

**Data collection**

Rigaku AFC-5R diffractometer	630 reflections with $I > 2\sigma(I)$
$\omega$ - $2\theta$ scans	$R_{\text{int}} = 0.033$
Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968)	$\theta_{\text{max}} = 26^\circ$ $h = 0 \rightarrow 6$ $k = 0 \rightarrow 10$ $l = -9 \rightarrow 9$
$T_{\text{min}} = 0.366$ , $T_{\text{max}} = 0.580$	3 standard reflections
774 measured reflections	every 100 reflections
691 independent reflections	intensity decay: 1.2%

**Refinement**

Refinement on $F^2$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.036$	$\Delta\rho_{\text{max}} = 0.739 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.102$	$\Delta\rho_{\text{min}} = -0.816 \text{ e } \text{\AA}^{-3}$
$S = 1.173$	Extinction correction: <i>SHELXL93</i>
691 reflections	Extinction coefficient: 0.020 (6)
62 parameters	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
H atoms not refined	
$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 0.3653P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$			
	x	y	z	$U_{\text{eq}}$
V1	0.4162 (2)	1/4	0.57407 (11)	0.0085 (3)
V2	-0.06299 (11)	0.05451 (7)	0.68499 (7)	0.0087 (3)
O1	0.6192 (7)	1/4	0.4308 (5)	0.0146 (8)
O2	0.1859 (5)	0.0866 (3)	0.5052 (3)	0.0121 (6)
O3	0.6143 (5)	0.0987 (3)	0.7329 (3)	0.0113 (6)
O4	0.0909 (7)	1/4	0.7566 (5)	0.0102 (7)
O5	0.0624 (5)	-0.0669 (3)	0.8295 (4)	0.0163 (7)
N1	0.4441 (11)	1/4	0.0633 (7)	0.0309 (13)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

V1—O1	1.597 (4)	V2—O3 <sup>i</sup>	1.736 (2)
V1—O2	1.835 (3)	V2—O4	1.876 (2)
V1—O3	1.971 (3)	V2—O2 <sup>ii</sup>	1.954 (3)
V1—O4	2.284 (4)	V2—O2	2.001 (3)
V2—O5	1.602 (3)	V2—O1 <sup>i</sup>	2.917 (3)
O1—V1—O2	102.6 (2)	O5—V2—O4	103.4 (2)
O2—V1—O2 <sup>iii</sup>	97.1 (2)	O3 <sup>i</sup> —V2—O4	96.1 (1)
O2—V1—O3 <sup>iii</sup>	157.6 (1)	O5—V2—O2 <sup>ii</sup>	102.6 (2)
O1—V1—O3	97.6 (2)	O3 <sup>i</sup> —V2—O2 <sup>ii</sup>	94.4 (1)
O2—V1—O3	87.5 (1)	O4—V2—O2 <sup>ii</sup>	147.8 (1)
O3 <sup>iii</sup> —V1—O3	80.5 (2)	O5—V2—O2	111.2 (1)
O1—V1—O4	174.1 (2)	O3 <sup>i</sup> —V2—O2	142.1 (1)
O2—V1—O4	73.7 (1)	O4—V2—O2	80.0 (2)
O3—V1—O4	86.8 (1)	O2 <sup>ii</sup> —V2—O2	73.1 (1)
O5—V2—O3 <sup>i</sup>	106.4 (2)		

Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $-x, -y, 1 - z$ ; (iii)  $x, \frac{1}{2} - y, z$ .Table 3. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...O4 <sup>i</sup>	0.97	1.86	2.823 (6)	175
N1—H2...O5 <sup>ii</sup>	0.89	2.15	2.949 (5)	150
N1—H3...O5 <sup>iii</sup>	0.89	2.51	3.156 (5)	130

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

All H atoms were located from a difference Fourier map and were fixed at ideal positions with common isotropic displacement parameters ( $U_{\text{iso}} = 0.05 \text{ \AA}^2$ ).

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1987a). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1987b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990a). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990b). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1075). Services for accessing these data are described at the back of the journal.

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## The low-temperature tetragonal phase of $\text{NiCr}_2\text{O}_4$

GO UENO, SHOICHI SATO AND YOSHIHIRO KINO

X-ray Research Laboratory, Rigaku Corporation, 3-9-12 Matsubara, Akishima, Tokyo 196-8666, Japan. E-mail: ueno@rigaku.co.jp

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**Abstract**

The title compound, normal spinel nickel chromite,  $\text{NiCr}_2\text{O}_4$ , undergoes a cubic to tetragonal phase tran-

sition at low temperature. The crystal structure of the tetragonal phase at 200 K was determined by single-crystal X-ray diffraction data. Details of the crystal information, including anisotropic displacement parameters, are reported.

### Comment

The phase transition of normal spinel NiCr<sub>2</sub>O<sub>4</sub> (space group  $Fd\bar{3}m$ ) to the tetragonal structure is interpreted in terms of a Jahn–Teller distortion of magnetic ions (Kino *et al.*, 1972). The site symmetry of the Ni<sup>2+</sup> ion is lowered from  $\bar{4}3m$  to  $\bar{4}m2$  at the transition and distortion of the NiO<sub>4</sub> tetrahedron is accompanied by an elongation of the unit cell. Although the crystal structure of the tetragonal phase has already been studied by powder diffraction (Armbruster *et al.*, 1983; Crottaz *et al.*, 1997), no single-crystal X-ray diffraction study has been carried out due to difficulties arising from crystal twinning. In the present study, X-ray diffraction data from a twinned crystal were measured at 200 K. The structure refinement was carried out based on a high-resolution data set of more than 400 independent reflections, adopting anisotropic atomic displacement parameters. The packing diagram of the tetragonal structure is shown in Fig. 1. For reference, the cubic structure was also refined at 300 K. The structure converged to sufficiently good  $R$  and  $wR$  values, and

was basically similar to those of the above-mentioned work. However, a few discrepancies were observed in the geometry of the NiO<sub>4</sub> tetrahedron. An unreasonably drastic change in the Ni—O bond distance reported by Crottaz *et al.* (1997) was not found, whereas the compressed O—Ni—O angle was more similar in value to that reported by Armbruster *et al.* (1983).

### Experimental

Single crystals of NiCr<sub>2</sub>O<sub>4</sub> were prepared by the flux method using a bismuth oxide (Bi<sub>2</sub>O<sub>3</sub>) flux. A mixture of Bi<sub>2</sub>O<sub>3</sub> and NiCr<sub>2</sub>O<sub>4</sub> (mass ratio 94:6) was ground and placed in a platinum crucible. A small amount of hematite (Fe<sub>2</sub>O<sub>3</sub>) with 5 wt% of NiCr<sub>2</sub>O<sub>4</sub> was added as an impurity to lower the transition temperature. The compounds were heated to 1553 K, held at that temperature for 5 h, cooled slowly to 1373 K at a rate of 0.5 K h<sup>-1</sup>, and finally cooled rapidly to room temperature. Black block-shaped crystals were obtained.

#### Cubic structure at 300 K

##### Crystal data

NiCr<sub>2</sub>O<sub>4</sub>  
 $M_r = 226.69$   
 Cubic  
 $Fd\bar{3}m$   
 $a = 8.3093(4) \text{ \AA}$   
 $V = 573.71(4) \text{ \AA}^3$   
 $Z = 8$   
 $D_x = 5.249 \text{ Mg m}^{-3}$   
 $D_m$  not measured

Mo  $K\alpha$  radiation  
 $\lambda = 0.7107 \text{ \AA}$   
 Cell parameters from 25 reflections  
 $\theta = 14.0\text{--}24.8^\circ$   
 $\mu = 13.754 \text{ mm}^{-1}$   
 $T = 302.0 \text{ K}$   
 Sphere  
 0.15 mm (radius)  
 Black

##### Data collection

Rigaku AFC-7R diffractometer  
 $\omega$ - $2\theta$  scans  
 Absorption correction: spherical (TEXSAN; Molecular Structure Corporation/Rigaku, 1998)  
 $T_{\min} = 0.067$ ,  $T_{\max} = 0.129$   
 2945 measured reflections  
 174 independent reflections

172 reflections with  $F^2 > 3\sigma(F^2)$   
 $R_{\text{int}} = 0.019$   
 $\theta_{\max} = 49.90^\circ$   
 $h = 0 \rightarrow 17$   
 $k = -17 \rightarrow 17$   
 $l = -17 \rightarrow 17$   
 3 standard reflections every 150 reflections  
 intensity decay: 1.2%

##### Refinement

Refinement on  $F$   
 $R = 0.022$   
 $wR = 0.058$   
 $S = 1.894$   
 172 reflections  
 8 parameters  
 $w = 1/[\sigma^2(F_o) + 0.0009|F_o|^2]$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 2.41 \text{ e \AA}^{-3}$  at  $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$   
 $\Delta\rho_{\min} = -1.04 \text{ e \AA}^{-3}$

Extinction correction: Zachariasen (1967) type 2, Gaussian isotropic  
 Extinction coefficient: 0.55 (7)  
 Scattering factors from *International Tables for Crystallography* (Vol. C)

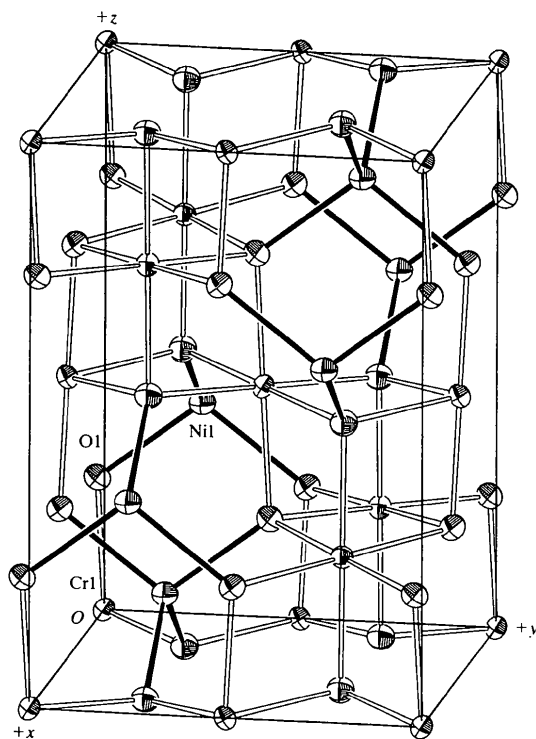


Fig. 1. A view of the unit cell of the tetragonal structure. Displacement ellipsoids are drawn at the 90% probability level.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for the cubic structure
$$U_{\text{eq}} = (1/3) \sum_i \sum_j U^{ij} a_i^j a_j$$

	x	y	z	$U_{\text{eq}}$
Ni1	3/8	3/8	3/8	0.00749 (4)
Cr1	1/4	1/4	0	0.00554 (4)
O1	0.2385 (1)	0.23855	0.23855	0.00766 (5)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for the cubic structure

Ni1—O1	1.964 (2)	Cr1—O1	1.987 (1)
O1—Ni1—O1 <sup>ii</sup>	109.471 (3)	O1—Cr1—O1 <sup>iii</sup>	95.62 (7)
O1—Cr1—O1 <sup>ii</sup>	84.38 (7)		

Symmetry codes: (i)  $x, \frac{3}{4} - y, \frac{3}{4} - z$ ; (ii)  $x, \frac{1}{4} - y, \frac{1}{4} - z$ ; (iii)  $\frac{1}{4} + x, \frac{1}{2} - y, z - \frac{1}{4}$ .

### Tetragonal structure at 200 K

#### Crystal data

NiCr<sub>2</sub>O<sub>4</sub>  
 $M_r = 226.69$   
 Tetragonal  
 $I4_1/amd$   
 $a = 5.8102 (8) \text{\AA}$   
 $c = 8.4806 (9) \text{\AA}$   
 $V = 286.29 (5) \text{\AA}^3$   
 $Z = 4$   
 $D_x = 5.259 \text{ Mg m}^{-3}$   
 $D_m$  not measured

Mo  $K\alpha$  radiation  
 $\lambda = 0.7107 \text{\AA}$   
 Cell parameters from 21 reflections  
 $\theta = 13.9\text{--}24.5^\circ$   
 $\mu = 13.781 \text{ mm}^{-1}$   
 $T = 200.2 \text{ K}$   
 Sphere  
 0.15 mm (radius)  
 Black

#### Data collection

Rigaku AFC-7R diffractometer  
 $\omega$ - $2\theta$  scans  
 Absorption correction: spherical (TEXSAN; Molecular Structure Corporation/Rigaku, 1998)  
 $T_{\text{min}} = 0.067$ ,  $T_{\text{max}} = 0.129$   
 2572 measured reflections  
 424 independent reflections

395 reflections with  $F^2 > 3\sigma(F^2)$   
 $R_{\text{int}} = 0.070$   
 $\theta_{\text{max}} = 49.97^\circ$   
 $h = 0 \rightarrow 12$   
 $k = -12 \rightarrow 12$   
 $l = -18 \rightarrow 18$   
 3 standard reflections every 150 reflections  
 intensity decay: 0.31%

#### Refinement

Refinement on  $F$   
 $R = 0.0226$   
 $wR = 0.0412$   
 $S = 1.862$   
 395 reflections  
 14 parameters  
 $w = 1/[\sigma^2(F_o) + 0.0004|F_o|^2]$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 1.00 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -2.23 \text{ e \AA}^{-3}$

Extinction correction: Zachariasen(1967) type  
 2, Gaussian isotropic  
 Extinction coefficient: 0.33 (7)  
 Scattering factors from International Tables for Crystallography (Vol. C)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for the tetragonal structure
$$U_{\text{eq}} = (1/3) \sum_i \sum_j U^{ij} a_i^j a_j$$

	x	y	z	$U_{\text{eq}}$
Ni1	0	1/4	3/8	0.00564 (4)
Cr1	0	0	0	0.00428 (6)
O1	0	-0.0179 (2)	0.2337 (1)	0.0059 (1)

Table 4. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for the tetragonal structure

Ni1—O1	1.965 (1)	Cr1—O1 <sup>i</sup>	1.9868 (6)
Cr1—O1	1.985 (1)		
O1—Ni1—O1 <sup>ii</sup>	104.81 (5)	O1—Cr1—O1 <sup>iv</sup>	96.20 (4)
O1—Ni1—O1 <sup>iii</sup>	111.85 (3)	O1 <sup>v</sup> —Cr1—O1 <sup>iv</sup>	94.52 (4)
O1—Cr1—O1 <sup>i</sup>	83.80 (4)		

Symmetry codes: (i)  $-\frac{1}{4} - y, -\frac{1}{4} - x, \frac{1}{4} - z$ ; (ii)  $x, \frac{1}{2} - y, z$ ; (iii)  $\frac{1}{4} - y, \frac{1}{4} - x, \frac{3}{4} - z$ ; (iv)  $-\frac{1}{4} - y, \frac{1}{4} + x, z - \frac{1}{4}$ ; (v)  $-\frac{3}{4} - y, -\frac{3}{4} - x, \frac{3}{4} - z$ .

The specimen was kept at  $200 \pm 1 \text{ K}$  using a cold nitrogen gas stream during the low-temperature experiment. Splitting of the Bragg peaks was observed below the transition temperature because of the formation of three twin components inside the crystal. The crystal orientation for the intensity measurement was determined by choosing one of these three twin components. The split peaks were clearly resolved, however, the separation between them was insufficient for some reflections. Thus, scan width and receiving-slit size had to be severely reduced to enable the measurement of as many of the individual reflections as possible. The data collection covered a hemisphere of the reciprocal space so that enough equivalent reflections could be obtained. For the structure refinement, reflections had to be selected carefully because there were some unreliable reflections affected by the other twin components. Therefore, reflections with an intensity deviation of more than 30% from the mean value of the equivalents were removed, then the rest of the equivalents were averaged and used for the structure refinement. Such a removal of unreliable reflections is justified in order to improve the precision of the observations under the difficult conditions mentioned above. Because of the iron impurity, the transition temperature (273 K) at which the splitting of peaks was observed is lower than that of pure nickel chromite (299 K; Kino *et al.*, 1973). Structure refinements with fractional inclusion of Fe atoms at the Ni or Cr sites were tried to see the influence of the impurity on the structure. However, no significant difference was observed in the refinements with and without impurity. The final refinement was performed on the simple structure without impurity.

For both compounds, data collection: *RigakuAFC Diffractometer Control Software* (Rigaku, 1995); cell refinement: *RigakuAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation/Rigaku, 1998). Program(s) used to solve structures: *SAPI91* (Fan, 1991) for 300 K data; *PATY* in *DIRDIF92* (Beurskens *et al.*, 1992) for 200 K data. For both compounds, program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1244). Services for accessing these data are described at the back of the journal.

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## A molecular tetraamminecopper(II)-*trans*-diamminocopper(II) tetracyanonickelate(II) coordination compound†

CHRISTOPH JANIAK,<sup>a\*</sup> HE-PING WU,<sup>a</sup> PETER KLÜFERS<sup>b\*</sup> AND PETER MAYER<sup>b</sup>

<sup>a</sup>Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstraße 21, D-79104 Freiburg, Germany, and <sup>b</sup>Institut für Anorganische Chemie, Universität Karlsruhe, Kaiserstraße 12, D-76131 Karlsruhe, Germany. E-mail: janiak@uni-freiburg.de

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### Abstract

The title complex, [Ni<sub>4</sub>Cu<sub>4</sub>(CN)<sub>16</sub>(NH<sub>3</sub>)<sub>12</sub>] or {[Cu(NH<sub>3</sub>)<sub>4</sub>][*cis*-Ni(CN)<sub>2</sub>(μ-CN)<sub>2</sub>]-*cyclo*-[*trans*-Cu(NH<sub>3</sub>)<sub>2</sub>]-[*cis*-Ni(CN)<sub>2</sub>(μ-CN)<sub>2</sub>]}<sub>2</sub>, is a dimeric C<sub>2h</sub> symmetrical entity built from square-planar [Ni(CN)<sub>4</sub>]<sup>2-</sup> anions as *cis* bridging ligands and (distorted) square-pyramidal copper centres. All of the atoms, except those of the three independent ammine groups, lie on a mirror plane. Copper is coordinated by ammine and tetracyanonickelate ligands. This is a rare example of a discrete molecular cyano-copper-nickel complex.

### Comment

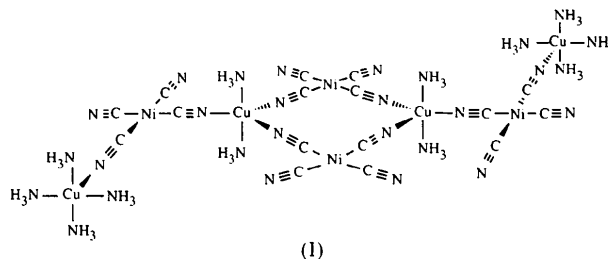
The interest in coordination polymers formed from metal ions and bridging ligands is fuelled by expectations of developing new materials with unique electronic properties (Robson *et al.*, 1992; Gardner *et al.*, 1995;

† Systematic name: dodecaammine-5κ<sup>4</sup>N,6κ<sup>2</sup>N,7κ<sup>2</sup>N,8κ<sup>4</sup>N-octa-μ-cyano-1:5κ<sup>2</sup>C:N;1:6κ<sup>2</sup>C:N;2:6κ<sup>2</sup>C:N;2:7κ<sup>2</sup>C:N;3:6κ<sup>2</sup>C:N;3:7κ<sup>2</sup>C:N;-4:7κ<sup>2</sup>C:N;4:8κ<sup>2</sup>C:N-octacyano-1κ<sup>2</sup>C,2κ<sup>2</sup>C,3κ<sup>2</sup>C,4κ<sup>2</sup>C-tetracopper(II)-tetranickel(II).

Janiak, Scharmann, Albrecht *et al.*, 1996). Polynuclear Cu<sup>II</sup> complexes have been studied intensely because they form diverse novel structural networks, including chains, sheets and matrices (Chui *et al.*, 1999; Smith, 1998; Janiak, Scharmann, Günther *et al.*, 1996).

Hoffman-type clathrates, M(NH<sub>3</sub>)<sub>2</sub>M'(CN)<sub>4</sub>·2(guest), have a layered structure of square-meshed *trans*-diamminometal [M<sup>II</sup>] tetra-*catena*-μ-cyanometallate-[M'<sup>II</sup>] sheets, with M' = Ni, Pd or Pt (Dunbar & Heintz, 1997). Only one of these structures is known where M = Cu (Miyoshi *et al.*, 1973). We therefore attempted crystallization of additional cyano-bridged tetracyanonickelate-copper compounds. Ni is the predominant M' metal in these framework structures (Park & Iwamoto, 1992, 1993; Yuge & Iwamoto, 1994; Yuge *et al.*, 1995, 1997).

From the reaction of Cu<sup>2+</sup> in NH<sub>3</sub> with [Ni(CN)<sub>4</sub>]<sup>2-</sup>, a molecular copper-nickel complex was isolated, *i.e.* bis{tetraamminecopper(II)[*cis*-(dicyano)(μ-dicyano)-nickelate(II)]}-*cyclo*-bis{*trans*-diammine[*cis*-(dicyano)(μ-dicyano)nickelate(II)]copper(II)}, (I). The formation of a discrete complex rather than a coordination polymer was unexpected in view of the known coordination chemistry of [Ni(CN)<sub>4</sub>]<sup>2-</sup> anions. Normally, two-dimensional frameworks result (Park & Iwamoto, 1992, 1993; Yuge & Iwamoto, 1994; Yuge *et al.*, 1995, 1997). A two-dimensional network was also found in the closely related compound Cu(NH<sub>3</sub>)<sub>2</sub>Ni(CN)<sub>4</sub>·2C<sub>6</sub>H<sub>6</sub> (Miyoshi *et al.*, 1973).



As shown in Fig. 1, the discrete units of (I), which display C<sub>2h</sub> symmetry, are octanuclear and built up from four amminecopper and four tetracyanonickelate moieties. The arrangement may also be viewed as a dimer, with the two molecular parts related by a C<sub>2</sub> axis or a centre of inversion. Intermolecular contacts between the discrete units are provided by weak hydrogen bonds of the form N—H···N (Table 2).

The Ni/Cu assignment is based on the established stability of the [Ni(CN)<sub>4</sub>]<sup>2-</sup> species; this in turn determines the C/N identity. We note that otherwise the neighbouring Ni/Cu and C/N elements cannot be distinguished easily by crystallographic means alone.

The [Ni(CN)<sub>4</sub>]<sup>2-</sup> anions act as *cis* bridges between the Cu centres, thereby utilizing two CN groups as donors. There are two types of Cu centres and two types of tetracyanonickelate anions. One type of Cu centre (Cu2) seems at first sight to possess a trigonal-