Cent. Eur. J. Chem. • 7(4) • 2009 • 923–928
DOI: 10.2478/s11532-009-0087-y

VERSITA

Central European Journal of **Chemistry**

Synthesis, structures, and spectroscopic properties of copper(I) complexes bearing 7-acetamido-4-methyl-1,8-naphthyridin-2-carbaldehyde azine and 1,2-bis(diphenylphosphino)ethane ligands

Research Article

Shao-Ming Chi[1], Yu-Fei Wang[2], Xin Gan[2], De-Hui Wang[2], Wen-Fu Fu[1,2*]

[1] *Graduate University of Chinese Academy of Sciences,*
Technical Institute of Physics and Chemistry,
Beijing, 100190 P.R China

[2] *College of Chemistry and Chemical Engineering,*
Yunnan Normal University,
Kunming, 650092 P.R China

Received 28 April 2009; Accepted 23 June 2009

Abstract: A new ligand napaa (napaa = 7-acetamido-4-methyl-1,8-naphthyridin-2-carbaldehyde azine) and its two dinuclear copper(I) complexes, $Cu_2(napaa)(dppe)_2(ClO_4)_2$ (**1**) and $Cu_2(napaa)(PPh_3)_4(BF_4)_2$ (**2**) (dppe = 1,2-bis(diphenylphosphino)ethane) and PPh_3 = triphenylphosphine) were synthesized and characterized, and the structure of **1** was determined by X-ray crystal analysis. Each copper atom in **1** has a distorted tetrahedral geometry in which the metal center is associated to napaa and dppe ligands displaying chelating coordination modes and the naphthyridine rings of napaa are almost coplanar. The two complexes exhibit similar electronic absorption spectra with λ_{max} at about 366 nm, which can be tentatively assigned to metal-to-ligand charge-transfer (MLCT) transition. The assignment was further supported by density functional theory (DFT) calculations.

Keywords: *Copper(I) complex • Phosphine ligand •Napaa • Crystal structure • Photophysical properties*

1. Introduction

Polynuclear transition metal complexes with heterocyclic ligands, such as pyrazole, pyridazine, phthalazine, pyridine, and triazole, display a variety of geometries, which have been extensively studied [1-6]. In general, structures of the complexes can be affected by the bulky auxiliary ligand. Bidentate 1,8-naphthyridine derivatives have generated many studies focused on the chemistry of the naphthyridine metal complexes exhibiting intriguing structures [7-10].This is due to their potential applications in luminescence-based sensors, display devices, and probes of biological systems [11-13]. However, the studies on 1,8-Naphthyridyl derivatives with flexible spacers and their metal complexes are rare. The spacers enable the ligand to rotate freely, thereby resulting in various coordination modes and interesting spectroscopic properties [14-18]. Herein, we report on the synthesis, structures and spectroscopic properties of a new ligand napaa with a N-N single bond as a linker (napaa = 7-acetamido-4-methyl-1,8-naphthyridin-2-carbaldehyde azine) and its two dinuclear copper(I) complexes, $Cu_2(napaa)(dppe)_2(ClO_4)_2$ (**1**) and $Cu_2(napaa)(PPh_3)_4(BF_4)_2$ (**2**) (dppe = 1,2-bis(diphenylphosphino)ethane and PPh_3 = triphenylphosphine).

---

* *E-mail: wf_fu@yahoo.com.cn*

2. Experimental Part

2.1. General techniques and apparatus

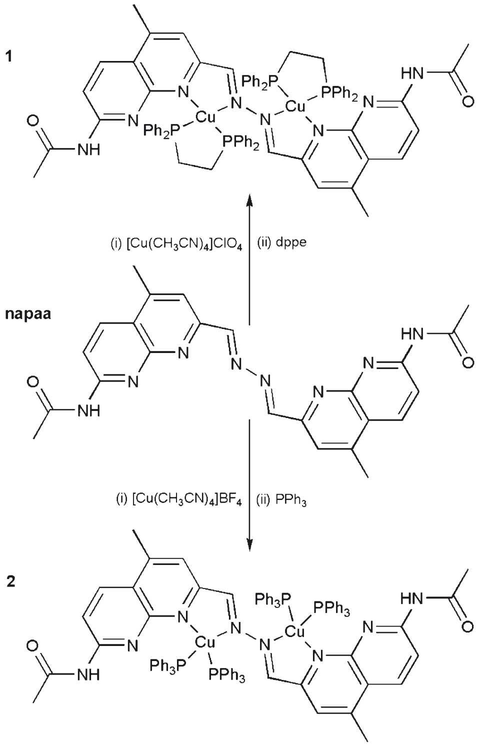
7-Amino-2,4-dimethyl-1,8-naphthyridine, 7-acetylamino-2,4-dimethyl-1,8-naphthyridine, 7-acetamiido-4-methyl-1,8-naphthyridine-2-aldehyde, $[Cu(CH_3CN)_4]BF_4$ and $[Cu(CH_3CN)_4]ClO_4$ were synthesized and purified following the literature procedures described previously (Scheme 1) [19-22]. Selenium dioxide, dppe and PPh_3 (Acros, 99%) were obtained commercially. Solvents used for spectroscopic studies and 1,4-dioxane were purified by standard methods [23]. All other chemicals and solvents were of A. R. grade and used as received. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 analyzer. Electronic absorption spectra were recorded on a HITACHI U-3010 spectrophotometer.

2.2. Synthesis of the ligand

7-acetamido-4-methyl-1,8-naphthyridin-2-carbaldehyde azine (napaa). Hydrazine hydrate (90 mg, 1.8 mmol) was added slowly with stirring to a solution of 7-acetamido-4-methyl-1,8-naphthyridin-2-carbaldehyde (802 mg, 3.5 mmol) in 40 mL of methanol (Scheme 1). The resulting solution was refluxed for 1 h under a nitrogen atmosphere. The mixture was cooled to room temperature, and the pale yellow crystals were obtained and filtered off, washed with MeOH and Et_2O, and dried; yield 0.450 g (57%). $C_{24}H_{22}N_8O_2$: Ms (m/z) 454 (M^+, 100%), 453 (M^+-1).

2.3. Synthesis of the complexes

$[Cu_2(napaa)(dppe)_2](ClO_4)_2$ (1). Ligand napaa (45.4 mg, 0.1 mmol) was dissolved in 30 mL of CH_2Cl_2, and $[Cu(CH_3CN)_4]ClO_4$ (65.4 mg, 0.2 mmol) was added under a nitrogen atmosphere at room temperature. The mixture gradually turned from pale yellow to a brown color. After stiring for 2 h, dppe (79.7 mg, 0.2 mmol) was added to the mixture. The resulting solution was filtered and the solvent was removed in vacuo. The deep brown prism crystals suitable for X-ray diffraction were obtained by diffusion of diethyl ether into a dichloromethane solution (56 mg, yield: 35%). Anal. Calcd for $C_{76}H_{70}N_8P_4Cu_2Cl_2O_{10}$ (powders): C, 57.87; H, 4.47; N, 7.10. Found: C, 57.82; H, 4.43; N, 7.15. (Scheme 2).

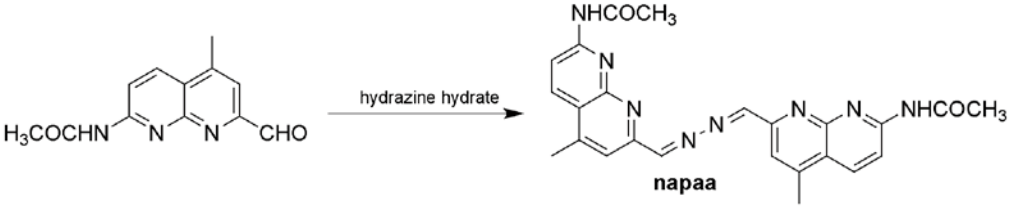


Scheme 2. Synthesis routes of **1** and **2**

$Cu_2(napaa)(PPh_3)_4(BF_4)_2$ (2) Complex **2** was prepared following the above procedure except that PPh_3 was used in place of dppe, and the reaction of napaa with $[Cu(CH_3CN)_4]BF_4$ and PPh_3 was in 1:2:4 molar ratios at room temperature. Despite numerous attempts at growing better crystals and collecting better data, but it was not successful (65 mg, yield: 36%). Anal. Calcd for $C_{96}H_{82}N_8P_4Cu_2B_2O_2F_8$ (powders): C, 63.90; H, 4.58; N, 6.21. Found: C, 63.84; H, 4.53; N, 6.29. (Scheme 2).

2.4. X-ray crystallography

Crystal suitable for X-ray structure determination was obtained by the diethyl ether diffusion into the CH_2Cl_2 solution of **1**. X-Ray data were collected on a Bruker SMART X-Ray diffractometer using a graphite monochromator with Mo-Kα radiation (λ = 0.071073 nm) at 298K. An absorption correction was applied by correction of symmetry-equivalent reflections using



Scheme 1. Synthesis route of napaa

Table 1. Summary of X-ray crystallographic data for **1**

Formula	$C_{76}H_{70}N_8P_4Cu_2Cl_2O_{10}$	Z	3
Fw	1577.25	T (K)	298(2)
Space group	P-1	ρcalcd (g cm^{-3})	1.249
Crystal system	Triclinic	θ range (deg)	1.38 to 25.01
a (Å)	11.067(2)	μ (mm^{-1})	0.704
b (Å)	13.513(3)	observed data	7172
c (Å)	16.076(4)	no. of parameters	462
α (deg)	66.604(3)	R^1	0.0759
β (deg)	87.088(3)	WR2^1	0.2408
γ (deg)	72.434(3)	Max, min peaks, (e Å^{-3})	1.082, -0.426
V (Å^3)	2096.9(7)		

[1] $I > 2\sigma(I)$, $R_1 = \Sigma||F_o| - |Fc||\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/ \Sigma[w(F_o^2)^2]\}^{1/2}$

Table 2. Selected bond lengths (Å) and angles (deg) for **1**

Cu(1)-N(1)	2.021(6)	P(2)-Cu(1)-P(1)	91.41(8)
Cu(1)-N(4)	2.115(5)	N(4A)-N(4)-Cu(1)	134.1(6)
Cu(1)-P(1)	2.273(2)	N(1)-Cu(1)-N(4)	78.8(2)
Cu(1)-P(2)	2.254(2)	N(1)-Cu(1)-P(2)	129.9(2)
N(4)-N(4A)	1.403(10)	N(1)-Cu(1)-P(1)	127.4(2)
N(4)-Cu(1)-P(2)	123.13(17)	C(15)-P(1)-Cu(1)	116.8(3)
N(4)-Cu(1)-P(1)	107.21(16)	C(10)-N(4)-N(4A)	112.8(7)

the ABSCOR program [24]. The structure was solved by direct methods using the SHELXS-97 program [25] and refined by full-matrix least-squares on F^2 using the SHELXL-97 software [26]. The hydrogen atoms were added using ideal geometries with a fixed C–H bond distance. The relevant crystallographic data as well as selected bond distances and angles for **1** are listed in Tables 1 and 2, respectively.

3. Results and Discussion

Complex **1** crystallizes in the triclinic space group P-1, a perspective view of which is shown in Fig. 1 along with the atom numbering scheme. Selected bond lengths and angles are given in Table 2. The copper(I) atoms in **1** are four-coordinate with a distorted tetrahedral geometry in which the ligand napaa as a tetradentate ligand chelate

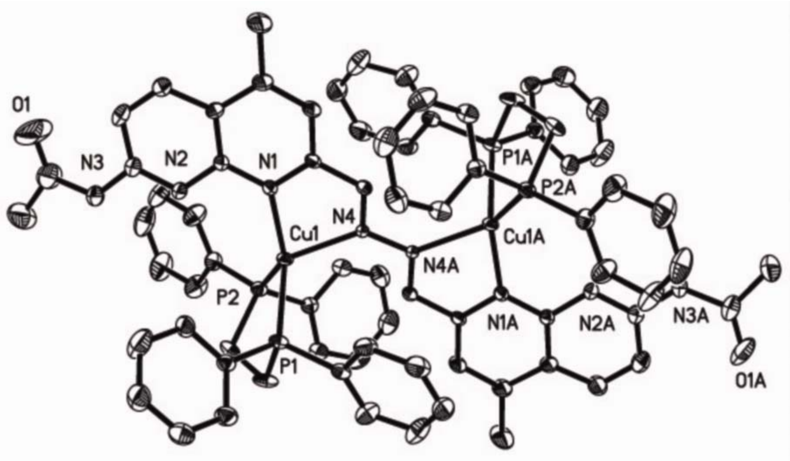


Figure 1. Perspective view of the structure of **1**

metal centers with a familiar pattern of "S-frame" forming two five-membered rings and the intermetallic separation of Cu(1)-Cu(1A) is 5.303 Å. Two naphthyridyl rings are almost at the same plane with a dihedral angle of 3.64°. This is similar with that of $[Cu_2(\mu\text{-paa})(PPh_3)_4](BF_4)_2$,(2.0°) and $\{[Cu_2(4,4'\text{-azpy})(\mu\text{-paa})(C_{18}H_{15}P)](BF_4)_2\}_\infty$,(0.7°) [27,28]. Interestingly, the ancillary ligand dppe exhibits a chelating *P^P* coordination mode instead of the usual bridging one, which can be ascribed to the limitation of their rigid structural framework. The average Cu-P bond length of 2.264(2) Å, which falls within the normal ranges for copper phosphine complexes. The average Cu-N and N-N bond lengths are 2.068(5) and 1.403(10) Å, respectively.

Napaa shows broad absorptions at 415 nm in CH_2Cl_2, which can be assigned to intraligand π–π^* transitions (Fig. 2). While **1** exhibits relative high-energy absorption with λ_{max} at 366 nm, this can be tentatively assigned to metal-to-ligand charge-transfer (MLCT) transition (d^{10}(Cu)–π^*). Compared to the absorption spectra of the free ligand napaa, the maximum of the low-energy absorption band of **1** is blue-shifted about 50 nm.

To verify the assignment of the electronic absorption spectrum of **1**, the frontier orbitals of **1** were calculated at the B3LYP/6-31G(d) level on the base of the crystal structural data by using the Gaussian 03 package [29]. All calculations were performed in Virtual Laboratory for Computational Chemistry, CNIC, CAS. As shown

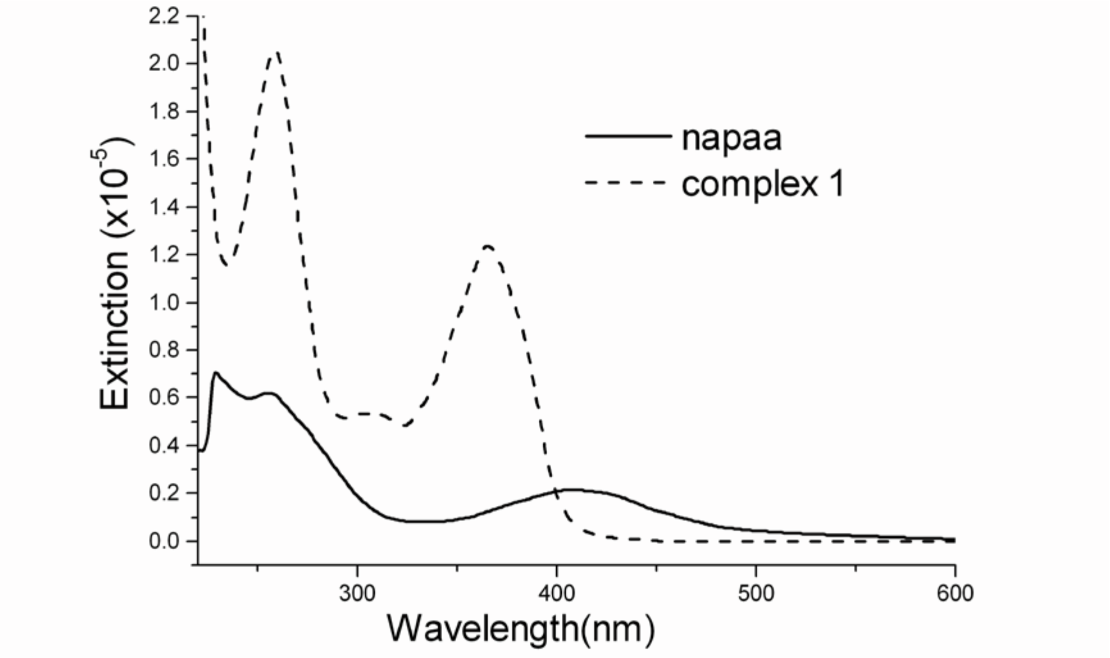


Figure 2. UV-visible spectra of complex **1** (dash line) and napaa (solid line) in CH_2Cl_2

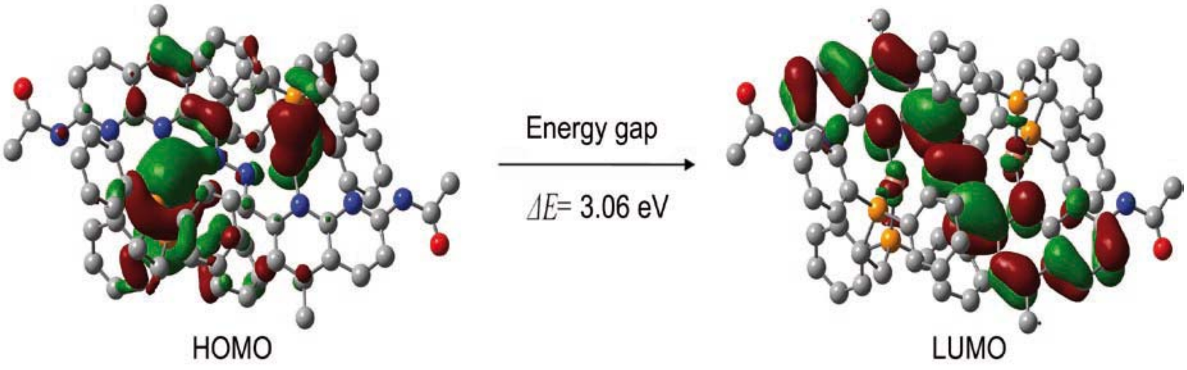


Figure 3. Contour plots of the HOMO and LUMO for **1**

in Fig. 3, the results of density functional theory (DFT) calculations for **1** reveal that the electronic density in the HOMO is distributed over the copper and phosphorus atoms, whereas that in the LUMO is localized mainly on –C=N-N=C- moiety of ligand napaa. A percentage of contribution for electronic density to Cu, P, N and C atoms were calculated using equation

$$[n^2/\sum n^2]\times 100 \qquad (1)$$

where n is the atomic orbital coefficient and $\sum n^2$ is the sum of the squares of all atomic orbital coefficients in a specific molecular orbital. Considering only AOs with more than 0.5% contribution to MO, the HOMO displays mainly Cu d orbital character mixed with P $3p_z$ orbitals (Cu, 41.74%; P, 19.31%). The LUMO has the π* orbital character of napaa, and it is mainly distributed over the azine bridge (–C=N-N=C-, 35.77%) and naphtyridin moieties (41.10%). Therefore, it is reasonable that the low-energy absorption band of **1** can be assigned to metal-to-ligand charge-transfer (MLCT) with a mixture of phosphine-to-ligand charge-transfer (PLCT) transition. TD-DFT calculations based on singlet orbitals showed that the electronic character of the absorption is dominated by one-electron transition from HOMO to LUMO (weight of the leading configurations, 82%), and the calculations HOMO–LUMO gap of 3.06 eV (405.2 nm) is essentially consistent with the experimental results described as MLCT mixed with PLCT transition character.

4. Conclusions

A new ligand napaa and its two novel dinuclear copper(I) complexes were synthesized. The structure of **1** was characterized by X-ray crystal analysis, in which each copper ion has distorted tetrahedral geometry. Complexes **1** and **2** with bulky ligands dppe and PPh_3, respectively, exhibit weak fluorescence. Their absorption maxima are attributed to come from metal-to-ligand charge-transfer state with a mixture of phosphine-to-ligand charge-transfer (PLCT) state, which is supported by the results of DFT calculatons.

Supplementary material

Supplementary data for the complex are available free of charge from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk), quoting the deposition number: CCDC-729118.

Acknowledgments

The work was supported by the National Natural Science Foundation of China (NSFC Grant No. 20671094, 20761006 and 90610034) and the foundation (GJHZ05) for Bureau of International Co-operation of Chinese Academy of Sciences.

References

[1] P.J. van Koningsbruggen, D. Gatteschi, R.A.G. de Graaff, J.G. Haasnoot, J. Reedijk, C. Zanchini, Inorg. Chem. 34, 5175 (1995)
[2] Z.Q. Xu, L.K. Thompson, D.O. Miller, Inorg. Chem. 36, 3985 (1997)
[3] J.C. Bayon et al., Inorg. Chem. 30, 2572 (1991)
[4] J. Xiang, Y.G. Yin, P. Mei, Inorg. Chem. Commun. 10, 1168 (2007)
[5] W.J. Stratton, D.H. Busch, J. Am. Chem. Soc. 80, 1286 (1958)
[6] J. Pons et al., Inorg. Chim. Acta 195, 61 (1992)
[7] H. Nakajima, H. Nagao, K. Tanaka, J. Chem. Soc., Dalton Trans. 1405 (1996)
[8] C. Bianchini, H.M. Lee, P. Barbaro, A. Meli, S. Moneti, F. Vizza, New J. Chem. 23, 929 (1999)
[9] C. He, S.J. Lippard, J. Am. Chem. Soc. 122, 184 (2000)
[10] C. He, J.L. DuBois, B. Hedman, K.O. Hodgson, S.J. Lippard, Angew. Chem. Int. Ed. 40, 1484 (2001)
[11] M.M. Yu, Z.X. Li, L.H. Wei, D.H. Wei, M.S. Tang, Org. Lett. 10, 5115 (2008)
[12] J.F. Zhang, W.F. Fu, X. Gan, J.H. Chen, Dalton Trans. 3093 (2008)
[13] R. Martinez, A. Espinosa, A. Tarraga, P. Molina, Org. Lett. 7, 5869 (2005)
[14] R.A. Henry, P.R. Hammond, J. Heterocyclic Chem. 14, 1109 (1977)
[15] V.A. Sauro, M.S. Workentin, J. Org. Chem. 66, 831 (2001)
[16] M. Chandra, A.N. Sahay, S.M. Mobin, D.S. Pandey, J. Organomet. Chem. 658, 43 (2002)
[17] A. Singh et al., J. Organomet. Chem. 689, 1821 (2004)
[18] I. Picón-Ferrer et al., J. Inorg. Biochem. 103, 94 (2009)
[19] Z.X. Li, W.F. Fu, M.M. Yu, X.J. Zhao, Y. Chen, Dyes and Pigments 75, 516 (2007)
[20] C. He, S.J. Lippard, Tetrahedron 56, 8245 (2000)

[21] R.A. Henry, P.R. Hammond, J. Heterocyclic Chem. 1109 (1977)
[22] G.J. Kubas, Inorg. Synth. 19, 90 (1979)
[23] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of laboratory chemicals, 2nd edition (Pergamon Press, Oxford, 1980)
[24] T. Higashi, ABSCOR, empirical absorption correction based on fourier series approximation (Rigaku Corporation, Tokyo, 1995)
[25] G.M. Sheldrick, HELXS 97, program for the solution of crystal structure (University of Gottingen, Gottingen, 1997)
[26] G.M. Sheldrick, HELXL 97, program for the refinement of crystal structure (University of Gottingen, Gottingen, 1997)
[27] M.M. Yu, W.F. Fu, Z.X. Li, Z.F. Yao, L.F. Jia, Acta Cryst. Sect. E: Struct. Rep. Online 60, M1897 (2004)
[28] Z.F. Yao, X. Gan, W.F. Fu, Cent. Eur. J. Chem. 6, 613 (2008)
[29] M.J. Frisch et al., Gaussian 03, Revision C.02. (Gaussian, Inc., Wallingford, CT, 2004)