

Poly[nickel(II)-di- μ -4,4'-bipyridyl- $\kappa^4 N:N'$ - μ -dichromato- $\kappa^2 O:O'$] and poly[copper(II)-di- μ -4,4'-bipyridyl- $\kappa^4 N:N'$ - μ -dichromato- $\kappa^2 O:O'$]

Amy L. Kopf,^a Paul A. Maggard,^b Charlotte L. Stern^a and Kenneth R. Poeppelmeier^{a*}

^aDepartment of Chemistry, Northwestern University, Evanston, IL 60208, USA, and

^bDepartment of Chemistry, North Carolina State University, Raleigh, NC 27695, USA

Correspondence e-mail: krp@northwestern.edu

Received 11 October 2004

Accepted 17 January 2005

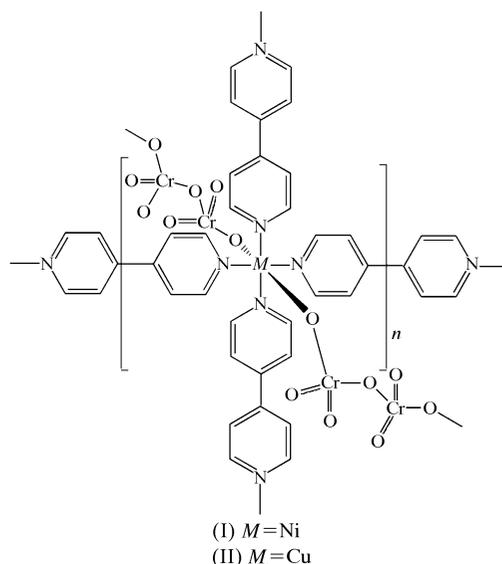
Online 11 March 2005

The novel title hybrid isomorphous organic–inorganic mixed-metal dichromates, $[\text{Ni}(\text{Cr}_2\text{O}_7)(\text{C}_{10}\text{H}_8\text{N}_2)_2]$ and $[\text{Cu}(\text{Cr}_2\text{O}_7)(\text{C}_{10}\text{H}_8\text{N}_2)_2]$, have been synthesized. A non-centrosymmetric three-dimensional (4,6)-net is formed from a linear chain of vertex-linked $[\text{Cr}_2\text{O}_7]^{2-}$ and $[\text{MN}_4\text{O}_2]^{2+}$ ($M = \text{Ni}$ and Cu) units, which in turn are linked by the planar bidentate 4,4'-bipyridine ligand through the four remaining vertices of the $[\text{MN}_4\text{O}_2]^{2+}$ octahedra. There are two such three-dimensional nets that interpenetrate with inversion symmetry.

Comment

Non-centrosymmetric solids, *i.e.* those without a center of inversion, may exhibit one or more interesting physical properties, such as ferroelectricity, pyroelectricity or piezoelectricity. A current approach to synthesizing non-centrosymmetric structures is to begin with asymmetric 'building blocks' (Halasyamani & Poeppelmeier, 1998). One example of an asymmetric building block is the dichromate anion, $[\text{Cr}_2\text{O}_7]^{2-}$, which is found in the compounds $[\text{M}(\text{Cr}_2\text{O}_7)(\text{py})_4]$ ($M = \text{Cu}^{2+}$ and Zn^{2+} , and py is pyridine) (Norquist *et al.*, 2001). These compounds consist of alternating vertex-linked CuN_4O_2 octahedra and $[\text{Cr}_2\text{O}_7]^{2-}$ polyhedra that form linear chain structures. In contrast, the dichromate-containing $[\text{Cu}(\text{Cr}_2\text{O}_7)(2,2'\text{-bpy})_2]$ (bpy is bipyridine) species forms isolated molecular species rather than chains (Maggard *et al.*, 2002). Both left- and right-handed enantiomers of isolated $[\text{Cu}(\text{Cr}_2\text{O}_7)(2,2'\text{-bpy})_2]$ molecules pack with inversion symmetry between layers in space group $P\bar{1}$. The structural difference between $[\text{Cu}(\text{Cr}_2\text{O}_7)(\text{py})_4]$ and $[\text{Cu}(\text{Cr}_2\text{O}_7)(2,2'\text{-bpy})_2]$ appears to be due to the modification evinced by the change of ligand. The different structures of the two compounds highlight the necessity for further studies to characterize the structure-directing features of organic mono- and bidentate ligands in relation to the dichromate anion.

Presented here is continuing synthetic work employing the late transition metal oxides of nickel and copper with asymmetric dichromate species (also referred to as the anion) and the 4,4'-bipyridine (4,4'-bpy) ligand.



$[\text{Ni}(\text{Cr}_2\text{O}_7)(4,4'\text{-bpy})_2]$, (I), and $[\text{Cu}(\text{Cr}_2\text{O}_7)(4,4'\text{-bpy})_2]$, (II), are isostructural compounds and are thus isostructural. An ellipsoid plot is shown in Fig. 1. The bond lengths and angles of the dichromate anion in both (I) and (II) (Table 1 and 2) are in good agreement with those reported for $\text{Na}_2\text{Cr}_2\text{O}_7$ (Panagiotopoulos & Brown, 1972). In both (I) and (II), a three-dimensional structure is generated from two bonding motifs, *viz.* (i) a linear chain that consists of alternating octahedra, centered on the late transition metal, joined

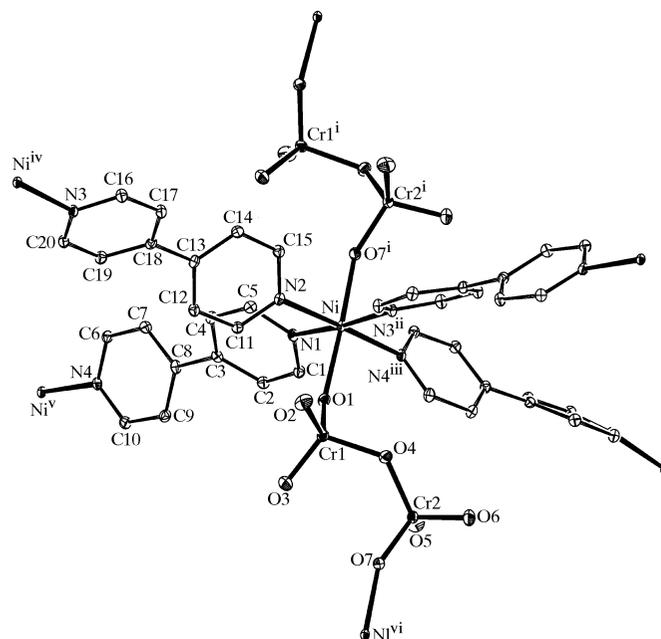


Figure 1
A displacement ellipsoid plot (50% probability level) of (I). [Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $x, -y, \frac{1}{2} + z$; (iii) $x, 1 - y, \frac{1}{2} + z$; (iv) $x, -y, z - \frac{1}{2}$; (v) $x, 1 - y, z - \frac{1}{2}$; (vi) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.]

to $[\text{Cr}_2\text{O}_7]^{2-}$ polyhedra, as shown in Fig. 2, and (ii) a two-dimensional square net of type (4,4) (Wells, 1977) composed of late transition metal cations coordinated by 4,4'-bpy ligands along the [200] plane (perpendicular to the chain; Fig. 3). The late transition metal cations are also bonded to O-atom vertices of the dichromate anions in a *trans* fashion. In addition, these opposing vertices are designated as the axial positions of the octahedra. As expected, the Cu–O bonds in (II) are elongated owing to the Jahn–Teller distortion of the Cu^{2+} ion. The average bond length between Cu and N atoms is 2.05 Å, while the average bond length of the Cu–O bonds is 2.32 Å. In comparison, the Ni^{2+} ion forms, on average, longer *M*–N bonds (2.12 Å) and shorter *M*–O bonds (2.02 Å). A general feature of the *M*–N bonds in both structures is that one *M*–N bond, for example, *M*–N1 (*M* = Ni and Cu) of a 4,4'-bpy ligand, is longer than the second *M*–N bond (*M*–N4) of the same 4,4'-bpy ligand (Fig. 1, and Tables 1 and 2). The difference between the two bonds is approximately 0.1 Å for both 4,4'-bpy ligands of (I) and (II). Similarly, for both (I) and (II), the shorter *M*–N bonds are *trans* to one another, as are the two longer *M*–N bonds. There are other examples of octahedrally coordinated Ni and Cu atoms having four bonds to N atoms and two bonds to O atoms exhibiting a similar trend (Prout *et al.*, 1971; Kulynych & Shimizu, 2002; Fritsky *et al.*, 2004). A search of the Cambridge Structural Database revealed that for octahedrally coordinated *M* (*M* = Cu and Ni) with four N-containing heterocyclic ligands and two O-containing ligands there is a correlation between the ionic character of the *M*–O bond (carbonate or dichromate *versus*

water, for example) and the variation of length within the four *M*–N bonds (Allen, 2002). The differences in *M*–O and *M*–N bond lengths of the title compounds are also accompanied by other distortions, such as a small displacement of the 4,4'-bpy molecule with respect to the equatorial plane.

Both compounds have chain structures composed of a late transition metal and coordinated dichromates. The chains are parallel to one another in the $[\bar{1}00]$ direction. Along the 2_1 screw axis there is a 180° rotation of each dichromate anion as the chain propagates; thus, the repeating segment in a chain is composed of two cations and two anions (Fig. 2).

The second bonding motif in $[\text{M}(\text{Cr}_2\text{O}_7)(\text{bpy})_4]$ (*M* = Ni^{2+} and Cu^{2+}) is a two-dimensional (4,4)-net composed of the bridging ligands and the late transition metal atoms. Each Ni/Cu atom forms bonds to four 4,4'-bpy ligands in the equatorial positions. These ligands serve as linkers and bridge each Ni/Cu atom to four other Ni/Cu-centered octahedra (Fig. 3). The linking of octahedra creates a two-dimensional square net composed of $\text{Ni}^{2+}/\text{Cu}^{2+}$ cations and 4,4'-bpy ligands.

The combination of this square net with the linear chain motif results in a three-dimensional net where the points of connectivity for both motifs are the $\text{Ni}^{2+}/\text{Cu}^{2+}$ -centered octahedra (*n* = 6) (Wells, 1977). The ligands act as spacers between the $\text{Ni}^{2+}/\text{Cu}^{2+}$ -centered octahedra centers. Each three-dimensional net is non-centrosymmetric with large cavities ($7.0 \times 7.0 \times 5.0$ Å) owing to the physical size and rigidity of the linking ligands. When a single non-centrosymmetric three-dimensional net is considered, the net is compatible with the polar or chiral-polar space group *Cc* or *C2*, respectively. However, the title compounds crystallize in the centrosymmetric space group *C2/c*, which indicates that the structures are composed of more than one three-dimensional net.

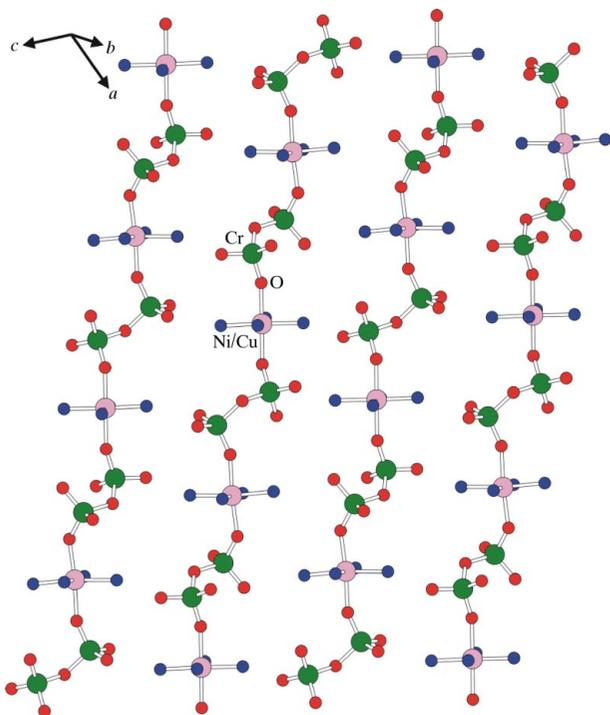


Figure 2
Linear chains of dichromate anions bonded to metal cations. The 4,4'-bpy rings have been omitted for clarity.

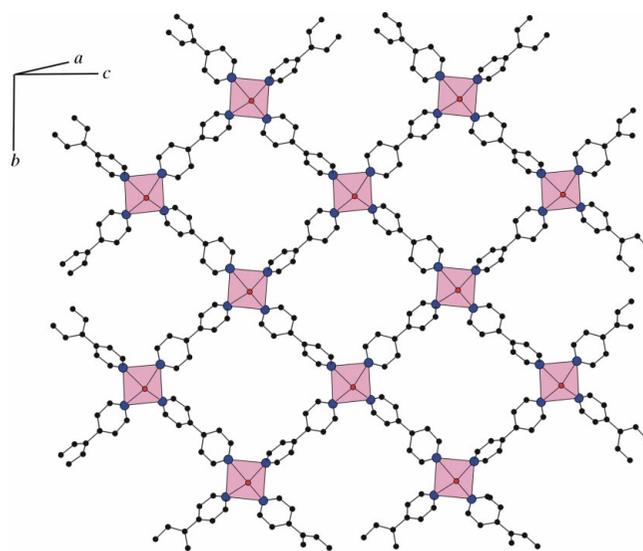


Figure 3
A two-dimensional net of $\text{Ni}^{2+}/\text{Cu}^{2+}$ -centered pseudo-octahedra and 4,4'-bpy ligands. The $[\text{Cr}_2\text{O}_7]^{2-}$ anions bonded to the axial position of the pseudo-octahedra have been omitted for clarity, except for the O atom directly coordinated to the metal.

Each parallel chain of late transition metal atoms and coordinated dichromate anions is surrounded by four other chains. These four surrounding chains are related to the central chain by an inversion center. The relationship between neighboring chains is shown in Fig. 4. Note that the Cr-centered tetrahedra have opposing facial directions. Additionally, the four closest neighboring chains are offset from the central chain by one-quarter of the repeating segment along the chain propagation direction. The chains of the net are

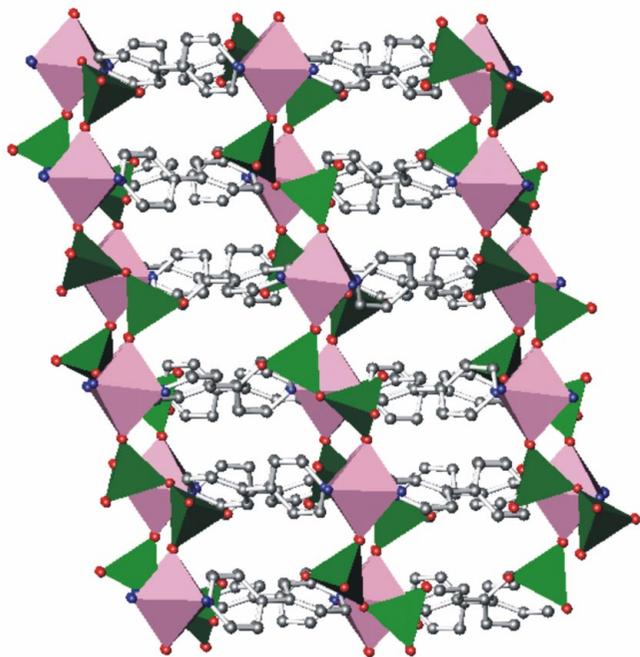


Figure 4
The overall structure of (I) and (II), including the 4,4'-bpy ligands.

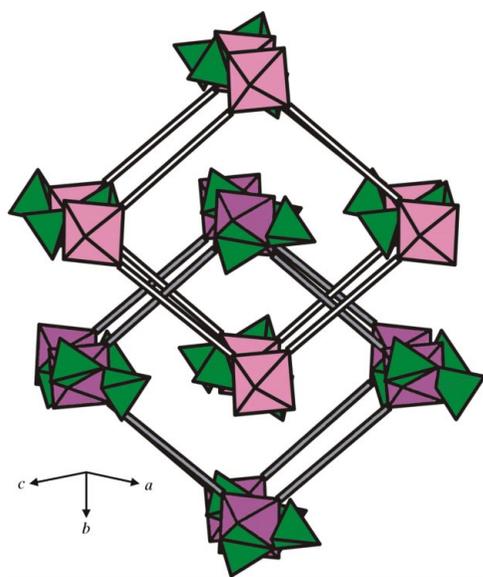


Figure 5
A view of two interpenetrating nets. The ligands, shown as bars, of one net are shaded. The two corner-sharing tetrahedra make up one dichromate anion.

related to their neighbors by an inversion center and, in three dimensions, the entire non-centrosymmetric three-dimensional net is related to the second net by an inversion center. In addition, the second independent three-dimensional net effectively fills the cavities as it interpenetrates the first net (Fig. 5).

It is evident that the three-dimensional net is created from late transition metal cations with coordinated dichromate anions in one direction and, most importantly, the linking 4,4'-bpy ligands in the other two directions. The rigidity and bidentate characteristics of the 4,4'-bpy and dichromate ligands bring about a stable three-dimensional net, while the length of the ligands affords enough space in the net to accommodate the interpenetration of an inversely related three-dimensional net.

Experimental

Single crystals of $[\text{Ni}(\text{Cr}_2\text{O}_7)(4,4'\text{-bpy})_2]$ were synthesized by placing NiO (44.1 mg, Aldrich, 99.99%), $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (291.6 mg, Aldrich, 99.5+%) and 4,4'-bpy (453.2 mg, Aldrich, 98%) in a Teflon (fluoroethylenepropylene) pouch (Harrison *et al.*, 1993). To the pouch were added aqueous HF (885.9 mg, Aldrich, 49% w/v) and deionized water (55.1 mg). The pouches were heat-sealed and placed in a 125 ml autoclave, which was back-filled with water (45 ml). The autoclave was heated in a convection oven for 24 h at 423 K and cooled to room temperature at a rate of 6 K h⁻¹. The pouch was opened in air and (I) was recovered by filtration in 39% yield based on Ni content. Single crystals of $[\text{Cu}(\text{Cr}_2\text{O}_7)(4,4'\text{-bpy})_2]$ were synthesized in a similar manner using Cu₂O (44.6 mg, Aldrich, 97%), $(\text{pyH})_2\text{Cr}_2\text{O}_7$ (234.5 mg, Fluka, 98.0%), 4,4'-bpy (195.1 mg, Aldrich, 98%), aqueous HF (112.3 mg, Aldrich, 49% w/v) and deionized water (1111.5 mg). Compound (II) was recovered by filtration in 75% yield based on Cu content. Crystals of (I) and (II) are isomorphous.

Compound (I)

Crystal data

$[\text{Ni}(\text{Cr}_2\text{O}_7)(\text{C}_{10}\text{H}_8\text{N}_2)_2]$
 $M_r = 587.08$
 Monoclinic, $C2/c$
 $a = 21.343$ (7) Å
 $b = 15.260$ (5) Å
 $c = 16.658$ (6) Å
 $\beta = 127.094$ (5)°
 $V = 4328$ (3) Å³
 $Z = 8$

$D_x = 1.802$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 5184 reflections
 $\theta = 4\text{--}28^\circ$
 $\mu = 1.90$ mm⁻¹
 $T = 153$ (2) K
 Column, blue
 $0.21 \times 0.16 \times 0.15$ mm

Data collection

Siemens SMART diffractometer
 ω - 2θ scans
 Absorption correction: analytical, face-indexed (PLATON; Spek, 2003)
 $T_{\text{min}} = 0.718$, $T_{\text{max}} = 0.874$
 19 357 measured reflections

5184 independent reflections
 4364 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.083$
 $\theta_{\text{max}} = 28.3^\circ$
 $h = -28 \rightarrow 28$
 $k = -20 \rightarrow 20$
 $l = -21 \rightarrow 22$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.099$
 $S = 1.08$
 5184 reflections
 307 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 7.5127P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.19$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.64$ e Å⁻³

Table 1

Selected geometric parameters (Å, °) for (I).

Ni—O1	2.0494 (19)	Cr1—O2	1.605 (2)
Ni—O7 ⁱ	2.0433 (19)	Cr1—O3	1.608 (2)
Ni—N1	2.160 (2)	Cr1—O4	1.7856 (19)
Ni—N2	2.086 (2)	Cr2—O4	1.7877 (18)
Ni—N3 ⁱⁱ	2.165 (2)	Cr2—O5	1.611 (2)
Ni—N4 ⁱⁱⁱ	2.0683 (19)	Cr2—O6	1.6115 (19)
Cr1—O1	1.6586 (18)	Cr2—O7 ⁱ	1.6439 (18)
O1—Ni—O7 ⁱ	174.48 (7)	O3—Cr1—O4	110.74 (9)
Ni—O1—Cr1	137.24 (10)	O4—Cr2—O5	109.69 (10)
Cr2—O7—Ni ^{iv}	156.82 (11)	O4—Cr2—O6	106.81 (10)
O1—Cr1—O2	110.00 (10)	O4—Cr2—O7 ⁱ	110.28 (9)
O1—Cr1—O3	109.82 (10)	O5—Cr2—O6	109.82 (11)
O1—Cr1—O4	108.82 (9)	O5—Cr2—O7 ⁱ	109.93 (10)
O2—Cr1—O3	109.74 (11)	O6—Cr2—O7 ⁱ	110.26 (9)
O2—Cr1—O4	107.70 (10)	Cr1—O4—Cr2	126.86 (10)

 Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $x, -y, \frac{1}{2} + z$; (iii) $x, 1 - y, \frac{1}{2} + z$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$

Compound (II)

Crystal data

 $[\text{Cu}(\text{Cr}_2\text{O}_7)(\text{C}_{10}\text{H}_8\text{N}_2)_2]$
 $M_r = 591.91$

 Monoclinic, $C2/c$
 $a = 21.603 (3) \text{ \AA}$
 $b = 14.8505 (18) \text{ \AA}$
 $c = 16.604 (2) \text{ \AA}$
 $\beta = 125.682 (2)^\circ$
 $V = 4326.8 (10) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.817 \text{ Mg m}^{-3}$

 Mo $K\alpha$ radiation

Cell parameters from 5221

reflections

 $\theta = 4\text{--}28^\circ$
 $\mu = 2.01 \text{ mm}^{-1}$
 $T = 153 (2) \text{ K}$

Cube, green

 $0.15 \times 0.15 \times 0.14 \text{ mm}$

Data collection

Siemens SMART diffractometer

 ω -2 θ scans

Absorption correction: analytical,

 face indexed (*PLATON*;
Spek, 2003)

 $T_{\min} = 0.769, T_{\max} = 0.816$

19 193 measured reflections

5221 independent reflections

 4526 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\max} = 28.3^\circ$
 $h = -28 \rightarrow 27$
 $k = -19 \rightarrow 19$
 $l = -21 \rightarrow 22$

Refinement

 Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.085$
 $S = 1.06$

5221 reflections

307 parameters

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0470P)^2$
 $+ 7.1233P]$

 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.73 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.78 \text{ e \AA}^{-3}$

H atoms were included in the final refinement model as riding atoms in idealized positions using the default *SHELXL97* (Sheldrick, 1997) settings at low temperature [$C-H = 0.95 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5U_{\text{eq}}(\text{C})$].

For both compounds, data collection: *SMART-NT* (Siemens, 1996); cell refinement: *SAINT-Plus* (Siemens, 1996); data reduction:

Table 2

Selected geometric parameters (Å, °) for (II).

Cu—O1	2.3238 (15)	Cr1—O2	1.6095 (17)
Cu—O7 ⁱ	2.3120 (16)	Cr1—O3	1.6132 (17)
Cu—N1	2.1102 (17)	Cr1—O4	1.7855 (15)
Cu—N2	2.0082 (16)	Cr2—O4	1.7898 (15)
Cu—N3 ⁱⁱ	2.1022 (16)	Cr2—O5	1.6135 (17)
Cu—N4 ⁱⁱⁱ	1.9923 (16)	Cr2—O6	1.6132 (16)
Cr1—O1	1.6432 (15)	Cr2—O7 ⁱ	1.6258 (16)
O1—Cu—O7 ⁱ	169.82 (6)	O3—Cr1—O4	110.90 (8)
Cu—O1—Cr1	128.01 (9)	O4—Cr2—O5	109.56 (9)
Cr2—O7—Cu ^{iv}	155.78 (9)	O4—Cr2—O6	107.42 (8)
O1—Cr1—O2	109.44 (8)	O4—Cr2—O7 ⁱ	109.77 (7)
O1—Cr1—O3	109.76 (9)	O5—Cr2—O6	110.04 (10)
O1—Cr1—O4	108.71 (7)	O5—Cr2—O7 ⁱ	110.21 (9)
O2—Cr1—O3	110.05 (9)	O6—Cr2—O7 ⁱ	109.79 (8)
O2—Cr1—O4	107.94 (9)	Cr1—O4—Cr2	125.96 (9)

 Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $x, -y, z - \frac{1}{2}$; (iii) $x, 1 - y, \frac{1}{2} + z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$

SAINT-Plus; structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1999); publication software: *SHELXL97*.

The authors acknowledge support from the National Science Foundation, Solid State Chemistry (award Nos. DMR-9727516 and DMR-0312136).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1225). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Dowty, E. (1999). *ATOMS*. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.
- Fritsky, I. O., Swiatek-Kozłowska, J., Dobosz, A., Sliva, T. Y. & Dudarenko, N. M. (2004). *Inorg. Chim. Acta*, **357**, 3746–3752.
- Halasyamani, P. S. & Poeppelmeier, K. R. (1998). *Chem. Mater.* **10**, 2753–2769.
- Harrison, W. T. A., Nenoff, T. M., Gier, T. E. & Stucky, G. D. (1993). *Inorg. Chem.* **32**, 2437–2441.
- Kulynych, A. D. & Shimizu, G. (2002). *CrystEngComm*, **4**, 102–105.
- Maggard, P. A., Kopf, A. L. & Poeppelmeier, K. R. (2002). *Acta Cryst.* **C58**, m207–m209.
- Norquist, A. J., Heier, K. R., Halasyamani, P. S., Stern, C. L. & Poeppelmeier, K. R. (2001). *Inorg. Chem.* **40**, 2015–2019.
- Panagiotopoulos, N. C. & Brown, I. D. (1972). *Acta Cryst.* **B28**, 1352–1357.
- Prout, C. K., Allison, G. B. & Rossotti, F. J. C. (1971). *J. Chem. Soc. A*, **21**, 3331–3335.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Siemens (1996). *SMART-NT* and *SAINT-Plus*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Wells, A. F. (1977). *Three-Dimensional Nets and Polyhedra*, pp. 12–172. New York: Wiley Interscience.