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Spectrometric measurements and DFT studies on new complex of copper (II) with 2-((E)-9-ethyl-3-(2-(6-(4-methylpyridin-2-yl)pyridin-3-yl)vinyl)-9H-carbazole

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ABSTRACT

The molecular structure of a new complex of copper (II) with (E)-9-ethyl-3-(2-(6-(4-methylpyridin-2-yl)pyridin-3-yl)vinyl)-9H-carbazole ($[Cu_2(emppc)_2Cl_2]Cl_2$) was optimized with B3LYP/LanL2DZ, PBE1PBE/LanL2DZ and M062X/LanL2DZ theoretical level. The ligand, (E)-9-ethyl-3-(2-(6-(4-methylpyridin-2-yl)pyridin-3-yl)vinyl)-9H-carbazole (emppc), binds to Cu(II) ions with a bi-dentate mode, two Cl^- serve as bridging ligand, each Cu(II) ion has a highly distorted tetrahedron coordination geometry. With M062X/LanL2DZ theoretical level, the calculated interaction energies of Cu(II) with coordination atoms N are between 183.3–200.0 kJ mol^{-1} for α spin and 319.4–324.9 kJ mol^{-1} for β spin, and interaction energies of Cu(II) with coordination atoms Cl atom are 248.0–252.4 kJ mol^{-1} for α spin and 332.6–333.6 kJ mol^{-1} for β spin. The experimental Fourier transform infrared spectrum was assigned. The calculated IR based on B3LYP/LanL2DZ, PBE1PBE/LanL2DZ and M062X/LanL2DZ methods were performed and compared with experimental results. The UV–Vis experimental spectra of $[Cu_2(emppc)_2Cl_2]Cl_2$ was measured in methanol solution. The calculated electronic spectrum was performed with TD/M062X and PCM-TD/M062X methods with LanL2DZ basis set. The nature bond orbital analysis and temperature dependence of the thermodynamic properties were calculated with the same methods.

1. Introduction

2,2′-Bipyridine and its derivatives are a kind of well known bidentate chelating agent for transition metal ions mainly for its availability, robust redox stability and relative ease of functionalization [1–4] and still continues to be of considerable interest as versatile starting material for organic, inorganic and supramolecular chemistry [5–9]. Their abilities to absorb visible light to act as electron reservoirs are promising factors in their applications as photosensitizers. For example, the ruthenium complexes with 2,2′-bipyridine derivatives are generally recognized as a class of the most excellent dye for dye-sensitized solar cells. M. Grätzel research group [10] reported *cis*-bis(2,2′-bipyridyl-4,4′-dicarboxylate)$(SCN)_2$ ruthenium(II)(N3) in 1993, the compound gives the photoelectric energy conversion efficiency reached 10%. If butyl ammonium salt introduced to N3, the photoelectric conversion efficiency reached 11.18% [11].

Transition metal complexes of 2,2′-bipyridine and their derivatives are of great interest also due to their ability to undergo facile electrochemical processes and can be used as efficiently catalysis. Lehn [12] reported the earliest metal complexes $[Re(bpy)(CO)_3Cl_2]$, the compound shown efficiently to catalyze the electrochemical conversion of CO_2 to CO. Kubiak [13] demonstrated that the activity of this complex could be vastly improved by utilizing a modified bpy ligand containing *tert*-butyl groups. More recently, Shunsuke Sato [14] reported an efficient photocatalyst, [Ir-Meppy], which has the TN_{CO} value up to 50, and the quantum yield F_{CO} up to 0.21.

Further, transition metal complexes of 2,2′-bipyridine and their derivatives can be used widely in extraordinary molecular architectures [15–17]. Many of these compounds have been designed to be used in the assembly of 0-D to 3-D polymeric complexes which consist of mononuclear building blocks bridged by transition metal or lanthanide ions [18–21]. Highlights include single molecule magnets [22,23], metal-organic frameworks [24,25] and materials which display organic electronic [26], spin crossover [27] and luminescence [28].

Although new developments in syntheses and applications have been reported, the spectroscopic properties of such compounds were not extensively studied [29,30]. We herein describe our results on a new binuclear compound, $[Cu_2(emppc)_2Cl_2]Cl_2$, concerning the structural, vibrational and electronic analyses through spectral measurements. Density Functional theory calculations have been performed to support our wavenumber assignments. The redistribution of Electron Density (ED) in various bonding, antibonding orbitals and E(2) energies have been calculated by natural bond orbital (NBO) analysis to provide

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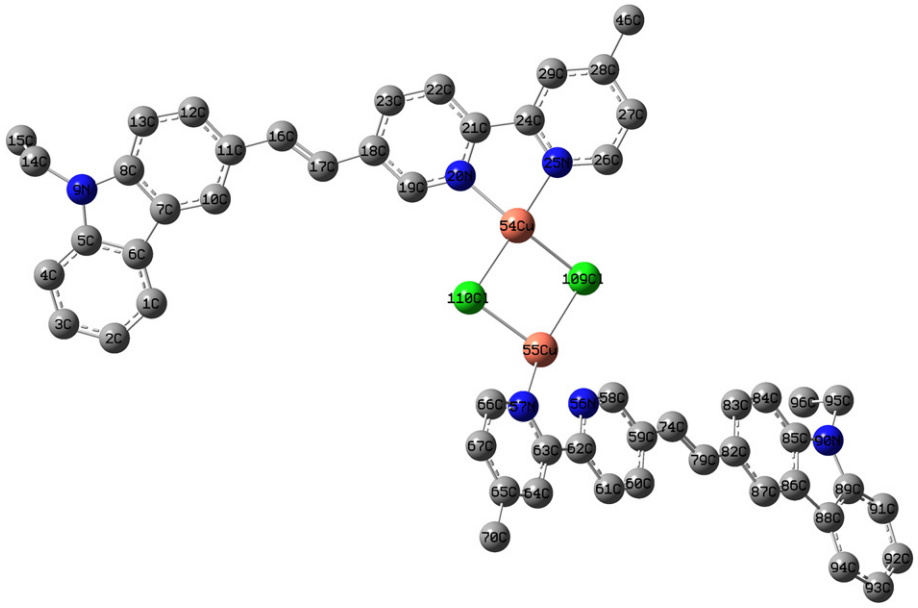

Fig. 1. Optimized structure of title compound with B3LYP/LanL2DZ level.

Table 1
Optimized and experimental bond distances (Å) and bond angles (°) for the compound.

Bond length	B3LYP	PBE1PBE	M062X	Bond angle	B3LYP	PBE1PBE	M062X
R(1,2)	1.4098	1.4014	1.3991	A(2,1,6)	118.8	118.8	118.8
R(1,6)	1.4037	1.4007	1.4029	A(7,8,9)	109.2	109.1	109.1
R(2,3)	1.4148	1.4108	1.4135	A(9,8,13)	129.6	129.6	129.5
R(3,4)	1.4075	1.4011	1.3999	A(5,9,8)	108.8	108.9	108.8
R(4,5)	1.4043	1.3989	1.4005	A(21,20,54)	113.3	113.0	112.9
R(5,6)	1.4276	1.421	1.4198	A(21,24,25)	115.3	115.1	115.1
R(5,9)	1.4137	1.4063	1.4059	A(24,25,54)	114.0	113.5	113.2
R(6,7)	1.4615	1.4536	1.4569	A(20,54,25)	81.6	82.9	83.3
R(7,8)	1.4419	1.4361	1.4346	A(25,54,109)	98.1	97.2	96.5
R(8,9)	1.3866	1.3781	1.3801	A(25,54,110)	158.8	163.9	168.4
R(8,13)	1.4116	1.4066	1.4065	A(109,54,110)	89.5	86.7	85.2
R(9,14)	1.4748	1.4637	1.4642	A(56,55,57)	81.6	82.8	83.4
R(10,11)	1.4264	1.4188	1.4148	A(56,55,109)	98.0	97.9	96.9
R(11,12)	1.4322	1.4273	1.4254	A(56,55,110)	159.5	163.7	169.3
R(11,16)	1.4546	1.4456	1.452	A(57,55,109)	158.4	162.3	168.3
R(12,13)	1.3951	1.3893	1.3909	A(109,55,110)	89.4	86.2	85.1
R(14,15)	1.5436	1.5335	1.536	A(55,56,62)	113.3	113.0	112.8
R(16,17)	1.3718	1.3698	1.3651	A(55,57,63)	113.9	113.5	113.2
R(17,18)	1.457	1.4459	1.4512	A(55,57,66)	126.1	126.4	126.6
R(18,19)	1.4226	1.4193	1.4183	A(56,58,59)	122.9	122.9	122.8
R(18,23)	1.4239	1.4203	1.4185	A(56,58,75)	116.2	116.5	116.9
R(19,20)	1.3467	1.3415	1.3448	A(59,58,75)	120.8	120.7	120.3
R(20,21)	1.3693	1.3659	1.3664	D(19,20,54,110)	−21.6	−17.3	−12.6
R(20,54)	2.0398	1.9938	1.9884	D(24,25,54,109)	160.4	165.3	169.7
R(21,22)	1.4105	1.4041	1.4006	D(20,54,109,55)	−119.7	−110.6	−104.4
R(21,24)	1.4784	1.466	1.4739	D(25,54,109,55)	152.5	160.2	167.0
R(22,23)	1.3967	1.3908	1.394	D(110,54,109,55)	−7.7	−4.1	−1.5
R(24,25)	1.3698	1.3657	1.3664	D(20,54,110,55)	169.4	169.8	170.9
R(24,29)	1.4071	1.4012	1.3979	D(25,54,110,55)	−103.8	−100.5	−97.5
R(25,26)	1.3557	1.3524	1.3548	D(109,54,110,55)	7.7	4.1	1.5
R(25,54)	2.0269	1.9844	1.9836	D(109,55,56,58)	−21.8	−18.5	−13.1
R(26,27)	1.3998	1.3928	1.3933	D(109,55,56,62)	157.6	161.6	167.9
R(27,28)	1.4156	1.4114	1.4104	D(110,55,56,58)	88.5	85.2	87.6
R(28,29)	1.4108	1.405	1.4065	D(109,55,57,63)	−90.9	−93.8	−91.3
R(28,46)	1.5108	1.5015	1.5051	D(109,55,57,66)	91.0	88.1	87.2
R(54,109)	2.4076	2.3762	2.3728	D(110,55,57,63)	159.0	163.2	170.3
R(54,110)	2.402	2.3721	2.3722	D(110,55,57,66)	−19.2	−14.9	−11.2
R(55,56)	2.0402	2	1.9882	D(56,55,109,54)	168.5	168.3	170.9
R(55,57)	2.0279	1.9891	1.983	D(57,55,109,54)	−104.1	−100.7	−98.1
R(55,109)	2.4038	2.3846	2.3724	D(56,55,110,54)	−119.4	−109.3	−103.3
R(55,110)	2.4087	2.3885	2.375	D(57,55,110,54)	152.1	158.7	166.9
R(56,58)	1.3466	1.3413	1.3444	D(109,55,110,54)	−7.7	−4.1	−1.5