

Note

Synthesis, molecular structure and intramolecular aromatic-ring stacking interaction of a novel binuclear Cu(II) complex with 1, 10-phenanthroline and phenylacetate

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The complex $[\text{Cu}(\text{phen})_2(\text{POAc})_3]\text{ClO}_4 \cdot 4\text{H}_2\text{O}$ has been synthesized and investigated by elemental analysis, IR spectroscopy and X-ray diffraction methods, where phen = 1, 10-phenanthroline, POAc = phenylacetate group). The complex crystallizes in the triclinic space group P1 with two molecules in a unit cell of dimensions $a = 1.0579(2)$ nm, $b = 1.2423(3)$ nm, $c = 1.9190(4)$ nm, $\alpha = 71.84(1)^\circ$, $\beta = 80.50(2)^\circ$, $\gamma = 88.60(1)^\circ$, $V = 2.3625(9)$ nm³, $R = 0.0407$ and $R_w = 0.0656$. The complex results from bridging of two $\text{Cu}(\text{phen})^{2+}$ units by three carboxylate groups, and each Cu^{2+} ion is in a distorted square pyramidal geometry with two nitrogen atoms of phen and three carboxylate oxygen atoms of POAc. It has been showed that intramolecular stacking interactions occur between the phenyl moieties of POAc and aromatic rings of phen, leading to a novel molecule structure with two coordinating modes of carboxylate ligands, of which two phenylacetates are μ_2 -carboxylate-*O*-bridging ligands, and the other is a μ_2 -carboxylate-*O*, *O'*-bridging ligand.

Keywords Phenanthroline, phenylacetate, copper(II) complex, stacking interaction, crystal structure

Introduction

Weak interactions play vital roles in highly efficient and specific biological reactions¹ and are essential for molecular recognition and self-organization of molecules

in supramolecular chemistry inspired by biology.^{2,3} Among the interactions, the intramolecular stacking interaction between suitable aromatic moieties of the two-coordinated ligands in the mixed-ligand complexes is especially fascinating because this interaction may be regarded as a model for metalloenzyme-substrate or metalloenzyme-inhibitor⁴ and used to interpret the antitumor mechanism of a new class of antitumor compounds with the general formula $\text{cis-}[\text{Pt}(\text{NH}_3)_2(\text{N-het})\text{Cl}]$.⁵

Mixed-ligand complexes involving 1, 10-phenanthroline and phenylalkancarboxylate ligands have been the object of extensive investigations in solution,⁶⁻¹² but very few reports have appeared concerning their characterization in the solid state.⁶ The wide interest of investigators in these complexes arises essentially from two reasons: (a) phenylalkancarboxylates are of biological importance,^{13,14} and transition metal ion-phen systems are used as reagents to degrade deoxyribonucleic acids or to modify microsomal proteins;¹⁵ (b) they form good systems suitable for the systematical study of the effect of structural alterations on the intramolecular aromatic-ring stacking interaction,⁷ and many of the results obtained with these complexes may be generalized and extrapolated to the situation with other complexes.

In order to get detailed information on the structure

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dependence of stacking interaction in the complexes, in the present investigation, the title compound was synthesized and characterized by elemental analysis, IR spectroscopy and X-ray diffraction methods.

Experimental

Synthesis

1,10-Phenanthroline (0.5 mmol) and $C_6H_5CH_2COONa$ (0.5 mmol) were dissolved in 30 mL of warm 50% (V/V) ethanol-water. To this solution was added $Cu(ClO_4)_2 \cdot 6H_2O$ (0.5 mmol) under stirring, and then the pH of the resulting solution was adjusted to about 4.5 with dilute NaOH solution. This solution was allowed to stand at room temperature. Blue green precipitate was produced after 1 d. Dark blue crystals formed within 3 weeks when resulting precipitate was recrystallized in

50% (V/V) ethanol-water. The crystals were filtered and air-dried. Anal. $C_{48}H_{45}N_4ClCu_2O_{14}$. Calcd.: C, 54.16; H, 4.26; N, 5.26. Found: C, 54.10; H, 4.19; N, 5.31.

Physical measurements

The IR spectrum (KBr disc) was recorded in the 400–4000 cm^{-1} range on a Nicolet 170SX spectrophotometer. The elemental analyses (carbon, nitrogen and hydrogen contents) were performed on a Perkin-Elmer 240C microanalyser.

X-Ray structural determination of the complex

Crystal data and some experimental details of data collection and refinement for the complex are listed in Table 1.

Table 1 Crystallographic data of the molecule $[Cu_2(phen)_2(POAc)_3]ClO_4 \cdot 4H_2O$

Formula	$C_{48}H_{45}ClCu_2N_4O_{14}$
<i>M</i>	1064.41
Colour	dark blue
Crystal size (mm)	0.40 × 0.40 × 0.36
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 1.0579(2)$ nm $\alpha = 71.84(1)^\circ$ $b = 1.2423(3)$ nm $\beta = 80.50(2)^\circ$ $c = 1.9190(4)$ nm $\gamma = 88.60(1)^\circ$
Volume (nm ³), <i>Z</i>	2.3625(9), 2
<i>D_c</i> (g/cm ³)	1.496
μ (mm ⁻¹)	1.029
<i>F</i> (000)	1096
Temperature (K)	295(2)
Diffractometer	Simens P4
Radiation, λ (nm)	Mo- K_α , 0.071073
θ range for data collection	1.73 to 25.00°
Range of <i>h</i> , <i>k</i> , <i>l</i>	$0 \leq h \leq 12$, $-14 \leq k \leq 14$, $-22 \leq l \leq 22$
Reflections measured	8996
Independent reflections	8221 ($R_{int} = 0.0134$)
Reflections used in the refinement	8215
Reflections with $I > 2\sigma(I)$	5023
Absorption correction type	ψ -scans
Refined parameters	622
Goodness of fit on F^2	0.916
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0407$, $wR_2 = 0.1022^b$
<i>R</i> indices (all data)	$R_1 = 0.0656$, $wR_2 = 0.1194$
Max., min. height in final ΔF map (e/nm ³)	581, -428

$$^a R = \sum [\| F_o \| - | F_c \|] / | F_o |. \quad ^b wR = [\sum w (| F_o | - | F_c |)^2 / \sum w (F_o)^{1/2}], \quad w^{-1} = [\sigma^2 (F_o^2) + (0.0682 P)_2],$$

$$P = (F_o^2 + 2 F_c^2) / 3.$$

The structure was solved by direct methods (SHELXS-86), refinements were carried out by full-ma-

trix least-squares on all F_2 data using the SHELXL-93 software.¹⁶ All non-hydrogen atoms were assigned to anisotropic displacement parameters. All the hydrogens located from a ΔF map (except the hydrogen atoms of the water molecules) were isotropically refined in the last

cycle. The atomic scattering factors were taken from the literature.¹⁷ All calculations were performed on an IBM 586 computer by using the SHELXTL system of computer program.¹⁶ Selected bond lengths and angles are listed in Table 2.

Table 2 Selected bond lengths (nm) and angles ($^\circ$) with e. s. d. s in parentheses

Cu(1)—O(1)	0.1937(2)	Cu(1)—O(5)	0.1964(2)
Cu(1)—N(1)	0.1996(3)	Cu(1)—N(2)	0.2003(3)
Cu(1)—O(3)	0.2279(2)	Cu(2)—O(2)	0.1931(2)
Cu(2)—O(3)	0.1949(2)	Cu(2)—N(4)	0.2002(3)
Cu(2)—N(3)	0.2003(3)	Cu(2)—O(5)	0.2360(2)
Cl—O(10)	0.1235(6)	Cl—O(9)	0.1338(6)
Cl—O(8)	0.1355(5)	Cl—O(7)	0.1373(6)
O(1)-Cu(1)-O(5)	95.15(9)	O(1)-Cu(1)-N(1)	90.84(10)
O(5)-Cu(1)-N(1)	170.21(10)	O(1)-Cu(1)-N(2)	172.40(10)
O(5)-Cu(1)-N(2)	91.47(10)	N(1)-Cu(1)-N(2)	82.10(11)
O(1)-Cu(1)-O(3)	91.33(9)	O(5)-Cu(1)-O(3)	83.48(9)
N(1)-Cu(1)-O(3)	104.15(10)	N(2)-Cu(1)-O(3)	93.12(9)
O(2)-Cu(2)-O(3)	93.78(9)	O(2)-Cu(2)-N(4)	171.87(10)
O(3)-Cu(2)-N(4)	94.18(10)	O(2)-Cu(2)-N(3)	89.81(10)
O(3)-Cu(2)-N(3)	168.74(10)	N(4)-Cu(2)-N(3)	82.07(11)
O(2)-Cu(2)-O(5)	88.79(9)	O(3)-Cu(2)-O(5)	81.66(9)
N(4)-Cu(2)-O(5)	93.95(9)	N(3)-Cu(2)-O(5)	109.10(10)
Cu(2)-O(3)-Cu(1)	94.02(9)	Cu(1)-O(5)-Cu(2)	91.16(9)
O(3)-C(33)-C(34)	116.2(3)	C(35)-C(34)-C(33)	111.0(3)
O(5)-C(41)-C(42)	115.3(3)	C(43)-C(42)-C(41)	112.9(3)
O(10)-Cl-O(9)	111.9(7)	O(10)-Cl-O(8)	110.8(7)
O(9)-Cl-O(8)	108.8(5)	O(10)-Cl-O(7)	114.6(6)
O(9)-Cl-O(7)	105.2(5)	O(8)-Cl-O(7)	105.0(4)

Results and discussion

The result of chemical analyses of the complex agrees well with the following formula: $[\text{Cu}_2(\text{phen})_2(\text{POAc})_3]\text{ClO}_4 \cdot 4\text{H}_2\text{O}$.

IR spectroscopy

The important IR spectral bands provide evidence for the structure of the complex. The absence of any bands in the region 1750–1700 cm^{-1} in the IR spectrum of the isolated complex suggests the coordination of the COO^- group of the phenylacetate to the metal ion.

The bands at 1608 and 1343 cm^{-1} are ascribed, respectively, to $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ of the μ_2 -carboxylate-*O*-bridging phenylacetate ligands, with a difference value of about 263 cm^{-1} . Moreover, the bands at 1568 and 1429 cm^{-1} are indicative of another coordinating mode of phenylacetate ligands, *i. e.*, μ_2 -carboxylate-*O, O'*-bridging phenylacetate ligands.¹⁸

The band at 3441 cm^{-1} can be attributed to the stretching vibration of uncoordinated water molecules, which is in agreement with the obtained result by X-ray diffraction method.

Crystal structure of $[\text{Cu}_2(\text{phen})_2(\text{POAc})_3]\text{ClO}_4 \cdot 4\text{H}_2\text{O}$

A summary of crystal data of the complex is given in Table 2. The structure consists of binuclear $[\text{Cu}_2(\text{phen})_2(\text{PhCH}_2\text{COO})_3]^+$ cations, considerably disordered ClO_4^- anions and H_2O molecules hydrogen-bonded to the carboxylate oxygens of the cations (Fig. 1). The cations result through bridge formation between two Cu^{2+} ions by two coordinating modes of carboxylate ligands, of which two phenylacetates are μ_2 -carboxylate- O bridging ligand, and the other is μ_2 -carboxylate- O, O' -bridging ligands, which is in striking contrast with the

similar binuclear $\text{Cu}(\text{II})$ complexes reported in the reference.⁶ The coordination sphere around each $\text{Cu}(\text{II})$ is approximately square pyramidal by two phen nitrogens and two carboxylate oxygens occupying basal sites and an axial carboxylate oxygen with a bond significantly longer than that of the basal atoms. The $\text{Cu}^{2+} - \text{Cu}^{2+}$ distance of the complex is 0.3007 nm, which is similar to that found for $[\text{Cu}_2(\text{phen})_2(\text{PPr})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$.⁶

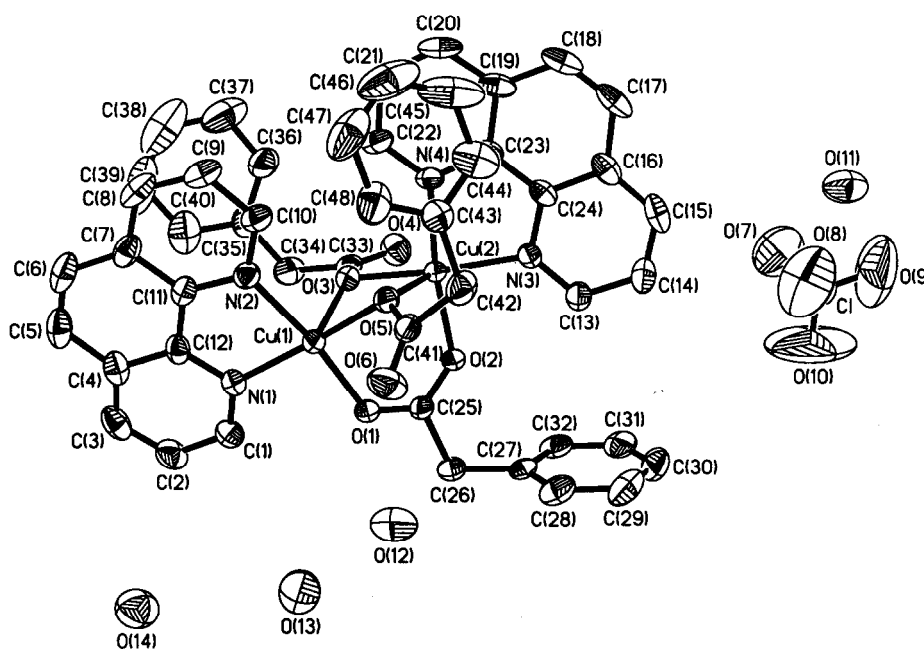


Fig. 1 ORTEP drawing of the complex $[\text{Cu}_2(\text{phen})_2(\text{POAc})_3]\text{ClO}_4 \cdot 4\text{H}_2\text{O}$.

From Fig. 1 it is evident that there is a pronounced interaction between the 1,10-phenanthroline and phenyl ring of phenylacetates in the complex. This interaction is usually called an intramolecular aromatic-ring stacking interaction.⁸ The two stacked phenylacetates are bent at C(33) and C(34) and at C(41) and C(42), respectively, resulting in an optimal fit of the planes of phenanthrolines and phenyl ring of the phenylacetates. The shortest atom to atom distances within the stacking aromatic rings are 0.320 and 0.323 nm, which is comparable with those for related stacking complexes,^{6,19} and the dihedral angles between the aromatic rings amount to 33.3 and 33.2°. This shows that the two intramolecular phenyl-phen stacking interactions are of almost the same strength. However, the fashion of stacking interaction in the complex is in contrast with the similar complex in the literature.⁶ This shows that the struc-

ture of the stacked molecules has a great influence on the interaction.

One interesting feature of the stacking interaction is that the two stacked phenylacetates form a μ_2 -carboxylate- O -bridging ligand, and the other unstacked phenylacetate forms a μ_2 -carboxylate- O, O' -bridging ligand, leading to a binuclear $\text{Cu}(\text{II})$ complex with a novel molecular structure.

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