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Structure of *cis*-Diaquabis(1,10-phenanthroline)zinc Sulfate Hexahydrate

BY NING-HAI HU AND YONG-SHENG LIU

Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

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Abstract. $[\text{Zn}(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]\text{SO}_4 \cdot 6\text{H}_2\text{O}$, $M_r = 665.98$, triclinic, $P\bar{1}$, $a = 10.070$ (4), $b = 12.280$ (3), $c = 13.358$ (2) Å, $\alpha = 109.12$ (2), $\beta = 92.58$ (2), $\gamma = 110.85$ (2)°, $V = 1433.9$ (7) Å³, $Z = 2$, $D_x = 1.54$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 10.1$ cm⁻¹, $F(000) = 692$, $T = 293$ K, $R = 0.044$ for 3985 observed reflections. The Zn atom is coordinated in a distorted octahedral geometry by four N atoms from two 1,10-phenanthroline (phen) ligands and two water molecules. The intermolecular ring-stacking interactions between the phen ligands occur in two forms: infinite chains and discrete dimers. Hydrogen bonds further stabilize the structure.

Introduction. Phenanthroline, as an excellent planar π system, has often been involved in model compounds to mimic non-covalent interactions in biological processes. Transition-metal complexes of phenanthroline and its substituted derivatives have been found to be probes for examining distinctive conformations along the DNA helix (Barton, 1989). These cationic complexes bind to DNA through weak interactions such as the π stacking associated with intercalation of the aromatic heterocyclic groups between the base pairs, and exhibit a high level of specificity in the recognition of different sites (Pyle, Rehmann, Meshoyrer, Kumar, Turro & Barton, 1989). It is of interest, therefore, to understand the structural features of these compounds. We describe here the structure of *cis*-diaquabis(1,10-phenanthroline)zinc sulfate hexahydrate.

Experimental. The complex was obtained from an aqueous acetone solution of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and 1,10-phenanthroline monohydrate. Crystal $0.48 \times 0.36 \times$

0.32 mm; Nicolet R3m/E diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω scan, scan speed $7.32^\circ \text{ min}^{-1}$, scan width 1.4° ; $3 < 2\theta < 56^\circ$, $h -12 \rightarrow 12$, $k -15 \rightarrow 15$, $l 0 \rightarrow 17$; lattice parameters from 20 reflections within the range $12 < 2\theta < 24^\circ$; Lp and empirical absorption corrections, minimum and maximum transmission coefficients 0.87 and 0.96; two intensity monitors varied $< 2\%$; total 6748 unique reflections, 3985 with $I > 3\sigma(I)$. Structure solved by direct methods and Fourier synthesis; block-diagonal least-squares refinement on F for non-H atoms (anisotropic thermal parameters); H atoms were located on a difference map, except some from the water molecules, and were fixed with $U = 0.06$ Å². $R = 0.044$, $wR = 0.062$, $S = 1.13$, where $w = 1/[\sigma^2(F_o) + 0.0017(F_o)^2]$, $(\Delta/\sigma)_{\text{max}} = 0.06$, maximum and minimum heights in final difference map 0.55 and -0.36 e Å⁻³, respectively. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). The calculations were performed with the *SHELXTL* program system (Sheldrick, 1983) on an Eclipse S/140 computer.

Discussion. Final atomic coordinates with their e.s.d.'s are listed in Table 1.* Bond lengths and angles are given in Table 2. The compound consists of a discrete $[\text{Zn}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$ cation, sulfate anion and six water molecules. Figs. 1 and 2 show the structure of the cation and the crystal packing.

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and hydrogen bonds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54269 (47 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
Zn	2469.5 (5)	5604.4 (4)	2534.4 (3)	33.8 (2)
N(1)	3717 (3)	6062 (3)	4108 (2)	38 (1)
N(2)	957 (3)	4462 (3)	3232 (3)	41 (1)
C(1)	5050 (4)	6902 (4)	4556 (3)	44 (2)
C(2)	5715 (5)	7113 (4)	5593 (3)	56 (2)
C(3)	4984 (5)	6431 (5)	6149 (3)	61 (2)
C(4)	3591 (5)	5533 (4)	5705 (3)	51 (2)
C(5)	734 (5)	3785 (4)	4748 (4)	53 (2)
C(6)	-679 (6)	2972 (4)	4266 (4)	67 (3)
C(7)	-1257 (5)	2920 (4)	3313 (4)	67 (2)
C(8)	-416 (4)	3673 (4)	2789 (4)	53 (2)
C(9)	1516 (4)	4509 (4)	4196 (3)	39 (2)
C(10)	2993 (4)	5392 (4)	4676 (3)	39 (2)
C(11)	2744 (6)	4753 (5)	6227 (4)	67 (3)
C(12)	1401 (6)	3923 (5)	5782 (4)	67 (3)
N(3)	4402 (3)	6489 (3)	2014 (2)	38 (1)
N(4)	3075 (3)	4042 (3)	1688 (2)	36 (1)
C(13)	5055 (5)	7702 (4)	2158 (3)	46 (2)
C(14)	6406 (5)	8212 (4)	1932 (4)	58 (2)
C(15)	7144 (5)	7466 (4)	1546 (4)	55 (2)
C(16)	6496 (4)	6179 (4)	1362 (3)	44 (2)
C(17)	5082 (4)	3606 (4)	976 (3)	44 (2)
C(18)	4309 (5)	2322 (4)	796 (3)	54 (2)
C(19)	2971 (5)	1935 (4)	1039 (4)	54 (2)
C(20)	2389 (4)	2821 (4)	1485 (3)	45 (2)
C(21)	4399 (4)	4421 (4)	1416 (3)	35 (2)
C(22)	5112 (4)	5739 (3)	1613 (3)	34 (2)
C(23)	7171 (5)	5324 (5)	940 (3)	59 (2)
C(24)	6482 (5)	4072 (5)	738 (3)	53 (2)
S(1)	1328 (1)	8165.0 (9)	938.5 (8)	45.7 (4)
O(1)	788 (4)	6818 (3)	392 (3)	67 (2)
O(2)	408 (4)	8664 (3)	529 (3)	71 (2)
O(3)	2787 (4)	8712 (4)	790 (4)	105 (3)
O(4)	1346 (6)	8438 (4)	2098 (3)	107 (3)
O(W1)	907 (3)	5213 (2)	1290 (2)	49 (1)
O(W2)	2138 (3)	7295 (3)	3266 (2)	50 (1)
O(W3)	3754 (4)	9277 (3)	5279 (3)	71 (2)
O(W4)	1976 (4)	10646 (4)	5468 (3)	99 (3)
O(W5)	4956 (4)	9405 (4)	7417 (4)	95 (2)
O(W6)	404 (5)	10149 (4)	3395 (3)	102 (2)
O(W7)	-574 (4)	10529 (4)	1480 (4)	110 (3)
O(W8)	3199 (6)	9248 (5)	8989 (4)	127 (3)

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Both phen ligands have normal bond lengths and angles as observed in the free molecule (Nishigaki, Yoshioka & Nakatsu, 1978) and zinc complex (Bencini, Midollini & Zanchini, 1989). The maximum deviations of the atoms from least-squares planes are 0.063 (6) Å for phen(1) [containing N(1) and N(2)] and 0.045 (3) Å for phen(2) [containing N(3) and N(4)].

The Zn atom is octahedrally coordinated by the two bidentate phen ligands with usual acute bites [N—Zn—N = 76.8 (1)° for both ligands] and by two water molecules. The complex cation exhibits a *cis* configuration with a dihedral angle of 85.1 (1)° between the phen planes and an O(W1)—Zn—O(W2) angle of 85.6 (1)°. The average Zn—N bond length [2.17 (1) Å] is in agreement with that observed in the six-coordinated [Zn(phen)₃]²⁺ complex [2.17 (1) Å] (Bencini, Midollini & Zanchini, 1989) but apparently greater than that in Zn(phen)Cl₂ [2.06 (1) Å] (Khan & Tuck, 1984) due to the change in coordination number from four to six. The Zn—N bonds fall into two sets depending on the electronegativity of the *trans* ligand, that is, the Zn—N

Table 2. Bond lengths (Å) and angles (°) with *e.s.d.*'s in parentheses

Zn—N(1)	2.191 (3)	C(11)—C(12)	1.331 (7)
Zn—N(2)	2.149 (4)	N(3)—C(13)	1.340 (5)
Zn—N(3)	2.136 (3)	N(3)—C(22)	1.351 (6)
Zn—N(4)	2.192 (4)	N(4)—C(20)	1.333 (5)
Zn—O(W1)	2.043 (3)	N(4)—C(21)	1.356 (5)
Zn—O(W2)	2.138 (3)	C(13)—C(14)	1.374 (7)
N(1)—C(1)	1.327 (4)	C(14)—C(15)	1.366 (8)
N(1)—C(10)	1.347 (6)	C(15)—C(16)	1.408 (7)
N(2)—C(8)	1.341 (5)	C(16)—C(22)	1.403 (5)
N(2)—C(9)	1.356 (6)	C(16)—C(23)	1.427 (8)
C(1)—C(2)	1.412 (6)	C(17)—C(18)	1.418 (6)
C(2)—C(3)	1.346 (7)	C(17)—C(21)	1.401 (7)
C(3)—C(4)	1.390 (6)	C(17)—C(24)	1.415 (6)
C(4)—C(10)	1.407 (6)	C(18)—C(19)	1.353 (7)
C(4)—C(11)	1.428 (8)	C(19)—C(20)	1.393 (7)
C(5)—C(6)	1.385 (6)	C(21)—C(22)	1.442 (5)
C(5)—C(9)	1.392 (7)	C(23)—C(24)	1.367 (8)
C(5)—C(12)	1.439 (8)	S(1)—O(1)	1.448 (3)
C(6)—C(7)	1.349 (9)	S(1)—O(2)	1.453 (5)
C(7)—C(8)	1.407 (8)	S(1)—O(3)	1.435 (4)
C(9)—C(10)	1.453 (5)	S(1)—O(4)	1.471 (4)
N(1)—Zn—N(2)	76.8 (1)	N(1)—C(10)—C(9)	117.4 (4)
N(1)—Zn—N(3)	90.5 (1)	C(4)—C(10)—C(9)	119.5 (4)
N(1)—Zn—N(4)	95.0 (1)	C(4)—C(11)—C(12)	122.1 (5)
N(1)—Zn—O(W1)	165.5 (1)	C(5)—C(12)—C(11)	120.8 (5)
N(1)—Zn—O(W2)	86.2 (1)	Zn—N(3)—C(13)	127.8 (3)
N(2)—Zn—N(3)	161.5 (2)	Zn—N(3)—C(22)	114.1 (3)
N(2)—Zn—N(4)	90.8 (1)	C(13)—N(3)—C(22)	117.7 (3)
N(2)—Zn—O(W1)	92.5 (1)	Zn—N(4)—C(20)	129.6 (3)
N(2)—Zn—O(W2)	98.0 (1)	Zn—N(4)—C(21)	113.0 (2)
N(3)—Zn—N(4)	76.8 (1)	C(20)—N(4)—C(21)	117.2 (4)
N(3)—Zn—O(W1)	102.0 (1)	N(3)—C(13)—C(14)	123.1 (5)
N(3)—Zn—O(W2)	94.5 (1)	C(13)—C(14)—C(15)	119.6 (4)
N(4)—Zn—O(W1)	95.0 (1)	C(14)—C(15)—C(16)	119.5 (4)
N(4)—Zn—O(W2)	171.2 (1)	C(15)—C(16)—C(22)	116.9 (4)
O(W1)—Zn—O(W2)	85.6 (1)	C(15)—C(16)—C(23)	123.5 (4)
Zn—N(1)—C(1)	128.6 (3)	C(22)—C(16)—C(23)	119.6 (4)
Zn—N(1)—C(10)	113.6 (2)	C(18)—C(17)—C(21)	116.9 (4)
C(1)—N(1)—C(10)	117.8 (4)	C(18)—C(17)—C(24)	122.8 (5)
Zn—N(2)—C(8)	127.1 (3)	C(21)—C(17)—C(24)	120.3 (4)
Zn—N(2)—C(9)	114.6 (2)	C(17)—C(18)—C(19)	120.0 (5)
C(8)—N(2)—C(9)	118.1 (4)	C(18)—C(19)—C(20)	118.8 (4)
N(1)—C(1)—C(2)	122.4 (4)	N(4)—C(20)—C(19)	123.8 (4)
C(1)—C(2)—C(3)	119.2 (4)	N(4)—C(21)—C(17)	123.3 (4)
C(2)—C(3)—C(4)	120.3 (4)	N(4)—C(21)—C(22)	116.7 (4)
C(3)—C(4)—C(10)	117.2 (4)	C(17)—C(21)—C(22)	120.0 (3)
C(3)—C(4)—C(11)	124.2 (4)	N(3)—C(22)—C(16)	123.1 (4)
C(10)—C(4)—C(11)	118.7 (4)	N(3)—C(22)—C(21)	118.2 (3)
C(6)—C(5)—C(9)	117.2 (5)	C(16)—C(22)—C(21)	118.7 (4)
C(6)—C(5)—C(12)	123.3 (5)	C(16)—C(23)—C(24)	121.5 (4)
C(9)—C(5)—C(12)	119.5 (4)	C(17)—C(24)—C(23)	119.8 (5)
C(5)—C(6)—C(7)	120.3 (5)	O(1)—S(1)—O(2)	110.3 (2)
C(6)—C(7)—C(8)	120.1 (4)	O(1)—S(1)—O(3)	108.9 (3)
N(2)—C(8)—C(7)	120.9 (5)	O(1)—S(1)—O(4)	108.1 (2)
N(2)—C(9)—C(5)	123.3 (3)	O(2)—S(1)—O(3)	111.2 (3)
N(2)—C(9)—C(10)	117.3 (4)	O(2)—S(1)—O(4)	110.2 (3)
C(5)—C(9)—C(10)	119.3 (4)	O(3)—S(1)—O(4)	108.1 (3)
N(1)—C(10)—C(4)	123.1 (3)		

bonds *trans* to N [2.149 (4) and 2.136 (3) Å] are significantly shorter than those *trans* to O [2.191 (3) and 2.192 (4) Å]. This fact was also found in phen-Cu^{II}-amino acid complexes (Antolini, Battaglia, Corradi, Marcotrigiano, Menabue, Pellacani, Saladini & Sola, 1986; Hu, Aoki & Yamazaki, 1989), where the longer metal—N(phen) bonds occur when N(phen) atoms are *trans* to O atoms. The two five-membered chelate rings have envelope conformations with the folded angles between the N—Zn—N and N—C—C—N planes being 4.1 (1)° [phen(1)] and 9.6 (2)° [phen(2)].

The crystal packing is dominated by hydrogen-bonding and ring-stacking interactions. There are two different modes of phen ring stacking. The

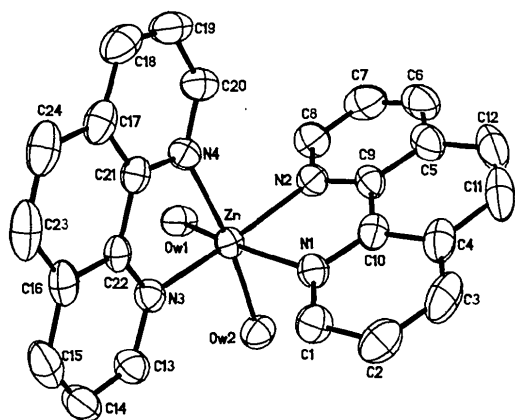


Fig. 1. Structure of the [Zn(phen)₂(H₂O)₂]²⁺ complex cation with the atomic numbering scheme.

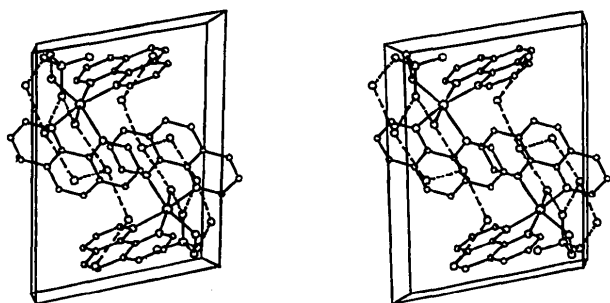


Fig. 2. Stereoview of the crystal packing as viewed down *b*. Broken lines denote hydrogen bonds.

phen(1) ligand makes contacts with one of its centrosymmetric partners on either side of the ring plane, with average spacings of 3.37 and 3.45 Å, thus forming a linear chain of stacking interactions running along the *a* axis. The two phen(2) ligands related by a center of symmetry stack themselves at an average spacing of 3.44 Å to create a discrete self dimer. An extensive hydrogen-bonding system forms involving the sulfate anions and all the water molecules. The coordinated O(*W*1) interacts with two sulfate anions through hydrogen bonds, while the O(*W*2) is hydrogen bonded to a sulfate anion and a hydrate water O(*W*3). The different packing environments may be responsible for non-equivalent Zn—O(water) bonds [2.043 (3) and 2.138 (3) Å].

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Geometry of the Iminium Moiety. II. Structures of Four Cycloalkylidene Derivatives of a Dihydropyrazolium Salt

BY L. R. NASSIMBENI, A. M. STEPHEN AND T. G. D. VAN SCHALKWYK*

Department of Chemistry, University of Cape Town, Rondebosch 7700, South Africa

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Abstract. Compound (I; PENT), bis(1-cyclopentylidene-4,5-dihydro-3,5,5-trimethylpyrazolium) hexachlorostannate, [C₁₁H₁₉N₂]₂[SnCl₆], *M_r* = 690.0, monoclinic, *P*2₁/*n*, *a* = 13.363 (1), *b* = 11.857 (1), *c* = 9.572 (1) Å, β = 93.15 (2)°, *V* = 1514.3 (2) Å³, *Z* = 2, *D_m* = 1.50 (1), *D_x* = 1.513 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 12.8 cm⁻¹, *F*(000) = 700, *T* = 294 K, *R* = 0.026 for 1382 observed

reflections. Compound (II; MHEX), bis[4,5-dihydro-3,5,5-trimethyl-1-(4-methylcyclohexylidene)pyrazolium] hexachlorostannate, [C₁₃H₂₃N₂]₂[SnCl₆], *M_r* = 746.1, monoclinic, *P*2₁/*c*, *a* = 19.223 (1), *b* = 10.803 (1), *c* = 16.990 (1) Å, β = 106.88 (2)°, *V* = 3376.2 (5) Å³, *Z* = 4, *D_m* = 1.47 (1), *D_x* = 1.468 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 11.52 cm⁻¹, *F*(000) = 1528, *T* = 294 K, *R* = 0.035 for 3336 observed reflections. Compound (III; HEPT), bis(1-cycloheptylidene-4,5-dihydro-3,5,5-trimethyl-

* Author to whom correspondence should be addressed.