metal-organic compounds

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

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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 $N-H\cdots O$ 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 which are in the unusual *syn* conformation. The copper complex exhibits *syn/anti* disorder of the $=CH_2$ group in one pair of symmetry-related AA ligands. The Cu^{II} and Mn^{II} centres are both situated on centres of inversion. The copper complex cation has octahedral coordination geometry with typical Jahn–Teller distortions.

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.*, 2005*a*), 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.*, 2005*a,b,c,d*, 2006*a,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.

(I)

(II)
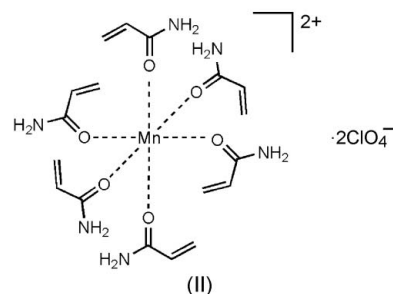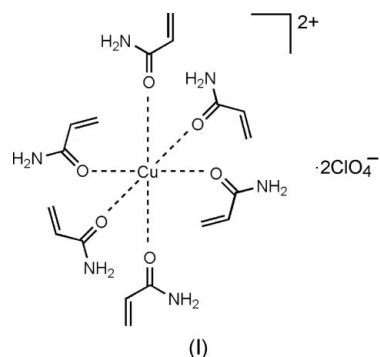
The crystal structure of (I) consists of two crystallographically independent Cu^{II} centres, both situated on centres of inversion (Figs. 1 and 2). The $Cu-O$ distances in the two molecules occur in two distinct ranges, *viz.* short [1.9338 (9)–1.9735 (10) Å] and long distances [2.4535 (10)–2.5241 (11) Å]. This is typical of Jahn–Teller distortions observed in d^9 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 approximately 64% 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,
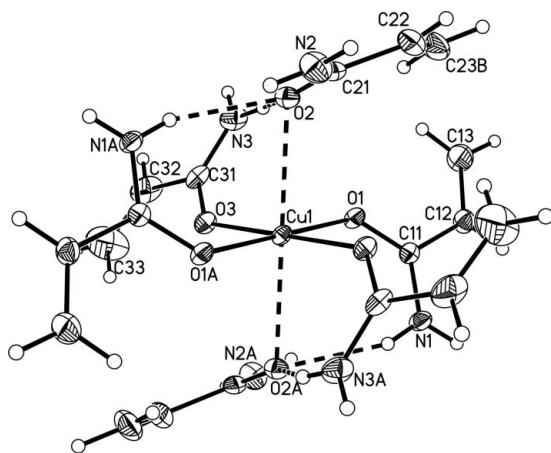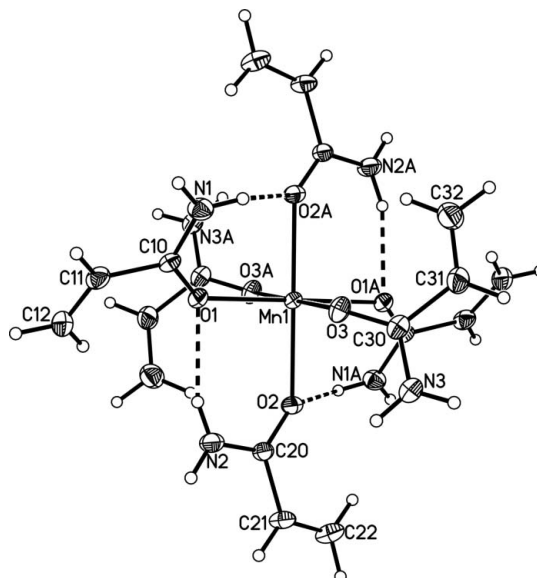
Figure 1
A perspective view of one of the crystallographically independent molecules in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The suffix 'A' denotes the symmetry operation ($-x + 2, -y + 1, -z$). Counter-ions and the minor disorder component in the $=CH_2$ fragment have been omitted for clarity. H atoms are shown as small spheres of arbitrary radii. Intramolecular hydrogen bonds are shown as dashed lines.
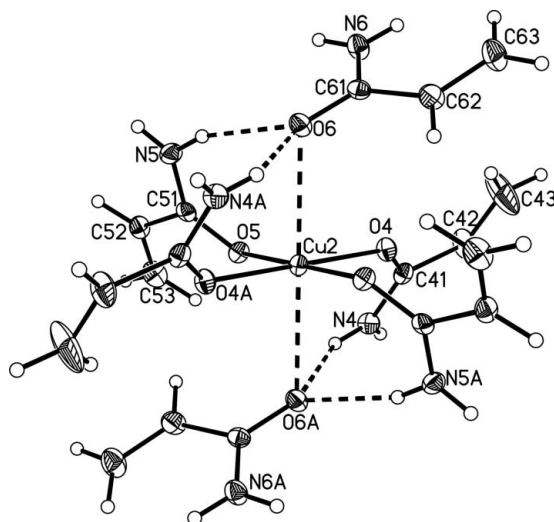
Figure 2
A perspective view of the second crystallographically independent molecule of (I), showing the atom-numbering scheme. Counter-ions have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. The suffix 'A' denotes the symmetry operation ($-x, -y + 2, -z + 1$). 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.

but there is no residual electron density greater than 0.5 e Å^{-3} associated with the AA atoms that would suggest additional *syn/anti* disorder. One perchlorate ion is noticeably disordered and was modelled with two O4 orientations, yet four of the eight O-atom positions take part in hydrogen bonding. Three of the four O atoms in the other ordered perchlorate take part in hydrogen bonding.

In the manganese complex, (II), the Mn^{II} 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) Å], as would be expected for an Mn^{II} 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 Cu2 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.*, 2005*b*) and iron (Girma *et al.*, 2006*a*) 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 Fe^{II} analogue (Girma *et al.* 2006*b*), while in the Co^{II}, Ni^{II} and Zn^{II} structures (Girma *et al.* 2006*b*), all amines are involved in intermolecular hydrogen bonding. The solely intermolecularly hydrogen-bonded 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
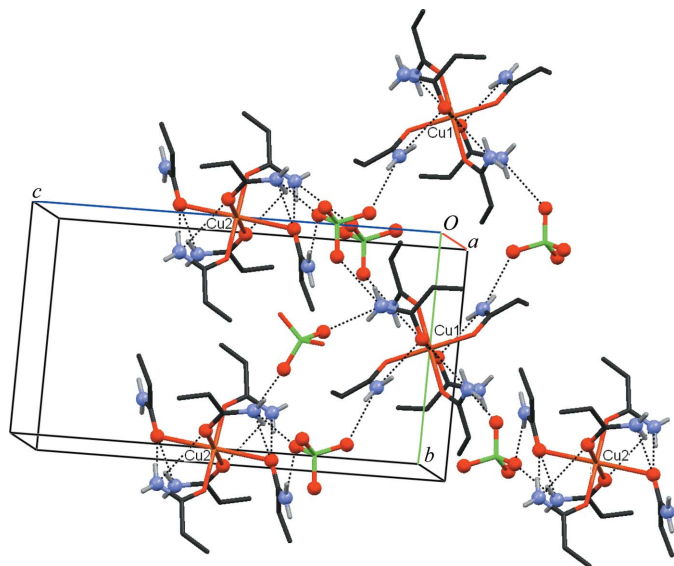
Figure 4
The hydrogen bonding of (I), showing both intra- and intermolecular hydrogen bonds (dashed lines).
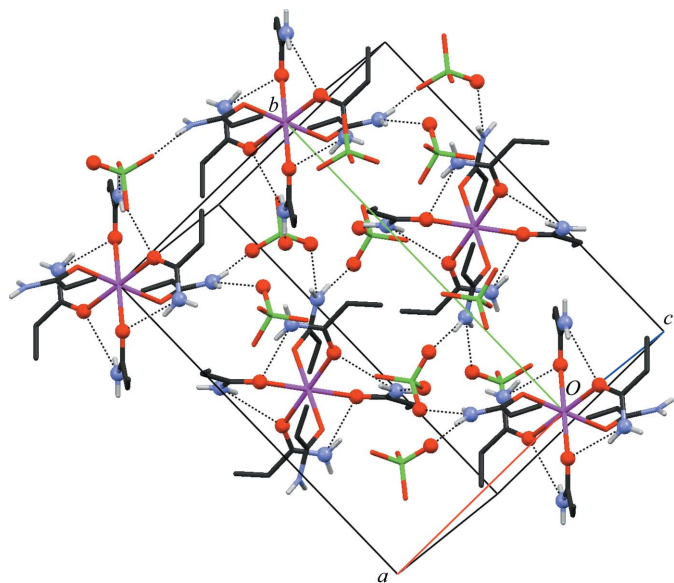

Figure 5
The hydrogen bonding of (II), showing both intra- and intermolecular hydrogen bonds (dashed lines).

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 −80.87 (16) and −107.33 (14)°. The Fe[II] species with the perchlorate counter-ion (Girma *et al.*, 2006*b*) has a similar combination of intra- and intermolecular hydrogen-bonding patterns to the Cu[II] and Mn[II] structures described here. However, in the Fe[II] analogue with μ_2-oxido-hexachlorido-diiron(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.* $R_4^2(20)$] 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 $R_4^4(24)$. Both these rings are over centres of inversion and involve two identical Cu[II] centres. Complex cations containing Cu1 and Cu2 are joined to form dimers *via* perchlorate O atoms, with graph-set notation $D_3^3(14)$. 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 $R_8^8(36)$, 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

Compound (I)

Crystal data

[Cu(C3H5NO)6](ClO4)2	$\gamma = 83.690\ (3)°$
$M_r = 688.92$	$V = 1472.77\ (15)$ Å^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.4577\ (5)$ Å	Mo $K\alpha$ radiation
$b = 9.8762\ (6)$ Å	$\mu = 1.00$ mm^{-1}
$c = 17.7889\ (11)$ Å	$T = 100$ K
$\alpha = 88.392\ (3)°$	$0.80 \times 0.58 \times 0.32$ mm
$\beta = 85.871\ (3)°$	

Table 1
Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1$B\cdots$O4S^{i}	0.83 (1)	2.21 (2)	2.9997 (18)	159 (2)
N1—H1$A\cdots$O2^{ii}	0.84 (1)	2.12 (2)	2.9049 (17)	155 (2)
N2—H2$A\cdots$O8T^{iii}	0.83 (2)	2.21 (3)	2.97 (2)	153 (2)
N2—H2$B\cdots$O1S^{iii}	0.83 (2)	2.24 (2)	2.9952 (18)	151 (2)
N3—H3$B\cdots$O2	0.83 (1)	2.15 (2)	2.8759 (17)	147 (2)
N3—H3$A\cdots$O1S	0.85 (1)	2.20 (2)	3.0219 (17)	162 (2)
N4—H4$A\cdots$O6S	0.83 (1)	2.23 (2)	3.037 (8)	164 (2)
N4—H4$A\cdots$O5T	0.83 (1)	2.38 (2)	3.19 (2)	166 (2)
N4—H4$B\cdots$O6^{iv}	0.84 (1)	2.21 (2)	2.9362 (16)	145 (2)
N5—H5$B\cdots$O6S^{v}	0.84 (1)	2.27 (2)	3.100 (6)	171 (2)
N5—H5$B\cdots$O5T^{v}	0.84 (1)	2.19 (2)	3.027 (15)	179 (2)
N5—H5$A\cdots$O6	0.85 (1)	2.05 (2)	2.8676 (17)	161 (2)
N6—H6$B\cdots$O2S^{vi}	0.86 (1)	2.15 (2)	3.0019 (18)	170 (2)
N6—H6$A\cdots$O8S^{vi}	0.85 (1)	2.25 (2)	3.080 (9)	166 (2)
N6—H6$A\cdots$O8T^{vi}	0.85 (1)	2.32 (3)	3.15 (2)	166 (2)

Symmetry codes: (i) $x-1, y+1, z$; (ii) $-x, -y+1, -z$; (iii) $-x+1, -y+1, -z$; (iv) $-x, -y+2, -z+1$; (v) $-x+1, -y+2, -z+1$; (vi) $-x+1, -y+1, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1$A\cdots$O2^{i}	0.88	2.28	2.9678 (15)	135
N1—H1$A\cdots$O1S^{ii}	0.88	2.30	3.1153 (15)	155
N2—H2$A\cdots$O1	0.88	2.10	2.9241 (14)	155
N2—H2$B\cdots$O1S^{iii}	0.88	2.46	3.2343 (16)	147
N2—H2$B\cdots$O2S^{iv}	0.88	2.55	3.2121 (18)	133
N3—H3$A\cdots$O1S^{iv}	0.88	2.24	3.0030 (16)	145
N3—H3$B\cdots$O3S	0.88	2.15	3.0206 (16)	168

Symmetry codes: (i) $-x, -y, -z+2$; (ii) $x-1, -y+\frac{1}{2}, z+\frac{1}{2}$; (iii) $x, y, z+1$; (iv) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.

Data collection

Bruker APEXII CCD area-detector diffractometer	34176 measured reflections
	9130 independent reflections
Absorption correction: multi-scan	7503 reflections with $I > 2\sigma(I)$
($SADABS$; Bruker, 2008)	$R_{int} = 0.031$
$T_{min} = 0.503$, $T_{max} = 0.741$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.081$	
$S = 1.01$	
9130 reflections	$\Delta\rho_{max} = 0.52$ e Å^{-3}
457 parameters	$\Delta\rho_{min} = -0.58$ e Å^{-3}
165 restraints	

Compound (II)

Crystal data

[Mn(C$_3$H$_5$NO)$_6$](ClO$_4$)$_2$	$V = 1470.79$ (16) Å^3
$M_r = 680.32$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.2804$ (6) Å	$\mu = 0.70$ mm^{-1}
$b = 15.9533$ (10) Å	$T = 100$ K
$c = 10.6876$ (7) Å	$0.64 \times 0.58 \times 0.42$ mm
$\beta = 111.642$ (3)°	

Data collection

Bruker APEXII CCD area-detector diffractometer	43193 measured reflections
	5063 independent reflections
Absorption correction: multi-scan	4083 reflections with $I > 2\sigma(I)$
($SADABS$; Bruker, 2008)	$R_{int} = 0.042$
$T_{min} = 0.662$, $T_{max} = 0.757$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	187 parameters
$wR(F^2) = 0.090$	H-atom parameters constrained
$S = 1.08$	$\Delta\rho_{max} = 0.52$ e Å^{-3}
5063 reflections	$\Delta\rho_{min} = -0.52$ e Å^{-3}

In (I), the =CH$_2$ group in one of the unique AA ligands was disordered through an approximately 180° rotation about the C21—C22 bond, with relative occupancies of the two orientations of 0.644 (5) and 0.356 (5), and these were labelled as C23B and C23C, respectively. The displacement parameters of some atoms were restrained using rigid-bond restraints (DELU; Sheldrick, 2008),

namely (C31/C32/C33), (C41/C42/C43) and (C21/C22/C23C/C23B), or similarity restraints (SIMU), namely (C22/C23C/C23B), (C32/C33) and (C42/C43); atoms in parentheses were restrained together. All Cl—O and O$\cdots$O distances in both perchlorate anions were restrained to be similar within a standard uncertainty of 0.02 Å. One perchlorate anion has disordered O atoms and two orientations were modelled for all four O atoms with occupancies of 0.74 (2) for the major component. For both (I) and (II), all amine H atoms were located in difference Fourier maps. Their coordinates were refined in (I), with N—H distances restrained to 0.85 (2) Å, but fixed in geometrically idealized positions in (II) and treated as riding on the parent N atom, with U_{iso}(H) = 1.2U_{eq}(N). The positions of all H atoms bound to C atoms were calculated and constrained to idealized geometries, with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(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*.

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metal-organic compounds

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