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Synthesis and Crystal Structure of a Novel Copper (II) Complex with Acetylenedicarboxylate and 2, 2′-Bipyridine

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Abstract: The title compound [Cu (ADC) (2, 2′-bipy)]$_n$ (ADC = $C_2(COO)_2^{2-}$) was prepared and characterized by elemental analysis, IR spectroscopy, X-ray analysis, respectively. The analysis of the crystal structure reveals that the copper atom is five-coordinated with two nitrogen atoms of 2, 2′-bipy and three oxygen atoms of different acetylenedicarboxylate dianions. ADC as bridging ligands link the Cu (II) ions, forming coordination polymer structure.

Keywords: Copper complex, crystal structure, coordination polymer, acetylenedicarboxylate acid.

The construction of molecular-based crystalline solids using coordination polymer has become a very active research field in recent years, not only due to their intriguing structural motifs, but also due to their potential applications in optical, electronic and magnetic materials[1, 2].

Many of the most interesting coordination polymers are based on polycarboxylate ligands, such as maleate[3], malonate[4], 1,4-benzenedicarboxylate[5], 1,3,5-benzenetricarboxylate[6] and 1, 2, 4, 5-benzenetetracarboxylate[7], which have been used successfully. These polycarboxylates mediate magnetic interactions owing to their different coordination modes, accomplishing the transmission of magnetic coupling to different degree[8]. Recently we have started to investigate the possible coordination polymers of the acetylenedicarboxylate dianion. To the best of our knowledge, there are only few reports involving the acetylenedicarboxylate ligand[9,10]. Here we report a novel coordination polymer [Cu (ADC) (2, 2′-bipy)]$_n$, where acetylenedicarboxylate is present as a bridging ligand. Its preparation and structural characterization are presented herein.

A 5 mL aqueous solution containing 0.0570 g (0.5 mmol) acetylenedicarboxylate and 0.0852 g (1 mmol) piperidine was added dropwise to the 5 mL aqueous solution of copper nitrate trihydrate (0.0121 g, 0.5 mmol) with constant stirring. To the resulting reaction mixture, 5 mL methanol solution of 0.0780 g (0.5 mmol) 2, 2′-bipyridine was added dropwise and stirring was continued for 2 h. The reaction solution was left undisturbed at room temperature. After three weeks, blue single crystals suitable for

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X-ray crystal diffraction were obtained. The crystals were filtered, washed with a small amount of cold water, and dried in vacuum; Yield: 0.12 g (73%). Found: C, 51.12; H, 2.41; N, 8.39. Calcd. for $C_{14}H_8N_2O_4Cu$: C, 50.68; H, 2.43; N, 8.44%. IR (KBr pellet, cm^{-1}): 3060 (w), 1641 (vs), 1620 (s), 1600 (sh), 1474 (w), 1444 (m), 1333 (s), 1295 (s), 1153 (w), 1004 (w), 764 (m), 728 (w), 687 (m).

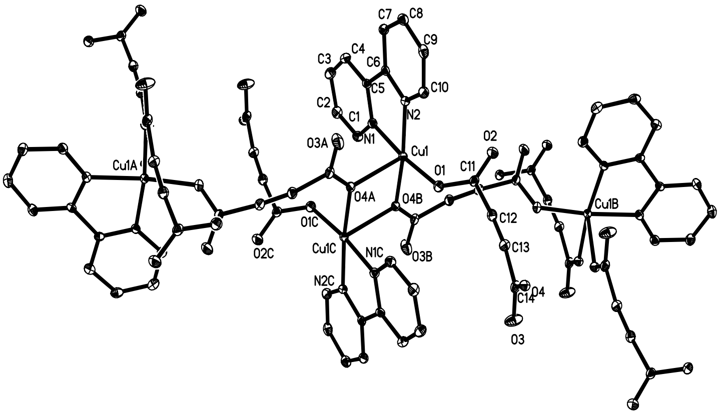
A single crystal of dimensions 0.20 x 0.18 x 0.16 mm was used to determine the crystal and molecular structure of the complex by X-ray structure analysis. The complex forms monoclinic crystals with space group P2 (1)/c, a = 9.842 (2), b = 14.782 (3), c = 8.5491 (17) Å, β = 102.34 (3) °, V=1215.0 (4) $Å^3$, Z = 4, Dc = 1.814 g cm^{-3}, F (0 0 0) = 668, reflections collected = 4195, independent reflections = 2468, R_{int} = 0.0587, GOF on F^2 = 1.123, R_1 = 0.0502 [I >2σ(I)], wR2 = 0.1199 and R_1 (all data) = 0.0734, wR2 = 0.1294. Intensity data were collected on a Rigaku RAXIS-IV IP diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation. The structure was solved by direct methods using SHELXS-86 program and refined by the full-matrix least-squares calculation on F^2 with SHELXL-97 program. The largest peak and hole on the final difference-Fourier map had the value of 0.654 and –0.775 e.$Å^{-3}$, respectively.

The elemental analysis suggested that the complex had the formula [Cu (ADC) (2, 2′-bipy)]$_n$. The IR spectra of the complex clearly showed the existence of acetylenedicarboxylate dianion and 2, 2′-bipyridine ligand. Strong absorptions at 1641, 1620 cm^{-1} are assigned to υ_{as} (COO^-) stretching vibration of acetylenedicarboxylate dianion, and strong absorptions at 1333, 1295 cm^{-1} are assigned to υ_{as} (COO^-) stretching vibration, respectively. Absorptions at 1600, 764 cm^{-1} are assigned to the υ(C=C) and δ(C-H) vibration of the ligand 2, 2′-bipyridine.

Carboxylate group can coordinate to metal ions in different ways. IR spectroscopy is a useful tool in diagnosing the nature of carboxylate coordination. If the separation between υ_{as}(COO^-) and υ_s(COO^-) is significantly less than the free carboxylate anion value, that indicated a bidentate bridging or chelating carboxylate group, if the separation is more than the free anionic value, that is indication of a unidentate ligand[11]. Here the IR spectra of the complex [Cu (ADC) (2, 2′-bipy)]$_n$ displays υ_{as}(COO^-) absorptions at 1641, 1620 cm^{-1} and υ_s(COO^-) absorptions at 1333, 1295 cm^{-1}. Separations of 308 cm^{-1} (1641-1333) and 325 cm^{-1} (1620-1295) were both significantly larger than the value of free acetylenedicarboxylate (200 cm^{-1}). This indicated that the carboxylate groups of the ADC may coordinate with Cu (II) ions in an unidentate mode. Interesting, the complex showed two υ_{as} (COO^-) absorptions and two υ_s (COO^-) absorptions, which indicated that the carboxylate groups may coordinate with Cu (II) ions in two different unidentate modes. The single crystal structural analysis further revealed that the carboxylate groups coordinated with Cu (II) in two unidentate bridging modes.

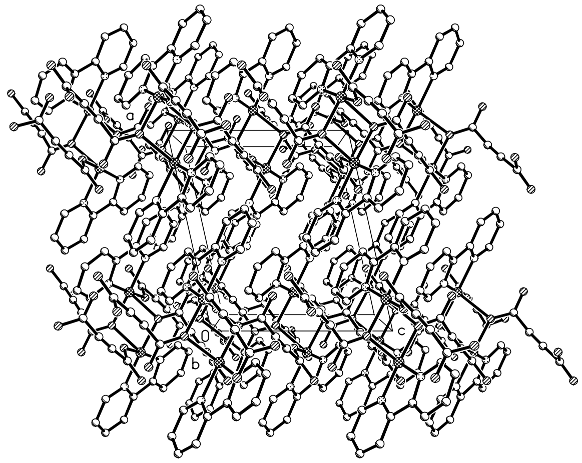
The coordination environment of Cu (II) and the crystal-packing pattern of the complex are shown in **Figure 1** and **Figure 2**, respectively. Each copper (II) ion is five-coordinated with two nitrogen atoms of 2, 2′-bipy and three oxygen atoms of carboxylate groups. These oxygen atoms O (1), O (4A) and O (4B) belong to three different ADC ligands. Cu (1), N (1), N (2), O (1) and O (4B) were in the plane position. Cu (1) – O (4A) was vertical with the coordinate plane and the distance (2.350 (3) Å) was obviously longer than Cu (1) – O (1) distance (1.931 (3) Å) and Cu (1) – O

Figure 1 The molecule structure of [Cu (ADC) (2, 2′-bipy)]$_n$



Selected bond lengths (Å) and angles (°) Cu (1)-O (1) 1.931 (3), Cu (1)-O (4B) 1.978 (3), Cu (1)-O (4A) 2.350 (3), Cu (1)-N (2) 2.008 (3), Cu (1)-N (1) 2.013 (3), C (11)-C (12) 1.473 (6), C (12)-C (13) 1.197 (6), C (13)-C (14) 1.475 (7), O (1)-Cu (1)-O (4B) 90.42 (12), O (4B)-Cu (1)-N (2) 172.52 (13), O (4B)-Cu (1)-N (1) 91.07 (13), N (2)-Cu (1)-N (1) 81.67 (13), N (2)-Cu (1)-O (4A) 100.15 (11), O (1)-Cu (1)-N (2) 97.00 (13), O (1)-Cu (1)-N (1) 172.87 (13), O (1)-Cu (1)-O (4A) 94.80 (12), O (4B)-Cu (1)-O (4A) 78.20 (12), N (1)-Cu (1)-O (4A) 92.33 (12).

Figure 2 Crystal packing pattern of [Cu (ADC)(2, 2′-bipy)]$_n$ (viewed from b axis)



(4B) distance (1.978 (3) Å). This indicated that O (4A) was coordinated to the Cu (II) ion in the apical position, forming a square pyramidal structure.

In addition, the two-carboxylate groups of the acetylenedicarboxylate dianion exhibited two kinds of coordination modes. One carboxylate group acted as an unidentate ligand. While the other carboxylate group exhibited an unusual unidentate-bridging mode, linking two Cu (II) ions by its one oxygen atom. This result was rarely observed in previous reports[12]. The C-C distances in the acetylenedicarboxylate dianion were as expected. For C-C single bond, C (11)-C (12) bond length was 1.473

(6) Å and C (13)-C (14) 1.475 (7) Å. C ≡ C triple bond C (12)-C (13) was 1.197 (6) Å. These data were similar to that found in H_3C-C ≡ C-H (1.460 Å and 1.20 Å for C-C and C ≡ C respectively) [13]. The dianion was almost linear C (11)-C (12)-C (13) = 175.5 (5)°, C (12)-C (13)-C (14) = 171.7 (5)°.

References

1. V. V. Pavlishchuk, I. A. Koval, E. Goreshnik, *et al.*, *Eur. J. Inorg. Chem.,* **2001**, 297.
2. S. Skoulika, P. Dallas, M. G. Siskos, *et al.*, *Chem. Mater.*, **2003,** *15*, 4576.
3. M. X. Li, G. Y. Xie, S. L. Jin, Y. D. Gu, *Polyhedron,* **1996**, *15*, 535.
4. C. Ruiz-Pérez, Y. Rodríguez-Martín, M. Hernández-Molina, *et al.*, *Polyhedron,* **2003**, *22*, 2111.
5. H. J. Choi, M. P. Suh, *Inorg. Chem.,* **1999**, *38*, 6309.
6. H. Li, M. Eddaoudi, T. L. Groy, O. M. Yaghi, *J. Am. Chem. Soc.,* **1998**, *120*, 8571.
7. Q. Shi, R. Cao, D. F. Sun, M. C. Hong, Y. C. Liang, *Polyhedron,* **2001**, *20,* 3287.
8. S. Konar, P. S. Mukherjee, M. G. B. Drew, *et al.*, *Inorg. Chem.,* **2003**, *42*, 2545.
9. I. Pantenburg, U. Ruschewitz, *Acta Crystallogr. Sect. C,* **2002,** *58*, 483.
10. H. Billetter, F. Hohn, I. Pantenburg, U. Ruschewitz, *Acta Crystallogr.*, **2003**, C59, 130.
11. G. B. Deacon, R. J. Phillips, *Coord. Chem. Rev.,* **1980**, *33*, 227.
12. I. G. Muro, F. A. Mautner, M. Insausti, *et al.*, *Inorg. Chem.,* **1998,** *37*, 3243.
13. J. March, *Advanced Organic Chemistry,* Mcgraw-Hill Inc., 2nd ed., **1977**, 17.

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