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Mixed ligand tris-chelate of copper(II) with *N*,*N*-donor ligands – Synthesis, structure and spectra of $[Cu(en)(phen)_2]X_2{\cdot}2phen{\cdot}8H_2O$ ($X = Cl^-, NO_3^-$)

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ABSTRACT

$[Cu(en)(phen)_2]^+$ is crystallized along with two phenanthroline and eight lattice water molecules either as a chloride or a nitrate salt. The cation has almost identical structural and spectral properties which correspond to a tetragonally elongated octahedral geometry with the en ligand in the equatorial plane. EPR parameters reveal a slight rhombicity in the coordination polyhedron. Even though both compounds have the same composition (except for the anions), the hydrogen bond networks involving the lattice water molecules and anions are quite different in the two compounds. There are also extensive π-stacking interactions involving the phenanthroline molecules, both coordinated and non-coordinated. The nonbonding interactions have a major directing role in the crystallization of the tris-chelate cation. The analogous mixed ligand complex of 2,2-bipyridine could not be crystallized.

1. Introduction

Tris-chelates of copper(II) with *N*,*N*-donor ligands [1] as well as mixed ligand tris-chelates [2] are few in number. While the Cu(II)-tris-chelates of 1,10-phenanthroline (phen) [3], 2,2-bipyridene (bipy) [2,4] and 1,2-diaminoethane (en) [5,6] have been prepared several decades ago, no mixed ligand tris-chelate involving any two of these common ligands have been structurally characterized till now. Since the Cu(II)-tris-chelates are expected to show Jahn–Teller distortion, it is of interest to see which ligand in a mixed chelate will occupy the equatorial position. While entropy change should favor mixed chelates when more than one type of chelating ligands are present, the difficulty in the isolation of mixed tris-chelates is probably related to the greater stability of the crystals of homoleptic tris-chelates and the tendency of Cu(II) to form five or six-coordinate bis-chelates in which the remaining coordination sites are occupied by anions or solvent (usually water) molecules. Even though metathesis reactions between chloride bound Cu(II) mono-chelates and Ag(I) bis-chelates had yielded several mixed tris-chelates, only one complex could be structurally characterized due to difficulty in getting good quality crystals [2]. We have previously reported mixed ligand complexes of copper with acetylacetonate and diimine ligands [7]. They were not tris-chelates, but rather anion or water bound five coordinate complexes. In this paper we report the synthesis, structure and spectral studies of $[Cu(en)(phen)_2](NO_3)_2{\cdot}2phen{\cdot}8H_2O$ (**1**) and $[Cu(en)(phen)_2](Cl)_2{\cdot}2phen{\cdot}8H_2O$ (**2**). The complex cations in these crystals appear to be stabilized by an extensive network of hydrogen bonded lattice water molecules and π-stacking interactions. The fact that mixed ligand cation is preferentially formed irrespective of the mole ratio of the ligands used in the preparation, coupled with the non-formation of similar complex of bipy demonstrates the decisive role played by non-bonded interactions in the crystallization of the mixed tris-chelate.

2. Experimental

2.1. Materials and physical measurements

All chemicals were reagent grade commercial samples and were used without further purification. IR spectra were recorded using KBr disks on a Jasco FT/IR 5300 spectrometer in the range 4000–400 cm^{-1}. Elemental analysis for C, H and N was performed on a Perkin–Elmer 240C elemental analyzer. Electronic spectral measurements were obtained using a Shimadzu UV-3101 PC spectrophotometer and the diffuse reflectance spectra with an ISR-3100 integrating sphere attachment. The EPR spectra of the frozen solutions at 130 K in ethanol were collected on a JEOL JES – FA 200 spectrometer operating at X-band frequency. Spectra were simulated using a previously described computer program [8].

2.2. Synthesis

2.2.1. $[Cu(en)(phen)_2](NO_3)_2(phen)_2(H_2O)_8$ (**1**)

$Cu(NO_3)_2{\cdot}3H_2O$ (0.060 g, 0.25 mmol) and 1,2-diaminoethane (0.017 mL, 0.25 mmol) were dissolved in 25 mL water and heated

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Table 1
Crystallographic data and structure refinement for **1** and **2**.

	1	**2**
Formula	$C_{50}H_{56}CuN_{12}O_{14}$	$C_{50}H_{56}Cl_2CuN_{10}O_8$
Formula weight	1112.61	1059.49
Crystal system	Monoclinic	Monoclinic
a (Å)	19.338(3)	19.061(8)
b (Å)	19.233(3)	19.972(9)
c (Å)	15.003(3)	14.886(7)
α (°)	90	90
β (°)	114.602(3)	116.255(6)
γ (°)	90	90
V (Å^3)	5073.5(15)	5082(4)
Z	4	4
Space group	$C2/c$	$C2/c$
ρ_{calcd} (g cm^{-3})	1.457	1.385
μ(mm^{-1})	0.511	0.598
F(0 0 0)	2324	2212
Crystal size (mm)	0.32 × 0.30 × 0.25	0.45 × 0.45 × 0.36
θ range (°)	1.80–28.29	1.57–26.02
$h/k/l$ indices	−25, 24/−25, 25/−19, 19	−23, 23/−24, 24/−18, 18
Reflections collected	29086	25221
Unique reflections, R_{int}	6084, 0.0535	4968, 0.0634
Goodness-of-fit	0.936	1.049
R (F_0^2)[I > 2σ(I)]	0.0531	0.0606
R_w (F_0^2)[I > 2σ(I)]	0.1362	0.1575
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.364, −0.299	0.874, −0.537

at 80 °C for 10 min with stirring. To this 5 mL methanolic solution of 1,10-phenanthroline monohydrate (0.198 g, 1.00 mmol) was added and stirred for another 5 min and the solution was filtered. The filtrate was kept for evaporation at room temperature. Blue prismatic crystals were formed after 3 days. Yield: 165 mg (0.148 mmol, 59%). *Anal.* calc. for $C_{50}H_{56}CuN_{12}O_{14}$: C, 53.98; H, 5.07; N, 15.11 *Found*: C, 53.99; H, 5.08; N, 15.21. IR (KBr disk, cm^{-1}): 3427, 1626, 1587, 1516, 1350, 842.

2.2.2. Synthesis of [Cu(en)(phen)$_2$](Cl)$_2$(phen)$_2$(H$_2$O)$_8$ (**2**)

The procedure was similar to that of **1**, except for the use of $CuCl_2 \cdot 2H_2O$ (0.043 g, 0.25 mmol). Blue crystals in the form of square shaped blocks were obtained after 1 week. Yield: 160 mg (0.151 mmol, 60%). *Anal.* calc. for $C_{50}H_{56}Cl_2CuN_{10}O_8$: C, 56.68; H, 5.33; N, 13.22 Found: C, 56.69; H, 5.21; N, 13.35. IR (KBr disk, cm^{-1}): 3402, 1622, 1587, 1508, 1419, 844, 727.

2.3. X-ray crystallography

X-ray data were collected on a Bruker SMART APEX CCD X-ray diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 298 K (Table 1). Data were reduced using SAINT-PLUS [9] and a multi-scan absorption correction using SADABS [10] was performed. The structures were solved by direct method using

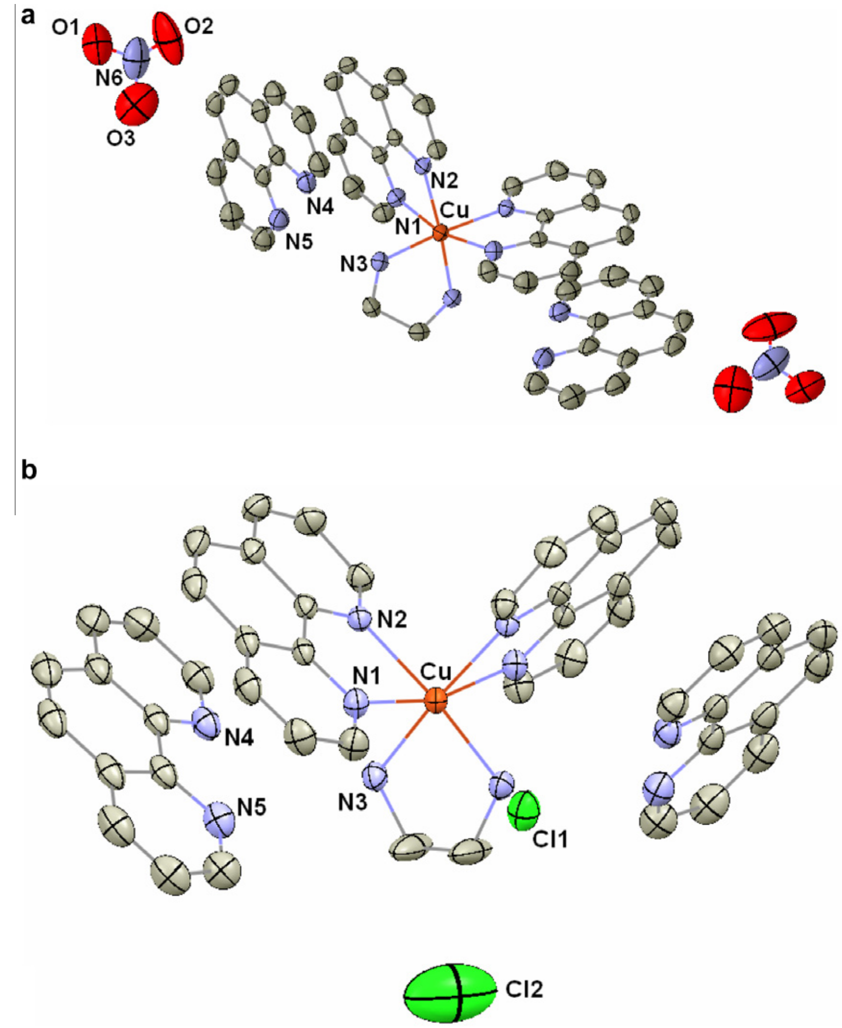

Fig. 1. Thermal ellipsoid plots drawn at 50% probability level showing atom labeling. (a) compound **1**; (b) compound **2**. Hydrogen atoms and solvent water molecules have been omitted for clarity.