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 \([\text{MN}_4\text{O}_2]^{2+}\) (\(\text{M} = \text{Ni} \text{ and Cu}\)) 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 \([\text{M}(\text{Cr}_2\text{O}_7)(\text{py})_4]\) (\(\text{M} = \text{Cu}^{2+} \text{ and Zn}^{2+}, \text{and py is pyridine}\)) (Norquist et al., 2001). These compounds consist of alternating vertex-linked CuN$_4$O$_2$ 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 \(P\overline{1}\). The structural difference between \([\text{Cu}(\text{Cr}_2\text{O}_7)(\text{py})]_2\) 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 monodentate and bidentate ligands in relation to the dichromate anion.
to [Cr$_2$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 [T00] 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 [M(Cr$_2$O$_7$)(bpy)$_4$]$_n$ (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 Ni$^{2+}$/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 Ni$^{2+}$/Cu$^{2+}$-centered octahedra (n = 6) (Wells, 1977). The ligands act as spacers between the Ni$^{2+}$/Cu$^{2+}$-centered octahedra centers. Each three-dimensional net is non-centrosymmetric with large cavities (7.0 x 7.0 x 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.
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 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 [Ni(Cr₂O₇)(C₁₀H₈N₂)₂] were synthesized by placing NiO (44.1 mg, Aldrich, 99.99%), (NH₄)₂Cr₂O₇ (291.6 mg, Aldrich, 99.5+%) and 4,4'-bpy (453.2 mg, Aldrich, 98%) in a Teflon (fluorinated ethylenepropylene) 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 [Cu(Cr₂O₇)(C₁₀H₈N₂)₂] were synthesized in a similar manner using Cu₂O (44.6 mg, Aldrich, 97%), (pyH)₂Cr₂O₇ (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

\[ \text{[Ni(Cr}_2\text{O}_7)(\text{C}_10\text{H}_8\text{N}_2)_2] \]

\[ M_r = 587.08 \]

Monoclinic, \( C2/c \)

\[ a = 21.343 (7) \text{ Å} \]

\[ b = 15.260 (5) \text{ Å} \]

\[ c = 16.658 (6) \text{ Å} \]

\[ \beta = 127.094 (5)^\circ \]

\[ V = 4328 (3) \text{ Å}^3 \]

\[ Z = 8 \]

Data collection

Siemens SMART diffractometer

\( \omega-2\theta \) scans

Absorption correction: analytical, face-indexed (PLATON; Spek, 2003)

\( T_{\text{min}} = 0.718, T_{\text{max}} = 0.874 \)

19 357 measured reflections

Reflinement

Refinement on \( F^2 \)

\( R[F^2 > 2\sigma(F^2)] = 0.038 \)

\( wR(F^2) = 0.099 \)

5 184 reflections

307 parameters

H-atom parameters constrained

\( w = 1/[\sigma^2(F^2) + (0.048P)^2 + 7.5127P] \)

where \( P = (F^2 + 2F'^2)/3 \)

\( \Delta f_{\text{max}} = 0.001 \)

\( \Delta f_{\text{min}} = 1.19 \text{ e Å}^{-3} \)

\( \Delta f_{\text{max}} = -0.64 \text{ e Å}^{-3} \)

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.
metal-organic compounds

Table 1
Selected geometric parameters (Å, °) for (I).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Bond Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni—O1</td>
<td>2.0494 (19)</td>
<td>Cr1—O2 1.605 (2)</td>
</tr>
<tr>
<td>Ni—O7^a</td>
<td>2.0433 (19)</td>
<td>Cr1—O3 1.608 (2)</td>
</tr>
<tr>
<td>Ni—N1</td>
<td>2.160 (2)</td>
<td>Cr1—O4 1.7856 (19)</td>
</tr>
<tr>
<td>Ni—N2</td>
<td>2.086 (2)</td>
<td>Cr2—O4 1.7877 (18)</td>
</tr>
<tr>
<td>Ni—N3^a</td>
<td>2.165 (2)</td>
<td>Cr2—O5 1.631 (2)</td>
</tr>
<tr>
<td>Ni—N4^a</td>
<td>2.0863 (19)</td>
<td>Cr2—O6 1.6115 (19)</td>
</tr>
<tr>
<td>Cr1—O1</td>
<td>1.6568 (18)</td>
<td>Cr2—O7^a 1.6439 (18)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) x, -y, -z, z; (ii) x, -y, 1+z; (iii) x, 1-y, -z; (iv) x+y, -y, z+1.

Table 2
Selected geometric parameters (Å, °) for (II).

<table>
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<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Bond Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu—O1</td>
<td>2.3238 (15)</td>
<td>Cr1—O2 1.6095 (17)</td>
</tr>
<tr>
<td>Cu—O7^a</td>
<td>2.3120 (16)</td>
<td>Cr1—O3 1.6132 (17)</td>
</tr>
<tr>
<td>Cu—N1</td>
<td>2.1102 (17)</td>
<td>Cr1—O4 1.7855 (15)</td>
</tr>
<tr>
<td>Cu—N2</td>
<td>2.0082 (16)</td>
<td>Cr2—O4 1.7898 (15)</td>
</tr>
<tr>
<td>Cu—Ni^a</td>
<td>2.1022 (16)</td>
<td>Cr2—O5 1.6135 (17)</td>
</tr>
<tr>
<td>Cu—Ni^a</td>
<td>1.9923 (16)</td>
<td>Cr2—O6 1.6132 (16)</td>
</tr>
<tr>
<td>Cr1—O1</td>
<td>1.6432 (15)</td>
<td>Cr2—O7^a 1.6258 (16)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) x, 1-y, z, -z; (ii) x, -y, 1+z; (iii) x, 1-y, z; (iv) x+y, -y, z+1.

Compound (II)

Crystal data

\[
\text{[CuCr}_2\text{O}_4\text{(C}]_{10}\text{H}_{18}\text{N}_2\text{]_2\}}
\]

\[M_r = 591.91\]

Monoclinic, C2/c

\[a = 21.603 (3) \text{ Å}\]
\[b = 14.8505 (18) \text{ Å}\]
\[c = 16.604 (2) \text{ Å}\]
\[\beta = 125.682 (2)^\circ\]
\[V = 4326.8 (10) \text{ Å}^3\]
\[Z = 8\]

Data collection

Siemens SMART diffractometer

\[\omega-2\theta\) scans\]

Absorption correction: analytical, face indexed (PLATON; Spek, 2003)

\[T_{\text{max}} = 0.769, T_{\text{min}} = 0.816\]
\[19\text{,}193\text{ measured reflections}\]

Refinement

Refinement on \(F^2\)

\[R(F^2) = 0.031\]
\[wR(F^2) = 0.085\]
\[S = 1.06\]
\[5221\text{ reflections}\]
\[307\text{ parameters}\]

H-atom parameters constrained

\[D_c = 1.817 \text{ Mg m}^{-3}\]

Mo Kα radiation

Cell parameters from 5221 reflections

\[\theta_{\text{max}} = 28.3^\circ\]
\[h = -28 \rightarrow 27\]
\[k = -19 \rightarrow 19\]
\[l = -21 \rightarrow 22\]

\[w = 1/\sigma^2(F^2) + (0.0470P)^2 + 7.1235 P\]

where \(P = (F^2 + 2F^2)/3\)

\[\Delta \rho_{\text{max}} = 0.73 \text{ e Å}^{-3}\]
\[\Delta \rho_{\text{min}} = -0.78 \text{ e Å}^{-3}\]

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 Å 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:

SAINT-Plus; structure solution: SHELX97 (Sheldrick, 1997); structure refinement: SHELXL97 (Sheldrick, 1997); molecular graphics: ATOMS (Dowty, 1999); publication software: SHELXL97.

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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.

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