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Trans-dichlorotetrakis(1*H*-pyrazole-κN^2)copper(II): Synthesis, crystal structure, hydrogen bonding graph-sets, vibrational and DFT studies

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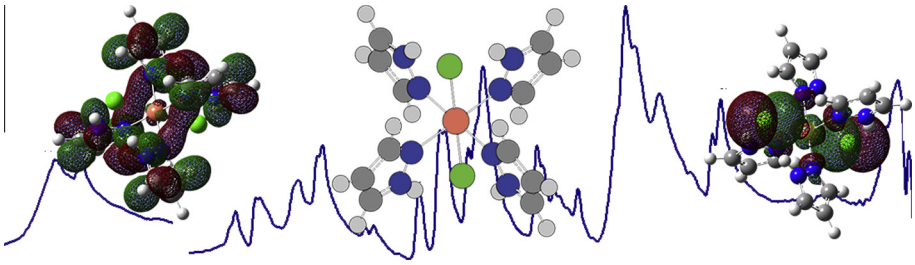
HIGHLIGHTS

- *Trans*-dichlorotetrakis(1*H*-pyrazole-κN^2)copper(II) were synthesized and characterized.
- The complex crystallizes in the monoclinic system, space group C2/c.
- The C_i symmetry is more stable than the C_1 symmetry.
- Structure is held together through N—H···Cl hydrogen bonds.

GRAPHICAL ABSTRACT



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ABSTRACT

The copper complex $[Cu(HPrz)_4]Cl_2$ (HPrz = Pyrazole) was synthesized and its structure was characterized by FT-IR, Raman and single-crystal X-ray diffraction (XRD) techniques. The structural conformers, optimized geometric parameters, normal mode frequencies and corresponding vibrational assignments of the compound were examined by means of the density functional theory (DFT) method, the Becke-3-Lee–Yang–Parr (B3LYP) functional, the 6-311+G(3df,p) and lanl2dz basis sets. Reliable vibrational assignments were investigated by the potential energy distribution (PED) analysis. The compound crystallizes in the monoclinic space group C2/c with the unit cell parameters $a = 13.5430$ (10) Å, $b = 9.1480$ (10) Å, $c = 14.6480$ (10) Å and $\beta = 116.7°$ (5). There is a good agreement between the theoretically predicted structural parameters and vibrational frequencies and those obtained experimentally. The findings of this work reveals further insight into molecular copper(II) pyrazole systems.

Introduction

Metal organic frameworks (MOFs) consist of metal ions or clusters often coordinated to rigid organic molecules to form one-, two-, or three-dimensional structures. MOFs are also known as coordination polymers which are the inorganic or organometallic polymer structures containing metal cation centers linked by organic ligands. The chemical and pharmacological properties of the pyrazoles have been investigated extensively, due to their chelating ability with metal ions [1] as terminal [2,3] or bridging ligands [4–6] and, precursors for synthesis of various multi-nitrogen donor ligands in the coordination, bio-inorganic and organometallic chemistry [7]. They are well known for the discovery of new catalyst precursors [8] and, for their potentially benefic chemical, biological and medicinal activities reported in the literature; including analgesic [9], anti-inflammatory [10] and other therapeutic functions. Furthermore, the pyrazoles are widely used for their ability to participate in hydrogen bonding interactions

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[11,12], as bridging units for two metal centers [13,14], and for the synthesis of complexes with spin crossover behavior [15].

The discrete complex *trans*-dichlorotetrakis(1*H*-pyrazole-κN^2)copper(II) had been mentioned in the earlier literature. In the early seventies, Reedijk [16] first published serial investigations about pyrazole and its derivatives. Mighell and coworkers also synthesized this complex and found the same unit cell [17]. It was synthesized by Sun and coworkers [18] in 2001, reacting hydrated copper chloride with a hydrotris(pyrazolyl)borate (Tp) derivative $[FeTp_2][TpFe(SCN)_3]$ in a methanolic solution. The UV–Vis and X-band ESR spectroscopic parameters of the complex were reported. Synthesis of $[Cu(HPrz)_4Cl_2]$ was performed again in 2006 by Xing and coworkers [19], by direct treatment of copper chloride with pyrazole in a methanolic solution.

In view of the above and in continuation with its synthesis, in this study, $[Cu(HPrz)_4]Cl_2$ complex was synthesized as single crystal. The structure of the complex was characterized by FT-IR, Raman and, confirmed by single-crystal XRD studies. The graph-set descriptors of the intra- and intermolecular hydrogen bonding interactions stabilizing the title coordination compound were also reported. Although literature reveals some syntheses and experimental studies of this complex, there is lack of information on the detailed experimental and theoretical vibrational properties together with theoretical molecular structure. In addition, this research work was complemented using DFT method in conjunction with the B3LYP/6-311+G(3df,p) and B3LYP/lanl2dz levels. The highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of the complex were also predicted. The findings of these spectroscopic and theoretical studies are herein reported.

Experimental

Instrumentation

A dark blue block-like crystal of the complex, with dimensions of 0.10 × 0.10 × 0.15 mm was selected and mounted on an Oxford Diffraction Xcalibur CCD diffractometer with a fine-focus sealed tube graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) using φ and ω scans at 170 K in the range of $2.8° \leqslant \theta \leqslant 31.7°$. The unit cell determination and data reduction were performed using the CrysAlis program [20]. A total of 8144 reflections were collected, of which 2741 were independent and 2120 reflections with $I > 2\sigma(I)$. The structure was solved by direct methods using the program SIR2008 [21] and was refined by full-matrix least squares technique on F^2 including all reflections with SHELXL-2013 program [22]. Both softwares were included within the WingX crystallographic software package [23]. All non-hydrogen atoms were anisotropically refined. All of the hydrogen atoms were located from the difference Fourier map and were fixed in calculated positions with distances constraints of C—H = 0.93 Å and N—H = 0.86 Å, and refined in riding mode with $U_{iso}(H) = 1.2\ U_{eq}$(C, N). The refinements converged at conventional *R* factor of 0.0249 and *wR* of 6.66%. Maximum and minimum peaks in the final

Table 2
Crystal data and parameters for structure refinement.

Crystal data	Complex
Empirical formula	$C_{12}\ H_{16}\ Cu\ N_{12}\ Cl_2$
Formula weight (g mol^{-1})	M_r = 406.76
Temperature (K)	170(2)
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions (Å,°)	
a	13.5430(10)
b	9.1480(10)
c	14.6480(10)
β	116.700(5)
Volume (Å^3)	1621.3(3)
Z[a]	4
Calculated density (g/cm^3)	1.667
Absorption coefficient (mm^{-1})	1.688
F(000)	828
Crystal size (mm^3)	0.10 × 0.10 × 0.15
Color	Dark blue
Shape	Block-like crystal
Cell parameters from	8144 reflections
Wavelength (Mo Kα) (Å)	0.71073
$\theta_{max} - \theta_{min}$	31.679° − 2.791°
Measured reflections	8144
Independent reflections	2741
Reflections with $I > 2\sigma(I)$	2120
R_{int}	0.0328
Limiting indices	
h	−19 → 20
k	−13 → 11
l	−20 → 21
Refinement method	Full-matrix Least-squares on F^2
Final *R* indices [b] [$F^2 > 2\sigma(F^2)$]	
R_1, wR_2	0.0249, 0.0666
R indices (all data)	
R_1, wR_2	0.0328, 0.0685
Goodness-of-fit on F^2[c]	1.019
Data/restraints/parameters	2548/0/106
H atoms	a constrained refinement
Largest difference peak and hole (e Å^{-3})	
$\Delta\rho_{max}$, $\Delta\rho_{min}$	0.344, −0.293

[a] The asymmetric unit contains 0.5 of the chemical formula.
[b] $R_1 = \sum|Fo - Fc|/Fo$. $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.
[c] GOF = $\{\sum[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{var})\}^{1/2}$.

Table 1
Energetic and molecular parameters of the complex.

Parameters	B3LYP/6-311+G(3df,p)		B3LYP/lanl2dz	
	C_i	C_1	C_i	C_1
Δ*G* (Hartree)	−3466.031387	−3466.031299	−1130.673014	−1130.673018
Dipole moment (Debye)	0	0.0048	0	0.0113
Thermal total energy (kcal/mol)	199.787	199.789	201.367	201.371
Heat capacity (cal/mol K)	83.431	83.435	82.497	82.495
Entropy (kcal/mol K)	175.001	174.81	171.789	171.812
Vibrational energy (kcal/mol)	198.01	198.011	199.589	199.594
Zero point vibrational energy (kcal/mol)	184.68488	184.69229	186.51305	186.51753
Rotational constant (GHz)				
a	0.22432	0.22433	0.22298	0.22303
b	0.22331	0.22337	0.22058	0.22061
c	0.16829	0.16828	0.16693	0.16694
Relative stability (kcal/mol)	0	0.05522	0.0025	0
Mole fractions (%)	52.33	47.67	49.89	50.11