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Supramolecular Hydrogen Bonded 3D Molecular Self Assembly Constructed from [(Co (nicotinamide)$_2$(thiocyanate)$_2$(H$_2$O)$_2$] Complex Showing Anti-ferromagnetic Character

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ABSTRACT

A new three dimensional hydrogen bonded cobalt frame work from [Co(nicotinamide)$_2$(thiocyanate)$_2$(H$_2$O)$_2$] was synthesized and characterized by X-ray diffraction, magnetism ,TGA and IR spectroscopy. The compound crystallizes in Triclinic space group *P-1* with *a* = 7.5475(19), *b* = 8.054(2), *c* =8.932(2). Alpha=73.347(4), beta=70.067(4), gamma=66.559(4) with space group P-1*Z* = 1, '$C_{14} H_{16} N_6 Co O_4 S_2$', *Mr* =455.38, *F*(000) = 233 and μ(Mo*Kα*) =0.71073 mm^{-1}. The final *R* = 0.0497 and *wR* = 0.1461 for 4185 observed reflections with $I > 2\sigma(I)$ and *R* = 0.0721 and *wR* = 0.1619 for all data. X-ray diffraction analyses revealed that Co(1) is linked by the nicotinamide ligands to form the ladder shape along the *c* axis, which is further extended into two-dimensional networks *via* the joint of Co(2) along the *a* axis. Moreover, these two dimensional motifs are interconnected by the thiocyanate S...H bridges to form a complicated 3-D polymeric framework. The magnetic susceptibility data at 1000Oe external field in the temperature range

2-300 K obeys the Curie-Weiss law, giving θ = -24.12 K and C =2.43 thus indicating a dominant strong antiferromagnetic interaction and/or spin orbital coupling between the Co (II) ions.

Indexing terms/Keywords

Hydrogen bonded 3D structure; spin orbital coupling.

1 INTRODUCTION

Metal–organic frameworks (MOF) have received much attention in recent years due to their potential applications in non-linear optics, magnetism, molecular recognition and gas storage [1,2] Based on current research, to select a multifunctional organic ligand is crucial in an assembly of a MOF with a desired framework because the multi-functional organic ligands can provide not only versatile binding sites to connect metal ions but also hydrogen bond donor or acceptor to form supramolecular interactions.[3,4] As is known, hydrogen bonds and p–p interaction are powerful supramolecular interactions and they can connect the low-dimensional frameworks into high dimensional supramolecular architectures. Pseudo halide anions are excellent ligands for obtaining discrete, one-dimensional, two-dimensional or three-dimensional systems.[5] As one of the most important pseudo halide anions, SCN^- presents multiform coordination modes connecting the metal ions with terminal and/or bridging fashions. . The thiocyanate ligand, with the ambidentate ability, seems to play an important role in the design of extended one, two, and three-dimensional compounds with specific magnetic properties. According to the concept of hard–soft acid–base [6,7, 8], the SCN_ ion prefers to bind to Cd(II) center in both N- and S-bonded fashion, whereas in the only N-terminal mode to Co(II) ion. Many thiocyanate complexes have been reported in combination with different ligand via-{[Cu(4,4_-bpy)_(BF4)2(H2O)2]_(4,4_-bpy)}*n* [9], {[Mn(4,4_-bpy)(NCS)2(H2O)2]_(4,4_-bpy)}*n*[10], and {[Cu(4,4_-bpy)(pyz)(H2O)2]_(PF6)}*n*H2O[11].

Nicotinamide is also well played as coligand documented in literature. Nicotinamide is known as a component of the vitamin B complex as well as a component of the coenzyme, nicotinamide adenine dinucleotide (NAD). These are more important for transfer of hydrogen in the cell breath. The presence of pyridine ring in numerous naturally abundant compounds, adducts of nicotinamide are also scientific interest. Therefore, the structure of nicotinamide has been the subject of many studies [12-15].

Our current interest is the construction of thiocyanate complexes containing anionic SCN^- ligand and nicotinamide as coligand with d^6 , d^7 , d^8 ,d^9, d^{10} metal ions. This strategy is anticipated to affect the crystal structure and obtain complexes with a new type of stacking structure. Previously we report the crystal structure with d^8 metal ions and their characterization and magnetic properties (16). As a continuance of our research work in the assemblies and properties of coordination polymers, here we report the synthesis, crystal structure and magnetic properties of the new thiocyanato S.... H bridged 3D coordination motifs, built by complex, $[Co\ (SCN)_2(\text{nicotinamide})_2\ (H_2O)_2]$.

2 EXPERIMENTAL

2.1 Materials and Physical Measurements

Nickel(II) acetate tetra hydrate (Sigma Aldrich), Potassium thiocyanate (Sigma Aldrich), Nicotinamide(Sigma Aldrich), were purchased and used without further purification. IR spectra were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the 4000～400 cm^{-1} region. Variable-temperature magnetic susceptibility data were collected using a Quantum Design MPMS SQUID magnetometer. Magnetic susceptibility of complex was corrected for diamagnetism of the ligand molecules using Pascal's constant (-302×10^{-6} cgs.).

2.2 Synthesis of the complex

An aqueous solution (10 ml) of Cobalt nitrate tetrahydrate (0.2460g, 1mmol) and Potassium thiocyanate (0.196g, 2mmol) was slowly added drop wise to hot aqueous solution (10ml) of Nicotinamide (0.244g, 2mmol) with stirring. Pinkish color solution was obtained. After filtration the final clear solution left undisturbed t room temperature for slow evaporation. Next day, needle shaped greenish blue crystals were collected and dried in vacuo over silica gel. Crystals suitable for single crystals X-ray diffraction was manually selected and immersed in silicon oil. (Yield-87 %) $C_{14}H_{16}CoN_6O_4S_2$: C 36.9, H 3.5, N 18.4, S 14.1 Found: C 36.8, H 3.5, N 18.6, S 14.0%.

2.3 Crystal structure determination

A selected greenish blue single crystal of the title compound with approximate dimensions of 0.48 x 0.32 x 0.26 mm^3 was mounted on a glass fibre. Crystal data of complex were collected on a SCXmini CCD diffractometer equipped with a graphite-monochromatic Mo*Kα* radiation (λ = 0.71073 Å) using an ω-2θ scan mode in the range of 5.05 $\le\theta\le$37.78° (-12<=h<=11, -13<=k<=14, -15<=l<=15) at 123(2) K. A total of 8114 reflections including 4752 unique ones were collected. Out of which 3477 with $I > 2\sigma(I)$ were considered as observed and used for the succeeding refinement. The data sets were corrected for absorption by multi-scan technique. The structure was solved by direct methods using SHELXS-97 program and refined with SHELXL-97 by full-matrix least-squares techniques on *F*2 [17-20]. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms of lattice water molecules were found in the electron density map and refined by riding, and the other hydrogen atoms were generated with idealized geometries and treated as riding. The final R =0.0462, wR =0.1105 ($w =1/[\sigma^2(F_o^2) + (0.0466P)^2 + 0.6377P]$, where $P = (F_o + 2F_c^2)/3$). S = 1.031, $(\Delta\rho)_{\max}$ = 0.501 e/Å^3 $(\Delta\rho)_{\min}$ = –0.710 e/Å^3 and $(\Delta/\sigma)_{\max}$=1.00000.Selected bond length and angles are listed in table 1and 2.

Table. 1.

Bond	Bond length (Å)
Co-O(1W)#1	2.117(3)
Co-O(1W)	2.117(3)
Co-N#1	2.075(2)
Co-N	2.075(2)
Co-N(1)#1	2.049(3)
Co-N(1)	2.049(3)
Bond	**Bond angles (°)**
N(thiocyanate)-Co-N(nicotinamide)	87.48°
O(water)-Co-N(thiocyanate),	91.9°
O(water)-Co-N(nicotinamide)	90.50°

3. RESULTS AND DISCUSSIONS

3.1 IR Spectrum

The IR spectrum of the complex as can be seen in fig. (1) exhibits the characteristic bands of the thiocyanate and nicotinamide ligands. The strong and broad absorption bands occurred in the frequency range 3318–3132 cm^{-1} are assigned to the antisymmetric and symmetric stretching vibrations of the NH_2 group of nicotinamide molecules involved in hydrogen bonding, while the relatively weak bands in the frequency range 3000–3100 cm^{-1} are due to the absorption of the CH groups(21,22). The broad bands observed in the range 3400 and 1675 cm^{-1} are attributable to v_{str} (O–H) stretching and δ (O–H) bending frequency of the coordinated water molecule. A characteristic peak for v_{str}(C–N) stretching frequency was found at 2000 and 2100 cm−1, corresponding to N-bonded terminal thiocyanate ligand [23, 24].

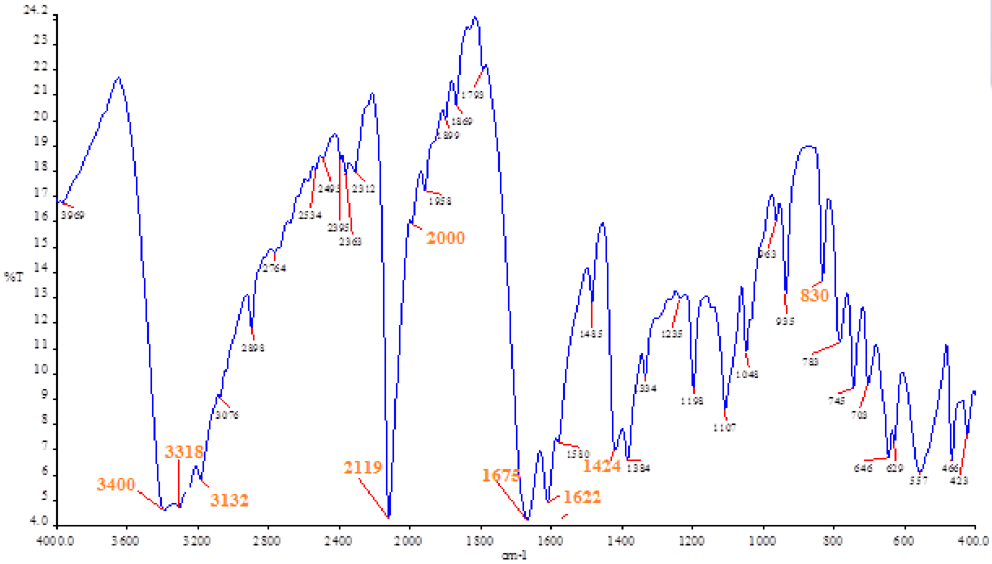


Fig. 1 IR Spectrum of Complex

3.2 Crystal structure

The structural unit of hydrogen bonded framework of cobalt is depicted in Figure (2). Co (II) is at a slightly distorted octahedral coordination environment. The equatorial positions are occupied by two nitrogen atoms from two nicotinamide ligands, the Co-N(nicotinamide) bond length is 2.117(3) Å, and two oxygen atoms from two water molecules, the Co-O(water) bond length is 2.075(2)Å and two nitrogen atoms from NCS- groups occupy the axial positions with bond length of 2.049(3) Å for Co-N(thiocyanate).

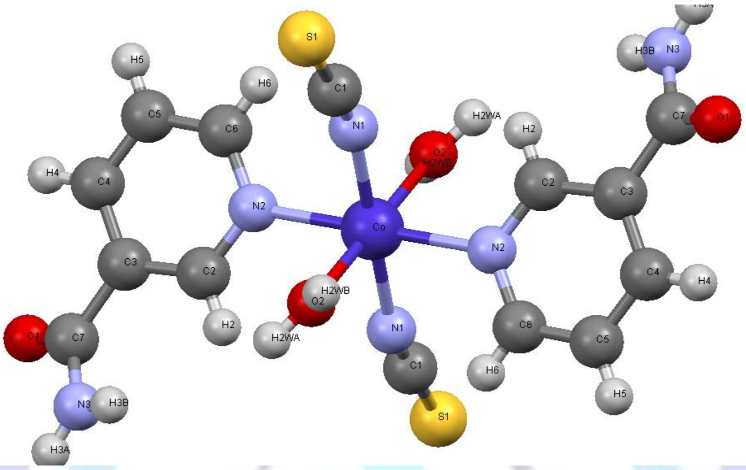


Fig. 2 Ortep view of complex$[Co(nicotinamide)_2(thiocynate)_2(H_2O)_2]$ with atom labelling

The O(water)-Co-O(water), N(thiocyanate)-Co-N(thiocyanate), and N(nicotinamide)-Co-N(nicotinamide) angles are constrained by symmetry to 180°. The N(thiocyanate)-Co-N(nicotinamide), O(water)-Co-N(thiocyanate), and O(water)-Co-N(nicotinamide) angles are 87.48°, 91.9°, and 90.50° respectively, indicating a slightly distorted octahedral coordination for the Co ion.

Both ligands generally acts as bidentate, however in this polymer plays as unidentate. The thiocyanate SCN presents multiform coordination modes connecting the metal ions with terminal and/or bridging fashions. According to the concept of hard–soft/ acid–base the SCN ion prefers to bind to Cd(II) center in both N- and S-bonded fashion, whereas in the only N-terminal mode to Co(II)ion.

As expected, the SCN anion is almost linear angle: 178° and coordinates in a little bent fashion to Co, exhibiting a Co-N-C angle of 159.56°. These structural features have already been observed in other thiocyanato-containing metal complexes.[25] As a result of the *trans* orientation of two terminal N-bonded thiocyanate groups around the Co(II) atom, the bond angle N(1)–Co(1)–N(1) is 180°. The S-C and C-N distances of 1.638(2) Å and 1.158(2)Å in the SCN- moiety show the normal structure of the thiocyanate in the complex which is also observed in other thiocyanate complexes. The N--C bond length is little larger than the corresponding value [1.140(11)A] found in the $[Mn(H\text{-}quin)(quin)(NCS)(H20)_2]$ complex (H-quin is quinaldic acid) with terminal nitrogen-bonded thiocyanato ligands [r].The nicotinamides molecules are trans to each other with angle N(2)-Co-N(2) is 180°. The nicotinamide ligand generally acts as a bidentate chelating ligand, coordinating to the metal ion through the carbonyl O and pyridine N atoms , but in this structure it acts as a unidentate ligand in which the pyridine N is coordinated to the Co ion while the carbonyl O is involved in hydrogen bonding with another water molecule. Water used as solvent whereas it involved in coordination with metal ions and act as ligand.

The coordination of nitrogen atoms of each thiocynate molecules and nicotinamide molecules results in the formation of two symmetrical axis N1···Co···N1, N2···Co···N2 respectively. The oxygen atoms of water molecules describe the third axis O(1)WA···Co···O(1)WB. The Co–Co distance spaced by the thiocyanate ligand is 7.548Å.

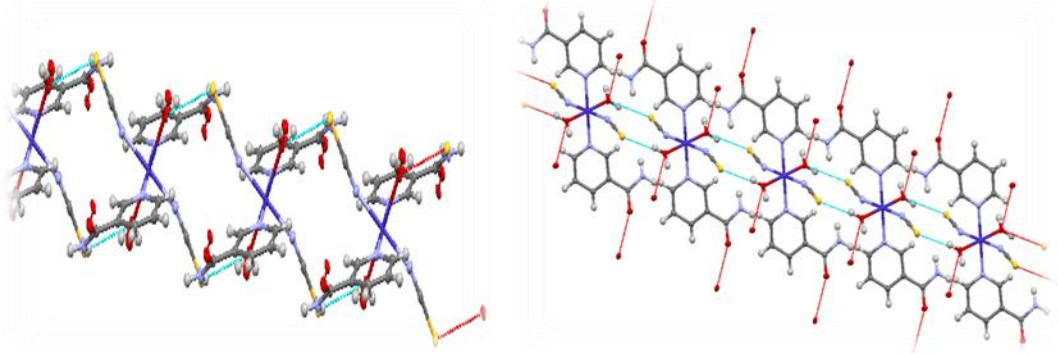


Fig. 3 Views of the complex $[Co(nicotinamide)_2(thiocyanate)_2(H_2O)_2]$: (a) 1D single polymeric chain running along the b axis (110 plane).(two cobalt centres attached through S- - H-O hydrogen bond and form ladder like structure.)

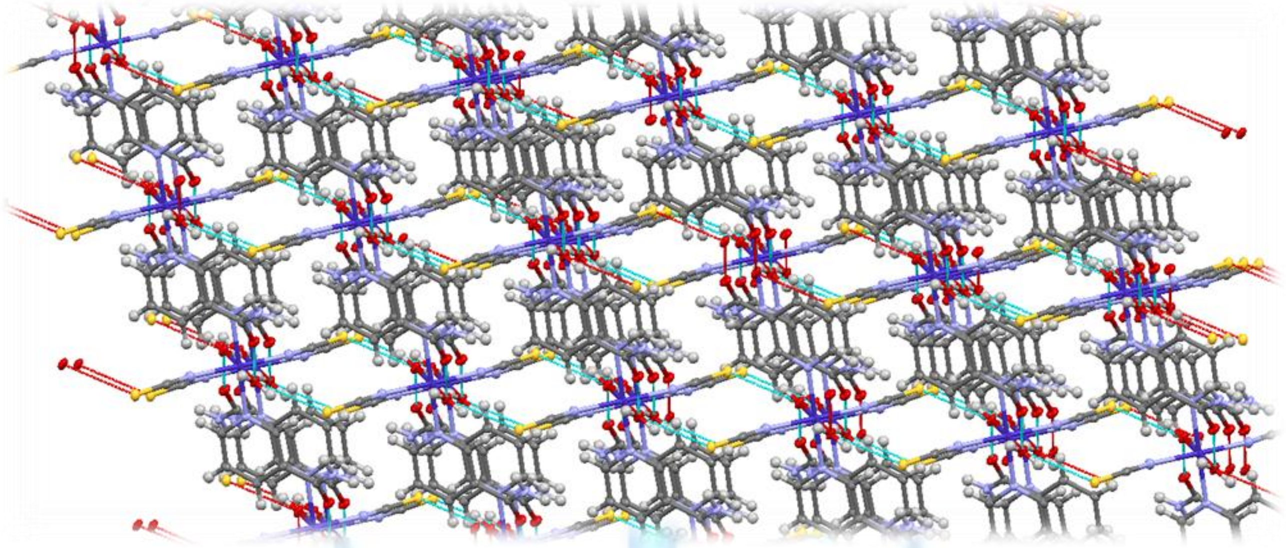


Fig. 4 2D polymeric chain running along the b axis (attached through N-H- -S hydrogen bonding between amide group of nicotinamide & S atom of thiocyanate molecule)

The discrete units are connected by bifurcated hydrogen bonds between the coordinated water molecules and terminal thiocyanate sulfur atoms forms O(2)-H(2)WA----S(1) interlayer hydrogen bonding gives 1D chain and forming ladder like structure can be seen in fig.(3). Further oxygen atom of amide group from nicotinamide molecule makes hydrogen bonding with hydrogen atom of water molecule C(7)-O(1)---H(2)WB to afford a 2-D layered architecture as depicted in Fig.(4)

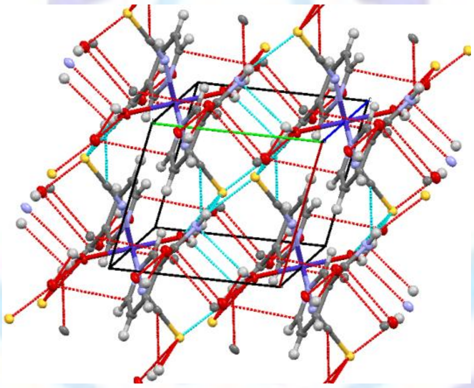


Fig. 5 A packing diagram of Compound. Hydrogen bonds are shown as dashed lines.

As can be seen from the packing diagram fig(5), the Co atoms are located at the centre of the axis of the unit cell and the molecules of polymer are linked by intermolecular hydrogen bond O—H---O, O-H----S and N—H----S hydrogen bonds, forming a supramolecular structure. Dipole–dipole and van der Waals interactions are also effective in the molecular packing.

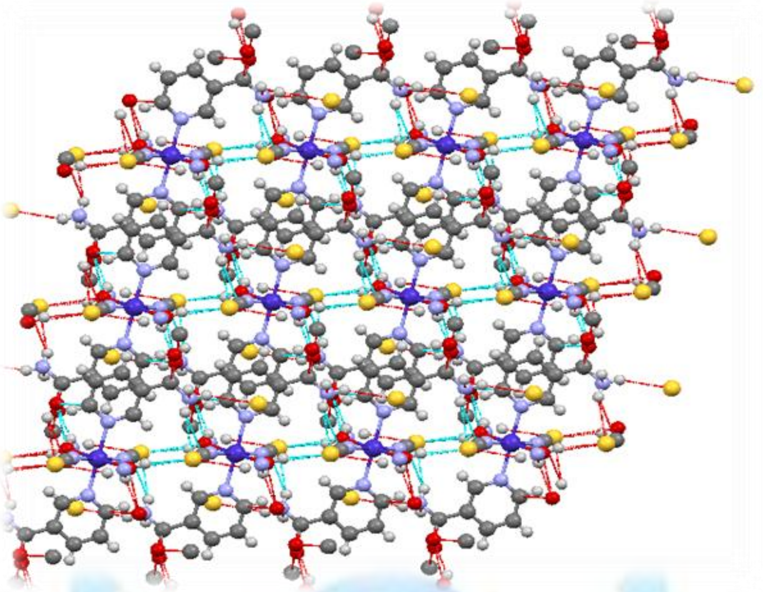


Fig. 6 Perspective three-dimensional view of the complex along the *b*-axis.

Remarkably, each sulphur atom of thiocyanate molecule plays a trifurcated role to be involved in the hydrogen bonding with one hydrogen atom from water molecules and two hydrogen atoms from nicotinamide molecules thus formation of three S(1)---H2WA, S(1)---H3A and S(1)---H3B interlayer respectively. With the aid of these contacts polymer affords 3D structure fig.(6). Carbonyl oxygen of amide group taking part in bonding gives three interlayer C(7)-O(1)---C(7), C(7)-O(1)---H(2)WB, C(7)-O(1)---H(6)C(6).These bonds also helps in making 3d structure.

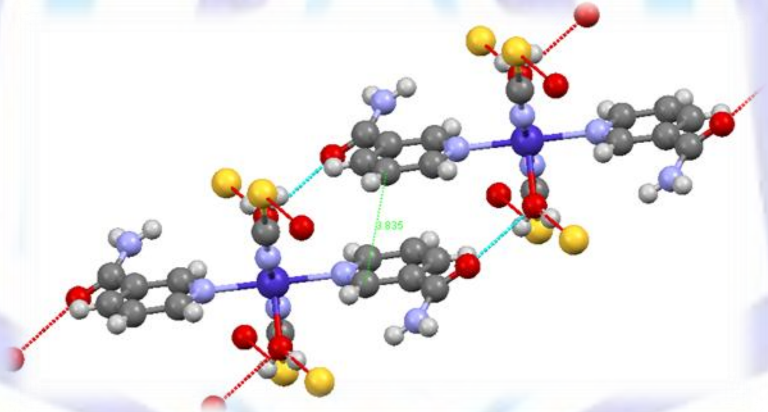


Fig. 7 Stacking of two pyridine rings of the neighbouring ligands through π-π interactions running along the c axis.

Additionally the structure stabilized through pi-pi interaction exists between parallel edges.

The shortest distance between two parallel benzene rings from the parallel nicotinamide ligands of the ladder structure is 3.865 Å show in fig. (7). which is in good with the literature, indicating a significant *pi-pi* interaction.[27]

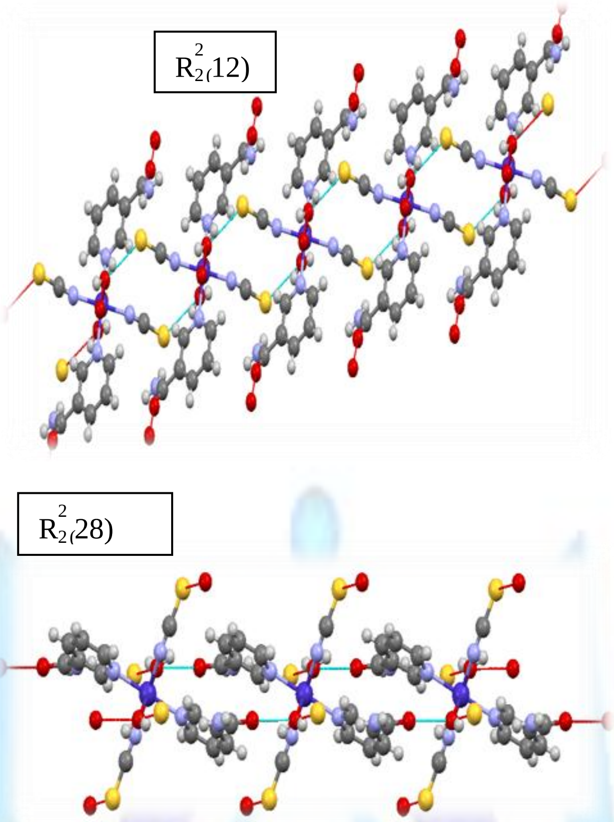


Fig. 8 Intermolecular hydrogen bonding & R_2^2 (12) and R_2^2 (28) motifs (View of the 1D single polymeric chain along the b axis) (a) nicotinamide positioned axial.(b) nicotinamide positioned equatorial).light blue dotted line shows intermolecular hydrogen bonding.

As can be seen in fig. (8) the intermolecular hydrogen bonding gives the molecular units R_2^2(12) and R_2^2 (28) appears to have reliable utility for construction of high dimensions of polymer.

3.3 Thermogravimetric analysis

In order to reveal the thermal stability of complex, TGA measurement has been carried out on a Perkin-Elmer Diamond TG/DTA instrument with a flow of dry air at a heating rate of 5°C/min from room temperature to 1000°. As shown in Fig. (9), TGA curve indicates that complex is stable up to about 150°C. The weight loss in the temperature range of 150～170°C is 8.4%, which is attributed to the elimination of disassociated water molecules (cacld.8.1%). With the temperature increasing, the ligands of nicotinamide and associated thiocyanate molecules are lost. Above 500°C, it is possible that Co (II) was oxidized to CoO. The black residual weight of the sample is *ca*.20.9% (calcd. for CoO: 18.4%).

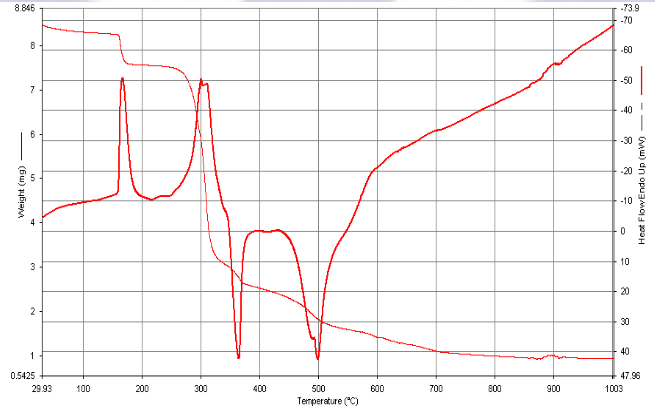


Fig. 8 Thermo- gravimetric graph of Compound

3.4 Magnetism

The variable temperature magnetic susceptibility data of the title complexes were measured in the range of 2–300 K under a magnetic field of 1 T. The plots of Xm and XmT versus T are shown in Figs. 10(a) and (b), respectively. It can be seen from Fig.10 (a) that the Xm value increases gradually upon cooling and the μeff value at 300 K is 4.35 ,which is much larger than that expected for the spin only case of Co (μeff = 3.87), indicating that an important orbital contribution is involved. Complex can be regarded as 1-D chains built by nicotinamide and Co(II) ions, and the magnetic interactions transferred by nicotinamide and hydrogen bonds should be very weak

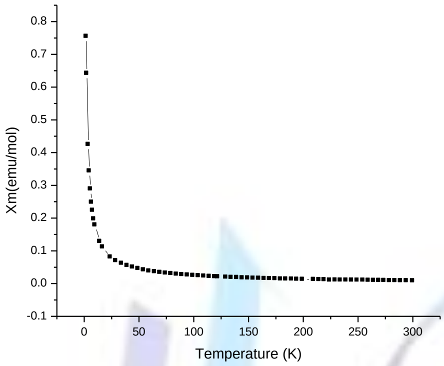


Fig10.(a)Shows plot between Xm versusT

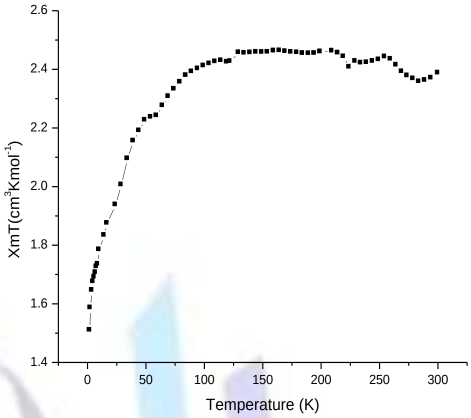


Fig.10 (b)Shows plot betweenXmT versusT

The value of XmT gradually decreases on cooling, indicating the overall antiferromagnetic exchange between the Co(II) ions. The XmT value at room temperature is 2.38 cm^3 mol^{-1} K, greater than the spin-only value expected for an isolated Co(II) ion. The magnetic susceptibility data at 1000Oe external field in the temperature range 2-300 K obeys the Curie-Weiss law, giving θ = -24.12 K and C =2.43 thus indicating a dominant strong antiferromagnetic interaction and/or spin orbital coupling between the Co (II) ions.

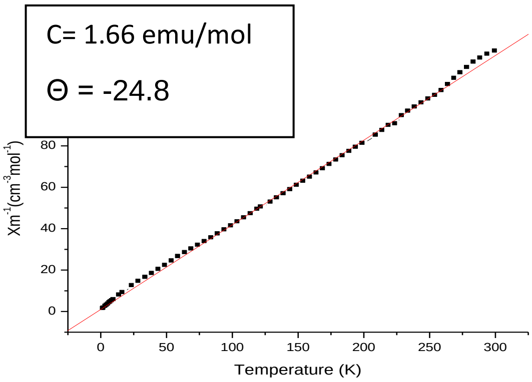
Magnetic susceptibility of complex was corrected for diamagnetism of the constituent atoms, which was calculated using Pascal's constant [28] and the temperature-independent paramagnetism of Co (II) ion. The variable temperature magnetic susceptibility data in the temperature range 300K to 2K was fitted to the formula (Equation 2), which was obtained based on isotropic Hamiltonian for two coupled Ni(II) ions as presented in Equation 1.

$$\mathrm{H} = -2\mathrm{J}\mathrm{S}_1\mathrm{S}_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

$$X_m = \frac{2Ng^2\beta^2}{k\,T}\,\frac{5+\exp\,(-4\mathrm{J}/\mathrm{kT})}{5+3\,\exp\,(-4\mathrm{J}/\mathrm{kT})+\exp\,(-6\mathrm{J}/\mathrm{kT})}\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

Equation (2) gave a good fit to the experimental data and the relevant fitting parameters are: g = 2.2 and 2J = –1.6 cm^{-1} and the agreement factor R=5.4×10^{-3}.The value 2J = –1.6 cm^{-1} further indicates that there is a strong antiferromagnetic interaction between adjacent Co (II)

ions.



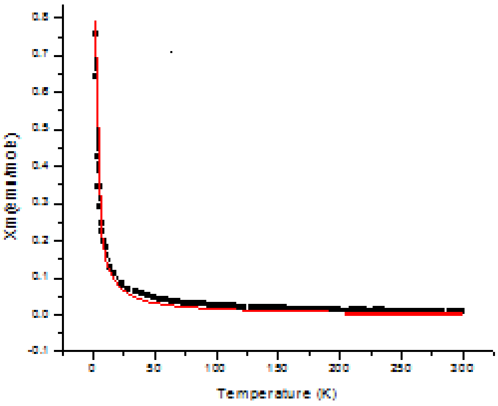


Fig. 10. (c) shows 1/Xm versus T plot

(the red line Curie Weiss fit)

Fig. 10. (d) shows Xm versus T plot

(the red line shows curve fitting)

4. Conclusion

In summary new [(Co (nicotinamide)$_2$ (thiocynate)$_2$(H$_2$O)$_2$] complex having 3D structure was synthesized & characterized by IR, TGA-DTA, Low temperature magnetic measurement . IR spectrum shows 2110cm^{-1} peak which indicates N—coordinated terminal thiocyanate ion. The crystal structure determined by X-ray diffraction shows a distorted octahedral geometry. Cobalt ion coordinated with four nitrogen atoms and two oxygen atoms, two nitrogen atoms from nicotinamide, two nitrogen atoms from thiocyanate and two oxygen atoms from water molecules respectively. Water used as solvent, however, it act as ligand. Most appealing point in this structure is sulphur atom of thiocyanate molecule showing trifurcated hydrogen bonding. Magnetic measurements indicate the existence of antiferromagnetic interaction with θ = -24.12 K and C =2.43 value.

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REFERENCES

[1] Eddaoudi, M., Moler, D.B Chen,. Li.H.B. Reineke,T.M. O'Keefee, M. and Yaghi, O. M. Acc. Chem. Res. 34(2001)319. (b) Batten S.R. and Robson, R., Angew. Chem., Int. Ed., 1998, 37,1460; (c) Fe´rey, G., Mellot-Draznieks, C., Serre, C., Millange, F., Dutour, J., Surble S., ´ and Margiolaki, I., Science, 309(2005)2040. (d) Zhao, X., Xiao, B., A. Fletcher, J.K., Thomas, M., Bradshaw D., and Rosseinsky, M.J., Science, 306(2004) 1012.

[2] C. Janiak, Dalton Trans. (2003) 2781.

[3] Cao, R,. Sun, D.F., Liang, Y.C., Hong, M.C., Tatsumi, K., and Shi, Q., Inorg. Chem. 41(2002)2087.

[4] Juan C.M.R. and . Lee, B. Coord. Chem. Rev. 183(1999)43. (b) Tse, M.C., Cheung, K. K., Chan, M.C., and Che, C.M., Chem. Commun.(1998)3245; (c) Tadokoro, M., Isobe K., H. Uekusa, Y. Ohashi, J. Toyoda, K. Tashiro and K. Nakasujhi, Angew. Chem. Int. Ed., 1999, 38, 95; (d) G. R. Desiraju, Angew Chem., Int. Ed. Engl., 1995, 34, 2311; (e) D. F. Sun, R. Cao,Y. Q. Sun, X. Li, W. H. Bi, M. C. Hong and Y. J. Zhao, Eur.J. Inorg.Chem., (2003) 94; (f) M. L. Tong, H. K. Lee, X. M. Chen,R. B. Huang and Mak, T.C.W. J. Chem. Soc., Dalton Trans.(1999)3657.

[5] Ducruix, Giege, A.R. Crystallization of proteins and nucleic acids, IRL IOxford Press (1992).

[6] Mondal, A., Pariya, C., Chaudhuri, Ray, N., Nayak, N. P., Mukherjee, A. K., Ghosh, A., Synthesis of [Ni(II)(Dien)$_{(2)}$ (NCS)$_{(4)}$ (H2O)] and Ni(Aepn)(NCS)(2)](N)(Dien=BIS(2-Aminoethyl)amine and AEPN=N-(2- Aminoethyl)-1,3-propanediamine) - Single-Crystal- Structure-analysis and thermal-behavior in the solid state. Polyhedron. 1997, 16, 39-45.

[7] Burmeister, J.L. Coord. Chem. Rev. 3 (1968) 225.

[8] Sailaja, S., Reddy, K., Rajasekharan, R M.V., Hureau, C., Riviere, E., Cano, J., Inorg. Chem. 42 (2003) 180. .

[9] Dey, S.K., Mondal, N., El Fallah, M.S., Vicente, R., Escuer, A., Solans, X., Font-Bardia, M., Matsushita, T. V., Mitra, Gramlich S., Inorg. Chem. 43 (2004) 2427.

[10] Blake, A. J., Hill, S. Y., Hubberstey, P., Rectangular grid two-dimensional sheets of copper (II) bridged by both co-ordinated and hydrogen bonded 4,4_-bipyridine(4,4_-bipy) in {[Cu(□-4,4_-bipy)(H2O)2][BF4]2}4,4-bipy), J. Chem. Soc. Dalton Trans. (1997) 913-914.

[11] Li, M. X., Xie, G. Y., Gu, Y. D., Synthesis, characterization and magnetic properties of one-dimensional 4,4_-bipyridinebridged manganese (II) complex: crystal structure of [Mn(□-4,4_-bipy)(4,4_-bipy)(NCS)2(H2O)2]*n*, Polyhedron, 1995, 14:1235_1239.

[12] Tong, M.L., Chen, X.M., Yu, X.L., A novel two-dimensional rectangular network, Synthesis and structure of {[Cu(4,4_-bpy)(pyz)(H2O)2][PF6]2}*n* (4,4_-bpy = 4,4_-bipyridine, pyz = pyrazine), J. Chem. Soc. Dalton Trans., (1998) 5-6.

[13] Mitwa, Y., Mizuno, T., Tsuchiya, K.,Taga, T., Iwata, Y., Experimental charge density and electrostatic potential in nicotinamide ,Acta Crystallogr Acta Crystallogr. B 55(1999) 78–84.

[14] Vogalsanger B., Brown, R. D., Godfrey, P. D., and Pierlot, A. P., J. Mol. Spectrosc. 145 (1991) 1.

[15] Purcell, P. J. Phys. Chem., 68 (1964) 2666.

[16] Purcell, P. and Siger, A.J. J. Phys. Chem., 69 (1965) 4097.

[17] Pandey, Deepanjali, Narvi, S. Shahid, Mehrotra, K. Gopal, and Butcher J. Raymond, Diaquabis(Nicotinamide-κN^1) bis (Thiocyanato-κS)Nickel(II) Acta Cryst. (2014). E70, m183

[18] Sheldrick, M. G.; SHELX97. Programs for Crystal Structure Analysis (Release 97-2). University of Göttingen, Germany. (1997).

[19] Wilson, C. J. A.; Ed., International Tables for Crystallography, Volume C, Kluwer Academic Publishers, Dordrecht, The Netherlands, (1995).

[20] SAINT: Area-Detector Integration Software. Siemens Industrial Automation, Inc.: Madison, WI. (1995).

[21] SADABS: Area-Detector Absorption Correction Siemens Industrial Automation, Inc.: Madison, WI. (1996).

[22] Sabbani, Supriya, Das, Samark. A simple coordination complex exhibiting colour change on slight structural modification: Synthesis and crystal structures of violet and yellow forms of [NiII(opda)2(NCS)2] (opda = orthophenylenediamine).J. Chem. Sci., Vol. 122, No. 5, September 2010, pp. 731–737.

[23] Bailey, R. A., Kozak, S. L., Michelsen, T.W., Mills, W.N., Coord. Chem. Rev. 6(1971)407-445.

[24] Tramer, A.C.R. Acad. Sei. 250 (1960) 3150-3153.

[25] Nesterova, O. V., Petrusenko, S. P., Kokozay, V. N.,Skelton, B.W., Inorg. Chem.Commun. 7 (2004) 450.

[26] Du, Miao.Li, Cheng-Peng.; Guo, Jian-Hua. Inorganica Chimica Acta. 359 (2006) 2575–2582.

[27] Dubler, E., Haring, U. K., Scheller, K. H., Baltzer, P., Sigel, H., *Inorg.Chem*. *23*, (**1984**)3785.

[28] Marshall, S. R., Incarvito, C. D., Manson, J. L. et al., Synthesis, structure and magnetic properties of Co2{[N(CN)2]4bpym}_H2O andM{[N(CN)2]2bpym}_H2O (M = Mn, Fe, Co; bpym = 2,2_-bipyrimidine), Inorg. Chem.39(2000) 1969-1973.