$S = 1.100$
7583 reflections
378 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.6916P]$
where $P = (F_o^2 + 2F_c^2)/3$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0021 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Mn1—O1	2.0980 (18)	O2—C1	1.249 (3)
Mn1—O4^{i}	2.1208 (17)	O3—C2	1.262 (3)
Mn1—O3	2.1297 (17)	O4—C2	1.262 (3)
Mn1—N1	2.236 (2)	O1*a*—C1*a*	1.306 (3)
Mn1—N2	2.245 (2)	O2*a*—C1*a*	1.224 (3)
Mn1—O5	2.4868 (16)	O3*a*—C2*a*	1.325 (4)
O1—C1	1.264 (3)	O4*a*—C2*a*	1.201 (4)
O1—Mn1—O4^{i}	101.10 (7)	O3—Mn1—N2	98.00 (7)
O1—Mn1—O3	88.36 (7)	N1—Mn1—N2	73.01 (8)
O4^{i}—Mn1—O3	96.25 (7)	O1—Mn1—O5	80.95 (6)
O1—Mn1—N1	97.09 (8)	O4^{i}—Mn1—O5	177.21 (7)
O4^{i}—Mn1—N1	97.96 (7)	O3—Mn1—O5	81.88 (6)
O3—Mn1—N1	163.49 (7)	N1—Mn1—O5	83.61 (7)
O1—Mn1—N2	164.12 (8)	N2—Mn1—O5	85.54 (7)
O4^{i}—Mn1—N2	92.69 (7)		
C2—C3—C4—C1	2.4 (3)	C2*a*—C3*a*—C4*a*—C1*a*	−14.9 (3)
C1—C4—C5—C6	−163.1 (2)	C1*a*—C4*a*—C5*a*—C6*a*	−154.1 (2)
C2—C3—C8—C7	163.7 (2)	C2*a*—C3*a*—C8*a*—C7*a*	170.4 (2)

Symmetry code: (i) $x, \frac{3}{2} - y, \frac{1}{2} + z$.

The quadrants $\pm h+k+l$ and $\pm h-k-l$ were measured. H-atom positions at C atoms were calculated geometrically and treated as riding, those at O atoms were located by a difference Fourier synthesis and refined with isotropic displacement parameters.

Data collection: *STADI*4 (Stoe & Cie, 1996*a*). Cell refinement: *STADI*4. Data reduction: *X-RED* (Stoe & Cie, 1996*b*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP/PC* (Siemens, 1990). 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: KA1307). Services for accessing these data are described at the back of the journal.

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Cadmium isopropylxanthate

David W. Tomlin,[a]† Thomas M. Cooper,[a] David E. Zelmon,[a] Zewdu Gebeyehu[b] and John M. Hughes[c]

[a]*Materials and Manufacturing Directorate, Air Force Research Laboratory, AFRL/MLPJ, Wright-Patterson AFB, OH 45433-7702, USA,* [b]*Department of Chemistry, Tuskegee University, Tuskegee, AL 36088, USA, and* [c]*Department of Geology, Miami University, Oxford, OH 45056, USA. E-mail: tomlindw@ml.wpafb.af.mil*

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Abstract

The crystal structure of bis(*O*-isopropyl dithiocarbonato-*S*)cadmium(II), $[\mathrm{Cd}(\mathrm{C_4H_7OS_2})_2]$, has been determined by X-ray crystallography. The crystals are orthorhombic (space group *Aba*2). The coordination about cadmium is distorted tetrahedral.

Comment

In our laboratories, we have been investigating the optical properties of novel metal–organic complexes. Some of the synthesized material was separated into powders of sizes in the range 12–350 µm and subjected to the Kurtz powder test (Kurtz & Perry, 1968; Kurtz & Dougherty, 1978). The powders were irradiated with an Nd:YAG laser operating at 1.064 µm and the intensity of the second harmonic (0.532 µm) was measured as a function of powder size. The results indicated that the title compound will phase match for 1.06 µm frequency doubling. Also, large single crystals can be grown from these materials, making them possible candidates for non-linear optical materials. Second-order non-linear optical materials have numerous applications as second-

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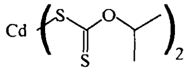
† Technical Management Concepts Inc., PO Box 340345, Beavercreek, OH 45434, USA.

harmonic generators, optical parametric oscillators and electro-optic modulators.



(I)

In the title complex, (I), the coordination about the Cd atom is a distorted tetrahedron, with the Cd atom nearly equidistant from the four S atoms. Each of the four S atoms coordinated to the Cd atom is associated with a different xanthic group. The material exhibits a polymer zigzag chain structure which runs along the crystallographic *a* axis, similar to that found by Iimura (1973). The isopropylxanthate moieties form infinite zigzag chains parallel to one another, with Cd···Cd distances of 5.85 Å. The S2—Cd distance of 2.536 (1) Å is shorter than the S1—Cd distance of 2.585 (1) Å. However, the S1—C1 distance of 1.680 (3) Å is shorter than the corresponding S2—C1 distance of 1.697 (3) Å. The Cd—S1—C1 angle of 108.3 (1)° is larger than the Cd—S2—C1 angle of 101.4 (1)°. These observations suggest large partial π delocalization of these chains. The highly polarizable Cd^{2+} ion, the partial π delocalizations within the isopropylxanthate ligands and the absence of inversion symmetry suggests that this material will exhibit promising non-linear optical properties.

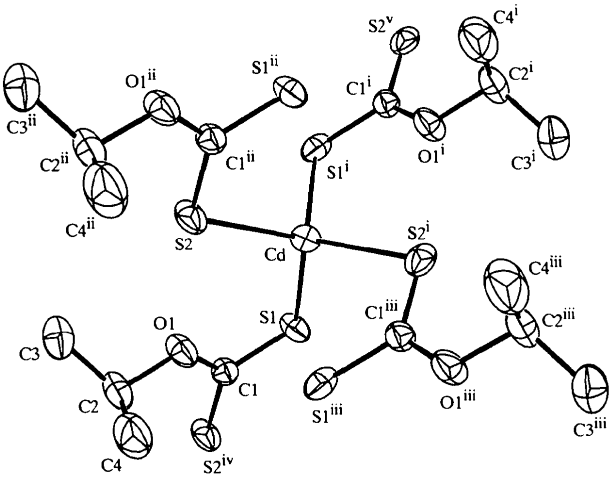


Fig. 1. The molecular structure of cadmium isopropylxanthate along with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $1-x$, $1-y$, z; (ii) x, $\frac{1}{2}+y$, $\frac{1}{2}+z$; (iii) $1-x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$; (iv) x, $y-\frac{1}{2}$, $z-\frac{1}{2}$; (v) $1-x$, $\frac{3}{2}-y$, $z-\frac{1}{2}$.]

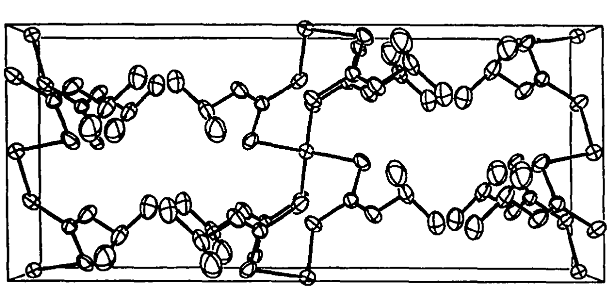


Fig. 2. The unit cell of the title compound illustrating the A-centering. The *a* and *b* axes are horizontal and vertical, respectively, with the *c* axis perpendicular to the page. Displacement ellipsoids are drawn at the 50% probability level.

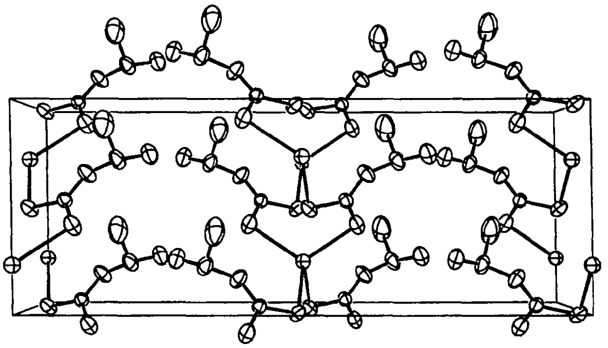


Fig. 3. The unit cell of the title compound illustrating parallel packing of the chains. The *a* and *c* axes are horizontal and vertical, respectively, with the *b* axis perpendicular to the page. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Cadmium isopropylxanthate, $[Cd(S_2COC_3H_7)_2]$, was prepared by the reaction of $CdCl_2$ with potassium isopropylxanthate in aqueous solution in a 1:2 molar ratio. A pale-yellow precipitate usually forms, although a white precipitate has been isolated on some occasions. The yellowish color may be due to the presence of small amounts of dixanthogens arising from oxidation of the xanthate ion during the reaction. The isolated compounds are insoluble in most organic solvents. However, $[Cd(S_2COC_3H_7)_2]$ dissolves very well in tetrahydrofuran, and it was possible to grow X-ray quality crystals from this solution.

Crystal data

$[Cd(C_4H_7OS_2)_2]$
$M_r = 382.86$
Orthorhombic
*Aba*2
$a = 20.652\ (2)$ Å
$b = 8.8934\ (6)$ Å
$c = 7.5917\ (5)$ Å
$V = 1394.3\ (2)$ Å^3
$Z = 4$
$D_x = 1.822$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 19–27°$
$\mu = 2.14$ mm^{-1}
$T = 297$ K
Parallelepiped
0.4 × 0.3 × 0.2 mm
Pale yellow

Data collection

Enraf–Nonius CAD-4 diffractometer

1903 reflections with $I > 2\sigma(I)$

$\omega/2\theta$ scans
Absorption correction:
empirical ψ scan (*SDP/PDP*; Enraf–Nonius, 1985)
$T_{\min} = 0.55$, $T_{\max} = 0.65$
3485 measured reflections
2012 independent reflections

$R_{\text{int}} = 0.012$
$\theta_{\max} = 30°$
$h = -4 \rightarrow 29$
$k = -4 \rightarrow 12$
$l = -10 \rightarrow 10$
3 standard reflections
frequency: 240 min
intensity decay: 1.2%

Refinement

Refinement on F
$R = 0.025$
$wR = 0.034$
$S = 1.27$
2012 reflections
70 parameters
H-atom parameters not refined
$w = 4F_o^2/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{\max} = 0.050$

$\Delta\rho_{\max} = 0.73$ e Å^{-3}
$\Delta\rho_{\min} = -0.80$ e Å^{-3}
Extinction correction: secondary Zachariasen (1967)
Extinction coefficient: $4.5(1) \times 10^{-7}$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

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

	x	y	z	U_{eq}
Cd†	1/2	1/2	0.2300	0.03054 (6)
S1	0.48845 (3)	0.29468 (8)	−0.0090 (1)	0.0311 (2)
S2	0.39918 (4)	0.54239 (9)	0.4142 (1)	0.0339 (2)
O1	0.3828 (1)	0.2498 (2)	0.1585 (2)	0.0360 (7)
C1	0.4204 (1)	0.1972 (3)	0.0315 (3)	0.0283 (7)
C2	0.3258 (1)	0.1655 (3)	0.2226 (4)	0.0387 (9)
C3	0.2731 (2)	0.2818 (4)	0.2498 (5)	0.052 (1)
C4	0.3446 (2)	0.0849 (5)	0.3852 (7)	0.092 (2)

† Site occupancy = 0.50.

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

Cd—S1	2.585 (1)	O1—C1	1.323 (3)
Cd—S2	2.536 (1)	O1—C2	1.479 (3)
S1—C1	1.680 (3)		
S1—Cd—S1^{i}	90.86 (2)	S1^{i}—Cd—S2^{i}	114.60 (2)
S1—Cd—S2	114.60 (2)	S2—Cd—S2^{i}	113.07 (3)
S1—Cd—S2^{i}	110.96 (2)	Cd—S1—C1	108.3 (1)
S1^{i}—Cd—S2	110.96 (2)	Cd—S2—C1^{ii}	101.4 (1)

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

All non-H atoms were located from electron-density maps and were refined anisotropically by full-matrix least squares. H atoms were calculated and were not refined.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP for Windows* (Frenz, 1998). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985) as implemented in *SDP for Windows*. Program(s) used to refine structure: *SDP for Windows*. Molecular graphics: *Xtal*3.4 (Hall *et al.*, 1995) *ORTEP*. Software used to prepare material for publication: *SDP for Windows*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1413). Services for accessing these data are described at the back of the journal.

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[1,3-Bis(pyridine-2-carboxamido)propane]palladium(II) monohydrate and its nickel(II) analogue

Masana Tamura,[a] Yuji Kajikawa,[a] Nagao Azuma,[a] Hiroyuki Tani,[b] Kunihiko Tajima,[c] Kenji Kanaori,[c] Keisuke Makino[c]† and Toshio Takayama[d]

[a]*Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790-8577, Japan,* [b]*Advanced Instrumentation Center for Chemical Analysis, Ehime University, Matsuyama 790-8577, Japan,* [c]*Department of Polymer Science & Engineering, Kyoto Institute Technology, Sakyo-ku, Kyoto 606-8585, Japan, and* [d]*Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, Kanagawa-ku, Yokohama 221-1293, Japan.*
E-mail: azuma@dpc.ehime-u.ac.jp

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Abstract

The title compounds, [*N*,*N*′-bis(2-pyridylcarbonyl)propane-1,3-diaminato-κ^4N]palladium(II) monohydrate, $[Pd(C_{15}H_{14}N_4O_2)]\cdot H_2O$, and [*N*,*N*′-bis(2-pyridylcarbonyl)propane-1,3-diaminato-κ^4N]nickel(II) monohydrate, $[Ni(C_{15}H_{14}N_4O_2)]\cdot H_2O$, were investigated by means of X-ray diffraction and high-resolution NMR. The Pd^{II} and Ni^{II} ions have regular and distorted square-planar

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† Current address: Institute of Advanced Energy, Kyoto University, Uji 611-0011, Japan.