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Synthesis, structure, spectral characterization and thermal analysis of the tetraaquabis (isothiocyanato-κN) cobalt (II)-bis(caffeine)-tetrahydrate complex

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ABSTRACT

The complex $2(C_8H_{10}N_4O_2).[Co(H_2O)_4(NCS)_2].4H_2O$ was prepared in the water-ethanol solution at room temperature and characterized by the single crystal X-ray diffraction analysis, ^{1}H, ^{13}C NMR, TGA/DTA and IR spectroscopy. This complex was crystallized in the monoclinic system (P 21/c). The unit cell parameters are a = 10.65854 (19) A°, b = 8.16642 (14) A°, c = 18.0595 (3) A° with β = 96.4701° (15). The cobalt (II) cation is coordinated by four oxygen atoms of the water molecules and two nitrogen in isothiocyanato a trans octahedral geometry, stabilized by hydrogen bonds with caffeine molecule and free water molecule, The intermolecular hydrogen bonds: O—H···N, O—H···O, C—H···S, π···π interactions are together playing a vital role in the stabilization of the crystal packing.

1. Introduction

In recent years, metal-organic supramolecular complexes are known for their diversity and structural applications [1–7]. These complexes are characterized by much weaker intermolecular interactions than the covalent bonds in their formation. The principal interactions between the organic structures and inorganic components are established through hydrogen bonding and Van Der Waals forces, which are significantly weaker if compared to the covalent or ionic bonds, these interactions are sufficient to provide the building and stabilization of frameworks in these materials [8].

Moreover, mode sensitivity of thiocyanate ion such as a bidentate chelate ligand has attained great interest. The linear triatomic pseudo halide, SCN^-, is an ambidentate ligand with two donor atoms, which may coordinate through either S or N atom or both. In coordination polymers, a thiocyanate ion must take action as a rigid bridging ligand and link a pair of metal centers [9,10].

The thiocyanate moiety was reported to possess an capacity to modify the biochemical behaviour when present in mixed ligand coordination complexes [9,11].

Caffeine (3,7-dihydro-1,3,7-trimethyl-1H-purine-2,6-dione) has been known to have attractive effects on diverse biological systems such as gastrointestinal, cardiovascular, respiratory and muscle systems [12,13]. Its complexes have different coordination with transition metals, moreover, the biological properties such as antibacterial and anti-inflammatory.

In this study, a new complex was synthesized and the interaction of caffeine with tetraaquabis (Isothiocyanato-κN)cobalt (II) was studied. The prepared complex was characterized by spectral studies (IR, ^{1}H, ^{13}C NMR and UV–vis). The thermal stabilities of the complex were discussed. The structure of the complex was determined by single-crystal XRD method (Fig. 1).

2. Materials and methods

2.1. Materials

The initial products were analytical grade chemicals and used without any purification.

Fourier transform infrared spectroscopy (FT-IR) spectra were obtained by using the FT/IR-4100 Fourier transform infrared spectrophotometer (JASCO Corporation, Tokyo, Japan) over a range of 400–4000 cm^{-1}. Before each measurement, the sample was finely ground, mixed with KBr by using a mortar and pressed into pellets.

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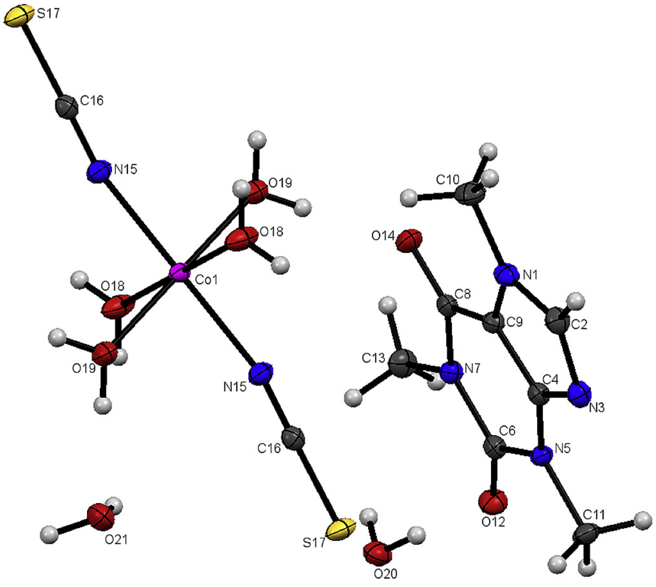

Fig. 1. The asymmetric unit [expanded for the cobalt (II) cation to show the full co-ordination sphere; primed atoms are related to the non-primed atoms by the symmetry operation -x + 2, -y + 1, -z + 1] of the title compound, with displacement ellipsoids drawn at the 50% probability level.

The ^{1}H, ^{13}C NMR spectra of complex were recorded with the Bruker AVANCE 300 at 25 °C. All chemical shifts ^{1}H and ^{13}C are given in ppm using tetramethylsilane (TMS) as internal reference and DMSO as solvent. The thermal decomposition process of complex was studied by TGA and DTA (DTG-60H, Shimadzu).

2.2. Crystallographic data collection and structure determination

X-ray diffraction data for the complex were collected at 120 K on a Oxford Diffraction Gemini diffractometer using a graphite monochromated Mo-K*α* radiation source (k = 0.71073 Å).

Data collection: Apex2 (Bruker AXS, 2006); cell refinement: Apex2 (Bruker AXS, 2006); data reduction: Apex2 (Bruker AXS, 2006); program(s) used to solve structure: Superflip (Palatinus & Chapuis, 2007); program(s) used to refine structure: CRYSTALS [14]; molecular graphics: CAMERON [15].

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms could be located in a difference Foutier map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined based on the bonds lengths and angles to regularize their geometry (C—H = 0.98 Å, O—H = 0.82 Å) and Uiso(H) set at 1.2–1.5 times of the Ueq of the parent atom, after which the positions were refined with riding constraints [16].

2.3. Preparation of complex

Caffeine (194.19 mg, 1 mmol) was dissolved in ethanol (10 ml). An aqueous solution (5 ml) of $CoCl_2,6H_2O$ (237 mg, 1 mmol) was added slowly. Then, the potassium thiocyanate (190 mg, 2 mmol) in water solution (5 ml) was added. The crystals of the complex suitable for X-ray analysis were crystallized after some months by slow evaporation of the solvent at room temperature. The most important details of the structure are summarized in Table 1.

Table 1
Experimental details.

Crystal data	
Chemical formula	$2(C_8H_{10}N_4O_2).[Co(H_2O)_4(NCS)_2].4H_2O$
Mr	707.61
Crystal system, space group	Monoclinic, *P*2$_1$/*c*
Temperature (K)	120
a, b, c (Å)	10.65854 (19), 8.16642 (14), 18.0595 (3)
β (°)	96.4701 (15)
V (Å3)	1561.93 (3)
Z	2
Radiation type	Mo *Kα*
μ (mm−1)	0.75
Crystal size (mm)	0.25 × 0.20 × 0.20
Data collection	
Diffractometer	Oxford Diffraction Gemini diffractometer
Absorption correction	Multi-scan *CrysAlis PRO* [17]
Tmin, Tmax	0.78, 0.86
No. of measured, independent and observed [I > 2.0σ(I)] reflections	62568, 4002, 3693
R_{int}	0.023
(sin θ/λ)max (Å−1)	0.689
Refinement	
R [F2> 2σ(F2)], w*R* (F2), S	0.023, 0.022, 1.13
No. of reflections	3586
No. of parameters	196
H-atom treatment	H-atom parameters not refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.36, −0.24

3. Results and discussion

3.1. Structural description

The X-ray structural determination of complex confirmed the assignments of the structure from spectroscopic data. The bond lengths, angles and Hydrogen bonds are represented in Tables 2 and 3 respectively. The molecular structure with atom-numbering

Table 2
Geometric parameters (Å, °).

N1—C2	1.3469 (12)	N7—C13	1.4723 (11)
N1—C9	1.3820 (11)	N15—C16	1.1610 (12)
N1—C10	1.4616 (12)	N15—Co1	2.0981 (8)
N3—C2	1.3407 (12)	C4—C9	1.3749 (12)
N3—C4	1.3588 (12)	C6—O12	1.2291 (11)
N5—C4	1.3727 (11)	C8—C9	1.4226 (12)
N5—C6	1.3792 (11)	C8—O14	1.2314 (11)
N5—C11	1.4672 (11)	C16—S17	1.6476 (9)
N7—C6	1.4006 (11)	O18—Co1	2.0981 (7)
N7—C8	1.4027 (11)	O19—Co1	2.0732 (7)
C2—N1—C9	105.49 (7)	C9—C8—O14	126.29 (8)
C2—N1—C10	126.68 (8)	C8—C9—N1	131.30 (8)
C9—N1—C10	127.76 (8)	C8—C9—C4	122.88 (8)
C2—N3—C4	103.21 (8)	N1—C9—C4	105.77 (8)
C4—N5—C6	119.42 (7)	N15—C16—S17	177.81 (8)
C4—N5—C11	119.83 (7)	O18i—Co1—O18	179.995
C6—N5—C11	120.37 (7)	O18i—Co1—N15i	87.69 (3)
C6—N7—C8	126.55 (7)	O18—Co1—N15i	92.31 (3)
C6—N7—C13	116.65 (7)	O18i—Co1—N15	92.31 (3)
C8—N7—C13	116.77 (7)	O18—Co1—N15	87.69 (3)
C16—N15—Co1	167.35 (8)	N15i—Co1—N15	179.995
N1—C2—N3	113.89 (8)	O18i—Co1—O19	89.86 (3)
N5—C4—N3	126.58 (8)	O18—Co1—O19	90.14 (3)
N5—C4—C9	121.78 (8)	N15i—Co1—O19	92.36 (3)
N3—C4—C9	111.64 (8)	N15—Co1—O19	87.64 (3)
N7—C6—N5	117.28 (8)	O18i—Co1—O19i	90.14 (3)
N7—C6—O12	120.99 (8)	O18—Co1—O19i	89.86 (3)
N5—C6—O12	121.70 (8)	N15i—Co1—O19i	87.64 (3)
N7—C8—C9	111.93 (7)	N15—Co1—O19i	92.36 (3)
N7—C8—O14	121.76 (8)	O19—Co1—O19i	179.994

Symmetry code: (i) −x+2, −y+1, −z+1.