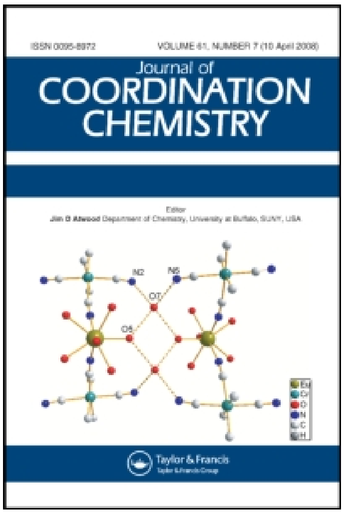

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Syntheses and characterization of Zn(II), Cd(II) and Hg(II) complexes with 5-methyl-1-(2′-pyridyl)pyrazole-3-carboxamide (MP_yP_zCA) ligand

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From the reaction between Zn(II), Cd(II) and Hg(II) with 5-methyl-1-(2′-pyridyl)pyrazole-3-carboxamide (MP_yP_zCA) in ethanol, the complexes $[Zn(MP_yP_zCA)_2(NO_3)]^+[(NO_3)_{0.60}(ClO_4)_{0.40}]^- \cdot H_2O$, $Cd(MP_yP_zCA)_2Cl_2$ and $Hg(MP_yP_zCA)(SCN)_2$ were obtained. These compounds have been characterized by IR and CHN analyses. The structure of $[Zn(MP_yP_zCA)_2NO_3]^+[(NO_3)_{0.60}(ClO_4)_{0.40}]^- \cdot H_2O$ has been solved by X-ray crystallopgraphy. The coordination environment around the Zn(II) may be described as a trigonal bipyramid in which the ligands are both bidentate, but coordinated differently. The coordination sphere is completed with the oxygen atom of a nitrate anion as a unidentate ligand.

Keywords: Pyridyl pyrazolyl carboxamide; X-ray crystal structure; Coordination chemistry; Zinc(II); Cadmium(II); Mercury(II)

1. Introduction

Numerous zinc(II), cadmium(II) and mercury(II) complexes with nitrogen or oxygen donor ligands have been synthesized and studied [1–3]. Some of these complexes are structural models for the active site in enzymes [2]. The well-documented bioactivity of pyrazole derivatives is often related to chelation with trace metal ions [4], generating substantial work on the coordination chemistry of pyrazole-derived ligands [5]. Recently, Saha and coworkers [6] reported the synthesis and spectroscopic characterization of copper(II) complexes with 5-methyl-1-(2′-pyridyl)pyrazole-3-carboxamide (MP_yP_zCA) together with an X-ray crystal structure of $[Cu(MP_yP_zCA)_2(H_2O)](ClO_4)_2$.

The general structure of the ligand can be represented by MP_yP_zCA. This ligand is interesting because of the structural chemistry of its multifunction coordination modes. The presence of a pyrazole nitrogen at the adjacent position of the amide linkage and the pyridyl group helps the ligand (MP_yP_zCA) to bind to a metal ion

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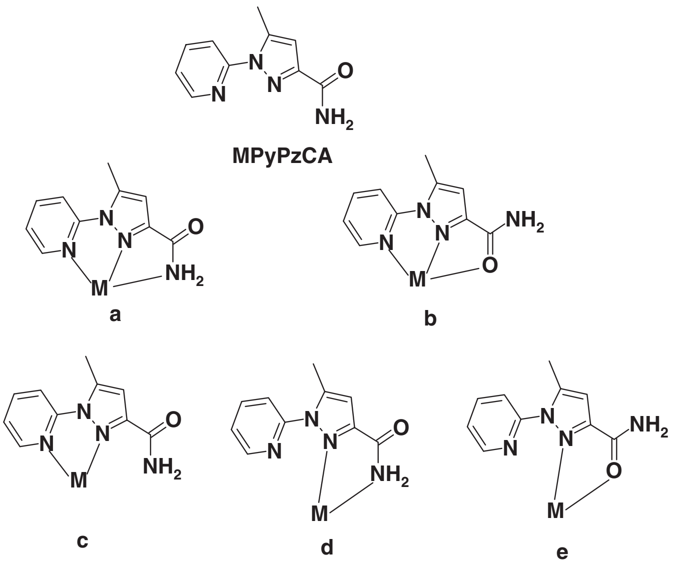

Figure 1. The general structure of the MP_yP_zCA ligand and its modes of coordination.

in a tridentate fashion, forming two five-membered chelate rings through either N-bonding (figure 1a) or O-bonding (figure 1b). MP_yP_zCA can also be bidentate, forming a five-membered chelate ring in the three forms shown in figure 1c–e.

In this work, we describe the syntheses and characterization of Zn(II), Cd(II) and Hg(II) complexes with this ligand and the X-ray crystal structure of $[Zn(MP_yP_zCA)_2NO_3]^+[(NO_3)_{0.60}(ClO_4)_{0.40}]^- \cdot H_2O$, an unusual zinc(II) complex.

2. Experimental

2.1. *Physical measurements*

Melting points were measured on an Electrothermal 9100 instrument and are uncorrected. IR spectra were recorded on a Nicolet-55XC FTIR spectrophotometer using KBr pellets (4000–400 cm^{-1}). Microanalyses were performed on a Heraeus CHN-O-Rapid analyzer. The ligand (MP_yP_zCA) was prepared by the procedure of Saha and coworkers [6].

2.2. *Preparation of the complex $[Zn(L)_2NO_3]^+[(NO_3)_{0.60}(ClO_4)_{0.40}]^- \cdot H_2O$*

To a magnetically stirred solution of the ligand MP_yP_zCA (0.404 g, 2 mmol) in ethanol (95%) (10 mL) was added dropwise a mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.297 g, 1 mmol) and $NaClO_4 \cdot H_2O$ (0.421 g, 3 mmol) in ethanol (95%) (20 mL) at room temperature over 10 min. The reaction mixture was stirred for 24 h at room temperature. The white powder was filtered off, washed with cold ethanol (95%) (5 mL) and then diethyl-ether (5 mL). The product was dried in vacuum over silica gel at room temperature, and then in vacuum over P_4O_{10} at 50°C. Yield 0.46 g, 73%; m.p. 220–220.1°C.

A single crystal suitable for X-ray analysis was obtained by slow evaporation of acetonitrile solution of the product at room temperature. IR (cm^{-1}) selected bands, ν(N–H) 3412 m and 3335 m, $\nu(C–H)_{ar}$ 3170 m, ν(C=C), ν(C=N) 1682 s, 1480 m, ν(C=O) 1635 s, $\nu(NO_3)$ 1370 vs and $\nu(ClO_4)$ 1105 s. Anal. Calcd for $C_{20}H_{22}Cl_{0.40}N_{9.60}O_{9.40}Zn$(%): C, 38.32; H, 3.54; N, 21.45. Found: C, 38.4; H, 3.6; N, 21.5.

Complexes $[Cd(MP_yP_zCA)_2Cl_2]$ and $[Hg(MP_yP_zCA)(SCN)_2]$ were prepared by analogous methods to that used for the synthesis of the zinc complex.

2.2.1. $[Cd(MP_yP_zCA)_2Cl_2]$. Reactant materials: 5-methyl-1-(2′-pyridyl)pyrazole-3-carboxamide (0.404 g, 2 mmol), cadmium(II) chloride (0.183.4 g, 1 mmol). White crystals. Yield 0.381 g, 65%; m.p. 215°C. Anal. Calcd for $C_{20}H_{20}N_8O_2Cl_2Cd$(%): C, 49.7; H, 3.40; N, 19.08. Found: C, 49.50; H, 3.25; N, 19.30. IR (cm^{-1}) selected bands, ν(N–H) 3415 m and 3330 m, $\nu(C–H)_{ar}$ 3180 m, ν(C=C), ν(C=N) 1680 s, 1480 m, ν(C=O) 1645 s.

2.2.2. $[Hg(MP_yP_zCA)(SCN)_2]$. Reactant materials: 5-methyl-1-(2′-pyridyl)pyrazole-3-carboxamide (0.404 g, 2 mmol), mercury(II) thiocyanate (316.5 g, 1 mmol). Yellow–white crystals. Yield 0.285 g, 55%; m.p. 218°C. Anal. Calcd for $C_{12}H_{10}N_6OS_2Hg$(%): C, 27.77; H, 1.93; N, 16.21. Found C, 27.80; H, 1.70; N, 16.40. IR (cm^{-1}) selected bands: ν(N–H) 3420 m and 3325 m; $\nu(C–H)_{ar}$ 3130; ν(C=C), ν(C=N) 1620, 1568; ν(C=O) 1640, ν(SCN) 2090 vs.

2.3. *Crystallography*

2.3.1. Determination of the structure. Crystallographic measurements were carried out at 293(2) K using a Siemens R3m/V diffractometer. Intensity data were collected within the range $2.85 \leq \theta \leq 26.06°$ using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Accurate unit cell parameters and orientation matrix for data collection were obtained from least-squares refinement. Intensities of 4617 unique reflections were measured, from which 3435 with $I > 2\sigma(I)$ were used in the refinement. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2.

The positions of hydrogen atoms were idealized and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotopic thermal parameter. The values of R, R_w, with a goodness-of-fit on F^2 of 1.051 were 0.0557, 0.1437, respectively. The final difference density map showed a maximum peak and hole of 0.859 and -0.794 e Å^{-3}, respectively. Corrections for Lorentz and polarization effects as well as an empirical correction for absorption using the semiempirical from equivalents programs were applied. All structural calculations were carried out with a PDP-11/23+ computer using the SDP-PLUS program package [7, 8].

Crystal data and structure refinement are presented in table 1 and selected bond lengths and angles are given in table 2. Atomic coordinates, anisotropy thermal parameters, observed and calculated structure factors, full lists of bond distances, bond angles and torsion angles are given in the supplementary material.

Table 1. Crystal data and structure refinement for the complex.

Empirical formula	C20 H22 C10.40 N9.60 9.40 Zn
Formula weight	626.82
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 7.5884(14)$ Å, $\alpha = 95.375(16)^\circ$
	$b = 9.688(2)$ Å, $\beta = 98.866(15)^\circ$
	$c = 18.538(4)$ Å, $\gamma = 106.313(15)^\circ$
Volume	1278.9(4) Å^3
Z	2
Density (calculated)	1.628 Mg m^{-3}
Absorption coefficient	1.074 mm^{-1}
$F(000)$	642
Crystal size	0.2 × 0.2 × 0.1 mm^3
Theta range for data collection	2.85 to 26.06°
Index ranges	$0 \le h \le 6$, $-11 \le k \le 11$, $-22 \le l \le 22$
Reflections collected	4617
Independent reflections	4219 [$R(\text{int}) = 0.0273$]
Completeness to $\theta = 26.06^\circ$	83.7%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4219/8/443
Goodness-of-fit on F^2	1.051
Final R indices [for 3435 reflections with $I > 2\sigma(I)$]	$R1 = 0.0557$, $wR2 = 0.1437$
R indices (all data)	$R1 = 0.0705$, $wR2 = 0.1531$
Largest diff. Peak and hole	0.859 and −0.794 e Å^{-3}

Table 2. Selected bond lengths (Å) and angles (°) for the complex.

Zn(1)–O(2)	2.053(4)	O(1)–C(12)	1.235(5)
Zn(1)–N(1′)	2.063(4)	N(7)–C(8)	1.352(7)
Zn(1)–N(7)	2.066(4)	O(1′)–C(12′)	1.240(5)
Zn(1)–N(1)	2.084(4)	N(7′)–C(8′)	1.340(7)
Zn(1)–O(1′)	2.191(3)	N(4)–O(2)	1.281(5)
O(2)–Zn(1)–N(1′)	115.39(15)	C(6)–N(7)–Zn(1)	117.2(3)
O(2)–Zn(1)–N(7)	128.19(15)	C(8)–N(7)–Zn(1)	124.5(3)
N(1′)–Zn(1)–N(7)	116.22(16)	C(12′)–O(1′)–Zn(1)	111.6(3)
O(2)–Zn(1)–N(1)	94.73(16)	C(5′)–N(1′)–Zn(1)	114.6(3)
N(1′)–Zn(1)–N(1)	104.06(15)	N(2′)–N(1′)–Zn(1)	137.1(3)
N(7)–Zn(1)–N(1)	77.20(15)	N(1)–Zn(1)–O(1′)	177.41(14)
O(2)–Zn(1)–O(1′)	87.55(15)	C(5)–N(1)–Zn(1)	139.9(3)
N(1′)–Zn(1)–O(1′)	75.98(13)	N(2)–N(1)–Zn(1)	114.1(3)
N(7)–Zn(1)–O(1′)	100.43(14)	N(4)–O(2)–Zn(1)	107.6(3)

3. Results and discussion

3.1. *Synthesis and spectroscopic properties of the complexes*

Reaction of $Hg(SCN)_2$, $Zn(ClO_4)_2$ and $CdCl_2$ with 5-methyl-1-(2′-pyridyl)pyrazole-3-carboxamide (MP_yP_zCA) provided powders analyzing as $[Hg(MP_yP_zCA)(SCN)_2]$, $[Zn(MP_yP_zCA)_2NO_3]^+[(NO_3)_{0.60}(ClO_4)_{0.40}]^- \cdot H_2O$ and $[Cd(MP_yP_zCA)_2Cl_2]$, respectively. The IR spectrum of the $[Hg(MP_yP_zCA)(SCN)_2]$ complex shows $\nu(SCN)$ at 2090 cm^{-1} and that of the $[Zn(MP_yP_zCA)_2NO_3]^+[(NO_3)_{0.60}(ClO_4)_{0.40}]^- \cdot H_2O$ complex shows $\nu(NO_3)$ at 1370 and $\nu(ClO_4)$ at 1105 cm^{-1}. Attempts to isolate

[Hg(MP_yP_zCA)$_2$(SCN)$_2$] were not successful; each time a 1 : 1 adduct was isolated. Comparison of IR spectrum of the free ligand with that of the complexes shows a negative shift in the ν(C=O) of the amide linkage in the complexes [1680 cm^{-1} (MP_yP_zCA) compared with 1645 cm^{-1} [Cd(MP_yP_zCA)$_2$Cl$_2$], 1635 cm^{-1} [Zn(MP_yP_zCA)$_2$](NO$_3$)$_2$ and 1640 cm^{-1} Hg(MP_yP_zCA)(SCN)$_2$], indicating [9] that the oxygen atom of the amide linkage is coordinated to the metal centers. The IR spectrum of the [Hg(MP_yP_zCA)(SCN)$_2$] complex reveals ν(SCN) at *ca* 2090 cm^{-1}, which is a significant change compared to the lead(II) complexes [10–12], suggesting that the thiocyanate anion coordinates differently in the lead(II) and mercury(II) complexes, possibly through sulfur for mercury(II) and through nitrogen the atom for lead(II).

3.2. *Crystal structure of* $[Zn(MP_yP_zCA)_2NO_3]^+[(NO_3)_{0.60}(ClO_4)_{0.40}]^-\cdot H_2O$

An ORTEP diagram of the complex together with the atom-numbering scheme is shown in figure 2, and a perspective view of the crystal structure is presented in figure 3. Selected bond distances and angles around the Zn(II) ion are shown in table 2. The two MP_yP_zCA ligands in the complex are both bidentate; however, one of them coordinates to Zn(II) through the pyrazole nitrogen and carboxamide oxygen atoms, and the other is coordinated through its pyrazole and pyridyl nitrogen atoms. The coordination environment around Zn(II) is distorted trigonal bipyramid [ZnN$_3$O(carboxamidic)O(nitrate anion)]. The atoms N(1) and O(1′) are axial, with an N(1)–Zn(1)–O(1′) angle of 177.41(14)°, and the atoms N(1′), N(7) and O(2) are distorted equatorial, with angles O(2)–Zn(1)–N(1′) = 115.39(15)°, O(2)–Zn(1)–N(7) = 128.19(15)° and N(1′)–Zn(1)–N(7) = 116.22(16)°.

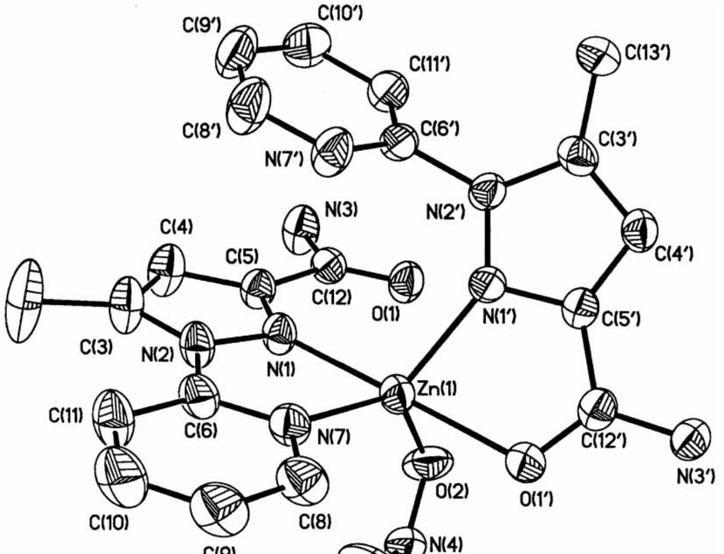

Figure 2. ORTEP plot of the molecule showing the atom-numbering scheme.

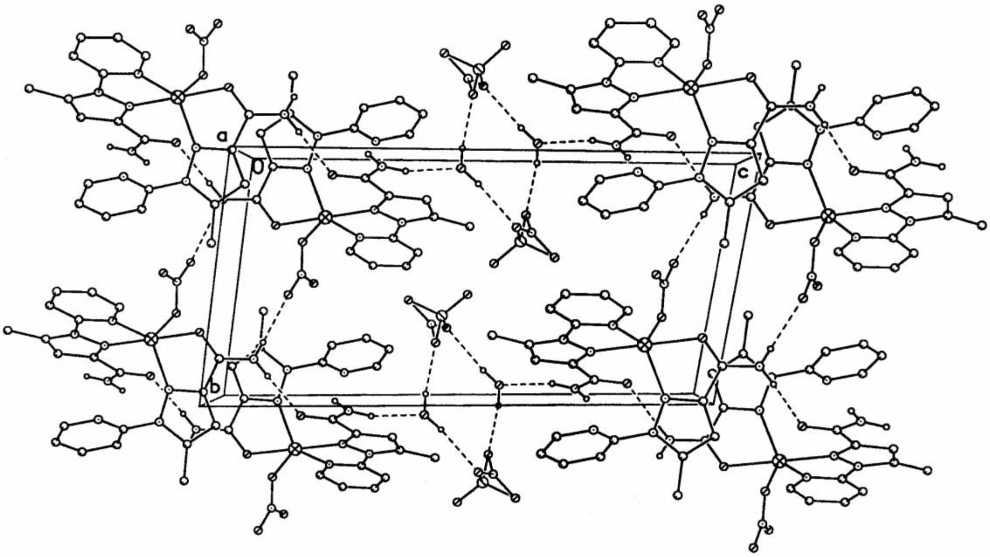

Figure 3. Unit cell showing the intermolecular hydrogen bonding of the molecules.

Table 3. Intermolecular H-bonds in the complex.

D–H···A	D···A (Å)	D–H (Å)	H···A (Å)	DHA (°)
O1W–H2W···O3S ($-x+1$, $-y$, $-z+1$)	2.74(l)	0.85	2.04	139.66
O1W–H1W···O2S	2.95(l)	0.85	2.15	158.08
N3–H3B···O1W ($-x+1$, $-y$, $-z+1$)	2.930(7)	0.90(6)	2.05(6)	165(5)
N3′–H3D···O1 ($-x$, $-y$, $-z$)	2.949(6)	0.82(6)	2.17(6)	159(5)
N3′–H3C···O4 ($-x$, $-y+1$, $-z$)	3.023(6)	0.75(5)	2.28(5)	170(5)
N3–H3A···N7′ ($x+1$, y, z)	3.0573(6)	0.98(7)	2.16(7)	151(6)

The crystal contains perchlorate and nitrate anions with two independent NO_3^- anions in the structure, one coordinating the Zn and another crystallographically independent NO_3^- anion is disordered, sharing one position in the crystal with the ClO_4^- anion. Final refinement showed that 40% of these positions in the crystal are occupied by ClO_4^- and 60% of positions contain NO_3^-. The crystal structure shows a high degree of stabilization through extensive hydrogen bonding (figure 3). The coordinated MP_yP_zCA and water molecules are involved in hydrogen-bonding, acting as hydrogen-bond acceptors with O atoms from nitrate or perchlorate anions as hydrogen-bond donors. As shown in figure 3, the hydrogen bonding yields infinite chains parallel to the crystallographic vectors *a* and *b*. Each complex is bonded to three neighbors, assembling molecules into a two-dimensional chain (table 3).

There is a π–π stacking [13, 14] interaction between parallel aromatic rings belonging to adjacent chains in this complex, as shown in figure 4. The pyridyls are almost parallel with the pyrazolyl groups and separated by a distance of about 3.5 Å, close to that of the planes in graphite. Parallel arrays of planes of the aromatic moieties indicate that these interactions are of the π-stacking type, rather than edge-to-face or vertex-to-face types [15–18]. Projection of the structure perpendicular to the ring plane

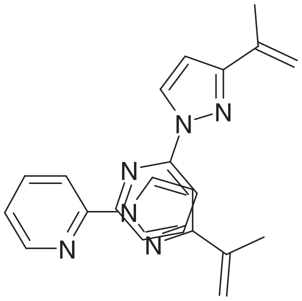

Figure 4. Projection of nearest neighbor pairs in the π–π stacks of the heteroaromatic bases in $[Zn(MP_yP_zCA)_2NO_3]^+[(NO_3)_{0.60}(ClO_4)_{0.40}]^-$.

shows the overall form of ''slipped'' stacking [18, 19], which can be rationalized qualitatively in terms of optimizing the attraction between atoms of opposite charges [20].

A simple model to describe the nature of π–π interactions has been developed by Hunter and Sanders [20]. This model predicts that face-to-face π-stacked interactions will be disfavored due to dominance of π–π repulsion. However, in offset π-stacked, and edge-on or T-shaped geometries, favorable π–σ attractions dominate. The polarization of aromatic systems through the introduction of heteroatoms, electron-withdrawing groups or electron-donating groups alters the nature of any π–π interactions. Hence, it can be expected that within the molecule discussed here, the electron-poor pyrazolyl rings will interact with less electron-poor rings such as pyridyl groups (figure 4).

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 163978. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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