Articles

Materials Synthesis and Applications

Hexakis(prop-2-enamide)copper(II) bis(perchlorate) and hexakis(prop-2- enamide)manganese(II) bis(perchlorate)

Mary McNamara
Technological University Dublin, Mary.McNamara@tudublin.ie

Andrew Kellett
Technological University, andrew.kellett@tudublin.ie

Georgina Rosair
Heriot-Watt University

See next page for additional authors

Recommended Citation

Authors

Mary McNamara, Andrew Kellett, Georgina Rosair, Michael Devereux, and Malachy McCann

Hexakis(prop-2-enamide)copper(II) bis(perchlorate) and hexakis(prop-2-enamide)manganese(II) bis(perchlorate)

Andrew Kellett,[a] Georgina Rosair,[b*] Michael Devereux,[a] Mary McNamara[a] and Malachy McCann[c]

a Inorganic Pharmaceutical and Bio-mimetic Research Laboratory and Focas Research Institute, Dublin Institute of Technology, Kevin Street, Dublin 8, Ireland, b Perkin Building, School of Engineering and Physical Sciences, Heriot–Watt University, Edinburgh EH14 4AS, Scotland, and c Chemistry Department, National University of Ireland Maynooth, Maynooth, Co. Kildare, Ireland

Correspondence e-mail: g.m.rosair@hw.ac.uk

The structures of $[Cu(AA)_6](ClO_4)_2$, (I), and $[Mn(AA)_6](ClO_4)_2$, (II) (AA is acrylamide, also known as prop-2-enamide; C_3H_5NO), display both intra- and intermolecular N—H_ _ _O hydrogen bonding. A three-dimensional network is propagated via the perchlorate counter-ions. There are two crystallographically independent molecules in the copper complex, with the most significant difference between them being the conformation of one symmetry-related pair of AA ligands. The copper complex exhibits syn/anti disorder of the CH_2 group in one pair of symmetry-related AA ligands. The CuII and MnII centres are both situated on centres of inversion. The copper complex cation has octahedral coordination geometry with typical Jahn–Teller distortions. [see Note 3]

Comment

Acrylamide (prop-2-enamide, AA) is a versatile nucleophile containing olefinic, carbonyl and amine groups. Consequently, AA can form a variety of metal complexes (Reedijk, 1971; Girma et al., 2005a), predominantly coordinating through the carbonyl O atom, with the monodentate geometries of divalent transition metals being octahedral for $[M(AA)_6]$ species. $[MX_2(AA)_4]$ species also adopt an octahedral geometry, with counter-ions or, in some cases, water molecules, occupying the ancillary coordinating positions (Girma et al., 2005a,b,c,d, 2006a,b). As yet, the structures of the copper(II) and manganese(II) AA complexes, (I) and (II), have not been published and both structures are described herein. AA has sparked worldwide debate within food safety circles due to its discovery within thermally treated foodstuffs (Rosen & Hellenas, 2002; Tareke et al., 2002; Mottram et al., 2002). It has been classified as a probable human carcinogen by the International Agency for Research on Cancer (1994) and is implicated in tumour formation (Rice, 2005), neurotoxicity (Chen et al., 2009) and mutagenesis (Martins et al., 2007; Baum et al., 2005). While AA and its metabolites, especially glycidamide, have been the subject of intensive investigations, the possibility of any of these species forming metal complexes in vivo through interaction with either free metal ions or metal cations within metalloenzymes has yet to be investigated. The relative ease with which metal

adducts of AA are formed, along with their apparent water solubility, makes us believe that compounds of this type may be worthy of further investigation from both synthetic and toxicological standpoints. The crystal structure of (I) consists of two crystallographically independent CuII centres, both situated on centres of inversion (Figs. 1 and 2). The Cu—O distances in the two molecules occur in two distinct ranges, viz. short [1.9340 (10)–1.9736 (10) A ˚] and long distances [2.4534 (10)–2.5241 (10) A ˚]. This is typical of Jahn–Teller distortions observed in d9 metal centres. The Cu2 centre has the greater spread of Cu—O distances but it is the other crystallographically independent molecule containing Cu1 which has disorder in one of the symmetry-independent CH_2 groups. In this disordered group, there are two possible positions for the CH_2 group, the major component being occupied 68% of the time. The major component has the CH_2 group anti with respect to NH_2, as in the ordered AA ligands, whereas the minor component is of the unusual syn conformation. In the other crystallographically independent molecule, one pair of AA ligands exists solely in this syn form, the rest have the anti configuration. None of the AA complexes found in the May 2010 version of the Cambridge Structural Database (Allen,2002) has the syn form. Several CH_2 C-atom displacement ellipsoids are rather anisotropic, but there is no residual electron density greater than 0.5 e A ˚ _3 associated with the AA atoms that would suggest additional syn/anti disorder. One perchlorate ion is noticeably disordered in one position, which is not involved in hydrogen bonding. All the O atoms in the other ordered perchlorate take part in hydrogen bonding. [see Note 5] In the manganese complex, (II), the MnII centre also lies on a centre of inversion but with the six Mn—O bond lengths in a tighter range [2.1357 (9)–2.1976 (9) A ˚], as would be expected for an MnII ion. All AA ligands are in the usual anti conformation (Fig. 3). All amine H atoms of (I) and (II) participate in hydrogen bonding, either intermolecularly with perchlorate O atoms to form a three-dimensional network, or intramolecularly with neighbouring AA O atoms. The N—H_ _ _O hydrogen bonds involving amides bound to the Cu_2 centre of (I) are closer to linearity than those emanating from the molecule containing Cu1 (see Table 1). In (I) and (II), and also in the cobalt (Girma et al., 2005b) and iron (Girma et al., 2006a) hexaacrylamide analogues, the intermolecular hydrogen bonds all involve the counter-ion. There are no direct cation-to-cation contacts in any of these four complexes. In (I) and (II), only four of the six amine groups take part in intramolecular hydrogen bonding (see Figs. 1, 2 and 3). These form six-membered rings with graph-set notation S(6) (Bernstein et al., 1995). The H atoms of the other two amines take part in intermolecular hydrogen bonding only. This is also the case in the FeII analogue (Girma et al. 2006b), while in the CoII, NiII and ZnII structures (Girma et al. 2006b), all amines are involved in intermolecular hydrogen bonding. The solely intermolecularly hydrogenbonded ligand (and its symmetry equivalent) in (I) has the longest Cu—O distance at both Cu centres, whereas conversely in (II), the shortest Mn—O bonds are made by the solely intermolecularly hydrogen-bonded ligand. The three shortest N_ _ _O distances are all intramolecular hydrogen bonds in (I), but there is no such distinction in (II). Two pairs of O atoms in (I) do not participate in hydrogen bonding (O3, O4 and their symmetry equivalents), whereas atoms O2 and O6

make bifurcated hydrogen bonds with neighbouring amine groups (see Figs. 1 and 2). The pattern in (II) differs subtly in that although one pair of O atoms (O3 and its symmetry equivalent) is not involved in N—H_ _ _O hydrogen bonding, no bifurcated hydrogen bonds are made by the other O atoms. The torsion angles M—O—C—N in (I) and (II) vary such that when this intramolecular hydrogen bond is present the range of values is 3.33 (19)–19.9 (2)_, but when the amine does not make this type of bond the torsion angle is between _80.89 (16) and _107.32 (14)_. The FeII species with the perchlorate counter-ion (Girma et al., 2006b) has a similar combination of intra- and intermolecular hydrogen-bonding patterns to the CuII and MnII structures described here. However, in the FeII analogue with _2-oxido-hexachloridodiiron(III) as the counter-ion (Girma et al., 2008), the amides all have intramolecular N—H_ _ _O contacts, although, in addition, two amine groups make intermolecular contacts with the bridging oxide atom in the counter-ion. The intermolecular hydrogen bonding in (I) and (II) is extensive and propagates in three dimensions (see Figs. 4 and 5, and Tables 1 and 2). The N—H_ _ _O linkages joining the complex cations to the counter-ions form a series of rings. One type of ring [viz. R24(20)] involves one perchlorate O atom in a bifurcated hydrogen bond as the link between complex cations, and another requires two O atoms in the counter-ion to form the ring R44 (24). Both these rings are over centres of inversion and involve two identical CuII centres. Complex cations containing Cu1 and Cu2 are joined to form dimers via perchlorate O atoms, with graph-set notation D33 (14). In (II), the intermolecular hydrogen bonding differs from (I) in that chains are more apparent than rings. The smallest ring which includes the metal centres has graph-set notation R88 (36), where four manganese complex cations are needed to form a ring with four perchlorates. In conclusion, metal complexes of AA display a significant degree of variation in intramolecular hydrogen bonding, even between chemically identical molecules. Such variation increases the capacity for yet more diversity in intermolecular interactions for complexes containing relatively simple ligands.

Experimental
For the preparation of [Cu(AA)6](ClO4)2, (I), acrylamide (1.15 g, 16.2 mmol) was added to a solution of copper(II) perchlorate hexahydrate (1.0 g, 2.7 mmol) in a 50:50 mixture of acetonitrile and triethylorthoformate (14 ml). The resulting blue solution was stirred at room temperature for 1 h and then allowed to stand for one week, resulting in the formation of the product as blue crystals (yield 1.17 g, 63%). Analysis calculated: C 31.38, H 4.39, N 12.20, Cl 10.29%; found: C 31.38, H 4.36, N 12.04, Cl 10.04%. IR (KBr, _, cm_1): 3335, 3196, 1667, 1429, 1353, 1281, 1089, 985, 811, 626, 508; Raman (cm_1): 3103, 3033, 3011, 2923, 1682, 1637, 1588, 1435, 1284, 1144, 1052, 959, 941, 844, 812, 627, 506, 462, 303, 126, 98; solubility: water; UV–Vis: _d_d = 808 nm, " = 12 dm3 mol_1 cm_1.

For the preparation of [Mn(AA)6](ClO4)2, (II), acrylamide (1.17 g, 16.6 mmol) was added to a solution of manganese(II) perchlorate hexahydrate (1.0 g, 2.8 mmol) in a 50:50 mixture of acetonitrile and triethylorthoformate (14 ml). The resulting colourless solution was stirred at room temperature for 1 h and then

allowed to stand for one week, resulting in the formation of the product as colourless crystals which were stored at 253 K (yield 1.21 g, 64%). Analysis calculated: C 31.78, H 4.44, N 12.35, Cl 10.42%; found: C 29.68, H 4.74, N 11.05, Cl 7.65%. IR (KBr, _, cm_1): 3333, 3189, 2745, 1665, 1621, 1589, 1436, 1436, 1360, 1282, 1105, 979, 811, 629; Raman (cm_1): 3363, 2932, 1667, 1606, 1459, 1324, 1122, 933, 842, 764, 624, 458, 134; solubility: water.

In (I), the CH2 group in one pair of AA ligands was disordered, with relative occupancies of 0.682 (5) and 0.318 (5) [may change with new refinement], and these were labelled as C23B and C23C, respectively. The O atoms (O6S and O6T) in one perchlorate ion were disordered and refined with relative occupancies of 0.80 (2) and 0.20 (2), respectively. [Sheldrick, 2008) distance restraints were applied to all Cl—O distances, and isotropic restraints (ISOR 0.01 in SHELXL97) were applied to one perchlorate O atom (O6T) and one AA C atom (C43). For both (I) and (II), all amine H atoms were located in difference Fourier maps. Their coordinates were refined freely in (I) but fixed in idealized positions in (II), and their isotropic displacement parameters were treated as riding on the parent N atom, with Uiso(H) = 1.2Ueq(N). The positions of all H atoms bound to C atoms were calculated and constrained to idealized geometries, with C—H=0.95 A ˚ and Uiso(H) = 1.2Ueq(C). For both compounds, data collection: APEX2 (Bruker, 2008); cell refinement: SAINT (Bruker, 2008); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

References
Allen, F. H. (2002). Acta Cryst. B58, 380–388. Baum,M., Fauth, E., Fritzen, S., Herrmann, A.,Mertes, P., Merz, K., Rudolphi, M., Zankl, H. & Eisenbrand, G. (2005). Mutat. Res. 580, 61–69.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). Angew. Chem. Int. Ed. Engl. 34, 1555–1573.

Bruker (2008). APEX2. Version 2009-5. Bruker AXS Inc., Madison, Wisconsin, USA. Chen, J.-H., Wu, K.-Y., Chiu, I.-M., Tsou, T.-C. & Chou, C.-C. (2009). Toxicol. In Vitro, 23, 855–861. doi:10.1016/j.tiv.2009.04.015.
]
Girma, K. B., Lorenz, V., Blaurock, S. & Edelmann, F. T. (2005a). Coord. Chem. Rev. 249, 1283–1293.

Girma, K. B., Lorenz, V., Blaurock, S. & Edelmann, F. T. (2005b). Z. Anorg. Allg. Chem. 631, 1419–1422.

Girma, K. B., Lorenz, V., Blaurock, S. & Edelmann, F. T. (2005c). Z. Anorg. Allg. Chem. 631, 2763–2769.

Girma, K. B., Lorenz, V., Blaurock, S. & Edelmann, F. T. (2005d). Z. Anorg. Allg. Chem. 631, 1843–1848.

Girma, K. B., Lorenz, V., Blaurock, S. & Edelmann, F. T. (2006a). Inorg. Chim. Acta, 359, 364–368.

Girma, K. B., Lorenz, V., Blaurock, S. & Edelmann, F. T. (2006b). Z. Anorg. Allg. Chem. 632, 1874–1878.

Girma, K. B., Lorenz, V., Blaurock, S. & Edelmann, F. T. (2008). Inorg. Chim. Acta, 361, 346–348.

International Agency for Research on Cancer (1994). IARC Monogr. Eval. Carcinog. Risks Hum. 60, 389–433.

Martins, C., Oliveira, N. G., Pingarilho, M., daCosta, G. G., Martins, V., Marques, M. M., Beland, F. A., Churchwell, M. I., Doerge, D. R., Rueff, J. & Gaspar, J. F. (2007). Toxicol. Sci. 95, 383–390.

Mottram, D. S., Wedzicha, B. L. & Dodson, A. T. (2002). Nature (London), 419, 448–449.

Reedijk, J. (1971). Inorg. Chim. Acta, 5, 687–690.

Rice, J. M. (2005). Mutat. Res. 580, 3–20.

Rosen, J. & Hellenas, K. E. (2002). Analyst, 127, 880–882.

Sheldrick, G. M. (2008). Acta Cryst. A64, 112–122.

Tareke, E., Rydberg, P., Karlsson, P., Eriksson, S. & To¨ rnqvist, M. (2002). J. Agric. Food Chem. 50, 4998–5006.

Compound (I)

Crystal data
$[Cu(C_3H_5NO)_6](ClO_4)_2$
Mr = 688.92
Triclinic, P1
a = 8.4577 (5) Å
b = 9.8762 (6) Å
c = 17.7889 (11) Å
_ = 88.392 (3)_
_ = 85.871 (3)_
_ = 83.690 (3)_
V = 1472.77 (15) Å 3
Z = 2
Mo K_ radiation
_ = 1.00 mm_1
T = 100 K
0.80 _ 0.58 _ 0.32 mm
Data collection
Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2008)
Tmin = 0.503, Tmax = 0.741
34176 measured reflections
9130 independent reflections
7503 reflections with I > 2_(I)
Rint = 0.031

Table 1

Hydrogen-bond geometry (Å , _) for (I).

D—H_ _ _A	D—H	H_ _ _A	D_ _ _A	D—H_ _ _A
N1—H1A_ _ _O2i	0.83 (2)	2.13 (2)	2.9048 (18)	155.3 (18)
N1—H1B_ _ _O4Sii	0.80 (2)	2.23 (2)	3.0001 (19)	159.7 (18)
N2—H2A_ _ _O5Si	0.82 (2)	2.29 (2)	3.043 (2)	153 (2)
N2—H2B_ _ _O1Si	0.81 (2)	2.26 (2)	2.9955 (19)	151 (2)
N3—H3A_ _ _O2	0.81 (2)	2.16 (2)	2.8758 (19)	147 (2)
N3—H3B_ _ _O1Siii	0.86 (2)	2.19 (2)	3.0215 (18)	161.7 (19)
N4—H4A_ _ _O6iv	0.83 (2)	2.21 (2)	2.9359 (17)	145.6 (17)
N4—H4B_ _ _O7S	0.80 (2)	2.28 (2)	3.0691 (19)	165.3 (18)
N5—H5A_ _ _O6	0.84 (2)	2.06 (2)	2.8673 (18)	160.6 (18)
N5—H5B_ _ _O7Sv	0.82 (2)	2.27 (2)	3.0784 (19)	172.8 (18)
N6—H6A_ _ _O2Svi	0.86 (2)	2.15 (2)	3.0021 (19)	169.7 (18)
N6—H6B_ _ _O5Svi	0.85 (2)	2.27 (2)	3.0978 (18)	166.4 (18)

Symmetry codes: (i) _x þ 2;_y þ 1;_z; (ii) x; y þ 1; z; (iii) x þ 1; y; z; (iv) _x;_y þ 2;_z þ 1; (v) _x þ 1;_y þ 2;_z þ 1; (vi) _x þ 1;_y þ 1;_z þ 1.

Refinement
$R[F2 > 2\_(F2)] = 0.032$
$wR(F2) = 0.084$
$S = 1.04$
9130 reflections
426 parameters
33 restraints
H atoms treated by a mixture of independent and constrained refinement
_   max = 0.79 e A ˚ _3
_   min = _0.59 e A ˚ _3

Compound (II)

Crystal data
$[Mn(C_3H_5NO)_6](ClO_4)_2$
$Mr = 680.32$
Monoclinic, $P21=c$
$a = 9.2804$ (6) A ˚
$b = 15.9533$ (10) A ˚
$c = 10.6876$ (7) A ˚
_ = 111.642 (3)_
$V = 1470.79$ (16) A ˚ 3
$Z = 2$
Mo K_ radiation
_ = 0.70 mm_1
$T = 100$ K
0.64 _ 0.58 _ 0.42 mm
Data collection
Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2008)
Tmin = 0.662, Tmax = 0.757
43193 measured reflections
5063 independent reflections
4083 reflections with I > 2_(I)
Rint = 0.042
Refinement
$R[F2 > 2\_(F2)] = 0.034$
$wR(F2) = 0.090$
$S = 1.08$
5063 reflections
187 parameters
H-atom parameters constrained
_   max = 0.52 e A ˚ _3
_   min = _0.52 e A ˚ _3

Table 2
Hydrogen-bond geometry (A˚ , _) for (II).

D—H_ _ _A	D—H	H_ _ _A	D_ _ _A	D—H_ _ _A
N1—H1A_ _ _O2i	0.88	2.28	2.9678 (15)	135
N1—H1B_ _ _O1Sii	0.88	2.30	3.1153 (15)	155
N2—H2A_ _ _O1	0.88	2.10	2.9241 (14)	155
N2—H2B_ _ _O1Siii	0.88	2.46	3.2343 (16)	147
N2—H2B_ _ _O2Siv	0.88	2.55	3.2121 (18)	133
N3—H3A_ _ _O1Siv	0.88	2.24	3.0030 (16)	145
N3—H3B_ _ _O3S	0.88	2.15	3.0206 (16)	168

Symmetry codes: (i) _x;_y;_z þ 2; (ii) x _ 1;_y þ 1
2; z þ 1
2; (iii) x; y; z þ 1; (iv)
x;_y þ 1
2; z þ 1
2.
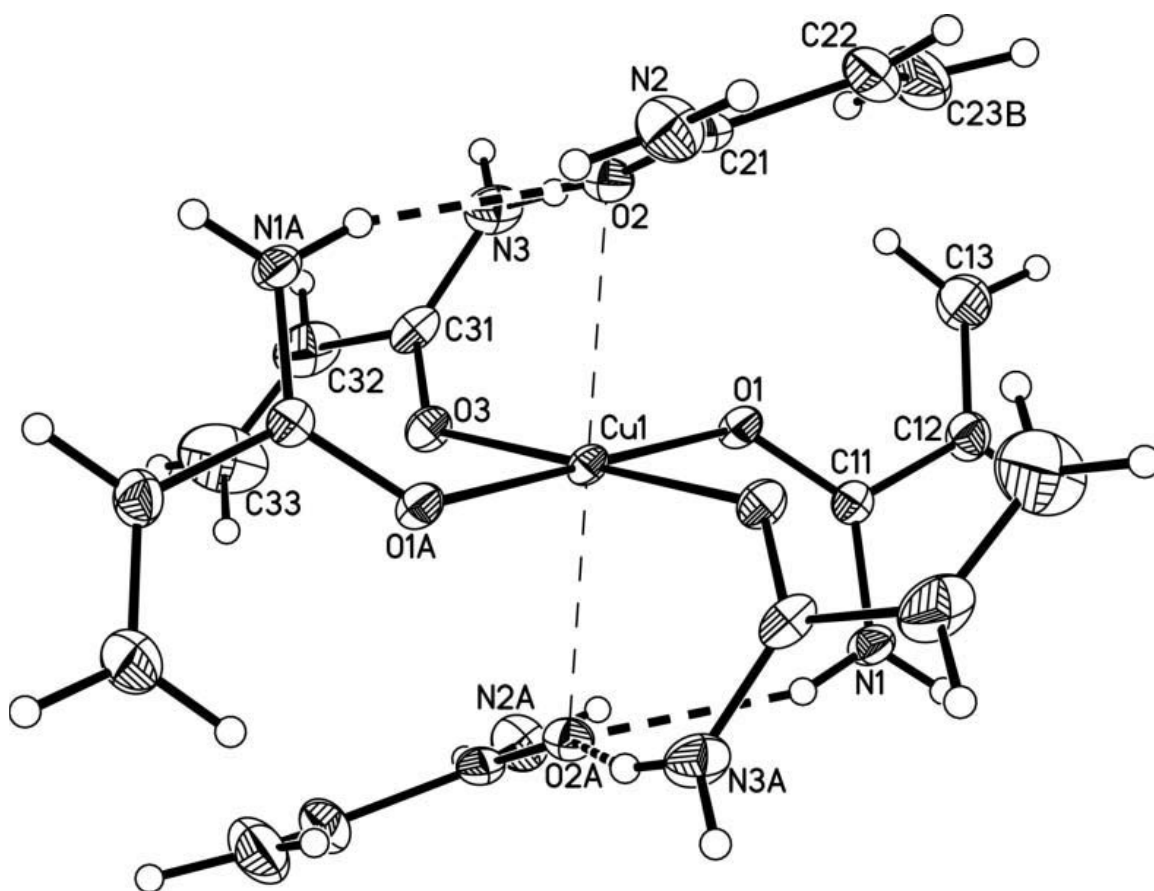
Figure 1
A perspective view of one of the crystallographically independent molecules in
(I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at

the 50% probability level. The suffix 'A' denotes the symmetry operation (_x + 2, _y + 1, _z). Counter-ions and the minor disorder component in the CH2 fragment have been omitted for clarity. H atoms are shown as small spheres of arbitrary radii. Intramolecular hydrogen bonds are shown as dashed lines.
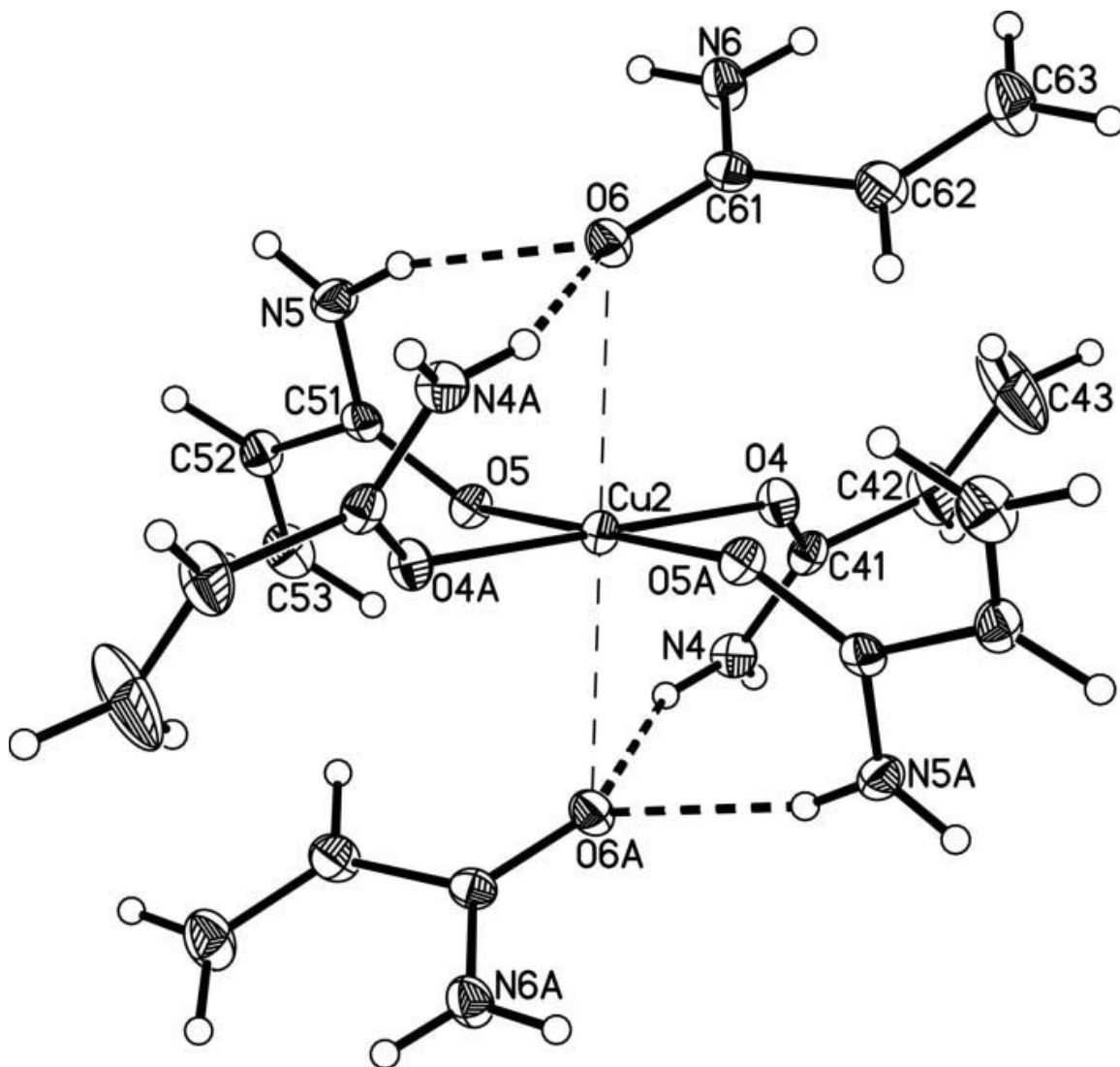

Figure 2
A perspective view of the second crystallographically independent molecule of (I), showing the atom-numbering scheme. Counter-ions have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. The suffix 'A' denotes the symmetry operation (_x, _y + 2, _z + 1). H atoms are shown as small spheres of arbitrary radii. Intramolecular hydrogen bonds are shown as dashed lines.
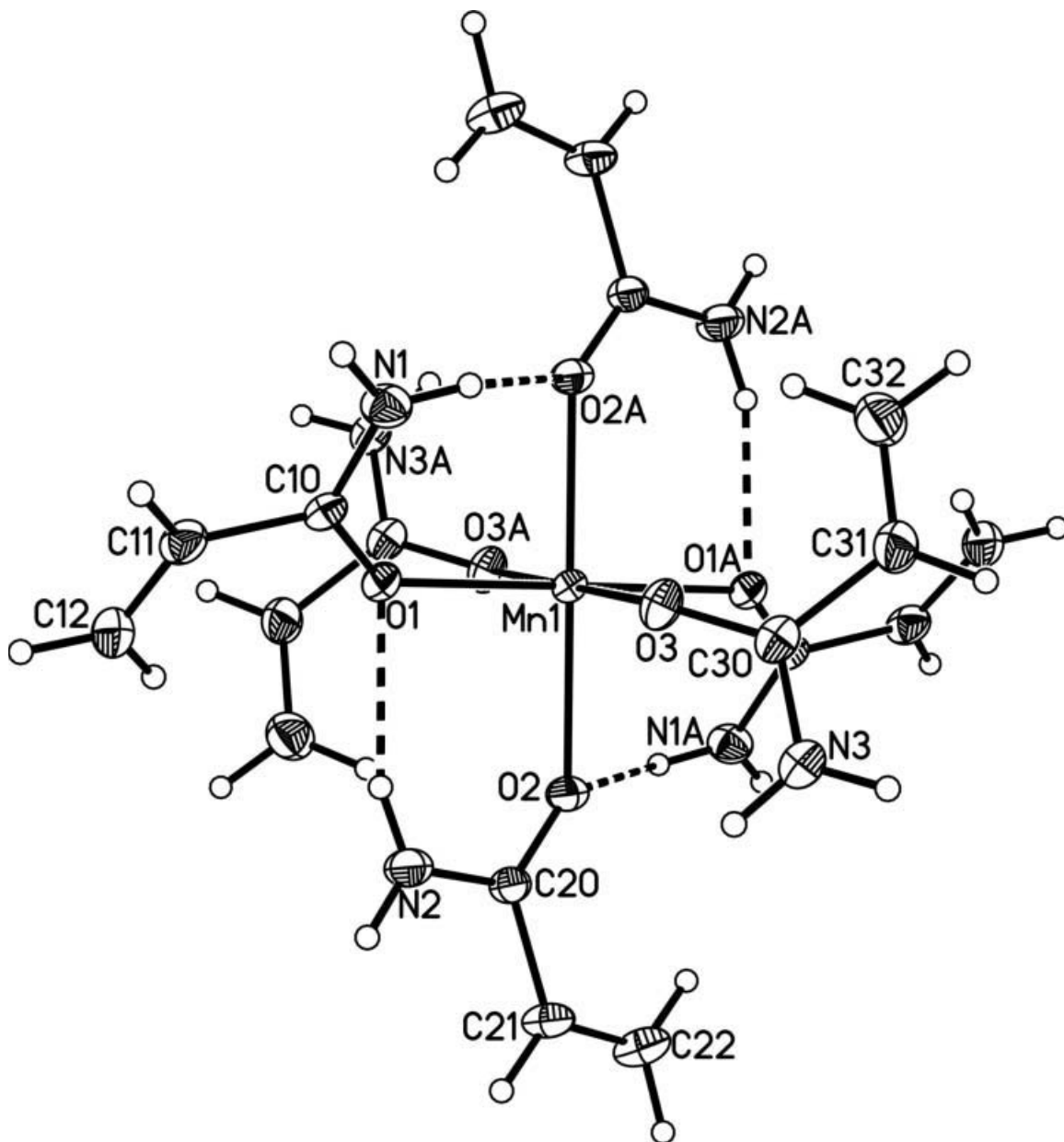
Figure 3
A perspective view of (II), showing the atom-numbering scheme. Counter-ions have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. The suffix 'A' denotes the symmetry operation (_x, _y, _z + 2). H atoms are shown as small spheres of arbitrary radii. Intramolecular hydrogen bonds are shown as dashed lines
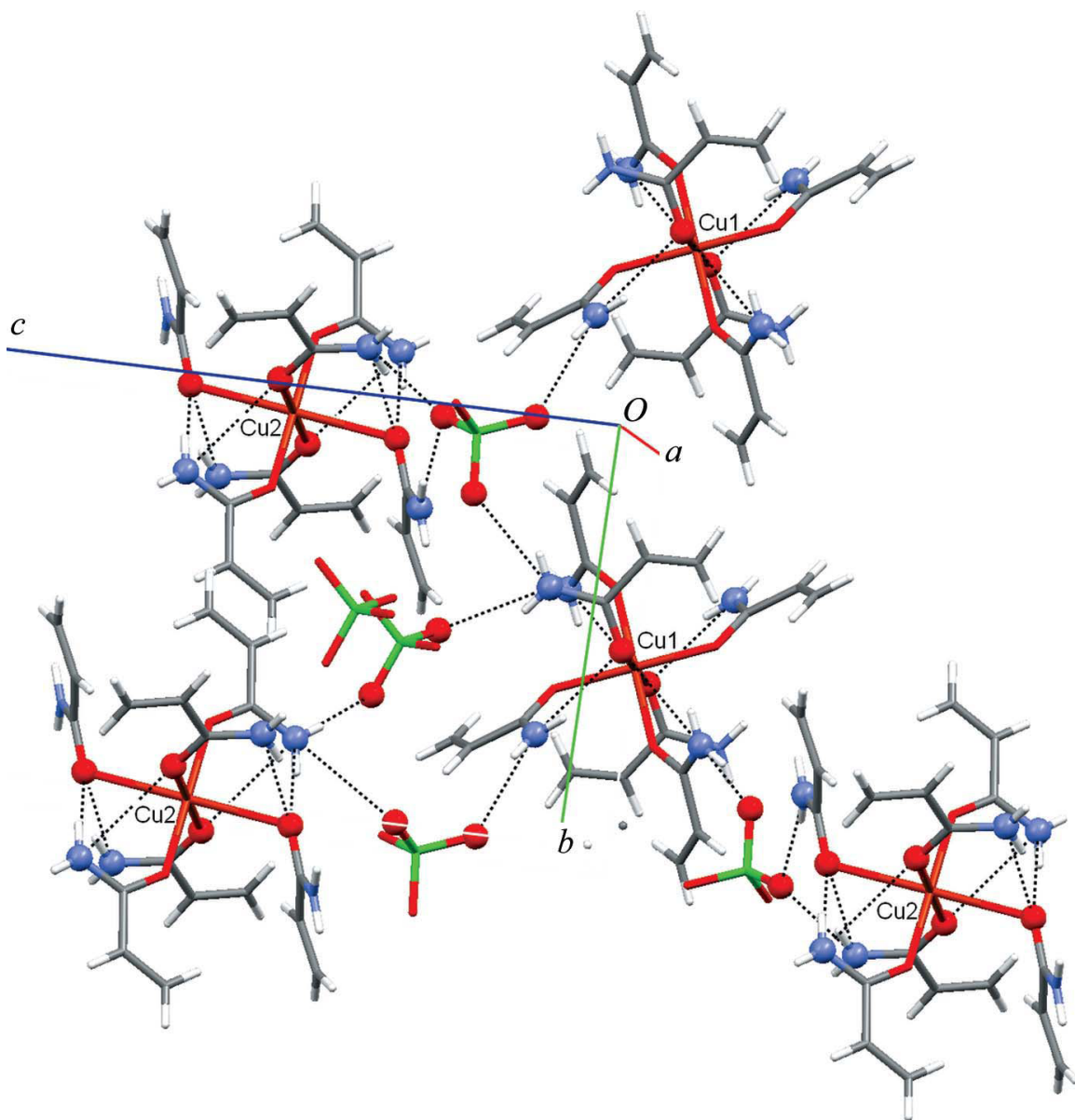
Figure 4
The hydrogen bonding of (I), showing both intra- and intermolecular hydrogen bonds (dashed lines). [see Note 6]
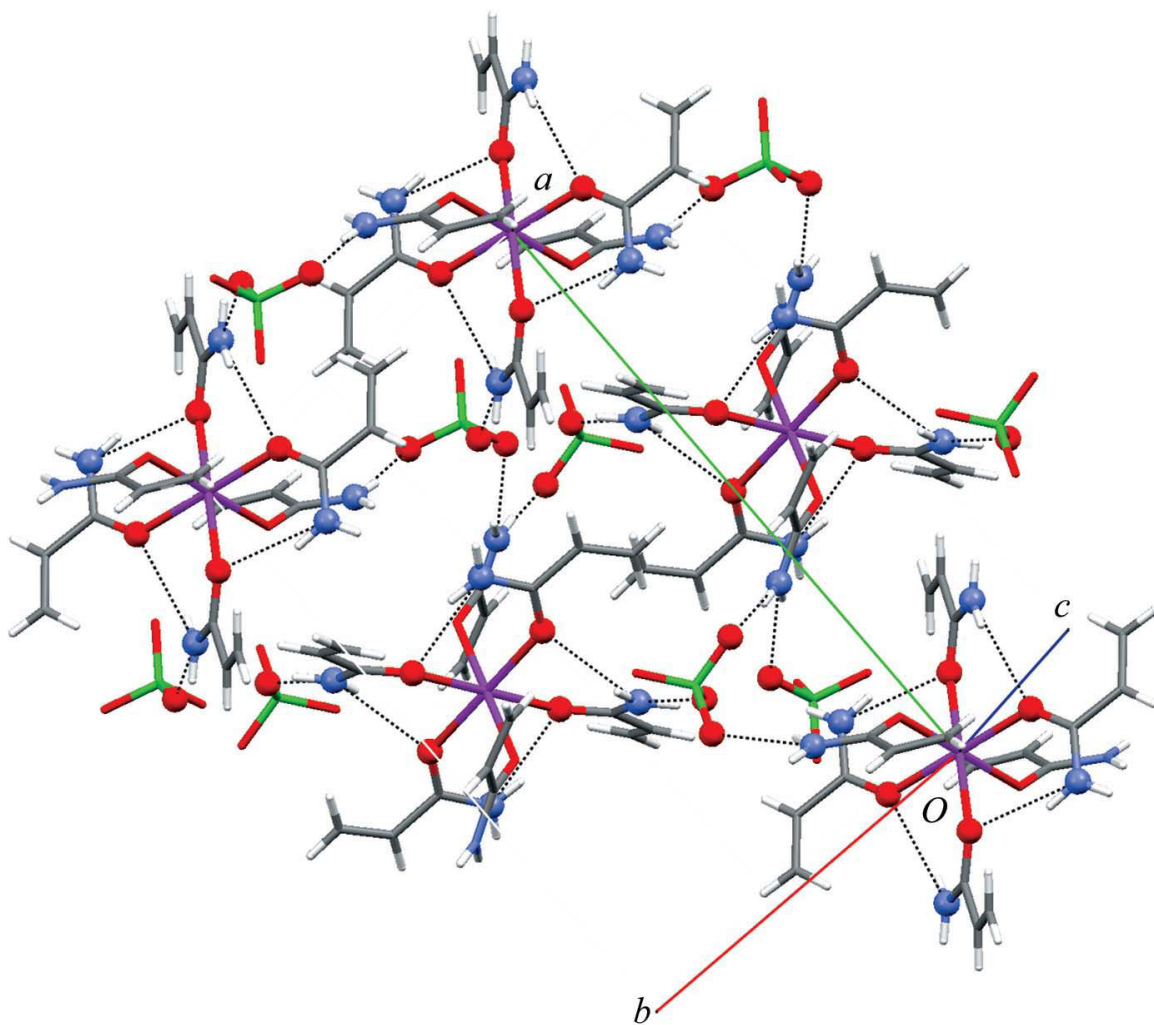
Figure 5
The hydrogen bonding of (II), showing both intra- and intermolecular
hydrogen bonds (dashed lines). [see Note 6]