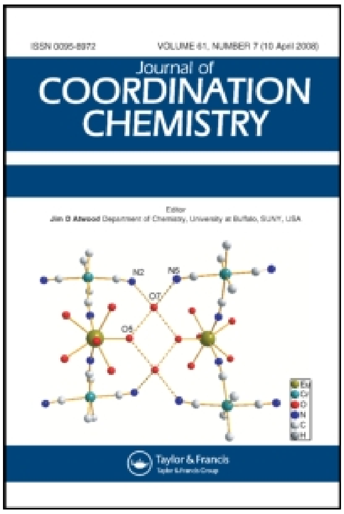

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Synthesis and structural characterization of *tris*(ethylenediamine)nickel(II) dichromate

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

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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 $[Ni(en)_3][Cr_2O_7]$ (**1**) (en = ethylenediamine) and *tris*(ethylenediamine)nickel(II) chromate $[Ni(en)_3][CrO_4]$ (**2**). Both compounds were characterized by analysis, spectra, magnetic susceptibility, and the structure of **1** was determined. $[Ni(en)_3][Cr_2O_7]$ (**1**) crystallizes in the centrosymmetric monoclinic space group *P2(1)/c* and its structure consists of a $[Ni(en)_3]^{2+}$ dication and a dichromate dianion, with all the atoms situated in a general position. Two carbons of one coordinated (en) in **1** and the hydrogens attached to the amine nitrogen in the same ligand are disordered over two positions. In the crystal structure, *tris*(ethylenediamine)nickel(II) cations are linked to the $[Cr_2O_7]^{2-}$ anions with several weak hydrogen bonding interactions resulting in an extended network. The χ *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 tetraoxidochromate(VI) tetrahedra, [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_4 tetrahedron has been exploited by the Poeppelmeier group to create new non-centrosymmetric materials [3–5]. The flexibility of CrO_4 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, 46–49]. In the present study, we have investigated the reactions of potassium dichromate and potassium chromate with *tris*(ethylenediamine)nickel(II) dichloride dihydrate and characterized two new Cr(VI) compounds.

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2. Experimental

2.1. *Materials and methods*

Doubly-distilled water was used as a solvent. All chemicals used in this study were of reagent grade and were used as received. $[Ni(en)_3]Cl_2 \cdot 2H_2O$ (en = ethylenediamine) was prepared by a literature procedure [50]. The starting materials and reaction products are air-stable and hence were prepared under normal laboratory conditions. Infrared (IR) spectra were recorded using Shimadzu (IR Prestige-21) FT-IR and ATI Mattson Genesis infrared spectrometers in the range 4000–400 cm^{-1}. Samples for the IR were prepared as KBr diluted pellets in the solid state and the signals were referenced to polystyrene bands. Raman spectra were recorded in the region 100–3500 cm^{-1} on a Bruker FRA 106 Fourier Transform Raman spectrometer. Magnetic susceptibility data were measured using a Faraday balance.

2.2. *Preparation of $[Ni(en)_3][Cr_2O_7]$ (1) and $[Ni(en)_3][CrO_4]$ (2)*

$K_2[Cr_2O_7]$ (294 mg, 1 mmol) was dissolved in water (~25 mL) and $[Ni(en)_3]Cl_2 \cdot 2H_2O$ (345 mg, 1 mmol) in water (~25 mL) was slowly added at room temperature. The clear reaction mixture was set aside for crystallization; 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 $K_2[CrO_4]$ (194 mg, 1 mmol) instead of $K_2[Cr_2O_7]$ in the above reaction yielded polycrystalline *tris*(ethylenediamine) nickel(II) chromate **2** in ~60% yield.

Anal. Calcd for $[Ni(en)_3][Cr_2O_7]$ (**1**) (%): C, 15.84; H, 5.32; N, 18.47. Found: C, 15.48; H, 5.25; N, 17.96%.

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

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

Anal. Calcd for $[Ni(en)_3][CrO_4]$ (**2**) (%): C, 20.30; H, 6.81; N, 23.67. Found: C, 20.28; H, 6.85; N, 23.13%.

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

Raman data: 3151, 2939, 2917, 2876, 1457, 1330, 1272, 1109, 1029, 882 $\nu_{Cr–O}$, 859 $\nu_{Cr–O}$, 845 $\nu_{Cr–O}$, 377, 347, 218, 119 cm^{-1}.

2.3. *X-ray crystallography and magnetic susceptibility*

Intensity data for $[Ni(en)_3][Cr_2O_7]$ (**1**) were collected on an Image Plate Diffraction System (IPDS-1) from Stoe using graphite-monochromated Mo-Kα radiation. A numerical absorption correction was applied to the collected reflections. The structure was solved with direct methods using SHELXS-97 [51] and refinement was done

Table 1. Crystal data and structure refinement for $[Ni(en)_3][Cr_2O_7]$.

Empirical formula	$C_6H_{24}Cr_2N_6NiO_7$
Formula weight	455.02
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*P2(1)/c*
Unit cell dimensions (Å, °)	
a	8.2655(7)
b	14.9360(9)
c	13.8821(12)
β	102.005(10)
Volume (Å^3), Z	1676.3(2), 4
Calculated density (mg m^{-3})	1.795
Absorption coefficient (mm^{-1})	2.421
$F(000)$	932
Crystal size (mm^3)	$0.14 \times 0.11 \times 0.07$
θ range for data collection (°)	2.86–28.15
Limiting indices	$-10 \leq h \leq 10$, $-19 \leq k \leq 19$, $-18 \leq l \leq 18$
Reflections collected	16,003
Independent reflection	4035 [R(int) = 0.0380]
Completeness to $\theta = 28.15°$	98.2%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4035/0/218
Goodness-of-fit on F^2	1.048
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0415$, $wR_2 = 0.1119$
R indices (all data)	$R_1 = 0.0495$, $wR_2 = 0.1195$
Extinction coefficient	0.0160(19)
Largest difference peak and hole (e Å^{-3})	0.810 and −0.724

against F^2 using SHELXL-97 [51]. All non-hydrogen atoms were refined using anisotropic displacement parameters. Both the carbons (C3 and C4) of one unique (en) coordinated to Ni(II) were disordered over two positions and refined using a split model. The hydrogens attached to N3 and N4 are disordered over two positions. The C–H (0.970 Å) and N–H (0.900 Å) hydrogens were positioned with idealized geometry and refined using a riding model. Details of data acquisition and selected crystal refinement results for **1** are given in table 1.

Variable temperature magnetic susceptibility data were measured using a Faraday balance (Bruker BSU45 – System Kiel) using powdered samples of **1** (13.58 mg) or **2** (13.17 mg) in a quartz sample container. The magnetic property of the sample was then measured from 80 to 320 K in an applied field of 15 kGauss. The susceptibility data were corrected for the diamagnetism of the sample holder, and for the diamagnetism of the constituent ligands and atoms using Pascal's constants.

3. Results and discussion

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 yielding **1** and **2** as shown below:

$$K_2(Cr_2O_7) + [Ni(en)_3]Cl_2 \cdot 2H_2O \longrightarrow [Ni(en)_3][Cr_2O_7](1) + 2KCl$$

$$K_2(CrO_4) + [Ni(en)_3]Cl_2 \cdot 2H_2O \longrightarrow [Ni(en)_3][CrO_4](2) + 2KCl$$

Table 2. Compounds containing $[Ni(en)_3]^{2+}$.

Compound	Synthesis	Space group	Reference
$[Ni(en)_3][MoO_4]$	Solvothermal	$P\bar{3}cl$	[52]
$[Ni(en)_3][MoS_4]$	Solvothermal	$Pna2_1$	[53]
$[Ni(en)_3][WS_4]$	Solvothermal	$Pna2_1$	[54]
$[Ni(en)_3]_2[SbS_4](NO_3)$	Solvothermal	$I\text{-}42d$	[55]
$(enH)[Ni(en)_3][SbSe_4]$	Solvothermal	$P\bar{1}$	[56]
$[Ni(en)_3][Sn_2Se_6]$	Solvothermal	$Pbca$	[57]
$[Ni(en)_3][CdI_4]$	Cation exchange	$P3c1$	[58]
$[Ni(en)_3][CrO_4]$	Cation exchange	–	This work
$[Ni(en)_3][Cr_2O_7]$	Cation exchange	$P2(1)/c$	This work
$\{[Ni(en)_3][Cd(C_4N_2S_2)_2] \cdot H_2O\}_n$	Ambient conditions	$P2(1)/n$	[59]
$[Ni(en)_3][Ni(C_3HN_3O_2)_2] \cdot H_2O$	Ambient conditions	$C2/c$	[60]
$[[Ni(en)_3][Na(NCS)_3(H_2O)]]_n$	Ambient conditions	$P\bar{3}cl$	[61]
$[Ni(en)_3](2,6\text{-nds}) \cdot H_2O$	Ambient conditions	$P2(1)/n$	[62]
$[Ni(en)_3](NO_3)_2$	Ambient conditions	$P6_322$	[63]
$[Ni(en)_3]_n[\{Ni(en)_2(NCS)Cr(NCS)_5\}_{2n}]$	Ambient conditions	$C2/c$	[64]

Abbreviations: $(C_4N_2S_2)$ = 1,2-dicyanoethylenedithiolato; $(C_3HN_3O_2)$ = 2-cyano-2-(oxidoimino)acetamidato]; (2,6-nds) = naphthalene-2,6-disulfonate.

The more soluble KCl remains in solution and **1** or **2** crystallizes 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 = ethylenediammonium) [40]. The compounds thus prepared are analyzed satisfactorily for the proposed formula. Both compounds exhibit sharp signals in their powder pattern indicating their crystalline nature. The *tris*(ethylenediamine)nickel(II) dication has been used to stabilize other tetrahedral dianions like molybdate, tetrasulfidomolybdate, selenate, antimonate, and other dianionic compounds [52–64] (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 [59–64]. 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 [52–57].

IR spectra of **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 cm^{-1} in **1** can be assigned for $\nu_{N–H}$; in **2**, signals at 3250 and 3129 cm^{-1} are attributed to $\nu_{N–H}$. Signals around 2900 cm^{-1} in both compounds are assigned to $\nu_{C–H}$. The intense signal at 936 cm^{-1} in **1** originates from the anion and can be assigned as $\nu_{Cr–O}$. This signal appears weak in its Raman spectrum, while two intense signals are observed in the Raman in the $\nu_{Cr–O}$ region at 899 and 880 cm^{-1}. In **2**, an intense signal for $\nu_{Cr–O}$ is observed at 861 cm^{-1}. In the Raman spectrum, a weak signal at 859 cm^{-1} and an intense signal at 845 cm^{-1} are observed.

Compound **1** crystallizes in the centrosymmetric monoclinic space group $P2(1)/c$ and all atoms are located in general positions. The structure of **1** consists of an octahedral *tris*(ethylenediamine)nickel(II) dication and a dichromate dianion (figure 1). Compounds listed in table 2, which contain the $[Ni(en)_3]^{2+}$ moiety, crystallize in both

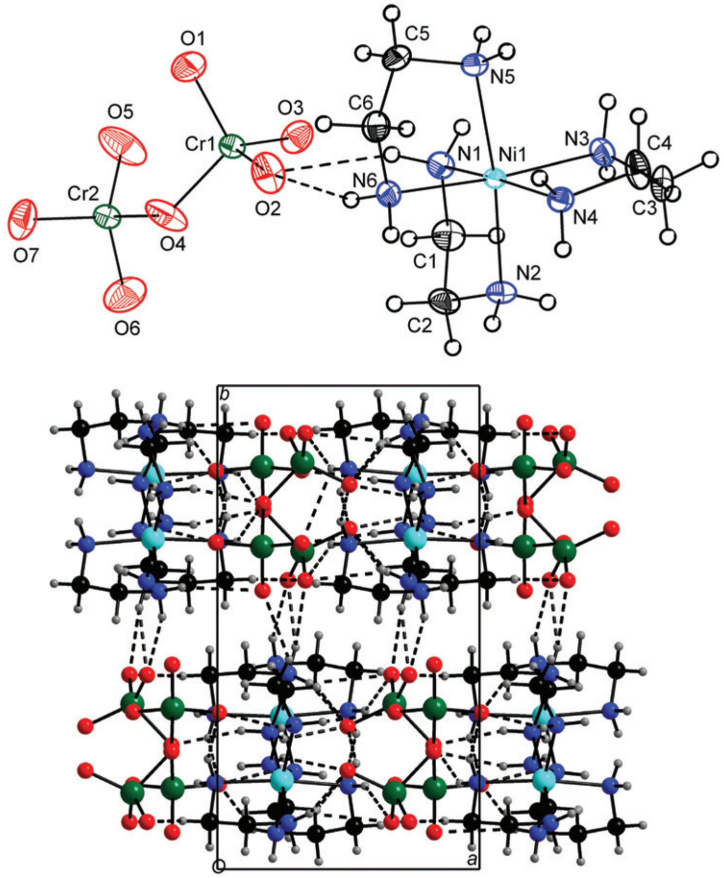

Figure 1. Crystal structure of **1** showing the atom-labeling scheme. The carbon atoms C3 and C4 and the hydrogen atoms attached to N3 and N4 are disordered over two positions (Supplementary material). Displacement ellipsoids are drawn at the 30% probability level except for the H atoms, which are shown as circles of arbitrary radius (top). A view of the crystallographic packing of **1** along the *c*-axis (bottom). H-bonds are shown as broken lines. Color code: Ni, Cyan; C, black; H, medium grey; N, blue; Cr, green; O, red.

centrosymmetric as well as non-centrosymmetric space groups. The bond lengths and angles for (en) in **1** are in the normal range (table 3). The *cis* N–Ni–N angles of the $\{NiN_6\}$ octahedron range from 81.22(9)° to 94.09(10)° while the *trans* N–Ni–N angles scatter in a narrow range between 171.67(9)° and 173.34(10)°, 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 Δ of 0.055 Å between the longest and the shortest Ni–N bonds. The Δ value observed here is slightly longer than that reported recently [65] for a distorted $\{NiN_6\}$ octahedron where N corresponds to a monodentate imidazole.

In dichromate, each Cr(VI) is tetrahedral surrounded by four oxygens, with one oxygen (O4) functioning as a bridging ligand. The O–Cr–O bond angles in one tetrahedron range from 107.26(14)° to 111.82(16)°, while in the other values lie between 105.12(17)° and 113.1(2)°. 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

Table 3. Selected bond lengths [Å] and angles [°] for **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)

Table 4. Hydrogen-bonding geometry (Å, °) for **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	$-x+2, y+1/2, -z+3/2$

significantly longer Cr–O distances at 1.766(2) and 1.794(3) Å. Dichromate anions are involved in several N–H···O interactions with $[\mathrm{Ni(en)_3}]^{2+}$. 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 (figure 1). The non-availability of a suitable crystal for single crystal study of **2** prohibited its structure determination.

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

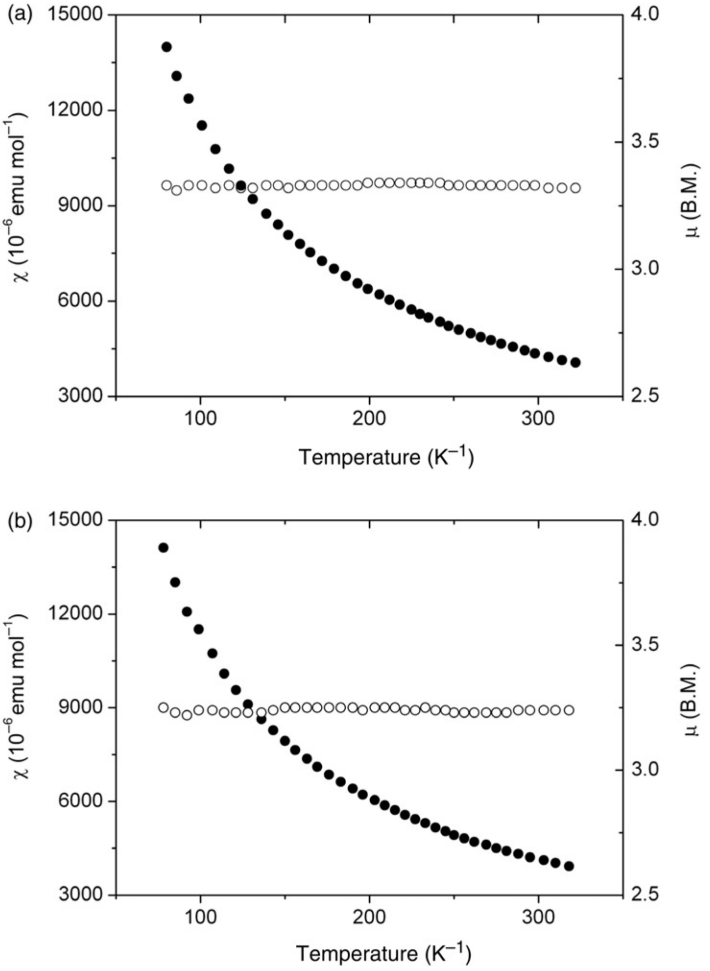

Figure 2. χ *vs*. T plot (solid circle) and μ *vs*. T plot (open circles) for $[Ni(en)_3][Cr_2O_7]$ **1** (a) and $[Ni(en)_3][CrO_4]$ **2** (b).

4. Conclusions

We have described the synthesis, spectral characteristics, and magnetic properties of two new Cr(VI) compounds that are 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 here 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 article. 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].

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