

Quinolinium trichloro(quinoline)zinc(II)

Wenguo Wang, Xiaofeng Zhang,
Deguang Huang, Hongping Zhu,
Changneng Chen and Qiutian
Liu*

State Key Laboratory of Structural Chemistry,
Fujian Institute of Research on the Structure of
Matter, Fuzhou, Fujian 350002, People's
Republic of China

Correspondence e-mail: lqt@ms.fjirsm.ac.cn

Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$

R factor = 0.045

wR factor = 0.147

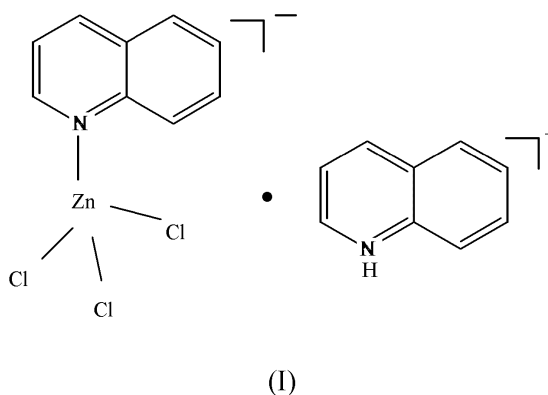
Data-to-parameter ratio = 14.0

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the title compound, $(\text{C}_9\text{H}_8\text{N})[\text{ZnCl}_3(\text{C}_9\text{H}_7\text{N})]$, the Zn^{II} atom is coordinated by three chloride ions and one N atom of the quinoline ligand to form a distorted tetrahedral coordination geometry, with a $\text{Zn}-\text{N}$ bond length of $2.090(4)\text{ \AA}$, $\text{Zn}-\text{Cl}$ bond lengths ranging from $2.2319(14)$ to $2.2707(13)\text{ \AA}$ and zinc bond angles ranging from $102.89(11)$ to $115.41(11)^\circ$.

Comment

Since hindered nitrogen bases give a variety of structural types for metal complexes, a series of adducts of transition metal halides with monodentate nitrogen bases has been studied (Healy *et al.*, 1985; Savariault *et al.* 1988). We chose quinoline as the nitrogen base to react with Zn^{II} and Mn^{II} salts to obtain heterometallic Zn/Mn nitrogen base complexes; consequently the title Zn^{II} complex, (I), was isolated.



The crystal structure of (I) consists of a $[\text{ZnCl}_3(\text{C}_9\text{H}_7\text{N})]^-$ monoanion and a discrete quinolinium cation as shown in Fig. 1. Within the $[\text{ZnCl}_3(\text{C}_9\text{H}_7\text{N})]^-$ anion, the Zn atom is coordinated by three chloride anions and one quinoline N atom in a distorted tetrahedral arrangement, the $\text{Zn}-\text{N}$ bond length being $2.090(4)\text{ \AA}$ and the $\text{Zn}-\text{Cl}$ bond lengths $2.2319(14)$, $2.2512(15)$ and $2.2707(13)\text{ \AA}$. The bond angles around Zn range from $102.89(11)$ to $115.41(11)^\circ$ for $\text{N}-\text{Zn}-\text{Cl}$ angles and from $105.86(6)$ to $114.49(6)^\circ$ for $\text{Cl}-\text{Zn}-\text{Cl}$ angles. The $\text{Zn}-\text{N}$ and $\text{Zn}-\text{Cl}$ distances are in accord with the corresponding distances in the $(\text{Hcin})\text{ZnCl}_3$ complex (cin is cinchonine; Hubel *et al.*, 1999) and other Zn complexes reported in the literature (Cui *et al.*, 1998; Lundberg, 1966; Bharadwaj *et al.*, 1991; Laity & Taylor, 1995; Parvez & Rusiewicz, 1995). There are no unexpected geometrical features associated with the coordination structure of the zinc. However, the most notable difference between the structure of (I) and $(\text{Hcin})\text{ZnCl}_3$ is the protonation position, which was found to occur at the tertiary N atom for the latter. In complex

Received 22 October 2001

Accepted 31 October 2001

Online 10 November 2001

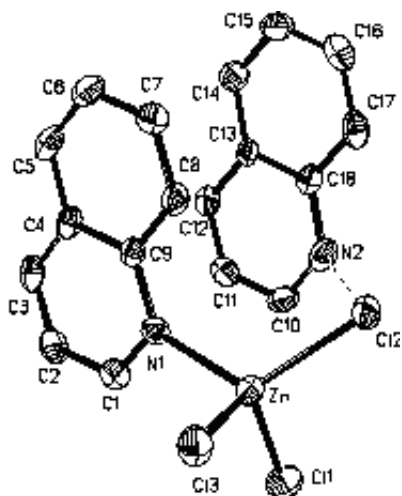


Figure 1
Structure of (I) showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level. H atoms have been omitted for clarity.

(I), the shortest distance between the uncoordinated quinoline and the complex anion is $\text{Cl2} \cdots \text{N2} = 3.303(5) \text{ \AA}$, showing the existence of a $\text{Cl} \cdots \text{H} - \text{N}$ hydrogen bond, and indicating protonation occurring at the pyridine-N atom of the uncoordinated quinoline. It is obvious that quinoline plays a double role in the structure, *i.e.* coordinating to the metal atom as a Lewis donor and balancing the minus charge by protonation. Interestingly, all the quinoline rings in the structure are nearly parallel to each other, as shown in Fig. 2, with a dihedral angle of $176.7(5)^\circ$. It is also noted that the existence of the $\text{Cl2} \cdots \text{H} - \text{N}$ hydrogen bond lengthens the $\text{Zn} - \text{Cl2}$ bond to $2.2707(13) \text{ \AA}$, which is the longest of the three $\text{Zn} - \text{Cl}$ bonds.

Experimental

A mixture of $\text{Zn}(\text{OAc})_2$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CH}_3\text{CH}_2\text{COOH}$ and quinoline were dissolved in ethanol and refluxed for 12 h. The resulting solution was allowed to stand at room temperature and colorless crystals of (I) were obtained.

Crystal data

$(\text{C}_9\text{H}_8\text{N})[\text{ZnCl}_3(\text{C}_9\text{H}_7\text{N})]$	$Z = 2$
$M_r = 431.04$	$D_x = 1.618 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.2360(7) \text{ \AA}$	Cell parameters from 2580 reflections
$b = 9.5392(7) \text{ \AA}$	$\theta = 1.7\text{--}25.0^\circ$
$c = 11.9512(10) \text{ \AA}$	$\mu = 1.84 \text{ mm}^{-1}$
$\alpha = 98.499(1)^\circ$	$T = 293(2) \text{ K}$
$\beta = 94.670(1)^\circ$	Prism, colorless
$\gamma = 106.104(1)^\circ$	$0.32 \times 0.20 \times 0.18 \text{ mm}$
$V = 884.76(12) \text{ \AA}^3$	

Data collection

Siemens SMART CCD diffractometer	3047 independent reflections
ω scans	2232 reflections with $I > 2\sigma(I)$
Absorption correction: multiscan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.029$
$T_{\text{min}} = 0.453$, $T_{\text{max}} = 0.718$	$\theta_{\text{max}} = 25.0^\circ$
4503 measured reflections	$h = -9 \rightarrow 8$
	$k = -11 \rightarrow 9$
	$l = -14 \rightarrow 13$

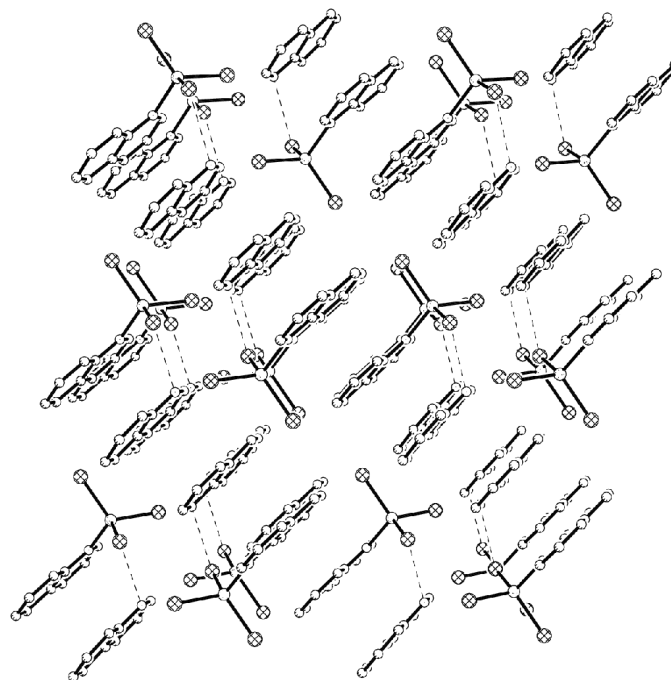


Figure 2
A packing diagram of (I) viewed along the b axis.

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.045$	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
$wR(F^2) = 0.147$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.91$	$(\Delta/\sigma)_{\text{max}} < 0.001$
3047 reflections	$\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$
217 parameters	$\Delta\rho_{\text{min}} = -0.45 \text{ e \AA}^{-3}$

Table 1

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

$\text{Zn} - \text{N1}$	2.090 (4)	$\text{Cl1} - \text{N1}$	1.330 (6)
$\text{Zn} - \text{Cl3}$	2.2319 (14)	$\text{Cl1} - \text{C2}$	1.398 (7)
$\text{Zn} - \text{Cl1}$	2.2512 (15)	$\text{C9} - \text{N1}$	1.379 (5)
$\text{Zn} - \text{Cl2}$	2.2707 (13)	$\text{Cl10} - \text{N2}$	1.322 (7)
$\text{N1} - \text{Zn} - \text{Cl3}$	106.18 (11)	$\text{Cl3} - \text{Zn} - \text{Cl2}$	111.92 (5)
$\text{N1} - \text{Zn} - \text{Cl1}$	102.89 (11)	$\text{Cl1} - \text{Zn} - \text{Cl2}$	105.86 (6)
$\text{Cl3} - \text{Zn} - \text{Cl1}$	114.49 (6)	$\text{Cl1} - \text{N1} - \text{C9}$	118.4 (4)
$\text{N1} - \text{Zn} - \text{Cl2}$	115.41 (11)	$\text{Cl10} - \text{N2} - \text{C18}$	123.9 (4)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D - \text{H} \cdots A$	$D - \text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D - \text{H} \cdots A$
$\text{N2} - \text{H2B} \cdots \text{Cl2}$	0.86	2.75	3.303 (5)	124

H atoms were located from difference Fourier syntheses and were refined with a riding model.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1994); data reduction: SHELXTL XPREP (Siemens, 1994); program(s) used to solve structure: SHELXTL; program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

This work was supported by The State Key Basic Research and Development Plan (No. G1998010100) and NNSFC (Nos. 29733090 and 29973047).

References

- Bharadwaj, P. K., Schugar, H. J. & Potenza, J. A. (1991). *Acta Cryst.* **C47**, 754–757.
- Cui, Y., Long, D., Chen, W. & Huang, J. (1998). *Acta Cryst.* **C54**, 1605–1607.
- Healy, P. C., Pakawatchai, C. & White, A. H. (1985). *Aust. J. Chem.* **38**, 669–675.
- Hubel, R., Polborn, K. & Beck, W. (1999). *Eur. J. Inorg. Chem.* pp. 471–482.
- Laity, H. L. & Taylor, M. R. (1995). *Acta Cryst.* **C51**, 1791–1793.
- Lundberg, B. K. S. (1966). *Acta Cryst.* **21**, 901–909.
- Parvez, M. & Rusiewicz, M. (1995). *Acta Cryst.* **C51**, 2277–2279.
- Savariault, J., Galy, J., Gutierrez-Zorrilla, J. & Roman, P. (1988). *J. Mol. Struct.* **176**, 313–322.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Siemens (1994). *SHELXTL* (Version 5.0) and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1996). *SMART*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.