

(2-Methylquinolin-8-olato)iron(III) and -copper(II) complexes

Fangfang Jian,^a Ying Wang,^a Lude Lu,^a Xujie Yang,^a Xin Wang,^a Suchada Chantrapromma,^{b*} Hoong-Kun Fun^c and Ibrahim Abdul Razak^c

^aMaterials Chemistry Laboratory, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China, ^bDepartment of Chemistry, Faculty of Science, Prince of Songkhla University, Hat-Yai, Songkhla 90112, Thailand, and ^cX-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia

Correspondence e-mail: suchada@ratree.psu.ac.th

Received 23 February 2001

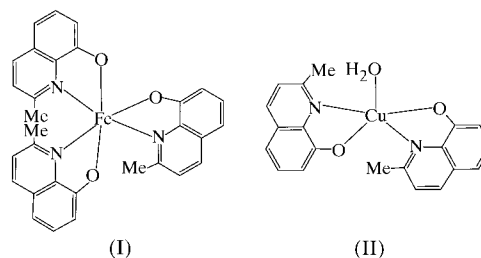
Accepted 29 March 2001

The crystal structures of tris(2-methylquinolin-8-olato-*N,O*)-iron(III), [Fe(C₁₀H₈NO)₃], (I), and aquabis(2-methylquinolin-8-olato-*N,O*)copper(II), [Cu(C₁₀H₈NO)₂(H₂O)], (II), have been determined. Compound (I) has a distorted octahedral configuration, in which the central Fe atom is coordinated by three N atoms and three O atoms from three 2-methylquinolin-8-olate ligands. The three Fe–O bond distances are in the range 1.934 (2)–1.947 (2) Å, while the three Fe–N bond distances range from 2.204 (2) to 2.405 (2) Å. In compound (II), the central Cu^{II} atom and H₂O group lie on the crystallographic twofold axis and the coordination geometry of the Cu^{II} atom is close to trigonal bipyramidal, with the three O atoms in the basal plane and the two N atoms in apical positions. The Cu–N bond length is 2.018 (5) Å. The Cu–O bond length in the basal positions is 1.991 (4) Å, while the Cu–O bond length in the apical position is 2.273 (6) Å. There is an intermolecular OW–H···O hydrogen bond which links the molecules into a linear chain along the *b* axis.

Comment

8-Quinolinol and its substituted analogues have been widely used as extracting agents for transition metals and for the fluorescence analysis of group 3A elements, as well as in the preparation of non-linear optical materials with second harmonic generation at high intensity and stability at room temperature (Sanz-Medel *et al.*, 1987; Sugiyama *et al.*, 1991; Kato *et al.*, 1988). Its complexes with transition metals have also found extensive applications. For example, bis(8-quinolinolato-*N,O*)nickel(II) has been used as a free-resistant additive for olefin polymers and as a fungicide for leather (Uma & Krishnamurthi, 1984). Also, tris(8-quinolinolato)-cobalt(III) has been synthesized and used to assist in the metal–ligand assignments which are further based on Zn labelling of the Zn complex, and on the effects of metal-ion

substitution in relation to expectations based on crystal-field theory (Nakamoto & Ohkaku, 1971). In this paper, we report the crystal structures of tris(2-methylquinolin-8-olato-*N,O*)-iron(III), (I), and aquabis(2-methylquinolin-8-olato-*N,O*)-copper(II), (II).



The molecular structures of compounds (I) and (II) are illustrated in Figs. 1 and 2, respectively. Selected bond lengths and angles are listed in Tables 1 and 2. In compound (I), the three 2-methylquinolin-8-olate ligands are coordinated to the central Fe atom through their O and N atoms, forming five-membered chelate rings. The Fe^{III} atom has a slightly distorted octahedral configuration as a result of the forced configuration of the five-membered chelate rings. Its structure is similar to that of tris(8-quinolinolato)chromium(III) (Folting *et al.*, 1968) and tris(8-quinolinolato)manganese(III) (Xiong *et al.*, 1995). The Fe–O bond distances in compound (I) are normal (Table 1) and are shorter than those in [Fe(OCH₃)₆(acac)₄(N₃)₂] [1.986 (5) Å; Li *et al.* (1997)]. The Fe–N bond distances are in agreement with those in [Fe(phen)₂(PhCOO)₂]⁴⁺ [2.200 (4) Å; Li *et al.* (1995)]. Because of the methyl-group steric effect, the Fe–N3 bond length is apparently longer than Fe–N1 and Fe–N2. Also, the chelate angle Fe–O3–C12 is the largest, Fe–N3–C11 is intermediate and the bite angle O3–Fe–N3 is the smallest.

In compound (II), the central pentacoordinated Cu^{II} atom and H₂O group lie on a crystallographic twofold axis and the

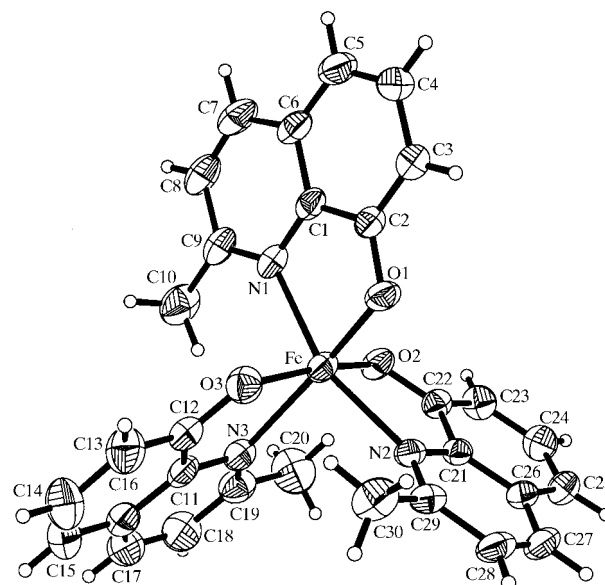


Figure 1
A view of compound (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

geometry of the Cu^{II} atom is close to trigonal bipyramidal. The basal coordination positions are occupied by three O atoms and the apical positions are occupied by two N atoms. The Cu—O1 and Cu—N1 distances fall within the normal range (Table 2), corresponding to the bond lengths in other five-coordinative Cu complexes [Cu—O 1.910 (9)–1.997 (8) Å (Chen *et al.*, 1997); Cu—N 1.979 (2)–2.029 (2) Å (Liu *et al.*, 1997); Cu—O 2.01 (1) Å and Cu—N 1.95–2.01 Å (Chen *et al.*, 1995); Cu—O 1.942–1.958 Å and Cu—N 2.016–2.019 Å (Bu *et al.*, 1990)]. The axial Cu—O1W bond, however, is significantly longer than the equatorial Cu—O1 bond, and is in agreement with that found in a similar compound (Liu *et al.*, 1997). The five-membered chelate ring (Cu, O1, N1, C1 and C2) and the 2-methyl-8-quinolinolate ligand are coplanar, with the maximum deviation of atoms being 0.039 (4) Å. The dihedral

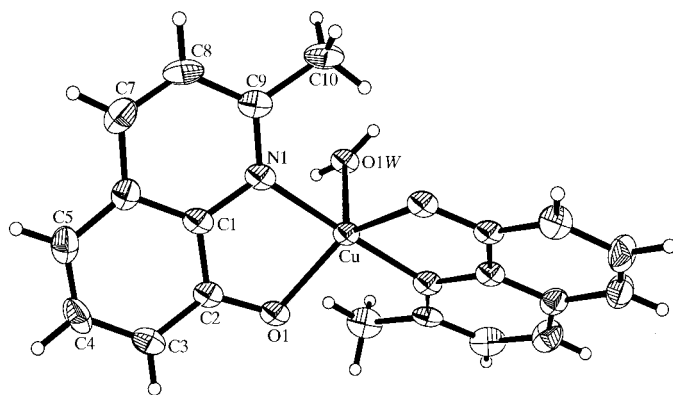


Figure 2

A view of compound (II) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

angle between the two quinolinolate ligand planes is 48.5 (1)°. The structure of CuO₂N₂ is obviously a distorted tetrahedron. The coordination plane comprising Cu, O1, O1ⁱ and O1W makes a dihedral angle of 81.8 (2)° with the plane formed by atoms Cu, N1, N1ⁱ and O1W [symmetry code: (i) $-x, y, \frac{1}{2} - z$]. They form dihedral angles of 85.0 (2) and 66.9 (2)° with the chelate ring plane, respectively.

For compound (II), there is an intermolecular hydrogen bond, O1W—H...O1, with an O...O separation of 2.752 (5) Å. This hydrogen bond links the molecules into a linear chain along the *b* axis.

Experimental

The title complexes were prepared by mixing an aqueous solution of metal nitrate ($M = \text{Fe}^{\text{III}}$ and Cu^{II}) and 2-methyl-8-hydroxyquinoline with heating. The deposits were collected by filtration, washed with water and dried overnight. Deep-red compound (I) and blue-green compound (II) were subsequently obtained. Single crystals suitable for X-ray analysis were obtained by recrystallization from EtOH solutions at room temperature. It was very difficult to get good quality crystals of compound (II), though many attempts were made. The crystal used for this report was the best attained after several attempts.

Compound (I)

Crystal data

[Fe(C₁₀H₈NO)₃]
 $M_r = 530.37$
 Monoclinic, *C2/c*
 $a = 23.8220$ (3) Å
 $b = 16.0839$ (3) Å
 $c = 15.6819$ (3) Å
 $\beta = 123.571$ (1)°
 $V = 5006.31$ (15) Å³
 $Z = 8$

$D_x = 1.407$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 8192 reflections
 $\theta = 1.6$ – 29.5°
 $\mu = 0.64$ mm⁻¹
 $T = 293$ (2) K
 Block, dark purple
 0.48 × 0.40 × 0.08 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
 $T_{\text{min}} = 0.749$, $T_{\text{max}} = 0.951$
 16 629 measured reflections

5734 independent reflections
 3729 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.072$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -30 \rightarrow 30$
 $k = -20 \rightarrow 11$
 $l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.142$
 $S = 0.94$
 5734 reflections
 337 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0718P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.45$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.96$ e Å⁻³

Table 1

Selected geometric parameters (Å, °) for (I).

Fe—O3	1.934 (2)	Fe—N2	2.204 (2)
Fe—O1	1.939 (2)	Fe—N1	2.220 (2)
Fe—O2	1.947 (2)	Fe—N3	2.405 (2)
O3—Fe—O1	94.51 (8)	O1—Fe—N1	80.01 (8)
O1—Fe—O2	99.67 (8)	O2—Fe—N1	87.20 (8)
O1—Fe—N2	86.80 (8)	O3—Fe—N3	75.36 (8)
O2—Fe—N2	79.69 (8)	C12—O3—Fe	123.2 (2)
O3—Fe—N1	93.13 (8)	C11—N3—Fe	106.7 (2)

Compound (II)

Crystal data

[Cu(C₁₀H₈NO)₂(H₂O)]
 $M_r = 397.90$
 Orthorhombic, *Pbcn*
 $a = 7.5388$ (2) Å
 $b = 9.1091$ (1) Å
 $c = 24.8514$ (6) Å
 $V = 1706.59$ (6) Å³
 $Z = 4$
 $D_x = 1.549$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 3814 reflections
 $\theta = 1.6$ – 28.4°
 $\mu = 1.30$ mm⁻¹
 $T = 293$ (2) K
 Rectangular slab, orange
 0.34 × 0.16 × 0.06 mm

Table 2

Selected geometric parameters (Å, °) for (II).

Cu—O1	1.991 (4)	Cu—O1W	2.273 (6)
Cu—N1	2.018 (5)		
O1 ⁱ —Cu—N1	98.4 (2)	O1 ⁱ —Cu—O1W	112.5 (1)
O1—Cu—N1	83.1 (2)	N1 ⁱ —Cu—O1W	88.1 (1)

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

Data collection

Siemens SMART CCD area-detector diffractometer	1500 independent reflections
ω scans	1056 reflections with $I > 2\sigma(I)$
Absorption correction: empirical (SADABS, Sheldrick, 1996)	$R_{\text{int}} = 0.119$
$T_{\text{min}} = 0.666$, $T_{\text{max}} = 0.926$	$\theta_{\text{max}} = 25.0^\circ$
8856 measured reflections	$h = -8 \rightarrow 8$
	$k = -10 \rightarrow 7$
	$l = -29 \rightarrow 26$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.088$	$w = 1/[\sigma^2(F_o^2) + (0.1587P)^2]$
$wR(F^2) = 0.239$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1500 reflections	$\Delta\rho_{\text{max}} = 1.84 \text{ e } \text{\AA}^{-3}$
104 parameters	$\Delta\rho_{\text{min}} = -1.52 \text{ e } \text{\AA}^{-3}$

Table 3

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O1W-H1W1 \cdots O1^i$	0.82	1.970	2.752 (5)	159

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

For both compounds, after checking their presence in the difference map, all H atoms were fixed geometrically and allowed to ride on their attached atoms with $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the attached atoms (except for the CH_3 moieties where $U_{\text{iso}} = 1.5U_{\text{eq}}$). The H atoms of the CH_3 moieties were refined as rigid rotators. For compound (II), restraints were applied to the displacement parameters of atoms C1, N1 and O1W.

For both compounds, data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT and SADABS (Sheldrick, 1996); program(s) used to solve structure: SHELXTL (Sheldrick, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to

prepare material for publication: SHELXTL and PLATON (Spek, 1990).

The authors would like to thank the Malaysian Government and Universiti Sains Malaysia for research grant R&D No. 305/PFIZIK/610942.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1467). Services for accessing these data are described at the back of the journal.

References

- Bu, X. R., You, X. Z. & Meng, Q. J. (1990). *Comments Inorg. Chem.* **9**, 221–244.
- Chen, Z. N., Wang, J. L., Qiu, J., Miao, F. M. & Tang, W. X. (1995). *Inorg. Chem.* **34**, 2255–2257.
- Chen, X. Y., Zhan, S. Z., Hu, C. J., Meng, Q. J. & Liu, Y. J. (1997). *J. Chem. Soc. Dalton Trans.* pp. 245–250.
- Folting, K., Cox, M. M., Moore, J. W. & Merritt, J. L. L. (1968). *Chem. Commun.* pp. 1170–1171.
- Kato, H., Kanemitsuya, K. & Futagami, T. (1988). *Jpn Kokai Tokkyo Koho JP* 63,128,041 [88,128,041], 19 November 1986.
- Li, H., Zhong, Z. J., Chen, W. & You, X. Z. (1997). *J. Chem. Soc. Dalton Trans.* pp. 463–464.
- Li, J., Zou, J. Z., Wu, M. F., Xu, Z., You, X. Z. & Mak, T. C. W. (1995). *Polyhedron*, **14**, 3519–3523.
- Liu, C. M., Xiong, R. G., You, X. Z., Fun, H.-K. & Sivakumar, K. (1997). *Polyhedron*, **16**, 119–123.
- Nakamoto, K. & Ohkaku, N. (1971). *Inorg. Chem.* **10**, 798–805.
- Sanz-Medel, A., Fernandez, C. R. & Garcia, A. J. I. (1987). *Analyst*, **11**, 493–497.
- Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). SHELXTL. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Siemens (1996). SMART and SAINT. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- Sugiyama, T., Shigemoto, T., Kamiya, M. & Ota, T. (1991). *Jpn Kokai Tokkyo Koho JP*, 02,262,627 [90,262,627], 8 December 1988.
- Uma, L. & Krishnamurthi, V. S. (1984). *Leather Sci. Madras*, **31**, 15–16.
- Xiong, R.-G., You, X.-Z., Wu, Q.-J. & Huang, X.-Y. (1995). *Acta Cryst.* **C51**, 1978–1980.