O5—Ni—O1	176.75 (8)	N2—C4—C5	113.9 (3)
O6—Ni—O1	87.63 (8)	C6—C5—C4	114.8 (3)
O3—S—O4	110.98 (13)	N3—C6—C5	111.8 (3)
O3—S—O2	110.59 (12)		

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
N2—H(N2*A*)···O4	2.24 (2)	3.075 (3)	161 (3)
N3—H(N3*B*)···O3	2.24 (3)	3.048 (3)	155 (3)
O5—H(O5*A*)···O4^{i}	1.91 (4)	2.763 (4)	172 (4)
O6—H(O6*B*)···O2^{i}	1.90 (3)	2.724 (3)	167 (3)
O7—H(O7*B*)···O2^{i}	2.05 (3)	2.823 (4)	153 (4)
N1—H(N1*B*)···O6^{ii}	2.28 (3)	3.131 (3)	172 (3)
O6—H(O6*A*)···O1^{ii}	1.87 (3)	2.711 (3)	159 (4)
O7—H(O7*A*)···O3^{iii}	1.97 (4)	2.791 (4)	165 (4)
N1—H(N1*A*)···O7^{iv}	2.37 (3)	3.111 (4)	144 (3)
O5—H(O5*B*)···O7^{iv}	1.88 (3)	2.741 (3)	175 (4)

Symmetry codes: (i) $1+x, y, z$; (ii) $-x, -y, 1-z$; (iii) $-x, 1-y, 1-z$; (iv) $1-x, -y, 1-z$.

Table 4. *A comparison of* Ni—N(*primary/secondary*) *distances* (Å) *and* N(*primary*)—Ni—N(*primary*) *bond angles* (°) *in octahedral* Ni^{II}*–triamine complexes*

	Ni—N(pr.)	Ni—N(sec.)	N(pr.)—Ni—N(pr.)
$Ni(dpt)_2$-$(ClO_4)_2$*	2.12 (2)–2.17 (2)	2.22 (2)–2.23 (2)	175.5 (3)–176.9 (3)
$[Ni(dpt)(H_2O)_2$-$(SO_4)].H_2O$†	2.084 (2)–2.099 (3)	2.088 (2)	170.0 (1)
$[Ni(dien)_2]$-$(NCS)_2$‡	2.096 (1)–2.134 (1)	2.110 (1)	92.6 (1)
$[Ni(NCO)_2$-$(terpy)(H_2O)]$§	2.152 (2)–2.165 (2)	2.047 (3)	154.8 (1)
$[Ni(bamp)_2]$-$Cl_2.1.67H_2O$¶	2.128 (3)–2.168 (3)	2.001 (3)–2.025 (3)	157.1 (1)–159.1 (1)

* Biagini & Cannas (1970).

† This work.

‡ dien = diethylenetriamine; Mukherjee *et al.* (1994).

§ terpy = 2,2′:6′,2″-terpyridine; Cortes *et al.* (1988).

¶ bamp = 2,6-bis(aminomethyl)pyridine; Bonhote, Ferigo, Stoeckli-Evans & Marty (1993).

The metal position was obtained from a Patterson synthesis and the remaining non-H atoms were located by successive Fourier difference syntheses. The structure was refined on F^2 by full-matrix least squares with anisotropic displacement parameters for non-H atoms. All H atoms were clearly visible in a difference map computed in the final stage of refinement and refined isotropically. All calculations were performed using a VAX 3400 computer at the Computer Center, Indian Association for the Cultivation of Science.

Data collection: *SHELXTL* (Sheldrick, 1985*b*). Cell refinement: *SHELXTL*. Data reduction: *SHELXTL*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93. Program(s) used for geometric calculations: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1131). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tris(2,2′-bipyridine)zinc(II) Perchlorate

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Abstract

The crystal structure of tris(2,2′-bipyridine)zinc(II) perchlorate, $[Zn(C_{10}H_8N_2)_3](ClO_4)_2$, has been established by X-ray crystallography. The Zn^{II} atom is coordinated by three chelating 2,2′-bipyridine ligands in a highly distorted octahedral arrangement with Zn—N bond lengths ranging from 2.135 (2) to 2.172 (3) Å.

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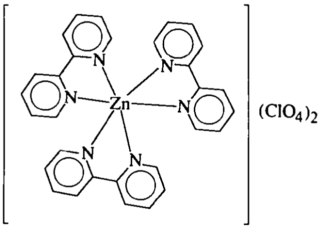
Comment

In an attempt to synthesize a zinc(II) complex containing both 2,2′-bipyridine (bpy) and carbonato ligands, we obtained an unusual μ_3-carbonato-bridged trinuclear zinc complex $[Zn_3(bpy)_6(CO_3)(H_2O)_2](ClO_4)_4(bpy).2H_2O$, along with some pink polyhedral crystals which were isolated as a minor product (Chen, Deng, Wang & Xu, 1995). The latter pink compound has been characterized by elemental analysis as the monomeric complex $[Zn(bpy)_3](ClO_4)_2$, (I). We report here the single-crystal structure of this complex.



The crystal structure of $[Zn(bpy)_3](ClO_4)_2$ is composed of monomeric $[Zn(bpy)_3]^{2+}$ cations and perchlorate anions. As illustrated in Fig. 1, the metal atom, being located at Wyckoff position 4*e* of symmetry 2, is surrounded by six N atoms from three chelating bpy ligands in a highly distorted octahedral arrangement with Zn—N bond lengths ranging from 2.135 (2) to 2.172 (3) Å, significantly longer than those (1.932–2.089 Å) found for the analogous cations $[Co(bpy)_3]^{3+}$ (Yanagi, Ohashi, Sasada, Kaizu & Kobayashi, 1981), $[Fe(bpy)_3]^{3+}$ (Figgis, Skelton & White, 1978) and $[Ni(bpy)_3]^{2+}$ (Wada, Katayama & Tanaka, 1976). The most distorted bond angles are seen for the chelating bpy ligands. It is notable that the pyridine rings of the bpy ligand that is bisected by the twofold axis are significantly non-coplanar, with a dihedral angle between them of *ca* 17°, markedly smaller than that (*ca* 29°) of the uncoordinated bpy molecule found in the crystal structure of the trinuclear zinc complex (Chen *et al.*, 1995). The non-coplanarity of this bpy ligand results in the significantly larger intraligand binding angle N—Zn—N [88.1 (1)°] in comparison to the other N—Zn—N angles [75.8 (1) and 77.2 (1)°] in the structure.

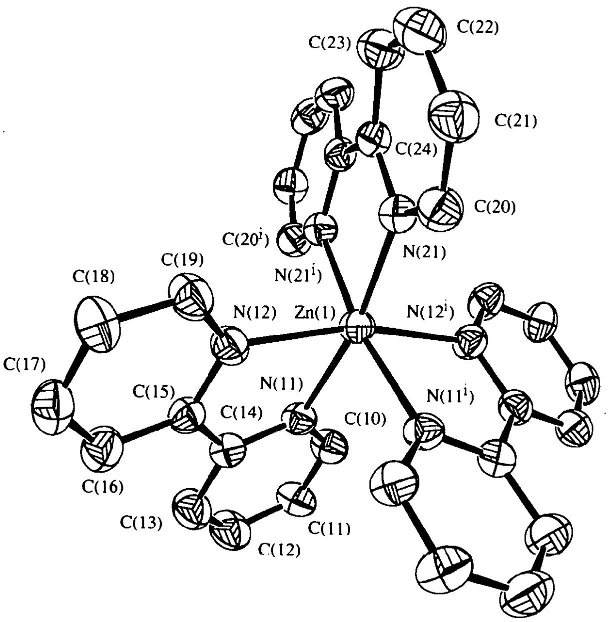


Fig. 1. *ORTEX* drawing (McArdle, 1993) of the $[Zn(bpy)_3]^{2+}$ cation with 45% probability displacement ellipsoids [symmetry code: (i) $-x, y, \frac{1}{2} - z$].

Experimental

Crystal data

$[Zn(C_{10}H_8N_2)_3](ClO_4)_2$
$M_r = 732.8$
Monoclinic
$C2/c$
$a = 17.473\ (3)$ Å
$b = 10.926\ (2)$ Å
$c = 16.163\ (3)$ Å
$\beta = 91.17\ (3)°$
$V = 3085\ (1)$ Å^3
$Z = 4$
$D_x = 1.578$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15–23°$
$\mu = 1.034$ mm^{-1}
$T = 295$ K
Polyhedral
0.42 × 0.40 × 0.36 mm
Pink

Data collection

Siemens *R*3*m*/*V* diffractometer
ω scans
Absorption correction: ψ scan (Kopfmann & Huber, 1968)
$T_{min} = 0.467$, $T_{max} = 0.562$
3678 measured reflections
3566 independent reflections

2763 observed reflections $[F \geq 6\sigma(F)]$
$R_{int} = 0.0212$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 14$
$l = -20 \rightarrow 20$
2 standard reflections monitored every 120 reflections intensity decay: 1.5%

Refinement

Refinement on *F*
$R = 0.0470$
$wR = 0.0646$
$S = 2.05$
2763 reflections
213 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.0005F^2]$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.60$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Zn(1)	0	0.0273 (1)	1/4	0.041 (1)
N(11)	−0.0633 (1)	−0.1152 (2)	0.1853 (1)	0.044 (1)
N(12)	−0.1021 (1)	0.0027 (2)	0.3225 (2)	0.045 (1)
C(10)	−0.0427 (2)	−0.1699 (3)	0.1149 (2)	0.053 (1)
C(11)	−0.0825 (2)	−0.2659 (3)	0.0792 (2)	0.060 (1)
C(12)	−0.1459 (2)	−0.3083 (3)	0.1186 (2)	0.070 (1)
C(13)	−0.1677 (2)	−0.2550 (3)	0.1917 (2)	0.064 (1)

C(14)	−0.1253 (2)	−0.1578 (3)	0.2239 (2)	0.045 (1)
C(15)	−0.1447 (2)	−0.0950 (3)	0.3022 (2)	0.043 (1)
C(16)	−0.2037 (2)	−0.1337 (3)	0.3523 (2)	0.056 (1)
C(17)	−0.2188 (2)	−0.0692 (3)	0.4238 (2)	0.062 (1)
C(18)	−0.1766 (2)	0.0325 (3)	0.4435 (2)	0.059 (1)
C(19)	−0.1185 (2)	0.0669 (3)	0.3910 (2)	0.055 (1)
N(21)	0.0422 (1)	0.1800 (2)	0.3196 (2)	0.043 (1)
C(20)	0.0797 (2)	0.1736 (3)	0.3939 (2)	0.051 (1)
C(21)	0.0911 (2)	0.2738 (3)	0.4434 (2)	0.056 (1)
C(22)	0.0655 (2)	0.3862 (3)	0.4156 (2)	0.061 (1)
C(23)	0.0299 (2)	0.3958 (3)	0.3381 (2)	0.056 (1)
C(24)	0.0193 (2)	0.2901 (2)	0.2916 (2)	0.041 (1)
Cl(1)	0.3241 (1)	−0.0087 (1)	0.3642 (1)	0.061 (1)
O(1)	0.3360 (2)	−0.0728 (4)	0.2919 (2)	0.124 (2)
O(2)	0.2499 (2)	0.0451 (3)	0.3623 (2)	0.103 (1)
O(3)	0.3812 (2)	0.0834 (4)	0.3734 (3)	0.133 (2)
O(4)	0.3315 (2)	−0.0861 (5)	0.4326 (2)	0.151 (2)

Table 2. *Selected geometric parameters* (Å, °)

Zn(1)—N(11)	2.166 (2)	Zn(1)—N(12)	2.172 (3)
Zn(1)—N(21)	2.135 (2)	N(11)—C(10)	1.341 (4)
N(11)—C(14)	1.345 (4)	N(12)—C(15)	1.339 (4)
N(12)—C(19)	1.346 (4)	C(10)—C(11)	1.379 (5)
C(11)—C(12)	1.370 (5)	C(12)—C(13)	1.377 (5)
C(13)—C(14)	1.390 (5)	C(14)—C(15)	1.485 (4)
C(15)—C(16)	1.390 (4)	C(16)—C(17)	1.384 (5)
C(17)—C(18)	1.368 (5)	C(18)—C(19)	1.389 (5)
N(21)—C(20)	1.359 (4)	N(21)—C(24)	1.343 (4)
C(20)—C(21)	1.367 (5)	C(21)—C(22)	1.379 (5)
C(22)—C(23)	1.392 (5)	C(23)—C(24)	1.388 (4)
C(24)—C(24$^{\rm i}$)	1.492 (5)		
N(11)—Zn(1)—N(12)	75.8 (1)	N(11)—Zn(1)—N(21)	169.5 (1)
N(12)—Zn(1)—N(21)	95.2 (1)	N(11)—Zn(1)—N(11$^{\rm i}$)	88.1 (1)
N(12)—Zn(1)—N(11$^{\rm i}$)	93.9 (1)	N(21)—Zn(1)—N(11$^{\rm i}$)	98.1 (1)
N(12)—Zn(1)—N(12$^{\rm i}$)	165.8 (1)	N(12)—Zn(1)—N(21$^{\rm i}$)	95.9 (1)
N(21)—Zn(1)—N(21$^{\rm i}$)	77.2 (1)	Zn(1)—N(11)—C(10)	125.9 (2)
Zn(1)—N(11)—C(14)	115.7 (2)	Zn(1)—N(12)—C(15)	115.1 (2)
Zn(1)—N(12)—C(19)	124.7 (2)	Zn(1)—N(21)—C(20)	125.5 (2)
Zn(1)—N(21)—C(24)	115.2 (2)	C(10)—N(11)—C(14)	118.2 (3)
C(15)—N(12)—C(19)	119.4 (3)	N(11)—C(10)—C(11)	123.5 (3)
C(10)—C(11)—C(12)	117.9 (3)	C(11)—C(12)—C(13)	119.8 (3)
C(12)—C(13)—C(14)	119.3 (3)	N(11)—C(14)—C(13)	121.3 (3)
N(11)—C(14)—C(15)	115.8 (2)	C(13)—C(14)—C(15)	122.9 (3)
N(12)—C(15)—C(14)	116.2 (2)	N(12)—C(15)—C(16)	121.0 (3)
C(14)—C(15)—C(16)	122.8 (3)	C(15)—C(16)—C(17)	119.3 (3)
C(16)—C(17)—C(18)	119.8 (3)	C(17)—C(18)—C(19)	118.4 (3)
N(12)—C(19)—C(18)	122.1 (3)	C(20)—N(21)—C(24)	118.6 (2)
N(21)—C(20)—C(21)	122.5 (3)	C(20)—C(21)—C(22)	118.7 (3)
C(21)—C(22)—C(23)	119.8 (3)	C(22)—C(23)—C(24)	118.4 (3)
N(21)—C(24)—C(23)	121.8 (3)	N(21)—C(24)—C(24$^{\rm i}$)	115.4 (2)
C(23)—C(24)—C(24$^{\rm i}$)	122.7 (2)		

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

A crystal of suitable size was cut and mounted on a glass fibre for data collection. Lp corrections were applied. The structure was solved by direct methods using *SAPI*91 (Fan, Yao, Zheng, Gu & Qian, 1991) and refined anisotropically with *SHELXL*93 (Sheldrick, 1993). The H atoms were generated geometrically (C—H 0.96 Å), assigned isotropic displacement parameters and included in structure-factor calculations.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1001). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hexakis(dimethyl sulfoxide)mercury(II) Trifluoromethanesulfonate, a Standard for Solid-State ^{199}Hg NMR

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Abstract

In the title compound, $[Hg\{(CH_3)_2SO\}_6](CF_3SO_3)_2$, the discrete cations have $\bar{3}$ symmetry. For the octahedral HgO_6 kernel, the compression ratio and polar angle are 1.39 and 58.1°, respectively. Within the cations, intramolecular Hg···H distances range from 4.00 to 5.48 Å, while there are no intermolecular Hg···H distances shorter than 4.34 Å.

Comment

The title compound, (1), was first synthesized by Peringer (1980). Its physical, chemical and NMR-

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