown in Figure 1. The co-ordination around the Co^{III} centres is
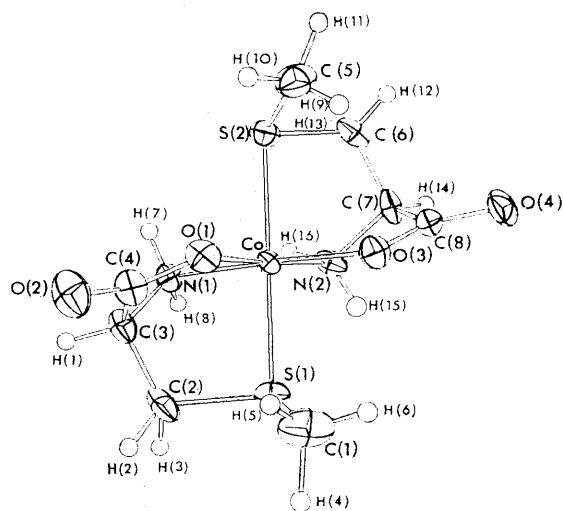

FIGURE 1 View of the $[Co(smc)_2]^+$ cation showing the atom numbering system used. Thermal vibration ellipsoids are reduced to include 40% probability for the sake of clarity (those of hydrogen atoms are arbitrary)

approximately octahedral, the smc ligands being terdentate with the S atoms *trans*. Thus, the geometry of this isomer is qualitatively that deduced by Hidaka and co-workers from electronic absorption and c.d. spectroscopy. The cobalt–ligand bond lengths (Table 3), are all very similar to the sums of the appropriate covalent radii.[28] Moreover the mean distances (Co–S 2.272, Co–N 1.946, Co–O 1.906 Å) are similar to the means of recently determined values for a variety of cobalt(III) complexes [Co–S 2.272(1) (ref. 29), Co–N 1.912(7)—1.966(6) (refs. 30—32), and Co–O 1.884(5)—1.92(3) Å

* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

28 L. Pauling, ' The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.
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30 L. F. Druding and F. D. Sancilio, *Acta Cryst.*, 1974, **B30**, 2386.

(refs. 31—33)]. The bond angles (Table 3) are slightly distorted from their idealized values, with *cis* angles in the range 83.8(3)—98.9(3)° and *trans* angles from 176.0(3) to 176.8(1)°.

Bond lengths (Å) and bond angles (°), with standard deviations in parentheses

(a) Distances

Co–S(1)	2.270(2)	Co–N(2)	1.943(6)
Co–S(2)	2.273(2)	Co–O(1)	1.903(5)
Co–N(1)	1.948(6)	Co–O(3)	1.908(5)
C(1)–S(1)	1.813(11)	C(5)–S(2)	1.773(9)
S(1)–C(2)	1.835(10)	S(2)–C(6)	1.838(10)
C(2)–C(3)	1.514(16)	C(6)–C(7)	1.526(15)
C(3)–C(4)	1.573(11)	C(7)–C(8)	1.502(13)
C(3)–N(1)	1.483(11)	C(7)–N(2)	1.506(9)
C(4)–O(1)	1.233(10)	C(8)–O(3)	1.310(10)
C(4)–O(2)	1.209(10)	C(8)–O(4)	1.203(10)
Cl–O(11)	1.387(8)	Cl–O(13)	1.305(12)
Cl–O(12)	1.406(14)	Cl–O(14)	1.361(12)

(b) Angles

S(1)–Co–S(2)	176.8(1)	C(3)–C(4)–O(1)	113.3(7)
N(1)–Co–O(3)	176.0(3)	C(3)–C(4)–O(2)	119.2(7)
N(2)–Co–O(1)	176.5(4)	O(1)–C(4)–O(2)	127.3(8)
S(1)–Co–N(1)	84.2(2)	C(4)–O(1)–Co	115.4(5)
S(1)–Co–N(2)	92.2(2)	C(5)–S(2)–C(6)	103.2(4)
S(1)–Co–O(1)	90.0(2)	C(5)–S(2)–Co	104.9(3)
S(1)–Co–O(3)	92.7(2)	C(6)–S(2)–Co	96.1(3)
S(2)–Co–N(1)	93.7(2)	S(2)–C(6)–C(7)	107.8(6)
S(2)–Co–N(2)	85.6(2)	C(6)–C(7)–C(8)	110.1(7)
S(2)–Co–O(1)	92.2(2)	C(6)–C(7)–N(2)	107.3(7)
S(2)–Co–O(3)	89.5(2)	C(8)–C(7)–N(2)	106.3(7)
N(1)–Co–N(2)	98.9(3)	C(7)–N(2)–Co	101.4(5)
N(2)–Co–O(3)	83.8(3)	C(7)–C(8)–O(3)	113.6(7)
O(3)–Co–O(1)	93.4(2)	C(7)–C(8)–O(4)	121.7(8)
O(1)–Co–N(1)	84.0(3)	O(3)–C(8)–O(4)	124.6(9)
C(1)–S(1)–C(2)	104.5(6)	C(8)–O(3)–Co	113.1(5)
C(1)–S(1)–Co	104.4(4)		
C(2)–S(1)–Co	95.5(4)	O(11)–Cl–O(12)	105.7(7)
S(1)–C(2)–C(3)	109.3(6)	O(11)–Cl–O(13)	113.4(7)
C(2)–C(3)–C(4)	108.1(8)	O(11)–Cl–O(14)	112.4(7)
C(2)–C(3)–N(1)	107.0(7)	O(12)–Cl–O(13)	102.9(1.2)
C(4)–C(3)–N(1)	105.3(6)	O(12)–Cl–O(14)	102.7(1.1)
C(3)–N(1)–Co	102.2(5)	O(13)–Cl–O(14)	117.7(8)

(c) Hydrogen bonding

A–B $\cdots$ C	A $\cdots$ C	B $\cdots$ C	A–B–C
N(1)–H(7) $\cdots$ W^I	2.922(10)	2.118	146
N(1)–H(8) $\cdots$ O(4^{II})	3.031(9)	2.166	149
N(2)–H(15) $\cdots$ O(12)	2.850(15)	2.003	155
N(2)–H(16) $\cdots$ W	3.300(11)	2.142	165
W–H(17) $\cdots$ O(14^{II})	2.955(14)	1.946	153
W–H(18) $\cdots$ O(2^{III})	2.768(11)	1.970	139

Roman superscripts refer to atom in the following equivalent positions: I $2 - x, \frac{1}{2} + y, 1.5 - z$ II $1.5 - x, 1 - y, -\frac{1}{2} + z$ III $x, 1 - y, z$.

The geometry of the smc ligands is normal,[34] although the apparent shortness of the co-ordinated carbonyl bond C(4)–O(1) and the associated lengthening of C(4)–C(3) suggests that the location of atom C(4) may be imperfect. The ligand dihedral angles are normal,[4] and are compared (Table 4) with those found in a dimeric complex of cysteine and molybdenum(v).[4]

31 R. M. Magee, W. Mazurek, M. J. O'Connor, and I. T. Phillip, *Austral. J. Chem.*, 1974, **27**, 1629.
32 W. H. Watson, D. R. Johnson, M. B. Celap, and B. Kamberi, *Inorg. Chim. Acta*, 1972, **6**, 591.
33 R. Herak, B. Prelesnik, L. J. Manojlovic-Muir, and K. W. Muir, *Acta Cryst.*, 1974, **B30**, 229.
34 K. A. Kerr, presented at American Cryst. Assocn. Meeting, Albuquerque, New Mexico, 1972.

The hydrogen bonding in the crystals is extensive, with every available donor atom participating. Figure 2 is a stereoview of the packing in the cell, and probable

Dihedral angle	L(I) †	L(II) †	Mo$_2$(cyst)$_2$ ¶
O*–C–C^a–C$^\beta$	78.9 ‡	83.8	93
O*–C–C^a–N$^\beta$	–34.6	–32.5	–23
N–C^a–C$^\beta$–S	44.7	49.2	57
M–N–C^a–C$^\beta$	–69.7	–70.9	–66
M–N–C^a–C	45.0	47.2	50
C^a–C$^\beta$–S–M	–3.7	–8.6	
C^a–C$^\beta$–S–CH$_3$	78.0	98.7	

* Carboxy–oxygen bonded to metal. † L(I) is C^1–S^1–C^2–C^3(:N^1)–C^4(:O^1)–O^3, L(II) is C^5–S^2–C^6–C^7(:N^2)–C^3(:O^2)–O^4. ‡ Values taken as positive when the far atom rotates anticlockwise relative to near atom. ¶ From ref. 4.

hydrogen bonds are listed in Table 3. The amino-groups are each involved in two probable hydrogen bonds to oxygen atom acceptors. N(1) Interacts with the water

view of the hydrogen bonding (*vide supra*), one might expect that the Cl–O(12) and Cl–O(14) bonds would be slightly longer than the remaining Cl–O bonds,[35] but this is apparently not the case since, to the precision available, Cl–O(14) is shorter than Cl–O(13). The nominally tetrahedral bond angles at chlorine are in the range 102.7(1.1)—117.7(8)°, mean 109.1°. The Cl–O bond lengths are in the range 1.305—1.406 Å, mean 1.37(4) Å.

While cysteine and its derivatives are potentially terdentate ligands, this is the first structural investigation of an octahedral complex with all six co-ordination sites occupied by two cysteine or cysteine derivative molecules. Terdentate cysteine has been established [4] in the molybdenum(v) complex Na$_2$[Mo$_2$O$_4$(SCH$_2$·CH·NH$_2$·CO$_2$)$_2$]·5H$_2$O, but the Mo–O bond is apparently substantially weaker than are the Mo–S and Mo–N bonds; in a variety of other cysteinato-complexes of molybdenum the amino-acid acts as a bidentate chelate.[8,11,12] Similarly, while D-penicillamine has been observed [5] to be terdentate towards lead(II), it forms a complicated
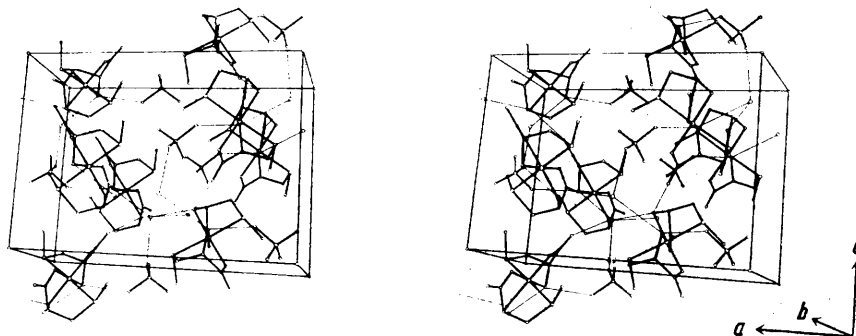

FIGURE 2 Stereoscopic view of the packing of the molecules in the cell showing the hydrogen bonding scheme. Hydrogen bonds are represented by thinner lines

molecule with N(1) · · · W and N(1)-H · · · W of 2.922 Å and 146°, and the terminal carboxy-oxygen atom O(4) of a neighbouring molecule with N(1) · · · O(4) and N(1)-H · · · O(4) 3.031 Å and 149°. N(2) Is hydrogen bonded to the water molecule [N(2) · · · W 3.30 Å, N(2)-H · · · W 165°] and to an oxygen atom of the perchlorate anion [N(2) · · · O(12) 2.850 Å, N(2)-H · · · O(12) 155°]. In addition to accepting the two N–H · · · O hydrogen bonds above, the water molecule acts as a donor to the terminal carboxy-oxygen atom O(2) and to another perchlorate oxygen atom O(14), with O · · · O 2.768 and 2.995 Å, and O–H · · · O 153 and 139°, respectively.

The geometry of the perchlorate anion is similar to that found in a number of recent structural studies.[35-39] In

polymeric structure [40] with cadmium(II) and acts [3] as a bidentate bridge towards methylmercury(II). Methionine, which is analogous to smc, has only been observed crystallographically as a bidentate ligand,[9,13-15] co-ordinating through O and N to copper(II) and through S and N to palladium and platinum(II), but Hidaka and co-workers have presented compelling spectroscopic evidence for the existence of terdentate complexes of methionine and cobalt(III).[7]

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