Crystallographic disorder in mixed-valent dioxo-bridged Mn^{III,IV} complexes. [Mn$_2$O$_2$(bpy)$_4$]-[Ce(NO$_3$)$_6$].5H$_2$O

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Abstract

The structure of tetrakis(2,2′-bipyridine)di-μ-oxo-dimanganese(3+) hexanitratocerate(3−) pentahydrate, [Mn$_2$O$_2$(bpy)$_4$][Ce(NO$_3$)$_6$].5H$_2$O, is described; M_r = 1368.88, monoclinic, $C2/c$, a = 12.940 (3), b = 18.060 (2), c = 22.54 (1) Å, β = 96.29 (2)°, V = 5237 (3) Å^3, T = 132 K, Z = 4, F(000) = 2752, D_x = 1.736 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, μ = 1.429 mm^{-1}, $R(F^2)$ = 0.0358, $wR(F^2)$ = 0.0783 for 4877 reflections with $I > 2\sigma(I)$. The cation does not have crystallographically distinguishable Mn atoms. An analysis of the atomic displacement ellipsoids and Mn—N bond distortions has been used to develop a model for the disorder in this type of mixed-valent complex. The anion, Ce(NO$_3$)$_6^{3-}$, has a distorted icosahedral geometry.

1. Introduction

Mixed-valent metal complexes are generally classified as class I, class II or class III compounds (Robin & Day, 1967). This scheme may be clarified with reference to a dinuclear metal complex $M_A M_B$ (ligands not shown). The term 'mixed valence' is used when the metal ions M_A and M_B are of the same element but differ in their formal oxidation states, most commonly by unity. In class I compounds the extra electron is localized on one of the metal sites, while in class III compounds the electron is fully delocalized over the two sites. In class II compounds, which are an intermediate case, there is partial electron delocalization which may lead to temperature-dependent hopping of the electron between the two sites. Class I and class II compounds are expected to have distinct coordination environments for the two metal centres with different metal–ligand bond distances, while in class III compounds the two metal sites will be indistinguishable at all temperatures.†

Numerous dimanganese complexes having one Mn atom in the +3 oxidation state and the other in the +4 state have been structurally characterized during the past two decades (for a review see Manchanda *et al.*,

1995). Many of these complexes have crystallographically indistinguishable Mn centres. For example, complexes of the type Mn$_2^{III,IV}$O$_2$L$_4^{3+}$, where L = bpy or phen (bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline), may have distinguishable (Plaksin *et al.*, 1972; Manchanda *et al.*, 1994; Jensen *et al.*, 1995) or indistinguishable (Stebler *et al.*, 1986) Mn sites depending on the counter anion. On the other hand, spectroscopic and chemical evidence suggests class II behaviour for all Mn^{III,IV} complexes (for a review see Wieghardt, 1989). In all cases of indistinguishable Mn centres, the mixed-valent cation is found to be situated on a crystallographic symmetry element. In an important paper Stebler *et al.* (1986) analysed this problem in [Mn$_2$O$_2$(phen)$_4$](PF$_6$)$_3$ using atomic displacement data and concluded that crystallographic indistinguishability arises because of disorder about the symmetry element imposed by the space group. Since the publication of this work several other Mn^{III,IV} complexes have been reported (Wieghardt *et al.*, 1987; Oki *et al.*, 1990; Goodson *et al.*, 1990, 1992). The present paper reports the structure of [Mn$_2^{III,IV}$O$_2$(bpy)$_4$][Ce^{III}(NO$_3$)$_6$].5H$_2$O, (1), based on low-temperature (132 K) data. The cation of (1) has been structurally characterized twice before: in the perchlorate salt by Plaksin *et al.* (1972) and in the tetrafluoroborate salt by Jensen *et al.* (1995). In both cases geometrically distinct Mn centres were observed. However, in (1) the Mn atoms are not crystallographically distinguishable. Analysis of the atomic displacement data indicates disorder about the monoclinic symmetry axis. The reasons for the widespread occurrence of disorder in Mn^{III,IV} complexes are examined based on the Jahn–Teller nature of Mn^{3+} and the strong *trans* influence of the oxo ligands.

2. Experimental

[Mn$_2$O$_2$(bpy)$_4$][Ce(NO$_3$)$_6$].5H$_2$O, (1), was prepared as follows. To a solution of Mn(CH$_3$CO$_2$)$_2$.4H$_2$O (0.508 g, 2.07 mmol) and 2,2′-bipyridine (0.648 g, 4.15 mmol) in methanol (5 ml), a solution of (NH$_4$)$_2$Ce(NO$_3$)$_6$ (2.16 g, 3.94 mmol) in methanol (10 ml) was added dropwise with stirring. The solution initially turned yellow and on further addition a green solution was obtained, which was allowed to stand for 10 min. The green precipitate

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† Classification of a given complex using the Robin & Day scheme is often not a trivial problem. The interesting case of the Creutz–Taube complex [μ-pyrazine-bis(pentaammineruthenium)]$^{5+}$, studied using several different techniques, is discussed by Furholz *et al.* (1984).

that formed was filtered, dried under vacuum and recrystallized from water to give dark green rectangular rod-shaped crystals. Yield: 0.770 g (0.562 mmol, 54%). IR (KBr disc, cm^{-1}): 3383 (b), 3088 (w), 1605 (s), 1566 (w), 1445 (vs), 1314 (vs), 1161 (s), 1111 (w), 1020 (s), 820 (s), 770 (s), 731 (s), 693 (s), 656 (s).

Intensity data were collected at the University of Canterbury, New Zealand. Experimental details are given in Table 1. Data collection, cell refinement and data reduction were carried out using *P4 Software* (Siemens, 1990). The structure was solved by direct methods with *SHELXS*86 (Sheldrick, 1990) and refined with *SHELXL*93 (Sheldrick, 1993).

Based on systematic absences, the space group was either *Cc* or *C2/c*. The structure could be solved in both space groups, but attempts to refine it in *Cc* led to instability owing to severe correlations between the two halves of the cation related by the (pseudo) twofold axis. Therefore, the centrosymmetric space group *C2/c* was chosen. This choice, unfortunately, imposes crystallographic symmetry on the cation as well as the anion. H atoms are labelled according to the atom to which they are attached. Non-H atoms were refined anisotropically and all ring H atoms were included in calculated positions using a riding model. The H atoms on water molecules were located from difference maps and refined using bond-length constraints. One of the lattice water molecules, O*W*1, lies on the twofold axis at a distance of 2.724 (3) Å from the bridging oxygen O1. The H atoms for this water molecule were located from a Fourier map at a distance of 1 Å from O*W*1, but were fixed at 0.97 Å owing to extreme shortening of the bonds on free refinement. H*W*1*A* lies on a twofold axis, while H*W*1*B* is disordered about this axis. All H atoms except H*W*1*A*, H*W*1*B*, H*W*2*A* and H*W*2*B* were assigned fixed U_{iso} values 1.5 times the U_{eq} value of the atom to which they are attached. Yet another water molecule, O*W*3/ O*W*4, suffers from positional disorder and was refined with fractional site-occupancy factors at two independent sites. Positional parameters are listed in Table 2 and selected bond distances and angles are given in Table 3.†

3. Results and discussion

3.1. Cation

The [Mn$_2$O$_2$(bpy)$_4$]$^{3+}$ ion is shown in Fig. 1(*a*) and in Fig. 1(*b*) a water molecule hydrogen-bonded to one of the bridging O atoms is also shown. Unlike in the previously reported ClO$_4^-$ (Plaksin *et al.*, 1972) or BF$_4^-$ (Jensen *et al.*, 1995) salts, in (1) the two Mn atoms are not distinguishable because of the crystallographic twofold axis passing through the two O atoms. Bearing this in mind it is possible to compare the parameters for

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS0004). Services for accessing these data are described at the back of the journal.

Table 1. *Experimental details*

Crystal data

Chemical formula	[Mn$_2$O$_2$(C$_{10}$H$_8$N$_2$)$_4$]-[Ce(NO$_3$)$_6$].5H$_2$O
Chemical formula weight	1368.88
Cell setting	Monoclinic
Space group	*C2/c*
a (Å)	12.940 (3)
b (Å)	18.060 (2)
c (Å)	22.544 (11)
β (°)	96.29 (2)
V (Å^3)	5237 (3)
Z	4
D_x (Mg m^{-3})	1.736
D_m (Mg m^{-3})	1.75
Density measured by	Flotation
Radiation type	Mo *Kα*
Wavelength (Å)	0.71073
μ (mm^{-1})	1.429
Temperature (K)	132 (2)
Crystal form	Rectangular rod
Crystal size (mm)	0.35 × 0.30 × 0.26
Crystal colour	Dark green–black

Data collection

Diffractometer	Siemens *P4*
Data collection method	ω–2θ scans
Absorption correction	Semi-empirical (North *et al.*, 1968)
T_{min}	0.257
T_{max}	0.327
No. of measured reflections	6034
No. of independent reflections	6021
No. of observed reflections	4877
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.0281
θ_{max} (°)	27.5
Range of *h, k, l*	$-16 \rightarrow h \rightarrow 16$
	$0 \rightarrow k \rightarrow 23$
	$0 \rightarrow l \rightarrow 29$
No. of standard reflections	3
Frequency of standard reflections	Every 100 reflections
Intensity decay (%)	0

Refinement

Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0358
$wR(F^2)$	0.0783
S	1.136
No. of reflections used in refinement	5645
No. of parameters used	409
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0342P)^2 + 13.2986P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	-0.157 for *y* of H*W*3*A*, < 0.03 for all non-H atoms
$\Delta\rho_{max}$ (e Å^{-3})	0.925
$\Delta\rho_{min}$ (e Å^{-3})	-0.589
Extinction method	None
Source of atomic scattering factors	*International Tables for Crystallography* (Vol. C, Tables 4.2.6.8 and 6.1.1.4)

(1) with those of the previous reports and its phen analogue. There are two main factors which influence the geometry of a dioxo-bridged Mn^{III,IV} complex:

(i) The Mn^{III} centre is susceptible to the Jahn–Teller effect, which usually manifests itself as a tetragonal elongation (Reddy *et al.*, 1996; Swarnabala *et al.*, 1994). The elongation direction will be perpendicular to the Mn_2O_2 plane.

(ii) The bonds opposite the oxo ligand for both Mn centres experience a strong *trans* influence leading to their elongation. This effect is more pronounced for Mn^{IV}, which has the shorter Mn—O distance.

The net result is that for the Mn^{III} site the axial Mn—N bonds are longer than the corresponding equatorial bonds, while the reverse is true for the Mn^{IV} site. This is borne out by the average bond-length differences shown in Table 4. Similar differences have also been observed for $Mn^{III,IV}$ complexes containing other ligands (Glerup *et al.*, 1994; Frapart *et al.*, 1996). As expected, for the crystallographically averaged structures the axial–equatorial difference is less, but still significant.

From a detailed analysis of the atomic displacement parameters for $[Mn_2O_2(phen)_4](PF_6)_3.CH_3CN$ it has been shown that the averaged structure results from a dynamic or static disorder about a crystallographic symmetry element, and not from any electron delocalization (Stebler *et al.*, 1986). In this analysis, the difference displacement parameter $\Delta U(z)$ is calculated for the axial and equatorial Mn—N bonds using the diag-
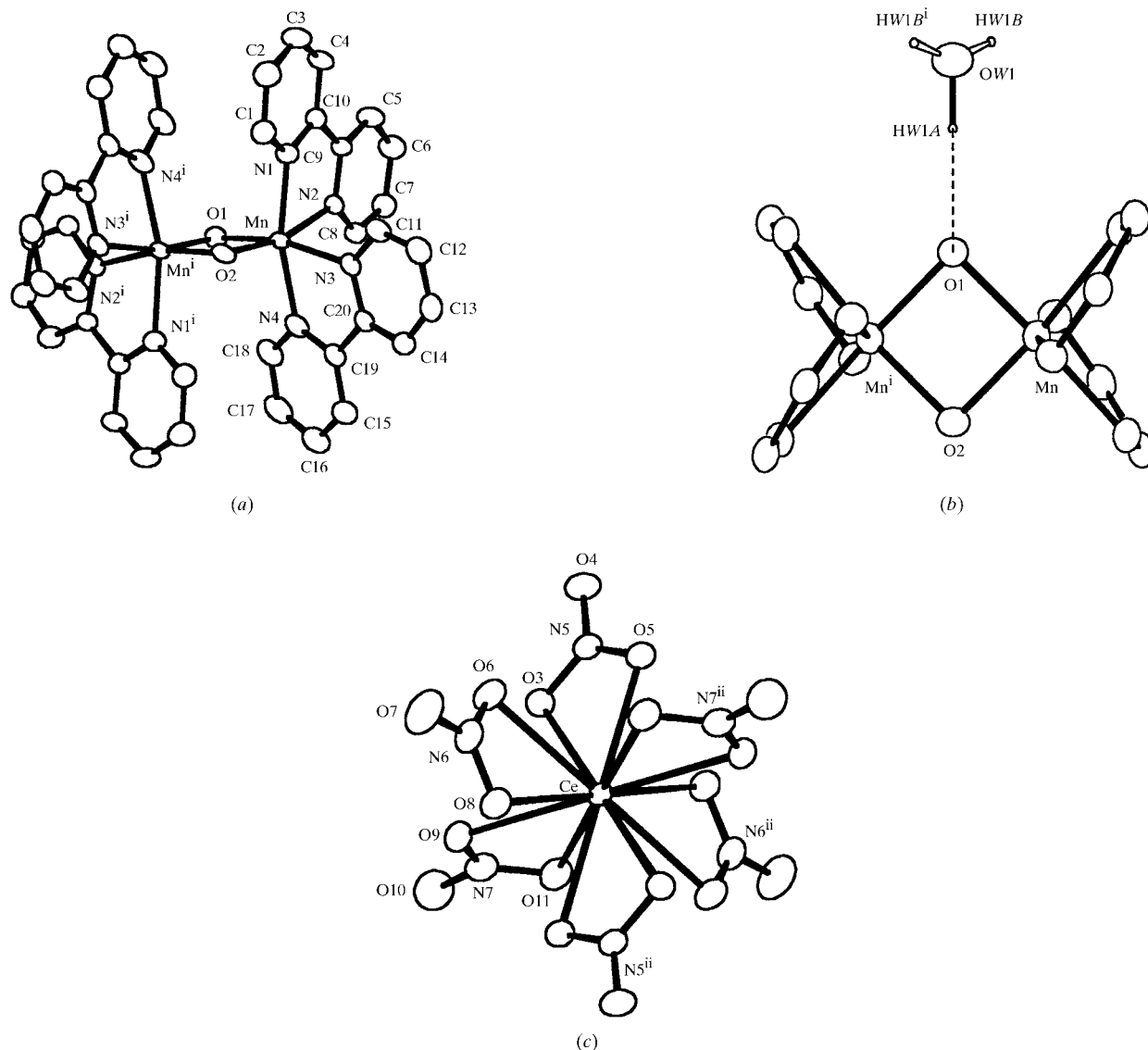

Fig. 1. *ORTEPII* (Johnson, 1976) view of (1) (50% probability ellipsoids). (*a*) The $[Mn_2O_2(bpy)_4]^{3+}$ cation [symmetry code: (i) $-x, y, -z + \frac{1}{2}$]. (*b*) The cation showing hydrogen bonding between the oxo group and a lattice water molecule [symmetry code: (i) $-x, y, -z + \frac{1}{2}$]. The disordered H atoms are connected by hollow bonds. (*c*) The $Ce(NO_3)_6^{3-}$ anion [symmetry code: (ii) $-x, -y, -z$].

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Mn	0.10205 (3)	−0.31120 (2)	0.27211 (2)	0.01864 (8)
O1	0	−0.37795 (13)	1/4	0.0236 (6)
O2	0	−0.24494 (13)	1/4	0.0231 (6)
N1	0.1644 (2)	−0.29545 (12)	0.18985 (9)	0.0241 (5)
N2	0.2151 (2)	−0.39399 (11)	0.27394 (9)	0.0218 (5)
N3	0.2023 (2)	−0.23294 (12)	0.31588 (10)	0.0247 (5)
N4	0.0801 (2)	−0.32638 (12)	0.36371 (10)	0.0279 (5)
C1	0.1366 (2)	−0.24126 (15)	0.15081 (12)	0.0288 (6)
C2	0.1768 (2)	−0.2361 (2)	0.09620 (13)	0.0341 (7)
C3	0.2476 (2)	−0.2889 (2)	0.08194 (13)	0.0366 (7)
C4	0.2766 (2)	−0.3455 (2)	0.12229 (12)	0.0306 (6)
C5	0.3286 (2)	−0.4612 (2)	0.21593 (13)	0.0332 (7)
C6	0.3474 (2)	−0.5126 (2)	0.26134 (13)	0.0368 (7)
C7	0.2997 (2)	−0.5039 (2)	0.31275 (12)	0.0326 (6)
C8	0.2352 (2)	−0.4442 (2)	0.31778 (12)	0.0272 (6)
C9	0.2615 (2)	−0.40292 (14)	0.22310 (11)	0.0228 (5)
C10	0.2340 (2)	−0.34700 (14)	0.17646 (11)	0.0233 (6)
C11	0.2668 (2)	−0.1883 (2)	0.28910 (13)	0.0323 (7)
C12	0.3204 (2)	−0.1306 (2)	0.31851 (14)	0.0363 (7)
C13	0.3070 (2)	−0.1175 (2)	0.37704 (14)	0.0339 (7)
C14	0.2419 (2)	−0.1634 (2)	0.40556 (13)	0.0296 (6)
C15	0.1064 (2)	−0.2737 (2)	0.46118 (13)	0.0344 (7)
C16	0.0441 (2)	−0.3279 (2)	0.48282 (15)	0.0407 (8)
C17	0.0018 (2)	−0.3818 (2)	0.44388 (15)	0.0390 (7)
C18	0.0210 (2)	−0.3794 (2)	0.38509 (14)	0.0341 (7)
C19	0.1242 (2)	−0.27452 (14)	0.40150 (12)	0.0259 (6)
C20	0.1917 (2)	−0.22138 (15)	0.37445 (12)	0.0247 (6)
Ce	0	0	0	0.01991 (4)
N5	0.0230 (2)	0.07341 (12)	−0.11877 (9)	0.0235 (5)
O3	0.01358 (14)	0.00350 (10)	−0.11422 (8)	0.0265 (4)
O4	0.03210 (15)	0.10318 (11)	−0.16699 (8)	0.0306 (5)
O5	0.02212 (14)	0.11081 (10)	−0.07128 (8)	0.0263 (4)
N6	−0.2367 (2)	0.02987 (13)	−0.01468 (10)	0.0289 (5)
O6	−0.19677 (14)	−0.00094 (12)	0.03188 (9)	0.0325 (4)
O7	−0.3317 (2)	0.03582 (15)	−0.02636 (11)	0.0506 (7)
O8	−0.17629 (14)	0.05590 (11)	−0.05042 (9)	0.0311 (5)
N7	0.0548 (2)	0.14382 (13)	0.06822 (10)	0.0312 (5)
O9	−0.03740 (15)	0.12916 (10)	0.04789 (9)	0.0305 (4)
O10	0.0757 (2)	0.19869 (13)	0.09999 (11)	0.0530 (6)
O11	0.12523 (14)	0.10117 (11)	0.05393 (9)	0.0322 (5)
OW1	0	−0.52877 (9)	1/4	0.0433 (8)
OW2	−0.0493 (2)	0.26400 (14)	0.19167 (8)	0.0646 (8)
OW3†	−0.4372 (2)	0.0877 (2)	−0.13899 (10)	0.0566 (14)
OW4‡	−0.3942 (2)	0.1105 (2)	−0.15369 (14)	0.069 (3)

† Site occupancy = 0.611.   ‡ Site occupancy = 0.389.

Table 3. *Selected geometric parameters ($\mathring{A}$, °)*

Mn—O2	1.811 (2)	Ce—O3	2.601 (2)
Mn—O1	1.817 (2)	Ce—O5	2.602 (2)
Mn—N2	2.089 (2)	Ce—O8	2.636 (2)
Mn—N3	2.091 (2)	Ce—O9	2.637 (2)
Mn—N1	2.121 (2)	Ce—O11	2.648 (2)
Mn—N4	2.133 (3)	Ce—O6	2.720 (2)
Mn—Mn^i	2.7188 (9)		
O2—Mn—O1	82.92 (8)	O1—Mn—N2	90.97 (8)
O2—Mn—N3	94.53 (8)	N2—Mn—N3	94.46 (8)
O2—Mn—N1	90.36 (6)	O1—Mn—N1	100.59 (6)
N2—Mn—N1	77.34 (8)	N3—Mn—N1	92.66 (9)
O2—Mn—N4	100.41 (6)	O1—Mn—N4	90.59 (6)
N2—Mn—N4	93.23 (8)	N3—Mn—N4	76.80 (9)
Mn—O1—Mn^i	96.87 (11)	Mn^i—O2—Mn	97.29 (11)
O3—Ce—O5	49.15 (6)	O9—Ce—O11	48.10 (6)
O8—Ce—O6	47.58 (6)		

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

4+ oxidation states to a great extent. On the other hand, the Jahn–Teller effect magnifies this difference for the axial bonds. Denoting, for example, the Mn^{III}—N_{axial} bond distance as $N_{ax}(III)$, $N_{ax}(III) - N_{ax}(IV)$ lies in the range 0.19–0.21 Å for the three complexes with distinguishable sites, while the range for $N_{eq}(III) - N_{eq}(IV)$ is only 0.03–0.06 Å. The same trend is observed on comparing the $\Delta U^{1/2}(z)$ values for the disordered structure. The values along the axial bonds are in the range 0.09–0.14 Å. Along the equatorial bonds the values lie in the range 0.05–0.06 Å, and are in the range normally seen in the absence of any disorder. Therefore, to build a simplified picture of disorder in this type of complex, one need consider only the axial bonds.

The three resulting possibilities for cation disorder in a monoclinic crystal are shown schematically in Fig. 2. In Fig. 2(a) the symmetry element involved is the monoclinic symmetry axis, normal to the Mn_2O_2 mean plane, while in Fig. 2(b) it is the inversion centre and in Fig. 2(c) the b axis passes through the two O atoms. Of the seven previously reported disordered structures two (Stebler et al., 1986; Wieghardt et al., 1987) belong to type (a) and five (Oki et al., 1990; Goodson et al., 1990, 1992) to type (b). In (c) the symmetry axis is perpendicular to the axial (disorder) direction of the molecule. The present structure belongs to this category. This mode is obtained here because of the presence of a water molecule hydrogen-bonded to only one of the O atoms. The other modes (a or b) in this situation would have meant a two-dimensional disorder in the lattice which is probably energetically costlier.† The Mn_2O_2 plane is strictly planar, while in the ordered structures

onalized displacement tensor U of the Mn and N atoms $[\Delta U(z) = U(N,z) - U(Mn,z)$, where z is the bond direction]. In an ordered structure, the quantity $\Delta U^{1/2}(z)$ is a measure of the difference in the intramolecular vibration amplitudes of the metal and ligand atoms and is usually ~0.05 Å (Chandrasekhar & Bürgi, 1984; Ammeter et al., 1979). Large deviations from this value can be caused by either static or dynamic disorder of the structure. The $\Delta U^{1/2}(z)$ values for the present compound are given in Table 4. It is worth emphasizing that the greater *trans* influence of the oxo ligands attached to Mn^{IV} smears out the expected differences for the equatorial Mn—N bond distances for the 3+ and

† In $[Mn_2O_2L_2](ClO_4)_3.H_2O$, where $L = N,N'$-dimethyl-N,N'-bis(imidazol-4-ylmethyl)ethane-1,2-diamine (Frapart et al., 1996), the monoclinic symmetry axis passes through the two Mn atoms. The presence of only one water molecule (which is said to be close to one of the dioxo O atoms) implies a disorder about the Mn–Mn axis, which, nevertheless, does not lead to averaging of the oxidation states.

Table 4. *Distortion parameters (Å) and difference displacement parameters (Å) for dioxo-bridged $[Mn_2O_2L_4]^{3+}$ systems*

Distortion parameters are bond-length differences for Mn—N bonds where, for example, $N_{ax}(III)$ represents the Mn^{III}—N_{axial} bond distance. Difference displacement parameters are along Mn—N bonds for averaged structures calculated as given in Stebler *et al.* (1986). The values are averages for chemically equivalent bonds in a structure. The two standard deviations in parentheses are calculated according to $\sigma^2[f(p_1\ldots)] = \Sigma(\partial f/\partial p_i)^2\sigma_i^2$ and $\sigma^2_{mean} = \Sigma(x_i - \bar{x})^2/(n-1)$, respectively.

Compounds with distinct Mn sites

	$N_{ax}(III) - N_{eq}(III)$	$N_{ax}(IV) - N_{eq}(IV)$	$N_{ax}(III) - N_{ax}(IV)$	$N_{eq}(III) - N_{eq}(IV)$
$[Mn_2O_2(bpy)_4](ClO_4)_3.3H_2O^{(a)}$	0.085 (7,14)	−0.053 (7,9)	0.195 (7,16)	0.057 (7,4)
$[Mn_2O_2(bpy)_4](BF_4)_3.2.8H_2O^{(b)}$	0.089 (4,6)	−0.070 (4,20)	0.207 (4,11)	0.048 (4,18)
$[Mn_2O_2(phen)_4](ClO_4)_3.2CH_3COOH.2H_2O^{(c)}$	0.107 (6,14)	−0.061 (6,12)	0.195 (6,14)	0.028 (6,12)

Compounds with equivalent Mn sites

	$N_{ax} - N_{eq}$	$\Delta U^{1/2}(z)N_{ax}$	$\Delta U^{1/2}(z)N_{eq}$
$[Mn_2O_2(bpy)_4][Ce(NO_3)_6].5H_2O^{(d)}$	0.037 (2,9)	0.093 (5); 0.136 (5)	0.050 (5); 0.060 (5)
$[Mn_2O_2(phen)_4](PF_6)_3.CH_3CN^{(e)}$	0.023 (2,21)	0.116 (10)	0.037 (33)

References: (*a*) Plaksin *et al.* (1972); (*b*) Jensen *et al.* (1995); (*c*) Manchanda *et al.* (1994); (*d*) this work; (*e*) Stebler *et al.* (1986).

small deviations ($\sim$0.03 Å) from planarity are seen. The equatorial N atoms show large deviations ($\pm$0.48, $\pm$0.49 Å) from this plane; this has also been observed for the ordered structures.

3.2. *Anion*

$Ce(NO_3)_6^{3-}$ has a distorted icosahedral structure with Ce located on a crystallographic inversion centre (Fig. 1*c*). Two of the three independent NO_3^- ions conform closely to the symmetric chelating mode [average Ce—O 2.622 (2) Å], while the third NO_3^- ion shows considerable asymmetry in chelation [Ce—O 2.720 (2), 2.636 (2) Å]. This ion has been previously characterized in $Ce_2Mg_3(NO_3)_{12}.24H_2O$ (Zalkin *et al.*, 1963) and more recently in $K_3Ce_2(NO_3)_9$ (Guillou, Auffrédic & Louër, 1995). The latter compound has a three-dimensional network of irregular icosahedra linked by NO_3^- ions. The $Ce(NO_3)_6^{3-}$ ion in all these compounds is more distorted than the $Ce(NO_3)_6^{2-}$ ion in $(NH_4)_2Ce(NO_3)_6$ (Beineke & Delgaudio, 1968) and $K_2Ce(NO_3)_6$ (Guillou, Louër *et*

al., 1995). It is tempting to ascribe this difference to the Jahn–Teller effect in the Ce^{III} complex ion. However, the weak distortions expected for the f^1 configuration might be comparable in magnitude to distortions arising from hydrogen bonding and other lattice perturbations.

3.3. *Hydrogen bonding*

One lattice water molecule forms a strong hydrogen bond with an O atom of the dioxo bridge [O1$\cdots$HW1*A* 1.754 (3), O1$\cdots$OW1 2.724 (3) Å], while another water molecule forms a hydrogen-bonded network [OW2$\cdots$HW2*A*^{i} 1.933 (4), OW2$\cdots$OW2^i 2.795 (3) Å; symmetry code: (i) $-x, y, -z + \frac{1}{2}$] and also interacts with the anion [O10$\cdots$HW2*B* 2.071 (7), O10$\cdots$OW2 3.002 (3) Å]. The third water molecule is disordered and interacts with OW1 as well as the O7 atom of the anion. There appear to be no significant contacts between the anion and the $Mn^{III,IV}$ complex ion except *via* the hydrogen-bond network involving two water molecules (OW1, OW4).
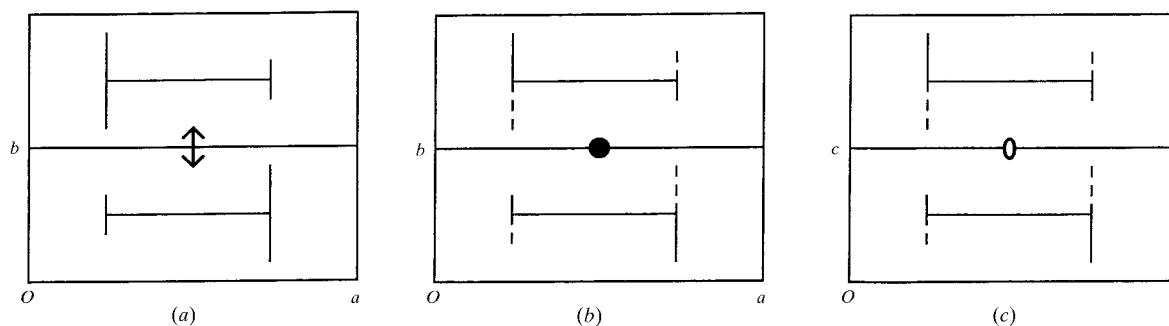

Fig. 2. Simplified model of disorder of an $[Mn_2O_2L_4]^{3+}$ ion in monoclinic crystals. The horizontal line represents the Mn_2O_2 core while the vertical lines denote the axial direction of the coordination 'octahedra'. Two adjacent unit cells are shown in projection down the *c* axis for (*a*) and (*b*), and down the *b* axis for (*c*). For (*c*) the monoclinic angle is taken to be 90° for convenience. The disorder is about an inversion centre in (*b*) while the other two cases correspond to disorder about the *b* axis.

4. Conclusion

The widespread occurrence of dioxo-bridged $Mn^{III,IV}$ complexes with averaged geometries is a consequence of crystallographic disorder. While the energetics of disorder will vary from system to system and will also depend upon the anion packing, it is reasonable to expect that the difference between the metric parameters at the two Mn atoms will play an important role. The combined effect of Jahn–Teller elongation (at Mn^{III}) and the *trans* influence of the oxo ligands makes this difference more pronounced along the axial coordination direction than in the Mn_2O_2 plane. This seems to favour a disorder about an inversion centre or a twofold axis perpendicular to the Mn_2O_2 plane. The hydrogen bonding with a lattice water molecule leads to a novel type of disorder in (1) wherein the crystallographic twofold axis passes through the dioxo O atoms.

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