

[Cu(CN)(py)₂], RN 102499-39-8, was obtained from tetracyanoethylene (0.516 g, 4.03 mmol) dissolved in pyridine (10 ml) and stirred with copper powder (0.51 g, 8.02 mmol) under argon at room temperature for 0.5 h. The originally brown solution became dark red and as the slightly exothermic reaction proceeded the copper metal dissolved to give a clear solution. On standing overnight pale-yellow crystals separated (yield 0.73 g, 39% based on copper). The crystals are stable under an inert atmosphere but are hygroscopic in air [m.p. > 573 K; $\nu(\text{CN})$ 2100 cm^{-1} (KBr)].

The space group was found to be *Cc* not *C2/c* by successful solution of the structure in *Cc* by direct methods. The coordinates of *x* and *z* for Cu(1) were held to fix the origin during refinement. H atoms were treated as riding on bonded atoms (C—H 0.96 Å, $U_{\text{iso}} = 1.2 \times U_{\text{eq}}$ of the bonded C atom). The absorption correction was applied using *XABS*, a program which provides an empirical correction based on F_o and F_c differences (Hope & Moezzi, 1987).

The absolute configuration was determined by *SHELXTL-Plus* (Sheldrick, 1989). This method is similar to that suggested by Rogers (1981).

Redundant data were collected and merged after determination of hand and application of the absorption correction.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55499 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1021]

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Structure of Aquabis(2,2'-bipyridyl)zinc(II) Diperchlorate

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Abstract

The Zn atom is pentacoordinated involving four N atoms of the bipyridyl ligands and an O atom in nearly trigonal bipyrimidal arrangement. The 2,2'-bipyridyl groups are planar and make an angle of 115.2° with each other. Hydrogen bonding exists involving O(9) of the cation and O(5) of a perchlorate anion.

Comment

The final atomic coordinates are given in Table 1. The bond lengths and angles involving the Zn atom are given in Table 2. An *ORTEPII* (Johnson, 1976) drawing of the structure is shown in Fig. 1. The atoms of the bidentate ligand 2,2'-bipyridyl (bpy) occupy *cis* positions in the pentacoordinated Zn complex. The Zn—N(2) and Zn—N(3) bonds are long and collinear, while the Zn—N(1) and Zn—N(4) bonds are short and non-collinear. The Zn—N distances are in close agreement with those found in bis(2,2'-bipyridyl)mononitritozinc(II) nitrate (Walsh, Walsh, Murphy & Hathaway, 1981). The bond distances and angles in the bipyridyl groups have normal values (Stephens, 1969) except

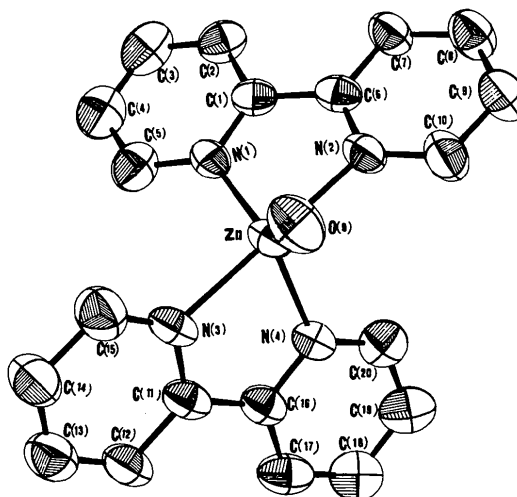


Fig. 1. Thermal ellipsoid plot of the cation.

C(3)—C(4) and C(18)—C(19), both of which have values of 1.44 Å. The C—H and O—H distances vary between 0.8 and 1.2 Å. The Zn coordination is nearly trigonal bipyramidal with N(1), N(4) and O(9) in the trigonal plane and N(2) and N(3) at the vertices of the pyramids.

The pyridine rings in each of the bpy ligands are reasonably coplanar with dihedral angles of 2.2 and 7.0° for the N(1)/N(2) and N(3)/N(4) ligands respectively. The bipyridyl rings are approximately planar with the mean planes of the bpy ligands inclined *ca* 115.2° to each other. The perchlorate ions exhibit large thermal motion, which is common among perchlorates of bulky organic cations, and their geometry is normal within the accuracy of the experiment.

There is a hydrogen bond between O(9) of the chelate and O(5) of the perchlorate with a length of 2.77 Å. There are also short contacts between O(2) and O(3) of one of the perchlorates and O(9) with values of 3.05 and 3.09 Å, respectively. These distances are too large for O—H...O hydrogen bonding even though there is a free donor proton on O(9). The molecules are packed with perchlorate channels separating the cations parallel to the *c* direction of the unit cell.

Experimental

Crystal data

[Zn(C₁₀H₈N₂)₂(H₂O)]-(ClO₄)₂

M_r = 594.6

Monoclinic

*P*2₁/*n*

a = 9.177 (2) Å

b = 13.393 (2) Å

c = 19.624 (3) Å

β = 102.09°

V = 2358.4 (7) Å³

Z = 4

D_x = 1.675 Mg m⁻³

D_m = 1.668 Mg m⁻³

Density measured by flotation in CH₃I-acetone

Mo *K*α radiation

λ = 0.71069 Å

Cell parameters from 19 reflections

θ = 7–15°

μ = 1.356 mm⁻¹

T = 293 K

Needles

0.3 × 0.1 × 0.1 mm

Pink

Crystal source: hot methanol solution of 2,2'-bipyridyl and zinc perchlorate

wR = 0.065

S = 1.5

2919 reflections

261 parameters

Only coordinates of H atoms refined

w = 1/σ²(*F*)

(Δ/σ)_{max} = 0.002

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Anomalous-dispersion corrections for Zn and Cl atoms

Program(s) used to solve structure: *SHELX76* (Sheldrick, 1976).

Program(s) used to refine structure: *MULTAN* (Germain, Main & Woolfson, 1971).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å²)

$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>
Zn	0.0881 (1)	0.2423 (1)	0.1351 (1)	4.01 (1)
Cl(1)	-0.2949 (3)	0.4085 (2)	0.4688 (1)	4.01 (3)
Cl(2)	-0.0188 (4)	0.0416 (3)	0.3052 (1)	5.33 (3)
O(1)	-0.2406 (13)	0.3175 (8)	0.4452 (6)	8.37 (7)
O(2)	-0.2174 (14)	0.4366 (13)	0.5311 (5)	11.64 (8)
O(3)	-0.2836 (22)	0.4777 (11)	0.4176 (8)	14.38 (9)
O(4)	-0.4490 (12)	0.3997 (10)	0.4685 (6)	9.17 (7)
O(5)	-0.0900 (13)	0.0439 (12)	0.2348 (5)	9.69 (7)
O(6)	0.1353 (13)	0.0400 (11)	0.3138 (6)	9.11 (7)
O(7)	-0.0666 (15)	-0.0410 (13)	0.3350 (8)	12.32 (8)
O(8)	-0.0696 (20)	0.1244 (12)	0.3364 (9)	14.71 (9)
N(1)	0.1282 (7)	0.3345 (5)	0.0552 (3)	3.86 (4)
N(2)	-0.1261 (7)	0.2508 (5)	0.0700 (3)	4.01 (5)
C(1)	0.0097 (18)	0.3481 (5)	0.0023 (4)	3.91 (4)
C(2)	0.0222 (11)	0.4015 (6)	-0.0571 (4)	4.83 (5)
C(3)	0.1592 (14)	0.4415 (7)	-0.0621 (5)	6.25 (5)
C(4)	0.2853 (13)	0.4273 (7)	-0.0047 (6)	6.35 (6)
C(5)	0.2622 (11)	0.3725 (7)	0.0526 (5)	5.43 (5)
C(6)	-0.1322 (9)	0.3035 (6)	0.0105 (4)	3.92 (4)
C(7)	-0.2657 (10)	0.3119 (6)	-0.0388 (4)	4.57 (5)
C(8)	-0.3951 (10)	0.2656 (7)	-0.0256 (5)	5.37 (5)
C(9)	-0.3874 (10)	0.2098 (7)	0.0353 (5)	5.56 (5)
C(10)	-0.2506 (10)	0.2049 (7)	0.0828 (5)	5.21 (5)
O(9)	0.0755 (7)	0.0889 (4)	0.1357 (3)	5.56 (5)
N(3)	0.3027 (7)	0.2337 (5)	0.2001 (3)	4.99 (5)
N(4)	0.0520 (7)	0.3195 (4)	0.2220 (3)	3.78 (5)
C(11)	0.3136 (9)	0.2841 (5)	0.2610 (3)	3.91 (5)
C(12)	0.4497 (9)	0.2856 (6)	0.3095 (4)	4.71 (5)
C(13)	0.5725 (10)	0.2341 (7)	0.2948 (4)	5.54 (5)
C(14)	0.5593 (10)	0.1785 (8)	0.2328 (5)	5.63 (5)
C(15)	0.4201 (10)	0.1816 (7)	0.1856 (5)	5.87 (5)
C(16)	0.1771 (9)	0.3302 (5)	0.2729 (4)	4.08 (5)
C(17)	0.1691 (11)	0.3818 (6)	0.3349 (4)	5.09 (5)
C(18)	0.0328 (12)	0.4183 (6)	0.3450 (5)	5.51 (5)
C(19)	-0.0998 (12)	0.4059 (7)	0.2916 (4)	5.73 (5)
C(20)	-0.0801 (10)	0.3549 (6)	0.2302 (4)	4.36 (5)

Table 2. *Geometric parameters* (Å, °)

Zn—N(1)	2.088 (6)	Zn—N(4)	2.079 (6)
Zn—N(2)	2.111 (9)	Zn—O(9)	2.058 (6)
Zn—N(3)	2.113 (9)		
N(1)—Zn—N(2)	78.6 (2)	N(3)—Zn—N(4)	79.7 (2)
N(1)—Zn—O(9)	127.9 (2)	Zn—N(1)—C(1)	114.7 (2)
N(1)—Zn—N(3)	101.4 (2)	Zn—N(1)—C(5)	124.1 (2)
N(1)—Zn—N(4)	113.9 (2)	Zn—N(2)—C(6)	114.5 (2)
N(2)—Zn—O(9)	90.6 (2)	Zn—N(2)—C(10)	125.0 (2)
N(2)—Zn—N(3)	179.9 (2)	Zn—N(3)—C(11)	113.1 (2)
N(2)—Zn—N(4)	100.5 (2)	Zn—N(3)—C(15)	125.4 (2)
O(9)—Zn—N(3)	89.3 (2)	Zn—N(4)—C(16)	113.5 (2)
O(9)—Zn—N(4)	118.2 (2)	Zn—N(4)—C(20)	125.3 (2)

Data collection

Syntex *P*2₁ diffractometer

w/2θ scans

Absorption correction:

none

4150 measured reflections

3852 independent reflections

2919 observed reflections

[*I* > 3σ(*I*)]

*R*_{int} = 0.018

θ_{max} = 25°

h = 0 → 10

k = 0 → 15

l = -22 → 22

3 standard reflections

frequency: 100 min

intensity variation: 2.2%

Refinement

Refinement on *F*

Final *R* = 0.063

Δρ_{max} = 0.27 e Å⁻³

Δρ_{min} = -0.23 e Å⁻³

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55517 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SP1002]

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Dimanganese Octacarbonyl Compounds with Bridging Cyclohexylphosphanes

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Abstract

Octacarbonyl-bis- μ -(cyclohexylphosphanido)-dimanganese, $[\text{Mn}_2\{\mu\text{-PH}(\text{C}_6\text{H}_{11})\}_2(\text{CO})_8]$ (I), and octacarbonyl-bis- μ -(dicyclohexylphosphanido)-dimanganese, $[\text{Mn}_2\{\mu\text{-P}(\text{C}_6\text{H}_{11})_2\}_2(\text{CO})_8]$ (II), have as a common structural fragment two edge-sharing Mn coordination octahedra with a planar Mn_2P_2 ring. In (I), the hydrido and cyclohexyl ligands adopt *anti* positions. The average Mn—P bond lengths in (I) and (II) are 2.372(1) and 2.408(1) Å, respectively. The dicyclohexyl compound (II) has already been described [Flörke & Haupt (1993). *Acta Cryst.* C49. In the press] as a triclinic structure. Here we report a monoclinic modification.

Comment

Both compounds belong to a series which contain Mn_2P_2 rings and have the formula $[\text{Mn}_2(\mu\text{-PLL}')_2(\text{CO})_8]$ [$L = L' = \text{phenyl}$ (Masuda, Taga, Machida & Kawamura, 1987); $L = L' = \text{H}$ (Deppisch, Schäfer, Binder & Leske, 1984);

$L = L' = \text{methyl}$ (Vahrenkamp, 1978); $L = \text{H}$, $L' = \text{phenyl}$ (Flörke & Haupt, 1993)]. As the geometrical centres of both molecules are situated on special sites [$\bar{1}$ for (I), $2/m$ for (II)], the rings are planar. This is also true for the other structures with the phosphorus substituents dimethyl, dihydrido, and hydrido/phenyl; the exception is the diphenyl compound which has a dihedral angle of 4.1° .

Both the triclinic and the new monoclinic structure of the dicyclohexyl compound exhibit the same bonding parameters. The average Mn—P bond lengths for the triclinic and monoclinic forms are 2.411(2) and 2.408(1) Å, respectively. The Mn—P—Mn and P—Mn—P angles are $101.0(1)$ and $79.0(1)^\circ$, respectively, in the triclinic structure, $101.4(1)$ and $78.6(1)^\circ$ in the monoclinic. On going from the dicyclohexyl (II) to the monocyclohexyl compound (I), a decrease of the average Mn—P bond from 2.408(1) to 2.372(1) Å is evident. The corresponding endocyclic ring angles are $103.0(1)^\circ$ at P and $77.0(1)^\circ$ at Mn. The same effects apply in the phenyl compounds in which the average Mn—P distances decrease from 2.388(2) to 2.358(1) Å from the diphenyl to the hydrido/phenyl ligands. The ring angles are $101.2(1)$ and $103.1(1)^\circ$ at the P atom, $78.7(1)$ and $76.9(1)^\circ$ at Mn. As already pointed out by Deppisch *et al.* (1984), these endocyclic angles seem not to be affected to a great extent by the kind of phosphorus ligand. Even in the dihydrido compound with the sterically least demanding ligands, these angles remain nearly the same [$103.9(1)$ and $76.1(1)^\circ$]. The Mn—P bond distances, however, are strongly affected. These related alterations are the result of the different electronic properties of the ligands which, on going from the substitution pattern H/L to L_2 ($L = \text{phenyl}$ or cyclohexyl), lead in each case to an increasing +I effect at the μ -P atom. As a result, the Mn—P bonds in the phenyl compounds are elongated by 0.030 Å and in the cyclohexyl compounds by 0.036 Å. In addition, the substitution of the L_2 compounds (phenyl *versus* cyclohexyl) increases the bonds by 0.020 Å. This electronic effect has also been observed in $(\mu_3\text{-H})_2(\mu\text{-PL}_2)(\text{CO})_6\text{Re}_3$ ($L = \text{phenyl}$, cyclohexyl; Haupt, Flörke & Schnieder, 1991).

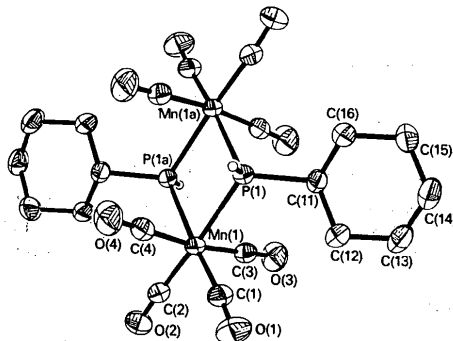


Fig. 1. Molecular structure of (I).