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Caesium Nickel(II) Trichloride, $CsNiCl_3$, and Tricaesium Nickel(II) Pentachloride, Cs_3NiCl_5

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Abstract

There are two congruently melting compounds in the $CsCl–NiCl_2$ system: orange $CsNiCl_3$ (absorption maximum 466 nm) and turquoise Cs_3NiCl_5 (654 nm). The different colours are caused by the different coordination polyhedra of the nickel(II) ions. In Cs_3NiCl_5, which crystallizes in the tetragonal space group *I4/mcm*, there are isolated $NiCl_4^{2-}$ tetrahedra, whereas in $CsNiCl_3$, which crystallizes in the hexagonal space group $P6_3/mmc$, the Ni^{2+} ions are octahedrally coordinated. These octahedra run parallel to [001] and share triangular faces.

Comment

There are two congruently melting compounds in the $CsCl–NiCl_2$ system: $CsNiCl_3$ and Cs_3NiCl_5 (Iberson *et al.*, 1962). Only powder data are available for the hexagonal perovskite $CsNiCl_3$ (Tishchenko, 1955; Minkiewicz *et al.*, 1970). Because of their similar X-ray powder patterns, Cs_3NiCl_5 was assumed to be isostructural with Cs_3CoCl_5 (Iberson *et al.*, 1962). If Cs_3NiCl_5 is isotypic with Cs_3CoCl_5 (Reynolds *et al.*, 1981), it is a rare example of a compound containing tetrahedrally coordinated Ni^{II} (Venanzi, 1958; Gill & Nyholm, 1959). Its structure is therefore of special interest.

$CsNiCl_3$ is stable at ambient temperature. At low temperatures, one-dimensional antiferromagnetic ordering occurs (Trudeau *et al.*, 1993). Cs_3NiCl_5 is metastable at room temperature, decomposing below 690 K to CsCl and $CsNiCl_3$, but can be quenched to ambient temperature (Iberson *et al.*, 1962). The instability of Cs_3NiCl_5 at ambient temperature may be caused by the much higher crystal-field stabilization energy of $NiCl_6$ octahedra compared to $NiCl_4$ tetrahedra (122.1 and 35.9 kJ mol^{-1}, respectively; Dunitz & Orgel, 1960). Some months after our measurements, the crystal we had studied had decomposed.

In $CsNiCl_3$ (Fig. 1), Ni^{II} is octahedrally coordinated by six Cl^- ions with an Ni—Cl distance of 2.4169 (6) Å. The slightly distorted octahedra run parallel to [001] and share triangular faces. Cs is anticuboctahedrally coordinated by 12 Cl^- ions with Cs—Cl distances between 3.5893 (5) and 3.7181 (12) Å.

In Cs_3NiCl_5 (Fig. 2), Ni is surrounded by four $Cl2^-$ ions at a distance of 2.245 (2) Å, establishing a nearly regular tetrahedron. The Cl2—Ni—Cl2 angles, 106.01 (11) and 111.23 (6)°, differ slightly from the ideal value of 109.47°. The two crystallographically non-equivalent Cs ions have different coordination. Cs1 displays a bicapped quadratic antiprismatic coordination by 10 Cl^- ions (8Cl2, 2Cl1) whereas the coordination of

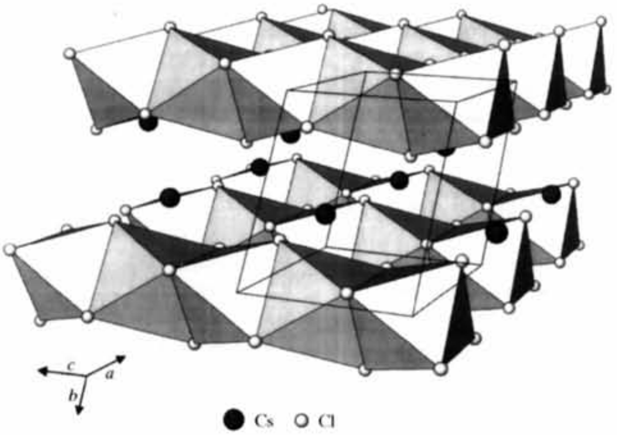

Fig. 1. The crystal structure of $CsNiCl_3$.

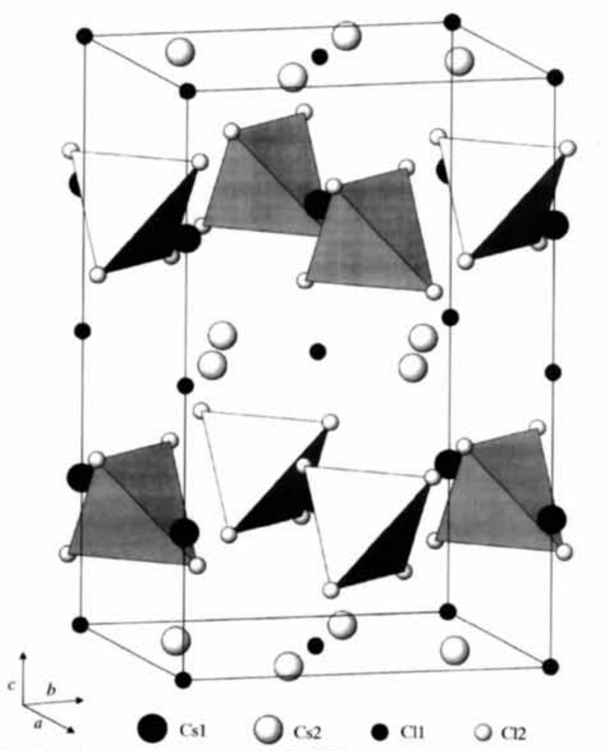

Fig. 2. The crystal structure of Cs_3NiCl_5.

Cs2 corresponds to a distorted bicapped trigonal prism (6Cl2, 2Cl1).

The different coordination of the Ni ions in these compounds results in different colours. Thus, Cs_3NiCl_5 is turquoise with an absorption maximum at 654 nm, whereas $CsNiCl_3$ is orange with an absorption maximum at 466 nm (Sassmannshausen, 1998). The Ni—Cl distances found in these compounds are significantly smaller than the characteristic *M*—Cl distances of all other bivalent metal ions (Lutz *et al.*, 1997) with the exception of tetrahedral Be—Cl bonds (2.028 Å; Gaebell & Meyer, 1984).

Experimental

Single crystals of $CsNiCl_3$ were obtained by melting a stoichiometric mixture of CsCl and $NiCl_2$ at 1043 K in a sealed glass ampoule and annealing the sample at 973 K for two weeks. Crystals of Cs_3NiCl_5 were obtained by melting a stoichiometric mixture of CsCl and $NiCl_2$ at 833 K in a sealed glass ampoule and annealing the sample at 803 K for two weeks. The sample was then quenched in ice–water.

$CsNiCl_3$

Crystal data

$CsNiCl_3$
$M_r = 297.97$
Hexagonal
$P6_3/mmc$
$a = 7.171$ (1) Å
$c = 5.944$ (3) Å
$V = 264.71$ (14) Å^3
$Z = 2$
$D_x = 3.738$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 15 reflections
$\theta = 7.1$–$42.0°$
$\mu = 11.774$ mm^{-1}
$T = 293$ (2) K
Needle
0.32 × 0.10 × 0.10 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{\min} = 0.245$, $T_{\max} = 0.308$
2344 measured reflections
247 independent reflections

227 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$
$\theta_{\max} = 34.60°$
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 9$
3 standard reflections
frequency: 120 min
intensity decay: 1.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.014$
$wR(F^2) = 0.031$
$S = 1.437$
247 reflections
10 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0146P)^2 + 0.0391P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.660$ e Å^{-3}
$\Delta\rho_{\min} = -0.783$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.061 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $CsNiCl_3$*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cs	1/3	2/3	3/4	0.02572 (10)
Ni	0	0	0	0.01536 (11)
Cl	0.15346 (4)	$2x$	1/4	0.01883 (11)

Table 2. *Selected geometric parameters (Å, °) for $CsNiCl_3$*

Cs—Cl$^{\rm i}$	3.5893 (5)	Ni—Cl	2.4169 (6)
Cs—Cl$^{\rm ii}$	3.7181 (12)		
Cl—Ni—Cl$^{\rm iii}$	93.84 (2)	Cl$^{\rm iii}$—Ni—Cl$^{\rm iv}$	180
Cl—Ni—Cl$^{\rm iv}$	86.16 (2)		

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

Cs_3NiCl_5

Crystal data

Cs_3NiCl_5
$M_r = 634.69$
Tetragonal
$I4/mcm$
$a = 9.224$ (2) Å
$c = 14.551$ (8) Å
$V = 1238.0$ (8) Å^3
$Z = 4$
$D_x = 3.405$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 16 reflections
$\theta = 11.2$–$28.5°$
$\mu = 11.276$ mm^{-1}
$T = 293$ (2) K
Plate
0.41 × 0.20 × 0.10 mm
Turquoise

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{\min} = 0.084$, $T_{\max} = 0.324$
1975 measured reflections
1055 independent reflections

650 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.074$
$\theta_{\max} = 39.86°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 26$
3 standard reflections
frequency: 120 min
intensity decay: 5.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.132$
$S = 1.070$
1055 reflections
18 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0610P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 2.17$ e Å^{-3}
$\Delta\rho_{\min} = -1.48$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0016 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for Cs_3NiCl_5*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cs1	0	0	1/4	0.0404 (2)
Cs2	0.16643 (4)	$x + 1/2$	0	0.0298 (2)
Ni	0	1/2	1/4	0.0265 (3)
Cl1	0	0	0	0.0335 (6)
Cl2	0.1374 (2)	$x + 1/2$	0.65716 (12)	0.0429 (4)

Table 4. *Selected geometric parameters (Å, °) for Cs_3NiCl_5*

$Cs1—Cl1^{i}$	3.638 (2)	$Cs2—Cl1^{iv}$	3.4386 (8)
$Cs1—Cl2^{ii}$	3.8231 (14)	$Cs2—Cl2^{v}$	3.627 (2)
$Cs2—Cl2^{iii}$	3.431 (2)	$Ni—Cl2^{vi}$	2.245 (2)
$Cl2^{vi}—Ni—Cl2^{vii}$	111.23 (6)	$Cl2^{vii}—Ni—Cl2^{viii}$	106.01 (11)

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

For Cs_3NiCl_5, residual electron density greater than 1 e Å^{-3} was observed. The largest positive peak in the final difference Fourier map was 0.70 Å from Cs2 and the largest negative peak was 0.69 Å from Cs2.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *LSUCR* (Evans *et al.*, 1963); data reduction: *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ATOMS* (Dowty, 1995); software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1253). Services for accessing these data are described at the back of the journal.

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New Compounds Containing the Complex Anion $[Ta_2S_{11}]^{4-}$; $A_4Ta_2S_{11}$ (A = Rb, Cs)

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Abstract

The new tetra(alkali metal) ditantalum undecasulfides $A_4Ta_2S_{11}$ (A = Rb, Cs) were prepared at low temperature *via* the molten-flux method. The crystal structures consist of well separated A^+ and $[Ta_2S_{11}]^{4-}$ ions. Within the anions, the Ta atoms display a sevenfold coordination by S_2^{2-} units and S^{2-} anions; the coordination polyhedra can be described as distorted pentagonal bipyramids. Two such bipyramids share common faces, thus forming the $[Ta_2S_{11}]^{4-}$ anion.

Comment

Reactions in molten alkali–polychalcogenide melts (Sunshine *et al.*, 1987) have led to a wide variety of new compounds with interesting new structures (Kanatzidis & Sutorik, 1995). During our investigations into the reaction of group V metals with such melts, we were able to prepare a number of new ternary chalcogenometallates, *e.g.* $K_4Nb_2S_{11}$ (Bensch & Dürichen, 1996*a*), $K_6Nb_4S_{25}$ (Bensch & Dürichen, 1996*b*), $K_4Nb_2S_{14}$ (Bensch & Dürichen, 1997), $A_6Nb_4S_{22}$ (A = Rb, Cs; Bensch & Dürichen, 1996*c*) and $NaNbS_6$ (Bensch *et al.*, 1998). Most of these contain an Nb_2S_{11} unit of two face-sharing pentagonal bipyramids as a main structural 'building block'. The tendency to form this unit is also documented for the lighter homologue vanadium, for example, $[V_2S_{20}O_4]^{6-}$ (Simonnet-Jegat *et al.*, 1996), and for group VI chalcogenometallates as in the complex anions $[Mo_2S_9O_2]^{2-}$ (Coucouvanis & Hadjikyriacou, 1987) and $[W_2S_{11}]^{2-}$ (Manoli *et al.*, 1987).

The title compounds $Rb_4Ta_2S_{11}$ and $Cs_4Ta_2S_{11}$ are isotypic with the previously reported sulfides $K_4Ta_2S_{11}$ (Schreiner *et al.*, 1989) and $K_4Nb_2S_{11}$ (Bensch & Dürichen, 1996*a*). Their structures consist of complex $[Ta_2S_{11}]^{4-}$ anions that are well separated from the alkali cations. The complex anion $[Ta_2S_{11}]^{4-}$ is best described as two face-sharing distorted pentagonal TaS_7 bipyramids. In both bipyramids, one apical position is occupied by a terminal monosulfide S^{2-} anion and the second by one S atom of a neighbouring S_2^{2-} dumbbell. Within the pentagonal plane, two η^2-bound S_2^{2-} units and one μ_2-S^{2-} unit bridging the two Ta^{5+} centres are

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