Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Setting ambiguity in *C*2/*c* with dibromidotetrakis(1*H*-pyrazole-κN^2)-manganese(II) as an example

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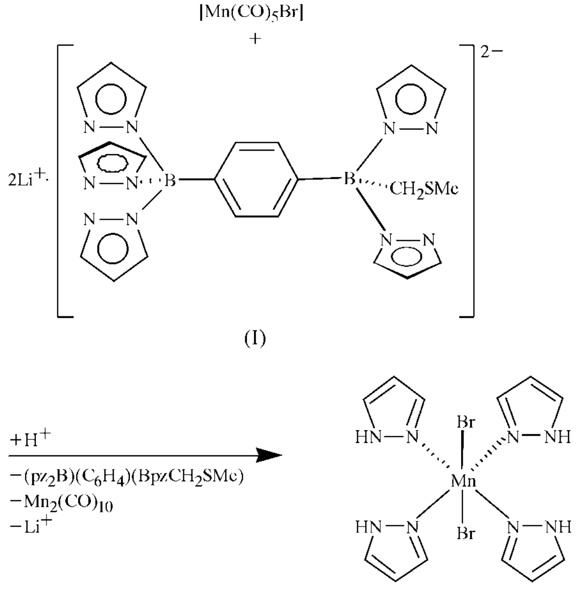
Received 5 October 2007
Accepted 22 October 2007
Online 14 November 2007

trans-Dibromidotetrakis(1*H*-pyrazole-κN^3)manganese(II), $[MnBr_2(C_3H_4N_2)_4]$, crystallizes in the *C*2/*c* space group with the Mn atom located on a centre of inversion. As a result, there is just one half-molecule in the asymmetric unit. Geometric parameters are in the usual ranges. The Mn centre is octahedrally coordinated by four pyrazole residues in the equatorial plane and by two bromide ligands in the axial positions. The molecular conformation is stabilized by N—H···Br hydrogen bonds. The structure of the title compound had already been described [Lumme & Lindell (1987). *J. Coord. Chem.* **15**, 383–392] in a different setting, with the Mn atoms located on inversion centres on Wyckoff position *d* ($\frac{1}{4}, \frac{1}{4}, \frac{1}{2}; \frac{3}{4}, \frac{1}{4}, 0; \frac{3}{4}, \frac{3}{4}, \frac{1}{2}; \frac{1}{4}, \frac{3}{4}, 0$). In the conventional setting, however, the Mn atoms are situated on Wyckoff position *a* ($0, 0, 0; 0, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). In this special case, if the *c* axis has the same length as the short diagonal of the *ac* plane, the transformation from one setting into the other yields almost indistinguishable cell parameters, and the possibility of confusion arises. This setting ambiguity could be the reason why two structures in different settings might be taken as polymorphs even though they can easily be transformed. As a result of this, care should always be taken to use the conventional setting.

Comment

Following the first synthesis of a scorpionate complex, considerable progress has been made towards extending this area of chemistry (Trofimenko, 1993). Our studies have shown that an important factor influencing the stability of scorpionates appears to be the degree of steric crowding around the boron centre (Bieller *et al.*, 2004). Another reason for the deboronation of scorpionates may be the low difference in Lewis acidity of the metal centre in MX_2 on one side and of the B centre in the corresponding borane of the pyrazolyl borate on the other side. The results of investigations in our group show that ditopic heteroscorpionates decompose in the presence of transition metal salts much more easily than monotopic homoscorpinates (Bieller *et al.*, 2006).

It is interesting to note that the manganese complex $[MnBr(CO)_5]$ can be transformed easily into Mn^{II} and $Mn_2(CO)_{10}$ in the presence of strong nucleophiles such as $NaSSi^tBu_3$ or $Na_2PSi^tBu_3$ (Kückmann 2007; Lerner *et al.*, 2005). In attempting to synthesize the 1,4-phenylene-bridged Mn^I scorpionate from the corresponding lithium scorpionate, (I), and $[MnBr(CO)_5]$, we obtained the title compound, namely dibromido(tetrapyrazole)manganese(II), (II), as a by-product (see reaction scheme below).



(I)

(II)

A perspective view of compound (II) is shown in Fig. 1. The Mn centre is located on a centre of inversion. It is octahedrally coordinated by two Br atoms in a *trans* configuration occupying the axial positions and by four pyrazole ligands in the equatorial plane. The pyrazole (pz) ligands are almost perpendicular [85.7 (3) and 88.9 (3)° for the rings containing atoms N1 and N11, respectively] to the equatorial plane consisting of the Mn centre and the four coordinating N atoms. The molecular conformation is stabilized by N—H···Br hydrogen bonds (Table 1).

In the monoclinic space group *C*2/*c*, there are two different sets of inversion centres which are not equivalent because they have different environments. One set is on Wyckoff position *a* ($0, 0, 0; 0, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) which can be transformed on to Wyckoff position *b* ($0, \frac{1}{2}, 0; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, 0; \frac{1}{2}, 0, \frac{1}{2}$) by an origin shift which is permitted in the monoclinic crystal system. Another set of inversion centres is on Wyckoff position *c* ($\frac{1}{4}, \frac{1}{4}, 0; \frac{3}{4}, \frac{1}{4}, \frac{1}{2}; \frac{3}{4}, \frac{3}{4}, 0; \frac{1}{4}, \frac{3}{4}, \frac{1}{2}$) and Wyckoff position *d* ($\frac{1}{4}, \frac{1}{4}, \frac{1}{2}; \frac{3}{4}, \frac{1}{4}, 0; \frac{3}{4}, \frac{3}{4}, \frac{1}{2}; \frac{1}{4}, \frac{3}{4}, 0$). The latter two sets can, similar to *a* and *b*, be transformed into one another by a permitted origin shift. We have found for (II) that the Mn atoms are located on Wyckoff position *a*. This setting is hereinafter referred to as (II*a*). The structure of the title compound has already been described (Lumme & Lindell, 1987) at 295 K in the same space group, *C*2/*c*, with cell parameters a = 14.208 (2) Å, b = 9.454 (1) Å and c =

DOI: 10.1107/S0108270107052419

15.015 (3) Å, β = 118.68 (1)° and V = 1769.4 (5) Å^3, but the Mn atoms are located on inversion centres of Wyckoff position d. This setting is hereinafter referred to as (IId).

At first glance, the packing diagrams of the two settings (Figs. 2 and 3) look completely different. However, closer inspection of the packing patterns reveals that there are striking similarities. A superposition of both cells (Fig. 4) shows that they can be transformed into one another by the matrix $(\bar{1}00/0\bar{1}0/101)$ and an additional origin shift of $(\frac{1}{4}, \frac{1}{4}, 0)$. The transformation of the symmetry elements is shown in Fig. 5. The conventional setting as given in *International Tables for Crystallography* Vol. A is shown in Fig. 5(a). By applying the matrix $(\bar{1}00/0\bar{1}0/101)$, which is equivalent to a twofold rotation about the [102] vector, screw axes are interchanged with rotation axes and c-glide planes become n-glide planes and *vice versa* (Fig. 5b). The origin shift of $\frac{1}{4}$ along a' (Fig. 5c) moves screw and rotation axes on to their correct positions. However, the height of the inversion centres and glide planes in the direction of the b axis is still not correct. This can be accomplished by an origin shift of $\frac{1}{4}$ along b (Fig. 5d). Thus, in the special case where the c axis has almost the same length as the short diagonal of the ac plane, the transformation from one setting into another yields almost indistinguishable cell parameters, and the possibility of confusion arises. Although refinement in each of these settings yields exactly the same results, only one of these settings is conventional. As a result of this, the cell parameters of (IId) should be transformed by the matrix $(\bar{1}00/0\bar{1}0/101)$ into a = 14.208 Å, b = 9.454 Å and c = 14.918 Å, and β = 117.99°, because the new c axis is shorter than the original one and the new β angle is smaller than the original one.

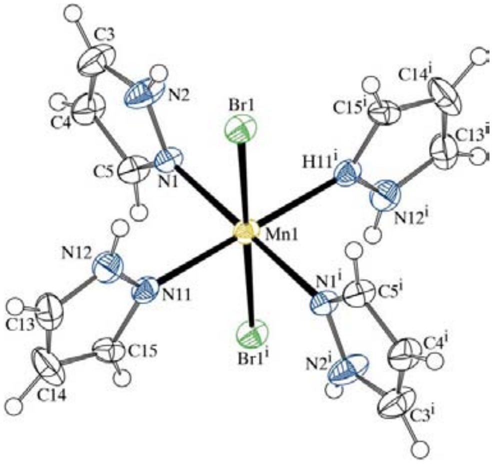


Figure 1

A perspective view of compound (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-x + 1$, $-y + 1$, $-z + 1$.]

A search of the Cambridge Structural Database (Version 5.28, November 2006 plus three updates; Allen, 2002) for structures in the space group $C2/c$ which are free of errors and not disordered yielded 29 279 hits. For 713 of these, the condition that the length of the c axis does not deviate by more than 1% from the length of the shorter diagonal of the ac plane is fulfilled. Checking these 713 structures for whether a cell transformation by $(\bar{1}00/0\bar{1}0/101)$ would give a shorter c axis and a smaller β angle revealed that 119 of these 713 would be better described in a different setting. If only one structure determination is concerned, the results are exactly the same for both settings. However, among these 119 structure determinations, there are three which should be revised. Bolotina *et al.* (2003) compared six structures of biguanidinium bis(dinitramide) determined at different temperatures. However, one setting was used for three of them and a different setting for the other three. Table 2 lists the original and corrected cell parameters. The original c axis at 150 K is the second longest (after that at 298 K). After transformation to a conventional setting, the length of the corrected c axis follows the expected trend of shortening when the temperature is lowered. Efe & Schlemper (1992) presented two structures of dichlorobis[3-(N-phenylamino)-3-methyl-2-butanone oxime]rhodium(III),

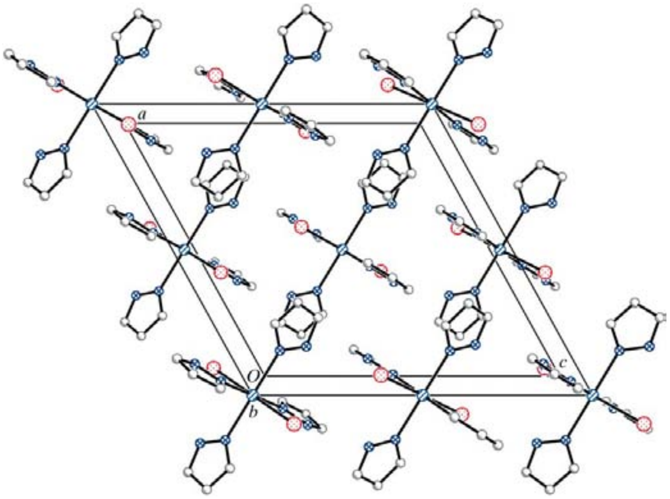


Figure 2

A packing diagram for (IIa), viewed in the ac plane. H atoms have been omitted for clarity.

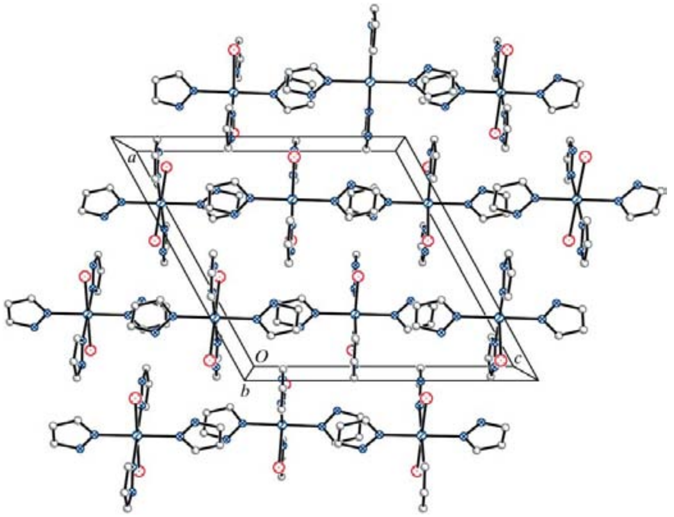


Figure 3

A packing diagram for (IId), viewed in the ac plane. H atoms have been omitted for clarity.

which are actually identical (Table 3). The same occurred with 3aβ,4α-dihydro-4β,10-dimethyl-2-phenyl-1*H*,3*H*,5*H*-pyrrolo-[3,4-*b*]carbazole-1,3-dione (Fischer *et al.*, 1995), where the two polymorphs presented are actually the same structure in a different setting (Table 4).

The nature of the problem described above is that some diffractometer programs might not calculate the correct conventional cell parameters and structure determination is performed in a nonconventional setting. A check for the conventional setting using the program *PLATON* (Spek, 2003) easily detects that a nonconventional setting has been used and lists the necessary transformation matrix. As far as just one single structure determination is concerned, it is just a question of sound crystallographic work. If, however, different determinations of the same structure are to be compared, care must be taken to use the same setting for all of these. And what is more obvious than using the conventional setting?

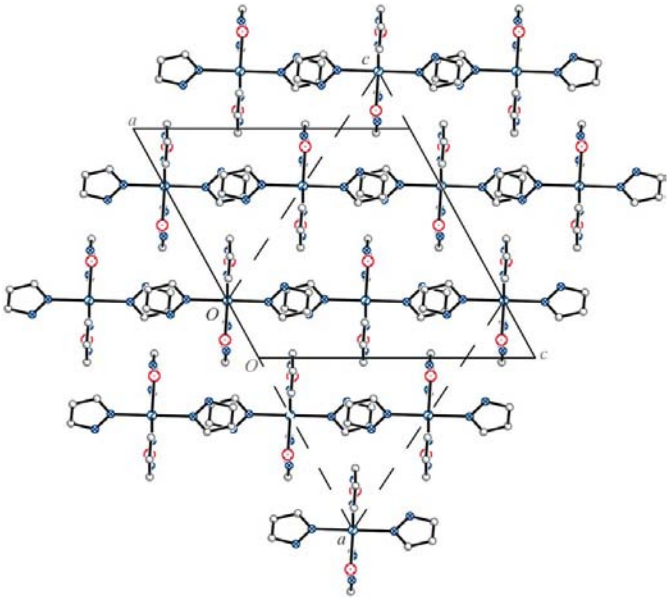


Figure 4
Superposition of the packing diagrams of (II*d*) (solid lines and dark labels) and (II*a*) (dashed lines and light labels), viewed in the *ac* plane. H atoms have been omitted for clarity.

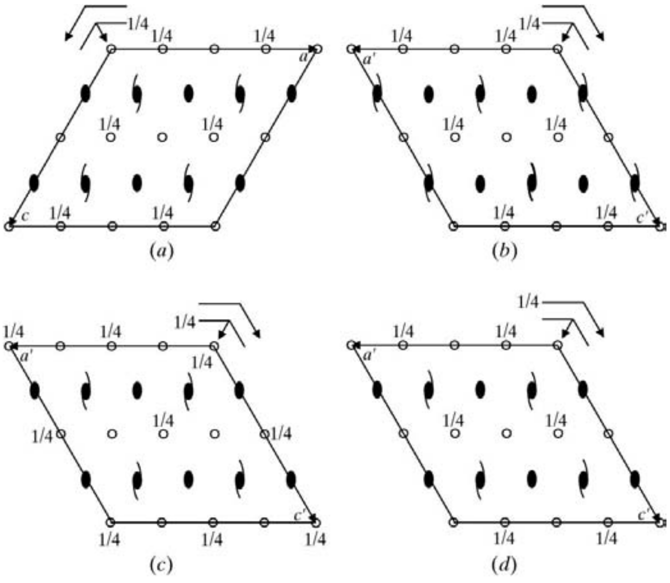


Figure 5
Transformation of the symmetry elements of the conventional setting in *C*2/*c*. (*a*) Original setting; (*b*) applying the matrix ($\bar{1}$00/0$\bar{1}$0/101); (*c*) applying an origin shift of $\frac{1}{4}$ in the direction of the *a* axis; (*d*) applying an origin shift of $\frac{1}{4}$ in the direction of the *b* axis.

Experimental

A solution of dilithium scorpionate (30.1 mg, 0.059 mmol) in tetrahydrofuran (9 ml) was treated with [MnBr(CO)$_5$] (31.8 mg, 0.116 mmol). The solution was separated *via* a cannula from the resulting precipitate. After removal of the solvent, the residue was dissolved in benzene. After several weeks, orange–yellow crystals of (II) suitable for X-ray diffraction were grown at room temperature by slow evaporation of the benzene solvent.

Crystal data

[MnBr$_2$(C$_3$H$_4$N$_2$)$_4$]
M_r = 487.09
Monoclinic, $C2/c$
a = 14.430 (2) Å
b = 9.4424 (8) Å
c = 14.725 (2) Å
β = 118.864 (11)°
V = 1757.1 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 5.31 mm^{-1}
T = 173 (2) K
0.17 × 0.16 × 0.14 mm

Data collection

Stoe IPDSII two-circle diffractometer
Absorption correction: multi-scan [*MULABS* (Spek, 2003; Blessing, 1995)]
$T_{\min}$ = 0.41, $T_{\max}$ = 0.47
8394 measured reflections
1644 independent reflections
1207 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.069

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.169
S = 1.02
1644 reflections
106 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 2.75 e Å^{-3}
$\Delta\rho_{\min}$ = −0.83 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···Br1	0.88	2.70	3.342 (8)	131
N12—H12···Br1	0.88	2.82	3.437 (8)	128
N12—H12···Br1$^{\rm i}$	0.88	2.91	3.568 (8)	133

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

Table 2
Original and corrected values for the *c* axis and β angle of biguanidinium bis(dinitramide) (Å, °).

Original data are taken from Bolotina *et al.* (2003). Corrections are not necessary for the data at 200, 250 and 298 K.

	85 K	100 K	150 K	200 K	250 K	298 K
Original *c*	13.0023	13.0111	13.0302	13.0286	13.0265	13.0359
Corrected *c*	12.8725	12.8987	12.9950			
Original β	117.407	117.337	117.005	116.639	116.225	115.806
Corrected β	116.270	116.354	116.699			

Table 3

Original and corrected values for the c axis and β angle of dichlorido-bis[3-methyl-3-(*N*-phenylamino)-2-butanone oxime]rhodium(III) (Å, °).

Original data are taken from Efe & Schlemper (1992). Corrections are not necessary for data set *A*.

	A	*B*
Original c	14.608	14.702
Corrected c		14.584
Original β	106.57	108.23
Corrected β		106.77

Table 4

Original and corrected values for the c axis and β angle of 3aβ,4α-dihydro-4β,10-dimethyl-2-phenyl-1*H*,3*H*,5*H*-pyrrolo[3,4-*b*]carbazole-1,3-dione (Å, °).

Original data are taken from Fischer *et al.* (1995). (I) and (II) here refer to structures (I) and (II) in the paper of Fischer *et al.* (1995). Corrections are not necessary for the data set for structure (II).

	(I)	(II)
Original c	23.729	23.663
Corrected c	23.661	
Original β	108.680	108.17
Corrected β	108.188	

H atoms were located in a difference map, but were positioned geometrically and refined using a riding model, with fixed individual displacement parameters [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N)] and with N—H = 0.88 Å or C—H = 0.95 Å. The highest peak (2.75 e Å^{-3}) in the final difference electron-density map is 1.36 Å from atom Br1.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3059). Services for accessing these data are described at the back of the journal.

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ISSN 0108-2701

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Received 19 March 2008
Accepted 28 March 2008
Online 26 April 2008

In the paper by Ruth *et al.* [*Acta Cryst.* (2007), C**63**, m566–m569], remarks regarding the results of Bolotina *et al.* [*J. Appl. Cryst.* (2003), **36**, 1334–1341] are withdrawn.

We wish to withdraw from our paper (Ruth *et al.*, 2007) our remarks concerning the results of Bolotina *et al.* (2003). Their results do not need to be revised because the same setting has been used for all structure determinations. Although three cells can be transformed to one with a shorter *c* axis and a smaller angle β, this transformation would change the setting and the six determinations would no longer be comparable.

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Ruth, K., Kunz, K., Lerner, H.-W. & Bolte, M. (2007). *Acta Cryst.* C**63**, m566–m569.

DOI: 10.1107/S0108270108009153