

M2_Nb‡	0.24700	0.2473	0.2528	0.0043
M2_Al†	0.24700	0.2473	0.2528	0.0043
As1_As§	0.49872 (5)	0.2519 (1)	0.32209 (6)	0.0062 (9)
As1_Nb¶	0.49872	0.2519	0.32209	0.0062
As2_As§	0.18725 (3)	0.50045 (12)	0.50368 (10)	0.0072 (10)
As2_Nb¶	0.18725	0.50045	0.50368	0.0072
O1	0.4870 (4)	0.1323 (5)	0.4882 (9)	0.0140 (13)
O2	0.5043 (4)	0.3811 (5)	0.4693 (11)	0.0107 (11)
O3	0.3930 (3)	0.2645 (6)	0.1779 (6)	0.0118 (11)
O4	0.6027 (3)	0.2332 (4)	0.1751 (6)	0.0062 (10)
OM1	0.2231 (4)	0.6249 (5)	-0.0559 (10)	0.0100 (13)
OM2	0.2204 (4)	0.3735 (5)	0.0585 (9)	0.0076 (12)
O5	0.1114 (3)	0.5397 (5)	0.3054 (6)	0.0103 (9)
O6	0.1088 (3)	0.4644 (4)	0.7011 (6)	0.0087 (10)
O7	0.2644 (4)	0.6224 (5)	0.5489 (10)	0.0091 (13)
O8	0.2616 (4)	0.3762 (5)	0.4538 (10)	0.0104 (13)

† Site occupancy = 0.980 (2). ‡ Site occupancy = 0.020 (2). § Site occupancy = 0.800 (10). ¶ Site occupancy = 0.200 (10).

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

M1—OM1'	1.823 (5)	M2—O4''	1.942 (4)
M1—OM2'	1.815 (5)	M2—O3	1.972 (4)
M1—O6''	2.035 (4)	As1—O4	1.677 (4)
M1—O5'	2.082 (4)	As1—O1	1.683 (6)
M1—O2'''	2.094 (5)	As1—O3	1.679 (4)
M1—O1	2.091 (5)	As1—O2	1.694 (6)
M2—OM1'	1.858 (6)	As2—O7	1.668 (5)
M2—OM2	1.892 (6)	As2—O8	1.671 (6)
M2—O7''	1.900 (6)	As2—O6	1.701 (4)
M2—O8	1.921 (6)	As2—O5	1.694 (4)
OM1'—M1—OM2'	99.8 (2)	OM1'—M2—O4''	88.9 (3)
OM1'—M1—O6''	91.9 (2)	OM2—M2—O4''	92.7 (4)
OM2'—M1—O6''	99.3 (2)	O7''—M2—O4''	92.6 (3)
OM1'—M1—O5'	97.4 (2)	O8—M2—O4''	88.8 (4)
OM2'—M1—O5'	91.3 (2)	OM1'—M2—O3	91.5 (4)
O6''—M1—O5'	164.4 (2)	OM2—M2—O3	86.9 (4)
OM1'—M1—O2'''	167.7 (2)	O7''—M2—O3	87.7 (4)
OM2'—M1—O2'''	96.0 (2)	O8—M2—O3	90.9 (4)
O6''—M1—O2'''	71.6 (2)	O4''—M2—O3	179.5 (5)
O5'—M1—O2'''	96.1 (2)	O4—As1—O1	111.1 (2)
OM1'—M1—O1	89.0 (2)	O4—As1—O3	109.9 (2)
OM2'—M1—O1	82.3 (2)	O1—As1—O3	111.2 (3)
O6''—M1—O1	89.0 (2)	O4—As1—O2	113.1 (2)
O5'—M1—O1	78.8 (2)	O1—As1—O2	104.0 (3)
O2'''—M1—O1	77.9 (2)	O3—As1—O2	107.0 (3)
OM1'—M2—OM2	178.1 (4)	O7—As2—O8	107.7 (3)
OM1'—M2—O7''	90.3 (3)	O7—As2—O6	113.5 (3)
OM2—M2—O7''	89.9 (4)	O8—As2—O6	108.7 (3)
OM1'—M2—O8	90.2 (4)	O7—As2—O5	107.3 (3)
OM2—M2—O8	89.0 (5)	O8—As2—O5	112.3 (3)
O7''—M2—O8	178.3 (4)	O6—As2—O5	107.6 (2)

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

Possible space groups assigned from X-ray photographs are $Pnma$ and $Pn2_1a$ for systematic absences $h = 2n + 1$ for $hk0$ and $k + l = 2n + 1$ for $0kl$. In this study, the same space group as KTP ($Pn2_1a$; Tordjman *et al.*, 1974) was assumed as the correct space group. The structure parameters of KTP were adopted as the initial parameters of KNAA. The Friedel pairs were averaged and 2698 reflections were obtained.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSCIAFC Diffractometer Control Software*. Program(s) used to refine structure: modified from the 1977 *ORXFLS4* version of *ORFLS* (Busing *et al.*, 1962).

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Zinc cadmium thiocyanate (ZCTC)

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Abstract

The title complex, zinc cadmium tetrathiocyanate, $[\text{ZnCd}(\text{SCN})_4]_n$, contains slightly flattened ZnN_4 and CdS_4 tetrahedra. The $-\text{S}=\text{C}=\text{N}-$ bridges connect Zn and Cd atoms, forming infinite three-dimensional $-\text{Cd}-\text{S}=\text{C}=\text{N}-\text{Zn}-$ networks, and are essentially linear at C and N, but bent at S. The structure exhibits a high non-linear optical property, and physical and chemical stability.

Comment

Recently, organometallic and coordination complexes have emerged as potential building blocks for second-order non-linear optical (NLO) materials (Long, 1995; Tian *et al.*, 1997). Compared with organic molecules,

metal complexes offer a large variety of structures, comparable or, in some cases, higher environmental stability, and a much greater diversity of tunable electronic properties by virtue of the coordinated metal centre. We have previously reported the NLO crystal structure of cadmium mercury thiocyanate (CMTC; Yuan *et al.*, 1997), which can generate second harmonic blue-violet light by using GaAlAs laser diodes to pump. As part of continuing work, we report here the crystal structure and properties of another thiocyanate complex, namely zinc cadmium thiocyanate, ZnCd(SCN)₄. The properties of the new crystal have some better characteristics than those of CdHg(SCN)₄, such as UV transparency, cutoff, thermal stability *etc.*

The thiocyanate ion can bind to metal ions through either the S or N atom (Yamaguchi *et al.*, 1985; Ozutsumi *et al.*, 1989). In this structure, the metal ions are surrounded tetrahedrally by four N atoms, with a Zn—N bond distance of 1.967 (5) Å and with angles of 107.09 (15) and 114.3 (3)° for Zn^{II}, and by four S atoms, with a Cd—S bond distance of 2.5640 (12) Å and with angles of 117.74 (6) and 105.50 (3)° for Cd^{II}. The hard and soft acid and base concept (Pearson, 1963; Balarew & Duhlew, 1984) rationalizes that the thiocyanate ions are coordinated *via* the hard N and soft S atoms in the formation of a tetrahedral complex with the hard Zn^{II} and soft Cd^{II} acceptors, respectively. The C—N bond distance is slightly longer than a normal triple bond, while the S—C bond is slightly shorter than a normal single bond due to the thiocyanate ion functioning as a bridging ligand. The thiocyanate bridges are essentially

linear at C and N, and bent at S. The structure contains two kinds of slightly distorted tetrahedral coordination; one is ZnN₄, the other CdS₄. The thiocyanate bridges lead to the formation of an infinite three-dimensional network and provide the crystal with a larger domain ion polarization, which in turn, we believe, induces a larger macroscopic non-linearity than that of the sum of the individual dipolar SCN, octupolar ZnN₄ and CdS₄ groups (Zyss, 1991). The second harmonic generation (SHG) effect of the crystals was studied on a powder sample; it was found to be superior to urea.

Experimental

Aqueous solutions of Zn(NCS)₂·2H₂O (2.18 g, 10 mmol, in 50 ml) and Cd(NCS)₂ (2.28 g, 10 mmol, in 50 ml) were mixed and stirred for 2 h. The resulting white solid was filtered off, washed with water, recrystallized from hot water, and dried over P₂O₅ (yield 2.8 g, 69%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of an aqueous solution.

Crystal data

ZnCd(SCN)₄

M_r = 410.09

Tetragonal

I $\bar{4}$

a = 11.135 (2) Å

c = 4.376 (1) Å

V = 542.6 (2) Å³

Z = 2

D_x = 2.510 Mg m⁻³

D_m not measured

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 3–12°

μ = 4.90 mm⁻¹

T = 293 (2) K

Parallelepiped

0.20 × 0.15 × 0.15 mm

Colourless

Data collection

Nicolet R3m/E diffractometer

ω–2θ scans

Absorption correction:

ψ scan (SHELXTL; Sheldrick, 1984)

T_{min} = 0.448, *T_{max}* = 0.479

807 measured reflections

554 independent reflections (plus 77 Friedel-related reflections)

612 reflections with

I > 2σ(*I*)

R_{int} = 0.048

θ_{max} = 32.51°

h = –6 → 16

k = –16 → 16

l = –6 → 6

3 standard reflections

every 97 reflections

intensity decay: none

Refinement

Refinement on *F*²

R [*F*² > 2σ(*F*²)] = 0.028

wR (*F*²) = 0.094

S = 1.264

631 reflections

33 parameters

w = 1/[σ²(*F_o*²) + (0.0619*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.575 e Å⁻³

Δρ_{min} = –0.680 e Å⁻³

Extinction correction:

SHELXL93

Extinction coefficient:

0.074 (6)

Scattering factors from

International Tables for Crystallography (Vol. C)

Absolute structure:

Flack (1983)

Flack parameter = 0.03 (4)

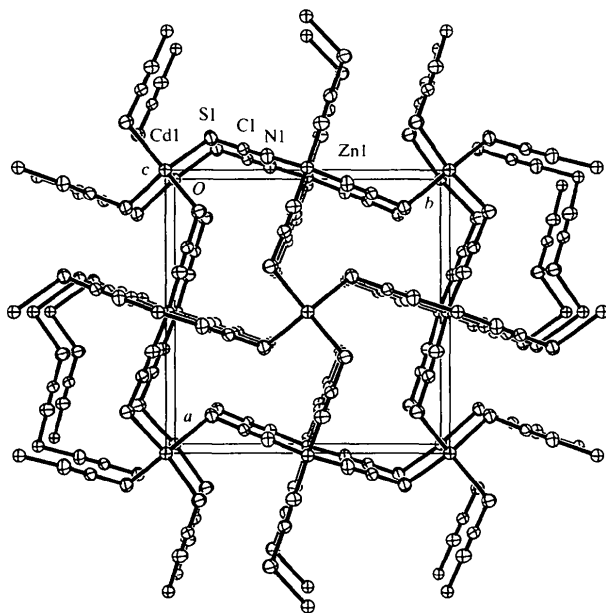


Fig. 1. The crystal structure of ZCTC with 50% probability ellipsoids and labelling of the unique atoms.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{\text{eq}} = (1/3) \sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Cd1	0	0	0	0.0318 (2)
Zn1	0	1/2	1/4	0.0305 (3)
S1	-0.12450 (11)	0.15280 (11)	-0.3029 (3)	0.0340 (3)
C1	-0.0783 (4)	0.2734 (4)	-0.1177 (11)	0.0298 (8)
N1	-0.0480 (4)	0.3596 (3)	0.0064 (13)	0.0385 (8)

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

Cd1—S1 ⁱ	2.5640 (12)	Zn1—N1 ^{iv}	1.967 (5)
Cd1—S1 ⁱⁱ	2.5640 (12)	Zn1—N1 ^v	1.967 (5)
Cd1—S1	2.5640 (12)	Zn1—N1 ^{vi}	1.967 (5)
Cd1—S1 ⁱⁱⁱ	2.5640 (12)	S1—C1	1.651 (5)
Zn1—N1	1.967 (5)	C1—N1	1.153 (6)
S1 ⁱ —Cd1—S1 ⁱⁱ	117.74 (6)	N1 ^{iv} —Zn1—N1 ^v	107.09 (15)
S1 ⁱ —Cd1—S1	105.50 (3)	N1 ^v —Zn1—N1 ^{vi}	107.09 (15)
S1 ⁱⁱ —Cd1—S1	105.50 (3)	N1 ^{iv} —Zn1—N1 ^{vi}	114.3 (3)
S1 ⁱ —Cd1—S1 ⁱⁱⁱ	105.50 (3)	N1 ^v —Zn1—N1 ^{vi}	107.09 (15)
S1 ⁱⁱ —Cd1—S1 ⁱⁱⁱ	105.50 (3)	C1—S1—Cd1	96.76 (15)
S1—Cd1—S1 ⁱⁱⁱ	117.74 (6)	N1—C1—S1	178.1 (4)
N1—Zn1—N1 ^{iv}	107.09 (15)	C1—N1—Zn1	175.2 (5)
N1—Zn1—N1 ^v	114.3 (3)		

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

Data collection: *P3* (Nicolet, 1985). Cell refinement: *P3*. Data reduction: *SHELXTL* (Sheldrick, 1984). Program(s) used to solve structure: *SHELXTL*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1297). Services for accessing these data are described at the back of the journal.

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Polyphosphates de strontium $\text{Sr}(\text{PO}_3)_2$ formes β et γ

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Abstract

Two polymorphic phases of strontium polyphosphate were prepared by solid-state reactions. The structure of β - $\text{Sr}(\text{PO}_3)_2$ is a redetermination. The structure of γ - $\text{Sr}(\text{PO}_3)_2$ was solved and contains $(\text{PO}_3)_n$ chains and SrO_8 polyhedra. $(\text{PO}_3)_n$ chains cross the cell along the *a* direction. Their repeat unit is two PO_4 tetrahedra. SrO_8 polyhedra are connected by edge-sharing to form infinite chains, which are further interconnected by edge-sharing to form double chains parallel to *a*. The $(\text{PO}_3)_n$ groups link these double chains to build three-dimensional networks.

Commentaire

On relève en bibliographie trois formes cristallines de polyphosphates de strontium: α - $\text{Sr}(\text{PO}_3)_2$ (Ropp *et al.*, 1959), β - $\text{Sr}(\text{PO}_3)_2$ (Durif *et al.*, 1972; Olbertz *et al.*, 1997; Jansen & Kindlery, 1997) et γ - $\text{Sr}(\text{PO}_3)_2$

(Ropp *et al.*, 1959). L'affinement de la structure de la forme β par Olbertz *et al.* (1997) a conduit au facteur de fiabilité $R(F) = 0,087$. Une redétermination de la structure par Jansen & Kindlery la même année, a conduit aux facteurs de fiabilité $R(F) = 0,053$ et $wR = 0,126$. La redétermination de la structure de β - $\text{Sr}(\text{PO}_3)_2$ a permis d'améliorer ces valeurs [$R(F) = 0,034$ et $wR = 0,086$]. Cette structure est formée de chaînes polyphosphates $(\text{PO}_3)_n$ de période quatre et de rubans $(\text{Sr}_4\text{O}_{22})_n$ se développant selon l'axe *a*. Ces rubans sont des chaînes simples de polyèdres $\text{Sr}(1)\text{O}_8$ et $\text{Sr}(2)\text{O}_7$ partageant des faces, assemblées latéralement en doubles chaînes par mises en commun d'arêtes (Fig. 1). Contrairement à la forme β de $\text{Sr}(\text{PO}_3)_2$, la forme γ n'a fait l'objet d'aucune étude structurale. Pourtant son existence a été signalée depuis 1959 (Ropp *et al.*, 1959). La structure de γ - $\text{Sr}(\text{PO}_3)_2$ établie dans ce travail, possède une charpente tridimensionnelle mixte formée de tétraèdres PO_4 et de bipyramides SrO_8 à bases carrés distordus, partageant des sommets et des arêtes. Cet empilement est caractérisé par une alternance de couches anioniques, où se disposent des chaînes polyphosphates non liées entre elles, et de couches cationiques formées de rubans $(\text{Sr}_2\text{O}_{10})_n$ également non liés entre eux (Fig. 2). Les chaînes polyphosphates se