

catena-Poly[copper(II)-di- μ -acetylacetonato-copper(II)-bis(μ -4-hydroxy-3-methoxybenzaldehyde picoloylhydrazone)] and (acetylacetonato)-(4-methoxybenzaldehyde picoloylhydrazone)copper(II)

Li-Fang Jiang

Department of Chemistry and Chemical Engineering, Minjiang University, Fuzhou, Fujian 350108, People's Republic of China
Correspondence e-mail: fanhue@gmail.com

Received 10 September 2010

Accepted 29 October 2010

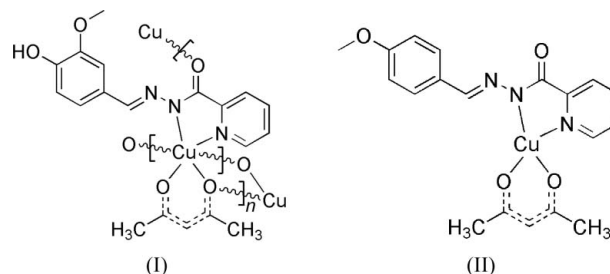
Online 10 November 2010

In the two title copper(II) complexes, $[\text{CuL}(\text{C}_5\text{H}_7\text{O}_2)]_n$, (I), and $[\text{CuL}'(\text{C}_5\text{H}_7\text{O}_2)]$, (II), respectively, where HL is 4-hydroxy-3-methoxybenzaldehyde picoloylhydrazone, $\text{C}_{14}\text{H}_{12}\text{N}_3\text{O}_3$, and HL' is 4-methoxybenzaldehyde picoloylhydrazone, $\text{C}_{14}\text{H}_{12}\text{N}_3\text{O}_2$, the Cu^{II} ions display a highly Jahn–Teller-distorted octahedral and a square-planar coordination geometry, respectively. In complex (I), two neighbouring Cu^{II} atoms are bridged by L^- and acetylacetonate, alternately, giving rise to a one-dimensional chain of CuN_2O_4 octahedra interconnected by these two ligands along the a axis. In addition, the hydroxy H atom of the vanillin group connects to the carboxyl O atom of the adjacent chain via an $\text{O}—\text{H}\cdots\text{O}$ hydrogen bond, giving rise to a three-dimensional supramolecular assembly. Complex (II) displays a discrete structure.

Comment

Studies of acylhydrazone Schiff bases and the construction of complexes with transition metals are of great interest, not only because of their intriguing structural motifs, but also because of their important potential applications (Pickart *et al.*, 1983; Sreekanth *et al.*, 2004) such as catalytic materials (Duda *et al.*, 2003) and magnetochemistry (Lin *et al.*, 2008). The use of carefully selected multidentate ligands and metal ions has allowed the construction of polymers with defined geometries and special properties. From the structural point of view, picoloylhydrazone and its derivatives have been used extensively as versatile ligands for building extended structures as they have potential N,O -donor sites, which give rise to different coordination modes (Domiano *et al.*, 1980; Wu & Liu, 2003). As part of continuing investigations of these types of Schiff base ligands, this work presents the syntheses and structural characterization of two copper(II) complexes,

catena-poly[copper(II)-di- μ -acetylacetonato-copper(II)-bis(μ -4-hydroxy-3-methoxybenzaldehyde picoloylhydrazone)], $[\text{CuL}(\text{C}_5\text{H}_7\text{O}_2)]_n$, (I), and acetylacetonato(4-methoxybenzaldehyde picoloylhydrazone)copper(II), $[\text{CuL}'(\text{C}_5\text{H}_7\text{O}_2)]$, (II), where HL and HL' are 4-hydroxy-3-methoxybenzaldehyde picoloylhydrazone and 4-methoxybenzaldehyde



picoloylhydrazone, respectively. To the best of our knowledge, the title complexes represent the first examples of structurally characterized CuL and CuL' complexes.

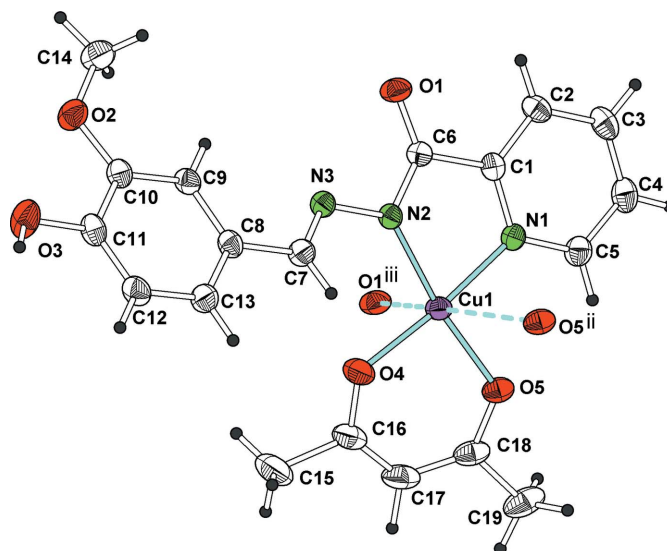


Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (ii) $1 - x, 1 - y, 1 - z$; (iii) $-x, 1 - y, 1 - z$.]

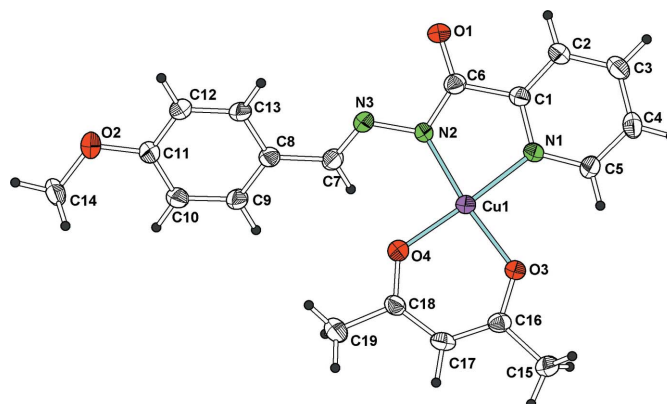
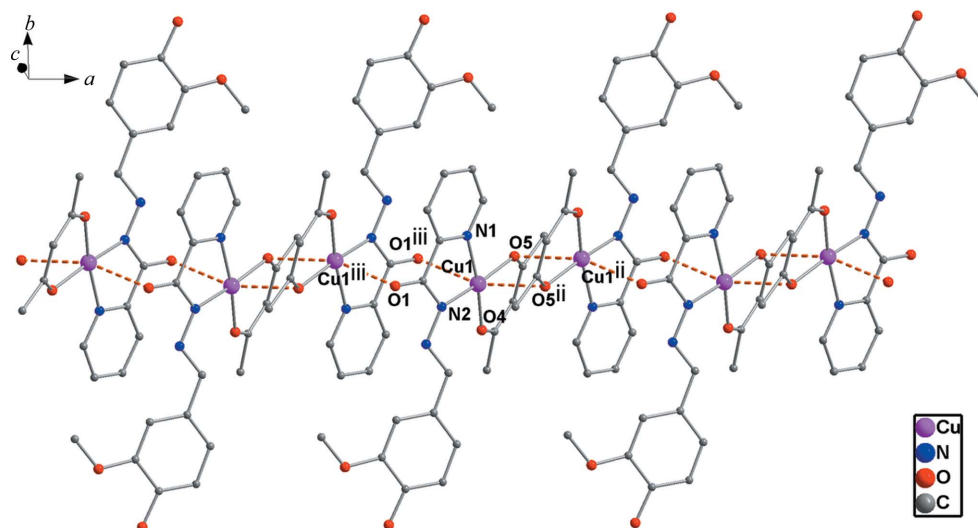


Figure 2

The molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.


Figure 3

The one-dimensional chain structure in (I). [Symmetry codes: (ii) $1 - x, 1 - y, 1 - z$; (iii) $-x, 1 - y, 1 - z$.]

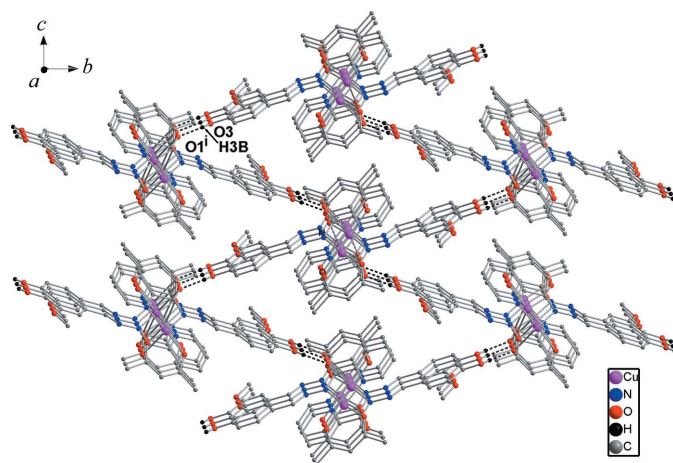
Structural views of (I) and (II) are shown in Figs. 1 and 2, respectively, and selected bond lengths and angles are given in Tables 1 and 3. In complex (I), the Cu^{II} ion displays a highly Jahn–Teller-distorted CuN_2O_4 octahedron, with the equatorial plane defined by the two N atoms (pyridyl N1 and hydrazine N2) of the L^- ligand and atoms O4 and O5 of the acetylacetonate ligand. The $\text{Cu1}-\text{N1}$ and $\text{Cu1}-\text{N2}$ distances are similar to the values reported for other copper complexes involving N -donor ligands (Table 4). The $\text{Cu1}-\text{O4}$ and $\text{Cu1}-\text{O5}$ bond lengths correspond to the distances observed in other Cu -acetylacetonate complexes (Heinze & Reinhart, 2006). There is no significant deviation of the metal centre from the N_2O_2 equatorial plane, which shows a small but significant tetrahedral distortion. The maximum displacements from the least-squares plane through atoms N1, N2, O4 and O5 are -0.0798 (15) and 0.0824 (15) Å for atoms N2 and N1, respectively; Cu1 is 0.0339 (16) Å below this plane. The two axial positions are occupied by carbonyl atom O5^{ii} of an acetylacetonate ligand [symmetry code: (ii) $1 - x, 1 - y, 1 - z$]

and carboxyl atom O1^{iii} of an L^- ligand [symmetry code: (iii) $-x, 1 - y, 1 - z$], with two weak coordination bonds of 2.847 (3) and 2.894 (3) Å, respectively (Das & Pal, 2005; Heinze & Reinhart, 2006).

The tridentate hydrazone ligand L^- is a bridging ligand to coordinating to two neighbouring Cu^{II} ions through its donors carboxyl atom O2, hydrazine atom N2 and phenolic atom O1. In addition, acetylacetonate atom O5 acts as a bridging atom linking Cu1 and Cu1^{ii} . Therefore, a one-dimensional chain is built up, consisting of CuN_2O_4 octahedra connected alternately by pairs of the different ligands along the a axis, shown in Fig. 3.

The planes through the acetylacetonate (O4/C15–C19/O5) and picoloylhydrazone (C1–C5/N1/C6/O1/N2/N3) groups make dihedral angles of 17.40 (18) and 8.60 (18)°, respectively, with the equatorial N_2O_2 plane. More buckling of acetylacetonate than picoloylhydrazone allows for a closer approach of atom O5 towards Cu1^{ii} and simultaneously reduces the steric interaction between the two ligands (Bhadrhade & Srinivas, 1993) (Fig. 3). The O–H function of the vanillin group connects to the carboxyl O atom of the adjacent chain *via* an $\text{O3}-\text{H3B}\cdots\text{O1}^{\text{i}}$ hydrogen bond [symmetry code: (i) $x, \frac{1}{2} - y, -\frac{1}{2} + z$], giving rise to a three-dimensional supramolecular assembly, as shown in Fig. 4.

In complex (II), atom Cu1 displays a square-planar coordination geometry (Fig. 2). The $\text{Cu1}-\text{N}$ and $\text{Cu1}-\text{O}$ bond lengths in the N_2O_4 plane are comparable with those found in (I) (Table 3). However, unlike (I), (II) does not form chains but is rather a simple discrete complex. The closest distance between a Cu^{II} ion and an O atom from a neighbouring molecule is 3.334 (4) Å for $\text{Cu1}\cdots\text{O3}^{\text{iii}}$, indicating that no intermolecular interactions are present. Just as in (I), there is no significant deviation of the metal centre from the N_2O_2 coordination plane and the distortion of this plane is even smaller. The maximum displacements from the least-squares plane through atoms N1, N2, O3 and O4 are -0.042 (2) and 0.043 (2) Å for atoms N2 and N1, respectively; Cu1 is


Figure 4

The three-dimensional supramolecular structure of (I). [Symmetry code: (i) $x, \frac{1}{2} - y, -\frac{1}{2} + z$.]

0.0054 (19) Å below this plane. It is worth noting that the acetylacetonate (C15–C19/O3/O4) and picoloylhydrazone (C1–C5/N1/C6/O1/N2/N3) planes make dihedral angles of 7.97 (18) and 6.43 (15)°, respectively, with the N₂O₂ plane. The approximately planar conformation of the Cu^{II} ion in complex (II) could be due to the absence of the Cu1···O3ⁱⁱⁱ interaction, which reduces the steric interaction between the ligands and a second molecule compared with (I).

Experimental

Ligand *HL* was prepared by the reaction of picolinohydrazide and 4-hydroxy-3-methoxybenzaldehyde in a 1:1 molar ratio under reflux in ethanol for 3 h. The yellow product obtained on cooling was washed with anhydrous ethanol. Ligand *HL'* was obtained by a similar procedure to that for *HL*, using 4-methoxybenzaldehyde in place of 4-hydroxy-3-methoxybenzaldehyde. Both complexes were prepared using the same method. Complex (I) was synthesized by adding Cu(acac)₂ (acac is acetylacetonate; 16.2 mg, 0.10 mmol) to a solution of *HL* (27.1 mg, 0.10 mmol) in methanol (15 ml). The resulting mixture was stirred for 3 h at room temperature to afford a green solution. The solution was allowed to stand at room temperature for about two weeks, during which time dark-green crystals of (I) were produced at the bottom of the vessel on slow evaporation of the methanol (yield 56.0%, based on Cu). Complex (II) was obtained by using *HL'* in place of *HL*. After two weeks, dark-green crystals of complex (II) appeared (yield 49.0%, based on Cu).

Compound (I)

Crystal data

[Cu(C ₁₄ H ₁₂ N ₃ O ₃)(C ₅ H ₇ O ₂)]	<i>V</i> = 1915.0 (5) Å ³
<i>M_r</i> = 432.91	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 8.4719 (15) Å	<i>μ</i> = 1.18 mm ⁻¹
<i>b</i> = 23.586 (3) Å	<i>T</i> = 293 K
<i>c</i> = 9.8635 (14) Å	0.42 × 0.31 × 0.18 mm
<i>β</i> = 103.683 (6)°	

Data collection

Bruker APEXII CCD area-detector diffractometer	18642 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	4358 independent reflections
<i>T</i> _{min} = 0.652, <i>T</i> _{max} = 0.809	2831 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.089

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.060	H atoms treated by a mixture of independent and constrained refinement
<i>wR</i> (<i>F</i> ²) = 0.138	<i>Δρ</i> _{max} = 0.47 e Å ⁻³
<i>S</i> = 1.04	<i>Δρ</i> _{min} = -0.63 e Å ⁻³
4358 reflections	
259 parameters	
1 restraint	

Compound (II)

Crystal data

[Cu(C ₁₄ H ₁₂ N ₃ O ₂)(C ₅ H ₇ O ₂)]	<i>V</i> = 1763.4 (6) Å ³
<i>M_r</i> = 416.91	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 7.4198 (15) Å	<i>μ</i> = 1.27 mm ⁻¹
<i>b</i> = 14.969 (3) Å	<i>T</i> = 293 K
<i>c</i> = 15.885 (3) Å	0.39 × 0.26 × 0.17 mm
<i>β</i> = 91.78 (3)°	

Table 1
Selected geometric parameters (Å, °) for (I).

Cu1–O4	1.902 (3)	Cu1–N1	1.979 (3)
Cu1–O5	1.931 (3)	Cu1–N2	1.996 (3)
O4–Cu1–O5	92.40 (12)	O4–Cu1–N2	95.14 (12)
O4–Cu1–N1	172.69 (14)	O5–Cu1–N2	172.15 (12)
O5–Cu1–N1	90.77 (12)	N1–Cu1–N2	81.99 (12)

Table 2
Hydrogen-bond geometry (Å, °) for (I).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O3–H3B···O1 ⁱ	0.79 (3)	1.93 (4)	2.636 (4)	149 (6)

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

Table 3
Selected geometric parameters (Å, °) for (II).

Cu1–O4	1.892 (3)	Cu1–N2	1.962 (4)
Cu1–O3	1.914 (3)	Cu1–N1	1.982 (4)
O4–Cu1–O3	91.81 (14)	O4–Cu1–N1	176.03 (16)
O4–Cu1–N2	95.25 (15)	O3–Cu1–N1	91.08 (15)
O3–Cu1–N2	172.67 (16)	N2–Cu1–N1	81.97 (15)

Table 4
Comparative geometric parameters (Å) for Cu–N in copper complexes.

Complex	Cu–N(pyridyl)	Cu–N(hydrazine)
(I) [†]	1.979 (3)	1.996 (3)
(II) [†]	1.982 (4)	1.962 (4)
[Cu(C ₁₅ H ₁₃ N ₄ O ₂)Cl] [‡]	1.989 (2)	1.921 (2)
[Cu ₂ (C ₁₂ H ₈ N ₄ O ₂)(H ₂ O) ₃ ·(NO ₃) ₂ ·2H ₂ O] [§]	1.980 (4), 1.996 (3)	2.008 (4), 1.919 (3)
[Cu ₄ (C ₁₅ H ₉ N ₃ O ₂) ₂ Cl ₄] _n [¶]	2.013 (6)	1.984 (6)

[†] This work. [‡] Grove *et al.* (2004). [§] Lagrenée *et al.* (1991). [¶] Bai *et al.* (2006).

Data collection

Bruker APEXII CCD area-detector diffractometer	16505 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	4005 independent reflections
<i>T</i> _{min} = 0.680, <i>T</i> _{max} = 0.806	1904 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.125

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.051	247 parameters
<i>wR</i> (<i>F</i> ²) = 0.154	H-atom parameters constrained
<i>S</i> = 0.91	<i>Δρ</i> _{max} = 0.39 e Å ⁻³
4005 reflections	<i>Δρ</i> _{min} = -0.51 e Å ⁻³

In both complexes, H atoms bonded to C atoms were positioned geometrically and refined using a riding model, with *Csp*²–H = 0.93 Å, with *U*_{iso}(H) = 1.2*U*_{eq}(C), and methyl C–H = 0.96 Å, with *U*_{iso}(H) = 1.5*U*_{eq}(C). The H atom bonded to the phenol O atom in (I) was located in a difference Fourier map and subsequently refined with the help of an O–H distance restraint of 0.82 (3) Å, and with *U*_{iso}(H) = 1.2*U*_{eq}(O).

For both compounds, data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT-Plus* (Bruker, 2007); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

The author thanks Minjiang University for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MX3036). Services for accessing these data are described at the back of the journal.

References

- Bai, Y., Dang, D.-B., Cao, X., Duan, C.-Y. & Meng, Q.-J. (2006). *Inorg. Chem. Commun.* **9**, 86–89.
- Bhadbhade, M. M. & Srinivas, D. (1993). *Inorg. Chem.* **32**, 6122–6130.
- Bruker (2007). *APEX2* and *SAINT-Plus*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Das, S. & Pal, S. (2005). *J. Mol. Struct.* **753**, 68–79.
- Domiano, P., Musatti, A., Nardelli, M., Pelizzi, C. & Predieri, G. (1980). *Inorg. Chim. Acta*, **38**, 9–14.
- Duda, D., Govindasamy, L., Agbandje-McKenna, M., Tu, C., Silverman, D. N. & McKenna, R. (2003). *Acta Cryst.* **D59**, 93–104.
- Grove, H., Kelly, T. L., Thompson, L. K., Zhao, L. A., Xu, Z. Q., Abedin, T. S. M., Miller, D. O., Goeta, A. E., Wilson, C. & Howard, J. A. K. (2004). *Inorg. Chem.* **43**, 4278–4288.
- Heinze, K. & Reinhart, A. (2006). *Inorg. Chem.* **45**, 2695–2703.
- Lagrenée, M., Sueur, S. & Wignacourt, J. P. (1991). *Acta Cryst.* **C47**, 1158–1160.
- Lin, P.-H., Burchell, T. J., Clérac, R. & Murugesu, M. (2008). *Angew. Chem. Int. Ed.* **47**, 8848–8851.
- Pickart, L., Goodwin, W. H., Burgua, W., Murphy, T. B. & Johnson, D. K. (1983). *Biochem. Pharmacol.* **32**, 3868–3871.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sreekanth, A., Kala, U. L., Nayar, C. R. & Kurup, M. R. P. (2004). *Polyhedron*, **23**, 41–47.
- Wu, W.-S. & Liu, S.-X. (2003). *Chin. J. Inorg. Chem.* **19**, 1065–1072.