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Research paper

Molecular and electronic structures of copper-cuprizone and analogues

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ABSTRACT

A paramagnetic dinuclear copper(II) complex, $[Cu^{II}(L^{-})Cl]_2$ (**1**) while LH = (*E*)-1,2-diphenyl-2-(2-(pyridine-2-yl)hydrozono)ethanone, an analogue of mono-hydrazone cuprizone ($L_{mcpz}H_2$), was isolated and substantiated by spectra, single crystal X-ray structure determination, unrestricted density functional theory (DFT) calculations and inter alia. Magnetic susceptibility measurement and EPR spectra confirmed the triplet state of **1** above 30 K because of two paramagnetic copper(II) centers. Unrestricted DFT calculations on copper cuprizone species with doublet spin state established similar electronic features and disclosed that bis-deprotonated NN-chelation, $[Cu(L_{mcpz})_2]^{2-}$, (*cis* or *trans*-$\mathbf{2^{NN}}$), is $\sim 3 \times 10^3$ kJ/mol higher in energy than the mono-deprotonated NO-chelation, $Cu(L_{mcpz}H)_2$, (*cis* or *trans*-$\mathbf{2^{NO}}$) precluding the existence of so far reported $\mathbf{2^{NN}}$ products. The calculations revealed that in all isomers, due to the mixing of $d^2_{x^2-y^2}$ orbital with a ligand group orbital as in **1**, 48–50% spin density is delocalized over the $L_{mcpz}H_2$ ligand. In fluid solution, **1** absorbs strongly at 527 nm due to LMCT elucidated by the time dependent (TD) DFT calculations and the excited LMCT state is fluorescent (λ_{ex} = 375 nm; λ_{em} = 405, 426 nm; Φ = 0.014).

1. Introduction

Mono-hydrazone cuprizone ($L_{mcpz}H_2$) is a bioactive molecule with neurotoxic properties leading to spongiosis and is used as a drug to induce that in laboratory animals [1–7]. Cuprizone has a strong affinity towards the redox active copper ion but the origin of the bioactivity of it is not clear so far [8–10]. To analyze the electronic and structural features mimicking the copper cuprizone complex, copper parent osazone (PhNHN = CH–CH = NNHPh) complex was given attention. Reaction of osazone with copper(II) ion salt under argon in methanol affords a dark red precipitate which is unstable even in solid state and decomposes spontaneously at 298 K [11].

However, the reaction of benzil with 2-hydrazino pyridine in methanol in air yields a two electron paramagnetic dinuclear copper complex, $(CuLCl)_2$, **1,** of (*E*)-1,2-diphenyl-2-(2-(pyridine-2-yl) hydrozono)ethanone (LH), an analogue of mono-hydrazone cuprizone ($L_{mcpz}H_2$) as shown in Chart 1. A complete experimental and theoretical study substantiated the complex **1** which incorporates NNO chelate. To compare the ground state energies of the various chelation modes of cuprizone to copper(II) ion and the compositions of the molecular orbitals were analyzed by DFT calculations. The calculations on the paramagnetic $[Cu(L_{mcpz})_2]^{2-}$, ($\mathbf{2^{NN}}$) or $Cu(L_{mcpz}H)_2$, ($\mathbf{2^{NO}}$ or $\mathbf{2^{OO}}$) considering all three types of chelation as illustrated in Scheme 1, likewise, established that the frontier molecular orbitals of **1** are very similar to those of $\mathbf{2^{NN}}$, $\mathbf{2^{NO}}$ and $\mathbf{2^{OO}}$ analogues.

In this article, synthesis, structure, spectra and the unrestricted DFT calculations on **1**, *cis/trans* isomers of $\mathbf{2^{NO}}$, $\mathbf{2^{NN}}$ and $\mathbf{2^{OO}}$ are reported.

2. Experimental

2.1. Materials and physical measurements

Reagents or analytical grade materials were obtained from *Sigma-Aldrich* and used without further purification. Spectroscopic grade solvents were used for spectroscopic measurements. After evaporating H_2O and MeOH solvents of the sample under high vacuum, elemental analyses and spectral measurements were performed. The C, H and N content of the compounds were obtained from *Perkin-Elmer 2400 series II* elemental analyzer. Infrared spectra of the samples were measured from 4000 to 400 cm^{-1} with the KBr pellet at 295 K on a *Perkin-Elmer Spectrum RX 1*, FT-IR Spectrophotometer. ESI mass spectra were recorded on a micro mass *Q-TOF mass spectrometer*. Electronic absorption spectra in solutions at 295 K were carried out on a *Perkin-Elmer Lambda 25* spectrophotometer

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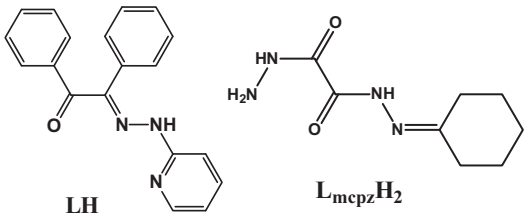


Chart 1. (*E*)-1,2-Diphenyl-2-(2-(pyridine-2-yl)hydrozono)ethanone (LH) and mono-hydrazone cuprizone ($L_{mcpz}H_2$).

in the range of 1100–200 nm. Variable temperature (3–300 K) magnetization data were recorded in a 1 T magnetic field on a *SQUID magnetometer* (MPMS Quantum Design). The experimental magnetic susceptibility data were corrected for underlying diamagnetism using tabulated Pascal's constants and fit using julX (Dr. Eckhard Bill). X-band EPR spectra were recorded on a *Bruker ELEXSYS E500* spectrometer and simulated with XSophe [12] distributed by Bruker Biospin GmbH. The electro analytical instrument, *BASi Epsilon-EC* for cyclic voltammetric experiments in CH_2Cl_2 solutions containing 0.2 M tetrabutylammonium hexafluorophosphate as supporting electrolyte was used. The BASi platinum working electrode, platinum auxiliary electrode, Ag/AgCl reference electrode were used for the measurements.

2.2. Syntheses

2.2.1. $[CuLCl]_2$ (**1**)

To a mixture of benzil (105 mg, 0.5 mmol) and 2-hydrazino pyridine (55 mg, 0.5 mmol) in a 100 mL round bottom flask, methanol (50 mL) was added and the reaction mixture was refluxed for 45 min (338 K). After cooling at room temperature (298 K), the solution mixture was filtered. To this solution anhydrous $CuCl_2$ (70 mg, 0.5 mmol) in methanol (~10 mL) was added carefully and the reaction mixture was allowed to evaporate slowly at 298 K. After a few days, a green crystalline solid of **1** separated out, which were filtered and dried in air and collected. Yield: 96 mg (~51% with respect to cupper). Mass spectrum (ESI, positive ion, CH_3CN); *m/z*: 363 for (CuL^+). Anal. Calc. for $C_{38}H_{28}Cl_2Cu_2N_6O_2$: C, 57.15; H, 3.53; N, 10.52; Found: C, 57.25; H, 3.55; N, 10.45. IR (KBr disk): ν 3474 (s), 1602 (vs), 1456 (m), 1514 (m), 1466 (s), 1438 (s), 1358 (s), 1327 (s), 1208 (vs), 1141 (s), 1092 (s), 1012 (s), 927 (m), 778 (m), 702 (s), 665 (vs) cm^{-1}.

2.3. Structure determination

Single crystals of **1** was picked up with nylon loops and was mounted on a *Bruker APEX-II CCD* diffractometer equipped with a Mo-target rotating-anode X-ray source and a graphite monochromator (Mo-Kα, λ = 0.71073 Å). Final cell constants were obtained from least squares fits of all measured reflections.

Table 1
Crystallographic data for **1**.

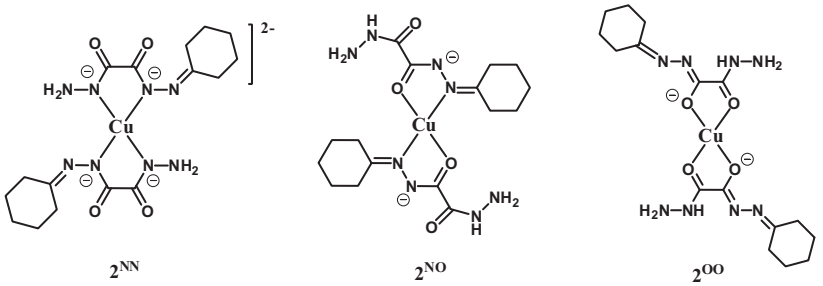
CCDC	840632	ρ_c/g cm^{-3}	1.525
Formula	$C_{38}H_{28}Cl_2Cu_2N_6O_2$	$2\theta_{max}$	50.0
F_w	798.64	Unique reflections	8375
Crystal colour	Green	Total reflections	12939
Crystal system	Monoclinic	λ/Å	0.71073
Space group	*C2/c*	μ/mm^{-1}	1.421
a/Å	21.9360(5)	*F*(0 0 0)	1624
b/Å	9.8104(2)	R_1[a] [$I>2\sigma(I)$]	0.0257
c/Å	17.5925(4)	GOF[b]	1.02
β/°	113.27(1)	R_1[a] (all data)	0.0297
V/$Å^3$	3477.87(13)	wR_2[c] [$I>2\sigma(I)$]	0.0743
Z	4	No. of Parameter	226
T/K	296(2)	$\Delta\rho_{max,min}$/$eÅ^{-3}$	0.508/−0.348

Observation criterion: $I > 2\sigma(I)$.
[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] GOF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$.
[c] $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$.

Intensity data were corrected for absorption using intensities of redundant reflections. The structure was readily solved by direct methods and subsequent difference Fourier techniques. The crystallographic data of **1** are listed in Table 1. The Siemens SHELXS97 [13] software package was used for solution and SHELXL97 [13] was used for the refinement. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at the calculated positions and refined as riding atoms with isotropic displacement parameters.

2.4. Density functional theory (DFT) calculations

All calculations reported in this chapter were done with the Gaussian 03W [14] program package supported by GaussView 4.1. The DFT [15] and TD DFT [16] calculations were performed at the level of Becke three parameter hybrid functional with the non-local correlation functional of Lee-Yang-Parr (B3LYP) [17]. The gas phase geometries of **1**, ***t*-2NO**, ***c*-2NO**, ***t*-2^{NN}**, ***c*-2^{NN}** and **2^{OO}** were optimized on theoretical coordinates using Pulay's Direct Inversion [18] in the Iterative Subspace (DIIS) convergent SCF procedure [19] ignoring symmetry. In all calculations, a LANL2DZ basis set along with the corresponding effective core potential (ECP) was used for copper metal [20]. Valence double zeta basis set, 6-31G [21] for H was used. For C, N, O and Cl non-hydrogen atoms valence double zeta plus diffuse and polarization functions, 6-31G (d,p) [22] as basis set were employed for the calculations. The percentage contribution of ligand and metal to the frontier orbitals of **1** and ***t*-2NO** were calculated using GaussSum program package [23]. The sixty lowest singlet excitation energies on the optimized geometries of **1** in CH_2Cl_2 using CPCM model [24] were elucidated by TD DFT method.



Scheme 1. Possible chelation modes of $L_{mcpz}H_2$: $[Cu(L_{mcpz})_2]^{2-}$ (**2^{NN}**) and $[Cu(L_{mcpz}H)_2]$ (**2NO** and **2^{OO}**).