

**(4,4'-Bipyridine)dichloroman-  
ganese(II), a two-dimensional  
coordination polymer**Ann M. Chippindale,<sup>a\*</sup> Andrew R. Cowley<sup>b</sup> and  
Katherine J. Peacock<sup>b</sup><sup>a</sup>Department of Chemistry, The University of Reading, Whiteknights, Reading  
RG6 6AD, England, and <sup>b</sup>Chemical Crystallography Laboratory, 9 Parks Road,  
Oxford OX1 3PD, England

Correspondence e-mail: a.m.chippindale@rdg.ac.uk

Received 7 December 1999

Accepted 3 March 2000

The title compound,  $[\text{MnCl}_2(\text{C}_{10}\text{H}_8\text{N}_2)]_n$ , crystallizes with a two-dimensional network constructed from linear chains of edge-sharing  $\text{MnCl}_4$  square-planar units cross-linked by bidentate 4,4'-bipyridine bridges. The Mn atom and the bipyridine moieties lie on sites with 222 crystallographic symmetry; the Cl atom lies on a twofold axis. The bipyridine molecule is twisted about the central C—C bond by 33.5 (3)°.

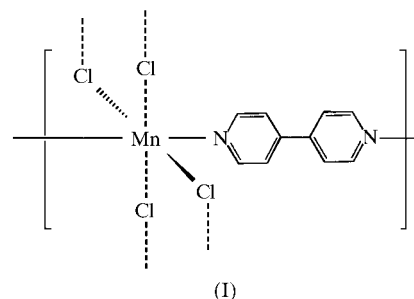
**Comment**

Divalent transition-metal dihalide complexes with 4,4'-bipyridine,  $[\text{MX}_2(4,4'\text{-bipyridine})]$  (where  $M = \text{Mn, Fe, Co, Ni}$  or  $\text{Cu}$  and  $X = \text{Cl, Br}$  or  $\text{I}$ ), were first prepared in the late 1960s (Musgrave & Mattson, 1968; Ferraro & Davis, 1969). IR and magnetic data confirmed that all the complexes were polymeric and contained octahedrally coordinated metal cations with both halide and 4,4'-bipyridine bridging ligands.

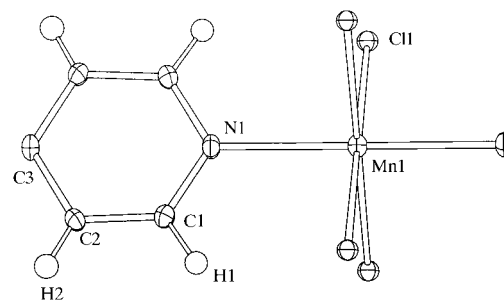
Given the poor solubility of these complexes in common organic solvents, it has proved difficult to obtain single crystals by conventional synthetic methods. The first structures were therefore determined *ab initio* from powder X-ray data for  $[\text{MX}_2(4,4'\text{-bipyridine})]$  ( $M = \text{Ni}$  or  $\text{Cu}$  and  $X = \text{Cl}$  or  $\text{Br}$ ; Masciocchi *et al.*, 1996). Recently, hydrothermal methods have been used to prepare single crystals of  $[\text{MCl}_2(4,4'\text{-bipyridine})]$  ( $M = \text{Fe}$  or  $\text{Co}$ ; Lawandy *et al.*, 1999). These compounds, and the Ni analogues  $[\text{NiX}_2(4,4'\text{-bipyridine})]$  ( $X = \text{Cl}$  or  $\text{Br}$ ), are isostructural and have an orthorhombic lattice ( $a \sim 11.5$ ,  $b \sim 11.9$ ,  $c \sim 3.6$  Å, space group  $Cmmm$ ). The structure consists of  $\text{MX}_2$  chains constructed from edge-sharing square-planar  $\text{MX}_4$  units. These are linked by planar bipyridine ligands occupying *trans* positions of the six-coordinate metal atoms to form a two-dimensional network.

We have prepared  $[\text{MnCl}_2(4,4'\text{-bipyridine})]$ , (I), as single crystals under solvothermal conditions in the presence of butan-2-ol. The lattice parameters at ambient temperature [shown by single-crystal X-ray diffraction to be  $a = 11.634$  (2),  $b = 11.979$  (2) and  $c = 3.6969$  (4) Å, and  $V = 515.23$  Å<sup>3</sup>] are

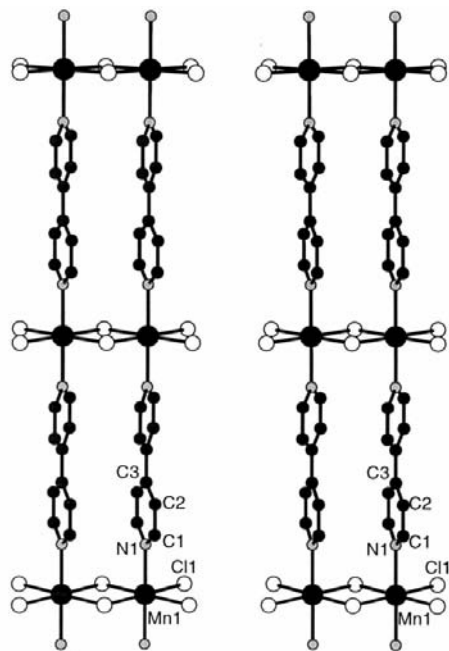
similar to those of the Fe, Co and Ni analogues, but the unit cell is primitive orthorhombic rather than  $C$ -centred. A crystal of (I) was rapidly cooled to 150 K for the structure determination presented here. The refinement was successful in space group  $Pban$ . Refinement was also attempted in the higher-symmetry space group  $Cmmm$ , but this led to unsatisfactory bipyridine-ring geometry and unreasonable displacement ellipsoids for the C atoms lying *ortho* and *meta* to the N atom, with elongation along the principal axes perpendicular to the ring plane. The primitive nature of the structure is further confirmed by the good agreement between the measured powder X-ray diffraction pattern and one simulated in  $Pban$ . The (121) reflection, which would be absent if the structure were  $C$ -centered, is clearly visible in the measured pattern. The anisotropic displacement parameters determined previously for the corresponding C atoms in the Fe and Co analogues (Lawandy *et al.*, 1999) are similar to those observed in our  $Cmmm$  refinement, suggesting that these structures may also be primitive rather than  $C$ -centered.



Compound (I) adopts a layer structure with identical connectivity to that of the Fe, Co and Ni analogues. The Mn, Cl, N and C3 atoms occupy special positions (Wyckoff labels  $2d$ ,  $4j$ ,  $4h$  and  $4h$ , respectively). The  $\text{Mn}^{2+}$  cation has a distorted octahedral coordination in which a pair of *trans* positions are occupied by the N atoms of two bipyridine ligands and the remaining positions occupied by four  $\text{Cl}^-$  anions. Although each aromatic  $\text{C}_5\text{N}$  ring is almost planar, the bipyridine molecule is twisted about the central C—C bond by *ca* 35°. This structural feature has not been observed in the previous  $[\text{MCl}_2(4,4'\text{-bipyridine})]$  structures, in which coplanarity of the rings is a consequence of the crystallographic symmetry.

**Figure 1**

A view of part of the molecule of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.


**Figure 2**

A stereoview (Dowty, 1997) of a single layer of (I) showing the non-coplanar C<sub>5</sub>N rings of the bipyridine unit. The *a* axis runs vertically and the *c* axis runs horizontally. The numbering scheme of one asymmetric unit is shown. H atoms have been omitted for clarity.

## Experimental

Compound (I) was synthesized under solvothermal conditions from a gel of composition MnCl<sub>2</sub>·4H<sub>2</sub>O:butan-2-ol:4,4'-bipyridine:Si(OEt)<sub>4</sub>:H<sub>3</sub>PO<sub>4</sub> (85% aqueous) in the ratio 1:17.5:2.4:0.1:2.3. MnCl<sub>2</sub>·4H<sub>2</sub>O (0.79 g) was dispersed in butan-2-ol (6.4 ml) by stirring and 4,4'-bipyridine (1.5 g) was added together with Si(OEt)<sub>4</sub> (0.1 ml) as crystallizing agent. After further stirring, aqueous H<sub>3</sub>PO<sub>4</sub> (85% by weight, 0.64 ml) was added and the mixture sealed in a Teflon-lined autoclave and heated for 7 d at 423 K. The solid product mixture consisted of clear colourless crystals of 4,4'-bipyridinium phosphate (Chippindale, 1997), very pale-green block-shaped crystals of (I) and a white powder. The organic phosphate was removed by washing in distilled water. Powder X-ray diffraction showed the washed product to consist almost entirely of (I).

### Crystal data

[MnCl<sub>2</sub>(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)]  
*M<sub>r</sub>* = 282.04  
 Orthorhombic, *Pbn*  
*a* = 11.641 (2) Å  
*b* = 11.955 (2) Å  
*c* = 3.678 (1) Å  
*V* = 511.86 Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.83 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 2342 reflections  
 $\theta = 0\text{--}26.57^\circ$   
 $\mu = 1.73\text{ mm}^{-1}$   
*T* = 150 K  
 Block, pale green  
 0.4 × 0.2 × 0.2 mm

### Data collection

Enraf–Nonius DIP2000 image-plate diffractometer  
 527 independent reflections  
 527 reflections with *I* > 0  
 $R_{\text{int}} = 0.024$   
 $\theta_{\text{max}} = 26.57^\circ$   
*h* = 0 → 14  
*k* = 0 → 14  
*l* = 0 → 4  
 Absorption correction: multi-scan (DENZO-SMN; Otwinowski & Minor, 1997)  
 $T_{\text{min}} = 0.501$ ,  $T_{\text{max}} = 0.708$   
 2342 measured reflections

### Refinement

*R* = 0.033  
*wR* = 0.038  
*S* = 1.0537  
 527 reflections  
 45 parameters  
 All H-atom parameters refined  
 Chebyshev polynomial with 3 parameters (294, 403, 112; Carruthers & Watkin, 1979)  
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.38\text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.79\text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Mn1—Cl1	2.5523 (4)	C1—C2	1.3823 (19)
Mn1—N1	2.2768 (19)	C2—C3	1.3958 (18)
N1—C1	1.3441 (18)	C3—C3 <sup>i</sup>	1.486 (4)
Cl1—Mn1—Cl1 <sup>ii</sup>	92.194 (18)	N1—C1—C2	123.23 (14)
Cl1—Mn1—N1	90	C1—C2—C3	119.18 (16)
Mn1 <sup>iii</sup> —Cl1—Mn1	92.194 (18)	C2—C3—C2 <sup>iv</sup>	117.7 (19)
Mn1—N1—C1	121.30 (9)	C2—C3—C3 <sup>i</sup>	121.1 (1)
C1—N1—C1 <sup>iv</sup>	117.40 (18)		

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

Data collection: *XPRESS* (MacScience, 1989); cell refinement: *DENZO-SMN*; data reduction: *DENZO-SMN* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 1996); molecular graphics: *ATOMS for Windows* (Dowty, 1997); software used to prepare material for publication: *CRYSTALS*.

ARC thanks the EPSRC for a Research Studentship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1389). Services for accessing these data are described at the back of the journal.

## References

- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.  
 Carruthers, J. R. & Watkin, D. J. (1979). *Acta Cryst.* **A35**, 698–699.  
 Chippindale, A. M. (1997). Unpublished work.  
 Dowty, E. (1997). *ATOMS for Windows*. Version 4.0. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.  
 Ferraro, J. R. & Davis, K. C. (1969). *Inorg. Chim. Acta*, **3**, 685–688.  
 Lawandy, M. A., Huang, X., Wang, R. J., Li, J., Lu, J. Y., Yuen, T. & Lin, C. L. (1999). *Inorg. Chem.* **38**, 5410–5414.  
 MacScience (1989). *XPRESS*. MacScience Co. Ltd, Yokohama, Japan.  
 Masciocchi, N., Cairati, P., Carlucci, L., Mezza, G., Ciani, G. & Sironi, A. (1996). *J. Chem. Soc. Dalton Trans.* pp. 2739–2746.  
 Musgrave, T. R. & Mattson, C. E. (1968). *Inorg. Chem.* **7**, 1433–1436.  
 Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.  
 Watkin, D. J., Prout, C. K., Carruthers, R. J. & Betteridge, P. (1996). *CRYSTALS*. Issue 10. Chemical Crystallography Laboratory, University of Oxford, England.