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Crystal structure, spectroscopy, DFT studies and thermal characterization of Cobalt(II) complex with 2-protonated aminopyridinium cation as ligand

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ABSTRACT

Single crystals of a new organic–inorganic hybrid compound $(2\text{-HAMP})_2[CoBr_4]$, (2-HAMP = 2-protonated aminopyridinium cation) was synthesized and characterized by X-Ray diffraction at room temperature, DTA–TG measurement, FT-IR and FT-Raman spectroscopies and optical absorption. Its crystal structure is a packing of alternated organic and inorganic layers parallel to (a, b) plane. The different components are connected by a network of N/C–H···Br hydrogen bonds and halogen···halogen interactions. These hydrogen bonds give notable vibrational effects. Theoretical calculations were performed using density functional theory (DFT) for studying the molecular structure, vibrational spectra and optical properties of the investigated molecule in the ground state. The optimized geometrical parameters obtained by DFT calculations are in good agreement with single crystal XRD data. The energy and oscillator strength calculated by Time-Dependent Density Functional Theory (TD-DFT) results complements with the experimental findings. The simulated spectra satisfactorily coincide with the experimental UV–Visible spectrum. The results show good consistent with the experiment and confirm the contribution of metal orbital to the HOMO–LUMO boundary. Thermal analysis studies indicate the presence of three phase transitions at 68, 125 and 172 °C, which are confirmed by X-ray powder diffraction as a function of temperature.

1. Introduction

A great deal of interest has arisen in the synthesis of hybrid materials as a result of their special functional properties such as magnetic or ferroelectric transitions, conductivity, electroluminescence and photoluminescence [1–6]. Furthermore, mixed organic-inorganic salts with the general formula A_2MX_4 (A: organic cation, M: transition metal and X: halogen = Cl, Br, I) have attracted considerable interest due to their multiple phase transitions related to the dynamics of the organic cations and inorganic anions. Interest in these compounds is rapidly increasing, as some of them exhibit interesting structural and physical properties like ferroelectricity, ferro-elasticity and low dimensional magnetism [7–16]. The current attention, herein, is the incorporation of metal halide systems and organic cations as counter-ions in the extremely interesting hybrid materials and this strategy is expected to affect their appealing structural, optical and photoluminescence properties, which should lead to new interesting functional compounds. The present work deals with the synthesis and the characterizations of a novel hybrid compound, $(2\text{-HAMP})_2[CoBr_4]$, with an organic layer of 2-aminopyridine ($C_5H_6N_2$), single X-ray diffraction study and detailed vibrational spectral analysis aided by Density Functional Theory (DFT) calculations. In the light of the theoretical calculations, correlation between FT-IR and FT-Raman spectra and computed results help unambiguous identification of vibrational modes and provide deeper insight into the bonding and structural features of the title compound. An optical absorption measurement and thermal studies were also performed.

2. Experimental details

2.1. Materials

All materials used in this work were of reagent grade purity and

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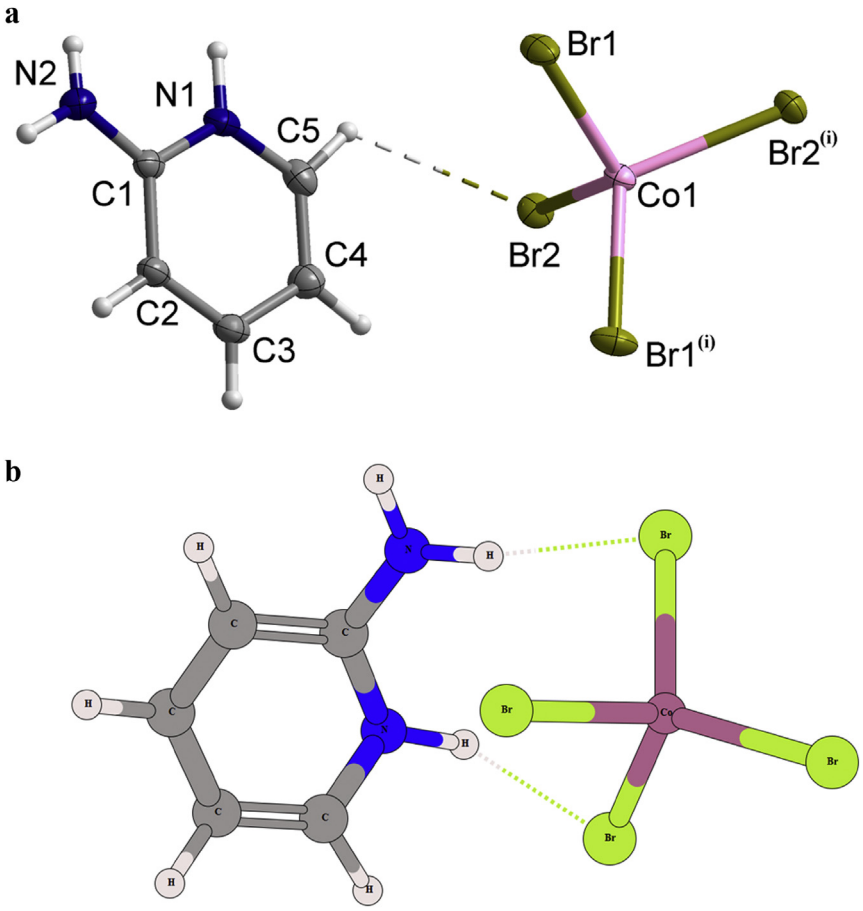

Fig. 1. (a): ORTEP plot (50% probability level) of $(2\text{-HAMP})_2[CoBr_4]$ with atom numbering (metal tetrahedron is completed by symmetry, symmetry code i = 2−x, y, 0.5−z). (b): B3LYP/LanL2DZ optimized geometry of $(2\text{-HAMP})[CoBr_4]$.

Table 1
Summary of crystallographic data for the structure of $(2\text{-HAMP})_2[CoBr_4]$.

Empirical formula	$(C_5H_7N_2)_2[CoBr_4]$
Formula weight (g mol^{-1})	568.78
Temperature (K)	298(2)
Crystal system	Monoclinic
Space group	C 2/c
a (Å)	8.339(4)
b (Å)	14.913(4)
c (Å)	13.637(5)
β (deg)	95.964(3)
V (Å$^{3)}$	1686.7(11)
Z	4
λ (MoKα) (Å)	0.71073
ρcal (g cm^{-1})	2.240
Absorption correction	Analytical
μ(mm^{-1})	10.485
Crystal size (mm^3)	0.38 × 0.28 × 0.16
Crystal color/shape	Blue, Needle
HKL range	$-13 \le h \le 10$ $-24 \le k \le 19$ $-18 \le l \le 21$
θ range for data collection (deg)	3–36.66
Diffractometer	Xcalibur
Refinement method	Full-matrix least-squares on F2
Programs system	SHELXL-97 and SHELXS-97
No. of reflection collected	9521
No. of independant reflection	4189
Reflexion numbers/variables parameters	3470/110
Rint	0.0365
F(000)	1076
No. of parameters	110
Goodness of fit	0.971
Transmission factors	$T_{min} = 0.303$, $T_{max} = 0.548$
Largest difference map hole and peak (e Å^{-3})	$\Delta\rho_{min} = -0.993$, $\Delta\rho_{min} = 0.721$
R indices	$R_1 = 0.033$, $wR_2 = 0.083$

were used as commercially obtained: $CoBr_2 \cdot xH_2O$ (99%, SIGMA ALDRICH), 2-aminopyridine ($C_5H_6N_2$) (98%, SIGMA ALDRICH) and Hydrobromic Acid HBr (48%, SIGMA ALDRICH). Distilled water was used in this synthesis.

Table 2
Main interatomic distances (Å) and angles (deg) of $(2\text{-HAMP})_2[CoBr_4]$.

Parametres	Observed	Calculated	Δ(%)
Co–Br1^i	2.4070(6)	2.46698	2.49
Co–Br1	2.4070(6)	2.53353	5.25
Co–Br2	2.4105(8)	2.57340	6.75
Co–Br2^i	2.4105(8)	2.61077	8.30
Br1^i–Co–Br1	108.79(3)	105.167	3.33
Br1^i–Co–Br2	103.42(3)	101.927	1.44
Br1–Co–Br2	116.40(2)	114.878	1.30
Br1^i–Co–Br2^i	116.40(2)	116.421	0.01
Br1–Co–Br2^i	103.42(3)	103.302	0.11
Br2–Co–Br2^i	108.93(3)	113.481	4.17
N1–C1	1.359(3)	1.3652	0.45
N1–C5	1.368(4)	1.3700	0.14
N2–C1	1.333(3)	1.3463	0.99
C1–C2	1.412(3)	1.4332	1.50
C2–C3	1.371(4)	1.3879	1.23
C3–C4	1.410(4)	1.4241	1.00
C4–C5	1.363(4)	1.3844	1.57
C1–N1–C5	123.1(2)	123.52	0.34
N2–C1–N1	119.2(2)	119.78	0.48
N2–C1–C2	123.0(2)	123.18	0.14
N1–C1–C2	117.8(2)	117.03	0.64
C3–C2–C1	119.5(2)	120.04	0.45
C2–C3–C4	121.0(2)	120.68	0.25
C5–C4–C3	118.5(3)	117.83	0.55
C4–C5–N1	120.1(2)	120.85	0.62

Symmetry codes: (i) 2−x. y. 0.5−z.