Copper(II)-Nickel(II) Induced Cyanide Bridged 2D Heterometallic Coordination Polymer: Synthesis, X-ray Structure and Magnetic Study

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One new two-dimensional heterometallic coordination polymer $[Cu_3Ni(L)_2(CN)_6]_n$ (**1**) [L = 2-methylethylenediamine, CN^- = cyanide ion] was synthesized and characterized by X-ray crystallography. Compound **1** crystallizes in the monoclinic $C2/c$ space group. The single crystal X-ray structure of compound **1** indicated that it is a 2D coordination polymer with three copper(II) ion embedded with $[Ni(CN)_4]^{2-}$ molecular ion in architecture through μ-CN/μ-NC bridges results heterometallic polymer. In compound **1**, each Cu^1 center with a CuN_5 chromophore is encompassed by four N atoms of the two different bidentate amine (L) and one N atom of μ-NC ion, while both Cu^2 and Cu^3 centres are connected by three N atoms of μ-NC ions having CuN_3 chromosphere and Ni^1 are coordinated by three μ-CN and one terminal CN ions with NiC_4 chromophore. Three copper centers and one nickel center are interlinked through μ-CN/μ-NC forming {-$Cu^1(L)_2$(μ-NC)Ni^1(CN)(μ-CN)$_2Cu^2$(μ-NC)Cu^3(μ-NC)-} unit to fabricate a 2D hetero metallic polymer. In the crystalline state of compound **1**, each 2D polymer is further propagated through intermolecular N-H···N hydrogen bonds corroborant a supramolecular 2D network structure. Variable temperature magnetic susceptibility study displayed a weak antiferromagnetic spin coupling presumably due to the diamagnetic tetracyanonickellate bridging among the Cu^{II} ions.

Keywords: Heterometallic, Coordination polymer, Terminal cyanide, Bridging cyanide, X-ray structure, Magnetic behaviour.

INTRODUCTION

Coordination polymers [1] subsume metal ions interlinked by coordinated ligands into sequential arrangement around molecular components to spawn inorganic-organic hybrid [2] functional materials [3-8] of various shapes and sizes [9] through judicious and strategic control and manipulation of covalent bonds [10] with malleable coordination spheres and multiple lateral non-covalent forces [11,12]. One-pot synthesis [13] of the building blocks is one of the time-consuming methods for assembling such complexes, with a large number of 1D, 2D and 3D extended arrays of homo and heterometallic polymers characterized with new structures and physico-chemical features [14]. In organometallic and coordination chemistry, cyanide anions with potential binding modes to various metal atoms are used to synthesize one, two or three-dimensional structures. The Lewis base behaviour of the cyanide ion's carbon and nitrogen terminals allows it to coordinate two distinct metal cations

that behave as the corresponding Lewis acids. Polyamine [15] or Schiff base [16] transition metal complexes, as complementary units with potential acceptor site(s) exhibiting polymeric structures, are driven extensively as multiple bridging units and cyanometallate complexes [17-22] with potent donor sites are driven extensively as multiple bridging units. [M(CN)x]n- [where x = 4 or 6; M(II) = Mn, Fe, Co, Ni, Cu, Zn, Cd, Pd, Pt, *etc*.] cyanometallate building blocks [14-16] containing cyanide groups have been extensively used to form multidimensional networks [23] and readily forms coordination polymers when reacted with transition-metal cations and can promote strong magnetic exchange [24]. Copper, is a better choice [25] because it has a variety of geometries with comparable stability, such as tetrahedral, square pyramidal and trigonal-bipyramidal, which leads to considerable changes in metal-ligand geometry and total molecule shape. Bioinorganic chemistry [26] and magnetism [27] are two other fields where this metal ion is useful. In this study, we prepared coordination polymer using

an unsymmetrical amine, 2-methylethylene-diamine (L) as a bidentate chelating ligand and successfully isolated one coordination polymer of heterometallic polymer [Cu$_3$Ni(L)$_2$(CN)$_6$]$_n$ (**1**) [CN$^-$ = cyanide ion]. To determine the exact coordination sphere, X-ray diffraction data were used to solve the structure of compound **1**. This study looked into the synthesis, characterization, X-ray structure and magnetic properties of this coordination polymer in further depth.

EXPERIMENTAL

High purity 2-methylethylenediamine (Sigma-Aldrich, USA), copper(II) nitrate trihydrate (Merck, India) and potassium tetracyanonickelate(II) (E. Merck, India) were all purchased and utilized as received from their respective companies. All other chemicals and solvents were of AR grade and had been distilled and dried prior to use. The synthetic reactions and work-up were carried out outside in the open air.

Physical measurements: A Perkin-Elmer 240C elemental analyzer was used to perform the analyses (carbon, hydrogen and nitrogen). A Bruker Alpha T200140 FT-IR spectrometer was used to record the IR spectra (KBr disc, 4000-200 cm^{-1}). Magnetic measurements of compound **1** were performed with a superconducting quantum interference device (SQUID) operating between 2 and 300 K at an applied field of 1T. Magnetic data were corrected for the diamagnetism of the sample holder, measured in the same range of temperature and field and for the intrinsic diamagnetism of the samples estimated through Pascal's constants [28].

Synthesis of [Cu$_3$Ni(L)$_2$(CN)$_6$]$_n$ (1): A 10 mL solution of potassium tetracyanonickelate(II) (0.482 g, 2.00 mmol) in MeCN was added dropwise to a mixture of copper(II) nitrate trihydrate (0.726 g, 3.00 mmol) and 2-methylethylenediamine (L, 0.148 g, 2.00 mmol) (15 mL) in MeCN, with constant stirring under magnetic stirrer for 3 h and the resultant combination was then maintained at room temperature for moderate evaporation. The violet single crystals of compound **1** formed and were recovered by filtration after 2 days, then washed with dehydrated alcohol and dried *in vacuo* over silica gel (**Scheme-I**). Yield: 0.332 g (60 %). Anal. calcd. (found) % for C$_{12}$H$_{20}$N$_{10}$Cu$_3$Ni (**1**): C, 26.03 (26.20); H, 3.64 (3.85); N, 25.30 (26.09). IR (KBr, cm^{-1}): ν(CN) 2085, 2115, 2135; Λ$_M$ (Ω^{-1} cm^2 mol^{-1}, DMF): 5.

**X-ray data collection and structure refinement:** To determine the coordination spheres of compound **1**, X-ray diffra-

ction data of compound **1** were obtained on a Bruker SMART 1000 CCD diffractometer using graphite monochromated MoK radiation (λ = 0.71073 Å) and cell dimensions and diffraction intensities were measured. The-scan technique was used to acquire data in the range of 1.82º25.25º to a maximum of 1.82º25.25º. The programme SAINT [29] was used for data reduction and cell refining. SADABS [29] was used to adjust for absorption. SIR97 [30] was used to solve the structure, while SHELXL-2018/3 [31] was used to refine it. As supplemental material, the final positional and thermal metrics are available. Table-1 provides an overview of the crystallographic data and structure determination parameters for compound **1**. Table-2 lists several bond lengths and angles that are relevant to metal coordination spheres. Table-3 lists the parameters of hydrogen bond interactions.

TABLE-1
CRYSTALLOGRAPHIC DATA FOR COMPOUND **1**

Empirical formula	C$_{12}$H$_{20}$N$_{10}$Cu$_3$Ni
Formula weight	553.70
Crystal system, space group	Monoclinic, *P* 2$_1$/n (No. 14)
Temperature	293(2) K
Wavelength	0.71073 Å
Unit cell dimensions	a = 9.744(5) Å, b = 16.859(10) Å, c = 12.275(7) Å, α = 90.00°, β = 93.522(9)°, γ = 90.00°
Volume	2013(2) Å^3
Z, calculated density	1.801 mg/cm^3
Absorption coefficient	2.475 mm^{-1}
F(000)	1412
Crystal size	0.15 × 0.10 × 0.07 mm^3
θ range	2.04 to 25.24°
Limiting indices	-11<= h <=11, -20<= k <=20, -14<= l <=14
Reflections collected/unique	21000/3642 [R(int) = 0.090]
Data/restraints/parameters	3642/4/177
Goodness-of-fit on F^2	2.197
Final R indices [I > 2σ(I)]	R = 0.1819 and wR = 0.5184
R indices (all data)	R = 0.2015 and wR = 0.5263
Largest peak and hole	0.432 and -1.428

Weighting scheme: R = Σ||F$_o$|–|F$_c$||/Σ|F$_o$|, wR = [Σw(F$_o^2$–F$_c^2$)^2/Σw(F$_o^2$)^2]$^{1/2}$, calcd w = 1/[σ^2(F$_o^2$) + (xP)^2 + yP]; x = 0.2000, y = 0.0000 for **1**, where P = (F$_o^2$ + 2F$_c^2$)/3

RESULTS AND DISCUSSION

Heteropolymer [Cu$_3$Ni(L)$_2$(CN)$_6$]$_n$ (**1**) [L = 2-methylethylenediamine] was prepared by the treatment of Cu(NO$_3$)$_2$·3H$_2$O, L and K$_2$[Ni(CN)$_4$] in 3:2:2 molar ratio in MeCN medium at room temperature. The principle involved is the union of one complementary units *viz.* [Ni(CN)$_4$]$^{2-}$, molecular ions with multi-connectors behaving as potential donors and the [Cu(L)$_2$(OH$_2$)]$^{2-}$, disolvento species [formed in medium by reaction of Cu(NO$_3$)$_2$·3H$_2$O and L] with two labile reaction sites acting as potential acceptors. The displacement of the weakly bound solvent molecules from the solvent complexes in [Cu(L)$_2$(OH$_2$)]$^{2-}$, by the putative cyanide bridging unit in [Ni(CN)$_4$]$^{2-}$ triggers such multi-nuclear heteropolymer formation. Microanalytical (C, H and N), spectroscopic magnetic and physico-chemical results were used to describe compound **1**. They remain powdery or crysta-
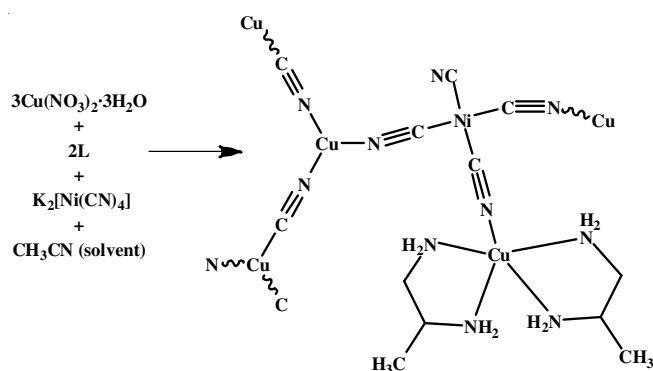
Scheme-I: Synthetic route for compound **1**

TABLE-2
SELECTED BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COMPOUND 1

Bond distances					
Cu1-N1	2.04(2)	Cu3-N6^{iii}	1.970(19)	Ni1-C10	1.85(2)
Cu1-N2	1.97(3)	Cu3-C11	1.94(3)	N5-C7	1.13(3)
Cu1-N3	2.01(2)	Cu3-C12^{iv}	1.903(19)	N6-C8	1.17(3)
Cu1-N4	2.06(2)	Cu3^{i}-N6	1.970(19)	N7-C9	1.12(3)
Cu1-N5	2.34(2)	Cu3^{i}-N12	1.903(19)	N8-C10	1.17(3)
Cu2-N8	1.96(2)	Ni1-C7	1.89(2)	N9-C11	1.08(3)
Cu2-N9	1.94(2)	Ni1-C8	1.86(2)	N10-C12	1.18(3)
Cu2-N10	1.88(2)	Ni1-C9	1.88(2)	–	–
Bond angles					
N1-Cu1-N2	85.3(11)	N8-Cu2-N10	118.2(9)	Cu1-N5-C7	146(2)
N1-Cu1-N3	172.7(9)	N9-Cu2-N10	126.1(9)	Cu2-N8-C10	161(2)
N1-Cu1-N4	96.3(9)	N6^{iii}-Cu3-C11	115.5(10)	Cu2-N9-C11	173(2)
N1-Cu1-N5	91.0(9)	N6^{iii}-Cu3-C12^{iv}	111.6(9)	Cu2-N10-C12	173(2)
N2-Cu1-N3	94.0(13)	C11-Cu3-C12^{iv}	131.1(10)	Cu3^{i}-N6-C8	174(2)
N2-Cu1-N4	171.2(13)	C7-Ni1-C8	89.9(10)	Cu3^{i}-C11-N9	176(3)
N2-Cu1-N5	98.3(13)	C7-Ni1-C9	178.0(9)	Cu3^{i}-C12-N10	168.8(18)
N3-Cu1-N4	83.3(10)	C7-Ni1-C10	91.5(10)	Ni1-C7-N5	173(2)
N3-Cu1-N5	96.3(8)	C8-Ni1-C9	90.6(9)	Ni1-C8-N6	176(2)
N4-Cu1-N5	90.4(9)	C8-Ni1-C10	177.3(10)	Ni1-C9-N7	177(2)
N8-Cu2-N9	113.2(10)	C9-Ni1-C10	87.9(10)	Ni1-C10-N8	177(2)

Symmetry code: (i) 3/2-x, 1/2+y, 3/2-z; (ii) 3/2-x, 1/2+y, 1/2-z; (iii) 3/2-x, -1/2+y, 0.5-z; (iv) 3/2-x, -1/2+y, 3/2-z.

TABLE-3
HYDROGEN BOND INTERACTION PARAMETERS (Å, °) FOR COMPOUND 1

D-H⋯A	D-H	H⋯A	D⋯A	D-H⋯A	Symmetry code
N3-H3A⋯N7	0.9000	2.3600	3.20 (4)	154.00	3/2-x, -1/2+y, 1/2-z

lline for lengthy periods of time and are insoluble in water and other common organic solvents such as heated dimethylformamide (DMF) and dimethylsulfoxide (DMSO). They function as non-electrolytes in dimethylformamide, as evidenced by their poor conductivity value [Λ_M (Ω^{-1} cm^2 mol^{-1}, DMF): 5]. In IR spectra, three well resolved ν(CN) stretching bands at 2085, 2115 and 2135 cm^{-1} in compound 1 are observed indicating the existence of different types of cyanide bridges [32,33] in the crystal lattice.

Crystal structure of [Cu$_3$Ni(L)$_2$(CN)$_6$]$_n$ (1): In order to define the coordination sphere of [Cu$_3$Ni(L)$_2$(CN)$_6$]$_n$ (1), single-crystal X-ray diffraction measurements were made. An ORTEP diagram with atom numbering scheme of asymetric unit, the 2D sheet structure found in the covalently bonded polymer perpendicular to the *a*-axis and perspective view of the hydrogen bonded crystalline architecture of compound 1 are shown in Figs. 1-3, respectively. Selected bond distances and bond angles relevant to the metal coordination spheres are given in Table-2. Hydrogen bond interaction parameters are shown in Table-3. Polymer 1 is an example of heteropolymer. The asymmetric unit of compound 1 contains the two different metal centres [copper(II) and nickel(II)] with varied coordination environments propagated in an alternate fashion bridged by cyanate ion. Each {Cu^1(L)$_2$(μ-NC)} is connected to one {Ni^1(CN)(μ-CN)$_3$}unit through μ-NC, which then bonded to {Cu^2(μ-NC)-Cu^3(μ-NC)} to constitute the heteropolymeric {-Cu^1(L)$_2$-(μ-NC)Ni^1(CN)(μ-CN)$_2$Cu^2(μ-NC)Cu^3(μ-NC)-} chain in one asymmetric unit (Fig. 1). In compound 1, Cu^1 centre adopts a distorted square pyramidal geometry (τ = 0.025)
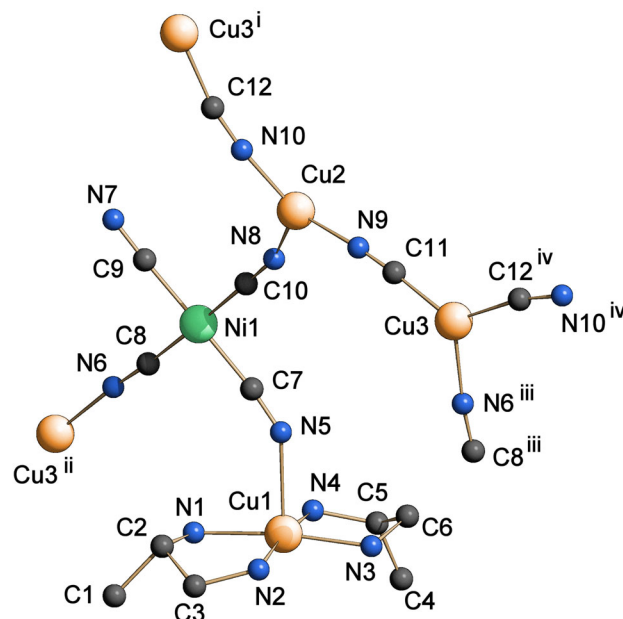

Fig. 1. Perspective view of the asymmetric unit of heteropolymeric compound [Cu$_3$Ni(L)$_2$(CN)$_6$]$_n$ (1) with displacement ellipsoid drawn at the 30% probability level [hydrogen atoms omitted for clarity]. Symmetry codes: (i) 3/2-x, 1/2+y, 3/2-z; (ii) 3/2-x, 1/2+y, 1/2-z; (iii) 3/2-x, -1/2+y, 0.5-z; (iv) 3/2-x, -1/2+y, 3/2-z

with the CuN$_5$ chromophore [34] surrounded by four N atoms (N1, N2, N3, N4) of the two different bidentate amine (L) and one N atom (N5) of μ-NC ion. The equatorial Cu-N distances [1.97(3)-2.06(2) Å] are somewhat shorter than apical Cu-N
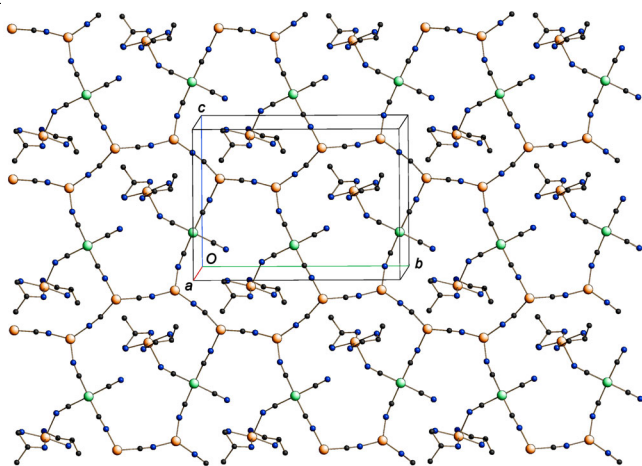
Fig. 2.   Packing diagram of 2D polymeric structure in compound **1** through both ν-CN/ν-NC bridging
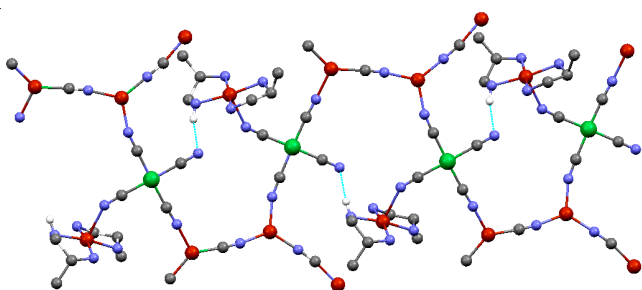

Fig. 3.   A segment of packing diagram of 2D polymeric structure in compound **1** through weak intermolecular N–H···N hydrogen bond along crystallographic *a* axis

distance [2.34(2) Å] (Table-2) around Cu^1. Each Cu^1 center deviates 0.305 Å from the mean plane. While Cu^2 and Cu^3 centres are in same triangular planar environment bearing the CuN_3 and $CuNC_2$ chromospheres connected by three N atoms (N8, N9, N10)/three C atoms (N6^{iii}, C11, C12^{iv}) of bridging cyanate in alternate modes. The Cu-N bond distances and N-Cu-N angles are 1.88(2)-1.96(2) Å and 113.2(10)-126.1(9)° around Cu^2 and the Cu-C and Cu-N bond distances are 1.903(19)-1.94(19) Å and 1.903(19)-1.970(19) Å, C-Cu-C/N angles are 111.6(9)-131.1(10)° around Cu^2 in distorted triangular planar geometry. In $[Ni(CN)_4]^{2-}$ molecular ion (which is incorporated), the geometry around Ni^1 is a distorted square planar with NiC_4 chromophore coordinated by four C atoms (C7, C8, C9, C9) of three μ-CN and one terminal CN ions. The Ni-C bond length are 1.85(2)-1.89(2) Å and C-Ni-C bond angles 87.9(10)-91.5(10)° in *cisoid* and 177.3(10)-178.0(9)° in *transoid* positions. The repeated {-Cu^1(L)$_2$(μ-NC)Ni^1(CN)-(μ-CN)$_2$Cu^2(μ-NC)Cu^3(μ-NC)-} units are interconnected to form a 2D heteropolymer (Fig. 2). The sequence of the arrangement of the atoms in polymeric **1** is {-Cu(1)-N(5)-C(7)-Ni(1)-C(10)-N(8)-Cu(2)-N(9)-C(11)-Cu(3)-}. In the polymeric framework, Cu^1···Ni^1, Cu^2···Ni^1 and Cu^2···Cu^3 separations in adjacent metal centres are 5.074, 4.913 and 4.951 Å, respectively which are smaller than Cu^1···Cu^2 (9.851 Å), Cu^1···Cu^3 (9.099 Å) and Cu^3···Ni^1 (8.200 Å) in non-adjacent metal centes. In the crystal packing of compound **1**, each 2D polymer is engaged in the intermolecular N-H···N hydrogen bonds (N3-H3A···N7: 2.3600

Å, 154.00°) interactions (Table-3) through involvement of H atoms (H3A) of -NH$_2$ group of L as the donor and the N (N7) of terminal cyanate as acceptor affording a supramolecular 2D network structure (Fig. 3).

Magnetic study of [Cu$_3$Ni(L)$_2$(CN)$_6$]$_n$ (1): A superconducting quantum interference device (SQUID) magnetometer was used to measure the magnetic susceptibility of a powdered monocrystalline sample of compound **1** in the temperature range of 2-300 K under a 1000 Oe external magnetic field the plots of χ_M *vs*. T and $1/\chi_M$T *vs*. T for compound **1** is delineated in Fig. 4. Because the eight *d*-electrons in the $[Ni(CN)_4]^{2-}$ unit are all coupled under a square-planar crystal field, Ni^{II} atoms with a d^8 configuration are diamagnetic. The c values increase slowly with the decrease of the temperature and a rapid increase of the molar susceptibility values is observed in the low temperature region without showing any peak. The χ_MT value at 300 K is 0.425 cm^3 mol^{-1} K for compound **1**, which is slightly larger than the expected value of 0.375 cm^3 mol^{-1} K for an uncoupled Cu^{II} ion with g = 2.0. The χ_MT value decreases slowly on cooling until 25 K. After that, the χ_MT value decreases rapidly with lowering temperature to a value of 0.120 cm^3 mol^{-1} K 2 K. The plot of χ *versus* T shows no maximum, thus indicating no long-range ordering. This characteristic feature is an indicative of feeble antiferromagnetic (AF) interactions exhibiting a quasi-Curie law. The fitting of the Curie-Weiss law in the temperature range 50-300 K imparts C = 0.423 cm^3 K mol^{-1} and θ = -6.56 K. The negative θ value signals antiferromagnetically coupled prioritized system. Because of the diamagnetic tetracyanonickellate bridging between the Cu^{II} ions, such magnetic behaviour shows that magnetic interactions exist between and within the chains *via* CN bridges and hydrogen bonds, resulting in weak antiferromagnetic spin coupling.
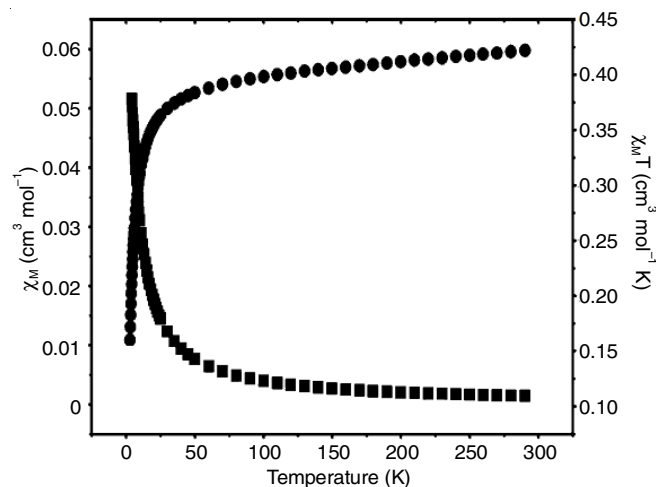

Fig. 4. Thermal dependence of (●) χ_MT and (■) χ_M for compound **1**

Conclusion

One new heterometallic coordination polymer (**1**) of copper(II)-nickel(II) has been synthesized and characterized using X-ray structural analysis. Compound **1** affords a 2D coordination polymer with three copper(II) ion with incorporated $[Ni(CN)_4]^{2-}$ architecture mediated through μ-CN/μ-NC bridging in {-Cu^1(L)$_2$(μ-NC)Ni^1(CN)(μ-CN)$_2$Cu^2(μ-NC)Cu^3(μ-

NC)-} unit resulting a heterometallic polymer. Each 2D polymer is further embedded in intermolecular N-H⋯N hydrogen bonds strengthening a supramolecular 2D network structure. Variable-temperature magnetic susceptibility study revealed a weak antiferromagnetic spin coupling presumably due to the diamagnetic tetracyanonickellate bridging among the Cu^{II} ions. Compound **1** is an ample paradigm of inorganic-organic hybrid polymer.

Supplementary material: Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre No. 2050948 for compound **1**. Copy of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0) 1223-336033; or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. M.J. Zaworotko, *J. Am. Chem. Soc.*, **132**, 7821 (2010); https://doi.org/10.1021/ja103305p
2. B. Moulton and M.J. Zaworotko, *Chem. Rev.*, **101**, 1629 (2001); https://doi.org/10.1021/cr9900432
3. J.S. Miller and M. Drillon, Magnetism: Molecules to Materials V, Wiley-VCH: Weinheim (2006).
4. O.R. Evans and W. Lin, *Acc. Chem. Res.*, **35**, 511 (2002); https://doi.org/10.1021/ar0001012
5. D.T. McQuade, A.E. Pullen and T.M. Swager, *Chem. Rev.*, **100**, 2537 (2000); https://doi.org/10.1021/cr9801014
6. B. Cornils, W.A. Herrmann and R. Schlogl, Catalysis from A to Z: A Concise Encyclopedia, John Wiley & Sons: New York (2000).
7. D. Demus, J.W. Goodby, G.W. Gray, H.-W. Spiess and V. Vill, eds., Handbbook of Liquid Crystals, Wiley-VCH: Weinheim (1998).
8. J.R. Farraro and J.M. Williams, Introduction to Synthetic Electrical Conductors, Academic Press: New York (1987).
9. S.T. Hyde, B. Ninham, S. Anderson, Z. Blum, T. Landh, K. Larsson and S. Liddin, The Language of Shape, Elsevier: Amsterdam (1997).
10. P. Comba and T.W. Hambley, Molecular Modelling of Inorganic and Coordination Compounds, VCH: Weinheim, Ed.: 2 (2001).
11. C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2781 (2003); https://doi.org/10.1039/b305705b
12. O. Almarsson and M.J. Zaworotko, *Chem. Commun.*, 1889 (2004); https://doi.org/10.1039/b402150a
13. H.-B. Yang, K. Ghosh, Y. Zhao, B.H. Northrop, M.M. Lyndon, D.C. Muddiman, H.S. White and P.J. Stang, *J. Am. Chem. Soc.*, **130**, 839 (2008); https://doi.org/10.1021/ja710349j
14. J.R. Sheats and P. Barbara, *Acc. Chem. Res.*, **32**, 191 (1999); https://doi.org/10.1021/ar990033n
15. M. Zbiri, S. Saha, C. Adhikary, S. Chaudhuri, C. Daul and S. Koner, *Inorg. Chim. Acta*, **359**, 1193 (2006); https://doi.org/10.1016/j.ica.2005.09.005
16. P.A. Vigato and S. Tamburini, *Coord. Chem. Rev.*, **252**, 1871 (2008); https://doi.org/10.1016/j.ccr.2007.10.030
17. M.S. El Fallah, E. Rentschler, A. Caneschi, R. Sessoli and D. Gatteschi, *Angew. Chem. Int. Ed. Engl.*, **35**, 1947 (1996); https://doi.org/10.1002/anie.199619471
18. H. Miyasaka, H. Ieda, N. Re, R. Crescenzi and C. Floriani, *Inorg. Chem.*, **37**, 255 (1998); https://doi.org/10.1021/ic9709640
19. M. Ohba, N. Usuki, N. Fukita and H. Okawa, *Inorg. Chem.*, **37**, 3349 (1998); https://doi.org/10.1021/ic9704748
20. T. Lu, H. Xiang, C. Su, P. Cheng, Z. Mao and L. Ji, *New J. Chem.*, **25**, 216 (2001); https://doi.org/10.1039/b007406n
21. R.J. Parker, L. Spiccia, S.R. Batten, J.D. Cashion and G.D. Fallon, *Inorg. Chem.*, **40**, 4696 (2001); https://doi.org/10.1021/ic001452f
22. H. Chowdhury, C. Rizzoli and C. Adhikary, *J. Coord. Chem.*, **74**, 663 (2021); https://doi.org/10.1080/00958972.2020.1861445
23. M. Ohba and H. Okawa, *Coord. Chem. Rev.*, **198**, 313 (2000); https://doi.org/10.1016/S0010-8545(00)00233-2
24. S. Sen, S. Mitra, D.I. Hughes, G. Rosair and C. Desplanches, *Polyhedron*, **261**, 740 (2007); https://doi.org/10.1016/j.poly.2006.12.015
25. C. Adhikary and S. Koner, *Coord. Chem. Rev.*, **254**, 2933 (2010); https://doi.org/10.1016/j.ccr.2010.06.001
26. S. Saha, D. Mal, S. Koner, A. Bhattacherjee, P. Gütlich, S. Mondal, M. Mukherjee and K.-I. Okamoto, *Polyhedron*, **23**, 1811 (2004); https://doi.org/10.1016/j.poly.2004.04.007
27. A. Escuer and G. Aromí, *Eur. J. Inorg. Chem.*, **2006**, 4721 (2006); https://doi.org/10.1002/ejic.200600552
28. E.A. Boudreaux and L.N. Mulay, Theory and Applications of Molecular Paramagnetism, Wiley-Interscience: New York (1976).
29. Bruker APEX2, (Version 2008.1-0), SAINT (Version 7.51A) and SADABS (Version 2007/4) Bruker AXS Inc: Madison, Wisconsin, USA (2008).
30. A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst.*, **32**, 115 (1999); https://doi.org/10.1107/S0021889898007717
31. G.M. Sheldrick, *ActaCryst.*, **C71**, 3 (2015); https://doi.org/10.1107/S2053229614024218
32. E. Colacio, J.M. Dominguez-Vera, F. Lloret, J.M. Moreno Sanchez, R. Kivekas, A. Rodriguez and R. Sillanpaa, *Inorg. Chem.*, **42**, 4209 (2003); https://doi.org/10.1021/ic034155u
33. K. Nakamoto, Infrared and Raman spectra of Inorganic and Coordination Compounds, Part A and B, Ed. 5: Wiley: New York (1997).
34. S.S. Massoud, F.A. Mautner, R. Vicente and H.N. Sweeney, *Inorg. Chim. Acta*, **359**, 1489 (2006); https://doi.org/10.1016/j.ica.2005.10.047