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Synthesis And Structural Characterization Of Three Hydrogen-Bonded Supramolecular Complexes Of Copper, Nickel And Zinc With 1-Phenyl-3-Methyl-4-(Salicylidene Hydrazide)-Acetyl-Pyrazolone-5 And 2,2´-Bipyridine

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Abstract: *A new set of supramolecular complexes, [Cu(PMAP-SHZ)(2,2´-bipy)$^{\cdot}$CH$_2$Cl$_2$] (1), [Ni (PMAP-SHZ) (2, 2´-bipy) CH$_3$OH] (2), [Zn (PMAP-SHZ) (2,2´-bipy)$^{\cdot}$CH$_3$OH] (3) (PMAP-SHZ=1-phenyl-3-methyl-4-(salicylidene hydrazide)-acetyl-pyrazolone-5, 2,2´-bipy= 2,2´-bipyridine) have been synthesized and characterized by elemental analysis, IR spectroscopy and X-ray crystallography. The X-ray diffraction analysis of the complexes shows that the Ni (II) and Zn (II) ion centers are six-coordinated while the Cu (II) ion center is five-coordinated. The three supramolecular complexes contain the same ligands, namely PMAP-SHZ and 2,2´-bipy. However, their hydrogen bonds are significantly different, and this variation apparently is responsible for the dissimilar structures of the three supramolecular complexes.*

Keywords: *Supramolecular complexes, 2,2´-bipyridine, 4-acyl-pyrazolones, crystal structures.*

I. INTRODUCTION

One of the recent developments in supramolecular chemistry is the application of reversible metal-ligand complexes for creation of new materials with advanced (photochemical, electrochemical, and catalytic) properties. In the recent years development of supramolecular coordination chemistry took place and many new supramolecular complexes based on the metal coordination centers have found their applications in catalysis, as advanced materials for molecular electronics, as molecular receptors used in sensor devices, light-harvesting materials for solar cells and in molecular machines. For the construction of supramolecular complexes, a metal template and an appropriate organic blocker are necessary. The heterocyclic-N donor ligands, especially pyridine, polypyridine, and their substituted derivatives, are important in maintaining the desired low dimensional coordination polymers and providing potential supramolecular recognition sites for p–p aromatic stacking interactions. In the present work, we had synthesized mixed-ligand complexes of transition metals with novel 4-acyl pyrazolone ligands and chelating heteroaromatic N-donor ligands such as 2,2´- bipyridine.

The acyl pyrazolones, which is an important class of β-diketones, contains a pyrazole ring fused to a chelate arm. Compounds derived from 4-acyl pyrazol-5-one have continued to receive considerable attention due to their pharmaceutical importance and high biological activity. They also enjoy a range of applications as a substructure in dye chemistry and synthesis. Here we report the synthesis and crystal structures of three mixed-ligand supramolecular complexes in which the components are 4-acetyl pyrazolone ligand and 2,2´-bipyridine(2,2´-bipy). The hydrogen bonds and π-π stacking interactions between 2,2´-bipyridine ligands play very important roles in the construction of the supramolecular architecture.

II. EXPERIMENTAL

A. MATERIALS AND PHYSICAL MEASUREMENTS

All the reagents were purchased from commercial sources and used as received. Elemental analysis of carbon, hydrogen and nitrogen were performed on a Perkin Elmer 2400 II elemental analyzer. IR spectra were recorded on a BRUKER EQUINOX-55 spectrophotometer in the 400–4000 cm^{-1} range using samples prepared as pellets with KBr. The crystal structures were analyzed using a Bruker Smart 1000 CCD and the SHELXTL 97 crystallographic software package of molecular structure.

B. SYNTHESIS OF THE LIGAND

Salicylic hydrazide (SHZ) was synthesized and purified according to the usual methods in the literature. 1-phenyl-3-methyl-4-acetyl-5-pyrazolone (PMAP) was synthesized using a modified Jensen’s method.

a. SYNTHESIS OF THE LIGAND PMAP-SHZ

The ligand PMAP-SHZ was prepared by refluxing equimolar PMAP and SHZ in methanol for 3 h, adding a few drops of glacial acetic acid as a catalyst. On cooling, the reddish brown solid obtained was filtered, washed with methanol, and dried in air. *Anal.* Calc. for $C_{19}H_{18}N_4O_3$: C, 65.20; H, 5.18; N, 16.00. Found: C, 65.20; H, 5.15; N, 15.99%. The synthetic procedure for the ligand PMAP-SHZ is shown in Scheme 1.

C. SYNTHESIS OF COMPLEXES

a. SYNTHESIS OF [CU (PMAP-SHZ) (2, 2´BIPY)]˙ 2CH$_2$CL$_2$

Cu (OAc) $_2$ ˙H_2O (1 mmol), PMAP-SHZ (1 mmol) and 2,2´-bipy (1 mmol) were reacted in methanol at 80^0C with continous stirring. The resulting green precipitate formed was filtered off, washed with methanol, and dried naturally. Dark green single crystals suitable for analysis were obtained by slowly evaporating the mixed solvent solution of CH_2Cl_2 and CH_3OH at room temperature for a few days. *Anal.* Calc. for $C_{29}H_{24}N_6O_3Cu$: C, 61.37; H, 4.26; N, 14.81. Found: C, 61.40; H, 4.15; N, 14.80%

b. SYNTHESIS OF [NI (PMAP-SHZ) (2, 2´-BIPY) CH$_3$OH]

Ni $(OAc)_2$˙$4H_2O$ (1 mmol), PMAP-SHZ (1 mmol) and 2,2´-bipy (1 mmol) were reacted in methanol at 70^0C with continuous stirring. The resulting mixture was filtered off, and the filtrate was kept at room temperature for several days, forming crystals of compound 1. *Anal.* Calc. for $C_{30}H_{28}N_6O_4Ni$: C, 60.58; H, 4.75; N, 14.13. Found: C, 60.55; H, 4.65; N, 14.12%.

c. SYNTHESIS OF [ZN (PMAP-SHZ) (2, 2´-BIPY) CH$_3$OH]

Compound 3 was prepared similarly to compound 1, by using Zn (OAc) $_2$˙ $2H_2O$ (1 mmol), PMAP-SHZ (1 mmol) and 2,2´-bipy (1 mmol). The resulting mixture was filtered off, and the filtrate was kept at room temperature for several days, forming crystals of compound 2. *Anal.* Calc. for $C_{30}H_{28}N_6O_4Zn$: C, 69.91; H, 4.69; N, 13.97. Found: C, 69.90; H, 4.64; N, 13.80%

D. X-RAY CRYSTALLOGRAPHY

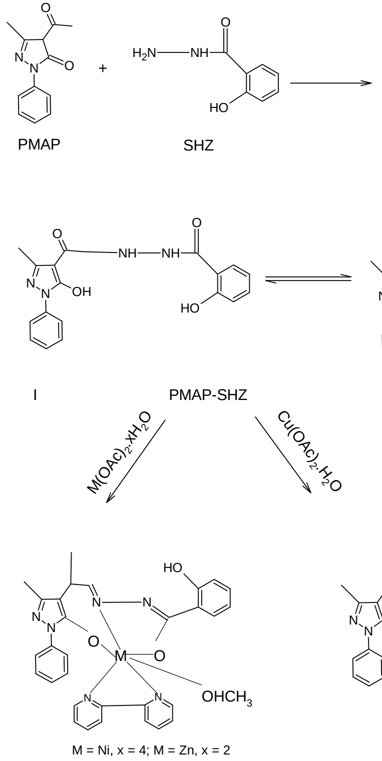
Suitable single crystals of the complexes 1, 2 and 3 were mounted on a Bruker Smart 1000 CCD diffractometer equipped with graphite monochromated Mo Ka (k = 0.71073A˚) radiation. Empirical absorption corrections were applied. The unit cell parameters were determined by least squares refinements of all reflections in all three of the cases. All the structures were solved by direct method and refined by full-matrix least squares on F2. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located from the difference map, then added geometrically. All calculations were performed using the SHELXTL 97 program package. Crystal data and experimental details for compounds 1, 2 and 3 are contained in Table 1. Selected bond distances and angles are listed in Table 2. H-bonding parameters are displayed in Table 3.

III. RESULTS AND DISCUSSION

A. IR SPECTRA

Selected IR bands are listed in Table 4. The spectrum of free ligand PMAP-SHZ shows a strong broad band at 3063 cm^{-}1, which is assigned to the v(NH) vibration. The strong bands at around 1609 and 1628 cm^{-}1 are assigned to v(C=O) of the pyrazolone-ring and v(C=O) of the lateral chain, respectively. All these suggest that hydrogen bonds exist in the free ligand molecule and the structure of the ligand in the solid state is the keto form II in Scheme 1.

The infrared spectra of the complexes exhibit characteristic bands for both pyrazolone and 2,2´-bipyridine. The v(NH), v(C=O) of the pyrazolone-ring, and v(C=O) of the lateral chain are all absent in the complexes, but a new band is observed at about 1367 cm^{-}1 due to (C-O). Meanwhile, there are two new bands between 1576 and 1600 cm^{-}1 in the complexes, which are assigned to (-C=N-N=C) of hydrazone and coordinated pyridine nitrogen. From these observations, it is concluded that the ligand reacts in the enol form with prototropy, which incorporates into two proton transfers, one occurs from the nitrogen atom N3 in the lateral moiety to the oxygen atom O1 of the pyrazolone-ring, and the other one is from the N4 atom to O2 (Scheme 1). Then the ligand loses the enolic protons and coordinates to the central metal atoms in the complex. In complexes 1–3, bands related to (M-O) are observed in the 515 cm^{-}1 region. The new bands at 451–468 cm^{-}1 for the complexes are assigned to (M-N). In addition, the presence of the 2,2´- bipy ligand is confirmed by bands arising from the skeletal vibrations of the pyridine ring. It is thus believed that the nitrogens of the azomethine group of hydrazone and 2,2′- bipyridine are coordinated to metal ions.



Scheme I

Figure 1

B. DESCRIPTION OF STRUCTURES

a. [CU (PMAP-SHZ) (2, 2′-BIPY)] ˙2CH$_2$CL$_2$

Selected bond distances and angles are listed in Table 2. The asymmetric unit contains a complete mononuclear complex molecule and two CH$_2$Cl$_2$ molecules. Both CH$_2$Cl$_2$ molecules are disordered over two sites. Hydrogen atoms are not attached to the disordered dichloromethane molecules. Geometric constraints were applied to these molecules to ensure stable refinement.

The Cu (II) ion center is five-coordinated involving two nitrogen atoms N5, N6 from 2, 2′-bipy, two oxygen atoms O1, O2, and one nitrogen atom N3 from one 4-acyl-pyrazolone ligand.

b. [NI (PMAP-SHZ) (2,2′-BIPY) CH$_3$OH]

The molecular view of [Ni (PMAP-SHZ) (2,2′-bipy) CH$_3$OH] unit with the atom-numbering scheme is shown in Fig. 1. Selected bond distances and angles are listed in Table 2. The geometry around the Ni(II) ion may be described as a distorted octahedron with two nitrogen atoms of 2,2′-bipy (N5, N6), one oxygen atom of the coordinating methanol molecule O4, two oxygen atoms (O1, O2) and one nitrogen atom N3 of PMAP-SHZ, respectively. In the complex, atoms O4, N3, N5 and N6 form the equatorial plane around Ni (II), and the axial positions are occupied by O1 and O2.

c. [ZN (PMAP-SHZ) (2,2′-BIPY) CH$_3$OH]

Selected bond distances and angles are reported in Table 2. The geometry around the zinc ion could be described as a distorted octahedron with two nitrogen atoms from 2,2′-bipy (N5 and N6), one oxygen atom O4 of the coordinated methanol molecule, two oxygen atoms O1, O2, and one nitrogen atom N3 of one PMAP-SHZ, respectively. In the complex, atoms O4, N3, N5 and N6 form an equatorial plane around Zn (II), and the axial positions are occupied by O1 and O2.

Complexes	1	2	3
Empirical formula	$C_{29}H_{24}N_6O_3Cu$	$C_{30}H_{28}N_6O_4Ni$	$C_{30}H_{28}N_6O_4Zn$
Formula weight	567.546	594.693	601.39
Crystal system	Monoclinic	monoclinic	Monoclinic
T (K)	293(2)	293(2)	293(2)
Wavelength (A˚)	0.71073	0.71073	0.71073
Space group	C2/c	P2(1)	P2(1)/n
a (A˚)	25.443(5)	9.9110(13)	12.919(2)
b (A˚)	12.732(2)	22.282(3)	15.426(3)
c (A˚)	21.467(4)	15.242(2)	16.294(3)
ɑ (_)	90	90	90
β (_)	105.514(3)	105.390(2)	102.418(3)
ɣ (_)	90	90	90
V (A˚ 3)	6606(2)	3195.5(7)	3168.9(9)
Z	8	4	4
Absorption coefficient (mm^{-}1)	0.868	0.656	0.824
Crystal size (mm)	0.40 x 0.20 x 0.10	0.20 x 0.20 x 0.06	0.30 x 0.18 x 0.14

Table 1: Crystal data and structure refinement parameters for 1–3

Compound 1			
Cu(1)–O(1)	1.931(2)	Cu(1)–N(5)	2.012(3)
Cu(1)–N(3)	1.933(3)	Cu(1)–N(6)	2.204(3)
Cu(1)–O(2)	1.992(2)		
O(1)–Cu(1)–N(3)	93.95(10)	O(2)–Cu(1)–N(5)	95.18(10)
O(1)–Cu(1)–O(2)	153.55(11)	O(1)–Cu(1)–N(6)	109.59(11)
N(3)–Cu(1)–O(2)	81.58(10)	N(3)–Cu(1)–N(6)	98.65(11)
O(1)–Cu(1)–N(5)	90.64(10)	O(2)–Cu(1)–N(6)	96.87(10)
N(3)–Cu(1)–N(5)	174.90(12)	N(5)–Cu(1)–N(6)	77.86(11)
Compound 2			
Ni(1)–O(1)	1.985(3)	Ni(1)–N(5)	2.071(4)
Ni(1)–N(3)	2.000(4)	Ni(1)-N(6)	2.095(4)
Ni(1)–O(2)	2.052(3)	Ni(1)–O(4)	2.148(3)
O(1)–Ni(1)–N(3)	92.31(14)	N(6)–Ni(1)–O(4)	169.88(16)
O(1)–Ni(1)–O(2)	172.57(15)	O(2)–Ni(1)–N(6)	90.88(16)
N(3)–Ni(1)–O(2)	80.35(15)	N(5)–Ni(1)–N(6)	78.60(17)
O(1)–Ni(1)–N(5)	88.99(15)	O(1)–Ni(1)–O(4)	89.24(13)
N(3)–Ni(1)–N(5)	174.51(17)	N(3)–Ni(1)–O(4)	94.06(15)
O(2)–Ni(1)–N(5)	98.43(15)	O(2)–Ni(1)–O(4)	90.12(14)
O(1)–Ni(1)–N(6)	91.05(15)	N(5)–Ni(1)–O(4)	91.30(16)
N(3)–Ni(1)–N(6)	96.05(17)		
Compound 3			
Zn(1)–O(1)	2.0245(19)	Zn(1)–N(6)	2.148(2)
Zn(1)–N(3)	2.108(2)	Zn(1)–O(4)	2.157(2)
Zn(1)–O(2)	2.110(2)	Zn(1)–N(5)	2.226(2)
O(1)–Zn(1)–N(3)	89.19(8)	O(2)–Zn(1)–O(4)	86.52(8)
O(1)–Zn(1)–O(2)	164.48(7)	N(6)–Zn(1)–O(4)	90.08(9)
N(3)–Zn(1)–O(2)	76.99(8)	O(1)–Zn(1)–N(5)	97.78(9)
O(1)–Zn(1)–N(6)	98.28(8)	N(3)–Zn(1)–N(5)	91.38(9)
N(3)–Zn(1)–N(6)	165.08(9)	O(2)–Zn(1)–N(5)	89.68(9)
O(2)–Zn(1)–N(6)	96.80(8)	N(6)–Zn(1)–N(5)	74.88(9)
O(1)–Zn(1)–O(4)	89.79(8)	O(4)–Zn(1)–N(5)	163.94(8)
N(3)–Zn(1)–O(4)	102.92(8)		

Table 2: Selected bond lengths (A˚) and angles (˚) for compounds 1–3

D–H---A	d(D–H)	d(H----A)	d(D ----A)	angle(DHA)
Compound 1				
O3–H3A …. N4	0.8500	1.8300	2.5611	143.00
C31–H31 ….O2	0.9300	2.5700	3.4604	161.00
C34–H34 ….. O3	0.9300	2.4800	3.2424	140.00
Compound 2				
O4–H4…..N8	0.9300	1.9900	2.761(5)	140.00
O8–H8…..N2	0.9300	1.9900	2.766(5)	140.00
C28–H28…..O6	0.9300	2.5500	3.286(7)	136.00
C66–H66….O2	0.9300	2.5400	3.328(7)	143.00
Compound 3				
O4–H4A…..N2	0.9300	1.9800	2.7515	139.00
C3–H3A…..O3	0.9300	2.5000	3.3357	149.00
C6–H6…..O4	0.9300	2.5800	3.4559	158.00

Table 3: Selected bond distance (A˚) and bond angle (^{o}) for complexes 1–3

Compounds	vNH	vC=O	vC-O	vC-N	vC=N(Bipy)	vM-N	vM-O
PMAP-SHZ	3063	1628, 1609					
[Cu(PMAP-SHZ)(2,2’-bipy)]			1367	1595, 1576	1489, 1455	451	518
[Ni(PMAP-SHZ)(2,2’-bipy)CH3OH]			1365	1600, 1579	1486, 1450	460	516
[Zn(PMAP-SHZ)(2,2’-bipy)CH3OH]			1367	1594, 1576	1488, 1454	468	515

Table 4: Some prominent IR bands for complexes 1–3 (cm^{-}1)

IV. CONCLUSION

4-acetyl-pyrazolone moiety may be considered important in the context of understanding the amount of metal ion complexation in the biological systems. The three different complexes contain supramolecular networks with identical structural topology due to the similar coordination mode of PMAP-SHZ and 2,2′-bipy, while the difference lies in the hydrogen-binding systems which always influence the crystal packing. [Ni (PMAP-SHZ) (2,2′-bipy) CH_3OH] and [Cu (PMAP-SHZ) (2,2′-bipy)]$^{\cdot}$2CH_2Cl_2 have one-dimensional supramolecular networks, but [Zn (PMAP-SHZ) (2,2′-bipy) CH_3OH] has a two-dimensional supramolecular network.

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