

## Synthesis and structural characterization of tris(ethylenediamine)nickel(II) dichromate

B R Srinivasan<sup>a\*</sup>, Ashish R Naik<sup>a</sup>, Christian Näther<sup>b</sup>, Herbert Pausch<sup>b</sup> & Wolfgang Bensch<sup>b</sup>

<sup>a</sup>Department of Chemistry, Goa University, Goa 403 206 India

email:srinigouri@rediffmail.com

<sup>b</sup>Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel, Olshausenstraße 40, D-24098 Kiel, Germany

### Abstract

The reaction of tris(ethylenediamine)nickel(II) dichloride dihydrate with potassium dichromate or potassium chromate results in the formation of mixed metallic compounds tris(ethylenediamine)nickel(II) dichromate  $[\text{Ni}(\text{en})_3][\text{Cr}_2\text{O}_7]$  **1** (en = ethylenediamine) and tris(ethylenediamine)nickel(II) chromate  $[\text{Ni}(\text{en})_3][\text{CrO}_4]$  **2**. Both compounds were characterized by analysis, spectra, magnetic susceptibility and the structure of **1** was determined.  $[\text{Ni}(\text{en})_3][\text{Cr}_2\text{O}_7]$  **1** crystallizes in the centrosymmetric monoclinic space group  $P2_1/c$  and its structure consists of a  $[\text{Ni}(\text{en})_3]^{2+}$  dication and a dichromate dianion, with all atoms situated in general position. Two carbon atoms of one of the coordinated en ligands in **1** and the hydrogen atoms attached to the amine nitrogen in the same en ligand are disordered over two positions. In the crystal structure, tris(ethylenediamine)nickel(II) cations are linked to the  $[\text{Cr}_2\text{O}_7]^{2-}$  anions with the aid of several weak hydrogen bonding interactions resulting in an extended network. The  $\chi$  versus T plots of **1** and **2** reveal simple paramagnetic behavior.

**Keywords:** tris(ethylenediamine)nickel(II); dichromate; chromate; crystal structure; paramagnetic.

## 1. Introduction

Chromates and dichromates whose structures are based on the tetraoxidochromate(VI) tetrahedron [1] constitute an important class of high valent chromium compounds and find application in organic syntheses and material science [2, 3] The acentric nature of the (CrO<sub>4</sub>) tetrahedron has been exploited by the Poeppelmeier group to create new non-centrosymmetric materials [3-5]. The flexibility of the (CrO<sub>4</sub>) tetrahedron to exist in several different structural environments can be evidenced by the structural characterization of dichromates and chromates with a variety of counter cations which include pure inorganic cations [6-26] organic ammonium cations [27-45] and hybrid organic-inorganic complex cations [3-5, 47-50]. In the present study, we have investigated the reactions of potassium dichromate and potassium chromate with tris(ethylenediamine)nickel(II) dichloride dihydrate and have characterized two new Cr(VI) compounds. The results of these investigations are described herein.

## 2. Experimental

### 2.1 Materials and Methods

Doubly distilled water was used as the solvent. All the chemicals used in this study were of reagent grade and were used as received. [Ni(en)<sub>3</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O (en = ethylenediamine) was prepared by a literature procedure [51] The starting materials and reaction products are air stable and hence were routinely prepared under normal laboratory conditions. Infrared (IR) spectra were recorded in a KBr matrix using a Shimadzu (IR Prestige-21) FT-IR spectrometer and a ATI Mattson Genesis infrared spectrometer in the range 4000-400 cm<sup>-1</sup>. The samples for the IR were prepared as KBr diluted pellets in the solid state and the signals referenced to polystyrene bands. Raman

spectra were recorded in the region 100 to 3500  $\text{cm}^{-1}$  on a Bruker FRA 106 Fourier Transform Raman spectrometer. Magnetic susceptibility data were measured using a Faraday balance.

## 2.2 Preparation of $[\text{Ni}(\text{en})_3][\text{Cr}_2\text{O}_7]$ **1** and $[\text{Ni}(\text{en})_3][\text{CrO}_4]$ **2**

$\text{K}_2[\text{Cr}_2\text{O}_7]$  (294 mg, 1 mmol) was dissolved in water (~25 ml) and  $[\text{Ni}(\text{en})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  (345 mg, 1 mmol) in water (~25 ml) was slowly added at room temperature. The clear reaction mixture was kept aside for crystallization. The orange red crystalline blocks which separated were filtered, washed with a little ice cold water (~2 ml) and dried in air to obtain tris(ethylenediamine)nickel(II) dichromate **1** in 60% yield. The product thus obtained was suitable for crystallography. The use of  $\text{K}_2[\text{CrO}_4]$  (194 mg, 1 mmol) instead of  $\text{K}_2[\text{Cr}_2\text{O}_7]$  in the above reaction afforded polycrystalline tris(ethylenediamine)nickel(II) chromate **2** in ~60% yield.

Anal.: Calc. for  $[\text{Ni}(\text{en})_3][\text{Cr}_2\text{O}_7]$  (**1**): C, 15.84; H, 5.32; N, 18.47. Found: C 15.48; H 5.25; N, 17.96 %.

IR data: 3316  $\nu_{\text{N-H}}$ , 3263  $\nu_{\text{N-H}}$ , 2939  $\nu_{\text{C-H}}$ , 2885  $\nu_{\text{C-H}}$ , 2356, 1569, 1466, 1328, 1277, 1108, 1025, 936  $\nu_{\text{Cr-O}}$ , 879  $\nu_{\text{Cr-O}}$ , 749, 677, 635, 544, 523, 485  $\text{cm}^{-1}$ .

Raman data: 3279, 2946, 2890, 1471, 1331, 1278, 1100, 932  $\nu_{\text{Cr-O}}$ , 899  $\nu_{\text{Cr-O}}$ , 880  $\nu_{\text{Cr-O}}$ , 372, 220  $\text{cm}^{-1}$

Anal.: Calc. for  $[\text{Ni}(\text{en})_3][\text{CrO}_4]$  (**2**): C, 20.30; H, 6.81; N, 23.67. Found: C 20.28; H 6.85; N, 23.13 %.

IR Data: 3250  $\nu_{\text{C-H}}$ , 3129  $\nu_{\text{C-H}}$ , 2914  $\nu_{\text{C-H}}$ , 2873  $\nu_{\text{C-H}}$ , 1588, 1451, 1331, 1106, 1035, 880, 861, 694, 530, 501, 411  $\text{cm}^{-1}$ .

1  
2  
3  
4 Raman data: 3151, 2939, 2917, 2876, 1457, 1330, 1272, 1109, 1029, 882  $\nu_{\text{Cr-O}}$ , 859<sup>4</sup>  
5  
6  $\nu_{\text{Cr-O}}$ , 845  $\nu_{\text{Cr-O}}$ , 377, 347, 218, 119  $\text{cm}^{-1}$   
7  
8  
9

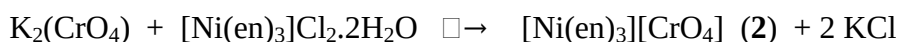
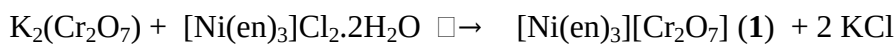
### 10 11 2.3 X-ray crystallography and magnetic susceptibility study 12 13

14  
15 Intensity data for  $[\text{Ni}(\text{en})_3][\text{Cr}_2\text{O}_7]$  **1** were collected on an Image Plate Diffraction  
16 System (IPDS-1) from Stoe using graphite-monochromated  $\text{Mo-K}\alpha$  radiation. A  
17 numerical absorption correction was applied to the collected reflections. The structure  
18 was solved with direct methods using SHELXS-97 [52] and refinement was done  
19 against  $F^2$  using SHELXL-97 [52]. All non-hydrogen atoms were refined using  
20 anisotropic displacement parameters. Both the carbon atoms (C3 and C4) of one of the  
21 unique en molecules coordinated to Ni(II) were disordered over two positions and were  
22 refined using a split model. The hydrogen atoms attached to N3 and N4 are disordered  
23 over two positions. The C-H (0.970 Å) and N-H (0.900 Å) hydrogen atoms were  
24 positioned with idealized geometry and were refined using a riding model. The details  
25 of data acquisition and selected crystal refinement results for **1** are given in Table 1.  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43

44 Variable temperature magnetic susceptibility data were measured using a Faraday  
45 balance using powdered samples of **1** (13.58 mg) or **2** (13.17 mg). The magnetic  
46 property of the sample was then measured from 80 to 320 K in an applied field of 15  
47 KGauss. The susceptibility data were corrected for diamagnetism of the sample holder,  
48 and for the diamagnetism of the constituent ligands and atoms using Pascal's constants.  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

### 3. Results and discussion

The reaction of equimolar solutions of  $K_2[Cr_2O_7]$  or  $K_2[CrO_4]$  with  $[Ni(en)_3]Cl_2 \cdot 2H_2O$  results in cation exchange affording compounds **1** and **2** as shown below:



The more soluble KCl remains in solution and the hybrid inorganic-organic mixed metal dichromate **1** or chromate **2** crystallizes out slowly from the reaction mixture. The synthetic methodology employed here is very similar to the one reported by us earlier for the synthesis of  $(enH_2)[Cr_2O_7]$  and  $(enH_2)[CrO_4]$  ( $enH_2$ ) is ethylenediammonium [40]. The compounds thus prepared analyzed satisfactorily for the proposed formula. Both compounds exhibit sharp signals in their powder pattern indicating their crystalline nature. It is interesting to note that the tris(ethylenediamine)nickel(II) dication has also been used to stabilize other tetrahedral dianions like molybdate, tetrasulfidomolybdate, selenate, antimonate, and other dianionic compounds [53-64] (Table 2). For the synthesis,  $[Ni(en)_3]^{2+}$  was used as the starting material for product formation via cation exchange as in the present work or alternatively the  $[Ni(en)_3]^{2+}$  dication was generated *in situ* under ambient conditions by using a nickel salt and en to stabilize the anion [60-64]. The compounds of  $[Ni(en)_3]^{2+}$  with  $[MoO_4]^{2-}$ ,  $[MoS_4]^{2-}$ ,  $[WS_4]^{2-}$ ,  $[SbS_4]^{3-}$ ,  $[SbSe_4]^{3-}$  and  $[Sn_2Se_6]^{2-}$  counter anions were prepared under solvothermal conditions [53-58].

The IR spectra of both **1** and **2** exhibit several signals in the mid infrared region many of which are also observed in  $[Ni(en)_3]Cl_2 \cdot 2H_2O$ . A comparison of the spectra of **1** and **2** with that of  $[Ni(en)_3]Cl_2 \cdot 2H_2O$  is very useful to identify the vibrations of the

oxidochromate moieties. The strong signals at 3316 and 3263  $\text{cm}^{-1}$  in **1** can be assigned for the N-H stretching vibration  $\nu_{\text{N-H}}$ . For compound **2** the signals at 3250 and 3129  $\text{cm}^{-1}$  are attributed to  $\nu_{\text{N-H}}$ . The signals around 2900  $\text{cm}^{-1}$  in both compounds can be assigned for  $\nu_{\text{C-H}}$  vibrations. The intense signal at 936  $\text{cm}^{-1}$  in **1** originates from the anion and can be assigned for  $\nu_{\text{Cr-O}}$  vibration. It is interesting to note that this signal appears weak in its Raman spectrum, while two intense signals are observed in the Raman in the  $\nu_{\text{Cr-O}}$  region at 899 and 880  $\text{cm}^{-1}$ . In the chromate compound **2**, an intense signal assignable for  $\nu_{\text{Cr-O}}$  is observed at 861  $\text{cm}^{-1}$ . In the Raman spectrum a weak signal at 859  $\text{cm}^{-1}$  and an intense signal at 845  $\text{cm}^{-1}$  is observed.

Compound **1** crystallizes in the centrosymmetric monoclinic space group  $P2_1/c$  and all atoms are located in general positions. The structure of compound **1** consists of an octahedral tris(ethylenediamine)nickel(II) dication and a dichromate dianion (Fig. 1). It is interesting to note that the compounds listed in Table 2 which contain the  $[\text{Ni}(\text{en})_3]^{2+}$  moiety, crystallize in both centrosymmetric as well as non-centrosymmetric space groups. The bond lengths and bond angles for the organic ligand en in **1** are in the normal range (Table 3). The cis N-Ni-N angles of the  $\{\text{NiN}_6\}$  octahedron range from 81.22(9) to 94.09(10) $^\circ$  while the trans N-Ni-N angles scatter in a narrow range between 171.67(9) to 173.34(10) $^\circ$  indicating a distorted octahedron. The distortion is also evident in terms of the Ni-N bond distances which range from 2.112(2) to 2.167(2) Å with a difference  $\Delta$  of 0.055 Å between the longest and the shortest Ni-N bonds. The  $\Delta$  value observed here is slightly longer than that reported recently [65] for a distorted  $\{\text{NiN}_6\}$  octahedron where the N corresponds to a monodentate imidazole.

In the dichromate anion, each Cr(VI) ion adopts tetrahedral geometry and is surrounded by four oxygen atoms with one oxygen (O4) functioning as a common (bridging) ligand for both metals. The O-Cr-O bond angles in one tetrahedron range from 107.26(14) to 111.82(16)<sup>o</sup>, while in the other tetrahedron these values lie between 105.12(17) to 113.1(2)<sup>o</sup>. The terminal Cr-O bond distances range from 1.590(3) to 1.621(3) Å (Table 3). As expected, the bridging oxygen atom (O4) is involved in two significantly longer Cr-O distances at 1.766(2) and 1.794(3) Å respectively. A scrutiny of the structure reveals that the dichromate anions are involved in several N-H...O interactions with the [Ni(en)<sub>3</sub>]<sup>2+</sup> dication. The geometric parameters of these weak interactions are listed in Table 4. As a result of the hydrogen bonding interactions the cations and anions are organized into alternating layers (Fig. 1). In view of the non availability of a suitable crystal for single crystal study of compound 2, its structure could not be determined. Efforts are under way in our laboratories to grow suitable crystals of 2 as well as related new chromates.

The  $\chi$  versus T plot for compound 1 (Fig 2) exhibits no maximum and is typical of a paramagnetic material with  $\chi$  decreasing on increase of T. The effective magnetic moment ( $\mu_{\text{eff}}$ ) remains virtually a constant over the entire temperature range measured indicating no significant exchange interactions. In compound 1 the paramagnetic Ni(II) centers are isolated from each other and the observed nearest nickel to nickel distance in 1 is 7.215 Å. The effective magnetic moment of 3.33 B.M. for 1 indicates orbital contribution for the magnetic moment and this value is in the expected range for Ni(II) compounds. Compound 2 (Fig. 2) exhibits an identical magnetic behavior.

#### 4. Conclusions

In the present study we have described the synthesis, spectral characteristics and magnetic properties of two new Cr(VI) compounds stabilized by tris(ethylenediamine)nickel(II). The structure of one of the new compounds has been determined. Both the compounds exhibit simple paramagnetic behavior. The simple cation exchange reaction described herein is a convenient method to prepare these compounds under ambient conditions.

#### Supplementary Material

CCDC 721290 contains the supplementary crystallographic data for the structure of tris(ethylenediamine)nickel(II) dichromate (**1**) reported in this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre 12 Union Road, Cambridge CB2 1EZ, UK. (fax: (+44) 1223-336-033 or email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

#### Acknowledgements

The authors thank Frau Maren Rasmussen for the magnetic measurements. B.R.S. thanks Indian National Science Academy (INSA) New Delhi, and Deutsche Forschungsgemeinschaft (DFG) for the sanction of a fellowship under the INSA-DFG bilateral exchange program.



## References

- [1] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry* (6<sup>th</sup> Edition) John Wiley & sons, Inc) 751-752.(1999)
- [2] B.S. Furniss, A.J. Hannaford, V. Rogers, P.W.G. Smith, A.R. Tatchell, *Vogel's textbook of practical organic chemistry*, 4<sup>th</sup> Edn (ELBS London) 1978.
- [3] A.J. Norquist, K.R. Heier, P.S. Halasyamani, C.L. Stern, K.R. Poeppelmeier, *Inorg. Chem.*, **40**, 2015-2019 (2001).
- [4] P.A. Maggard, A.L. Kopf, C.L. Stern, K.R. Poeppelmeier, *Acta Crystallogr.*, **C58**, m207-m209 (2002).
- [5] A.L. Kopf, P.A. Maggard, C.L. Stern, K.R. Poeppelmeier, *Acta Crystallogr.*, **C61**, m165-m168 (2005).
- [6] N.C. Panagiotopoulos, I.D. Brown, *Acta Crystallogr.*, **B28**, 2880-2882 (1972).
- [7] D. Blum, M.T. Averbuch-Pouchot, J.C. Guitel, *Acta Crystallogr.*, **B35**, 2685-2687 (1979).
- [8] Y. Gerault, A. Riou, Y. Cudennec, J.Y. Le Marouille, *Acta Crystallogr.*, **C40**, 220-222 (1984).
- [9] S.V. Krivovichev, E.V. Kir'yanova, S.K. Filatov, P.C. Burns, *Acta Crystallogr.*, **C56**, 629-630 (2000).
- [10] T.J.R. Weakley, E.R. Ylvisaker, R.J. Yager, J.E. Stephens, R.D. Wiegel, *Acta Crystallogr* **B60**, 705-715 (2004).
- [11] G. Collotti, L. Conti, M. Zocchi, *Acta Crystallogr.*, **12**, 416 (1959)
- [12] J.S. Stephens, D.W.J. Cruickshank, *Acta Crystallogr.*, **B26**, 437-439 (1970)
- [13] A. Hardy, F. Gaboriaud, *Acta Crystallogr.*, **B28**, 2329-2332 (1972).
- [14] P. Gravereau, A. Hardy, *Acta Crystallogr.*, **B28**, 2333-2337 (1972).
- [15] J.A. McGinnety, *Acta Crystallogr* **B28**, 2845-2852 (1972)
- [16] H. Ruben, I. Olovsson, A. Zalkin, D.H. Templeton, *Acta Crystallogr.* **B29**, 2963-2964 (1973).
- [17] H. Montgomery, *Acta Crystallogr.*, **B35**, 155-156 (1979); *Acta Crystallogr.*, **C40**, 14-15 (1984).
- [18] A. Riou, Y. Gerault, Y. Cudennec, *Acta Crystallogr.*, **B38**, 1693-1696 (1982), *Acta Crystallogr* **C46** 1915-1916 (1990).

- [19] B.M. Casari, V. Langer, *Acta Crystallogr.*, **C56**, e36-e37 (2000).
- [20] U. Kolitsch, *Acta Crystallogr* **E58**, i88-i90 (2002).
- [21] W. Klein, J. Curda, K. Friese, M. Jansen, *Acta Crystallogr.*, **C58**, i23-i24 (2002).
- [22] U. Kolitsch, *Acta Crystallogr.*, **C60**, i17-i19 (2004); *ibid* **C62**, i35-i37 (2006).
- [23] U. Kolitsch, K.Schwendtner, *Acta Crystallogr.*, **C60**, i89-i90 (2004).
- [24] W. Klein, J. Curda, M. Jansen, *Acta Crystallogr.*, **C61**, i63-i64 (2005).
- [25] T.A. Sullens, T.E. Albrecht-Schmitt, *Acta Crystallogr.*, **E62**, i258-i260 (2006).
- [26] J. Leppä-aho, *Acta Crystallogr.*, **C50**, 663-666 (1994).
- [27] M.R. Pressprich, R.D. Willett, R.M. Sheets, W.W. Paudler, G.L. Gard, *Acta Crystallogr.*, **C46**, 1635-1637 (1990).
- [28] M. Jannin, R. Puget, C. de Brauer, R. Perret, *Acta Crystallogr.*, **C49**, 749-751 (1993).
- [29] J. Pecaut, R. Masse, *Acta Crystallogr.*, **B49**, 277-282 (1993).
- [30] P.A. Lorenzo-Luis, P. Martin-Zarza, P. Gili, J.M. Arrieta, G. Germain, L. Dupont, *Acta Crystallogr.*, **C51**, 1073-1075 (1995)..
- [31] T.V. Sundar, V. Parthasarathi, S. Thamocharan, K.G. Sekar, *Acta Crystallogr.*, **E59**, (2003) m327-m329
- [32] Z.-M. Jin, H.-M. Zhang, H.-B. Wang, M.-L. Hu and L. Shen, *Acta Crystallogr* **C60**, m572-m574 (2004).
- [33] Z.-M. Jin, X.-J. Ma, Y. Zhang, B. Tu and M.-L. Hu, *Acta Crystallogr* **E62**, m106-m108 (2006).
- [34] H. Khadhrani, R. Ben Smail, A. Driss, T. Jouini, *Acta Crystallogr.*, **E62**, m146-m148 (2006).
- [35] R. Ben Smail, H. Chebbi, A. Driss, *Acta Crystallogr.*, **E63**, m1859-m1860 (2007).
- [36] L. Sieron, *Acta Crystallogr.*, **E63**, m2068 (2007); *ibid* m2336.
- [37] S. Akriche, M. Rzaigui, *Acta Crystallogr.*, **E65**, m123 (2009).
- [38] K. Ramaiah, P.K. Dubey, J. Ramanathan, C. Ravi Kumar, T.S. Grossert, S. Cameron, *Indian J. Chem.*, **41B**, 2136-2144 (2002).

- [39] B.R. Srinivasan, A.R. Naik, C. Näther, W. Bensch, *Acta Crystallogr.*, **E60**, m1384-m1386 (2004).
- [40] B.R. Srinivasan, S.N. Dhuri, C. Näther, W. Bensch, *Indian J. Chem.*, **42A**, 2735-2741.(2003).
- [41] B.R. Srinivasan, C. Näther, W. Bensch, *Acta Crystallogr.*, **E59**, m639-m641 (2003).
- [42] M. Cygler, M.J. Grabowski, A. Stepien, E. Wajzman, *Acta Crystallogr.*, **B32**, 2391-2395 (1976).
- [43] H. Chebbi, A.A. Hajem, A. Driss, *Acta Crystallogr.*, **C56**, e333-e334 (2000).
- [44] H. Chebbi, A. Driss, *Acta Crystallogr.*, **C57**, 1369-1370 (2001).
- [45] H. Chebbi, A. Driss, *Acta Crystallogr.*, **E58**, m147-m149 (2002); **E58**, m494-m496 (2002); **E60**, m904-m906 (2004).
- [46] F. Dahan, *Acta Crystallogr.*, **B31**, 423-426 (1975).
- [47] L. Pan, N. Zheng, X. Zhou, Y. Wu, Q. Wu, X. Jin, *Acta Crystallogr.*, **C54**, 1802-1804 (1998).
- [48] K. Ejsmont, M. Wasielewski, J. Zaleski, *Acta Crystallogr.*, **E58**, m200-m202 (2002).
- [49] P. Dagur, D. Chopra, A.S. Prakash, T.N. Guru Row, M.S. Hegde, *Acta Crystallogr.*, **E59**, m1129-m1130 (2003).
- [50] W. Bensch, N. Seferiadis, H.R. Oswald, *Inorg. Chim. Acta* **126**, 113-117 (1987).
- [51] H.M. State, *Inorg Synth.*, **6**, 200-202 (1950).
- [52] G.M. Sheldrick, *Acta Crystallogr.*, **64A**, 112-122 (2008).
- [53] B -Z. Lin, G -H, Han, F. Geng, C. Ding, *Acta Crystallogr.*, **E62**, m532-m534 (2006).
- [54] J. Ellermeier, C. Näther, W. Bensch, *Acta Crystallogr.*, **C55**, 501-503 (1999).
- [55] J. Ellermeier, *Ph.D. Dissertation*, University of Kiel 2002.
- [56] M. Schur, W. Bensch, *Acta Crystallogr.*, **C56**, 1107-1108 (2000).
- [57] M -L. Fu, W -T. Chen, L-Z. Cai, G -W. Zhou, G -C. Guo, J -G. Mao, J -S. Huang, *Acta Crystallogr* **E59**, m367-m369 (2003).

- 1  
2  
3  
4 [58] H -B Duan, Z. Hu, B. Jia, Y -L An, *Acta Crystallogr.*, **E62**, m2709-m2710  
5 (2006).  
6  
7  
8 [59] M. Sohail, K.C. Molloy, M. Mazhar, G. Kociok-Köhn, M.K. Khosa, *Acta*  
9 *Crystallogr.*, **E62**, m394-m396 (2006).  
10  
11 [60] A -F. Fu, D.-Q Wang, J -X. Xing, *Acta Crystallogr.*, **E61**, m2115-m2117 (2005).  
12  
13 [61] A.I. Buvaylo, N.M. Dudarenko, I.O. Fritsky, J.S. Kozłowska, *Acta Crystallogr.*,  
14 **C62**, m331-m333 (2006).  
15  
16 [62] L. Shen, M.Z. Jing, *Acta Crystallogr.*, **C58**, m591-m592 (2002).  
17  
18 [63] L -H. Huo, S. Gao, Z -Z. Lu, S -X. Xu, H. Zhao, *Acta Crystallogr* **C58**,  
19 m591-m592 (2002).  
20  
21 [64] L.J. Farrugia, P. Macchi, A. Sironi, *J Appl Cryst* **36**, 141-145 (2003).  
22  
23 [65] B.R. Srinivasan, J.V. Sawant, P. Raghavaiah, *Indian J Chem* **48A** 181-188 (2009).  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

Table 1. Crystal data and structure refinement for [Ni(en)<sub>3</sub>][Cr<sub>2</sub>O<sub>7</sub>] **1**

Empirical formula	C <sub>6</sub> H <sub>24</sub> Cr <sub>2</sub> N <sub>6</sub> NiO <sub>7</sub>
Formula weight	455.02
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
Unit cell dimensions	<i>a</i> = 8.2655(7) Å <i>b</i> = 14.9360(9) Å <i>c</i> = 13.8821(12) Å $\beta$ = 102.005(10)°.
Volume	1676.3(2) Å <sup>3</sup>
<i>Z</i>	4
Density (calculated)	1.795 Mg/m <sup>3</sup>
Absorption coefficient	2.421 mm <sup>-1</sup>
F(000)	932
Crystal size	0.14 x 0.11 x 0.07 mm <sup>3</sup>
Theta range for data collection	2.86 to 28.15°.
Index ranges	-10 ≤ <i>h</i> ≤ 10, -19 ≤ <i>k</i> ≤ 19, -18 ≤ <i>l</i> ≤ 18
Reflections collected	16003
Independent reflections	4035 [R(int) = 0.0380]
Completeness to theta = 28.15°	98.2 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4035 / 0 / 218
Goodness-of-fit on F <sup>2</sup>	1.048
Final R indices [I > 2σ(I)]	R1 = 0.0415, wR2 = 0.1119
R indices (all data)	R1 = 0.0495, wR2 = 0.1195
Extinction coefficient	0.0160(19)
Largest diff. peak and hole	0.810 and -0.724 e.Å <sup>-3</sup>

Table 2. Synthesis of compounds containing  $[\text{Ni}(\text{en})_3]^{2+}$  counter cation

Compound	Synthesis	Space Group	Reference
$[\text{Ni}(\text{en})_3][\text{MoO}_4]$	Solvothermal	$P\bar{1}$	53
$[\text{Ni}(\text{en})_3][\text{MoS}_4]$	Solvothermal	$Pna2_1$	54
$[\text{Ni}(\text{en})_3][\text{WS}_4]$	Solvothermal	$Pna2_1$	55
$[\text{Ni}(\text{en})_3]_2[\text{SbS}_4](\text{NO}_3)$	Solvothermal	$I-42d$	56
$(\text{enH})[\text{Ni}(\text{en})_3][\text{SbSe}_4]$	Solvothermal	$P\bar{1}$	57
$[\text{Ni}(\text{en})_3][\text{Sn}_2\text{Se}_6]$	Solvothermal	$Pbca$	58
$[\text{Ni}(\text{en})_3][\text{CdL}_4]$	Cation exchange	$P3c1$	59
$[\text{Ni}(\text{en})_3][\text{CrO}_4]$	Cation exchange	---	This work
$[\text{Ni}(\text{en})_3][\text{Cr}_2\text{O}_7]$	Cation exchange	$P2_1/c$	This work
$\{[\text{Ni}(\text{en})_3][\text{Cd}(\text{C}_4\text{N}_2\text{S}_2)_2 \cdot \text{H}_2\text{O}]\}_n$	Ambient conditions	$P2_1/n$	60
$[\text{Ni}(\text{en})_3][\text{Ni}(\text{C}_3\text{HN}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}]$	Ambient conditions	$C2/c$	61
$[[\text{Ni}(\text{en})_3][\text{Na}(\text{NCS})_3(\text{H}_2\text{O})]]_n$	Ambient conditions	$P\bar{1}$	62
$[\text{Ni}(\text{en})_3](2,6\text{-nds}) \cdot \text{H}_2\text{O}$	Ambient conditions	$P2_1/n$	63
$[\text{Ni}(\text{en})_3](\text{NO}_3)_2$	Ambient conditions	$P6_322$	64

Abbreviations:  $(\text{C}_4\text{N}_2\text{S}_2) = 1,2\text{-dicyanoethylenedithiolato}$ ;  $(\text{C}_3\text{HN}_3\text{O}_2) = 2\text{-cyano-2-(oxidoimino)acetamidato}$ ;  $(2,6\text{-nds}) = \text{naphthalene-2,6-disulfonate}$

Table 3. Selected bond lengths [Å] and angles [°] for [Ni(en)<sub>3</sub>][Cr<sub>2</sub>O<sub>7</sub>] **1**

Ni(1)-N(4)	2.112(2)	Ni(1)-N(5)	2.132(2)
Ni(1)-N(1)	2.117(2)	Ni(1)-N(2)	2.140(2)
Ni(1)-N(3)	2.132(2)	Ni(1)-N(6)	2.167(2)
N(4)-Ni(1)-N(1)	171.67(09)	N(3)-Ni(1)-N(2)	92.47(10)
N(4)-Ni(1)-N(3)	81.78(10)	N(5)-Ni(1)-N(2)	173.34(10)
N(1)-Ni(1)-N(3)	92.32(09)	N(4)-Ni(1)-N(6)	93.92(10)
N(4)-Ni(1)-N(5)	92.71(09)	N(1)-Ni(1)-N(6)	92.66(10)
N(1)-Ni(1)-N(5)	93.42(09)	N(3)-Ni(1)-N(6)	172.31(10)
N(3)-Ni(1)-N(5)	92.57(10)	N(5)-Ni(1)-N(6)	81.22(9)
N(4)-Ni(1)-N(2)	92.35(09)	N(2)-Ni(1)-N(6)	94.09(10)
N(1)-Ni(1)-N(2)	82.05(10)		
Cr(1)-O(2)	1.603(2)	Cr(2)-O(5)	1.590(3)
Cr(1)-O(3)	1.605(2)	Cr(2)-O(7)	1.592(3)
Cr(1)-O(1)	1.621(3)	Cr(2)-O(6)	1.599(3)
Cr(1)-O(4)	1.766(2)	Cr(2)-O(4)	1.794(3)
O(2)-Cr(1)-O(3)	109.99(15)	O(5)-Cr(2)-O(7)	112.7(2)
O(2)-Cr(1)-O(1)	111.82(16)	O(5)-Cr(2)-O(6)	113.1(2)
O(3)-Cr(1)-O(1)	108.17(14)	O(7)-Cr(2)-O(6)	108.0(2)
O(2)-Cr(1)-O(4)	107.26(14)	O(5)-Cr(2)-O(4)	111.10(14)
O(3)-Cr(1)-O(4)	110.88(15)	O(7)-Cr(2)-O(4)	106.24(18)
O(1)-Cr(1)-O(4)	108.74(16)	O(6)-Cr(2)-O(4)	105.12(17)
N(1)-C(1)	1.466 (4)	C(4)-N(4)	1.485(8)
C(1)-C(2)	1.512 (5)	C(3')-C(4')	1.541(12)
C(2)-N(2)	1.463 (4)	C(4')-N(4)	1.480(9)
N(3)-C(3')	1.461 (7)	N(5)-C(5)	1.465(4)
N(3)-C(3)	1.536 (8)	C(5)-C(6)	1.510(4)
C(3)-C(4)	1.472(11)	C(6)-N(6)	1.464(4)
N(1)-C(1)-C(2)	109.8(2)	N(3)-C(3')-C(4')	105.4(6)
N(2)-C(2)-C(1)	108.7(3)	N(4)-C(4')-C(3')	107.1(5)
C(4)-C(3)-N(3)	109.1(6)	N(5)-C(5)-C(6)	109.5(2)
C(3)-C(4)-N(4)	109.3(6)	N(6)-C(6)-C(5)	109.4(2)

Table 4. Hydrogen-bonding geometry (Å, °) for [Ni(en)<sub>3</sub>][Cr<sub>2</sub>O<sub>7</sub>] **1**

D-H...A	d(H...A)	d(D...A)	<DHA	Symmetry code
N1-H1N1...O2	2.250	3.110	160	x, y, z
N1-H2N1...O1	2.330	3.194	161	-x+1, -y+1, -z+1
N1-H2N1...O3	2.545	3.221	132	-x+1, -y+1, -z+1
N2-H1N2...O6	2.488	3.299	150	-x+2, -y+1, -z+1
N2-H2N2...O4	2.304	3.087	146	-x+2, y+1/2, -z+3/2
N5-H1N5...O1	2.463	3.253	147	-x+1, y+1/2, -z+3/2
N5-H2N5...O3	2.396	3.205	150	-x+1, -y+1, -z+1
N5-H2N5...O5	2.616	3.147	119	-x+1, -y+1, -z+1
N6-H1N6...O2	2.381	3.239	159	x, y, z
N6-H2N6...O7	2.519	3.329	150	-x+2, y+1/2, -z+3/2
N6-H2N6...O6	2.594	3.382	147	-x+2, y+1/2, -z+3/2
N3-H1N3...O6	2.241	2.996	141	-x+2, -y+1, -z+1
N3-H2N3...O5	2.269	3.144	164	-x+1, -y+1, -z+1
N3-H3N3...O6	2.097	2.996	177	-x+2, -y+1, -z+1
N3-H4N3...O5	2.520	3.144	127	-x+1, -y+1, -z+1
N3-H4N3...O1	2.538	3.302	143	-x+1, -y+1, -z+1
N4-H1N4...O1	2.253	2.991	139	-x+1, y+1/2, -z+3/2
N4-H2N4...O4	2.224	3.103	165	-x+2, y+1/2, -z+3/2
N4-H3N4...O1	2.092	2.991	177	-x+1, y+1/2, -z+3/2
N4-H4N4...O4	2.311	3.103	147	-x+2, y+1/2, -z+3/2
N4-H4N4...O6	2.540	3.307	143	-x+2, y+1/2, -z+3/2



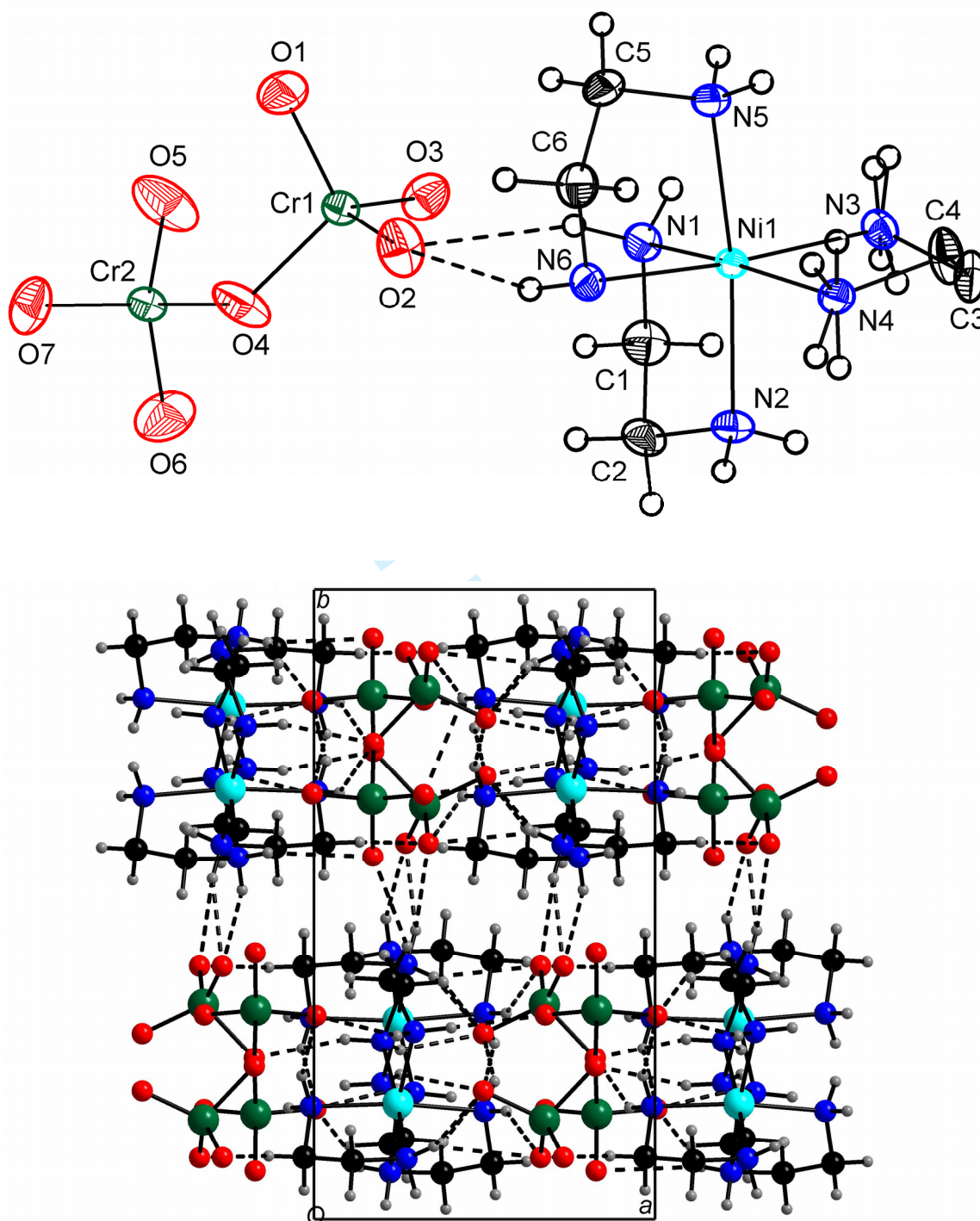


Fig. 1. Crystal structure of  $[\text{Ni}(\text{en})_3][\text{Cr}_2\text{O}_7]$  **1** showing the atom-labeling scheme. The carbon atoms C3 and C4 and the hydrogen atoms attached to N3 and N4 are disordered over two positions. For clarity, the disordered carbon atoms C3' and C4' are not shown. Displacement ellipsoids are drawn at the 30% probability level except for the H atoms, which are shown as circles of arbitrary radius (top). A view of the crystallographic packing of **1** along *c* axis (bottom). H-bonds are shown as broken lines.

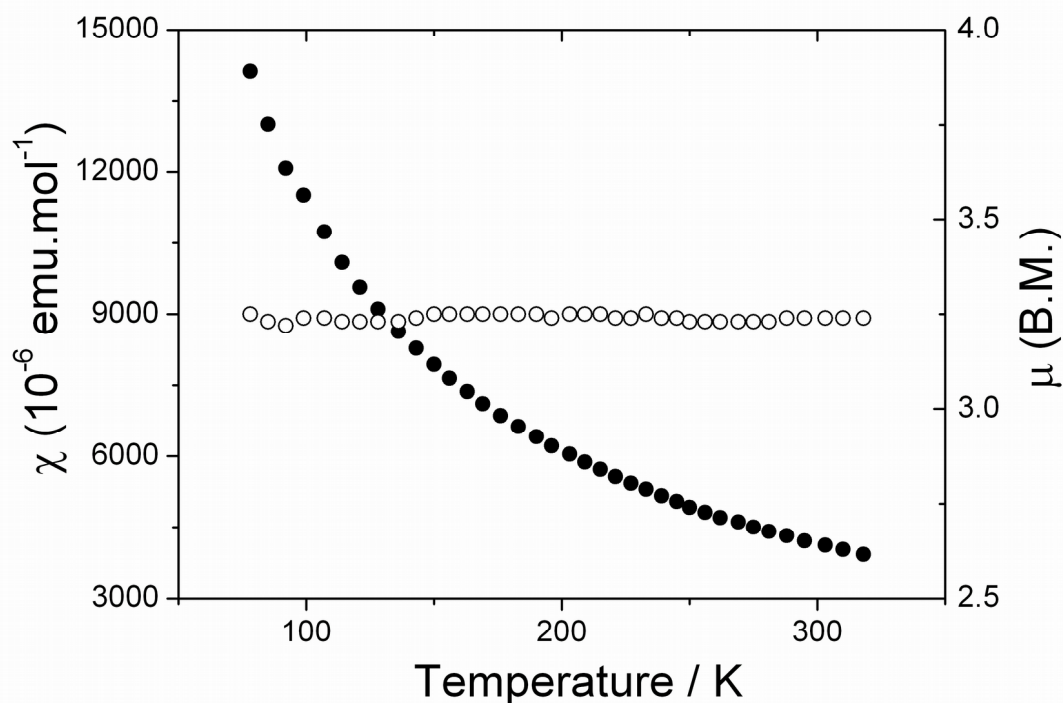
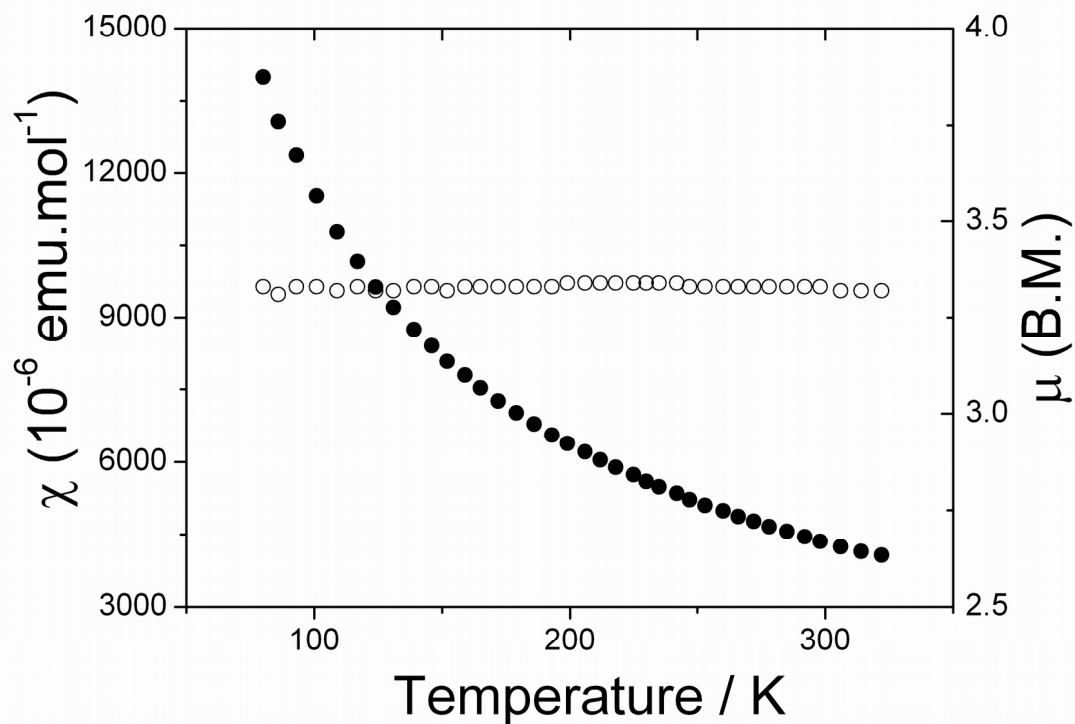


Fig. 2  $\chi$  versus T plot (solid circle) and  $\mu_{\text{eff}}$  versus T plot (open circles) for  $[\text{Ni}(\text{en})_3][\text{Cr}_2\text{O}_7]$  **1** (top) and  $[\text{Ni}(\text{en})_3][\text{CrO}_4]$  **2** (bottom)

## Supplementary Figures on structure for Review purpose

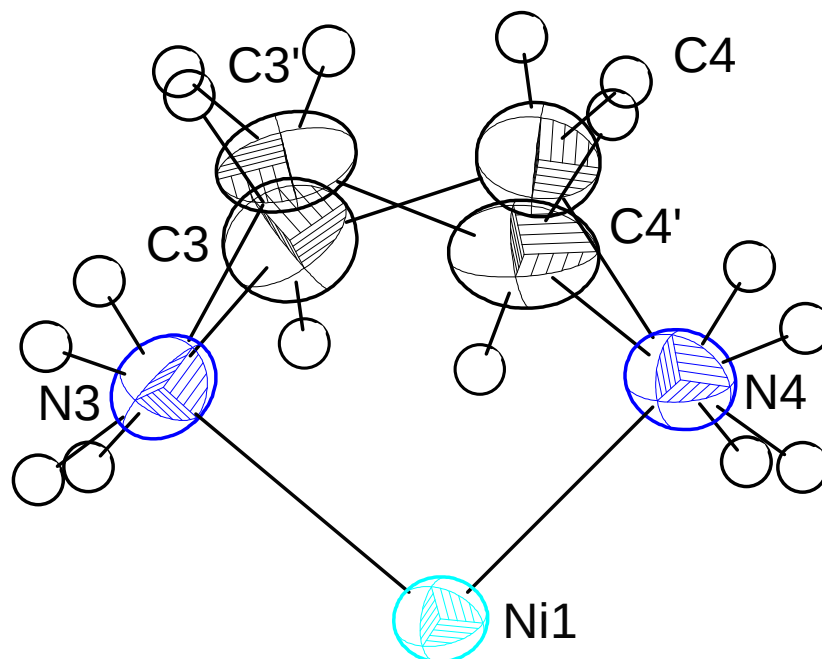


Figure S1 The disordered en ligand in  $[\text{Ni}(\text{en})_3][\text{Cr}_2\text{O}_7]$  **1**. The C3 and C4 atoms as well as the H atoms attached to N3 and N4 are disordered over to positions.

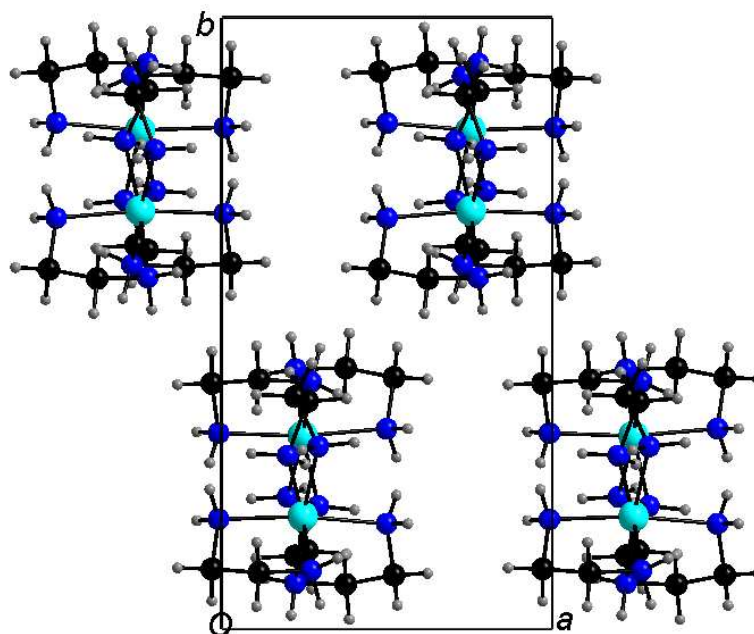


Figure S2A view of the crystallographic packing showing only the  $[\text{Ni}(\text{en})_3]^{2+}$  dications of **1**.

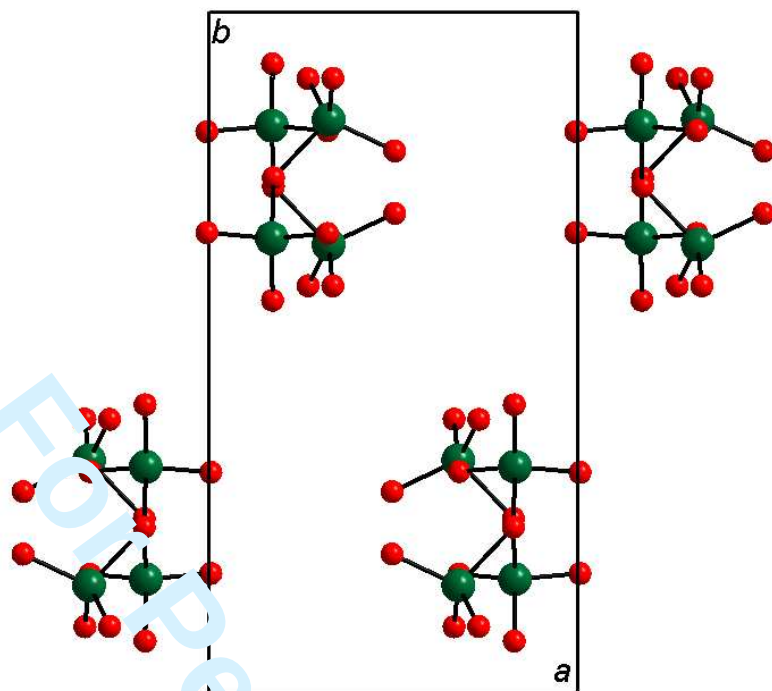


Figure. S3 A view of the packing of **1** showing only the  $[\text{Cr}_2\text{O}_7]^{2-}$  anions.

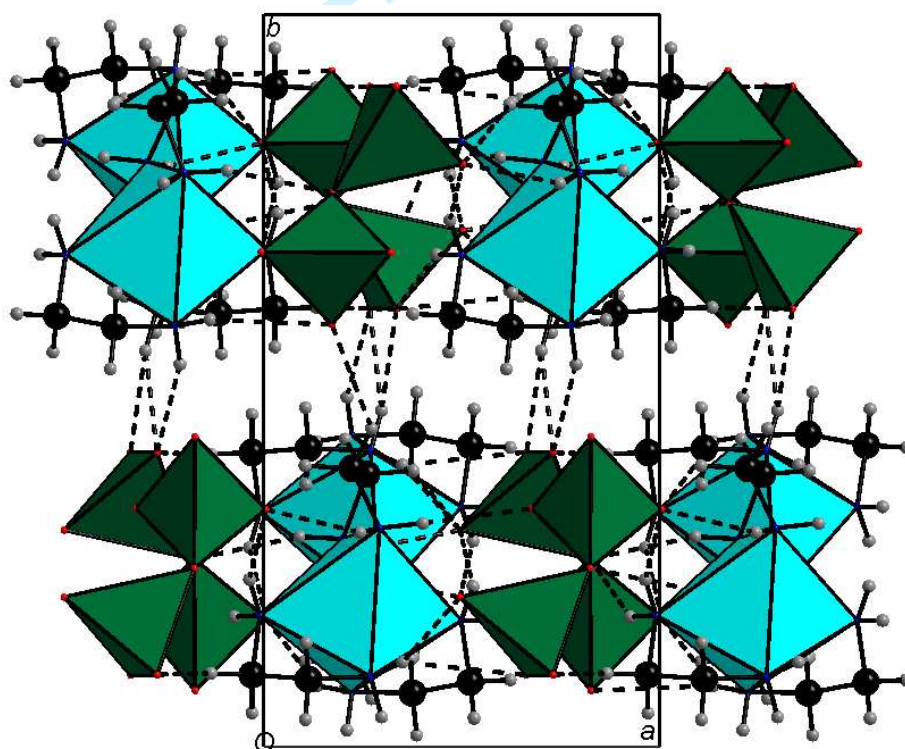


Figure S4 A view of the crystallographic packing of **1** showing the cations (cyan) and anions (green) as polyhedra. H-bonds are shown as broken lines.

Supplementary Table 1. Variable temperature magnetic data

Temperature K	$\chi_M(\text{corr}) \times 10^6$ (emu mol <sup>-1</sup> )	$1/\chi_M$ (mol.cm <sup>-3</sup> )	$\mu_{\text{effective}}$ (B.M.)
<b>[Ni(en)<sub>3</sub>][Cr<sub>2</sub>O<sub>7</sub>] 1</b>			
322	4065.37	245.98	3.32
314	4141.87	241.437	3.32
306	4237.5	235.988	3.32
298	4352.25	229.766	3.33
292	4447.88	224.826	3.33
285	4562.63	219.172	3.33
278	4658.26	214.672	3.33
272	4773.01	209.511	3.33
266	4868.64	205.396	3.33
260	4983.39	200.667	3.33
253	5098.14	196.15	3.33
247	5212.89	191.832	3.33
242	5346.77	187.029	3.34
235	5480.65	182.46	3.34
230	5595.4	178.718	3.34
225	5729.28	174.542	3.34
218	5882.28	170.002	3.34
212	6035.28	165.692	3.34
206	6207.41	161.098	3.34
199	6379.54	156.751	3.34
193	6551.67	152.633	3.33
186	6781.17	147.467	3.33
179	7010.68	142.64	3.33
172	7259.31	137.754	3.33
165	7527.06	132.854	3.33
159	7794.82	128.29	3.33
152	8081.7	123.736	3.32
146	8406.83	118.951	3.33
139	8751.08	114.272	3.33
131	9210.09	108.577	3.32
124	9630.849	103.833	3.32
117	10166.36	98.364	3.33
109	10778.37	92.778	3.32
101	11524.26	86.774	3.33
93	12365.77	80.868	3.33
86	13073.41	76.491	3.31
80	13991.43	71.472	3.33
<b>[Ni(en)<sub>3</sub>][CrO<sub>4</sub>] 2</b>			
318	3921.17	255.026	3.24
310	4028.88	248.208	3.24
303	4121.2	242.648	3.24
295	4213.52	237.331	3.23
288	4321.23	231.416	3.24

1				
2				
3				
4	281	4413.55	226.575	3.23
5	275	4505.87	221.933	3.23
6	269	4613.58	216.752	3.24
7	262	4705.9	212.499	3.23
8	256	4813.61	207.744	3.23
9	250	4921.31	203.198	3.23
10	245	5044.41	198.239	3.24
11	239	5167.5	193.517	3.24
12	233	5305.98	188.467	3.25
13	227	5429.08	184.193	3.24
14	221	5567.56	179.612	3.24
15	215	5721.43	174.782	3.25
16	209	5875.29	170.204	3.25
17	203	6044.55	165.438	3.25
18	196	6213.8	160.932	3.24
19	190	6413.83	155.913	3.25
20	183	6629.25	150.847	3.24
21	176	6860.05	145.772	3.24
22	169	7106.24	140.721	3.24
23	163	7367.81	135.725	3.24
24	156	7644.78	130.808	3.24
25	150	7937.13	125.99	3.24
26	143	8275.63	120.837	3.24
27	136	8629.53	115.881	3.23
28	128	9106.519	109.811	3.23
29	121	9568.13	104.514	3.23
30	114	10091.28	99.096	3.23
31	107	10737.52	93.13099	3.24
32	99	11506.86	86.905	3.24
33	92	12076.17	82.808	3.22
34	85	13014.77	76.836	3.23
35	78	14122.62	70.808	3.25
36				
37				
38				
39				
40				
41				
42				
43				
44				
45				
46				
47				
48				
49				
50				
51				
52				
53				
54				
55				
56				
57				
58				
59				
60				