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Two Unprecedented Cu(II) Complexes with Versatile Azide/Thiocyanate Bridging derived from Symmetrical Azo-Linked Schiff Base of 1-(5-Chloro-2-Hydroxy-Phenyl)-Ethanone and Propane 1,3-Diamine

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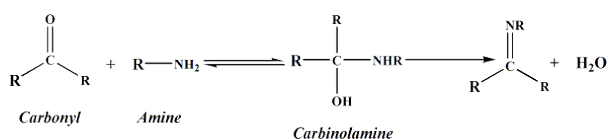
Magnetic Moment

ABSTRACT

Two new novel Cu(II) complexes with versatile azide or thiocyanate bridging derived from symmetrical azo-linked Schiff base of 1-(5-Chloro-2-hydroxy-Phenyl)-Ethanone and propane 1,3-diamine have been properly synthesized. The above two complexes are synthesized by direct reaction of ligand with appropriate concentration of copper metal salts and also the template method. The azo-linked Schiff base ligand and the metal complexes were characterized on the basis of common elemental analysis (C, H and N), and several popular micro analytical techniques like IR, UV-Vis, mass (m/e) spectroscopic study. The Schiff base ligand was further identified by using ¹H NMR spectra. Additional magnetic moment data was provided to establish probable geometry of the synthesized complexes. The electronic spectra and magnetic moment data suggests that environment of Cu(II) in the reference complexes must be square pyramidal and square planar. The molar conductivity values indicate that the two newly synthesized copper complexes are totally non-electrolyte. All the experimental results suggests that Cu(II) metal in both complexes bonded through the imino nitrogen of the respective ligand after proper incorporation of azide or thiocyanate pseudohalides. The copper complexes showed magnetic moment value within the range 1.85-1.88 μB.

1. Introduction

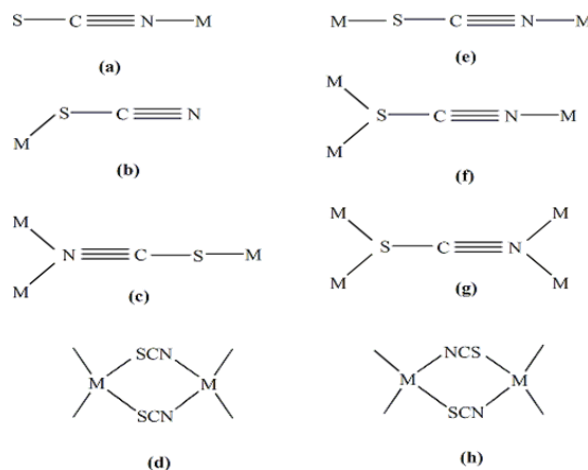
Prof. Hugo Schiff during 19th century [1] opened the beautiful research gate in the field of coordination chemistry after his novel discovery of Schiff base. Schiff bases also known as anils, imine or azomethine [2], generally synthesized by common condensation reaction between an aldehyde or ketone and a primary amine. The formation of Schiff base was characterized by the presence of azomethine (C=N) linkage. The azomethine linkage attached by R group which may be alkyl, aryl, heteroaryl or simply hydrogen. The classical method by which Schiff base synthesis to be carried out is the given type of reaction Scheme 1.



Scheme 1 Synthetic procedure of symmetrical azo-linked Schiff base

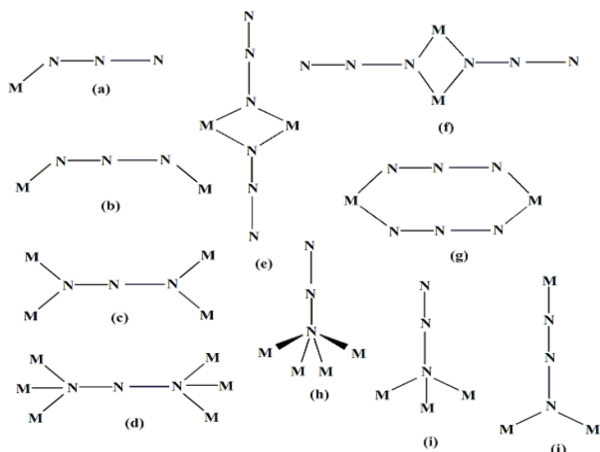
The above synthetic scheme imply that Schiff base formation proceed through beautiful carbinolamine intermediate formation followed by dehydration. The formation of Schiff base according to Scheme 1 is completely reversible and takes place in presence of acid, base or upon mild heating. After the discovery of novel Schiff base by Prof. Hugo Schiff, many inquisitive modern Inorganic chemists got interested to prepare different types of Schiff bases, and nowadays active and well-designed Schiff base ligands are considered 'privileged ligands' [3] because of their preparational accessibilities, structural varieties, varied denticities and mobility of donor center. Today, the endearing popularity of Schiff base is due to its beauteousness and bemusing versatility of wide range of complex formation with various metal ions which may be transition or post transition in nature. Such Schiff base metal complexes have numerous

applications in the field of cancer treatment, as antibactericide agents [4-5], as antiviral agents [6-8], as fungicide agents [9-10], and many other biological properties [11-13]. In the present scenario, Schiff base complexes applications are in the chemical analysis [14], absorption and transport of oxygen [15-16], in pesticides and hetero and homogeneous catalysis for oxidation and polymerization of organic compounds [17-18]. The design and synthesis of transition metal complexes are highly interesting in presence of Schiff base bridged by small conjugated ligands such as cyano, azido, thiocyanato and hence today modern inorganic chemists are currently under investigated in view of their structural diversity and in the context of molecule based magnets. The most common bridging ligands like SCN¹⁻, N₃¹⁻ exhibits versatile bridging modes during complex formation in presence of novel Schiff base Scheme 2.

Scheme 2a Different versatile binding modes of SCN¹⁻ during complex formation

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Scheme 2b Different versatile binding modes of N_3^{-1} during complex formation

Today plenty of research studies about azide or thiocyanate bridge have been dedicated to divalent transition- metal coordination complexes like Cu^{2+} , Ni^{2+} , Mn^{2+} etc, and thus possessing diverse structures from 1-D, 2-D to 3-D supramolecular polymers with different magnetic properties [19-28]. For a better understanding of magneto-structural correlation, it is necessary to prepare some specific complexes that should have the same Schiff base ligand and versatile pseudohalides azide, thiocyanate where structural variations are strongly affected. Keeping in mind, in the present research scenario, we synthesized a novel symmetrical azo Schiff base H_2L , two new $Cu(II)$ complexes using the same Schiff base having azide/thiocyanate versatile bridging modes. Further very carefully, Schiff base H_2L and respective two metal complexes were characterized by various spectroscopic techniques (IR, UV-Vis, 1H NMR), and magnetic studies were also conducted.

2. Experimental Methods

2.1 Materials

All chemicals were of reagent grade, purchased from commercial sources and used as received without further purification. 5-chloro-2-hydroxyacetophenone was purchased from Sigma Aldrich Company, USA. 1,3-Diaminopropane, Copper acetate both are purchased from Sigma Aldrich Company, USA. Sodium azide, Ammonium thiocyanate, were purchased from SDFCL, India. The total synthetic reactions and work-up were done in open air.

Caution! The azide complexes are highly explosive particularly in the presence of Schiff base ligand. Even though no such accident occurred during the course of my research work, since only a small amount of materials should be prepared and must be handled with utmost care.

2.2 Physical Measurement

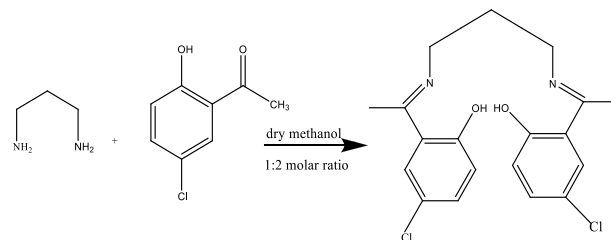
Elemental analyses (carbon, hydrogen and nitrogen) of the Schiff base H_2L and the metal $Cu(II)$ complexes were determined with a Perkin-Elmer CHN analyzer 2400. Mass spectra were done with a JEOLJMS-AX 500 mass spectrometer. IR spectra (KBr pellet, 400–4000 cm^{-1}) were recorded on a Perkin-Elmer model 883 infrared spectrophotometer. The electronic spectra of the complexes in organic solvent were recorded on a Hitachi model U-3501 spectrophotometer. The 1H NMR spectra of novel Schiff base H_2L were recorded on Bruker 300 MHz FT-NMR spectrophotometer using trimethylsilane as internal standard in $CDCl_3$ solvent. The magnetic susceptibility values of two $Cu(II)$ complexes were determined by Gouy method correction for diamagnetism of the constituent atoms was calculated, using common Pascal's constant. The effective magnetic moments values μ_{eff} , of two $Cu(II)$ complexes were calculated using the given equation:

$$\mu_{eff} = 2.83 (\chi_M T)^{1/2}$$

2.3 Synthesis

2.3.1 Synthesis of Novel Schiff Base H_2L

To a methanolic solution (30 mL) of 5-chloro-2-hydroxy acetophenone (0.171 g, 1 mmol), propylene diamine (0.0371 g, 0.5 mmol) in methanol (5 mL) was added with constant stirring. At this moment colour of the solution turned deep yellow and it was refluxed continuously for 3 hours. A yellow solid was immediately separated and collected by filtration after cooling the solution up to room temperature. Then the yellow solid was dried and preserved in a desiccator Scheme 3.



Scheme 3 Synthetic procedure of Schiff base H_2L

For novel Schiff base H_2L (Yield: 75%), M.Wt. (379.28), Exact Mass: 378.09, m/e: 379.00, Anal. Calc. for $C_{19}H_{20}N_2O_2Cl_2$: C, 60.17; H, 5.32; Cl, 18.69; N, 7.39; O, 8.44 Found: C, 60.1; H, 5.31; Cl, 18.62; N, 7.35; O, 8.42 IR (KBr: ν cm^{-1}): 1611 (ν C=N s), 1491.03(s), 1290.02(m), 1228.78(m); 1H NMR (in DMSO), UV-Vis spectrum, λ_{max} (CH_3OH): 272.89 nm, 334.10 nm, and 400.08 nm.

2.3.2 Synthesis of Complex

2.3.2.1 Complex 1- $[Cu_2(H_2L)_2(N_3)_4]$ Synthetic Procedure

To a methanolic (30 mL) solution of the ligand (0.379 g, 1 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (0.241 g, 1 mmol) taken in same solvent was added drop wise with constant stirring. After 10 min NaN_3 (0.065 g, 1 mmol) dissolved in 5 drops of water+methanol mixture was added and stirred for 2.5 h. A brown colored complex was immediately precipitated out and this was filtered under suction, washed with methanol, dried and preserved in a desiccator properly.

For Complex 1 (Yield: 65%), M.Wt. (1053.73), Exact Mass: 1050.10, m/e: 1052.08, Anal. Calc. for $[Cu_2(C_{19}H_{20}Cl_2N_2O_2)_2(N_3)_4]$: C, 43.31; H, 3.83; Cl, 13.46; N, 21.27; O, 6.07, Cu, 12.06. Found: C, 43.3; H, 3.82; Cl, 13.43; N, 21.25; O, 6.00, Cu, 12.00 IR (KBr, ν_{max}/cm^{-1}): $\nu(N-N) = 2054.00$; $\nu(C=N) 1602.49$, $\lambda_{max}(CH_3OH)$: 365.87 nm.

2.3.2.2 Complex 2- $[Cu_2(C_{19}H_{20}Cl_2N_2O_2)_2(NCS)_2(NO_3)]$ Synthetic Procedure

This compound was prepared in a similar procedure to that mentioned above for Complex 1 using $Cu(NO_3)_2 \cdot 3H_2O$ (0.241 g, 1 mmol) and NH_4SCN (0.076 g, 1 mmol) was added after 10 min and stirred for 2.5 h. A dark brown colored complex was immediately precipitated out and this was filtered under suction, washed with methanol, dried and preserved in a desiccator properly.

For Complex 2 (Yield: 67%), M.Wt. (1021.99), Exact Mass: 1125.83, m/e: 1123.9, Anal. Calc. for $[Cu_2(C_{19}H_{20}Cl_2N_2O_2)_2(NCS)_2(NO_3)_2]$: C, 43.31; H, 3.83; Cl, 13.46; N, 21.27; O, 6.07, Cu, 12.06. Found: C, 43.3; H, 3.82; Cl, 13.43; N, 21.25; O, 6.00, Cu, 12.00 IR (KBr, ν_{max}/cm^{-1}): $\nu(NCS) = 2364.65$; $\nu(C=N) 1602.49$, $\lambda_{max}(CH_3OH)$: 358.64 nm.

3. Result and Discussion

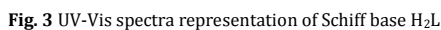
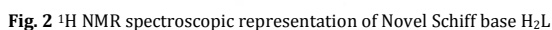
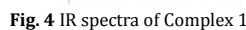
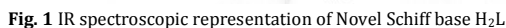
3.1 Synthesis

Novel Schiff base ligand (H_2L) and two new $Cu(II)$ azide/thiocyanate bridging complexes have been synthesized very carefully in our laboratory. They are lucidly characterized by different physicochemical techniques like elemental analyses, IR, UV-Vis, mass (m/e), and 1H NMR spectroscopic studies. Beside, additional magnetic moment data will be provided to establish probable structure of the synthesized two complexes.

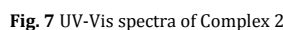
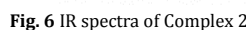
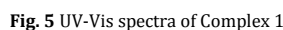
3.2 Individual Characterization of Novel Schiff Base (H_2L) and $Cu(II)$ Azide/Thiocyanate Bridging Complexes

3.2.1 Characterization of Novel Schiff Base Ligand (H_2L)

From IR studies, the presence of IR band near at 1611 cm^{-1} provides the evidence for formation of azomethine group (C=N) in the azo-linked symmetrical novel Schiff base (H_2L). Again the absence of C=O group, IR band around 1700-1800 cm^{-1} confirmed the Schiff base formation according to Scheme 1. The very weak band near 2800-2920 cm^{-1} indicates the presence of intramolecular hydrogen bond by -OH functional group participation. 1H NMR spectroscopic data was further confirmed the formation of novel Schiff base Figs. 1-2. The UV-Vis spectrum in methanol of novel symmetrical Schiff base (H_2L) reflects three main peaks at 272.89 nm, 334.10 nm and 400.08 nm. The first two UV-Vis spectrum are assigned due to benzene $\pi \rightarrow \pi^*$ and imino $\pi \rightarrow \pi^*$ transitions. Additional peak 400.08 nm is due to $n \rightarrow \pi^*$ transition Fig. 3.



Two unique azo based symmetrical Schiff base Cu(II) complexes shows IR frequency band near at 2054 cm^{-1} and 2364.65 cm^{-1} indicating the presence of versatile azide and thiocyanate linkage complex formation. In both Cu(II) complexes the peak being bifurcated, that's why azide and thiocyanate function as bridging moiety. The lowering frequency of C=N group indicates the coordination of C=N nitrogen to the Cu metal center. The literature [29] $\nu(\text{C}=\text{N})$ frequencies of SCN^{-1} could be used for differentiation purpose between S-bonded (2110-2140 cm^{-1}) and N-bonded (less than 2110 cm^{-1}) complexes. Hence here NCS^{-1} can be coordinated with Cu metal as terminal fashion through S atom. Since Cu(II) d^9 configuration, paramagnetic nature in both complexes exhibit d-d transition band. In both complexes shift of ligand $\pi-\pi^*$ and $n-\pi^*$ transition takes place due to complexation with Cu(II) metal center. The peak 358.64 nm in SCN^{-1} bridged complex is due to $\pi-\pi^*$ transition. The UV-Vis peak of Complex 1 365.87 nm directly confirmed N_3^{-1} bridged complex formation takes place with Cu(II) metal center Figs. 4-7.



3.3 Magnetic Moment Study

The copper(II) metal ion ($3d^9$) has one unpaired electron in the 3d shell, therefore all Cu(II) compounds were considered to have magnetic moments close to the spin-only value, $1.73 \mu_B$ but due to spin orbit coupling phenomenon, higher values are expected. The magnetic moment values calculated for Complex 1 are in the range of 1.85 – $1.88 \mu_B$. The environment around the copper in Complex 1 is square pyramidal. Complexes having a square pyramidal configuration, the five-fold degenerate 3d level of Cu(II) is split by a ligand field of C_{4v} symmetry into four components. The $d_{x^2-y^2}$, d_{z^2} and d_{xy} levels are non-degenerate, while (d_{xz} , d_{yz}) levels are four-fold degenerate, including spin. The spin-orbit coupling interaction splits this level into two components, each of which is further split into two sublevels by the external magnetic field. Boudreaux calculated theoretically the magnetic moment of square-pyramidal copper(II) complexes to be 2.11 – $2.21 \mu_B$ at room temperature. These values are slightly higher than those obtained during the experimental measurements ($1.88 \mu_B$). Again the colour of Complex 1 is brown suggesting strongly square pyramidal geometry (Fig. 8). Complex 2 is dark brown suggesting Cu(II) square planar geometry (Fig. 9).

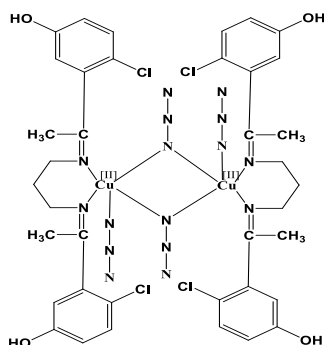


Fig. 8 Probable structure of Complex 1

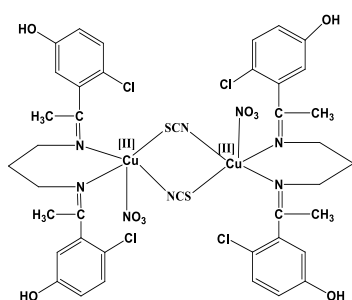


Fig. 9 Probable structure of Complex 2

4. Conclusion

We have successfully synthesized in our laboratory symmetrical azo-linked novel Schiff base H_2L , two new Cu(II) azide/ thiocyanate bridging complexes. Schiff base (H_2L) and Cu(II) complexes have been characterized by elemental analyses, FT-IR, UV-Vis, mass, and 1H NMR spectroscopic study. Additional magnetic moment study will be provided to guess the expected probable geometry of synthesized two complexes. Our aim for current research work is to investigate primarily the nature of bridging modes of versatile azide or thiocyanate around Cu(II) metal center. Hence we are very carefully consider microanalytical techniques for characterization of Schiff base H_2L , copper metal complexes and at the final stage magnetic moment study were conducted to find out probable structure of two complexes.

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References

- [1] H. Schiff, Condensation products of aldehydes and ketones with primary amines, *Ann. Suppl.* 3(343) (1864) 1864-1865.
- [2] B. Cohen, The interaction of alpha-1-antitrypsin with chymotrypsin, trypsin and elastase, *Biochim. Biophys. Acta* 391 (1975) 193-200.
- [3] T.P. Yoon, E.N. Jacobsen, Privileged chiral catalysts, *Science* 299 (2003) 1691-1693.
- [4] N.N. Gulerman, S. Rollas, H. Erdeniz, M. Khiraj, Antibacterial, antifungal and anticobacterial activities of some substituted thiosemicarbazides and 2, 5-disubstituted-1, 3, 4-thiadiazoles, *J. Pharm. Sci.* 26 (2001) 1-5.
- [5] K.H. Reddy, P.S. Reddy, P.R. Babu, Nuclease activity of 2-substituted heteroaromatic thiosemicarbazone and semicarbazone copper (II) complexes, *Trans. Met. Chem.* 25 (2000) 154-160.
- [6] H. Singh, L.D.S. Yadav, S.B.S. Mishra, Studies of some antifungal transition metal chelates of N-(5-Phenyl-1,3,4-thiadiazyl-2-yl) dithiocarbamic acid, *J. Inorg. Nucl. Chem.* 43 (1981) 1701-1704.
- [7] J. Charo, J.A. Lindencrona, L.M. Carison, J. Hinkula, R. Kiessling, Protective efficacy of a DNA influenza virus vaccine is markedly increased by the coadministration of a Schiff base-forming drug, *J. Virol.* 78 (2004) 11321-11326.
- [8] D.X. West, S.L. Dietrich, I. Thientananvanich, C.A. Brown, A.E. Liberta, Spectral and biological studies of copper(II) complexes of 2-acetylpyridine thiosemicarbazones with bulky N4-substituents, *Trans. Met. Chem.* 19 (1994) 319-320.
- [9] N.K. Singh, S.B. Singh, Synthesis, characterization and biological properties of manganese(II), cobalt(II), nickel(II), copper(II), zinc(ii), chromium(II) and iron(II) complexes with a new thiosemicarbazide derivative, *Ind. J. Chem.* 40 (2001) 1070-1075.
- [10] V. Mishra, S.N. Pandeya, S. Anathan, Antitubercular activity of thiosemicarbazones and semicarbazones, *Acta Pharm. Turc.* 42 (2000) 139-145.
- [11] E.J. Baran, Oxovanadium(IV) and oxovanadium(V) complexes relevant to biological systems, *J. Inorg. Biochem.* 80 (2000) 1-10.
- [12] F. Velde, I.W.C.E. Arends, R.A. Sheldon, Biocatalytic and biomimetic oxidations with vanadium, *J. Inorg. Biochem.* 80 (2000) 81-89.
- [13] X.D. Zhu, C.G. Wang, Y.L. Dang, H.B. Zhou, Z.S. Wu, et al, The Schiff base N-salicylidene-O,S-dimethylthiophosphorylimine and its metal Complexes: Synthesis, characterization and insecticidal activity studies, *Synth. React. Inorg. Met. Org. Chem.* 30 (2000) 625-636.
- [14] M. Kanthimathi, A. Dhathathreyan, B.U. Nair, Langmuir-Blodgett film properties of a donor-acceptor Schiff base, *Chem. Phys. Lett.* 324 (2000) 43-47.
- [15] H. Zhang, Y. Zhang, C. Li, Enantioselective Epoxidation of olefins catalyzed by the Mn (Salen) catalysts immobilized in the nanopores of mesoporous materials, *J. Catal.* 238 (2006) 369-381.
- [16] B. Bahramian, V. Mirkhani, M. Moghadam, S. Tangestaninejad, Selective alkene epoxidation and alkane hydroxylation with sodium periodate catalyzed by cationic Mn(III)-salen supported on Dowex MSC1, *Appl. Catal.* 301 (2006) 169-175.
- [17] J. Wen, J. Zhao, X. Wang, J. Dong, T. You, Asymmetric pinacol coupling reaction catalyzed by dipeptide-type Schiff base, *J. Mol. Catal.* 245 (2006) 242-247.
- [18] C.Y. Liao, H.H. Wei, S.C. Cheng, S. Mohanta, Antiferro and ferromagnetic behaviors of two new $\mu_{1,3}$ -N₃ and $\mu_{1,1}$ -N₃ bridged dinuclear Nickel(II) complexes with 2,6-Bis(2-pyridyl)-4(1H)-pyridine and 2,6-Dimethyl-2,3-bis(2-pyridyl) quinoxaline ligand, *Tamk. J. Sci. Eng.* 5 (2002) 201-208.
- [19] S. Banerjee, B. Wu, P.G. Lassahn, C. Janiak, A. Ghosh, Synthesis structure and bonding of cadmium (II) thiocyanate system featuring nitrogen based ligands of different denticity, *Inorg. Chem. Acta* 358 (2005) 535-544.
- [20] F. Meyer, P. Kircher, H. Pritzkow, Tetranuclear nickel(II) complexes with genuine μ_4 -1,1,3 and μ_4 -1, 1,3,3 azide bridges, *Chem. Commun.* 6 (2003) 774-775.
- [21] S. Ferlay, S. Mallah, R. Quahes, P. Veillet, M. Verdaguar, A room-temperature organometallic magnet based on Prussian blue, *Nature* 378 (1995) 701-703.
- [22] O. Sato, T. Iyoda, A. Fujishima, K. Hashimoto, Photoinduced magnetization of a cobalt-iron cyanide, *Science* 272 (1996) 704-705.
- [23] J. Ribas, A. Escuer, M. Monfort, R. Vcente, R. Cortes, et al., Polynuclear Ni^{II} and Mn^{II} azide bridging complexes: Structural trends and magnetic behavior, *Coord. Chem. Rev.* 1027 (1999) 193-195.
- [24] B.Q. Ma, S. Gao, G. Su, X.G. Xu, Cyano-Bridged 4f-3d coordination polymers with a unique two-dimensional topological architecture and unusual magnetic behavior, *Angew. Chem. Int. Ed.* 40 (2001) 434-437.
- [25] M. Yuan, F. Zhao, W. Zhang, F. Pan, Z. Wang, S. Gao, Hydrogencyanamide-bridged one-dimensional polymers built on Mn(III)-Schiff base fragments: synthesis, structure and magnetism, *Chem. Eur. J.* 13 (2007) 2937-2952.
- [26] J. Ribas, M. Monfort, B.K. Ghosh, R. Cortes, X. Solans, M. Fon Bardia, Two new Antiferromagnetic Nickel(II) complexes Bridged by Azido ligands in the cis position, effect of the counter anion on the crystal structure and magnetic properties, *Inorg. Chem.* 35 (1996) 864-868.
- [27] M. Goher, L.A. Al-Shatti, F.A. Mautner, A polymeric complex of copper (II) bridged simultaneously by tridentate glycinate and MU (N, S)-thiocyanato anions-synthesis, spectral and thermal properties of the complex [Cu (glycinato) (NCS) (H₂O)], *Polyhedron* 16 (1997) 889-895.
- [28] R. Cortes, J.L. Pizarro, L. Lezama, M.I. Arriortua, T. Rojo, Ferromagnetic interactions in the first Bis(μ -end-on-azido) Mn(II) dinuclear compound, *Inorg. Chem.* 33 (1994) 2697-2700.
- [29] K. Nakamoto, Infrared and Raman spectra of inorganic and coordination compounds, 5th Ed., Wiley, New York, 1986.