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Bis(1-carbamoylguanidinium) diaquatetrachloromanganate(II)

Colin A. Bremner and William T. A. Harrison*

Department of Chemistry, University of Aberdeen, Aberdeen AB24 3UE, Scotland

Correspondence e-mail: w.harrison@abdn.ac.uk

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Mn–O) = 0.001 Å
R factor = 0.031
wR factor = 0.078
Data-to-parameter ratio = 30.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $(C_2H_7N_4O)_2[MnCl_4(H_2O)_2]$, contains a molecular network of $C_2H_7N_4O^+$ cations and $[Mn(H_2O)_2Cl_4]^{2-}$ *trans*-octahedral anions (Mn site symmetry 2/*m*). An extensive network of N—H···Cl, N—H···(Cl,Cl), N—H···O, O—H···O and O—H···Cl links results in a structure with a three-dimensional hydrogen-bonding network. The compound is isostructural with its copper- and cobalt-containing congeners.

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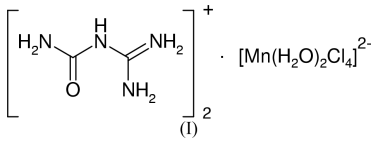
Comment

The title compound, (I), arose as a side product during a synthetic investigations of organically templated manganese–phosphate networks (Chippindale *et al.*, 2001). It is isostructural with $(C_2H_7N_4O)_2[Cu(H_2O)_2Cl_4]$ (Begley *et al.*, 1988) and $(C_2H_7N_4O)_2[Co(H_2O)_2Cl_4]$ (Bremner & Harrison, 2003).



(I)

In (I), Mn1 (site symmetry 2/*m*) has a flattened *trans*-octahedral coordination by two O (water) atoms and four Cl^- ions [range of *cis*-bond angles = 84.40 (3)–95.60 (3)°; d_{av}(Mn—Cl) = 2.5277 (4) Å]. Similar Mn—O (d_{av} = 2.183 Å) and Mn—Cl (d_{av} = 2.543 Å) separations have been seen in related compounds (Feist *et al.*, 1997). The 1-carbamoylguanidinium (guanylurea) cation has typical (Bremner & Harrison, 2002) geometrical parameters [d_{av}(N—C) = 1.334 (2) Å] and is essentially planar (for the non-H atoms, the r.m.s. deviation from the least-squares plane is 0.031 Å), indicating electronic delocalization over the non-H-atom skeleton (Begley *et al.*,

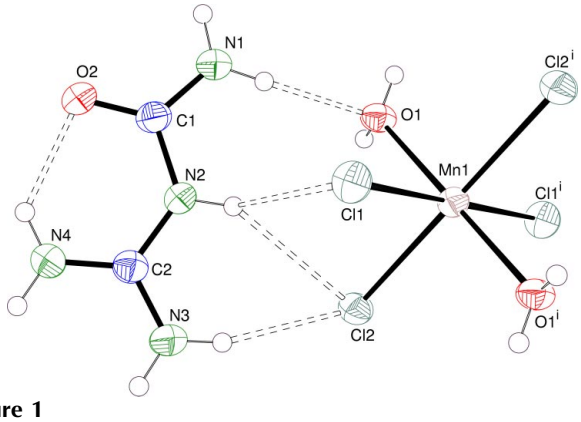


Figure 1
Component species in (I), shown with 50% displacement ellipsoids, arbitrary spheres for the H atoms and hydrogen bonds indicated by dashed lines. [Symmetry code: (vii) $-x, 1-y, -z$.]

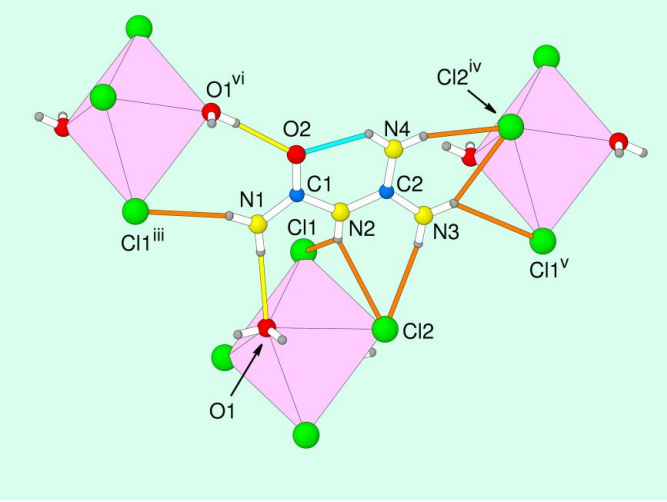


Figure 2
Detail of (I) showing the hydrogen-bonding interactions of the $C_2H_7N_4O^+$ species with nearby $[Mn(H_2O)_2Cl_4]^{2-}$ groups. Colour key: $[Mn(H_2O)_2Cl_4]^{2-}$ octahedra pink, Cl atoms green, C atoms blue, N atoms yellow, H atoms grey (all radii arbitrary). The intramolecular H···O, intermolecular H···O, and H···Cl portions of the hydrogen bonds are coloured light blue, yellow, and orange, respectively. Note that the chloride acceptors for bifurcated hydrogen bonds form octahedral edges. Symmetry codes as in Table 2; additionally (vi) $x+\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2}$.

1988). A typical (Bremner & Harrison, 2002) non-linear (θ = 129°) intramolecular N4—H9···O2 hydrogen bond is present (Fig. 1).

The component species in (I) interact by way of an extensive hydrogen-bonding network (Table 2 and Fig. 2), as described in more detail for the isostructural compound $(C_2H_7N_4O)_2[Co(H_2O)_2Cl_4]$ (Bremner & Harrison, 2003). The N—H···Cl hydrogen bonds involving atoms H5 and H6 are bifurcated [d_{av}(N···Cl) = 3.415 (2) Å, d_{av}(H···Cl) = 2.74 Å and θ_{av}(N—H···Cl) = 137°], whereas those involving atoms H3, H7 and H8 are simple N—H···Cl links [d_{av}(N···Cl) = 3.333 (2) Å, d_{av}(H···Cl) = 2.52 Å and θ_{av}(N—H···Cl) = 158°]. The 'synthon'-like role of N—H···Cl and N—H···(Cl,Cl) interactions in defining crystal structures containing different types of metal–chloride polyhedra has been discussed by Brammer *et al.* (2002).

Experimental

10 ml of a 1 *M* $MnCl_2$ solution, 10 ml of a 1 *M* H_3PO_4 solution and 0.5 g of dicyandiamide were mixed together in a plastic bottle and heated to 353 K for 24 h, resulting in a colourless solution. The solution was cooled to room temperature, and colourless rod-like crystals of (I) grew as the solvent slowly evaporated. The dicyandiamide was transformed to guanylurea cations by slow acid hydrolysis.

Crystal data

$(C_2H_7N_4O)_2[Mn(H_2O)_2Cl_4]$
M_r = 439.00
Monoclinic, $P2_1/n$
a = 6.4106 (3) Å
b = 11.4036 (6) Å
c = 11.5775 (6) Å
β = 103.640 (1)°
V = 822.49 (7) Å^3
Z = 2
D_x = 1.773 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2931 reflections
θ = 2.5–32.3°
μ = 1.48 mm^{-1}
T = 293 (2) K
Block, colourless
0.33 × 0.23 × 0.19 mm

Data collection

Bruker SMART1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.644, T_{max} = 0.768
8334 measured reflections
2947 independent reflections
2122 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 32.5°
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 17$
$l = -17 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.078
S = 0.95
2947 reflections
97 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0411P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Selected geometric parameters (Å).

Mn1—O1	2.1971 (10)	N2—C2	1.3529 (19)
Mn1—Cl1	2.5031 (4)	N2—C1	1.3839 (18)
Mn1—Cl2	2.5523 (4)	N3—C2	1.3147 (19)
O2—C1	1.2260 (17)	N4—C2	1.3011 (18)
N1—C1	1.317 (2)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^{i}	0.79	1.88	2.6499 (15)	167
O1—H2···Cl2^{ii}	0.87	2.29	3.1227 (11)	159
N1—H3···Cl1^{iii}	0.86	2.62	3.4649 (14)	166
N1—H4···O1	0.86	2.10	2.9415 (17)	165
N2—H5···Cl1	0.86	2.67	3.2944 (14)	131
N2—H5···Cl2	0.86	2.79	3.5170 (13)	143
N3—H6···Cl2^{iv}	0.86	2.57	3.3282 (15)	148
N3—H6···Cl1^{v}	0.86	2.93	3.5213 (14)	127
N3—H7···Cl2	0.86	2.46	3.2635 (14)	155
N4—H8···Cl2^{iv}	0.86	2.49	3.2692 (15)	152
N4—H9···O2	0.86	2.01	2.6441 (18)	129

Symmetry codes: (i) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $1-x, 1-y, -z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$; (v) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

The starting model for the non-H atoms was taken from the structure of $(C_2H_7N_4O)_2[Co(H_2O)_2Cl_4]$ (Bremner & Harrison, 2003), with Mn replacing Co. The H atoms attached to O1 were located in difference maps and refined as riding. The N-bound H atoms were placed in idealized positions [d(N—H) = 0.86 Å] and refined as riding. The constraint U_{iso}(H) = 1.2U_{eq}(parent atom) was applied in all cases.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: isostructural with Co complex; program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *ATOMS* (Shape Software, 1999); software used to prepare material for publication: *SHELXL*97.

References

Begley, M. J., Hubberstey, P., Martindale, S. P., Moore, C. H. M. & Price, N. S. (1988). *J. Chem. Res.* (*M*), pp. 101–128.
Brammer, L., Swearingen, J. K., Bruton, E. A. & Sherwood, P. (2002). *Proc. Natl Acad. Sci. USA*, **99**, 4956–4961.
Bremner, C. A. & Harrison, W. T. A. (2002). *Acta Cryst.* E**58**, m254–m256.
Bremner, C. A. & Harrison, W. T. A. (2003). *Acta Cryst.* E**59**, m467–m469.

Bruker (1999). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chippindale, A. M., Gaslain, F. O. M., Cowley, A. R. & Powell, A. V. (2001). *J. Mater. Chem.* **11**, 3172–3179.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Feist, M., Troyanov, S., Stiewe, A., Kemnitz, E. & Kunze, R. (1997). *Z. Naturforsch. Teil B*, **52**, 1094–1102.
Shape Software (1999). *ATOMS*. Shape Software, Kingsport, Tennessee, USA.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.