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Complexes with a tridentate aroylhydrazone ligand: Microwave solid-state synthesis, crystalline architectures through supramolecular interactions and electrochemical properties

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ABSTRACT

A series of complexes, $[CuLCl]\cdot 1\cdot 5H_2O$ (**1**); $[ML_2]\cdot X$ (X = 0, M = Cd, **2a**; X = DMF, M = Hg, **2b**; X = DMF, M = Ni, **2c**); $[Cu_2(OOCCH_3)_2L_2]\cdot 2CH_3OH$ (**3**) have been synthesized by microwave solid-state method with a tridentate aroylhydrazone ligand HL (HL = N^3-salicyloylpyridine-2-carboxamidrazone). All these compounds were characterized by element analysis, IR, X-ray diffraction and electrochemistry. Crystal analysis revealed that the coordination molecules extended to 3D supramolecular networks through plentiful H-bondings and weak molecular interactions between the ligand moieties and solvent molecules. Meanwhile, these compounds displayed diverse metal or ligand localized electrochemical properties.

1. Introduction

Hydrazone ligands, usually as transition metal binders in analytical chemistry [1], have been found to have wide applications not only in various chemical and photochemical reactions [2,3], but also in numerous industrial manufacture of science and technology [4]. Additionally, studies have also shown that the hydrazone derivatives have considerable importance in biological activities [5], which was reviewed by Rollas et al. [6]. Moreover, substituted aroylhydrazone complexes were known to provide useful models for elucidation of the mechanism of enzyme inhibition by hydrazine derivatives [7–9]. On the other hand, substituted aroylhydrazone ligands, owing to their structural flexibility, have quite diverse coordination modes and can act as a bidentate [10], tridentate or tetradentate [11] unit and a neutral or anionic ligand due to keto-enol tautomerization [12,13]. Such complexes of 2-pyridinecarboxaldehyde-salicyloyhydrazone and 2-acetylpyridine-salicyloylhydrazone have been well characterized [14–16].

The aroylhydrazone of N^3-salicylolylpyridine-2-carboxamidrazone, as a precursor of 1,2,4-triazole, affords several potential donor atoms and can occur in different chemical and structural conformations [17–20], exhibiting more facile and abundant coordination ability than triazoles. Otherwise, this asymmetric open-ring ligand owns groups readily forming hydrogen bondings, which play the main roles on the generation of unique supramolecular structures. Moreover, these supramolecular structures possess of significant potential use as magnetic materials, optical and thermal switches, host/guest properties and probes for DNA structures [21].

Nowadays, low-thermal solid-state reaction becomes one of energy-efficient, low-pollution synthetic methods advocated by green-chemistry industrial manufacture. Especially, the microwave-assistant solid-state synthesis becomes interested due to its advantages in reducing reaction steps, increasing yield and purity of products, shorting reaction time, convenience of separating products [22,23].

In this present paper, a series of compounds $[CuLCl]\cdot 1\cdot 5H_2O$ (**1**); $[ML_2]\cdot X$ (X = 0, M = Cd, **2a;** X = DMF, M = Hg, **2b**; X = DMF, M = Ni, **2c**); $[Cu_2(OOCCH_3)_2L_2]\cdot 2CH_3OH$ (**3**) based on the ligand N^3-salicylolylpyridine-2-carboxamidrazone have been synthesized by microwave solid-state method. The structures of all the compounds were determined and the expected dominance of the hydrogen bonding in the crystal packing was discussed in detail. Furthermore, the electrochemical properties were also investigated to explore the redox behaviors of these compounds.

2. Experimental

2.1. Materials

The ligand HL was synthesized following a literature procedure [24]. All chemicals were of reagent grade and were used without further purification.

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2.2. Physical measurements

The microwave radiation was realized in a domestic National NN-S570MFS oven with pulsed microwave control. The melting point was measured on a XT-5 micro melting point apparatus. Elemental analysis (carbon, hydrogen and nitrogen) was performed using a Perkin–Elmer 240C elemental analyzer. IR spectra in KBr (4500–500 cm^{-1}) were recorded using a Bruker Optics TENSOR 27 FT-IR spectrophotometer. Electrochemical measurements were performed in DMSO solution under a dry nitrogen atmosphere at ambient temperature. The CV data was collected in conventional three-electrode configurations using a Pt-disk working electrode, Pt auxiliary electrode and saturated calomel reference electrode (SCE), with tetra-butylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. The redox potentials were calibrated versus ferrocene, which was used as an internal potential standard for measurement to avoid the influence of liquid junction potential. The value for the F_c/F_c^+ couple under our conditions is 0.45 V. The final values were reported versus F_c/F_c^+ couple.

2.3. X-ray crystallography

Single crystals of **1–3** having suitable dimensions was used for data collection using a 'Bruker SMART APEX II' diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The molecular structures were solved by direct methods and refinement by full-matrix least squares on F^2 using the SHELX-97 package [25]. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. H atoms of hydroxy were located by difference Fourier maps and were kept fixed. Empirical absorption corrections were carried out with the ABSPACK program [26a]. Non-hydrogen atoms were refined anisotropically. The space group for compound **2a** was checked by PLATON software [26b] to $P2/c$. Significant crystallographic data were summarized in Table 1.

2.4. Preparations

2.4.1. Synthesis of [CuLCl]·1.5H₂O (**1**)

The solid-state mixture of ligand HL (4 mmol, 1.024 g) and $CuCl_2 \cdot 2H_2O$ (4 mmol, 0.682 g) was grinded by the agate mortar and dampened by several drops of water. Then, the mixture was radiated for 6 min in the microwave oven of 200 W. The resulting green powder was washed by water and ethanol for 2–3 times, dried in vacuum and recrystallized from DMF/water (V:V = 1:1). Yield: 1.239 g (80%), M. p. > 300 °C. *Anal.* Calc. for $C_{26}H_{28}Cl_2Cu_2N_8O_7$ (FW, 762.56): C, 40.91; H, 3.67; N, 14.69. Found: C, 40.98; H, 3.73; N, 14.49%. Selected IR data(KBr, cm^{-1}): 3452(b)(ν(OH)/ν(NH)), 1671(s), 1598(s)(ν(C=N)), 1552(s), 1515(s), 1477(s), 1420(s), 1254(m), 1237(m)(ν(Ar–O)), 1154(w), 1094(w), 1050(w), 964(w), 907(w), 853(w), 792(w), 750(m), 700(w), 643(w).

2.4.2. Synthesis of [ML₂]·X (X = 0, M = Cd, **2a;** X = DMF, M = Hg, **2b**; X = DMF, M = Ni, **2c**)

The solid-state mixture of ligand HL (4 mmol, 1.024 g) and $Cd(OOCCH_3)_2 \cdot 3H_2O$ (2 mmol, 0.462 g) was grinded by the agate mortar and dampened by several drops of ethanol. Then, the mixture was radiated for 3 min in the microwave oven of 200 W. The resulting brown powder was washed by water and ethanol for 2–3 times, dried in vacuum and colorless columnar crystals of **2a** suitable for single-crystal X-ray diffraction were recrystallized from DMF/ethanol (V:V = 1:1). Yield: 1.123 g (77%), M. p. > 300 °C. *Anal.* Calc. for $C_{26}H_{22}CdN_8O_4$ (FW, 622.92): C, 50.09;

Table 1
Crystallographic data for **1**, **2a**, **2b** and **3**.

	1	**2a**	**2b**	**3**
Formula	$C_{26}H_{28}Cl_2Cu_2N_8O_7$	$C_{26}H_{22}CdN_8O_4$	$C_{29}H_{29}HgN_9O_5$	$C_{32}H_{36}Cu_2N_8O_{10}$
Mr	762.56	622.92	784.2	819.75
Color and habit	green, block	colorless, columnar	orange-yellow, block	brown, block
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$C2/c$	$P2/c$	$P\bar{1}$	$P\bar{1}$
Crystal size (mm^3)	0.38 × 0.24 × 0.20	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1
T (K)	298(2)	296(2)	296(2)	296(2)
a (Å)	14.857(1)	10.9157(6)	10.6852(5)	8.9598(9)
B (Å)	12.456(1)	13.2344(7)	12.3580(6)	9.8977(9)
c (Å)	16.541(2)	20.1459(9)	12.6037(6)	12.253(1)
α (°)	90	90	101.224(2)	71.073(3)
β (°)	95.5770(10)	116.997(3)	113.369(2)	71.390(3)
γ (°)	90	90	99.075(2)	67.654(3)
V (Å³)	3046.6(5)	2593.1(2)	1446.64(12)	926.6(2)
Z	4	4	2	1
D_{calc} ($g\ cm^{-3}$)	1.663	1.596	1.800	1.466
μ (mm^{-1})	1.630	0.892	5.377	1.212
$F(000)$	1552	1256	772	420
θ (°)	2.40–25.02	1.54–27.97	1.74–28.27	2.52–26.00
Index ranges	$-17 \leqslant h \leqslant 17$, $-14 \leqslant k \leqslant 14$, $-19 \leqslant l \leqslant 10$	$-14 \leqslant h \leqslant 14$, $-17 \leqslant k \leqslant 17$, $-25 \leqslant l \leqslant 26$	$-14 \leqslant h \leqslant 14$, $-16 \leqslant k \leqslant 16$, $-16 \leqslant l \leqslant 16$	$-10 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 12$, $-15 \leqslant l \leqslant 15$
No. measured reflections	7631	24385	25984	11607
No. independent reflections (R_{int})	2705 (0.0370)	6198 (0.0209)	7095 (0.0234)	3566 (0.0266)
No. observed reflections, [$I > 2\sigma(I)$]	2109	5398	6578	2973
Parameters	216	352	397	237
S	1.024	1.059	0.972	1.035
R_1 ($I > 2\sigma(I)$)[a]	0.0337	0.0304	0.0246	0.0539
wR_2 (all data)[b]	0.0905	0.1286	0.0997	0.834
Maximum, minimum electron density ($e\ Å^{-3}$)	0.334, −0.372	1.440, −0.548	1.902, −1.635	1.587, −0.769

[a] $R_1 = ||F_o| - |F_c||/|F_o|$.

[b] $wR_2 = \{[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$ and $p = (F_o^2 + 2F_c^2)/3$.