C43	0.2658 (3)	0.6479 (3)	0.4375 (2)	0.0441 (7)
C44	0.3089 (4)	0.6858 (3)	0.3535 (3)	0.0674 (12)
C45	0.3596 (5)	0.6227 (4)	0.2784 (3)	0.081 (2)
C46	0.3674 (4)	0.5218 (4)	0.2859 (3)	0.0734 (13)
C47	0.3254 (4)	0.4837 (3)	0.3689 (3)	0.0693 (12)
C48	0.2741 (4)	0.5455 (3)	0.4434 (3)	0.0563 (9)
C49	0.2171 (3)	0.8495 (3)	0.5004 (3)	0.0481 (8)
C50	0.3020 (3)	0.8856 (3)	0.5212 (3)	0.0568 (9)
C51	0.3242 (4)	0.9765 (3)	0.4851 (4)	0.0762 (14)
C52	0.2611 (5)	1.0304 (4)	0.4326 (5)	0.088 (2)
C53	0.1760 (5)	0.9970 (4)	0.4146 (5)	0.093 (2)
C54	0.1535 (4)	0.9060 (3)	0.4487 (4)	0.0725 (13)
N1	0.4128 (3)	0.7185 (3)	0.6988 (3)	0.0641 (9)
C55	0.4835 (3)	0.7397 (3)	0.7230 (3)	0.0559 (9)
S1	0.58586 (10)	0.76794 (10)	0.75668 (12)	0.0858 (4)
C56	0.4851 (5)	0.0321 (4)	0.7830 (5)	0.093 (2)
Cl1	0.3948 (2)	0.0104 (2)	0.7154 (2)	0.1388 (8)
Cl2	0.5300 (2)	0.1431 (2)	0.7405 (2)	0.1490 (9)
Cl3	0.4293 (4)	0.0500 (3)	0.8981 (2)	0.231 (2)

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

Ag1—N1	2.319 (4)	P2—C25	1.816 (4)
Ag1—P1	2.5431 (9)	P2—C31	1.833 (4)
Ag1—P2	2.5967 (9)	P3—C37	1.828 (4)
Ag1—P3	2.5561 (9)	P3—C43	1.824 (4)
P1—C1	1.837 (4)	P3—C49	1.825 (4)
P1—C7	1.824 (4)	N1—C55	1.145 (5)
P1—C13	1.823 (4)	C55—S1	1.635 (4)
P2—C19	1.832 (4)		

N1—Ag1—P1	103.36 (10)	C43—P3—Ag1	122.95 (11)
N1—Ag1—P3	107.89 (10)	C49—P3—Ag1	112.07 (13)
P1—Ag1—P3	114.73 (3)	C2—C1—P1	117.2 (3)
N1—Ag1—P2	102.58 (10)	C6—C1—P1	123.9 (3)
P1—Ag1—P2	114.73 (3)	C12—C7—P1	122.5 (3)
P3—Ag1—P2	112.12 (3)	C8—C7—P1	118.7 (3)
C7—P1—C1	102.4 (2)	C18—C13—P1	118.5 (3)
C13—P1—C1	104.6 (2)	C14—C13—P1	122.3 (3)
C13—P1—C7	102.4 (2)	C20—C19—P2	123.0 (3)
C1—P1—Ag1	112.83 (11)	C24—C19—P2	118.3 (3)
C7—P1—Ag1	114.74 (11)	C26—C25—P2	123.7 (3)
C13—P1—Ag1	118.08 (12)	C30—C25—P2	117.7 (3)
C25—P2—C19	104.1 (2)	C32—C31—P2	122.9 (3)
C25—P2—C31	102.7 (2)	C36—C31—P2	117.4 (3)
C19—P2—C31	101.6 (2)	C38—C37—P3	123.0 (3)
C19—P2—Ag1	115.47 (11)	C42—C37—P3	117.8 (3)
C25—P2—Ag1	112.16 (12)	C44—C43—P3	123.5 (3)
C31—P2—Ag1	118.91 (12)	C48—C43—P3	118.6 (3)
C43—P3—C37	102.6 (2)	C54—C49—P3	123.6 (3)
C49—P3—C37	105.6 (2)	C50—C49—P3	117.1 (3)
C43—P3—C49	101.8 (2)	C55—N1—Ag1	159.6 (3)
C37—P3—Ag1	110.18 (12)	N1—C55—S1	178.8 (4)

The H atoms were placed in calculated positions and subsequently constrained to ride on the atoms to which they are attached. The extreme values in the final difference map occur around the Cl atoms of the chloroform molecule; otherwise the map is featureless.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990) (direct methods). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*, *PARST* (Nardelli, 1983). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1253). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Molecular Adducts of Inorganic Salts. VI. The Dimorphism of Cd(ReO4)2.2tu (tu = Thiourea)

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Abstract

The title compound, cadmium tetraoxorhenium bis(thiourea), $Cd(ReO_4)_2.2CH_4N_2S$, forms two polymorphs: monoclinic, (I), and triclinic, (II). Both are built up from infinite chains in which the Cd atoms are hexacoordinate. In (I), the centrosymmetric CdO_4S_2 octahedra are interlinked by double ReO_4 bridges, while in (II), CdO_3S_3 octahedra are connected by alternating double ReO_4 and S bridges. The Cd—S coordination bond length is 2.495 (2) Å in (I) and ranges from 2.576 (2) to 2.719 (2) Å in (II). The hydrogen bonding between chains is more developed in compound (II).

Comment

Among the thiourea (tu) addition compounds, polymorphic species have been found previously for Pb(ClO₄)₂.6tu (Boeyens & Herbstein, 1967; Goldberg & Herbstein, 1972) and suggested for Pb(ReO₄)₂.6tu (Angelova, 1995). Of the tu adducts of cadmium salts known so far, Cd(ReO₄)₂.2tu is the first example of dimorphic crystals coexisting under ambient conditions.

(I)

(II)
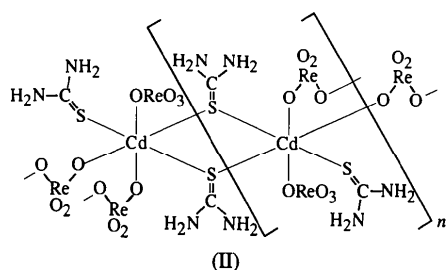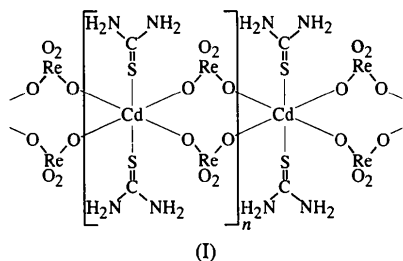
Both structures are built up from infinite chains in which the Cd atoms are octahedrally coordinated (Figs. 1 and 2). The Cd atom in the monoclinic form, (I), is located at a centre of symmetry and is coordinated by
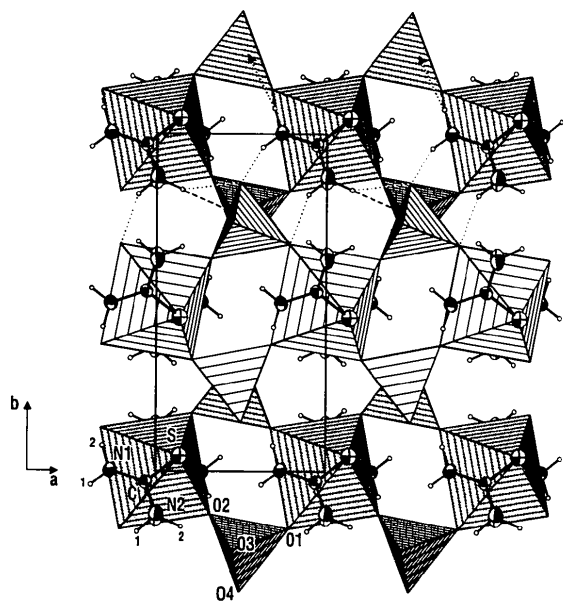

Fig. 1. A view of the packing in the monoclinic form of Cd(ReO₄)₂.2tu with the atom-numbering scheme. The displacement ellipsoids are drawn at the 30% probability level and H atoms are arbitrarily reduced. Dashed and dotted lines represent intra- and interchain hydrogen bonds, respectively.

Fig. 2. A view of the packing in the triclinic form of Cd(ReO₄)₂.2tu with the atom-numbering scheme. The displacement ellipsoids are drawn at the 30% probability level and H atoms are arbitrarily reduced. Dashed and dotted lines represent intra- and interchain hydrogen bonds, respectively.
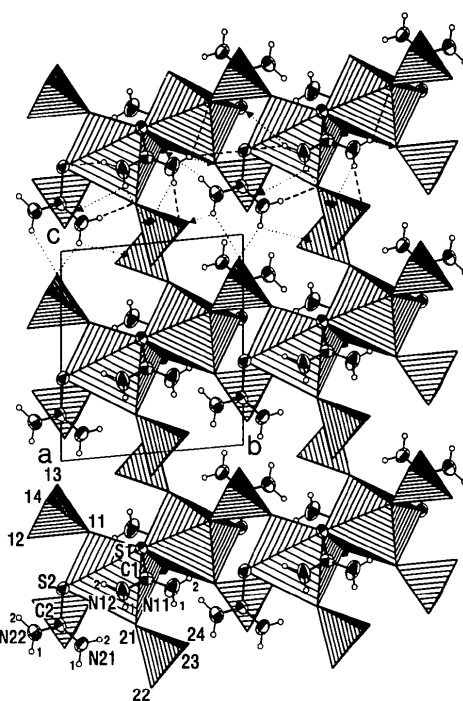
four perrhenate O atoms and two *trans*-disposed tu S atoms in an almost regular octahedral environment. In comparison, in the analogous Cd(ReO₄)₂.2(urea) adduct (Angelova, Macíček, Petrova, Todorov & Mihailova, 1996), the urea molecules are *cis* positioned. Cadmium polyhedra are linked by double T bridges (T = ReO₄) and the tu molecules are terminal. Thus, the chains in (I) differ from those in bis(thiourea)cadmium formate (Nardelli, Fava Gasparri & Boldrini, 1965) and bis-(thiourea)cadmium thiocyanate (Domiano, Manfredotti, Grossoni, Nardelli & Vidoni Tani, 1969), where the cadmium polyhedra are interlinked by S bridges and the counteranions are *trans*-terminal.

The coordination polyhedron of Cd in the triclinic form, (II), is a highly distorted octahedron of three perrhenate O and three S atoms in a *mer* configuration. The Cd octahedra share a common S···S edge and form centrosymmetric pairs which are linked by double T bridges in a zigzag chain. The remaining O and S vertices come from terminal groups (Fig. 2). An analogous chain type has been found in the structure of potassium tetrafluoro-tetraoxodisulfatodiuranate(VI) hydrate (Alcock, Roberts & Chakravorti, 1980). The topological schemes of the chain types in compounds (I) and (II) are given in Fig. 3.

The Cd—O distances of 2.406 (6) and 2.419 (6) Å for O1 and O2, respectively, in (I) are close to the Cd—S distance of 2.495 (2) Å; this bond length corre-
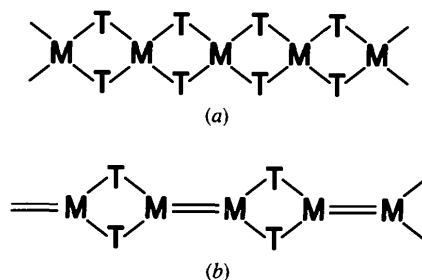
Fig. 3. Topological representation of the chain types (*a*) in compound (I) and (*b*) in (II). M=M denotes Cd–S$_2$–Cd thiourea bridges and M–T$_2$–M denotes Cd–(ReO$_4$)$_2$–Cd ReO$_4$-tetrahedra bridges.

sponds to a bond valence (Brown & Altermatt, 1985) of 0.598 v.u. compared with values of 0.247 and 0.257 v.u. for the corresponding Cd—O bonds. The Cd—S distance is slightly shorter than the typical terminal coordination bond length of 2.533 (1) Å at the hexacoordinated Cd atom in [Cd(CH$_3$COO)$_2$].2tu (Bondar, Rau, Struchkov, Akimov, Molodkin, Ilyuhin & Belov, 1980) and is close to the terminal bond lengths of between 2.496 (6) and 2.56 (1) Å at the tetrahedrally coordinated Cd atom in tetrakis(*N*,*N'*-dimethylthiourea)cadmium(II) nitrate (Rodesiler, Charles, Griffith & Amma, 1983), and values of 2.497 (1) and 2.499 (2) Å in (dinitrato)-bis(tetramethylthiourea)cadmium(II) (Griffith, Charles, Rodesiler & Amma, 1983). In compound (II), the Cd—O distances are shorter and vary between 2.338 (10) and 2.374 (6) Å, while the Cd—S distances are between 2.576 (2) and 2.719 (2) Å. Such a distribution of the Cd—S distances [2.52 (1)–2.63 (2) Å] has been found in the dimeric structure of tris(thiourea)cadmium sulfate (Corao & Baggio, 1969; Cavalca, Chiesi Villa, Mangia & Palmieri, 1970). The Cd—O bond-valence distribution at the Cd atom in compound (II) is between 0.281 and 0.309 v.u., and the Cd—S bond-valence distribution is between 0.326 and 0.480 v.u.

The Cd—S—C—N1 torsion angle of 72.6 (7)° in compound (I) shows that the Cd atom is well out of the plane of the terminal tu molecule; the Cd—S—C angle is 99.0 (3)°. In compound (II), the bridging tu molecule is tilted in the same manner with Cd—S1—C1—N12 −65.2 (8), Cd—S1—C1 99.4 (4) and Cd(1 − *x*, 1 − *y*, 1 − *z*)—S1—C1 112.9 (3)°, while the terminal tu molecule is exactly in-plane coordinated, with a Cd—S2—C2 angle of 113.1 (3)°. The angles within the four-membered Cd$_2$S$_2$ ring are S1—Cd—S1 85.5 (1) and Cd—S1—Cd 94.5 (1)°.

Although it was not possible to locate the H atoms, the rigid geometry of the tu molecules makes it feasible to place them in calculated positions and to discuss the corresponding hydrogen bonds (Table 5). The contacts have been divided into two groups, *i.e.* intra- and interchain hydrogen bonds, of which the former are of particular interest because they should contribute to the stabilization of the local atomic arrangement

of the corresponding polymorph after the coordination has occurred. As seen from Table 5 and the figures, the two intrachain hydrogen bonds in compound (I) are weak and part of bifurcated hydrogen bonds. In compound (II), the chains are embraced on both sides by continuous N11—H···S2···H—N12 hydrogen bonding. In addition, there is one almost linear intrachain N21—H212···O21 bond. Thus, it seems that the complicated hydrogen-bonding scheme is a significant stabilizing factor for the more irregular structure of the second polymorph, while stabilization of the structure of (I) comes from the strong *trans*-Cd—S bonding.

Experimental

The two title polymorphs crystallize simultaneously from an aqueous solution of stoichiometric amounts of Cd(ReO$_4$)$_2$ and thiourea. Pure phases were obtained from different solvents, *i.e.* compound (I) from cresol and compound (II) from ethanol.

Compound (I)

Crystal data

Cd(ReO$_4$)$_2$.2CH$_4$N$_2$S	Mo *K*α radiation
M$_r$ = 765.03	λ = 0.71073 Å
Monoclinic	Cell parameters from 22
*P*2$_1$/*c*	reflections
a = 5.935 (4) Å	θ = 20.53–21.89°
b = 11.358 (1) Å	μ = 19.18 mm^{-1}
c = 10.490 (2) Å	*T* = 292 K
β = 94.66 (1)°	Prismatic
V = 704.8 (3) Å^3	0.13 × 0.13 × 0.09 mm
Z = 2	Colourless
D$_x$ = 3.604 Mg m^{-3}	
D$_m$ not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	4469 measured reflections
Continuous profile scans	2050 independent reflections
Absorption correction: empirical based on ψ scans (North, Phillips & Mathews, 1968) and spherical (*r* = 0.06 mm; θ dependence)	1772 observed reflections [*I* > 3.0σ(*I*)]
	R$_{int}$ = 0.043
	θ$_{max}$ = 30.0°
	h = 0 → 8
	k = −16 → 16
T$_{min}$ = 0.035, *T$_{max}$* = 0.107	*l* = −14 → 14
	3 standard reflections frequency: 120 min intensity decay: none

Refinement

Refinement on *F*	(Δ/σ)$_{max}$ = 0.335
R = 0.031	Δρ$_{max}$ = 0.95 e Å^{-3}
wR = 0.044	Δρ$_{min}$ = −4.17 e Å^{-3}
S = 0.996	Extinction correction: none
1772 reflections	Atomic scattering factors
88 parameters	from *SDP/PDP* (Enraf–
H atoms refined as riding	Nonius, 1985)
w = 1/[σ^2(*F*) + (0.030*F*)^2]	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$) for (I)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cd	0	0	0	0.0252 (1)
Re	0.48415 (4)	0.22181 (2)	−0.06024 (2)	0.02115 (6)
O1	0.2124 (10)	0.1712 (5)	−0.0537 (6)	0.043 (1)
O2	0.6769 (10)	0.1266 (5)	0.0199 (6)	0.048 (1)
O3	0.5485 (12)	0.2355 (4)	−0.2159 (6)	0.041 (1)
O4	0.5023 (10)	0.3565 (4)	0.0144 (5)	0.036 (1)
S	0.1393 (3)	0.0457 (2)	0.2254 (2)	0.0323 (4)
N1	−0.2663 (11)	0.0035 (6)	0.3025 (7)	0.045 (2)
N2	0.0044 (14)	−0.1315 (8)	0.3599 (10)	0.078 (2)
C	−0.0579 (13)	−0.0325 (6)	0.3025 (7)	0.033 (1)

Table 2. *Selected geometric parameters ($\mathring{A}$, °) for (I)*

Cd—O1	2.409 (6)	Re—O3	1.714 (6)
Cd—O2^i	2.419 (6)	Re—O4	1.717 (5)
Cd—S	2.495 (2)	S—C	1.722 (8)
Re—O1	1.719 (6)	N1—C	1.303 (10)
Re—O2	1.741 (6)	N2—C	1.314 (11)
O1—Cd—O2^i	88.5 (2)	O2—Re—O3	109.1 (3)
O1—Cd—S	85.1 (2)	O2—Re—O4	108.6 (3)
O2^i—Cd—S	89.9 (1)	O3—Re—O4	110.1 (2)
O1—Re—O2	110.8 (3)	S—C—N1	121.3 (6)
O1—Re—O3	110.5 (3)	S—C—N2	118.6 (6)
O1—Re—O4	107.7 (3)	N1—C—N2	120.1 (7)

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

Compound (II)

Crystal data

Cd(ReO$_4$)$_2$.2CH$_4$N$_2$S	Mo $K\alpha$ radiation
$M_r = 765.03$	$\lambda = 0.71073\ \mathring{A}$
Triclinic	Cell parameters from 22
$P\bar{1}$	reflections
$a = 8.931$ (2) $\mathring{A}$	$\theta = 20.10-21.85°$
$b = 9.066$ (3) $\mathring{A}$	$\mu = 19.48\ \text{mm}^{-1}$
$c = 10.125$ (1) $\mathring{A}$	$T = 292$ K
$\alpha = 76.46$ (2)°	Prismatic
$\beta = 67.08$ (1)°	0.15 × 0.13 × 0.10 mm
$\gamma = 66.39$ (3)°	Colourless
$V = 689.0$ (2) $\mathring{A}^3$	
$Z = 2$	
$D_x = 3.688\ \text{Mg m}^{-3}$	
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	3210 observed reflections
	[$I > 3.0\sigma(I)$]
Continuous profile scans	$R_{int} = 0.030$
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)	$\theta_{max} = 30.0°$
	$h = 0 \rightarrow 12$
	$k = -12 \rightarrow 12$
	$l = -14 \rightarrow 14$
$T_{min} = 0.047,\ T_{max} = 0.100$	3 standard reflections frequency: 120 min
4257 measured reflections	intensity decay: none
4018 independent reflections	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.212$
$R = 0.038$	$\Delta\rho_{max} = 2.12\ \text{e}\ \mathring{A}^{-3}$
$wR = 0.054$	$\Delta\rho_{min} = -3.68\ \text{e}\ \mathring{A}^{-3}$
$S = 1.041$	Extinction correction: none

3210 reflections
172 parameters
H atoms refined as riding
$w = 1/[\sigma^2(F) + (0.040F)^2]$

Atomic scattering factors from *SDP/PDP* (Enraf–Nonius, 1985)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$) for (II)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cd	0.59543 (7)	0.28733 (7)	0.42273 (6)	0.0243 (1)
Re1	0.50486 (4)	−0.03097 (4)	0.75187 (3)	0.02072 (7)
Re2	0.70067 (4)	0.56670 (4)	0.05582 (4)	0.0280 (1)
S1	0.6939 (2)	0.4443 (2)	0.5491 (2)	0.0224 (5)
S2	0.8435 (3)	0.0119 (3)	0.3967 (2)	0.0312 (7)
O11	0.4783 (8)	0.1558 (8)	0.6495 (6)	0.031 (2)
O12	0.5595 (8)	−0.1830 (8)	0.6482 (8)	0.040 (2)
O13	0.3163 (9)	−0.0216 (9)	0.8921 (8)	0.039 (2)
O14	0.6706 (9)	−0.0807 (9)	0.8166 (8)	0.044 (2)
O21	0.6969 (9)	0.4101 (9)	0.1917 (8)	0.038 (2)
O22	0.7811 (10)	0.4933 (10)	−0.1095 (8)	0.047 (2)
O23	0.8295 (12)	0.6626 (10)	0.0595 (9)	0.056 (3)
O24	0.4977 (12)	0.7016 (13)	0.0811 (11)	0.081 (4)
N11	0.8784 (10)	0.6122 (10)	0.3506 (10)	0.041 (3)
N12	1.0097 (11)	0.3411 (10)	0.3582 (11)	0.043 (3)
N21	0.9916 (10)	0.1139 (10)	0.1250 (8)	0.032 (2)
N22	1.1329 (10)	−0.1431 (10)	0.2036 (9)	0.035 (2)
C1	0.8730 (10)	0.4694 (10)	0.4064 (8)	0.023 (2)
C2	1.0011 (10)	−0.0025 (10)	0.2264 (9)	0.023 (2)

Table 4. *Selected geometric parameters ($\mathring{A}$, °) for (II)*

Cd—S1	2.677 (3)	Re2—O21	1.731 (7)
Cd—S1^i	2.719 (2)	Re2—O22	1.722 (8)
Cd—S2	2.576 (2)	Re2—O23	1.712 (12)
Cd—O11	2.374 (6)	Re2—O24	1.690 (9)
Cd—O12^{ii}	2.338 (10)	S1—C1	1.742 (8)
Cd—O21	2.339 (7)	S2—C2	1.743 (7)
Re1—O11	1.745 (6)	N11—C1	1.298 (12)
Re1—O12	1.726 (8)	N12—C1	1.321 (10)
Re1—O13	1.714 (7)	N21—C2	1.290 (11)
Re1—O14	1.705 (9)	N22—C2	1.337 (10)
S1—Cd—S1^i	85.48 (7)	O11—Re1—O14	110.4 (4)
S1—Cd—S2	101.55 (9)	O12—Re1—O13	109.8 (4)
S1—Cd—O11	90.2 (2)	O12—Re1—O14	106.4 (4)
S1—Cd—O12^{ii}	165.6 (1)	O13—Re1—O14	109.9 (4)
S1—Cd—O21	94.6 (3)	O21—Re2—O22	110.3 (4)
S1^i—Cd—S2	172.1 (1)	O21—Re2—O23	109.8 (5)
S1^i—Cd—O11	94.7 (1)	O21—Re2—O24	109.5 (4)
S1^i—Cd—O12^{ii}	82.8 (2)	O22—Re2—O23	109.0 (4)
S1^i—Cd—O21	84.3 (2)	O22—Re2—O24	109.6 (5)
S2—Cd—O11	81.9 (1)	O23—Re2—O24	108.7 (5)
S2—Cd—O12^{ii}	89.7 (2)	S1—C1—N11	121.3 (6)
S2—Cd—O21	98.4 (2)	S1—C1—N12	119.6 (7)
O11—Cd—O12^{ii}	82.4 (3)	N11—C1—N12	119.1 (8)
O11—Cd—O21	175.1 (3)	S2—C2—N21	122.6 (5)
O12^{ii}—Cd—O21	92.6 (3)	S2—C2—N22	116.7 (6)
O11—Re1—O12	111.0 (3)	N21—C2—N22	120.7 (7)
O11—Re1—O13	109.3 (3)		

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

Table 5. *Hydrogen-bonding contacts ($\mathring{A}$, °) with the intra- or interchain type denoted in compounds (I) and (II)*

D—H···A	H···A	D···A	D—H···A	A···H···A	Type
Compound (I)					
N1—H11···O4^i	2.07 (1)	2.980 (9)	160.1 (4)		inter
N1—H12···O2^{ii}	2.58 (6)	3.269 (9)	129.5 (5)	85.0 (2)	intra
N1—H12···O3^{iii}	2.33 (6)	3.162 (8)	145.4 (5)		inter
N2—H21···O1^i	2.47 (1)	3.352 (11)	153.8 (5)		inter
N2—H22···O3^{iv}	2.55 (1)	3.372 (11)	145.2 (6)	75.7 (2)	intra
N2—H22···O4^v	2.35 (1)	3.115 (10)	137.4 (6)		inter

Compound (II)

N11—H111···O22^i	2.17 (1)	3.017 (10)	147.8 (6)	84.1 (3)	inter
N11—H111···O23	2.83 (1)	3.050 (15)	94.3 (7)		intra
N11—H112···O11^{ii}	2.32 (1)	3.035 (10)	132.0 (7)	75.4 (2)	inter
N11—H112···O12^{iii}	2.73 (1)	3.513 (10)	139.9 (6)	75.2 (2)	intra
N11—H112···S2^{iii}	3.05 (1)	3.636 (11)	121.6 (7)	94.1 (2)	intra
N12—H121···O14^{iv}	2.60 (1)	3.079 (10)	111.5 (6)	97.0 (3)	inter
N12—H121···O22^i	2.12 (1)	2.983 (12)	149.7 (5)		inter
N12—H122···S2	2.98 (1)	3.716 (12)	135.7 (8)	85.8 (1)	intra
N12—H122···S2^{iv}	2.92 (1)	3.684 (9)	138.4 (8)		inter
N21—H211···O13^v	2.06 (1)	2.942 (9)	153.6 (5)	85.2 (3)	inter
N21—H211···O23^i	2.44 (1)	2.941 (13)	112.4 (6)		inter
N21—H212···O21	1.95 (1)	2.898 (9)	175.0 (6)		intra
N22—H221···O13^v	2.31 (1)	3.104 (10)	140.8 (5)	86.4 (3)	inter
N22—H221···O24^{vi}	2.19 (1)	2.852 (11)	125.7 (6)		inter
N22—H222···S1^{iv}	2.70 (1)	3.543 (9)	147.9 (6)		inter

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

Thiourea H atoms were calculated in a riding geometry with fixed $U_{\text{iso}} = 0.506$ Å^2.

For both compounds, data collection: *CAD-4 User's Manual* (Enraf–Nonius, 1988); data reduction: *SDP/PDP* (Enraf–Nonius, 1985). Program(s) used to solve structures: *MULTAN*11/82 (Main *et al.*, 1982) for (I); *SHELXS*86 (Sheldrick, 1985) for (II). For both compounds, program(s) used to refine structures: *SDP/PDP*; molecular graphics: *ORTEP*II (Johnson, 1976), *STRUPLO*84 (Fischer, 1985); software used to prepare material for publication: *KAPPA* (Macíček, unpublished) in *SDP/PDP*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1219). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(μ-thiosulfato)-1κO,1:2κ²S;2κO,1:2κ²S-bis[(2,9-dimethyl-1,10-phenanthroline-N,N')cadmium(II)]

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Abstract

The title complex, [Cd$_2$(S$_2$O$_3$)$_2$(C$_{14}$H$_{12}$N$_2$)$_2$], presents a dimeric structure with the novel feature of having the thiosulfate group acting as both a bridging and a bidentate ligand. This unusual coordination mode leads to an S—S bond length in the mid-range of those found in the S-bridging thiosulfates, but longer than those observed in monodentate S-bonded complexes. The pentacoordinate Cd^{II} center exhibits a distorted environment.

Comment

As a part of a general study of metal complexes incorporating sulfur oxyanions, we describe here the structure of [Cd(dmph)(S$_2$O$_3$)], (I) (where dmph is