

C4a—C5a—O8a	128.9 (7)	N3d—C2d—N6d	121.4 (7)
C2b—N1b—C5b	105.0 (6)	C2d—N3d—C4d	108.9 (7)
N1b—C2b—N3b	113.3 (7)	C2d—N3d—C7d	129.5 (7)
N1b—C2b—N6b	122.8 (7)	C4d—N3d—C7d	121.6 (7)
N3b—C2b—N6b	123.9 (7)	N3d—C4d—C5d	100.1 (7)
C2b—N3b—C4b	108.7 (7)	N1d—C5d—C4d	108.7 (7)
C2b—N3b—C7b	127.0 (7)	N1d—C5d—O8d	126.1 (8)
C4b—N3b—C7b	122.8 (7)	C4d—C5d—O8d	125.2 (8)

The title structure was solved manually by the Patterson method. H atoms were calculated and refined in a riding geometry with fixed displacement parameters ( $U_{\text{iso}} = 0.0506 \text{ \AA}^2$ ).

Data collection: *CAD-4 Manual* (Enraf–Nonius, 1988). Data reduction: *SDP/PDP* (Enraf–Nonius, 1985). Program(s) used to refine structure: *SDP/PDP*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *KAPPA* (Macíček, 1992).

This work has been supported by the Bulgarian National Science Fund Project Ch-402.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1187). 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. VII. Cd(ReO<sub>4</sub>)<sub>2</sub>.4tu (tu = Thiourea)

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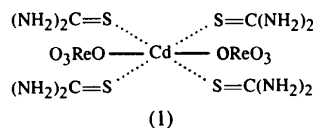
### Abstract

The crystal structure of cadmium tetraoxorhenium tetrakis(thiourea), Cd(ReO<sub>4</sub>)<sub>2</sub>.4CH<sub>4</sub>N<sub>2</sub>S, is comprised of isolated *trans*-[Cd(ReO<sub>4</sub>)<sub>2</sub>tu<sub>4</sub>] clusters consisting of a CdS<sub>4</sub>O<sub>2</sub> octahedron and two ReO<sub>4</sub> tetrahedra. The Cd—S—C—N torsion angles are  $-22.6(5)$  and  $69.1(4)^\circ$  for the two thiourea molecules which are inclined at an angle of  $10.8(5)^\circ$  with respect to one another. The structural units are held together by a complex network of hydrogen bonds.

### Comment

The crystal structures of only a few thiourea (tu) addition compounds of cadmium salts are known. These are CdCl<sub>2</sub>.*ntu*, with  $n = 2$  (Nardelli, Cavalca & Braibanti, 1957) and  $n = 4$  (Nardelli, Cavalca & Braibanti, 1956), and CdSO<sub>4</sub>.*ntu*.*mH*<sub>2</sub>O, with  $n = 1$  and  $m = 2$  (Cavalca, Domiano, Fava Gasparri & Boldrini, 1967), and  $n = 3$  and  $m = 0$  (Corao & Baggio, 1969; Cavalca, Chiesi Villa, Mangia & Palmieri, 1970). We have investigated the Cd(ReO<sub>4</sub>)<sub>2</sub>–tu–H<sub>2</sub>O system and have found several different adducts of formula Cd(ReO<sub>4</sub>)<sub>2</sub>.*ntu*, where  $n = 2, 4$  and  $6$ . For  $n = 2$ , two polymorphic phases have been identified (Petrova, Angelova & Macíček, 1996). One of these phases, (I), is built up of infinite kröhnkite-type chains (Hawthorne & Ferguson, 1975), while in the other, (II), the chains consist of CdS<sub>3</sub>O<sub>3</sub> octahedra linked by alternating double ReO<sub>4</sub> and tu bridges.

When  $n = 4$ , (1), the structure assumes finite dimensions and consists of isolated centrosymmetric ReO<sub>4</sub>–Cd(tu)<sub>4</sub>–ReO<sub>4</sub> clusters held together by an extensive hydrogen-bonding network. In the notation of Hawthorne (Hawthorne, 1985; Eby & Hawthorne, 1993), this can be represented as *trans*-[M(TO<sub>4</sub>)<sub>2</sub>φ<sub>4</sub>]. The same structural unit has been found in CdCl<sub>2</sub>.4tu (Nardelli, Cavalca & Braibanti, 1956), as well as in the



anapaite, bloedite, leonite and schertelite (Hawthorne, 1985), and henmilitite (Eby & Hawthorne, 1993) minerals.

The Cd—O distance in the centrosymmetric *trans*-CdS<sub>4</sub>O<sub>2</sub> octahedron of 2.407 (3) Å is similar to the distances found in the 'inversed' (S *versus* O) *trans*-CdS<sub>2</sub>O<sub>4</sub> octahedron in Cd(ReO<sub>4</sub>)<sub>2</sub>.2tu [phase (I)] but slightly longer than the distances found in the *mer*-CdO<sub>3</sub>S<sub>3</sub> octahedron in Cd(ReO<sub>4</sub>)<sub>2</sub>.2tu [phase (II)] [values range between 2.338 (10) and 2.374 (6) Å; Petrova, Angelova & Macíček, 1996] and the CdSO<sub>4</sub>.*ntu*.*m*H<sub>2</sub>O adducts [2.339 (15) Å for *n* = 3 and *m* = 0 (Corao & Baggio, 1969; Cavalca, Chiesi Villa, Mangia & Palmieri, 1970); average 2.28 (2) Å for *n* = 1 and *m* = 2 (Cavalca, Domiano, Fava Gasparri & Boldrini, 1967)]. The Cd—S distances of 2.646 (1) and 2.701 (1) Å are also a little longer than the distances found in the single-bonded cadmium adducts of tu, *i.e.* 2.576 (2) in Cd(ReO<sub>4</sub>)<sub>2</sub>.2tu [phase (II)], 2.495 (2) in Cd(ReO<sub>4</sub>)<sub>2</sub>.2tu [phase (I)], and 2.538 (6) and 2.627 (6) Å in CdSO<sub>4</sub>.3tu, but are of the same order as those found in the bridging Cd—tu adducts, *i.e.* 2.677 (3) and 2.719 (2) in Cd(ReO<sub>4</sub>)<sub>2</sub>.2tu [phase (II)], 2.627 (7) and 2.870 (7) in CdSO<sub>4</sub>.3tu, and 2.638 (4) and 2.647 (4) Å in CdSO<sub>4</sub>.tu.H<sub>2</sub>O.

The torsion angles Cd—S1—C1—N11 -22.6 (5) and Cd—S2—C2—N21 -69.1 (4)° show that the tu1 molecule tends to be coordinated within the plane (Lebioda, 1980), while the coordination bond to tu2 is realized with some contribution from the π-bonding component of the S=C double bond. These coordination modes have been found to occur in some addition compounds of urea also (Lebioda, 1980; Macíček, Angelova, Petrova, 1995*a,b*). Bond lengths and angles within both thiourea molecules have typical values (Elcombe & Taylor, 1968; Zuñuga, Madariaga, Paciorek, Pérez-Mato, Ezpeleta & Etxebarria, 1989). The two thiourea molecules are inclined at an angle of 10.8 (5)° with respect

to one another. This particular orientation favours formation of two intracomplex N—H...O1 hydrogen bonds to the coordinated O1 atom of the ReO<sub>4</sub> tetrahedron. One of these hydrogen bonds (N11—H111...O1) is almost linear, while the second (N21—H211...O1) is bent. In addition, there is an extensive network of intercomplex hydrogen bonds (Table 3 and Fig. 1).

**Experimental**

A powder sample of Cd(ReO<sub>4</sub>)<sub>2</sub>.4tu was synthesized by slow evaporation of an aqueous solution containing Cd(ReO<sub>4</sub>)<sub>2</sub> and thiourea in a 1:4 molar ratio at room temperature. Single crystals suitable for X-ray analysis were obtained after recrystallization from ethanol.

*Crystal data*

Cd(ReO<sub>4</sub>)<sub>2</sub>.4CH<sub>4</sub>N<sub>2</sub>S  
*M<sub>r</sub>* = 917.27  
 Monoclinic  
*P*2<sub>1</sub>/*c*  
*a* = 7.016 (2) Å  
*b* = 13.603 (2) Å  
*c* = 11.551 (2) Å  
 β = 107.16 (1)°  
*V* = 1053.3 (7) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 2.892 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo Kα radiation  
 λ = 0.71073 Å  
 Cell parameters from 22 reflections  
 θ = 20.04–21.85°  
 μ = 13.05 mm<sup>-1</sup>  
*T* = 292 K  
 Prismatic  
 0.26 × 0.13 × 0.13 mm  
 Colourless

*Data collection*

Enraf–Nonius CAD-4 diffractometer  
 ω/2θ scans  
 Absorption correction: empirical based on an ψ scan (North, Phillips & Mathews, 1968) and spherical  
*T<sub>min</sub>* = 0.163, *T<sub>max</sub>* = 0.232  
 5472 measured reflections

2726 independent reflections  
 2351 observed reflections [*I* > 3.0σ(*I*)]  
*R<sub>int</sub>* = 0.026  
 θ<sub>max</sub> = 28.0°  
*h* = 0 → 9  
*k* = -18 → 18  
*l* = -15 → 15  
 3 standard reflections frequency: 120 min intensity decay: 1.2%

*Refinement*

Refinement on *F*  
*R* = 0.024  
*wR* = 0.032  
*S* = 0.898  
 2351 reflections  
 124 parameters  
*w* = 1/[σ<sup>2</sup>(*F*) + (0.026*F*)<sup>2</sup>]

(Δ/σ)<sub>max</sub> = 0.710  
 Δρ<sub>max</sub> = 1.17 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -2.75 e Å<sup>-3</sup>  
 Extinction correction: none  
 Atomic scattering factors from SDP/PDP (Enraf–Nonius, 1985)

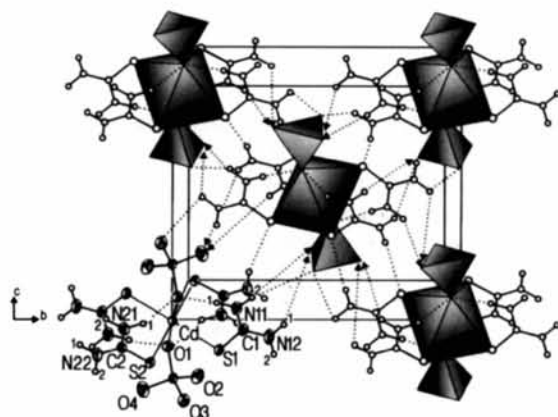


Fig. 1. Projection of the title structure down the *a* axis with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and hydrogen bonds are denoted by dashed lines.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
Re	-0.41843 (3)	-0.02234 (1)	-0.31132 (1)	0.02914 (5)
Cd	0	0	0	0.02382 (9)
O1	-0.3045 (5)	-0.0353 (2)	-0.1568 (3)	0.0333 (8)
O2	-0.6203 (6)	0.0556 (3)	-0.3374 (3)	0.053 (1)

O3	-0.2540 (7)	0.0275 (3)	-0.3780 (4)	0.056 (1)
O4	-0.4875 (7)	-0.1361 (3)	-0.3711 (3)	0.060 (1)
S1	0.0038 (2)	-0.16998 (8)	0.12148 (9)	0.0326 (3)
S2	0.2084 (2)	-0.06799 (8)	-0.13997 (9)	0.0309 (3)
C1	-0.0845 (6)	-0.2643 (3)	0.0222 (4)	0.030 (1)
C2	0.3323 (6)	-0.1656 (3)	-0.0550 (4)	0.0266 (9)
N11	-0.2022 (7)	-0.2481 (3)	-0.0897 (3)	0.041 (1)
N12	-0.0394 (7)	-0.3563 (3)	0.0578 (4)	0.045 (1)
N21	0.4742 (6)	-0.1495 (3)	0.0481 (3)	0.037 (1)
N22	0.2900 (7)	-0.2565 (3)	-0.0927 (4)	0.040 (1)

Table 2. Selected geometric parameters (Å, °)

Cd—O1	2.407 (3)	S1—C1	1.711 (4)
Cd—S1	2.701 (1)	C1—N11	1.330 (5)
Cd—S2	2.646 (1)	C1—N12	1.326 (6)
Re—O1	1.736 (3)	S2—C2	1.726 (4)
Re—O2	1.722 (4)	C2—N21	1.326 (5)
Re—O3	1.705 (5)	C2—N22	1.315 (6)
Re—O4	1.706 (4)		
O1—Cd—S1	95.20 (8)	O2—Re—O3	107.9 (2)
O1—Cd—S2	89.90 (9)	O2—Re—O4	111.5 (2)
S1—Cd—S2	95.49 (4)	O3—Re—O4	109.1 (2)
O1—Re—O2	110.3 (2)	N11—C1—N12	118.7 (4)
O1—Re—O3	109.7 (2)	N21—C2—N22	119.3 (4)
O1—Re—O4	108.3 (2)		

Table 3. Hydrogen-bonding geometry (Å, °)

D—H...A	H...A	D...A	D—H...A	A...H...A
N11—H111...O1	2.08 (1)	3.028 (5)	174 (1)	
N11—H112...O2 <sup>i</sup>	2.13 (1)	2.962 (6)	146 (1)	
N12—H121...O2 <sup>i</sup>	2.41 (1)	3.168 (5)	137 (1)	84 (1)
N12—H121...O3 <sup>ii</sup>	2.60 (1)	2.983 (6)	105 (1)	
N12—H122...S2 <sup>ii</sup>	2.62 (1)	3.562 (4)	168 (1)	
N21—H211...O1 <sup>iii</sup>	2.52 (1)	3.194 (5)	128 (1)	
N21—H211...S2 <sup>iv</sup>	2.81 (1)	3.667 (4)	150 (1)	82 (1)
N21—H212...O4 <sup>v</sup>	2.24 (1)	3.049 (6)	143 (1)	
N22—H221...O3 <sup>vi</sup>	2.41 (1)	2.961 (5)	117 (1)	93 (1)
N22—H221...O4 <sup>v</sup>	2.12 (1)	2.961 (5)	147 (1)	
N22—H222...S1 <sup>vii</sup>	2.54 (1)	3.467 (4)	164 (1)	

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

The H atoms were situated at calculated positions and refined as riding with  $U_{\text{iso}} = 0.0506 \text{ \AA}^2$ .

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Data reduction: *SDP/PDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SDP/PDP*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *KAPPA* (Macíček, unpublished).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1239). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Bis(*N*-2-propylsalicylideneamino-*N*,*O*)-cobalt(II)

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## Abstract

The title complex, bis[2-(2-propyliminomethyl)phenolato-*N*,*O*]cobalt(II), [Co(C<sub>10</sub>H<sub>12</sub>NO)<sub>2</sub>], has two chelating Schiff base ligands coordinating through their N and O atoms to give a tetrahedral geometry distorted mainly by reduction of the chelate O—Co—N angles and by expansion of the N—Co—N angle because of steric hindrance of the isopropyl substituents. The Co—O bonds [mean 1.906 (5) Å] are shorter than the Co—N bonds [mean 1.992 (8) Å].

## Comment

The reaction between Co<sup>II</sup> and bidentate anionic Schiff bases such as salicylidene results in stable organometal-