

**COORDINATION CADMIUM COMPOUNDS WITH
1,10-PHENANTHROLINE**Zhang WEIGUANG^{a1,b}, Jiang XUHONG^{a,c}, Zhong YUN^d, Tan MINGYU^{b1,*} and Wang SUELEIN^d^a Department of Chemistry, South China Normal University, Guangzhou 510631, China;
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Accepted August 28, 2002

[Cd(R-XA)₂]_n (XA = xanthate; R = Et, Bu) transformed upon reaction with 1,10-phenanthroline (phen) to [Cd(R-XA)₂(phen)]. The product with R = Et crystallizes in the orthorhombic space group *Pbcn*, while that with R = Bu belongs to the monoclinic system, space group *C2/c*. In two complexes, adjacent phenanthroline ligands form a layered array due to mutual π - π interactions.

Keywords: Xanthates; Cadmium(II) complexes; 1,10-Phenanthroline; Chelates; Crystal structure; X-Ray diffraction.

Metal xanthate complexes and their reaction products with a variety of Lewis bases have been extensively studied¹⁻⁴. Soluble alkali metal xanthates are widely used in extraction and separation of Hg, Ag, Cd and other metals⁵⁻⁷. Sodium and potassium ethylxanthate are antidotes in acute mercury poisoning⁸. Transition metal xanthate complexes for nonlinear optical application were investigated⁹, Cd xanthate showed phase matching for frequency doubling of 1.06 μm light and generated a very strong second harmonic signal. To our knowledge, reaction products of Cd xanthate with Lewis bases have been much less extensively studied than the others. In this paper, we report the syntheses and crystal structures of [Cd(R-XA)₂(phen)] (R = Et, Bu). Likewise the majority of complexes with bidentate dithiolate ligands, such as dithiocarbamate and dialkyldithiophosphate, the reaction of [Cd(R-XA)₂]_n with 1,10-phenanthroline reduces the original polymeric structure to monomeric adducts. Because of the π - π

interactions between adjacent phenanthroline groups, two different cadmium coordination compounds are formed.

EXPERIMENTAL

Instrumentation

The IR spectra (wavenumbers in cm^{-1}) were recorded with a Perkin-Elmer 17300 FTIR spectrometer. Carbon, nitrogen and hydrogen were determined by using a VARIO EL elemental analyzer. Cadmium was determined by using an American SP-I ICP analyzer. Thermal analyses (TGA) were performed on an American PE-DELTA thermobalance.

Syntheses

Sodium xanthate, Na(R-XA) ($\text{R} = \text{Et, Bu}$), was prepared by reaction of an excess of R-OH (10 ml) with NaOH (0.40 g) and CS_2 (1.4 ml). $[\text{Cd(R-XA)}_2]_n$ was prepared by the reaction of Na(R-XA) with $\text{Cd(NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.31 g). Complexes $[\text{Cd(R-XA)}_2(\text{phen})]$ ($\text{R} = \text{Et}$ (1), Bu (2)) were synthesized by stirring $[\text{Cd(R-XA)}_2]_n$ (1 mmol) with 1,10-phenanthroline (1 mmol) in acetone for 30 min. A pale-yellow columnar single crystal, suitable for X-ray structure determination, was obtained after evaporation of the solution at room temperature for a few days. IR spectra (KBr pellets): 3043 ($\nu(\text{C-H})$), 1200–1030 ($\nu(\text{C-O})$), 770–630 ($\nu(\text{C-S})$), 1600–1420 ($\nu(\text{C-C-C-N})$). Complex 1: For $\text{C}_{18}\text{H}_{18}\text{CdN}_2\text{O}_2\text{S}_4$ (535.0) calculated: 40.41% C, 3.39% H, 21.01% Cd, 5.24% N; found: 40.72% C, 3.48% H, 21.34% Cd, 5.47% N. Complex 2: For $\text{C}_{22}\text{H}_{26}\text{CdN}_2\text{O}_2\text{S}_4$ (591.1) calculated: 44.70% C, 4.43% H, 19.02% Cd, 4.74% N; found: 44.88% C, 4.58% H, 19.25% Cd, 4.96% N.

X-Ray Crystallography

Crystal data collections were performed on a CCD area diffractometer with graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.071073$ nm) at 295(2) K, using the $\omega/2\theta$ scan technique. The reflections were corrected for absorption, for Lorentz polarization and secondary extinction effects by the Gaussian integration method. The structure was solved by the Patterson method and subsequent difference Fourier techniques and refined by full-matrix least-squares methods with anisotropic thermal factors for all non-hydrogen atoms; a number of the hydrogen atoms were placed in calculated positions. All calculations were performed using the SHELXTL97 system¹⁰ of computer programs.

Compound 1 ($\text{C}_{18}\text{H}_{18}\text{CdN}_2\text{O}_2\text{S}_4$), $M = 534.98$, crystallizes in the orthorhombic system, space group $Pbcn$, with $a = 1.4855(10)$ nm, $b = 1.4541(9)$ nm, $c = 1.0257(7)$ nm, $V = 2.2156(3)$ nm³, $Z = 4$, $R_1 = 0.0571$ and $wR_2 = 0.1101$. Compound 2 ($\text{C}_{22}\text{H}_{26}\text{CdN}_2\text{O}_2\text{S}_4$), $M = 591.09$, belongs to the monoclinic system, space group $C2/c$ with $a = 0.6587(5)$ nm, $b = 1.9159(15)$ nm, $c = 2.0705(17)$ nm, $\beta = 97.112(2)^\circ$, $V = 2.5930(4)$ nm³, $Z = 4$, $R_1 = 0.0650$ and $wR_2 = 0.1616$. CCDC 181474 (for compound 1) and 181473 (for compound 2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

The selected bond lengths and bond angles are shown in Table I.

RESULTS AND DISCUSSION

The perspective view of the monomeric unit in complexes **1** and **2** and the atomic numbering scheme are shown in Figs 1 and 2, respectively. Figures 3 and 4 then present a perspective view of the crystal packing in the unit cells of **1** and **2**, respectively. The cadmium(II) centre of both complexes is in a distorted octahedral environment, surrounded by two chelating xanthate anions and one chelating phenanthroline ligand. The Cd–N, Cd–S1 and Cd–S2 bond lengths [0.2376(3), 0.2648(12) and 0.2728(12) nm, respectively] in compound **1** are in a good agreement with those in compound **2** [0.2369(4), 0.2653(14) and 0.2700(12) nm, respectively]. The ligand “bite angles” S–C–S is also similar [123.1(2) and 123.3(3)°]. The bond angle S1–Cd–S1^a [101.35(8)°] in compound **2** is smaller than that in compound **1** [115.03(6)°]. Hence, two butyl groups are closer than the two ethyl groups.

In compounds **1** and **2**, the S1–C7 and S2–C7 bond lengths trend to average; the C–S distances indicate the double bond character, probably delocalized over two C–S bonds. The O1–C7 bond lengths are shorter than O1–C8, which is a consequence of the carbon atom hybridization¹¹.

A stereoview of the unit cell packing of molecules **1** shows that the phenanthroline ligands form a layered array by π – π interactions between the adjacent ligands, being arranged in two different orientations. The molecules in the unit cell of **2** are arranged differently. Two and three molecules with phenanthroline ligands parallel to each other alternate in the

TABLE I
Selected bond lengths (in nm) and angles (in °) for compounds **1** and **2**

Bond	1	2	Angle	1	2
Cd1–N1	0.2376(3)	0.2369(4)	N1 ^a –Cd1–N1	70.08(16)	69.59(19)
Cd1–S1	0.2648(12)	0.2653(14)	N1–Cd1–S1	93.55(8)	98.03(10)
Cd1–S2	0.2728(12)	0.2700(17)	N1 ^a –Cd1–S2	88.03(7)	92.48(11)
S1–C7	0.1689(4)	0.1682(6)	S1–Cd1–S2	67.11(4)	67.34(5)
S2–C7	0.1676(5)	0.1675(5)	S2–Cd1–S2#1	160.69(6)	162.86(6)
O1–C7	0.1327(5)	0.1344(7)	S2–C7–S1	124.1(3)	124.3(3)
O1–C8	0.1454(6)	0.1430(2)	S1–Cd1–S1#1	115.03(6)	101.35(8)

Symmetry transformations used to generate equivalent atoms: #1: $-x + 1, y, -z + 3/2$.

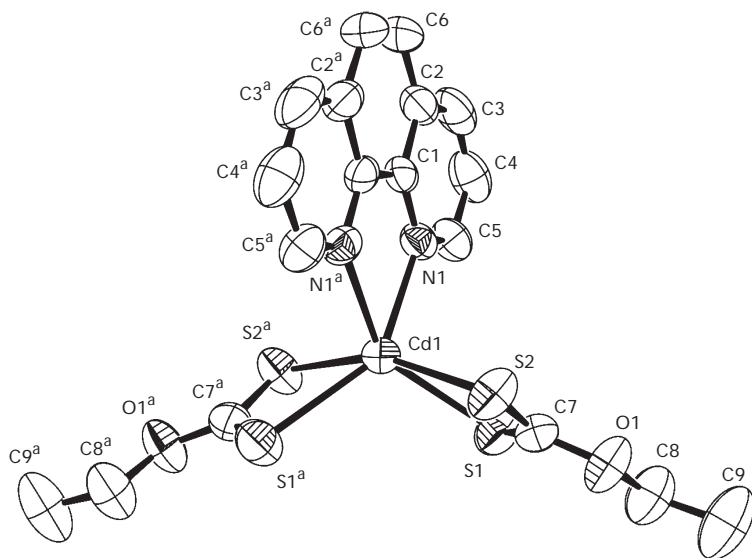


FIG. 1
ORTEP view of compound 1

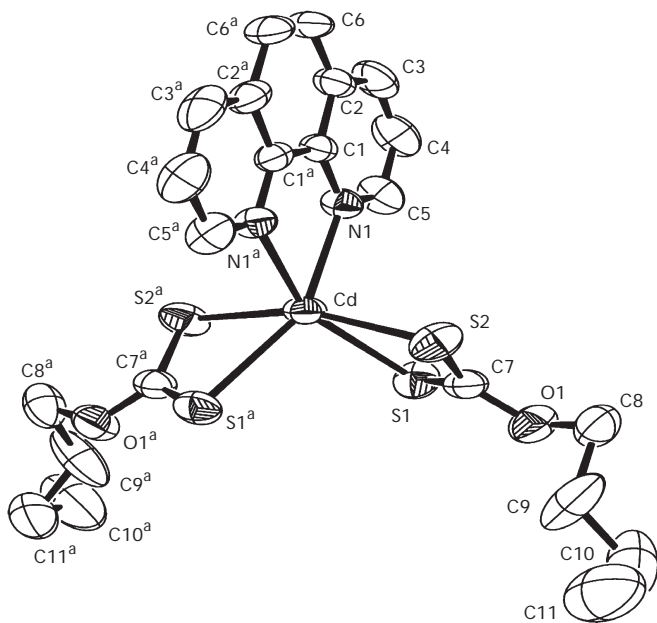


FIG. 2
ORTEP view of compound 2

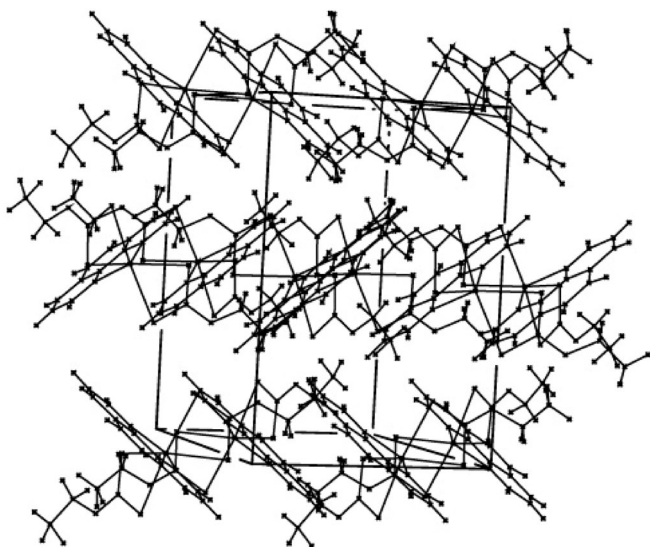


FIG. 3
Unit cell contents of compound 1

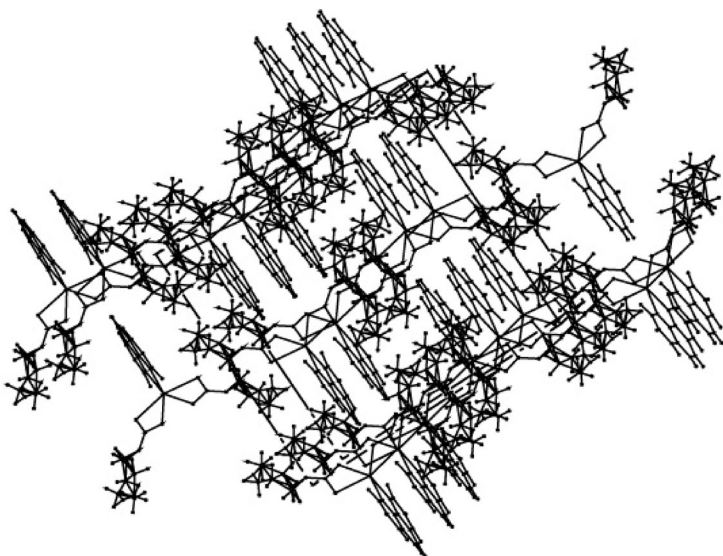


FIG. 4
Unit cell contents of compound 2

array and are arranged in two different orientations, because of the hindrance of the butyl groups. Thus, the interactions between the molecules of compound **1** are stronger compared to compound **2** and the former species has therefore higher melting point 140 °C than the latter 120 °C.

Thermogravimetric analysis (TGA) of $[\text{Cd}(\text{R-XA})_2(\text{phen})]$ reveals that thermal decomposition of compound **1** mainly takes place at 110 and 150 °C, and that of compound **2** mainly at 85 and 131 °C. This result again documents that compound **1** is more stable than **2**.

This work has been supported by Natural Science Foundation of Guangdong Province (990463) and National Natural Science Foundation of China (29561002).

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