Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Cocrystal of the $[Mn^{IV}(C_2H_7N_5)_3]^{4+}$ ion and biguanidium: a double hydrogen-bond interaction with guanidinium-recognizing anions

Li-Ping Lu, Miao-Li Zhu† and Pin Yang*

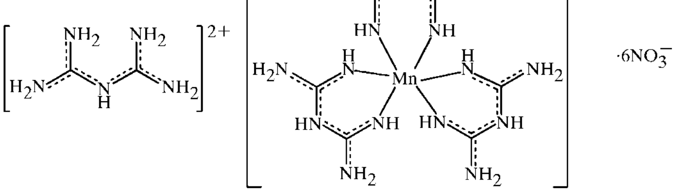
Institute of Molecular Science, Chemical Biology and Molecular Engineering Laboratory of Education Ministry, Shanxi University, Taiyuan, Shanxi 030006, People's Republic of China
Correspondence e-mail: yangpin@sxu.edu.cn

Received 16 October 2003
Accepted 29 October 2003
Online 13 December 2003

Biguanidium tris(biguanide-κ^2N^2,N^4)manganese(IV) hexanitrate, $(C_2H_9N_5)[Mn(C_2H_7N_5)_3](NO_3)_6$, is a cocrystal of the $[Mn^{IV}(C_2H_7N_5)_3]^{4+}$ ion and biguanidium. The cocrystal exhibits a double hydrogen-bonding interaction between the biguanide and nitrate groups, which is rarely observed in crystal structures but is proposed as a recognition mode for guanidinium-recognizing anionic groups in biological systems. In this cocrystal structure, biguanide moieties exist both as divalent cations and as neutral molecules.

Comment

Das *et al.* (2001, and additions and corrections) reported the synthesis and crystal structure of $[Mn^{IV}(C_2H_7N_5)_3]^{4+}$, a rare stable mononuclear complex of manganese(IV) in aqueous solution. We have also encountered this cation, but in crystals in which it co-exists with biguanidium, forming a complex structure of overall formula $(C_2H_9N_5)[Mn(C_2H_7N_5)_3](NO_3)_6$, which can be viewed as a mixture of $[Mn(C_2H_7N_5)_3](NO_3)_4$ and $(C_2H_9N_5)\cdot(NO_3)_2$. In this complex, (I), we find a double hydrogen-bond interaction between the biguanide and nitrate groups, which has rarely been observed in crystal structures but which is proposed as a molecular recognition mode for guanidinium-recognizing anionic entities, such as carboxylates, phosphates, sulfates and nitrates, in biological systems (Baggio *et al.*, 1997; Liu *et al.*, 2001; Lu *et al.*, 2001; Best *et al.*, 2003). We report here the structural characterization of (I).



(I)

A single crystal of (I) was prepared according to the procedure described by Das *et al.* (2001). However, not only is the stoichiometry of the present crystal different from that of Das *et al.*, but the quality of the present crystal is also much improved. The *R* value (0.046) for the present structure, with the triclinic space group $P\overline{1}$, is better than that (0.094) of the previously reported monoclinic crystal, with space group *I*2/*a* (Das *et al.*, 2001).

The geometric parameters of (I) are listed in Table 1 and the molecular conformation is illustrated in Fig. 1. The crystal structure of (I) consists of three different chemical moieties, namely the $[Mn^{IV}(C_2H_7N_5)_3]^{4+}$ cation, the $C_2H_9N_5^{2+}$ cation and six nitrate anions (Fig. 1). The $[Mn^{IV}(C_2H_7N_5)_3]^{4+}$ cation is similar to that reported by Das *et al.* In the complex tetracation, six N atoms from three neutral biguanide moieties coordinate to the Mn^{IV} atom, forming an octahedron. The Mn—N bonds range from 1.918 (2) to 1.952 (2) Å, and the bite angles of the biguanide ligands at the Mn^{IV} atom are 86.43 (10)° for N4—Mn1—N1, 85.68 (10)° for N11—Mn1—N14 and 84.30 (10)° for N9—Mn1—N6. The free biguanide

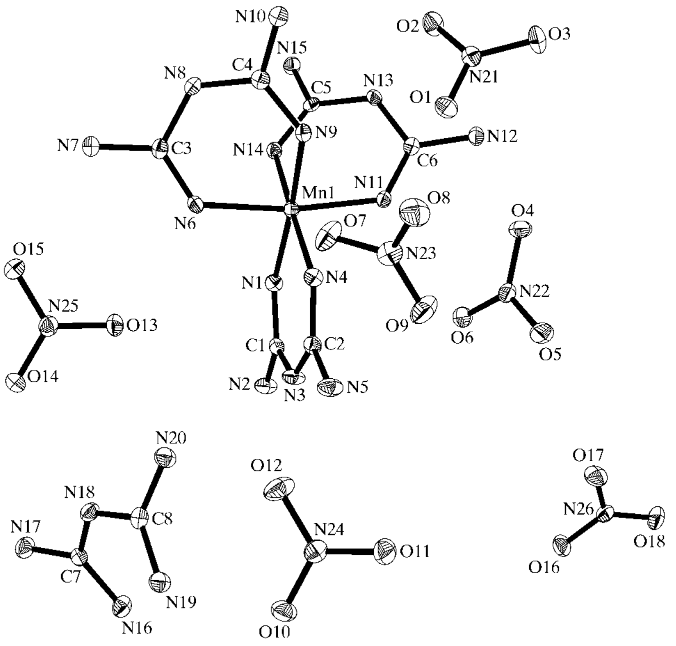


Figure 1
The structure of (I), with displacement ellipsoids drawn at the 30% probability level for non-H atoms.

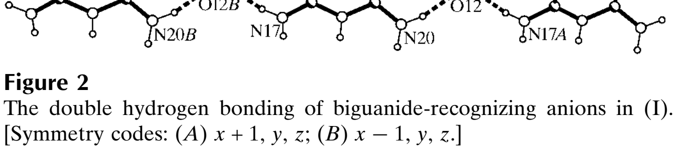


Figure 2
The double hydrogen bonding of biguanide-recognizing anions in (I). [Symmetry codes: (*A*) *x* + 1, *y*, *z*; (*B*) *x* − 1, *y*, *z*.]

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† Additional correspondence author, email: miaoli@sxu.edu.cn

DOI: 10.1107/S0108270103024892

moieties exist in the form of divalent cations, with charge balance achieved by six nitrate anions. Thus, two forms of biguanide moieties, *viz*. divalent cations and neutral molecules (as ligands), are present in the crystal.

There are hydrogen bonds between all biguanide and nitrate groups (Table 2). The biguanides, whether coordinated to the Mn^{IV} atom (neutral) or free (divalent cations), interact with the nitrate groups *via* strong double hydrogen bonds. In these bonds (Fig. 2), the $D\cdots A$ distances range between 2.820 (3) and 2.906 (3) Å, forming an elongated hexagon that was suggested for guanidinium-recognizing anions, such as amino acids (Galán *et al.*, 1992; Kanyo *et al.*, 1996; Metzger *et al.*, 1996) and nucleotides (Andreu *et al.*, 1994; Kato *et al.*, 1994; Schliessl & Schmidtchen, 1994; Lu *et al.*, 2001). In previous reports, the guanidinium group present in the side chain of the amino acid arginine, being a vital component of enzymatic catalytic domains that participate in the binding of anionic substrates (Cotton *et al.*, 1979; Christianson & Lipscomb, 1989), attracted great attention. An array of receptors containing guanidinium groups for the purpose of binding anions has been designed and synthesized (Best *et al.*, 2003). It has been proven that a strong interaction between the guanidinium groups and anions through charge pairing and hydrogen bonding facilitates the recognition of small target anions by receptors containing guanidinium groups in competitive solvent systems (Best *et al.*, 2003), but few crystal structure studies have been reported to date. Our results provides direct crystallographic evidence for this interaction.

Experimental

The title complex was prepared according to the procedure reported by Das *et al.* (2001).

Crystal data

$(C_2H_9N_5)[Mn(C_2H_7N_5)_3](NO_3)_6$
$M_r = 833.52$
Triclinic, $P\overline{1}$
$a = 9.4222\ (19)$ Å
$b = 12.803\ (3)$ Å
$c = 14.452\ (3)$ Å
$\alpha = 105.673\ (2)°$
$\beta = 104.037\ (2)°$
$\gamma = 104.891\ (2)°$
$V = 1528.3\ (5)$ Å^3

$Z = 2$
$D_x = 1.811$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2688 reflections
$\theta = 2.4$–26.5°
$\mu = 0.55$ mm^{-1}
$T = 184\ (2)$ K
Block, red
$0.25 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
$T_{min} = 0.874$, $T_{max} = 0.898$
6316 measured reflections

5274 independent reflections
4160 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 25.0°$
$h = -11 \rightarrow 11$
$k = -15 \rightarrow 15$
$l = -15 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.110$
$S = 0.98$
5274 reflections
479 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.058P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.55$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—N4	1.918 (2)	Mn1—N1	1.937 (2)
Mn1—N11	1.924 (2)	Mn1—N9	1.947 (2)
Mn1—N14	1.931 (2)	Mn1—N6	1.952 (2)
N4—Mn1—N11	91.80 (10)	N14—Mn1—N9	92.22 (10)
N4—Mn1—N14	175.03 (10)	N1—Mn1—N9	175.62 (10)
N11—Mn1—N14	85.68 (10)	N4—Mn1—N6	92.87 (10)
N4—Mn1—N1	86.43 (10)	N11—Mn1—N6	170.82 (10)
N11—Mn1—N1	96.47 (10)	N14—Mn1—N6	90.22 (10)
N14—Mn1—N1	89.59 (10)	N1—Mn1—N6	91.70 (10)
N4—Mn1—N9	91.95 (10)	N9—Mn1—N6	84.30 (10)
N11—Mn1—N9	87.65 (10)		
N4—Mn1—N1—C1	0.6 (3)	N14—Mn1—N11—C6	35.4 (2)
N9—Mn1—N6—C3	35.8 (2)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O3^{iii}	0.88	2.06	2.934 (3)	173
N3—H3$\cdots$O5^{iv}	0.88	1.94	2.788 (3)	161
N4—H4$\cdots$O7	0.88	2.00	2.848 (3)	160
N5—H5*A*$\cdots$O9	0.88	2.16	2.961 (4)	152
N5—H5*B*$\cdots$O6^{iv}	0.88	2.04	2.913 (3)	175
N6—H6$\cdots$O13	0.88	2.22	3.009 (3)	150
N7—H7*A*$\cdots$O15	0.88	2.10	2.854 (3)	143
N7—H7*B*$\cdots$O8^{vii}	0.88	2.29	3.060 (4)	146
N9—H9$\cdots$O1	0.88	2.21	3.077 (3)	167
N11—H11$\cdots$O6	0.88	2.16	2.984 (3)	157
N12—H12*B*$\cdots$O2^{vi}	0.88	2.04	2.919 (3)	177
N13—H13$\cdots$O3^{vi}	0.88	2.08	2.841 (3)	144
N14—H14$\cdots$O15^{v}	0.88	2.04	2.894 (3)	162
N16—H16*A*$\cdots$O11^{iii}	0.88	1.94	2.820 (3)	173
N16—H16*B*$\cdots$O4^{iv}	0.88	2.21	3.017 (3)	152
N17—H17*A*$\cdots$O12^{iii}	0.88	2.01	2.883 (3)	170
N17—H17*B*$\cdots$O16^{ii}	0.88	1.97	2.792 (3)	156
N18—H18$\cdots$O14	0.88	1.97	2.839 (3)	170
N19—H19*A*$\cdots$O10	0.88	1.98	2.841 (3)	165
N19—H19*B*$\cdots$O17^{i}	0.88	2.03	2.818 (3)	148
N20—H20*A*$\cdots$O12	0.88	2.05	2.906 (3)	165
N20—H20*B*$\cdots$O13	0.88	1.99	2.866 (3)	177

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

H atoms attached to N atoms were found in a difference map but were placed in idealized positions (N—H = 0.88 Å) and constrained to ride on their parent atoms [$U_{iso}(H) = 1.2U_{eq}(N)$].

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL*/*PC*.

This work was supported financially by the National Natural Science Foundation of China (grant No. 20171031 to PY), the Provincial Natural Foundation of Shanxi for Youth (grant No. 20011007 to LPL) and the Overseas Returned Scholar Foundation of Shanxi Province (in 2002 to MLZ).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1036). Services for accessing these data are described at the back of the journal.

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