

This work was in part supported by Grant-in-Aid for Scientific Research No. 09740489 from the Ministry of Education, Science and Culture, Japan.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1069). Services for accessing these data are described at the back of the journal.

References

- Coles, S. J., Edwards, P. G., Fleming, J. S. & Hursthouse, M. B. (1995). *J. Chem. Soc. Dalton Trans.* pp. 1139–1145.
- Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.
- Diel, B. N., Brandt, P. F., Haliwanger, C., Hackner, M. L. J. & Norman, A. D. (1989). *Inorg. Chem.* **28**, 2811–2816.
- Heinemann, F., Schmidt, H., Peters, K. & Thiery, D. (1992). *Z. Kristallogr.* **198**, 123–124.
- Johnson, C. K. (1970). *ORTEP*. Report ORNL-3794, 2nd revision. Oak Ridge National Laboratory, Tennessee, USA.
- Mak, T. C. W. (1984). *Z. Kristallogr.* **166**, 277–281.
- Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7-2. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Rigaku Co. Ltd (1985). *RigakuAFC Diffractometer Control Software*. Rigaku Co. Ltd, Akishima, Tokyo, Japan.
- Saum, S. E., Askham, F. R., Fronczek, F. R. & Stanley, G. G. (1988). *Organometallics*, **7**, 1409–1416.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Suzuki, T., Rude, M., Simonsen, K. P., Morooka, M., Tanaka, H., Ohba, S., Galsbøl, F. & Fujita, J. (1994). *Bull. Chem. Soc. Jpn.*, **67**, 1013–1023.
- Walter, O., Klein, T., Huttner, G. & Zsolnai, L. (1993). *J. Organomet. Chem.* **458**, 63–81.
- Whitaker, A. & Jeffery, J. W. (1967). *Acta Cryst.* **23**, 977–984.

Acta Cryst. (1999). **C55**, 186–188

Aquabis(2,2'-bipyridine-*N,N'*)(perchlorato-*O*)manganese(II) perchlorate

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(Received 23 June 1998; accepted 21 September 1998)

Abstract

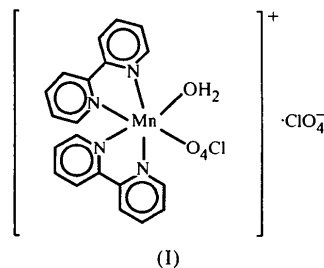
The crystal structure of the title compound, [Mn(ClO₄)-(C₁₀H₈N₂)₂(H₂O)]ClO₄, contains monomeric [Mn(bipy)₂-(ClO₄)(H₂O)]⁺ cations (bipy is 2,2'-bipyridine) in which

the Mn^{II} ion is surrounded by a pair of chelating bipy ligands [Mn—N 2.222 (5)–2.228 (5) Å], an aqua ligand [Mn—O 2.142 (4) Å] and a perchlorate ligand [Mn—O 2.289 (5) Å] in a distorted octahedral arrangement. Adjacent cations are linked into dimers by pairs of O···O hydrogen bonds [O···O 2.795 (7) Å].

Comment

Manganese complexes have attracted considerable interest recently because of the frequent occurrence of such metal centres in biological systems (Wieghardt, 1989). The complexation behaviour of 2,2'-bipyridine (bipy) or bipy-related ligands with Mn ions gives rise to a wide variety of coordination complexes, depending on the nature of the bipy ligand, the oxidation state of the Mn ion and the nature of the other coordinating ligands. Mn^{II} complexes with bipy-type ligands are well known: there are over 100 structures of this type in the Cambridge Structural Database (Allen & Kennard, 1993).

The crystal structure of the title compound, (I), consists of discrete [Mn(bipy)₂(ClO₄)(H₂O)]⁺ cations and perchlorate anions. As illustrated in Fig. 1, the Mn^{II} ion in each cation is in a distorted octahedral environment, coordinated by a pair of *cis*-related chelating bipy ligands, one aqua ligand and one O atom of the ClO₄⁻ ligand.



The bipyridine groups exhibit their usual acute N···N bite distance [N1···N2 2.670 (7) and N3···N4 2.652 (7) Å] and N—Mn—N angles [N1—Mn1—N2 73.75 (18) and N3—Mn1—N4 73.16 (17)°]. The values are very close to those found in [Mn(bipy)₂Cl₂] (Lumme & Lindell, 1988), [Mn(bipy)₂(NCS)₂] (Veidis *et al.*, 1981) and [MnCl(bipy)₂(H₂O)] (Chen *et al.*, 1995), in which pairs of bipy ligands are also *cis* related, but are markedly different from those of some other [M(bipy)₂L₂]ⁿ⁺ species, in which the two bipy ligands are *trans* related.

Both bipy molecules are nearly planar; the largest deviation from either mean plane is 0.131 (7) Å. The mean planes of the two bipy molecules are inclined at 97.77 (11)° with respect to one another. The aromatic bond distances of both bipy molecules are normal, within the range 1.324 (8)–1.353 (6) Å for aromatic N—C bonds and 1.343 (9)–1.389 (7) Å for aromatic

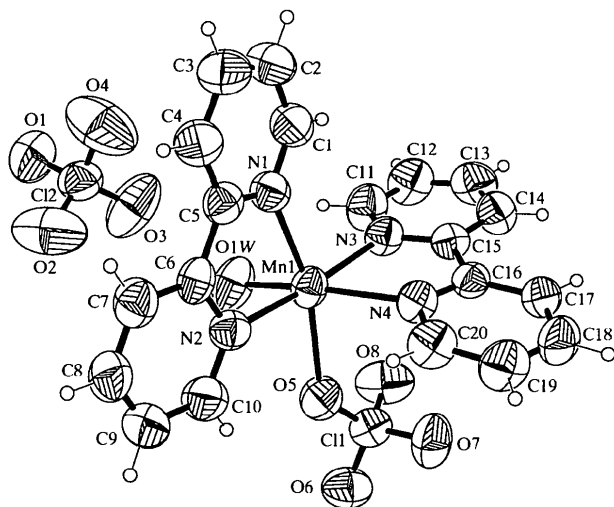


Fig. 1. A perspective view of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

C—C bonds, single C—C bonds being 1.470 (8) and 1.474 (7) Å. The values of the bond angles within each pyridine ring of both bipy molecules range from 117.7 (7) to 123.4 (6)°, while the values of the angles around the C—C bond between the two pyridine rings lie in a somewhat larger range.

The Mn—N bonds have lengths ranging from 2.222 (5) to 2.228 (5) Å, while the Mn—O bonds have lengths of 2.142 (4) and 2.289 (5) Å.

Hydrogen bonding plays an important role in consolidating the crystal structure. Each pair of adjacent [Mn(bipy)₂(ClO₄)(H₂O)]⁺ cations related by an inversion centre is linked by a pair of intermolecular hydrogen bonds between the aqua and the perchlorate ligands [O1W...O8ⁱ 2.795 (7) Å; symmetry code: (i) $-x, -y, -z$]. The aqua ligand also appears to have a single hydrogen-bonding interaction with the O3 atom of the perchlorate anion [O1W...O3 2.717 (8) Å].

Experimental

A mixture of MnCl₂·4H₂O (0.4 g, 2.0 mmol) and 2,2'-bipyridine (0.31 g, 2.0 mmol) was dissolved in warm distilled water (10 ml, 333 K). To the yellow solution, an aqueous solution of sodium perchlorate (0.3 g in 2 ml) was added. The resulting solution was allowed to stand in air overnight whereupon a yellow precipitate was deposited. Recrystallization from water gave the title complex.

Crystal data

[Mn(ClO₄)(C₁₀H₈N₂)₂·(H₂O)]ClO₄
 $M_r = 584.22$
 Monoclinic
 $P2_1/n$

Cu $K\alpha$ radiation
 $\lambda = 1.54179$ Å
 Cell parameters from 20 reflections
 $\theta = 5\text{--}25^\circ$

$a = 8.744$ (4) Å
 $b = 14.219$ (7) Å
 $c = 19.552$ (9) Å
 $\beta = 98.63$ (4)°
 $V = 2403$ (2) Å³
 $Z = 4$
 $D_x = 1.615$ Mg m⁻³
 D_m not measured

$\mu = 7.043$ mm⁻¹
 $T = 293$ (1) K
 Prism
 $0.30 \times 0.22 \times 0.18$ mm
 Yellow

Data collection

Siemens AED diffractometer
 $\omega/2\theta$ scans
 Absorption correction:
 numerical (NEWCORR;
 González-Platas & Ruiz-
 Pérez, 1997)
 $T_{\min} = 0.107$, $T_{\max} = 0.205$
 4741 measured reflections
 4429 independent reflections

2546 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.058$
 $\theta_{\max} = 69.85^\circ$
 $h = -10 \rightarrow 0$
 $k = 0 \rightarrow 17$
 $l = -23 \rightarrow 23$
 2 standard reflections
 frequency: 120 min
 intensity decay: <5%

Refinement

Refinement on F^2
 $R(F) = 0.068$
 $wR(F^2) = 0.211$
 $S = 1.079$
 4429 reflections
 326 parameters
 H atoms treated by a
 mixture of independent
 and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1141P)^2 + 1.2013P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.579$ e Å⁻³
 $\Delta\rho_{\min} = -0.716$ e Å⁻³
 Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Mn1—O1W	2.142 (4)	Mn1—N1	2.227 (5)
Mn1—N2	2.222 (5)	Mn1—N3	2.228 (5)
Mn1—N4	2.223 (5)	Mn1—O5	2.289 (5)
O1W—Mn1—N2	91.51 (19)	N4—Mn1—O5	86.67 (18)
O1W—Mn1—N4	159.35 (17)	N1—Mn1—O5	161.03 (16)
N2—Mn1—N4	105.12 (17)	N3—Mn1—O5	99.64 (18)
O1W—Mn1—N1	96.91 (18)	C1—N1—Mn1	125.0 (4)
N2—Mn1—N1	73.75 (18)	C5—N1—Mn1	116.1 (4)
N4—Mn1—N1	99.43 (17)	C10—N2—Mn1	124.4 (4)
O1W—Mn1—N3	91.83 (19)	C6—N2—Mn1	116.7 (4)
N2—Mn1—N3	172.63 (19)	C11—N3—Mn1	124.5 (4)
N4—Mn1—N3	73.16 (17)	C15—N3—Mn1	117.4 (3)
N1—Mn1—N3	99.32 (18)	C20—N4—Mn1	123.6 (4)
O1W—Mn1—O5	81.88 (19)	C16—N4—Mn1	117.2 (3)
N2—Mn1—O5	87.34 (17)	C11—O5—Mn1	131.9 (3)

The O atoms of the ClO₄⁻ anions are probably disordered, but it was not possible to resolve them into several sites. The elevated values of R and wR are a consequence of the disordered anions. The aromatic H atoms were included in calculated positions as riding atoms, with *SHELXL93* (Sheldrick, 1993) default parameters. The H atoms of the aqua ligand were not located.

Data collection: *DIF4* (Stoe & Cie, 1992a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1992b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *PARST95* (Nardelli, 1995).

YRM thanks the University of La Laguna for a collaboration fellowship (No. CO2/97).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1066). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
- Chen, X.-M., Shi, K.-L., Mak, T. C. W. & Luo, B.-S. (1995). *Acta Cryst.* **C51**, 358–361.
- González-Platas, J. & Ruiz-Pérez, C. (1997). *NEWCORR. A Program for Absorption Correction*. University of La Laguna, Spain.
- Lumme, P. O. & Lindell, E. (1988). *Acta Cryst.* **C44**, 463–465.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- Stoe & Cie (1992a). *DIF4. Diffractometer Control Program*. Version 6.2D. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (1992b). *REDU4. Data Reduction Program*. Version 6.2D. Stoe & Cie, Darmstadt, Germany.
- Veidis, M. V., Dockum, B., Charron, F. F. Jr, Reiff, W. M. & Brennan, T. F. (1981). *Inorg. Chim. Acta*, **53**, L197–199.
- Wieghardt, K. (1989). *Angew. Chem. Int. Ed. Engl.* **28**, 1153–1172.

Acta Cryst. (1999). **C55**, 188–190

A dichloropalladium(II) complex with a mixed donor bidentate ligand: dichloro[2-(diphenylphosphino)-1-(methylthio)ethane-P,S]palladium(II)

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(Received 21 July 1998; accepted 2 October 1998)

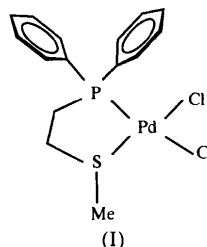
Abstract

The title compound, [PdCl₂(C₁₅H₁₇PS)], was prepared by the reaction of *cis*-dichlorobis(benzonitrile)-palladium(II) with the ligand 1-(thiomethyl)-2-(diphenylphosphino)ethane in acetone. The crystal structure of the resulting palladium(II) complex has been determined. The length of the Pd—Cl bonds is consistent with the *trans*-influence order: P > S.

Comment

The synthesis of symmetrical Pd^{II} complexes bearing bidentate P- or N-donor ligands, and their activity as catalyst precursors in homogeneous catalysis, have been extensively investigated (Abu-Surrah & Rieger, 1996). However, little research effort has been directed towards asymmetrical complexes with chelates that consist of mixed donor atoms, such as P and S or N.

In previous reports we described the use of symmetrical and unsymmetrical donor ligands (Abu-Surrah & Hodali, 1991), in complexes with late transition metals, in the preparation of potential catalyst precursors (Abu-Surrah & Rieger, 1998). A general feature of the coordination chemistry of complexes that carry mixed donor ligands is that a strong donor group at one end, such as an aryl phosphine, can stabilize the metal ion in low oxidation states, while a weakly coordinating site having an S or N atom can be substituted by a π-acceptor ligand (Abu-Surrah & Hodali, 1990; Kittaneh & Hodali, 1982). The presence of a vacant coordinating site is a fundamental property in homogeneous catalysis, since it permits organic substrates to enter the coordination sphere of the metal ion (Collman *et al.*, 1980), thereby generating catalytically active systems. The title compound, [Pd(S-P)Cl₂], (I), where (S-P) is 1-(thiomethyl)-2-(diphenylphosphino)ethane, was used successfully as a catalyst for homopolymerization of norbornene to poly(2,3-bicyclo[2.2.1]hept-2-ene) after activation with methylaluminumoxane (MAO). However, it showed a lower activity compared with the symmetrical Pd^{II} complex, [Pd(P-P)Cl₂], where (P-P) is 1,2-bis(diphenylphosphino)ethane (Abu-Surrah *et al.*, 1999).



The crystals of the title complex are monoclinic and belong to the space group $P2_1/n$. The Pd atom is at the center of a square-planar arrangement. The length of the Pd—Cl1 [2.3115(12) Å] and Pd—Cl2 [2.3719(13) Å] bonds are shorter in (I) than in the corresponding symmetrical biphosphine complex [Pd-(P-P)Cl₂] [2.415(3) and 2.394(3) Å, respectively; Singh *et al.*, 1995]. Furthermore, the metal-halide bond *trans* to the S atom [Pd—Cl1; 2.3115(12) Å] is shorter than that *trans* to the P atom [Pd—Cl2; 2.3719(13) Å]. This could be due to the stronger *trans* influence (Atwood, 1997) of the P donor atom compared to the S atom.

The increased length of the Pd—Cl bond when P is the *trans* group is in agreement with previous NMR