Note

Synthesis, Characterization and Molecular Structure of Ternary Cu(II) Complex with 1,4,8,9-Tetraazatriphenylene and L-Phenylaninate

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The complex [Cu(L-Phe)(TATP)(H₂O)]ClO₄·0.5H₂O has been synthesized and investigated by elemental analysis, molar conductivity, spectroscopic and X-ray diffraction methods, where TATP = 1,4,8,9-tetraazatriphenylene and L-phe = L-phenylaninate group. The complex crystallizes in the triclinic space group $P\bar{1}$ with two molecules in a unit cell of dimensions $a = 0.5730(1)$, $b = 1.0190(2)$, $c = 2.1430(4)$, $\alpha = 97.50$ $(1)°$, $\beta = 95.33(3)°$, $\gamma = 102.85(1)°$, $V = 1.1998(4)$ nm^3, $R_1 = 0.0360$, $wR_2 = 0.0400$. The crystal contains two independent [Cu(L-Phe)(TATP)(H₂O)]⁺ complexes Cu1 and Cu2, having essentially the same distorted square-pyramidal structure, where each Cu(II) ion coordinates two nitrogen atoms of TATP and the amino nitrogen and carboxylate oxygen atoms of L-Phe in the equatorial positions and one water oxygen at an axial position.

Keywords   1,4,8,9-Tetraazatriphenylene, L-phenylaninate, copper(II) complex, crystal structure

Introduction

It has been established[1,2] that ternary metal complexes with an aromatic amine as the primary ligand and amino acids as the second ligands can serve as useful models for ternary enzyme-metal ion-substrate complexes, which play an important role in metalloenzyme-catalysed biochemical reactions. To our knowledge, the complexes have been the object of extensive investigations in solution,[3] but a limited number of X-ray investigations are available.[3(m),4] As a continuation of our interest in this study field,[4(b)] in this work, the complex [Cu(L-Phe)(TATP)(H₂O)]ClO₄·0.5H₂O (TATP = 1,4,8,9-tetraazatriphenylene and L-Phe = L-phenylaninate group) has been synthesized and investigated by elemental analysis, molar conductivity, spectroscopic and X-ray diffraction methods.

Experimental

Materials

All starting materials were commercially available and of analytical grade quality. TATP and Cu(ClO₄)₂·6H₂O were, respectively, prepared according to the literatures.[5,6]

Synthesis of the Cu(II) complex

TATP (1 mmol) and Cu(ClO₄)₂·6H₂O (1 mmol) were dissolved in 25 mL of 80% (V/V) methanol-water

solvent with heating and stirring. To this solution was added dropwise an aqueous hot solution containing *L*-Phe (1 mmol). The pH of the mixture was adjusted to 4 with dilute aqueous NaOH solution. The resulting solution was left at room temperature. Dark blue crystals formed after a week. The crystals were filtered and air-dried. Anal.: $C_{23}H_{21}N_5ClCuO_{7.5}$. Calcd.: C, 47.10; H, 3.61; N, 11.94; Cu, 11.83. Found: C, 46.97; H, 3.54; N, 11.82; Cu, 11.71.

Caution: The solid complex is potentially explosive and should be handled with care.

Physical measurements

The analyses of carbon, nitrogen and hydrogen contents were performed on a Perkin-Elmer 240C microanalyser. The complex was nitrated by the mixture of concentrated nitric acid and perchloric acid, and then the copper content was measured by chelatometric titration with the disodium salt of EDTA standardized against standard zinc. Molar conductivity was measured in methanol with a DDS-11A conductometer. The infrared and far-infrared absorption spectra in KBr disks were recorded in the range 200—4000 cm^{-1} on a Nicolet 170SX spectrophotometer. The electronic absorption spectrum of the complex was measured in methanol on a Pharmacia 4000 UV-Vis spectrophotometer at room temperature. A prismatic well-shaped crystal was chosen and directions of axes were measured by X-diffraction analysis, and then anisotropic X-band ESR spectra of the complex in the crystalline state were recorded on a Bruker ECS 106 spectrometer at ambient temperature with a frequency modulation of 100 kHz.

X-Ray structural determination of the complex

A single crystal with size of 0.23 mm × 0.18 mm × 0.11 mm was mounted on a Bruker Smart 1K CCD system diffractometer with graphite monochromated Mo K_α radiation at $\lambda = 0.071069$ nm. The SMART program was applied to search for diffraction peaks to determine cell parameters, data collection and reduction. Absorption corrections were allied with the Siemens Area Detector Absorption program (SADABS).[7] The structure was solved by direct and Fourier methods, refinements were carried out by full-matrix least squares on F^2 with posi-

tional and anisotropic thermal parameters. All the parameters of atomic coordinates, anisotropic thermal parameters for hydrogen atoms were refined to converge. All calculations were performed on a PC computer with the Siemens SHELXS97[8] and SHELXL97[9] program packages, respectively. Absolute structure has been determined by Flack parameter of 0.0148.[10] Details of the structure solution and refinement are shown in Table 1. The selected bond lengths and angles are collected in Table 2.

Results and discussion

The result of chemical analyses of the title complex agrees well with the following formula: $[Cu(L$-Phe$)(TATP)(H_2O)]ClO_4 \cdot 0.5H_2O$. The complex is soluble in DMF, methanol or ethanol, but not in water or ether *etc*. Molar conductivity measurement in methanol would give credence to this idea, with the complex approaching 1:1 electrolyte value[11] ($\Lambda = 97.3$ S·cm^2/mol).

Crystal structure

The complex is composed of the discrete $[Cu(L$-Phe$)(TATP)(H_2O)]^+$ cations, perchlorate anions, and crystallization water molecules. Interestingly, the crystal of the complex contains two independent $[Cu(L$-Phe$)(TATP)(H_2O)]^+$ complexes **Cu1** and **Cu2**, having essentially the same compositions and coordination structure which is similar with the complex reported recently $[Cu(L$-Phe$)(bipy)(H_2O)]ClO_4$.[3(m)] Each Cu(II) ion coordinates two nitrogen atoms of TATP and one amino nitrogen and one carboxylate oxygen atoms of *L*-Phe in the equatorial positions [Cu(1)—N(3) = 0.2036(3), Cu(1)—N(4) = 0.2008(3), Cu(1)—N(5) = 0.1981(3), and Cu(1)—O(1) = 0.1932(3) nm for complex **Cu1** and Cu(2)—N(8) = 0.1998(3), Cu(2)—N(9) = 0.2006(3), Cu(2)—N(10) = 0.1995(3), and Cu(2)—O(3) = 0.1948(3) nm for complex **Cu2**] and one water oxygen at an axial position [Cu(1)—O(1w) = 0.2240(3) nm for complex **Cu1** and Cu(2)—O(2w) = 0.2308(3) nm for complex **Cu2**], the resulting coordination geometry being described as a distorted square pyramid (Fig. 1). The bond lengths around the Cu atom agree well with those for the complex $[Cu(L$-Phe$)(phen)(H_2O)]ClO_4$.[4(a)]

Table 1 Crystallographic data of the molecule [Cu(L-Phe)(TATP)(H$_2$O)]ClO$_4$·0.5H$_2$O

Formula	C$_{23}$H$_{21}$ClCuN$_5$O$_{7.5}$
M	586.44
Crystal size (mm^3)	0.23 × 0.18 × 0.11
Crystal system	triclinic
Space group	P1
Unit cell dimensions	a = 0.5730(1), b = 1.0190(2), c = 2.1430(4) nm
	α = 97.50(1)°, β = 95.33(3)°, γ = 102.85(1)°
Volume (nm^3), Z	1.1998(4), 2
D$_c$ (g/cm^3)	1.623
μ (mm^{-1})	1.080
F (000)	600
Temperature (K)	293(2)
θ range for data collection	4.09 to 30.05°
Reflections measured	8474
Independent reflections	7321 (R$_{int}$ = 0.0132)
Reflections used in the refinement	7321
Reflections with I > 2σ(I)	5023
Refined parameters	676
Goodness of fit on F^2	0.993
Final R indices [I > 2σ(I)]	R$_1$ = 0.0360, wR$_2$ = 0.0947
R indices (all data)	R$_1$ = 0.0400, wR$_2$ = 0.0971
Mar., min. height in final ΔF map (e/nm^3)	451, −437

Table 2 Selected bond lengths (nm) and angles (°) with e.s.d.s. in parentheses

Cu(1)—O(1)	0.1932(3)	Cu(2)—O(3)	0.1948(3)
Cu(1)—N(5)	0.1981(3)	Cu(2)—N(10)	0.1995(3)
Cu(1)—N(4)	0.2008(3)	Cu(2)—N(8)	0.1998(3)
Cu(1)—N(3)	0.2036(3)	Cu(2)—N(9)	0.2006(3)
Cu(1)—O(1W)	0.2240(3)	Cu(2)—O(2W)	0.2308(3)
N(5)···O(3Wa)	0.2887(6)	N(5)···O(2b)	0.2890(4)
N(10)···O(4d)	0.3073(5)	O(1w)···O(2b)	0.2980(4)
O(2w)···O(3d)	0.2860(4)	O(2w)···N(1e)	0.2967(5)
O(1)-Cu(1)-N(5)	84.68(12)	O(3)-Cu(2)-N(10)	83.92(11)
O(1)-Cu(1)-N(4)	91.89(12)	O(3)-Cu(2)-N(8)	94.81(12)
N(5)-Cu(1)-N(4)	173.19(13)	N(10)-Cu(2)-N(8)	178.54(14)
O(1)-Cu(1)-N(3)	160.34(12)	O(3)-Cu(2)-N(9)	164.31(14)
N(5)-Cu(1)-N(3)	99.48(12)	N(10)-Cu(2)-N(9)	98.73(12)
N(4)-Cu(1)-N(3)	81.83(12)	N(8)-Cu(2)-N(9)	82.31(12)
O(1)-Cu(1)-O(1W)	104.71(13)	O(3)-Cu(2)-O(2W)	105.75(13)
N(5)-Cu(1)-O(1W)	95.34(12)	N(10)-Cu(2)-O(2W)	88.69(12)
N(4)-Cu(1)-O(1W)	91.22(12)	N(8)-Cu(2)-O(2W)	92.35(12)
N(3)-Cu(1)-O(1W)	94.08(12)	N(9)-Cu(2)-O(2W)	89.81(13)

Symmetry transformations used to generate equivalent atoms: a. x + 1, y + 1, z; b. x + 1, y, z; c. x + 2, y, z + 1; d. x − 1, y, z; e. x + 2, y + 1, z + 1.

Although the two complex units are similar, a number of differences can be found on closer inspection, of which the most notable one is seen in intramolecular di-hedral angles between the side chain aromatic ring of L-Phe and the aromatic ring of TATP. The dihedral angle for complex **Cu1** is 48.6°, but that for complex **Cu2** is

81.5°, which may be caused by N(5)···O(2b) hydro-   gen bond.
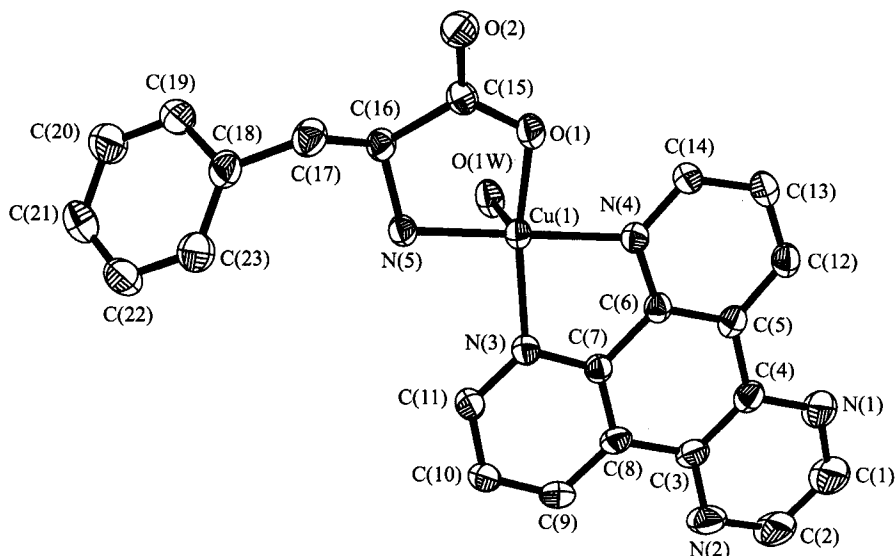
Fig. 1 Structure of one of two crystallographically independent molecules of [Cu(*L*-Phe)(TATP)(H₂O)]⁺.
The perchlorate ion, water molecule and hydrogen atoms were omitted for clarity.

It is noteworthy that there is no intramolecular aromatic stacking interaction between the *L*-Phe and TATP ligands in the complex, which is most probably due to the self-stacking of the aromatic rings of TATP ligands and the benzene rings of *L*-Phe ligands and intermolecular stacking interaction on each other throughout the crystal, thereby prohibiting the formation of intramolecular stacking between them (Table 3), and partly due to the existence of intermolecular hydrogen-bonding interaction between coordinated water O(2w) and nitrogen atom N(1) of TATP ligand [O(2w)···N(1) = 0.2967(5) nm in *x* + 2, *y* + 1, *z* + 1].

Table 3 Intermolecular aromatic-ring stacking interactions in the complex

Mode	Dihedral angle (°)	Average spacing (nm)
benzene ring (Cu1)—benzene ring (Cu1)	0	0.337
TATP ring (Cu1)—TATP ring (Cu1)	0	0.341
TATP ring (Cu2)—TATP ring (Cu2)	0	0.345
benzene ring (Cu1)—TATP ring (Cu2)	10.2	0.349

Infrared and far-infrared absorption spectra

The infrared spectrum of the complex shows a strong and broad band at 3441 cm⁻¹ which is most likely ascribed to the stretching vibrations of water molecules. The bands at 3310 and 3285 cm⁻¹ can be attributed to the stretching vibrations of the coordinated NH₂ group. The bands at 1636 and 1314 cm⁻¹ can be attributed, respectively, to the antisymmetric and symmetric stretching vibrations of the coordinated carboxylate, showing that the carboxylate is monodentate. Thus, one can deduce that the monovalent anions of *L*-Phe are coordinated to the metal ion as a bidentate N, O-ligand. The band at 1582 cm⁻¹ is most likely assigned to the stretching vibration of the C = N group of the TATP ligand and confirms its coordination to the metal ions.

In low frequency range, several new bands, which can not be observed in the *L*-Phe and TATP ligands, appear in the complex. The band at 441 cm⁻¹ can be assigned to the Cu—N (amino group) and Cu—O (water) stretching vibration. The bands at 251 and 350 cm⁻¹ can be attributed to the Cu—N (N = C group) and Cu—O (carboxylate) stretching vibrations, respectively.[12]

Electronic absorption spectra

The electronic absorption spectrum of the complex in the methanol solution presents two important absorption bands: the band at 257 nm [$\varepsilon = 55600$ L/(mol·cm)] can be attributed to the π-π^* transitions of the coordinated TATP and L-phenylaninate, and the broad absorption bond at 603 nm [$\varepsilon = 116$ L/(mol·cm)] to the d-d transition of the central Cu^{2+} ion.

In addition, a weak broad absorption band, which can not be observed in the spectra of TATP, L-Phe and [Cu(L-Ala)(TATP)(H_2O)]ClO$_4$, appears at 368 nm [$\varepsilon = 124$L/(mol·cm)]. The band may be assigned to the charge transfer (CT) between the aromatic ring of TATP and the benzene ring of L-Phe in the complex, which is usually called intramolecular aromatic-ring stacking interaction.[3(m),13] Therefore, we suggest the possibility of following conformational equilibrium in methanol for the complex:

$$\{[Cu(L\text{-Phe})(TATP)(H_2O)]^+\}_{op} =$$
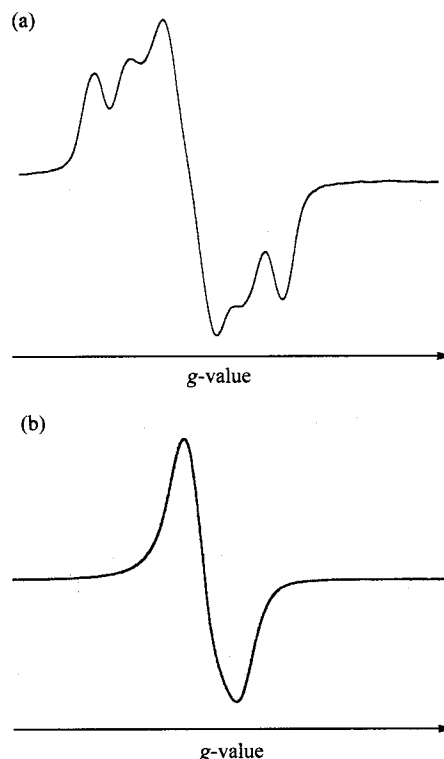$$\{[Cu(L\text{-Phe})(TATP)(H_2O)]^+\}_{cl}$$
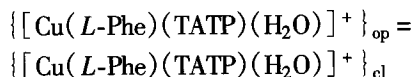
where op represents unstacked opened isomer and cl expresses closed one with the stacking interaction. The structural change between the unstacked and stacked structures may be principally responsible for the conformational change of the carbon backbond of the L-Phe ligand.

Electron paramagnetic resonance spectra

In order to yield more accurate crystal g-values, the single-crystal ESR spectra (Fig. 2) for the complex were measured at room temperature.

The g-values (> 2.03 G) of the spectra and $g_\parallel$ (2.14 G) > $g_\perp$ (2.07 G) indicate a distorted square-based pyramidal copper environment[14] (i.e., a $d_{x^2-y^2}$ ground state), which is in agreement with the obtained result by X-diffraction method. However, comparing the spectra of the complex with those of other copper complexes with a similar distorted square-based pyramidal structure, some differences can be found. The most notable one is that there are more absorption bands for the complex in the direction of magnetic field compared to other complexes with the similar structure, which may be attributed to the crystal containing two independent [Cu-

(L-Phe)(TATP)(H_2O)]$^+$ complexes **Cu1** and **Cu2**, having different bond lengths and angles.

Fig. 2   Single-crystal X-band ESR spectra of [Cu(L-Phe)-(TATP)(H_2O)]ClO$_4$·0.5H$_2$O at room temperature when (a) c (crystal axis of the complex) ‖ M (magnetic field) and (b) $c \perp M$.

Supplementary data

Crystallographic data have been deposited with the CCDC (12 Union Road, Cambridge, CB2 1EZ, UK) and are available on request quoting the deposition number CCDC 150441.

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