

- Mayr, A., Asaro, M. F. & Gilnes, T. J. (1987). *J. Am. Chem. Soc.* **109**, 2215–2216.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
- Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement*. Univ. of Göttingen, Germany.
- Spek, A. L. (1991). *PLUTON. Molecular Graphics Program*. Univ. of Utrecht, The Netherlands.
- Szklarzewicz, J., Samotus, A., Alcock, N. W. & Moll, M. (1990). *J. Chem. Soc. Dalton Trans.* pp. 2959–2963.

Acta Cryst. (1995). **C51**, 820–822

Tris(2,2'-bipyridine)manganese(II) Perchlorate Hemihydrate

XIAO-MING CHEN,* RUI-QIN WANG AND ZHI-TAO XU

Department of Chemistry, Zhongshan University,
135 Xingang Road W., Guangzhou,
People's Republic of China

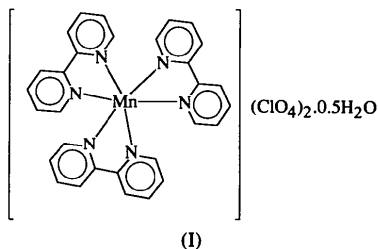
(Received 28 July 1994; accepted 28 October 1994)

Abstract

The crystal structure of tris(2,2'-bipyridine)manganese(II) perchlorate hemihydrate, [Mn(C₁₀H₈N₂)₃](ClO₄)₂·0.5H₂O, has been established by X-ray crystallography. The metal atom is coordinated by three chelating 2,2'-bipyridine ligands in a highly distorted octahedral MnN₆ arrangement with Mn—N bond lengths ranging from 2.219 (4) to 2.294 (4) Å.

Comment

In an attempt to prepare a manganese(II) complex containing 2,2'-bipyridine (bpy) and betaine ligands, we obtained an unusual singly carboxylato-bridged dinuclear manganese(II) complex [Mn₂(bpy)₄(Me₃NCH₂CO₂)(H₂O)₂](ClO₄)₄·2H₂O, together with golden needle-like crystals as a minor product (Chen & Mak, 1993). The latter complex has been characterized by IR spectral data and elemental analysis as the monomeric complex [Mn(bpy)₃](ClO₄)₂·0.5H₂O, (I). We report here the single-crystal structure of this complex.



The crystal structure of the title complex is composed of monomeric [Mn(bpy)₃]²⁺ cations, perchlorate anions and lattice water molecules. As illustrated in Fig. 1, the metal atom is surrounded by six N atoms from three chelating bpy ligands in a highly distorted octahedral MnN₆ arrangement. The Mn—N bond lengths range from 2.219 (4) to 2.294 (4) Å with the most distorted N—Mn—N angle (*ca* 73°) resulting from a chelating bpy ligand. The Mn—N bond lengths are significantly longer than those (1.932–2.172 Å) found for the analogous cations [Zn(bpy)₃]²⁺ (Chen, Wang & Yu, 1995), [Co(bpy)₃]³⁺ (Yanagi, Ohashi, Sasada, Kaizu & Kobayashi, 1981), [Fe(bpy)₃]³⁺ (Figgis, Skelton & White, 1978) and [Ni(bpy)₃]²⁺ (Wada, Katayama & Tanaka, 1976). The Mn—N bond lengths are longer than the *M*—N bond lengths found for analogous [M(bpy)₃]^{*n*+} complexes (*M* = Zn²⁺, Co³⁺, Fe³⁺, Ni²⁺); this may be attributed to the larger ionic radius of the Mn²⁺ cation. It is noteworthy that each pair of pyridine rings in the three bpy ligands are not coplanar, the dihedral angles between each pair ranging from 13 to 25°.

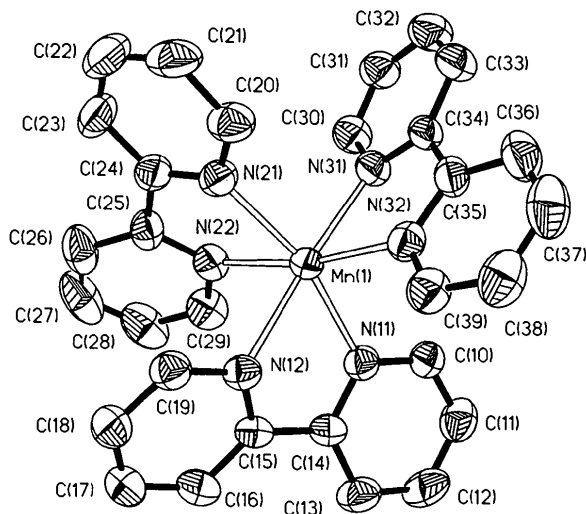


Fig. 1. ORTEP (Johnson, 1965) drawing of the [Mn(bpy)₃]²⁺ cation showing 45% probability ellipsoids.

Experimental

The crystals were a by-product of the work reported in XVI Congress and General Assembly of International Union of Crystallography (Chen & Mak, 1993).

Crystal data

[Mn(C₁₀H₈N₂)₃](ClO₄)₂·
0.5H₂O
M_r = 730.4
Triclinic
*P*1

Mo *K*α radiation
λ = 0.71073 Å
Cell parameters from 25
reflections
θ = 1.5–25°

$a = 8.133 (2) \text{ \AA}$
 $b = 11.056 (2) \text{ \AA}$
 $c = 18.658 (5) \text{ \AA}$
 $\alpha = 102.27 (2)^\circ$
 $\beta = 91.02 (2)^\circ$
 $\gamma = 99.77 (2)^\circ$
 $V = 1613.1 (7) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.504 \text{ Mg m}^{-3}$

$\mu = 0.636 \text{ mm}^{-1}$
 $T = 295 \text{ K}$
 Needle-like
 $0.50 \times 0.48 \times 0.40 \text{ mm}$
 Golden yellow

C(31)	-0.3828 (7)	0.2681 (6)	0.5784 (3)	0.081 (3)
C(32)	-0.3190 (9)	0.3796 (7)	0.5603 (3)	0.095 (3)
C(33)	-0.1601 (8)	0.4388 (5)	0.5842 (3)	0.084 (3)
C(34)	-0.0679 (7)	0.3863 (4)	0.6285 (3)	0.062 (2)
C(35)	0.1081 (7)	0.4429 (4)	0.6564 (3)	0.064 (2)
C(36)	0.2036 (9)	0.5388 (5)	0.6308 (3)	0.091 (3)
C(37)	0.3663 (10)	0.5784 (6)	0.6560 (4)	0.107 (3)
C(38)	0.4347 (8)	0.5270 (6)	0.7074 (4)	0.096 (3)
C(39)	0.3305 (7)	0.4349 (5)	0.7329 (3)	0.077 (2)
Cl(1)	-0.2699 (2)	0.3235 (1)	1.0854 (1)	0.080 (1)
O(11)	-0.2465 (5)	0.4550 (4)	1.0884 (3)	0.107 (2)
O(12)	-0.1560 (6)	0.2684 (5)	1.0402 (3)	0.138 (3)
O(13)	-0.2509 (8)	0.3028 (4)	1.1574 (2)	0.142 (3)
O(14)	-0.4355 (6)	0.2673 (4)	1.0549 (3)	0.124 (2)
Cl(2)	0.1999 (2)	0.2256 (1)	0.4378 (1)	0.071 (1)
O(21)	0.1924 (13)	0.0886 (6)	0.4356 (6)	0.111 (4)
O(22)	0.0525 (8)	0.2288 (7)	0.3926 (4)	0.093 (2)
O(23)	0.1899 (13)	0.2876 (9)	0.5135 (3)	0.140 (4)
O(24)	0.3475 (9)	0.2734 (8)	0.4055 (5)	0.134 (4)
O(21')	0.1678 (13)	0.2532 (9)	0.3665 (4)	0.135 (3)
O(22')	0.2448 (13)	0.1083 (6)	0.4306 (5)	0.109 (4)
O(23')	0.0640 (10)	0.2482 (9)	0.4818 (5)	0.149 (4)
O(24')	0.3431 (9)	0.3237 (7)	0.4702 (5)	0.131 (3)
O(1w)	0.0531 (23)	0.2953 (17)	0.2481 (10)	0.254 (8)

Data collection

Siemens R3m/V diffractometer
 $R_{\text{int}} = 0.0142$
 $\theta_{\text{max}} = 25^\circ$
 ω scans
 $h = 0 \rightarrow 9$
 Absorption correction: empirical
 $k = -13 \rightarrow 13$
 $l = -22 \rightarrow 22$
 $T_{\text{min}} = 0.724$, $T_{\text{max}} = 0.996$
 6198 measured reflections
 5759 independent reflections
 3875 observed reflections
 $[F > 6\sigma(F)]$
 2 standard reflections monitored every 100 reflections
 intensity decay: 1.0%

Refinement

Refinement on F^2
 $R = 0.0583$
 $wR = 0.0736$
 $S = 3.02$
 3875 reflections
 424 parameters
 H-atom parameters not refined
 $w = 1/[\sigma^2(F) + 0.002F^2]$
 $(\Delta/\sigma)_{\text{max}} = 0.63$
 $\Delta\rho_{\text{max}} = 0.63 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.41 \text{ e \AA}^{-3}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$
Mn(1)	0.0062 (1)	0.2370 (1)	0.7423 (1)	0.055 (1)
N(11)	0.1500 (5)	0.0930 (3)	0.6877 (2)	0.060 (2)
N(12)	0.1585 (4)	0.1886 (3)	0.8336 (2)	0.058 (2)
C(10)	0.1711 (6)	0.0648 (5)	0.6149 (3)	0.068 (2)
C(11)	0.2709 (7)	-0.0181 (5)	0.5847 (3)	0.084 (3)
C(12)	0.3522 (8)	-0.0746 (6)	0.6295 (4)	0.094 (3)
C(13)	0.3303 (7)	-0.0479 (5)	0.7041 (3)	0.081 (2)
C(14)	0.2286 (6)	0.0369 (4)	0.7315 (3)	0.057 (2)
C(15)	0.2039 (5)	0.0755 (4)	0.8118 (3)	0.057 (2)
C(16)	0.2196 (7)	-0.0008 (5)	0.8602 (3)	0.076 (2)
C(17)	0.1934 (7)	0.0404 (6)	0.9341 (3)	0.082 (3)
C(18)	0.1538 (7)	0.1577 (6)	0.9561 (3)	0.078 (2)
C(19)	0.1366 (6)	0.2285 (5)	0.9056 (3)	0.068 (2)
N(21)	-0.1445 (5)	0.3495 (4)	0.8202 (2)	0.063 (2)
N(22)	-0.2004 (5)	0.0973 (4)	0.7767 (2)	0.062 (2)
C(20)	-0.1313 (7)	0.4752 (5)	0.8305 (3)	0.080 (2)
C(21)	-0.2425 (10)	0.5386 (7)	0.8721 (3)	0.104 (3)
C(22)	-0.3694 (10)	0.4724 (9)	0.9027 (4)	0.115 (4)
C(23)	-0.3825 (7)	0.3438 (8)	0.8926 (3)	0.095 (3)
C(24)	-0.2695 (6)	0.2856 (5)	0.8510 (3)	0.067 (2)
C(25)	-0.2783 (6)	0.1476 (5)	0.8359 (3)	0.067 (2)
C(26)	-0.3551 (7)	0.0720 (8)	0.8812 (3)	0.097 (3)
C(27)	-0.3587 (9)	-0.0553 (8)	0.8632 (4)	0.117 (4)
C(28)	-0.2841 (9)	-0.1049 (7)	0.8019 (4)	0.105 (3)
C(29)	-0.2051 (7)	-0.0269 (5)	0.7603 (3)	0.081 (2)
N(31)	-0.1295 (5)	0.2783 (4)	0.6477 (2)	0.063 (2)
N(32)	0.1719 (5)	0.3920 (3)	0.7074 (2)	0.063 (2)
C(30)	-0.2873 (7)	0.2208 (5)	0.6226 (3)	0.073 (2)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Mn(1)—N(11)	2.219 (4)	Mn(1)—N(12)	2.294 (4)
Mn(1)—N(21)	2.230 (4)	Mn(1)—N(22)	2.280 (4)
Mn(1)—N(31)	2.233 (4)	Mn(1)—N(32)	2.214 (4)
N(11)—Mn(1)—N(12)	73.4 (1)	N(11)—Mn(1)—N(21)	164.3 (2)
N(12)—Mn(1)—N(21)	94.1 (1)	N(11)—Mn(1)—N(22)	95.3 (1)
N(12)—Mn(1)—N(22)	82.5 (1)	N(21)—Mn(1)—N(22)	73.2 (1)
N(11)—Mn(1)—N(31)	102.7 (1)	N(12)—Mn(1)—N(31)	175.9 (1)
N(21)—Mn(1)—N(31)	90.0 (2)	N(22)—Mn(1)—N(31)	99.3 (1)
N(11)—Mn(1)—N(32)	93.2 (1)	N(12)—Mn(1)—N(32)	105.0 (1)
N(21)—Mn(1)—N(32)	99.3 (1)	N(22)—Mn(1)—N(32)	170.0 (2)
N(31)—Mn(1)—N(32)	73.6 (2)	Mn(1)—N(11)—C(10)	124.5 (4)
Mn(1)—N(11)—C(14)	116.7 (3)	Mn(1)—N(12)—C(15)	111.5 (3)
Mn(1)—N(12)—C(19)	123.2 (3)	Mn(1)—N(21)—C(20)	123.6 (3)
Mn(1)—N(21)—C(24)	117.2 (3)	Mn(1)—N(22)—C(25)	113.7 (3)
Mn(1)—N(22)—C(29)	123.2 (3)	Mn(1)—N(31)—C(30)	123.8 (4)
Mn(1)—N(31)—C(34)	115.8 (3)	Mn(1)—N(32)—C(35)	117.0 (3)
Mn(1)—N(32)—C(39)	123.9 (4)		

A crystal was cut to a suitable size and mounted on a glass fibre for data collection. Lorentz and polarization corrections were applied. The lattice water molecule had a site occupation factor of 0.5. The H atoms were generated geometrically (C—H 0.96 \AA), assigned isotropic displacement parameters and included in the structure-factor calculations. The O atoms of one perchlorate anion were twofold disordered and were assigned site occupation factors of 0.5 and refined isotropically.

Data collection, cell refinement and data reduction: *SHELXTL-Plus* (Sheldrick, 1990b). Structure solution (direct methods) and structure refinement: *SHELXTL/PC* (Sheldrick, 1990a).

We acknowledge financial support by a grant from the National Education Commission of China for Returned Scientists from Abroad and a grant from Zhongshan University. We are also indebted to Professor Thomas C. W. Mak for the X-ray data collection.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1009). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Chen, X.-M. & Mak, T. C. W. (1993). *Acta Cryst.* **A49**, C-220.
 Chen, X.-M., Wang, R.-Q. & Yu, X.-L. (1995). *Acta Cryst.* **C51**. In the press.
 Figgis, B. N., Skelton, B. W. & White, A. H. (1978). *Aust. J. Chem.* **31**, 57–64.
 Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
 Sheldrick, G. M. (1990a). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc, Madison, Wisconsin, USA.
 Sheldrick, G. M. (1990b). *SHELXTL-Plus. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Univ. of Göttingen, Germany.
 Wada, A., Katayama, C. & Tanaka, J. (1976). *Acta Cryst.* **B32**, 3194–3199.
 Yanagi, K., Ohashi, Y., Sasada, Y., Kaizu, Y. & Kobayashi, H. (1981). *Bull. Chem. Soc. Jpn.* **54**, 118–126.

Acta Cryst. (1995). **C51**, 822–824

Bis(acetato)amminedichloro(cyclohexylamine)platinum(IV), an Orally Active Anticancer Drug

STEPHEN NEIDLE AND CHRIS F. SNOOK

The CRC Biomolecular Structure Unit at The Institute of Cancer Research, Sutton, Surrey SM2 5NG, England

BARRY A. MURRER AND CHRISTOPHER F. J. BARNARD

Johnson Matthey Technology Centre, Blount's Court, Sonning Common, Reading RG4 9NH, England

(Received 24 May 1994; accepted 23 November 1994)

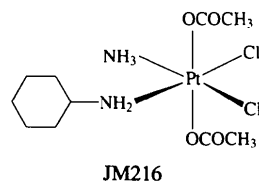
Abstract

The structure of the anticancer drug bis(acetato)-amminedichloro(cyclohexylamine)platinum(IV), [PtCl₂(C₂H₃O₂)₂(C₆H₁₃N)(NH₃)], is reported. The acetato groups are axial to the square plane composed of the chlorine and amine substituents. The cyclohexane ring may sterically hinder one of the acetato groups for metabolic attack. The amine groups are hydrogen bonded to the carbonyl O atoms of the acetato groups.

Comment

The platinum(II) complex cisplatin (*cis*-diamminedichloroplatinum) is an established and effective drug in the treatment of certain cancers, especially testicular and ovarian cancer (Horwich, 1989). However, because of its severe nephrotoxicity, relatively narrow spectrum of activity and lack of activity in tumours with acquired resistance, there has been a continuing search for new platinum compounds that circumvent these problems

(Kelland, 1993). It has been found that platinum(IV) alkylamines with axial carboxylate groups show selective cytotoxicity to cisplatin-resistant human tumour cell lines (Kelland *et al.*, 1992). This biological response is due mainly to the lipophilicity of the axial groups combined with activation of the complex *via* reduction to the platinum(II) species. The title compound, JM216, an outstandingly active member of the series (Kelland *et al.*, 1993), is currently being evaluated in clinical trials. Its crystal structure has been determined as part of a study relating structural features to possible patterns of metabolism.



The title complex has standard octahedral coordination around the Pt^{IV} atom. The two Cl atoms, the ammine group and the cyclohexylamine group are in a square-planar arrangement around the Pt atom. The two acetato groups are axial to this plane (Fig. 1) and the cyclohexane ring adopts a chair conformation. The angle N1—Pt—N2 is significantly greater than 90°.

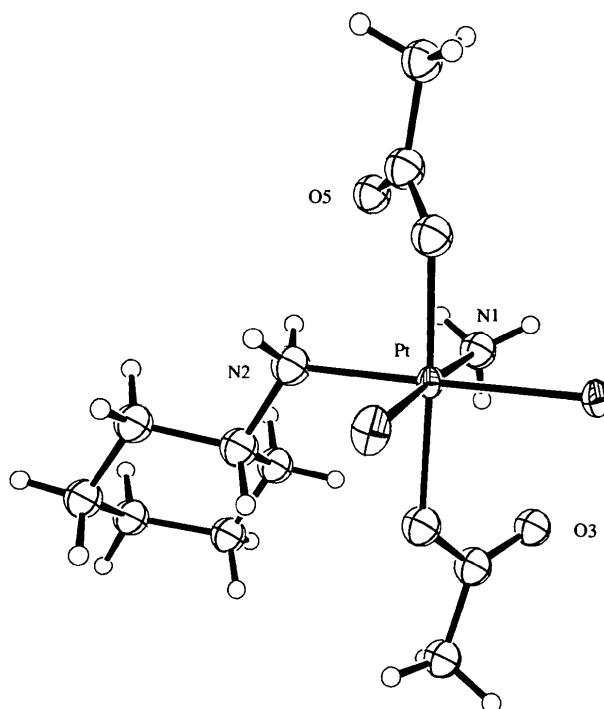


Fig. 1. View of the title molecule (ORTEX; McArdle, 1993) showing 50% displacement ellipsoids for the Pt and Cl atoms and the numbering scheme for selected non-H atoms. H atoms are plotted as spheres of arbitrary size.