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Synthesis and Structure of the Cadmium (II) Complex: $[Cd(C_5H_5N)_2(S_2CO\text{-}n\text{-}C_4H_9)_2]$

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Abstract: The $[Cd(C_5H_5N)_2(S_2CO\text{-}n\text{-}C_4H_9)_2]$ adduct of pyridine with $[Cd(S_2CO\text{-}n\text{-}C_4H_9)_2]_n$ was synthesized and characterized by IR, elemental analysis, ^{1}H-NMR and X-ray diffraction analysis. The crystasl belong to the monoclinic system, space group P2(1)/c with Z=2. Cell dimensions are a=1.1094(12), b=0.6152(6), c=1.7985(19) nm, • =96.148(2)°, V=1.2204(2)nm^3. The structure was refined to R=0.0246 and wR=0.0645 for 2624 reflections with I>2•(I). The complex has a centrosymmetric molecule structure.

Keywords: n-Butylxanthate, cadmium (II) complex, pyridine, crystal structure

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Introduction

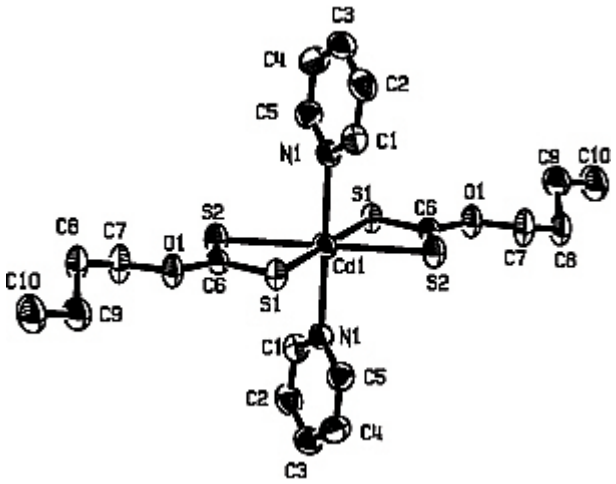
Metal xanthate complexes and their reaction products with a variety of Lewis bases have been extensively studied [1-3]. The soluble alkali metal xanthates are widely used in extraction and separation of Hg, Ag, Cd, etc., [4-6]. Sodium and potassium ethyl xanthate have antidotal effects in acute mercurial poisoning. Transition metal xanthate complexes have been investigated for nonlinear optical applications [7], and Cd xanthate was demonstrated to have nonlinear optical properties and

generated a very strong 2nd harmonic signal. To the best of our knowledge, the reaction products of Cd xanthate with Lewis bases have been much less extensively studied than other similar compounds. In this paper, we report the synthesis and X-ray crystal structure of $[Cd(C_5H_5N)_2(S_2CO\text{-}n\text{-}C_4H_9)_2]$. Like most bidentate dithiolate complexes, the reaction of $[Cd(S_2CO\text{-}n\text{-}C_4H_9)_2]_n$ with pyridine destroyed the original polymeric structure to yield the corresponding bis-(Lewis base) adduct.

Results and Discussion

The X-ray structure of the cadmium complex $[Cd(C_5H_5N)_2(S_2CO\text{-}n\text{-}C_4H_9)_2]$ is built up of centrosymmetric monomeric entities. Figure 1 shows a perspective view of the monomeric unit with the atomic numbering scheme. Figure 2, a perspective view of the crystal packing in the unit cell. The cadmium (II) atom is in an octahedral environment surrounded by two chelating xanthate anions and two pyridine ligands. Two nitrogen atoms occupy the apical site.

Figure 1. The atomic numbering scheme of the cadmium complex

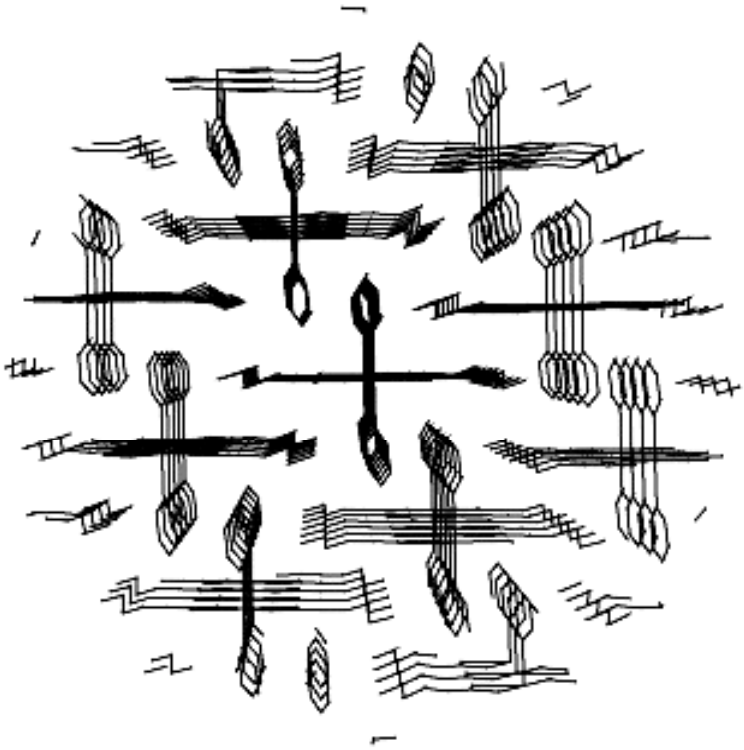


Selected bond lengths (nm) and bond angles (°)

Cd(1)-S(1)	0.2644(5)	N(1)#1-Cd(1)-N(1)	180.00(8)
Cd(1)-S(2)	0.2730(5)	N(1)-Cd(1)-S(1)#1	90.49(4)
S(1)-C(6)	0.1696(18)	N(1)-Cd(1)-S(1)	89.51(4)
S(2)-C(6)	0.1688(19)	S(1)#1-Cd(1)-S(1)	180.0
O(1)-C(6)	0.1337(2)	N(1)-Cd(1)-S(2)#1	90.10(4)
O(1)-C(7)	0.1446(2)	S(1)#1-Cd(1)-S(2)#1	67.654(15)
		S(1)-Cd(1)-S(2)#1	112.346(15)
		N(1)-Cd(1)-S(2)	89.90(4)
		S(1)-Cd(1)-S(2)	67.654(15)
		S(2)#1-Cd(1)-S(2)	180.00(3)

Four sulfur atoms and one cadmium atom are almost coplanar. The bond angles around Cd(II) are in the range 67.654(1)-180.00(3)°. The S(1)-S(2)-S(1)#1-S(2)#1 occupy the equatorial plane and the chelated planes composed by cadmium and xanthate are coplanar with it. The terminal n-butyl groups of xanthate take on a trans-configuration. Two pyridine rings are coplanar and almost perpendicular to the O(1)-S(1)-S(2)-O(1)#1-S(1)#1-S(2)#1 plane.

Figure 2. Cell contents of the complex



The S(1)-C(6) and S(2)-C(6) bond distances tend to average, and the C-S distances show double bond character due to delocalization over the two C-S bonds. The O(1)-C(6) bond distance [1.337(2)Å] is shorter than the O(1)-C(7) [1.446(2) Å] as a consequence of the hybridization of the carbon atom [8]. A stereoview of the unit cell packing of the compound shows that the molecules are parallel each other and form a layered array. In the ^{1}H-NMR spectra of the complexes in $CDCl_3$, the corresponding pyridine hydrogen resonances are shifted to lower field compared to those of the free pyridine (δ=7.16, 7.55, 8.52 ppm), thus indicating that the pyridines take part in coordination to the metal ion.

Conclusions

We have reported the first synthesis and X-ray crystal structure of $[Cd(C_5H_5N)_2(S_2CO\text{-}n\text{-}C_4H_9)_2]$.

Acknowledgments

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Experimental

General

All reagents and chemicals were used as received unless otherwise noted. Sodium n-butyl xanthate was prepared by reaction of n-butanol, NaOH, and CS_2. $[Cd(SSO\text{-}n\text{-}C_4H_9)_2]_n$ was prepared by reaction of sodium n-butyl xanthate and $Cd(NO_3)\cdot 4H_2O$. $[Cd(C_5H_5N)_2(S_2CO\text{-}n\text{-}C_4H_9)_2]$ was synthesized by stirring $[Cd(S_2CO\text{-}n\text{-}C_4H_9)_2]_n$ with excess pyridine in acetone for 30 minutes. IR(KBr): $\bullet_{=C\text{-}H}$ 3060, $\bullet_{C\text{-}O}$ 1200~1000, $\bullet_{C\text{-}S}$ 750~620, $\bullet_{C\text{-}C\ C\text{-}N}$ 1600~1440cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ(ppm): 0.93 (m, 3H, CH_3), 1.43 (m, 2H, CH_2CH_3), 1.79 (m, 2H, $CH_2CH_2CH_3$), 4.40 (t, J=2Hz, 2H, OCH_2), 7.42(m, 2H, Pyridine ring 3-H, 5-H), 7.82 (m, 1H, Pyridine ring 4-H), 8.76 (m, 2H, Pyridine ring 2-H, 6-H). Elemental analysis: C 41.47%, H 5.07%, N 5.16%. Calcd.: C 42.20%, H 4.96%, N 4.92%.

X-ray analysis

A pale–yellow columnar single crystal suitable for X-ray structure determination was obtained by evaporation of a suitable solution at room temperature for few days. Crystal data collections were performed on a Siemens P4 diffractometer using Mo-Kα radiation (λ=0.71073Å) and the ω/2θ (θ = 1.85-27.97) scan technique at 295(2) K. The reflections were corrected for absorption by the Gaussian integration method for Lorentz polarization and secondary extinction effects. The structure was solved by the Patterson method and subsequent difference Fourier techniques and refined by Full-matrix least-squares on F^2 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 SHELXTL [9] suite of computer programs.

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Sample Availability: Available from the authors**.**