ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2013, Vol. 39, No. 1, pp. 63–67. © Pleiades Publishing, Ltd., 2013.

# Synthesis, Crystal Structure, and Characterizations of a (6,3)-Connected Coordination Polymer Based on Cadmium(II) and Nickel(II)[1]

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Received July 7, 2011

**Abstract**—A novel heteronuclear coordination polymer Cd(1,3-μ-SCN)$_6$Ni$_2$(C$_2$H$_8$N$_2$)$_2$(H$_2$O)$_2$ (**I**) has been prepared and characterized by elemental analysis, EDS analysis, PXRD and IR spectrum and single-crystal X-ray diffraction. The single-crystal X-ray diffraction analysis revealed that compound **I** crystallizes in a monoclinic system of space group *C*2/*m* with $a = 19.427(8)$, $b = 9.622(3)$, $c = 7.261(3)$ Å, $\beta = 105.383(10)°$. The compound exhibits a (6,3)-connected two-dimensional layer which is built up from the strict alternation of 6-connected {CdS$_6$} octahedra and 3-connected {NiON$_5$} octahedra.

**DOI:** 10.1134/S1070328412100107

## INTRODUCTION

The interest in heteronuclear coordination polymers has been steadily growing in recent years due to their fascinating network topologies and potential applications in optical, electric, magnetic, catalytic properties [1–6]. Much effort at present has been devoted to the design and synthesis of Cd-containing heteronuclear coordination polymers because of their unusual topological frameworks and photoluminescent properties [7]. The bridging ligands play important role in the formation of such coordination polymers. The multidentate ligand, SCN$^-$, which may coordinate with metal ions through either S or N atom or both, always link two metal centers through the linkage 1,1-μ-SCN$^-$, 1,1-μ-NCS$^-$ or 1,3-μ-SCN$^-$ to finish the coordination number of the metal ion [8–10]. The flexible coordination behaviors of SCN$^-$ offer greater opportunities for the formation of novel heterometal thiocyanate compounds with new structures and interesting optical properties. Herein, we describe the synthesis, crystal structure, elemental analysis, EDS analysis, PXRD and IR spectrum of the new heteronuclear coordination polymer Cd(1,3-μ-SCN)$_6$Ni$_2$(C$_2$H$_8$N$_2$)$_2$(H$_2$O)$_2$ (**I**), which exhibits a two-dimensional (6,3)-connected network [(4$^3$)$_2$(4$^6$.6$^6$.8$^3$) topology] built up from the strict alternation of 6-connected {CdS$_6$} octahedra and 3-connected {NiON$_5$} octahedra.

## EXPERIMENTAL

**Materials and methods.** All chemicals were obtained from commercial sources and used without further purification. Elemental analyses (C, H, and N) were performed on a PerkinElmer 2400II elemental analyzer. Energy dispersive spectroscopy (EDS) analysis was performed on a FEI-Quanta 200 scanning electron microscope. XRD data of compound **I** were collected on a Bruker D8-advance with Cu$K_\alpha$ radiation ($\lambda = 1.5418$ Å). IR spectra were recorded on a Nicolet 170 FT-IR spectrometer using KBr pellets in a range of 4000–400 cm$^{-1}$.

**Synthesis of I.** A 30 mL methanol solution of NH$_4$SCN (0.15 g, 2 mmol), KCl (0.15 g, 2 mmol) and Cd(NO$_3$)$_2$ · 4H$_2$O (0.31 g, 1 mmol) were mixed. Then 10 mL aqueous solution of Ni(NO$_3$)$_2$ · 6H$_2$O (0.29 g, 1 mmol) and 0.5 mL ethylenediamine (En) were added. After stirring for half an hour, the mixture was filtrated and left for slowly evaporating at room temperature to obtain blue crystals suitable for X-ray structure determination. The yield was 63%.

For C$_{10}$H$_{20}$N$_{10}$O$_2$S$_6$CdNi$_2$

| | | | |
|---|---|---|---|
| anal. calcd., %: | C, 16.35; | H, 2.74; | N, 19.07. |
| Found, %: | C, 16.74; | H, 2.49; | N, 18.92. |

**X-ray crystallography.** Intensity data were collected on a Bruker APEX-II CCD detector at 296(2) K using Mo$K_\alpha$ radiation ($\lambda = 0.71073$ Å) in a range of $2.91° < \theta < 25.00°$ with $-22 \le h \le 23$, $-10 \le k \le 11$, $-8 \le l \le 8$.

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[1] The article is published in the original.

**Table 1.** Crystal data and structure refinement for **I**

| Parameter | Value |
|---|---|
| Formula weight | 734.54 |
| Temperature, K | 296(2) |
| Crystal system | Monoclinic |
| Space group | $C2/m$ |
| $a$, Å | 19.427(8) |
| $b$, Å | 9.622(3) |
| $c$, Å | 7.261(3) |
| β, deg | 105.383(10) |
| $V$, Å$^3$ | 1308.6(8) |
| $Z$ | 2 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.864 |
| μ, mm$^{-1}$ | 2.736 |
| $F$(000) | 732 |
| Scan mode | φ and ω scans |
| Crystal size, mm | 0.25 × 0.23× 0.18 |
| Reflections collected | 3285 |
| Unique data ($R_{int}$) | 1223 (0.0136) |
| Reflections with $I > 2\sigma(I)$ | 1090 |
| Parameters | 93 |
| Goodness-of-fit on $F^2$ | 1.089 |
| $R_1$ ($I > 2\sigma(I)$)* | $R_1 = 0.0333$, $wR_2 = 0.0912$ |
| $\Delta\rho_{min}/\Delta\rho_{max}$, $e$ Å$^{-3}$ | −0.624/1.082 |

* $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$.

The structure was solved by a direct method and refined by full matrix least squares on $F^2$ using the SHELXTL-97 software [11, 12]. All of the non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically. The sulfur site split into two disordered sites in the structure. Considering the disordered sulfur sites of the structure, several attempts have already been made to prepare the compound containing non-disordered sulfur sites, but despite all efforts, they were unsuccessful up to now. A summary of crystal data and structure refinement for compound **I** is provided in Table 1, selected bond lengths and angles of **I** are listed in Table 2. Crystallographic data for structurt have been deposited with the Cambridge Crystallographic Data Centre (no. 833629; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

## RESULTS AND DISCUSSION

The asymmetric unit of compound **I** consists of one octahedral Cd site and one octahedral Ni site. The Cd(II) atom is surrounded by six sulfur atoms from six 1,3-μ-SCN ligands to finish its distorted octahedral coordination geometry with Cd–S bond lengths ranging from 2.6934(19) to 2.755(2) Å (*av*. 2.730 Å). The Ni(II) atom adapts octahedral coordination by one water molecule (O(1*w*)) and five nitrogen atoms from three SCN ligands and one En molecule. The bond lengths of Ni–N and Ni–O(1*w*) are 2.052(4)–2.083(4) and 2.145(5) Å, respectively. These geometric parameters are in good agreement with those previously reported compounds [13]. The molecular structural unit of compound **I** is depicted in Fig. 1. The assignment of the oxidation state for Ni and Cd atoms in compound **I** is confirmed by the bond valence sum calculations [14], by which the valence sum for Cd(1) and Ni(1) is 1.81 and 2.39, respectively. The results indicate that Ni and Cd atoms are in +2 oxidation state.

Compound **I** contains a two-dimensional network which is built up from the strict alternation of 6-connected $\{CdS_6\}$ octahedra and 3-connected $\{NiON_5\}$ octahedra (Fig. 2). Each cadmium(II) center connects with six nickel(II) centers through six 1,3-μ-SCN ligands and each nickel(II) center connects three cadmium(II) centers through three 1,3-μ-SCN ligands, the distance of Cd···Ni is 6.1796(27) and 6.0332(15) Å, respectively, by means of this architecture, a two-dimensional framework comes into being. In other words, connectivity between the polyhedra

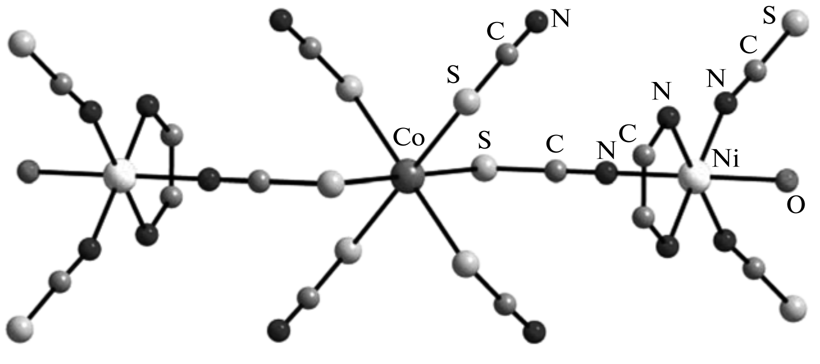

**Fig. 1.** The molecular structural unit of compound **I**.

**Table 2.** Bond lengths (Å) and angles (deg) for compound **I***

| Bond | *d*, Å | Bond | *d*, Å |
|---|---|---|---|
| Cd(1)–S(2)$^{\#1}$ | 2.6934(19) | Ni(1)–N(3)$^{\#2}$ | 2.083(4) |
| Cd(1)–S(2) | 2.6934(19) | Ni(1)–N(3) | 2.083(4) |
| Cd(1)–S(1) | 2.755(2) | Ni(1)–O(1*w*) | 2.145(5) |
| Cd(1)–S(1)$^{\#1}$ | 2.755(2) | N(1)–C(1) | 1.137(7) |
| Cd(1)–S(1)$^{\#2}$ | 2.755(2) | N(2)–C(2) | 1.118(6) |
| Cd(1)–S(1)$^{\#3}$ | 2.755(2) | N(3)–C(3) | 1.432(8) |
| Ni(1)–N(2)$^{\#2}$ | 2.052(4) | C(1)–S(2) | 1.640(6) |
| Ni(1)–N(2) | 2.052(4) | C(2)–S(1)$^{\#4}$ | 1.688(5) |
| Ni(1)–N(1) | 2.062(5) | C(3)–C(3)$^{\#2}$ | 1.317(16) |
| Angle | ω, deg | Angle | ω, deg |
| S(2)$^{\#1}$Cd(1)S(2) | 180.00(5) | N(2)Ni(1)N(1) | 93.10(15) |
| S(2)$^{\#1}$Cd(1)S(1) | 105.08(5) | N(2)$^{\#2}$Ni(1)N(3)$^{\#2}$ | 174.30(16) |
| S(2)Cd(1)S(1) | 74.92(5) | N(2)Ni(1)N(3)$^{\#2}$ | 92.47(17) |
| S(2)$^{\#1}$Cd(1)S(1)$^{\#1}$ | 74.92(5) | N(1)Ni(1)N(3)$^{\#2}$ | 90.48(15) |
| S(2)Cd(1)S(1)$^{\#1}$ | 105.08(5) | N(2)$^{\#2}$Ni(1)N(3) | 92.47(17) |
| S(1)Cd(1)S(1)$^{\#1}$ | 180.00(6) | N(2)Ni(1)N(3) | 174.30(16) |
| S(2)$^{\#1}$Cd(1)S(1)$^{\#2}$ | 105.08(5) | N(1)Ni(1)N(3) | 90.48(16) |
| S(2)Cd(1)S(1)$^{\#2}$ | 74.92(5) | N(3)$^{\#2}$Ni(1)N(3) | 83.1(2) |
| S(1)Cd(1)S(1)$^{\#2}$ | 100.90(10) | N(2)$^{\#2}$Ni(1)O(1*w*) | 87.50(16) |
| S(1)$^{\#1}$Cd(1)S(1)$^{\#2}$ | 79.10(10) | N(2)Ni(1)O(1*w*) | 87.50(16) |
| S(2)$^{\#1}$Cd(1)S(1)$^{\#3}$ | 74.92(5) | N(1)Ni(1)O(1*w*) | 179.1(2) |
| S(2)Cd(1)S(1)$^{\#3}$ | 105.08(5) | N(3)$^{\#2}$Ni(1)O(1*w*) | 88.88(17) |
| S(1)Cd(1)S(1)$^{\#3}$ | 79.10(10) | N(3)Ni(1)O(1*w*) | 88.88(17) |
| S(1)$^{\#1}$Cd(1)S(1)$^{\#3}$ | 100.90(10) | C(1)N(1)Ni(1) | 175.6(5) |
| S(1)$^{\#2}$Cd(1)S(1)$^{\#3}$ | 180.00(8) | C(2)N(2)Ni(1) | 163.5(5) |
| N(2)$^{\#2}$Ni(1)N(2) | 91.8(2) | C(3)N(3)Ni(1) | 108.1(4) |
| N(2)$^{\#2}$Ni(1)N(1) | 93.10(15) | N(1)C(1)S(2) | 177.5(5) |

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x, -y + 1, -z + 1$; $^{\#2}$ $x, -y + 1, z$; $^{\#3}$ $-x, y, -z + 1$; $^{\#4}$ $x - 1/2, y - 1/2, z$; $^{\#5}$ $x + 1/2, y + 1/2, z$.

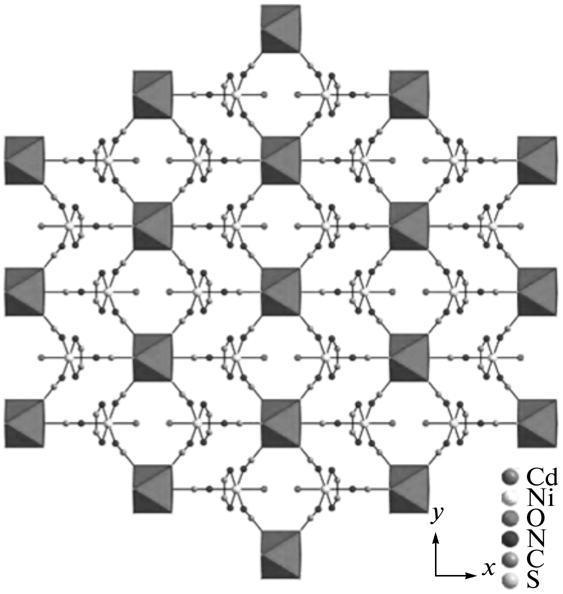

**Fig. 2.** View of the infinite two-dimensional layer containing 4-MRs along the *z* axis.

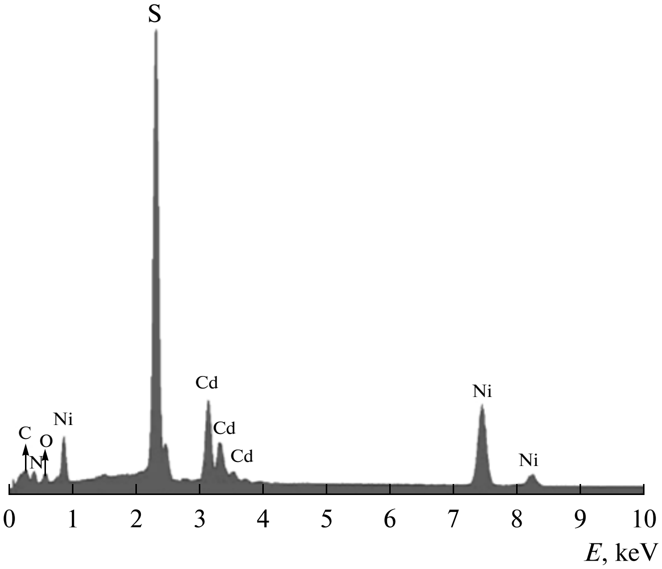

**Fig. 4.** Energy dispersive spectroscopy for **I**.

leads to 4-MRs via –Cd–SCN–Ni–NCS–Cd–SCN–Ni–NCS– (–Cd–Ni–Cd–Ni–) linkages and gives rise to the layer in which 6-connected $\{CdS_6\}$ octahedra strictly alternates with 3-connected $\{NiON_5\}$, as shown in Fig. 2. That is, within the layer, each $\{CdS_6\}$ octahedron is surrounded by six $\{NiON_5\}$ octahedra, whereas each $\{NiON_5\}$ octahedron is connected with three $\{CdS_6\}$ octahedra. To fully understand the structure of compound **I**, we also analyze the topology of layered structure of compound **I** [15]. If Cd and Ni atoms are respectively considered as 6-connected nodes and 3-connected nodes, the layered structure of compound **I** can be described as a (6,3)-connected two-dimensional network with $(4^3)_2(4^6.6^6.8^3)$ topology along the *z* axis (Fig. 3).

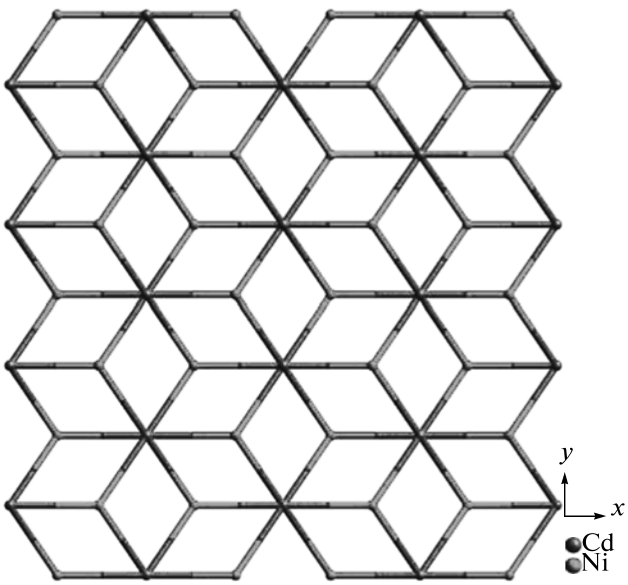

**Fig. 3.** View of the (6,3)-connected layer with $(4^3)_2(4^6.6^6.8^3)$ topology along the *z* axis (C, N, S, O, and H atoms are omitted for clarity).

In the IR spectrum of compound **I**, the vibrations at 2125 and 766 cm$^{-1}$ are attributed to $\nu_{CN}$ and $\nu_{CS}$, respectively. The result is in agreement with the relevant compounds [16, 17]. The vibrations at 3341, 3280, 2950, and 2883 cm$^{-1}$ are assigned to En molecule. Compared with 3400 cm$^{-1}$ assigned to the amine group of free En molecule, the 59 cm$^{-1}$ red-shifted indicates coordination of the En molecule with Ni atoms in the compound **I**. In addition, the peak at 3439 cm$^{-1}$ is assigned to the coordinated water molecule.

EDS for the single crystal of **I** indicated the presence of the elements Cd, Ni, S, O, N and C, as well as gave Cd, Ni and S elements in a molar ratio of 1 : 2.07 : 5.94 (Fig. 4). The EDS result accords with that from single-crystal X-ray structural analysis (Cd : Ni : S = 1 : 2 : 6). The powder XRD pattern is in agreement with the simulated XRD pattern based on single-crystal structural data, proving the phase purity of the as-synthesized product.

## REFERENCES

1. Chen, X.L., Zhang, B., Hu, H.M., et al., *Cryst. Growth Des.,* 2008, vol. 8, p. 3706.
2. Ferey, G., Mellot-Draznieks, C., Serre, C., and Millange, F., *Chem. Res.,* 2005, vol. 38, p. 217.

3. Wang, L.S., Sheng, T.L., Wang, X., et al., *Inorg. Chem.,* 2008, vol. 47, p. 4054.
4. Branzea, D.G., Guerri, A., Fabelo, O., et al., *Cryst. Growth Des.*, 2008, vol. 8, p. 941.
5. Karabach, Y.Y., Kirillov, A.M., Silva, M.F.C.G., et al., *Cryst. Growth Des.*, 2006, vol. 6, p. 2200.
6. Chaudhuri, P., *Coord. Chem. Rev.*, 2003, vol. 243, p. 143.
7. Bose, D., Mostafa, G., Walsh, R.D.B., et al., *Polyhedron*, 2006, vol. 25, p. 1477.
8. Silva, P.B., Frem, R.C.G., Netto, A.V.G., et al., *Inorg. Chem. Commun.*, 2006, vol. 9, p. 235.
9. Li, B.L., Zhu, X., Zhou, J.H., et al., *Polyhedron*, 2004, vol. 23, p. 3133.
10. Rahaman, S.H., Ghosh, R., Mostafa, G., and Ghosh, B.K., *Inorg. Chem. Commun.*, 2005, vol. 8, p. 700.
11. Sheldrick, G.M., *SHELXL-97, Program for Crystal Structure Refinement*, Göttingen (Germany): Univ. of Göttingen, 1997.
12. Sheldrick, G.M., *SHELXL-97, Program for Crystal Structure Solution*, Göttingen (Germany): Univ. of Göttingen, 1997.
13. Kong, D.M., Zhu, L.N., Wang, J., et al., *Inorg. Chim. Acta*, 2009, vol. 362, p. 1109.
14. Brown, I.D. and Altermatt, D., *Acta Crystallogr., B*, 1985, vol. 41, p. 244.
15. Batten, S.R., *CrystEngComm.*, 2001, vol. 18, p. 1.
16. Bala, R., Sarma, R.P., Sharma, R., and Kariuki, B.M., *Inorg. Chem. Commun.*, 2006, vol. 9, p. 852.
17. Nesterova, O.V., Petrusenko, S.P., Kokozay, V.N., and Skelton, B.W. *Inorg. Chem. Commun.*, 2004, vol. 7, p. 450.