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Crystal structure of (phenanthroline-*N*,*N*′)-*N*-carbamoylmethyl-iminodiacetato-copper(II) dihydrate, $[Cu(C_6H_8N_2)(C_{12}H_8N_2)] \cdot 2H_2O$

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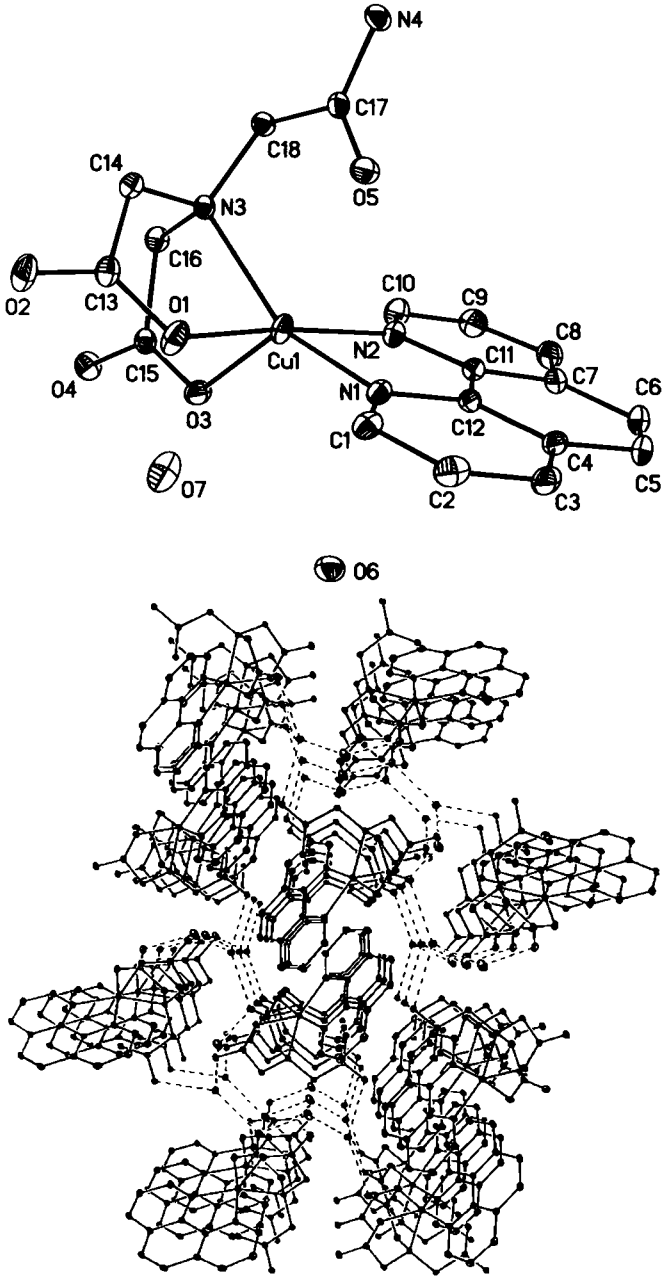

Abstract

$C_{18}H_{20}CuN_4O_7$, monoclinic, $P12_1/c1$ (no. 14), a = 8.802(1) Å, b = 22.493(3) Å, c = 9.885(1) Å, β = 97.163(2)°, V = 1941.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.033, $wR_{ref}(F^2)$ = 0.096, T = 291 K.

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Source of material

The mixture of $Cu(CH_3COO)_2 \cdot 5H_2O$ (0.5 mmol, 0.100 g) and H_2ADA (1 mmol, 0.190 g; $H_2NCOCH_2N(CH_2COOH)_2$, *N*-carbamoylmethyl-iminodiacetic acid or named *N*-(2-acetamido)iminodiacetic acid) was stirred into 6 mL 50 % methanolic solution at room temperature, which was refluxed about 20 min. Then the pH was adjusted to approximately 6 with NaOH solid, and 4 mL 50 % methanolic solution of 1,10 phenanthroline (0.5 mmol, 0.100 g) was added. The reaction mixture was heated on a water bath for 6 h at 60 °C and then filtered. The blue prismatic crystal was separated from the mother liquor by slow evaporation at room temperature after one week (yield 0.158 g, 65 %).

Experimental details

The water H atoms were freely refined due to their importance in the hydrogen bonding. The other H atoms were added geometrically and refined using rigid body approximation.

Discussion

Chelation of ADA (the divalent anion of H_2ADA) and metal(II) ions (such as Mg, Ca, Sr, Ba, Mn, Co, Ni, Cu, Zn, Cd, Hg, Pb etc.) in solution has been well researched for a long time [1]. H_2ADA acts as a polydentate ligand and presents a variety of coordination modes because of the presence of carbamoyl function and iminodiacetic group. It is not only a well-known chelating agent, but also used in biological buffers of pH 6.0-7.4 [2,3]. In recent studies, it was found that the investigation of ADA-metal chelates in solid state provides information about the chelating role of the divalent anion $H_2NCOCH_2N(CH_2COO^-)_2$. Therefore, some mixed-ligand complexes of transitional metal ions with ADA as primary ligand and water molecule, imidazole and 2,2′-bipyridine as secondary ligands have been reported [1,4-8]. However, crystal structures of the mixed-ligand metal(II) complexes with ADA and 1,10-phenanthroline compound have not been studied so far.

The asymmetric unit of the title crystal structure consists of a [Cu(ADA)(phen)] moiety and two hydrate water molecules (figure, top). The Cu(II) ion is five-coordinated (CuN_3O_2) and the coordination polyhedron is a distorted trigonal bipyramid in which the divalent ADA anion acts as tridentate chelating ligand. The bond lengths of Cu1—O1, Cu1—O3 and Cu1—N3 are 1.942(2) Å, 2.102(2) Å and 2.171(2) Å, respectively. The phen molecule serves as bidentate ligand chelating to the Cu(II) ion with Cu1—N1 and Cu—N2 bond distances of 2.007(2) Å and 2.032(2) Å, respectively. It should be pointed out that the Cu—N (imino) and Cu—O (carboxyl) bonds are longer than those reported in other metal-ADA complexes [1,6,7], but remarkable close to nickel(II) complex $[Ni(ADA)(bipy)(H_2O)] \cdot 4H_2O$ (I) [8], which is probably due to steric hindrance of phen (or 2,2′-bipyridine) weakening the bonding interaction of ADA with metal ions. The Cu(II)

ion is chelated by means of the N atom (imino) and two O (carboxyl) donor of the tridentate ADA ligand, and the *N*-carbamoylmethyl arm is not coordinated to the Cu(II) ion. The coordination mode is similar to that of the Ni complex [8], but different from in the other related metal-ADA mixed-ligand complexes. The crystal structure consists of mononuclear [Cu(ADA)(phen)] · $2H_2O$ complex units linked by a 3D hydrogen bond network (figure, bottom). Polar amido N–H bond, unionized carboxyl oxygen and two non-coordinated water molecules are involved in forming of hydrogen bonds. At the same time, there exist aromatic ring π-π stacking interactions between phen molecules. The dihedral angles between the coordinated phen molecules is 2.6°, showing that they are nearly parallel to each other. The average interplane distance is 3.46 Å, indicating π-π stacking interactions between these phen molecules.

Table 1. Data collection and handling.

Crystal:	blue block, size 0.21 × 0.31 × 0.39 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	11.75 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9516, 3499
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2957
$N(param)_{refined}$:	287
Programs:	SHELXS-97 [9], SHELXL-97 [10], SHELXTL [11]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(4A)	4*e*	−0.0368	0.4628	−0.1109	0.049
H(4B)	4*e*	−0.0264	0.4013	−0.1646	0.049
H(1)	4*e*	0.1355	0.4730	0.5176	0.048
H(2)	4*e*	0.1776	0.5707	0.5859	0.057
H(3)	4*e*	0.3591	0.6265	0.4977	0.058
H(5)	4*e*	0.5640	0.6325	0.3313	0.064
H(6)	4*e*	0.6965	0.5862	0.1828	0.066
H(8)	4*e*	0.7519	0.4898	0.0536	0.062
H(9)	4*e*	0.6934	0.3921	0.0092	0.060
H(10)	4*e*	0.4948	0.3476	0.1060	0.054
H(14A)	4*e*	−0.0323	0.2735	0.2185	0.045
H(14B)	4*e*	−0.0812	0.3387	0.1781	0.045
H(16A)	4*e*	0.2948	0.2652	0.1073	0.044
H(16B)	4*e*	0.1674	0.2340	0.1790	0.044
H(18A)	4*e*	0.0319	0.3193	−0.0196	0.040
H(18B)	4*e*	0.2031	0.3394	−0.0160	0.040
H(1W)	4*e*	0.911(4)	0.332(2)	0.634(1)	0.08(1)
H(2W)	4*e*	0.835(2)	0.322(1)	0.742(3)	0.06(1)
H(3W)	4*e*	0.698(5)	0.234(2)	0.318(3)	0.08(2)
H(4W)	4*e*	0.643(6)	0.220(3)	0.434(5)	0.22(4)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	4*e*	0.26378(4)	0.38782(1)	0.30958(3)	0.0422(2)	0.0246(2)	0.0467(2)	−0.0085(1)	0.0153(2)	−0.0077(1)
O(1)	4*e*	0.1071(2)	0.36842(9)	0.4244(2)	0.055(1)	0.047(1)	0.053(1)	−0.021(1)	0.024(1)	−0.020(1)
O(2)	4*e*	−0.0899(2)	0.30946(9)	0.4456(2)	0.059(1)	0.052(1)	0.057(1)	−0.023(1)	0.030(1)	−0.014(1)
O(3)	4*e*	0.3875(2)	0.31116(8)	0.3766(2)	0.049(1)	0.031(1)	0.052(1)	0.0003(9)	−0.0104(9)	0.0002(9)
O(4)	4*e*	0.3925(2)	0.21305(8)	0.3511(2)	0.051(1)	0.029(1)	0.061(1)	0.0104(9)	0.001(1)	0.0076(9)
O(5)	4*e*	0.0892(2)	0.44262(8)	0.1189(2)	0.063(1)	0.027(1)	0.043(1)	0.0046(9)	−0.0071(9)	−0.0028(8)
O(6)	4*e*	0.9130(3)	0.3366(1)	0.7168(2)	0.079(2)	0.053(1)	0.044(1)	−0.001(1)	0.001(1)	−0.006(1)
O(7)	4*e*	0.7128(3)	0.2103(1)	0.3862(5)	0.061(2)	0.061(2)	0.150(3)	0.002(1)	0.013(2)	−0.004(2)
N(1)	4*e*	0.2846(2)	0.47028(9)	0.3874(2)	0.030(1)	0.027(1)	0.041(1)	−0.0006(9)	−0.0010(9)	−0.0023(9)
N(2)	4*e*	0.4370(2)	0.41664(9)	0.2083(2)	0.036(1)	0.029(1)	0.045(1)	−0.0026(9)	0.007(1)	0.0002(9)
N(3)	4*e*	0.1434(2)	0.32362(8)	0.1714(2)	0.031(1)	0.022(1)	0.034(1)	0.0020(8)	0.0045(8)	0.0019(8)
N(4)	4*e*	−0.0089(3)	0.4264(1)	−0.0989(2)	0.054(1)	0.028(1)	0.039(1)	0.004(1)	−0.002(1)	0.0034(9)
C(1)	4*e*	0.2084(3)	0.4953(1)	0.4795(3)	0.034(1)	0.037(2)	0.049(2)	0.002(1)	0.001(1)	−0.006(1)
C(2)	4*e*	0.2340(3)	0.5543(1)	0.5217(3)	0.049(2)	0.039(2)	0.053(2)	0.013(1)	−0.001(1)	−0.012(1)
C(3)	4*e*	0.3410(4)	0.5876(1)	0.4688(3)	0.058(2)	0.024(1)	0.057(2)	0.003(1)	−0.014(2)	−0.005(1)
C(4)	4*e*	0.4243(3)	0.5629(1)	0.3703(3)	0.047(2)	0.026(1)	0.045(2)	−0.002(1)	−0.013(1)	0.002(1)
C(5)	4*e*	0.5420(4)	0.5930(1)	0.3091(3)	0.072(2)	0.028(1)	0.056(2)	−0.017(1)	−0.004(2)	0.008(1)
C(6)	4*e*	0.6209(4)	0.5653(1)	0.2205(3)	0.064(2)	0.044(2)	0.056(2)	−0.025(2)	0.003(2)	0.014(2)
C(7)	4*e*	0.5928(3)	0.5042(1)	0.1816(3)	0.046(2)	0.042(2)	0.042(2)	−0.012(1)	0.000(1)	0.011(1)
C(8)	4*e*	0.6736(3)	0.4717(2)	0.0937(3)	0.045(2)	0.061(2)	0.050(2)	−0.012(2)	0.010(1)	0.011(2)
C(9)	4*e*	0.6384(3)	0.4140(2)	0.0666(3)	0.043(2)	0.058(2)	0.051(2)	0.000(1)	0.013(1)	0.002(2)
C(10)	4*e*	0.5183(3)	0.3872(1)	0.1256(3)	0.045(2)	0.038(2)	0.053(2)	−0.000(1)	0.012(1)	−0.004(1)
C(11)	4*e*	0.4740(3)	0.4743(1)	0.2370(3)	0.034(1)	0.032(1)	0.037(1)	−0.005(1)	−0.003(1)	0.004(1)
C(12)	4*e*	0.3912(3)	0.5037(1)	0.3325(3)	0.036(1)	0.024(1)	0.038(1)	−0.001(1)	−0.007(1)	0.006(1)
C(13)	4*e*	0.0059(3)	0.3310(1)	0.3778(3)	0.040(1)	0.026(1)	0.045(2)	−0.000(1)	0.014(1)	−0.004(1)
C(14)	4*e*	−0.0022(3)	0.3149(1)	0.2295(3)	0.032(1)	0.039(2)	0.042(2)	−0.007(1)	0.003(1)	0.003(1)
C(15)	4*e*	0.3461(3)	0.2638(1)	0.3158(3)	0.032(1)	0.028(1)	0.042(1)	0.003(1)	0.007(1)	0.005(1)
C(16)	4*e*	0.2363(3)	0.2678(1)	0.1840(3)	0.047(2)	0.020(1)	0.042(1)	0.004(1)	0.003(1)	−0.003(1)
C(17)	4*e*	0.0607(3)	0.4089(1)	0.0203(3)	0.036(1)	0.026(1)	0.037(1)	−0.002(1)	0.005(1)	0.003(1)
C(18)	4*e*	0.1116(3)	0.3439(1)	0.0285(2)	0.040(1)	0.027(1)	0.032(1)	0.003(1)	0.003(1)	0.000(1)

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