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Unprecedented 2D Copper(I)-Cyanide Complex with 20-Member Metal Ring: the Effect of the Co-ligand 4,5-diazafluoren-9-one

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Hydrothermal reaction of $Cu(NO_3)_2$, 4,5-diazafluoren-9-one (L) and $K_3[Fe(CN)_6]$, which is used as environment friendly cyanide source, produces a two-dimensional copper cyanide complex $Cu_{10}(CN)_{10}L_4$ (1). In the complex, the L ligands act as corner and bridges ligands simultaneously. With the help of the corner ligands, infinite $Cu(CN)_\infty$ chains are formed. The chains are further bridged by another type of L ligand forming a 2D layer with a $Cu_{20}(CN)_{18}L_2$ macrocycle, which shows blue photoluminescence related to centered π-π* transitions of the L ligand.

The design, synthesis of novel structural coordination polymer with catalysis, adsorption, luminescence, nonlinear optics and magnetism properties is one of the most active subject in the field of inorganic chemistry.[1] Among various coordination complexes, cyanide complex is one of the most investigated families. The history of metal cyanides research can be traced to Prussian Blue $[Fe_4\{Fe(CN)_6\}_3]\cdot xH_2O$ with a typical *pcu* topological structure in the 18th century, and a great deal of work have been done in tailoring that structure,[2] for example in the field of molecule magnetism.[3] Other types of metal cyanides with building block from linear $M(CN)_2$,[4] trigonal $M(CN)_3$,[5] tetrahedral $M(CN)_4$[6] to high connected $M(CN)_7$[7a] and $M(CN)_8$[7b] units were reported with various metal ions. With the help of various co-ligands, metal cyanides, the structures of which are from discrete molecule cube to three-dimensional framework, and the properties of which are single molecule magnetism, spin-crossover, gas absorption and separation, luminescence and so on, were constructed under different assembling conditions.[2a,8] Thus, the study of the assembling, structure and properties of novel metal cyanides is an old subject but evergreen.

Among various metal cyanides, the Copper(I) cyanide complexes are very important in organic, organometallic, and supramolecular chemistry because of both the copper center and the versatile cyanide ligand.[9] The copper cyanide, CuCN, have been found so polymorphic that much attention from the structure study have been drawn. One structure of CuCN contains one-dimensional linear -Cu-(CN)-Cu- chains, similar to those of AgCN and AuCN.[4b,10] If the long linear structure architecture is slightly bent, macrocycles structure will be promisingly constructed.[11] Despite one 2D complex consisting $Cu_{18}(CN)_{16}(Pip)_2$ macrocycle was reported,[12] the macrocycle of copper cyanide with metal ions larger than 12 is very rare,[13] because in the most reported cyclic $[CuCN]_n$ (n = 4,6,7,8,10,12) structure, the trigonal $Cu(CN)_3$ and tetrahedral $Cu(CN)_4$ units in those complexes are apt to bring branches and prevent the growth of the chains into a larger ring.[5,14]

The co-ligands may also negatively influence the constructing of larger cycle, which either restricts the chain in one dimensional or forms additional linkage reducing the number of the metal ions in the macrocycle.[15] It is not an easy task for a co-ligand to overcome the two negative aspects at the same time. In this contribution, a 2D copper cyanide complex $Cu_{10}(CN)_{10}$**L**$_4$ (**1**) (**L**=4,5-diazafluoren-9-one) was formed by using a co-ligand **L**, which is a frequently used ligand but almost ignored in metal cyanide systems. The **L** ligand contains a five number ring, which makes the coordinated chemistry of **L** differs from that of its precursor 1, 10-phenanthroline, which contains a six number ring.[16] That difference makes the **L** ligand act as not only corner ligands but also bridge ligands in **1,** which result in the formation of a 2D layer with $Cu_{20}(CN)_{18}$**L**$_2$ macrocycle. Photoluminescence study of **1** indicated a blue emission of the π-π* transitions of the **L** ligands.

Light orange crystals of **1** were obtained through the hydrothermal reaction of $Cu(NO_3)_2$ and **L** which was synthesized by oxidizing 1,10-phenanthroline with $KMnO_4$,[17] and $K_3[Fe(CN)_6]$ in water. ‡ **1** was characterized by single-crystal *X*-ray diffraction§ and PXRD (Fig. S1). Usually, the KCN/CuCN is used directly as a cyanide source in assembling of copper cyanide complexes, and in few reactions the cyanide anions are generated in situ.[18] Different from the two method above, in obtaining **1** the $K_3[Fe(CN)_6]$ act as cyanide source, which is environmental friendly and used conveniently.[19]

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*†Electronic supplementary information (ESI) available: Additional crystallographic and photoluminescent data. Crystallographic data, PXRD for **1** CCDC 1420117. ESI and crystallographic data in CIF or other electronic format see:*

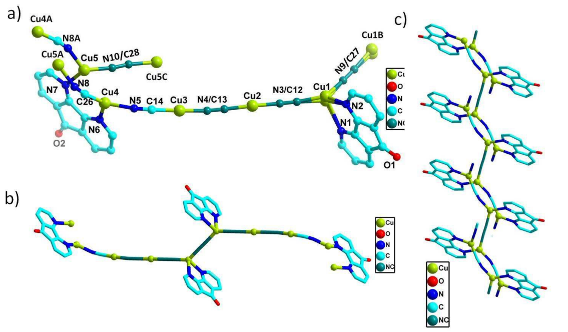

Fig. 1 a) The coordination mode and linkage of metal ions and ligands in **1**. b) The 1D chain constructed by the cyanide copper in **1**. c) The structure of the 1D chains formed by cyanide anions, copper ions and **L** ligand in bridge mode. Symmetry code: A: -1-x,1-y,-z; B:3-x,1-y,1-z;C: -x,1-y,-z.

The structure of **1** is a 2D layer containing two **L** ligands, five Cu(I) ions and six CN^- anions, in which N9/C27 and N10/C28 are half occupied. In **1**, The first type of Cu^I ion is disorder at two close position (Cu1 and Cu1'), in which Cu1 is adopts tetrahedral coordinated geometry coordinated by C12/N3 and N7/C27 atoms from two bridging CN^- groups and two N atoms N1 and N2 of one **L** ligand in chelating mode (Fig. 1a) (Table S1). While the coordinated geometry of Cu1' is different with that of Cu1 with a long Cu1'-N1 distance about 2.563 (9) Å. Cu2 is two-coordinated by N3/C12 and C13/N4 atoms from two CN^- groups forming a linear coordinated geometry (Fig. 1a). The coordination mode of Cu3 is same as that of Cu2 coordinated by N4/C13 and C14. Cu4 and Cu5 adopt a trigonal planar geometry, all coordinated by two CN^- and two N atoms (N7 for Cu5 and N6 for Cu4) from the same **L** ligand. In that way two different types of chain were formed. One chain is $[CuCN]_n$ with a [-Cu1-CN–Cu2–CN–Cu3–CN-Cu4-CN-Cu5-$]_2$ sequence, in which **L** ligand chelate with copper ions acting as corner ligand (Fig. 1b). The other type of chain is formed by **L** in bridge mode, copper ions and cyanide anions. In that chain two **L** ligands and two cyanide anions linked four copper ions forming a $Cu_4L_2(CN_2)_2$ units, which was further connected by cyanide anions to give a 1D structure (Fig. 1c). The two types of 1D chains share copper ions to generate 2D copper(I)-cyanide structure with 20-member metal ring (Fig. 2). And compared with the phen which usually has chelating coordinated mode, the **L** ligands have bridging,[20] chelating[16,21] and monodentate[22] mode in coordinating to metal ions. That is very important in obtaining **1**. And the structure of **1** is very different with that of the 1D complex $[Cu(CN)]_3(phen)$,[5b,23] in which the phen ligand only acts as a chelating ligand.

The 20-member metal ring structure could be comprehended in that way as presented in chart 1. Firstly, three cyanide groups connect the two coppers (Cu2 and Cu3) in the linear coordinated geometry to generate the linear CN-Cu-CN-Cu-CN units. Then the cyanide from one side of unit connects to the copper (Cu1) which is tetrahedral coordinated geometry formed by two cyanide groups and one chelated **L** ligand to form Cu_3 unit. Furthermore, one cyanide group links two Cu_3 units to form a Cu_6 unit. Finally two cyanide groups of the Cu_6 coordinated by two $Cu_4\mathbf{L}_2(CN_2)_2$ of the second type of chains to give the $Cu_{20}(CN)_{18}\mathbf{L}_2$ macrocycle. And it was worth noticing that the **L** ligand take very important roles in forming the macrocycle, first it take in chelating mode restrict the copper cyanide structure growth in one dimension, and then the other type of **L** ligand links those copper cyanide chains to form 2D layer with larger macrocycle structure.

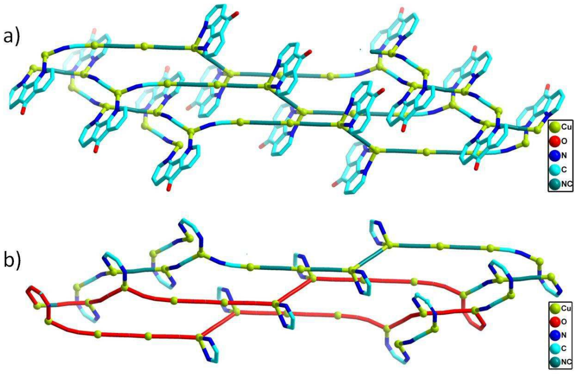

Fig. 2 a) View of the 2D structure of **1**. b) View of simplified 2D structure with 20-member metal ring (highlighted in red)**.**

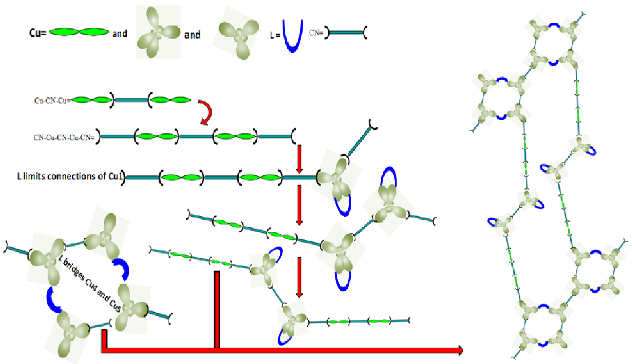

Chart. 1 Schematic representation of the formation of the long chain and the 20-member metal ring.

The photoluminescent properties of **1** and **L** ligand in the solid state at room temperature were studied, intense band in the emission spectra are observed at 389 nm (λ_{ex} =285 nm) for **L** ligand, 391 nm (λ_{ex} =287 nm) for complex **1** (Fig. 3). The bands might be assigned as the metal-to-ligand charge transfer (MLCT) with electrons being transferred from the Cu(I) centers to the unoccupied π* orbitals of the cyanide groups, according to the literature.[24]

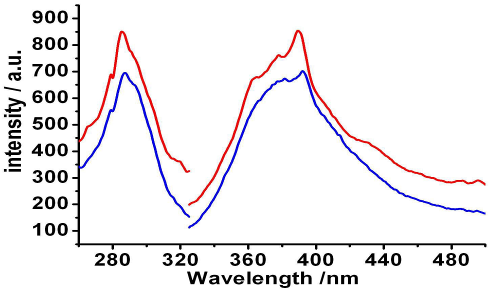

Fig. 3 Excitation spectrum (left) and emission spectrum (right) of the **L** ligand (red) and **1** (blue).

In summary, with the help of the **L** ligand a 20-member metal ring based 2D copper cyanide complex was obtained by using $K_3[Fe(CN)_6]$ as an environment friendly cyanide source. In the complex, it is very rare that the **L** ligand has two functions, one is as chelating ligand, and the other is as bridge ligand, which is the key to form the larger macrocycle structure. The luminescence study indicated blue photoluminescence of **1** related to π-π* transitions of the **L** ligand. This work may not only highlight the rich coordination chemistry of metal cyanide, but also give an impetus to the further synthesis of macrocycle complexes.

Notes and References

‡Synthesis of **1**: a mixture of $Cu(NO_3)_2{\cdot}6H_2O$ (1 mmol), ligand **L** (**L**=4,5-diazafluoren-9-one) (3 mmol), $K_3[Fe(CN)_6]$ (1 mmol), and H_2O (10 mL) was sealed in a Teflonlined autoclave, heated to 120 ℃, and kept for 72 h. Then, the reaction vessel was cooled to room temperature in 12 h. A yellow crystalline product was collected as a mixture of **1**.

§Crystal data for **1**: $C_{54}H_{24}Cu_{10}N_{18}O_4$, Mr = 1624.176, triclinic, space group: P-1, a = 8.0131(16) Å, b = 11.455(2) Å, c = 15.705(3) Å, α=86.68(3)° β=84.63(3)° γ=73.35(3)° V =1374.33 $Å^3$, Z = 1, ρ_{calcd} = 1.963 g cm^{-3} , μ(Mo Kα)=3.851 mm^{-1}, F(000)=11994, GOF=1.108, T=293(2) K, R_1 =0.0504, ωR_2 =0.0817 [I > 2σ(I)]. CCDC 1420117 .

1. (a) A. U. Czaja, T. Natalia and M Ulrich, *Chem. Soc. Rev.,* 2009, **38,** 1284; (b) J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.,* 2011, **112,** 869; (c) K. Mohamedally, *Chem. Soc. Rev.,* 2009, **38,** 1353; (d) C. Janiak, T. G. Scharmann, P. Albrecht, F. Marlow and R. Macdonald, *J. Am. Chem. Soc.*, 1996, **118,** 6307.
2. (a) S. S. Kaye and J. R. Long, *J. Am. Chem. Soc.*, 2005, **127,** 6506; (b) S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H. E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest and M. E. Thompson, *J. Am. Chem. Soc.*, 2001, **123,** 4304.
3. (a) S. Ferlay, T. Mallah, R. Ouahès, P. Veillet and M. Verdaguer, *Nature*, 1995, **378,** 701; (b) S. I. Ohkoshi and H. Tokoro, *Acc. Chem. Res.*, 2012, **45,** 1749.
4. (a) S. J. Hibble and A. M. Chippindale, *Z. Anorg. Allg. Chem.*, 2005, **631,** 542; (b) T. Okabayashi, E. Y.; Koto, F. Okabayashi, T. Ishida and M. Tanimoto, *J. Am. Chem. Soc.*, 2009, **131,** 11712.
5. (a) L.-L. Li, L.-L. Liu, A.-X. Zheng, Y.-J. Chang, M. Dai, Z.-G. Ren and J.-P. Lang, *Dalton Trans.*, 2010, **39,** 7659; (b) Z.-H. Su, Z.-F. Zhao, B.-B. Zhou, Q.-H. Cai and Y.-N. Zhang, *Cryst. Eng. Commun.*, 2011, **13,** 1474.
6. (a) R. Jószai, I. Beszeda, A. C. Bényei, A. Fischer, M. Kovács, M. Maliarik, P. Nagy, A. Shchukarev and I. Tóth, *Inorg. Chem*., 2005, **44,** 9643; (b) D. J. Chesnut, A. Kusnetzow and J. Zubieta, *J. Chem. Soc. Dalton.*, 1998, **24,** 4081.
7. (a) K. Qian, X.-C. Huang, C. Zhou, X.-Z. You, X.-Y. Wang and K. R. Dunbar, *J. Am. Chem. Soc.*, 2013, **135,** 13302; (b) S. Chorazy, R. Podgajny, W. Nitek, M. Rams, S. I. Ohkoshi and B. Sieklucka, *Cryst. Growth Des.*, 2013, **13,** 3036.
8. (a) V. Urban, T. Pretsch and H. Hartl, *Angew. Chem.-Int. Edit.*, 2005, **44,** 2794; (b) X. Liu, G.-C. Guo, A.-Q. Wu, L.-Z. Cai and J.-S. Huang, *Inorg. Chem.*, 2005, **44,** 4282; (c) E. J. Schelter, K. Ferdi, A. Carolina, A. V. Prosvirin, W. Wolfgang and K. R. Dunbar, *J. Am. Chem. Soc.*, 2007, **129,** 8139; (d) T. Delgado, A. Tissot, C. Besnard, L. Guénée, P. Pattison and A. Hauser, *Chem-Eur. J.*, 2015, **21,** 3664.
9. R. D. Pike, *Organometallics.*, 2012, **31,** 7647.
10. (a) S. J. Hibble, S. M. Cheyne, A. C. Hannon and S. G. Eversfield, *Inorg. Chem.*, 2002, **41,** 4990; (b) D. B. Grotjahn, M. A. Brewster and L. M. Ziurys, *J. Am. Chem. Soc.*, 2002, **124,** 5895.
11. J.-D. Lin, Z.-H. Li, T. Li; J.-R. Li and S.-W. Du, *Inorg. Chem. Commun.*, 2006, **9,** 675.
12. D. Chesnut, *Chem. Commun.*, 1998, **16,** 1707.
13. R. D. Pike, A. N. Ley and T. A. Tronic, *Chem. Commun.*, 2007, **36,** 3732.
14. (a) L. Hou, W.-J. Shi, Y.-Y. Wang, B. Liu, W.-H. Huang and Q.-Z. Shi, *Cryst. Eng. Commun.*, 2010, **12,** 4365; (b) A. C.Tsipis and A. V. Stalikas, *J. Comput. Chem.*, 2015, **36,** 1334; (c) B. Sieklucka, J. Szklarzewicz, T. J. Kemp and W. Errington, *Inorg. Chem.*, 2000, **39,** 5156.
15. (a) S. Cui, M. Zuo, H. Wang and J.-Z. Xu, *Anorg. Allg. Chem.*, 2015, **641,** 1540; (b) X.-P. Zhou, S.-H. Lin, D. Li and Y.-G. Yin, *Cryst. Eng. Commun.*, 2009, **11,** 1899.
16. J.-P. Zhao, R. Zhao, Q. Yang, B.-W. Hu, F.-C. Liu and X.-H. Bu, *Dalton Trans.*, 2013, **42,** 14509.
17. (a) L. J. Henderson Jr, F. R. Fronczek and W. R. Cherry, *J. Am. Chem. Soc.*, 1984, **106,** 5876; (b) K. Wright, M. Sarciaux, A. D. Castries, M. Wakselman, J. P. Mazaleyrat, A. Toffoletti, C. Corvaja, M. Crisma, C. Peggion, F. Formaggio and C. Toniolo, *Eur. J. Org. Chem.*, 2007, **19,** 3133.
18. (a) X.-P. Zhou, D. Li, T. Wu and X. Zhang, *Dalton Trans.*, 2006, **20,** 2435; (b) Y.-L. Zhu, L.-L. Qu, J. Zhang, G.-W. Ge, Y.-Z. Li, H.-B. Du and X.-Z. You, *Inorg. Chem. Commun.*, 2011, **14,** 1644.
19. Y.-L. Qin, J.-J. Hou, J. Lv and X.-M. Zhang, *Cryst. Growth Des.*, 2011, **11,** 3101.
20. (a) H.-J. Pang, C.-J. Zhang, J. Peng, Y.-H. Wang, J.-Q. Sha, A.-X. Tian, P.-P. Zhang, Y. Chen, M. Zhu and Z.-M. Su, *Eur. J. Inorg. Chem*, 2009, 5175. (b) H.-J. Pang, J.-Q. Sha, J. Peng, A.-X. Tian, C.-J. Zhang, P.-P. Zhang, Y. Chen, M. Zhu and Y.-H. Wang, *Inorg. Chem. Comm*, 2009, **12**, 735.
21. X.-H. Shi, X.-Z. You, C. Li, R.-G. Xiong and K.-B. Ye, *Transition,Met,Chem*, 1994, **20**, 191.
22. Z.-L. Lu, C.-Y. Duan, Y.-P. Tian, X.-Z. You and X.-Y. Huang, *Inorg, Chem,* 1996, **35**, 2253.
23. S.-W. Liang, M.-X. Li, M. Shao and Z.-X. Miao, *Inorg. Chem. Commun.*, 2006, **9,** 1312.
24. (a) A. Horvath, C. E. Wood and K. L. Stevenson, *Inorg. Chem.*, 1994, **33,** 5351; (b) V. W. W. Yam and K. K. W. Lo, *Chem. Soc. Rev.*, 1999, **28,** 323; (c) J.-P. Lang, Q.-F. Xu, Z.-N. Chen and B. F. Abrahams, *J. Am. Chem. Soc.*, 2003, **125,** 12682; (d) L.-L. Li, L.-L. Liu, Z.-G. Ren, H.-X. Li, Y. Zhang and J.-P. Lang, *Cryst. Eng. Commun.*, 2009, **11,** 2751.

Synopsis

Unprecedented 2D Copper(I)-Cyanide Complex with 20-Member Metal Ring: the Effect of the Co-ligand 4,5-diazafluoren-9-one

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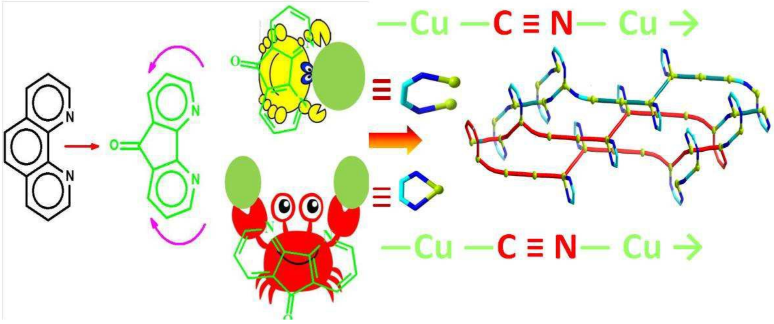

The effects of **L** ligand were illustrated in constructing copper(I)-cyanide complex with 20 member metal rings, in which the **L** ligands act as corner and bridges ligands simultaneously forming a 2D layer with a $Cu_{20}(CN)_{18}$**L**$_2$ macrocycle.