Synthesis, molecular and crystalline architectures, and properties of a mononuclear complex [Co^{II}(benzidine)$_2$(NCS)$_2$(OH$_2$)$_2$]

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Abstract. One mononuclear cobalt(II) compound of the type [Co(bnzd)$_2$(NCS)$_2$(OH$_2$)$_2$] (**1**) (bnzd = benzidine) has been isolated through a single-pot reaction of the molecular building components in MeOH–H$_2$O solvent mixture at room temperature and characterized by physico-chemical and spectroscopic methods. The crystal structure of complex **1** has an octahedral geometry with *trans*, *trans*, *trans* orientations in the order (N^a,N^a), (N^t,N^t), (O^w,O^w) [N^a = N(amine), N^t = N(thiocyanate) and O^w = O(water)]. In crystalline state, individual units of **1** are associated by weak cooperative O–H$\ldots$N, O–H$\ldots$S and N–H$\ldots$S hydrogen bonds resulting in a 3D network structure. The compound is redox active and shows luminescence in MeOH solution. Thermal decomposition pattern of **1** reveals the presence of two coordinated water molecules. Variable-temperature magnetic susceptibility measurement shows significant orbital contribution and numerical matrix diagonalization method gives the best fit parameters: α = A*k = 1.43; λ = $-130\,\text{cm}^{-1}$; Δ = $-864\,\text{cm}^{-1}$; TIP = 0.000975; R = 1.19×10^{-4}.

Keywords. Cobalt(II); thiocyanate; benzidine; X-ray structure; magnetism.

1. Introduction

The construction[1] of coordination compounds of cobalt(II) of different nuclearities is the centre of attraction due to interesting structural and physico-chemical properties.[1–5] One-pot synthesis[6] using the building units is an efficient synthetic approach to isolate such coordination molecules and supramolecular entities. Recently, we are active[7–10] in the isolation of different coordination compounds by variation of metal coordination environments, blocking ligand back-bones and mono-/multiatom bridging units; in this regard, 3d metal templates, polyamine/Schiff base spacers,[7–12] halide/pseudohalide terminal or bridging units[7–10,13–17] have been used. Recently, we have reported the syntheses, structural characterizations and molecular properties of some cobalt(II/III) halide/pseudohalide compounds in combination with Schiff bases of different denticities;[18–23] the special mention is the 1D cobalt(II) coordination polymer[23] containing dicyanamide and a tetradentate Schiff base, that shows interesting symmetry breaking SCO behaviour. Coordination chemistry

of benzidine (bnzd, scheme 1), is less explored.[10,24,25] The tailored aromatic diamine may act as a terminal or bridging unit. In a recent work from this group it has been reported that bnzd along with dicyanamide coordinates in a bridging fashion affording a luminous 2D coordination polymer of cadmium(II).[10] To extend the chemistry, we investigate here its coordination behaviour to cobalt(II) in concert with thiocyanate, that remains unexplored to date. We have isolated successfully a mononuclear compound of the type [Co(bnzd)$_2$(NCS)$_2$(OH$_2$)$_2$] (**1**). The synthesis, molecular and crystalline architectures, and spectroscopic, thermal, redox and magnetic properties of this complex are described in this paper.
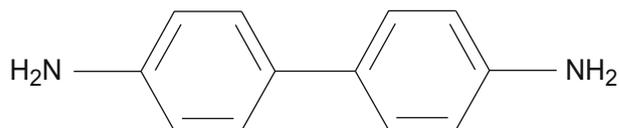
Scheme 1. Framework of benzidine.

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2. Experimental

2.1 *Materials*

High purity benzidine (SRL, India) and ammonium thiocyanate (Merck, India) were used as received. Cobalt(II) perchlorate hexahydrate was prepared[19] by treatment of cobalt(II) carbonate (Merck, India) with perchloric acid (Merck, India) followed by slow evaporation on a steam bath and filtration with a fine glass-frit. The salt was stored in a desiccator over concentrated sulphuric acid (Merck, India) for subsequent uses. All other chemicals and solvents used were AR grade and used as received. The synthetic reaction and work-up were done in open air.

2.2 *Physical measurements*

Elemental analyses (carbon, hydrogen and nitrogen) were done using a Perkin-Elmer 2400 CHNS/O elemental analyzer. IR spectrum (KBr disk, 4000–400 cm^{-1}) was recorded using a Perkin-Elmer FTIR model RX1 spectrometer. Molar conductance was measured using a Systronics conductivity meter, where the cell constant was calibrated with 0.01 M KCl solution and dry MeOH was used as solvent. Electrochemical measurement was made with a computer controlled CH (model CHI620D) electrochemical instrument using MeOH as solvent and tetrabutylammonium perchlorate as supporting electrolyte. Platinum and Ag/AgCl were the working and the reference electrodes, respectively in the process. The following parameters and relations were used: scan rate (v), 100 mVs^{-1}; formal potential $E° = 0.5 (E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; ΔE_p is the peak-to-peak separation. Ground state absorption (in MeOH) was made with a Shimadzu model UV-2450 UV-VIS spectrophotometer. Steady-state fluorescence and quantum yield measurements (in MeOH) were made with a Perkin Elmer LS55 Fluorescence Spectrometer. Thermal behaviour was investigated with a Perkin-Elmer Diamond TG/DT analyzer heated from 30–750°C under nitrogen. Magnetic measurement was carried out on polycrystalline sample with a Quantum Design SQUID MPMS-XL magnetometer working in the 2–300 K range. The magnetic field was 0.5 T.

Caution! Perchlorate salts are potentially explosive.[26] Only a small amount of these materials should be prepared and handled with care.

2.3 *Synthesis of [Co(bnzd)$_2$(NCS)$_2$(OH$_2$)$_2$] (1)*

Co(ClO$_4$)$_2$.6H$_2$O (0.365 g, 1 mmol) and bnzd (0.368 g, 2 mmol) were taken in methanol (each with 10 mL)

and mixed together slowly. To the resulting yellowish-pink solution, an aqueous solution (20 mL) of NH$_4$SCN (0.152 g, 2 mmol) was added drop-wise. The final bright pink solution was filtered and left for slow evaporation in air at room temperature. After a few days, pink crystals of **1** that separated, were collected by filtration with a fine glass-frit, washed with toluene and dried *in vacuo* over silica gel. Yield: 0.43 g (75%). Anal. Calc. for C$_{26}$H$_{28}$N$_6$O$_2$S$_2$Co (**1**): C, 53.8; H, 4.8; N, 14.4%. Found: C, 53.7; H, 4.7; N, 14.2. IR (KBr, cm^{-1}): ν(H$_2$O) 3401; ν(N-H) 3326, 3255; ν(C-H) 2929, 2852; ν(N=C=S) 2106; ν(C-S) 769. Λ_M (MeOH, ohm^{-1} cm^2 mol^{-1}): 6. UV-Vis in MeOH (λ, nm): 521, 295. E^0 (MeOH): 0.45 V.

2.4 *X-ray data collection and structure refinement*

Single crystal of **1** suitable for X-ray analysis was selected from those obtained by open evaporation of MeOH–H$_2$O (1:1) solution of the reaction mixture at 298 K. X-ray crystal data were collected on a Bruker AXS KAPPA APEX II diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 295(2) K. The detector frames were integrated by use of the program SAINT[27] and absorption corrections were performed with SADABS.[28] Of the 25183 total reflections, 3436 with [$I > 2\sigma(I)$] were used for structure solution. The structure was solved by direct method using SHELXTL.[29] All non-hydrogen atoms were refined with anisotropic displacement parameters whereas hydrogen atoms were placed in possible calculated positions and given isotropic U values 1.2 times that of the atom to which they are bonded. The final differences Fourier map showed the maximum and minimum peak heights at 0.547 and −0.458 eÅ^{-3} with no chemical significance. Materials for publication were prepared using SHELXTL, PLATON[30] and ORTEP-32[31] programs. The crystallographic data for the complex is summarized in table 1.

3. Results and discussion

3.1 *Synthesis and formulation*

The hexacoordinated mononuclear complex **1** was obtained as a pink crystalline product in MeOH–H$_2$O (1:1) solvent mixture containing a 1:2:2 molar ratio of Co(ClO$_4$)$_2$.6H$_2$O, bnzd and NH$_4$NCS. The moisture-insensitive complex is stable over long periods of time in powdery or crystalline state and is soluble in warm MeOH, MeCN, DMF and DMSO but is insoluble

Table 1. Crystallographic data for **1**.

|	
Compound	**1**
Formula	$C_{26}H_{28}N_6O_2S_2Co$
Formula weight	579.61
Crystal system	Orthorhombic
Space group	Pbca
$a/\text{Å}$	14.3765(2)
$b/\text{Å}$	6.88830(10)
$c/\text{Å}$	27.8646(4)
α^o	90.00
$\beta°$	90.00
γ^o	90.00
$V/\text{Å}^3$	2759.42(7)
$\lambda/\text{Å}$	0.71073
$\rho_{calcd}/\text{Mg/m}^3$	1.395
Z	4
Temp/K	295(2)
μ (mm^{-1})	0.808
$F(000)$	1204
Crystal size (mm^3)	$0.30 \times 0.20 \times 0.20$
θ ranges (°)	1.46 to 28.30
$h/k/l$	$-19,19/-9,9/-37,36$
Reflections collected	25183
Independent reflections	3436 [R(int) = 0.0524]
T_{max} and T_{min}	0.8551 and 0.7936
Data/restraints/parameters	3436/0/169
Goodness-of-fit on F^2	1.016
Final R indices [$I>2\sigma(I)$]	R1 = 0.0379 and wR2 = 0.0833
R indices (all data)	R1 = 0.0692 and wR2 = 0.0979
Largest peak and hole (eÅ^{-3})	0.547 and -0.458

Weighting scheme: $R1 = \Sigma \|Fo|-|Fc\| / \Sigma|Fo|$, wR2 $=[\Sigma w(F_o^2 - F_c^2)_2 / \Sigma w(F_o^2)^2]^{1/2}$, calcd w $= 1/[\sigma^2(F_o^2) + (0.0391P)^2 + 1.3330P]$; where P $= (F_o^2 + 2F_c^2)/3$

in H_2O. In MeOH solution, compound **1** behaves a non-electrolyte[32] as reflected from its low conductivity value (see Experimental section).

3.2 *Spectroscopic features*

In IR spectrum, ν(N-H) stretching frequencies of the -NH$_2$ groups of bnzd are observed at 3326 and 3255 cm^{-1}. A characteristic ν(O–H) stretching frequency for H_2O is seen at 3401 cm^{-1}. ν(C=N) stretching vibration of the thiocyanate group appears as a single and strong peak at 2106 cm^{-1}; the position and the number of signal strongly suggest mutual *trans* alignment as well as N-coordination of the pseudo-halide.[33] A band corresponding to ν(C–S) stretching frequency appears at 769 cm^{-1}. Light pink MeOH solution of **1** exhibits a distinct absorption band at 521 nm due to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition characteristic of a high-spin octahedral cobalt(II) environment.[34] A strong absorption band at 295 nm may be assigned to a ligand based transition.[35] The photoluminescence behaviour of the free bnzd and its corresponding cobalt(II) complex **1** are depicted in figure 1. Upon photoexcitation at the corresponding absorption band (286 nm) in MeOH solution, free bnzd exhibits a fluorescent emission centred at 393 nm; the corresponding cobalt(II) complex **1** shows a more intense photoluminescence with the main emission at the same position to that of free bnzd unit. The phenomenon of luminescence[36–38] may be attributed to the intraligand $^1(\pi-\pi*)$ transition. The greater intensity of **1** compared to that of free bnzd may be due to the increase in conformational rigidity of the ligand upon coordination. Luminescence quantum yields (Φ_{em}) of bnzd and complex **1** (in MeOH) were calculated using pyrene as the primary standard reference (Φ_{em} = 0.32 in cyclohexane),[39] and the values are 0.75 (bnzd) and 0.47 (**1**).
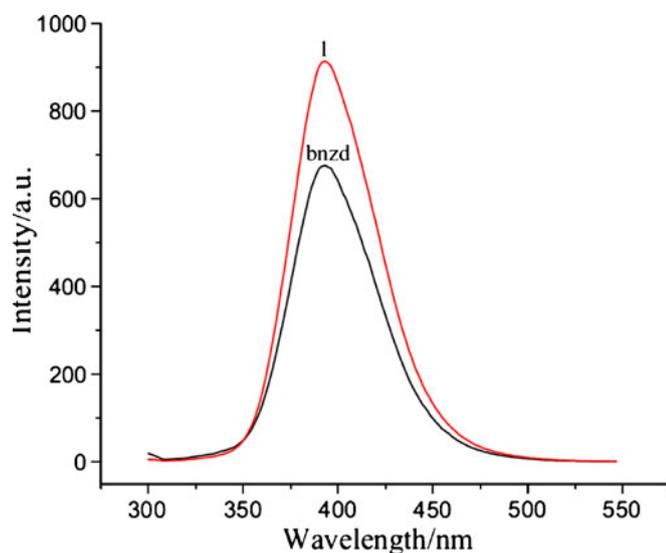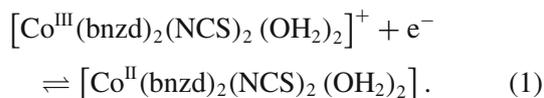
Figure 1. Emission spectra: fluorescence behaviour of free bnzd and **1** in MeOH solutions at 298 K.

3.3 *Thermal analysis*

To examine thermal stability of the compound, thermogravimetric analysis (TGA) was made between 30 and 750°C in a static atmosphere of dinitrogen. The compound shows (figure S1) weight loss in two successive steps within the temperature range 106–727°C. The first step is associated with the release of two coordinated water molecules (obs.: 5.56%; calc.: 6.21%) between 106–132°C. The second weight loss (obs.: 80.34%; calc.: 83.76%) in the 224–727°C range is due to the simultaneous decomposition of the remaining two benz and two thiocyanate anions.

3.4 *Electrochemical study*

The electron transfer property of the compound was examined in MeOH solution using CV at a platinum working electrode. Pink solution of **1** in MeOH shows a quasi-reversible ($\Delta E_p = 120$ mV) oxidative response (figure S2) presumably due to the Co^{II}–Co^{III} couple and as shown in equation (1):

$$\left[\text{Co}^{III}(\text{bnzd})_2(\text{NCS})_2(\text{OH}_2)_2\right]^+ + e^-$$
$$\rightleftharpoons \left[\text{Co}^{II}(\text{bnzd})_2(\text{NCS})_2(\text{OH}_2)_2\right]. \qquad (1)$$

The response is reproducible with no trace of decomposition after a number of cycles indicating appreciable stability of the electrogenerated species in CV time scale. The formal potential is ca. 0.45 V versus non-aqueous Ag/AgCl electrode in MeOH. The one-electron nature of the couple was verified by comparison with a standard cobalt(II) compound.[40]

3.5 *Magnetic properties*

Variable-temperature magnetic susceptibility measurement of **1** has been performed in the 2–300 K temperature range. Plot of $\chi_m T$ *vs* T is shown in figure 2. The experimental $\chi_m T$ value (3.4 cm^3 mol^{-1} K) at room temperature is significantly larger than that (1.875 cm^3 mol^{-1} K if g = 2.00) expected for an isolated high spin cobalt(II) ion reflecting significant orbital contribution. With decrease in temperature, $\chi_m T$ value decreases reaching a value of 2.2 cm^3 mol^{-1} K at low temperature.

The matrix diagonalization method including spin-orbit coupling effect based on a perturbational approach reported by Lloret *et al.* has been used for the interpretation the magnetic property of six-coordinated high spin cobalt(II) clusters;[41] the Hamiltonian used contains the parameters A, κ, λ, Δ and TIP, where k and A are orbital reduction factors associated respectively with the covalent metal-ligand bond character and with the interaction of the $^4T_{1g}(F)$ ground state with the $^4T_{1g}(P)$ from a P term, λ is spin-orbit coupling parameter, Δ is tetragonal distortion parameter from the pure octahedral geometry.[41] This Hamiltonian does not provide for an analytical expression of χ_m as a function of the parameters already commented; thus their values must be determined through a numerical matrix diagonalization process [see acknowledgement]. For complex **1**, the best fit values are: $\alpha = A*k = 1.43$ (noting that from
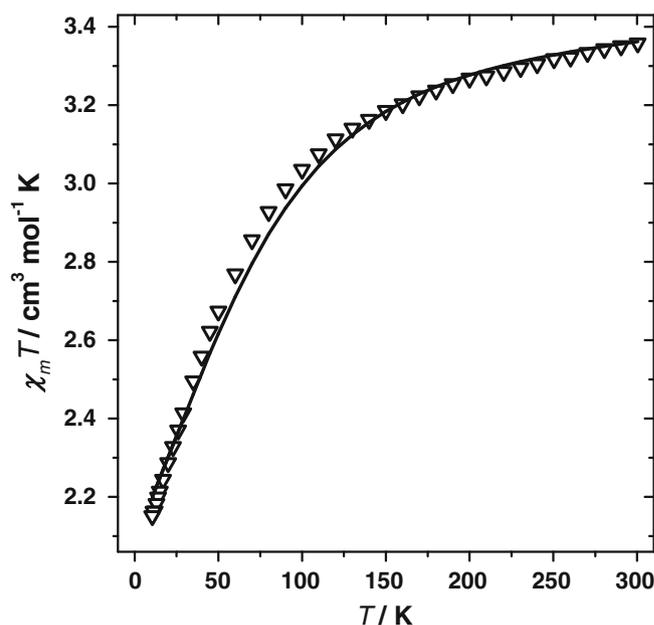

Figure 2. Plot of the $\chi_m T$ vs T for **1**; the solid line represents the best fit obtained (see the text for the method of fitting and the obtained parameters)

crystal field A must be between 1.0 and 1.5); $\lambda = -130\,cm^{-1}$; $\Delta = -864\,cm^{-1}$; TIP = 0.000975. R (agreement factor) = 1.19×10^{-4}, and is in good agreement with a mononuclear cobalt(II) complex.

3.6 *Description of the crystal structure of [Co(bnzd)₂(NCS)₂(OH₂)₂] (1)*

ORTEP plot with atom numbering schemes of complex **1** is shown in figure 3. Selected bond lengths and angles pertaining to the coordination sphere are set out in table 2. Structural analysis reveals an asymmetric unit consisting of [Co(bnzd)₂(NCS)₂(OH₂)₂] unit (figure 3). The coordination polyhedron around cobalt(II) is best described as an octahedron with a CoN_4O_2 chromophore. Metal(II) is located on a crystallographic inversion centre and one-half of the monomeric unit is symmetrical to the other half. The coordination includes two amine N atoms (N2 and N2a) of bnzd ligands, two N atoms (N1 and N1a) of terminal NCS units and two O atoms (O1 and O1a) of coordinated water

molecules. Two amine N atoms (N2 and N2a) of two different bnzd units along with two N atoms (N1 and N1a) of the pendent thiocyanato groups define the equatorial plane, while the two O atoms (O1 and O1a) of corresponding water molecules are in axial positions. Complex **1** adopts a molecular architecture corresponding to the gross geometry *trans, trans, trans* in the order (N^a,N^a), (N^t,N^t), (O^w,O^w), where N^a = N(amine), N^t = N(thiocyanate) and O^w = O(water). To the best of our knowledge, only one cobalt(II) compound, [Co(L1)₂(NCS)₂(H₂O)₂].2H₂O [L1 = 4-[3-(1,2,4-triazolyl)-1,2,4-triazole] is reported[33] in the literature which show similar gross geometry with the title compound. Co–N^a distances [2.2101(18) Å] are greater than Co–N^t bond distances [2.0712(19) Å], reflecting the stronger coordination of the anionic thiocyanate over the neutral amine. Co–O^w distances [2.1176(15) Å] lie in between Co–N^a and Co–N^t bond lengths (table 2). The thiocyanates are almost linear [S2-C6-N1 179.6(2)°] and in mutual *trans* alignment with N1–Co1–N1a angle of 180.000(1)°. N1–C6 [1.149(3) Å] and S2–C6 [1.637(2) Å] bond lengths are as expected
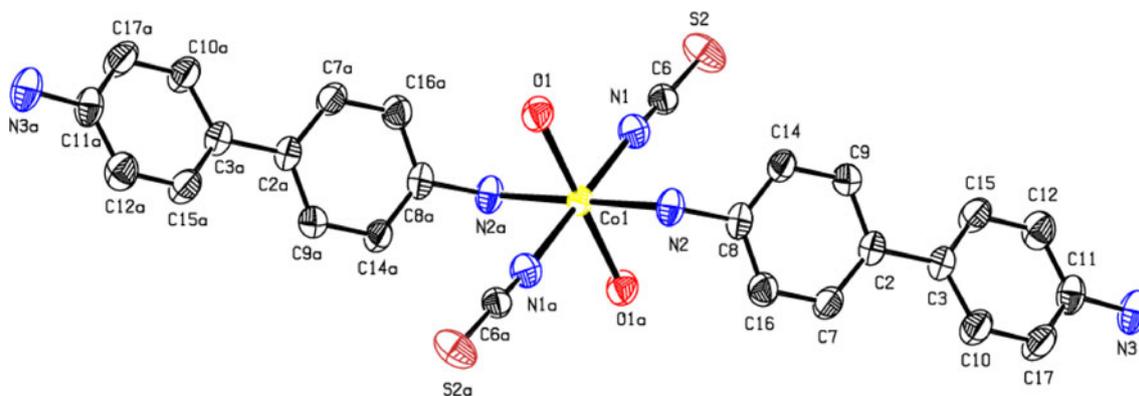
Figure 3. An ORTEP diagram of **1** with atom numbering scheme and 50% thermal ellipsoid probability for all non-hydrogen atoms.

**Table 2.** Selected bond distances (Å) and bond angles (°) for **1**.

Bond distances		Bond angles	
Co(1)-N(1)	2.0712(19)	N(1)-Co(1)-N(1a)	180.000(1)
Co(1)-N(2)	2.2101(18)	N(1)-Co(1)-O(1)	89.46(7)
Co(1)-O(1)	2.1176(15)	N(1a) -Co(1)-O(1)	90.54(7)
N(1)-C(6)	1.149(3)	N(1a) -Co(1)-O(1a)	89.46(7)
S(2)-C(6)	1.637(2)	O(1)-Co(1)-O(1a)	180.00(9)
		N(1)-Co(1)-N(2)	91.18(7)
		N(1a) -Co(1)-N(2)	88.82(7)
		O(1)-Co(1)-N(2)	91.21(6)
		O(1a)-Co(1)-N(2)	88.79(6)
		N(2a)-Co(1)-N(2)	179.999(1)
		C(6)-N(1)-Co(1)	171.30(18)

Symmetry transformation used to generate equivalent atoms: a = −x, −y, −z+1

Table 3. Hydrogen bond distances (Å) and angles (°) for **1**.

D-H...A	D-H	H...A	D...A	D-H...A
O(1)-H(1)...N(3)[b]	0.89	1.96	2.833(3)	167
O(1)-H(2)...S(2)[c]	0.93	2.40	3.3076(16)	165
N(2)-H(3)...S(2)[c]	0.95	2.55	3.476(2)	165
N(3)-H(6)...S(2)[d]	0.87	2.74	3.611(2)	176

Symmetry code: b = x, 1/2−y, 1/2+z; c = −x, 1−y, 1−z; d = 1/2+x, y, 1/2−z.
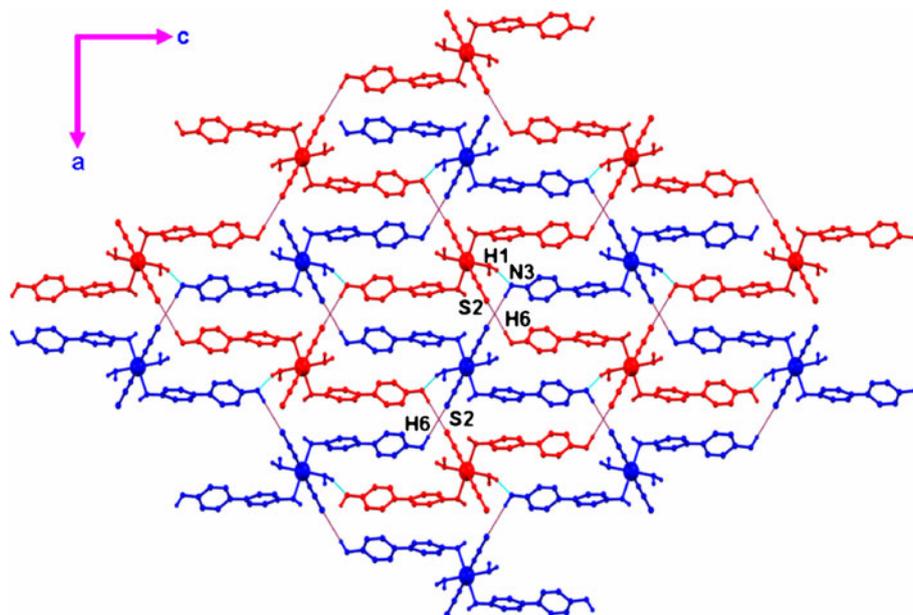
Figure 4. A view of 2D (4,4) square grid structure in **1** formed through weak N–H...S hydrogen bonds in *ac*-plane (viewed along crystallographic *b*-axis).
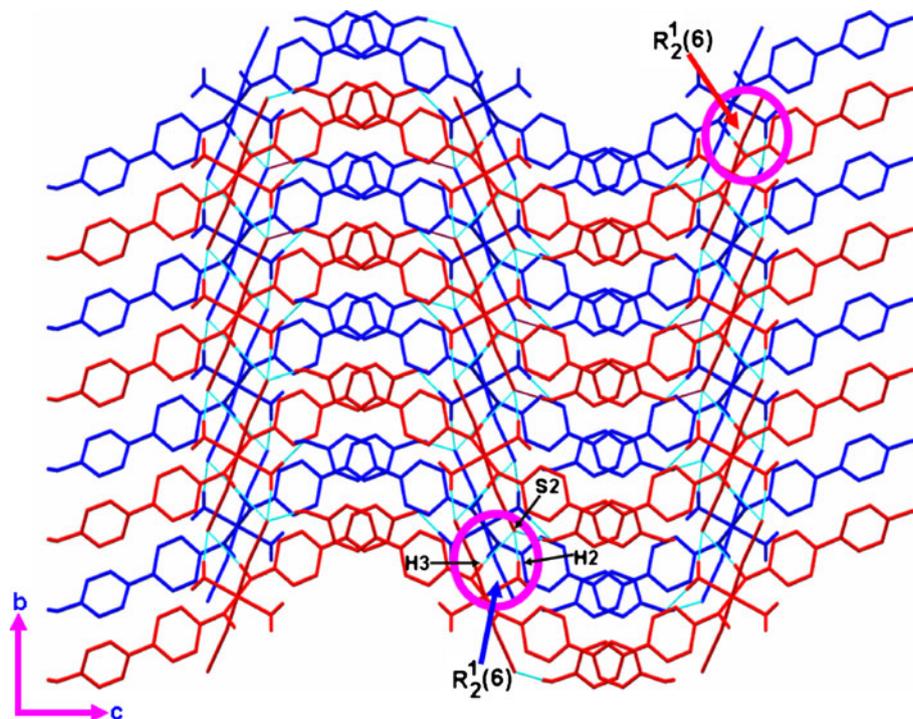
Figure 5. 3D network structure in **1** formed through cooperative O–H...N, O–H...S and N–H...S hydrogen bonds (viewed along crystallographic *c*-axis).

for N-coordination of this terminal pseudohalide. Both the thiocyanates are almost linearly coordinated to cobalt(II) with Co–N–C bond angles close to 180° [Co1-N1-C6 171.30(18)°].

In the crystalline state, individual units in **1** are associated by weak N–H...S hydrogen bonds (N3-H6...S2; table 3) forming 2D (4,4) square grid structures (figure 4) in *ac-plane* and connected to each other through strong cooperative O–H...N hydrogen bonds (O1-H1...N3, table 3). These 2D sheets are further extended along crystallographic *b-axis* through O(1)-H(2)...S(2) and N(2)-H(3)...S(2) hydrogen bonds resulting in a 3D network structure (figure 5; table 3) with a cyclic motif $R_2^1(6)$ in Etter's graph set notation. [42]

4. Conclusion

One mononuclear cobalt(II) bnzd complex in combination with a pseudohalide is isolated and characterized by X-ray crystallographically. The preparation of such compound illustrates a potentially versatile approach to the construction of uncharged metal-organic frameworks, which is an emerging area of research for the rational design of functional materials. The compound is electroactive and shows luminescence property. Variable-temperature magnetic property is in consonance with significant orbital contribution and the best fit parameters obtained as a function of χ_m are in good agreement for a mononuclear cobalt(II) complex. We are currently investigating bnzd chemistry with other paramagnetic 3d ions in combination with different pseudohalides and polycarboxylates for isolation of new magnetic materials.

Supplementary materials

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre No. 895740 (**1**). Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). For figures S1–S2, see online version www.ias.ac.in/chemsci website.

Acknowledgements

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