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Inorganica Chimica Acta 357 (2004) 1991-1996

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Synthesis, characterization and crystal structure of a monomeric and a macrocyclic copper (II) complex with a large cavity using benzylacetylacetone ligand ☆

Subrata Kumar Dey ^a, Bappaditya Bag ^a, Zhongyuan Zhou ^b, Albert S.C. Chan ^b, Samiran Mitra ^{a,*}

^a Department of Chemistry, Jadavpur University, Kolkata 700 032, West Bengal, India ^b Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Kowloon, Hong Kong

Received 2 July 2003; accepted 13 December 2003

Abstract

The bidentate ligand benzylacetylacetone was used to synthesize the Cu(II) complexes 1 and 2 without and with 4,4'-bipyridine ligand, respectively. The complexes were characterized by analytical and spectroscopic studies. The mononuclear complex $[Cu(C_{10}H_9O_2)_2]$ (1) has been synthesized by the reaction of copper acetate with the ligand whereas the tetranuclear complex $[Cu_4(4,4'-bpy)_4(C_{10}H_9O_2)_4(C_2H_3O_2)_4]$ (2) has been synthesized by the reaction of copper acetate with the ligand followed by the addition of 4,4'-bipyridine. The X-ray analysis shows that the complex 1 has square planar geometry and the complex 2 has square pyramidal geometry around the metal centers. The thermogravimetric studies showed that the complexes undergo decomposition in multiple steps.

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Keywords: Cu(II) monomeric and macrocyclic complexes; Benzylacetylacetone; 4,4'-Bipyridine; Crystal structures

1. Introduction

The ability of 4,4'-bipyridine (4,4'-bpy) and pyrazine (pyz) to act as exo-bidentate ligands, thus giving rise to the formation of oligomeric and polymeric metal complexes, is well established [1–4]. Furthermore, supramolecular chemistry and self-assembly with 4,4'-bpy, pyz and their derivatives are at the frontiers of molecular science, as demonstrated by the intense interest and near exponential growth of publications in this area in the last decade [5]. Many examples exist of 4,4'-bpy and pyz acting as a linear spacer between metal centers to form 1D-chain polymers and 2D square lattice, and three-dimensional (3D) motifs with rigid multitopic organic "spacer" ligand [6–8]. In the supramolecular chemistry of hydrogen-bonded organic molecule, coordination polymers [9] offer a higher potential because of the variety of coordination modes and the peculiarities of the metallic centers. Extending the scope of the crystal engineering to self-assembled metal systems containing two different organic ligands is much less explored, and it is generally not yet possible to predict either the composition or structure of the product of a reaction consisting of a metal center and two different organic ligands.

The deliberate design of a novel networks based on coordination compounds requires a careful selection of the polydentate ligand. In the present study, the synthesis of mononuclear four coordinated Cu(II) complex $[Cu(C_{10}H_9O_2)_2]$ (1) and 4,4'-bipyridine bridged tetranuclear complex $[Cu_4(4,4'-bpy)_4 (C_{10}H_9O_2)_4 (C_2H_3O_2)_4]$ (2) have been reported. Spectroscopic and thermal properties have been investigated for both the complexes along with the X-ray crystal structures.

[☆] Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2003.12.014.

^{*}Corresponding author. Tel.: +91-33-2668-2017/2414-6193; fax: +91-33-2414-6266.

E-mail address: smitra_2002@yahoo.com (S. Mitra).

2. Experimental

2.1. Materials

Benzylacetylacetone, copper acetate (Merck), were used as received.

2.2. Synthesis of the complex 1 and 2

2.2.1. $[Cu(C_{10}H_9O_2)_2]$ (1)

The complex **1** was synthesised by slowly adding a suspension of benzylacetylacetone (2 mmol) in 10 ml methanol to a 15 ml methanolic solution of copper acetate (0.199 g, 1 mmol) at room temperature with constant stirring. Shiny green rod like crystals appeared after 8 h, from which suitable crystals for X-ray analysis were separated. Yield: 54%. *Anal.* Calc. for $C_{20}H_{18}CuO_4$: C, 62.19; H, 5.05; Cu, 16.47. Found: C, 62.20; H, 5.14; Cu, 16.55%.

The complex $[Cu_4(C_{22}H_{20}N_2O_4)_4]$ (2) was prepared by slowly adding a 20 ml methanolic suspension of benzylacetylacetone (1 mmol) to a 20 ml methanolic solution of copper acetate (0.199 g, 1 mmol) at room temperature with constant stirring. To this resulting solution, 4,4'-bipyridine (1 mmol) in 15 ml methanol was added slowly and the resulting mixture was kept at room temperature, which afforded green colored needle shaped crystals after 10 h. The crystals were washed with methanol and air-dried. Yield: 45%. *Anal.* Calc. for $C_{88}H_{80}Cu_4N_8O_{16}$: C, 60.0; H, 4.58; N, 3.19; Cu, 14.44. Found: C, 60.12; H, 4.60; N, 3.17; Cu, 14.49%.

2.3. Physical measurements

Elemental analyses were carried out using a Perkin– Elmer 2400 II elemental analyzer. Infrared spectra were recorded on a Perkin–Elmer 883-IR spectrophotometer using KBr pellets as well as in solution. Electronic spectra were recorded on a Lamda-40 spectrophotometer. Thermal investigations (TGA) were carried out on a Shimadzu TGA-50 thermal analyser under a dynamic nitrogen environment. ¹H NMR spectra was recorded on a Bruker DPX-300 (300 MHz) NMR spectrometer in CDCl₃ using tetramethyl silane (TMS) as internal reference. The magnetic susceptibility were measured for the solid samples at room temperature using a vibrating sample magnetometer using mercury (tetrathiocyanato) cobaltate as a standard.

2.4. X-ray data collection and structure refinement

The pale blue needle shaped crystals of 1 (size $0.30 \times 0.06 \times 0.04 \text{ mm}^3$) and deep green needle shaped crystals of 2 (size $0.38 \times 0.10 \times 0.08 \text{ mm}^3$) were mounted

Table 1 Crystal data and structure refinement for 1 and 2

	1	2	
Empirical formula	$Cu(C_{10}H_9O_2)_2$	$(CuC_{22}H_{20}N_2O_4)_4$	
Formula weight	385.88	1759.76	
Temperature (K)	294(2)	294(2)	
Wavelength (Å)	0.71073	0.71073	
Crystal system	monoclinic	tetragonal	
Space group	$P2_{1}/n$	$I\overline{4}$	
Unit cell dimensions			
<i>a</i> (Å)	4.472(13)	22.466(2)	
b (Å)	10.616(3)	22.466(2)	
<i>c</i> (Å)	18.435(5)	7.472(11)	
β (°)	96.412(4)		
Volume (Å ³)	869.7(4)	3771.2(8)	
Ζ	2	2	
Density (Calc.) (Mg/m ³)	1.473	1.550	
Absorption coefficient (mm ⁻¹)	1.277	1.191	
F(000)	398	1816	
Crystal size (mm ³)	0.30 imes 0.06 imes 0.04	0.38 imes 0.10 imes 0.08	
θ Range for data collection	2.94–27.54°	2.87–27.52°	
Limiting indices	$-5 \leqslant h \leqslant 5, \ -13 \leqslant k \leqslant 13,$	$h \leqslant 5, -13 \leqslant k \leqslant 13, \qquad -27 \leqslant h \leqslant 29, -29 \leqslant k \leqslant 27,$	
	$-18 \leqslant 1 \leqslant 23$	$-9 \leq l \leq 9$	
Reflections collected	5721	12 835	
Independent reflections (R_{int})	1983 (0.0607)	4319 (0.0451)	
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	
Data/restrains/parameters	1983/0/116 4319/0/264		
Goodness-of-fit on F^2	1.030 1.020		
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0679, wR_2 = 0.1590$	$R_1 = 0.0465, wR_2 = 0.1085$	
R indices (all data)	$R_1 = 0.1208, wR_2 = 0.1782$	$R_1 = 0.0776, wR_2 = 0.1202$	
Largest difference in peak and hole (e \mathring{A}^{-3})	0.744 and -0.559	0.579 and -0.380	

on a fine-focus sealed tube of Bruker SMART CCD area detector. The Crystallographic data of 1 and 2 are listed in Table 1. Cell dimension and intensity data for the crystal 1 and 2 were measured at 294(2) K, fitted with graphite-monochromated Mo Ka radiation, $\lambda = 0.71073$ Å. For 1, a total of 5721 reflections in the θ range 2.94–27.54° were collected using ω scans, of these independent, 1983 were and satisfied the $I > 2\sigma(I)[R_{int} = 0.0607]$ criterion of observability and were used in the subsequent structure determination and refinement. For 2, total of 12835 reflections in the θ range 2.87–27.52° were collected using φ and ω scans, of these 4319 were independent, and satisfied the $I > 2\sigma(I)[R_{int} = 0.0451]$ criterion of observability and were used in the subsequent structure determination and refinement. The semi-empirical absorption was applied. The structures were solved by direct methods (SHELXS-97) [10] and refined on F^2 by full-matrix least-squares using all unique data (SHELXL-97) [11]. All the nonhydrogen atoms were refined anisotropically. The final R indices were 0.0679 and 0.1590 for 1, 0.0465 and 0.1085 for 2, respectively, for all observed reflections. Maximum and minimum peaks in the final difference Fourier synthesis were 0.744 and -0.599 for 1, 0.579 and -0.380 for **2** e A⁻³, respectively.

3. Results and discussion

3.1. Infrared spectra

A weak broad band in the region 3150-3300 cm⁻¹ due to OH group in free ligand (in solution) was not observed in the infrared spectra of complex 1 and 2. This indicates that the alcoholic oxygen is deprotonated and coordinated with Cu(II). Carboxylate groups can coordinate to metals in syn-syn, anti-anti, and syn-anti and in monoatomic fashion [12]. The bands of v_{as} (CO₂⁻) at 1680 cm⁻¹ and v_s (CO₂) at 1370 cm⁻¹, respectively, having 310 cm⁻¹ separation value (Δv) [12], is significantly higher than the free carboxylate group indicating the carboxylate group is coordinated with Cu in a monodentate fashion [13], which is unambiguously confirmed by the crystal structure of 2. The bands at 1596, 1535, 1414, 1224, 1074, 1028, 995, 822 cm⁻¹ indicated the presence of 4,4'-bipyridine for complex 2. The v(Cu-O) and all other bands appeared at their usual positions.

3.2. Electronic spectra

Although the electronic spectra of the copper complexes with multidentate Schiff base ligands are not in general good indicators of geometry [14], but help to support it. The spectrum of the complex 1 was recorded in chloroform. For the complex 1, bands appeared in the range 649 cm⁻¹, which assigned for d–d transition and supports the four coordinated square planar geometry around the copper (II) ion with the CuO₄ chromophoric group. The electronic spectrum of the complex **2** in CH₂Cl₂ solution exhibits a sharp band at 860 nm and a broad band with a maximum at 682 nm, characteristic of a distorted square pyramidal CuN₂O₃ coordination polyhedron [15].

3.3. NMR spectra

The ¹H NMR spectra of the copper(II) complexes derived from bidentate ligands have been recorded in CDCl₃. The ¹H NMR spectra of the complexes support the stoichiometric formula [Cu(C₁₀H₉O₂)₂] (1) and [Cu₄(4,4'-bpy)₄(C₁₀H₉O₂)₄(C₂H₃O₂)₄] (2). The aromatic and aliphatic proton signals are in their usual positions. In the ¹H NMR spectrum of the free ligand, the resonance signal due to the free OH group appears at δ 12.4 ppm. This signal is not present in the ¹H NMR spectra of the copper (II) complexes. This confirms that the bonding of the ligand oxygen atoms to Cu(II) occur through the replacement of alcoholic hydrogen, further supporting the observation recorded in infrared spectra.

3.4. Thermal studies

The thermogravimetric analyses of the complex 1 and 2 have been carried out non-isothermally under a flow of dry N₂. The complex 1 is stable up to 145 °C and 2 is stable up to 160 °C. The mass loss in the TGA curve corresponds to the release of coordinated acetate groups from 2 followed by the loss of the 4,4'-bpy molecules in between 161 and 275 °C. On further heating up to 510 °C the oxide residue is left, confirmed by qualitative test. The mass loss in the TGA curve corresponds to the release of two coordinated ligands from 1 between 146 and 450 °C resulting the oxide residue confirmed by qualitative test.

3.5. Magnetic moment

The room temperature magnetic moment of the compound **1** is $1.74\mu_B$ fits well with the spin only value for the copper (II) system. The magnetic moment value per copper atom of the compound **2** is $1.76\mu_B$ at RT slightly higher than the expected value for one unpaired electrons on each.

3.6. Description of the structures

The crystal structure of complex 1 consists of monomeric $[Cu(C_{10}H_9O_2)_2]$ units is shown in Fig. 1 and the molecular packing diagram is shown in Fig. 2, the bond distances and angles are given in the Table 2. Complex 1 crystallizes in monoclinic system with space group



Fig. 1. Perspective view of the complex 1 with atom labeling scheme.



Fig. 2. Molecular packing diagram of complex 1.

Table 2 Bond lengths (Å) and angles (°) for 1 and 2

1 Cu1–O1 Cu1–O2	1.924(3) 1.918(3)	Cu1–O1A Cu1–O2A	1.924(3) 1.918(3)
O1–Cu1–O1A O2A–Cu1–O1A O2–Cu1–O1A	180.00(1) 93.16(12) 86.84(12)	O1–Cu1–O2 O1–Cu1–O2A O2–Cu1–O2A	93.16(12) 86.84(12) 180.00(1)
2 Cu1-O1 Cu1-N3A Cu1-O2 O1 Cu1 O4	1.920(3) 2.015(3) 2.438(3) 91.92(10)	Cul-O4 Cul-N2	1.942(3) 2.051(3)
O4-Cu1-N3A O4-Cu1-N2 O1-Cu1-O2 N3A-Cu1-O2	91.92(10) 86.23(12) 174.03(19) 88.08(16) 97.10(16)	01–Cu1–N3A 01–Cu1–N2 N3A–Cu1–N2 04–Cu1–O2 N2–Cu1–O2	88.05(11) 93.26(12) 92.87(15) 93.10(16)

 $P2_1/n$. The coordination geometry around the Cu(II) ion is square planar with four oxygen donor set arising from two bidentate ligands and the central copper atom is sitting on the inversion center of symmetry. The mean deviation of the plane formed by Cu1, O1, O1A, O2 and O2A is 0, 0, 0, 0 Å. The displacement of the atoms O1, O1A, O2, O2A from the best plane are 0, 0, 0, 0 Å, respectively. The six-membered chelate rings formed by the ligand moiety with the Cu(II) ion are approximately coplanar (mean deviation from the plane is 0.0322 Å). The other angles for O1–Cu1–O2A and O1–Cu1–O2 are lying in between $86.84(12)^\circ$ –93.16(12)°, respectively. Two sets of bond distances are equal and comparable to the other Cu(II) square planar complexes [16,17].

$[Cu_4(4,4'-bpy)_4(C_{10}H_9O_2)_4(C_2H_3O_2)_4]$ (2)

A perspective view of the molecule with atom numbering scheme is shown in Fig. 3 and the molecular packing diagram is shown in Fig. 4 and the bond distances and bond angles are listed in Table 2. The complex has tetra-nuclear unit formed by Cu(II) atom with crystallographic centre of inversion as shown in Fig. 3. The local geometry around each copper atom is distorted square pyramidal which comprises the coordinate plane formed by two nitrogen atoms from two bridging 4,4'-bpy (N2 and N3A), one oxygen (O2) from free acetate ion and two oxygen atoms (O1 and O4) from the ligand. The environment around all the copper atoms are same. 4,4'-bpy and two oxygen atoms from the ligand occupy the basal plane and the axial position is occupied by the acetate ion. In the crystal lattice all the copper atoms have distorted square pyramidal geometry with the geometrical factor $\tau = 2.7^{\circ}$ for Cu1 (it is same for all the Cu atoms).



Fig. 3. Perspective view of the complex 2 with atom labeling scheme.



Fig. 4. Molecular packing diagram of complex 2.

The axial Cu1–O2 distance (2.438(3) A) is longer than equatorial bond distances [1.920(3), 1.942(3), 2.015(3), 2.051(3) for Cu1–O1, Cu1–O4, Cu1–N3A and Cu1–N2, respectively]. All the basal planes are almost parallel. The Cul-CulA and Cul-CulC separation in the tetrameric unit is 7.47 Å in both. Two bidentate ligands form the six edges of the hexagon defined by the four copper atoms and the ring planes lie approximately in the same plane to the square plane. The bond angles for O1-Cu1-N3A and O4-Cu1-N2 are 174.6(2)° and 174.03(2)°, respectively. All the bond distances are comparable to the other Cu(II) square pyramidal complexes [12,18,19]. Compound 2 posses large square cavities with dimensions of 11.470×11.470 Å enclosed by the 4,4'-bpy ligands. The deviation of Cu atom from the least square plane is 0.1297 A.

This design of square- or box-shaped macrocycles self-assembled from square planar metal centers and 4,4'-bpy has attracted much attention in the context of molecular recognition of guests by tailored hosts' [20–26]. Compound **2** is effectively a macrocyclic square that exhibits a clear preference for hydrophobic guests (i.e. arenes, CHCl₃, etc.). This study illustrates the importance of solvent medium upon anion coordination, interpenetration, and which polymeric motif is generated [27,28].

4. Supplementary materials

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic data center, CCDC Nos. 213166 for 1 and 213167 for 2. Copies of this information may be obtained free of charge from The Director, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; deposit@ccdc. cam.ac.uk or www.ccdc.cam.ac.uk).

Acknowledgements

We thank the Council of Scientific and Industrial Research, New Delhi, India for financial assistance to Dr. S.K. Dey. Thanks may also be extended to UGC, New Delhi, India for financial assistance.

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