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Thiocyanates of nickel and caesium: $Cs_2NiAg_2(SCN)_6{\cdot}2H_2O$ and $CsNi(SCN)_3$

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The crystal structures of dicaesium nickel disilver hexathiocyanate dihydrate, $Cs_2NiAg_2(SCN)_6{\cdot}2H_2O$, (I), and caesium nickel trithiocyanate, $CsNi(SCN)_3$, (II), have been determined by single-crystal X-ray diffraction at 273 K. Compounds (I) and (II) are monoclinic, with $P2_1/c$ and $P2_1/n$ symmetry, respectively. In (I), the Ni atom lies on an inversion centre; in (II), there are two independent Ni atoms, each of which lies on an inversion centre. The coordination polyhedra and the bonding schemes in the structures are discussed.

Comment

A detailed search of the literature revealed that more than 80 inorganic thiocyanates are known. They include two compounds containing nickel (*e.g.* Kuo Chan & Porai-Koshits, 1960) and 13 containing caesium (*e.g.* Bohatý & Fröhlich, 1992), but none that contain both. The NCS^- anion can interact with metal atoms in various ways, whereby both the N and S atoms can act as ligands forming covalent or ionic bonds, or simple van der Waals interactions. In the present structures, the Ni—N and Ag—S bonds are covalent, whereas the Ni—S bonds and all bonds to Cs are ionic.

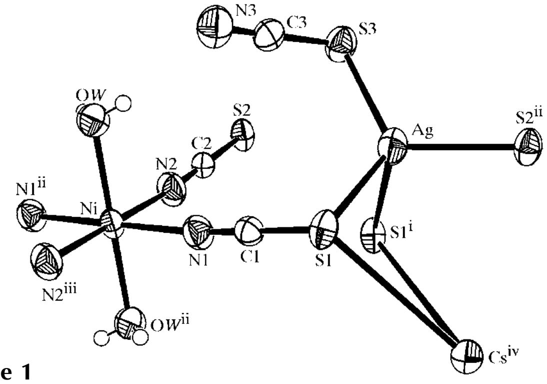

Figure 1
The connectivity in $Cs_2NiAg_2(SCN)_6{\cdot}2H_2O$, shown with displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) $x, -\frac{1}{2}-y, z-\frac{1}{2}$; (ii) $1-x, -y, 1-z$; (iii) $1-x, -y, 2-z$; (iv) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$.]

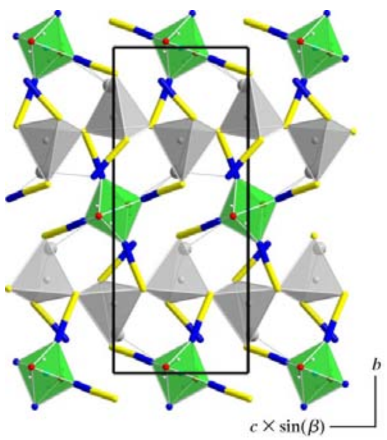

Figure 2
The structure of $Cs_2NiAg_2(SCN)_6{\cdot}2H_2O$, viewed along [100]. Note the star-like clusters of $Ni(SCN)_4(H_2O)_2$ connecting the infinite chains of Ag–S polyhedra. The S—C—N groups are represented as two-tone rods, and the Ag and Cs atoms are displayed as small and large grey spheres, respectively.

The structure of dicaesium nickel disilver hexathiocyanate dihydrate, (I) (Fig. 1), is characterized by corner-linked irregular $[AgS_4]$ tetrahedra forming chains along [001] (Fig. 3). The Ag—S1 bond length [2.7716 (14) Å] indicates an ionic rather than a covalent interaction, as estimated from the sums of the covalent and ionic radii of 2.55 and 2.84 Å, respectively (Sanderson, 1962; Sutton, 1965; Shannon, 1976). These polyhedral chains are interconnected by octahedral $[Ni(SCN)_4(H_2O)_2]$ groups, in which the central Ni atom forms four equatorial covalent Ni—N bonds and two apical Ni—O bonds. The Ag–(SCN)–Ni framework forms slightly puckered sheets parallel to (100). Cs atoms are located between these sheets and link them into a three-dimensional structure by forming ionic bonds with the thiocyanate groups (Fig. 2). In addition, hydrogen bonds are formed between the H atoms of the water molecules and the N atoms of adjacent sheets.

The structure of caesium nickel trithiocyanate, (II) (Fig. 3), is altogether different. The prominent features are the coordination polyhedra of the Ni atoms, which are of two different types. Atom Ni1 is [4+2]-coordinated, with four covalent Ni—N bonds [mean distance = 2.052 (2) Å; calculated sum of covalent radii = 1.96 Å] and two ionic Ni—S bonds [distances = 2.5411 (8) Å; calculated sum of ionic radii 2.53 Å]. The coordination polyhedron of atom Ni2 can be described as a [2+4] coordination, with two covalent Ni—N bonds [distances = 2.015 (2) Å] and four ionic Ni—S bonds [mean distance = 2.5204 (8) Å]. It is remarkable that the Ni atoms in the unit cell form a pseudo-tetragonal *F*-centred lattice. However, the irregularity of the polyhedra and the positions of the other atoms clearly show that the symmetry is monoclinic. The thiocyanate groups are all approximately parallel to the (010) plane, connecting the Ni polyhedra into sheets parallel to (010) (Fig. 4). The Cs atoms are located between these sheets and are connected to the thiocyanate groups by ionic bonds.

X-ray powder diffraction data have been collected for both compounds and the resulting data have been submitted to the powder diffraction file of the International Centre for Diffraction Data (JCPDS–ICDD).

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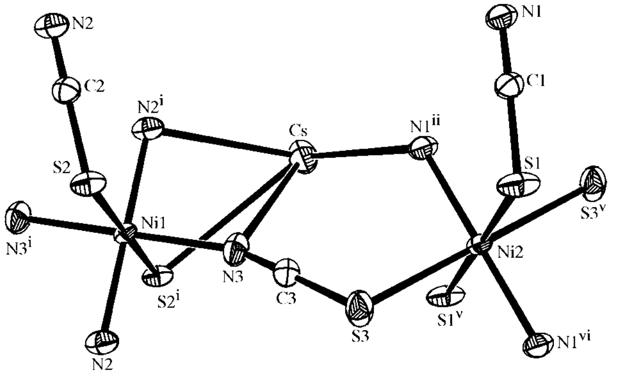

Figure 3
The connectivity in $CsNi(SCN)_3$, shown with displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) $2 - x, 2 - y, 2 - z$; (ii) $1 - x, 2 - y, 1 - z$; (v) $2 - x, 2 - y, 1 - z$; (vi) $1 + x, y, z$.]

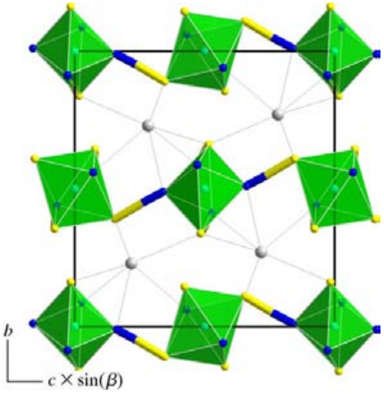

Figure 4
The structure of $CsNi(SCN)_3$, viewed along [100]. The $Ni(SCN)_2$ sheets parallel to (001) are orientated horizontally. The coding is as in Fig. 2.

Experimental

For compound (I), stoichiometric quantities of Cs_2CO_3 (1680 mg), $NiCl_2{\cdot}6H_2O$ (1089 mg), AgSCN (821 mg) and NH_4SCN (392 mg) were dissolved in approximately 150 ml of distilled water. For compound (II), stoichiometric quantities of Cs_2CO_3 (1702 mg), $NiCl_2{\cdot}6H_2O$ (1065 mg) and NH_4SCN (402 mg), and approximately 120 ml distilled water were used. The solutions were heated to a temperature of 353 K until the material had completely dissolved and the resulting solutions cooled to 293 K over a period of 14 d. The syntheses yielded small (up to 0.5 mm) blue [for (I)] or green [for (II)] crystals. In both cases, the products were accompanied by large colourless crystals of NH_4Cl. The products were picked manually from the supernatant liquors and washed carefully with distilled water.

Compound (I)

Crystal data

$Cs_2NiAg_2(SCN)_6{\cdot}2H_2O$
$M_r = 924.82$
Monoclinic, $P2_1/c$
$a = 7.503$ (2) Å
$b = 18.766$ (4) Å
$c = 7.733$ (2) Å
$\beta = 92.59$ (3)°
$V = 1087.7$ (5) Å^3
$Z = 2$
$D_x = 2.824$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3260 reflections
$\theta = 4.1$–30.0°
$\mu = 6.53$ mm^{-1}
$T = 293$ (2) K
Prism, blue
0.17 × 0.10 × 0.08 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (Otwinowski & Minor, 1997)
$T_{min} = 0.403$, $T_{max} = 0.623$
6227 measured reflections
3167 independent reflections
2538 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 30.0°$
$h = -10 \rightarrow 10$
$k = -26 \rightarrow 26$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.077$
$S = 1.05$
3167 reflections
124 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0279P)^2 + 2.7068P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 2.18$ e Å^{-3}
$\Delta\rho_{min} = -1.59$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0024 (2)

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

Ag—S3	2.5314 (13)	Cs—C2	3.573 (4)
Ag—S2^{i}	2.5316 (11)	Cs—S2^{iii}	3.5841 (15)
Ag—S1	2.5868 (13)	Cs—S1^{v}	3.6315 (12)
Ag—S1^{i}	2.7716 (14)	S1^{i}—Cs^{vi}	3.9860 (12)
Ni—N1	2.046 (3)	S1—C1	1.651 (4)
Ni—N2^{ii}	2.047 (3)	C1—N1	1.153 (5)
Ni—O*W*	2.126 (3)	S2—C2	1.645 (4)
Cs—O*W*	3.359 (3)	C2—N2	1.151 (5)
Cs—N3^{iii}	3.420 (5)	S3—C3	1.645 (4)
Cs—C2^{iv}	3.520 (4)	C3—N3	1.157 (6)
Cs—N2^{iv}	3.530 (4)		
N1—C1—S1	177.4 (4)	N3—C3—S3	177.4 (4)
N2—C2—S2	175.9 (4)		

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

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O*W*—H1*W*···N3	0.71 (8)	2.31 (8)	3.004 (6)	168 (8)
O*W*—H2*W*···N3^{i}	0.87 (5)	2.27 (5)	3.072 (5)	153 (4)

Symmetry code: (i) $2 - x, -y, 1 - z$.

Compound (II)

Crystal data

$CsNi(SCN)_3$
$M_r = 365.86$
Monoclinic, $P2_1/n$
$a = 5.5540$ (10) Å
$b = 13.294$ (3) Å
$c = 12.589$ (3) Å
$\beta = 96.87$ (3)°
$V = 922.8$ (3) Å^3
$Z = 4$
$D_x = 2.633$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2800 reflections
$\theta = 4.1$–30.0°
$\mu = 6.61$ mm^{-1}
$T = 293$ (2) K
Fragment, green
0.15 × 0.08 × 0.05 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (Otwinowski & Minor, 1997)
$T_{min} = 0.437$, $T_{max} = 0.734$
5137 measured reflections
2695 independent reflections
2441 reflections with $I > 2\sigma(I)$
$R_{int} = 0.014$
$\theta_{max} = 30.0°$
$h = -7 \rightarrow 7$
$k = -18 \rightarrow 17$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.057$
$S = 1.05$
2695 reflections
104 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0231P)^2 + 1.4456P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.40$ e Å^{-3}
$\Delta\rho_{\min} = -1.28$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0042 (4)

Table 3
Selected geometric parameters (Å, °) for (II).

Cs—N2^{i}	3.240 (2)	Ni1—S2	2.5411 (8)
Cs—N3	3.413 (3)	Ni2—N1^{vi}	2.015 (2)
Cs—C1^{ii}	3.462 (2)	Ni2—S3	2.4896 (8)
Cs—N1^{ii}	3.491 (2)	Ni2—S1	2.5511 (8)
Cs—S3^{iii}	3.5508 (9)	S1—C1	1.647 (2)
Cs—S2^{iv}	3.5798 (13)	C1—N1	1.154 (3)
Cs—S3^{v}	3.6317 (10)	S2—C2^{vi}	1.647 (2)
Cs—S2^{v}	3.6341 (10)	C2—N2	1.156 (3)
Cs—C2^{i}	3.702 (2)	S3—C3	1.651 (3)
Ni1—N2^{i}	2.043 (2)	C3—N3	1.152 (3)
Ni1—N3	2.061 (2)		
N1—C1—S1	178.4 (2)	N3—C3—S3	177.3 (2)
N2—C2—S2	179.6 (2)		

Symmetry codes: (i) $1-x, 2-y, 2-z$; (ii) $1-x, 2-y, 1-z$; (iii) $\frac{5}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iv) $2-x, 2-y, 2-z$; (v) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (vi) $1+x, y, z$.

The H atoms in (I) were refined freely. After the refinements, the residual electron-density maxima and minima were 2.18 (0.79 Å from Ag) and −1.59 e Å^{-3} (0.76 Å from Ag), respectively, for (I), and 1.40 (0.76 Å from Cs) and −1.28 e Å^{-3} (0.65 Å from Cs), respectively, for (II).

For both compounds, data collection: *COLLECT* (Nonius, 2003); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff *et al.*, 1996) and *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1042). Services for accessing these data are described at the back of the journal.

References

Bergerhoff, G., Berndt, M. & Brandenburg, K. (1996). *J. Res. Natl Inst. Stand. Technol.* **101**, 221–225.
Bohatý, L. & Fröhlich, R. (1992). *Z. Kristallogr.* **198**, 33–39.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Kuo Chan, C. & Porai-Koshits, M. A. (1960). *Kristallografiya*, **5**, 462–463. (In Russian.)
Nonius (2003). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sanderson, R. T. (1962). *Chemical Periodicity*. New York: Reinhold.
Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Sutton, L. E. (1965). *Table of Interatomic Distances and Configuration in Molecules and Ions*, Suppl. 1956–1959, Special Publication No. 18. London: Royal Chemical Society.