

[Pd(Me-Xanthate)₂]: Synthesis, Characterization, and X-Ray Structure

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Potassium methyl xanthate and its complex [Pd(Me-Xanthate)₂] were synthesized at room temperature under stirring conditions. The ligand and the complex were characterized by elemental analysis, IR, NMR (¹H, ¹³C) and XRD. NMR data revealed that potassium methyl xanthate acts as a bidentate specie and the complex exhibits 4-coordinated geometry in solution. In solid state, the palladium atom is coordinated to the 2 sulfur atoms of the xanthate ligand and the complex exhibits distorted square planar geometry.

Key Words: Palladium(II) xanthate, spectroscopy, X-ray structure.

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 the extraction and separation of Hg, Ag etc.^{4,5} Sodium and potassium ethyl xanthate have antidotal effects in acute mercurial poisoning. Transition metal xanthate complexes have been investigated for nonlinear optical applications.⁶

The chemistry of palladium(II) and platinum(II) with dithio ligands such as xanthate, dithiocarbamate, and dithiophosphate is well developed. Metal xanthates exhibit high efficiency for removal of metal ions.⁷

Metal xanthates are extensively used as fungicides, pesticides, accelerators, corrosion inhibitors, agricultural reagents, and quite recently in therapy for HIV infection.⁸

These ligands usually form bidentate chelate or monodentate discrete or network solids, showing a wide range of coordination behavior.⁹ Referring to various applications and as a continuation of our previous

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work,^{10–14} we report here the preparation of palladium(II) complex containing Me₂O₂C₂S₄ (Figure 1). This complex was characterized by elemental analysis, IR, NMR (¹H, ¹³C), and single crystal X-ray analysis.

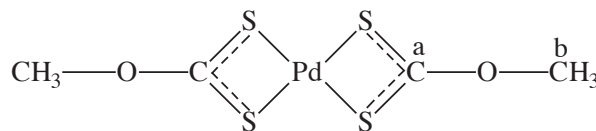


Figure 1. Chemical structure of [Pd(Me-Xanthate)₂].

Experimental

Materials and methods

All the chemical reagents used were of analytical grade. PdCl₂ and carbon disulphide were purchased from Aldrich. Melting points are uncorrected and were taken in a capillary tube on a MP-D Mitamura Rikero Kogyo (Japan). IR spectra were recorded on a Bio-Rad FTIR spectrophotometer as KBr discs. ¹H- and ¹³C-NMR spectra were recorded on a Bruker 300 MHz spectrometer using CDCl₃ as an internal reference. Elemental analysis was carried out with a CHN-932 Elemental Analyzer, Leco Corporation, USA. Solvents were purified and dried before use.¹⁵ X-ray single crystal data were collected on CCD area detector diffractometer with graphite monochromated MoK_α radiation.

Procedure for synthesis of potassium methyl xanthate

To a round bottom 2-necked flask were added (1 mmol) methanol and (1 mmol) potassium hydroxide and the solution was stirred at room temperature until the KOH dissolved. Then (1 mmol) carbon disulfide was added to the reaction mixture dropwise and it was stirred for 3-4 h. The yellow solution was concentrated to obtain a fluffy solid product. Yield = 88%; mp 237 °C; elemental analysis, % calcd. (found), C = 16.43 (16.50), H = 2.05 (2.11), S = 43.83 (43.79); IR (cm⁻¹), ν_{C=S} = 933s, ν_{C-S} = 1161m; δ ¹H-NMR (ppm), H_b = 3.65s; δ ¹³C-NMR (ppm), C_a = 202, C_b = 55.7.

Procedure for synthesis of Pd(II) complex

A solution of potassium methyl xanthate (2.0 mmol) and PdCl₂ (1.0 mmol) in distilled water (50 mL) was stirred in a round bottom flask overnight. The yellow solid obtained was filtered off, washed with distilled water, and air dried. The solid was recrystallized from chloroform. Yield = 65%; mp 188 °C; elemental analysis, % calcd. (found), C = 16.96 (16.88), H = 1.87 (1.79), S = 39.90 (40.11); IR (cm⁻¹), ν_{C=S} = 949s, ν_{C-S} = 1187m, ν_{Pd-S} = 439; δ ¹H-NMR (ppm), H_b = 3.84s; δ ¹³C-NMR (ppm), C_a = 206, C_b = 57.3.

X-ray crystallography

X-ray crystallographic data were collected on a CCD area detector diffractometer (Bruker SMART). The structure was solved by direct methods using the SHELXS97¹⁶ program and refined by a full-matrix least

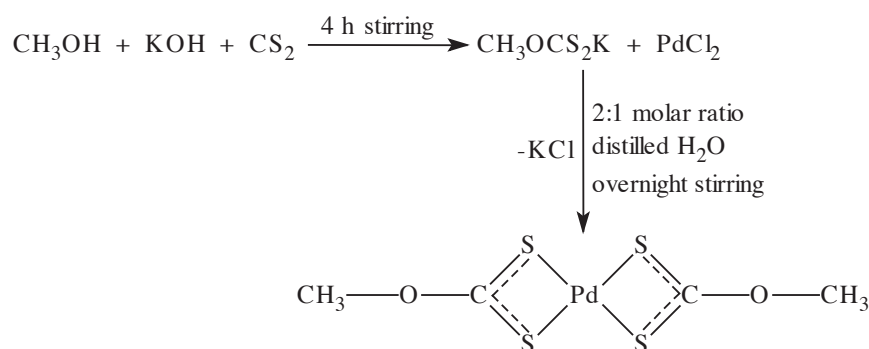
squares procedure based on F^2 using SHELXL97.¹⁶ All data were collected with graphite monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. H atom positions were calculated geometrically with $\text{C-H} = 0.96 \text{ \AA}$ for methyl H, and constrained to ride on their parent atoms, with $U_{iso}(\text{H}) = xU_{eq}(\text{C})$, where $x = 1.5$ for methyl H.

Results and Discussion

[Pd(Me-Xanthate)₂] complex was prepared by the reaction of the ligand and the corresponding palladium(II) chloride in 2:1 molar ratio in distilled water (Scheme). The complex is solid with a sharp melting point and more soluble in polar solvents than in non-polar ones.

Infrared spectroscopy

Characteristic IR bands of the ligand and its complex are given in the experimental part. In IR spectra, $\nu(\text{C}=\text{S})$ shifts to higher frequency on complexation showing the coordination of ligands through sulfurs. The band at 439 cm^{-1} is attributed to $\nu(\text{Pd}=\text{S})$ vibration.¹⁴



Scheme

NMR spectroscopy

The ^1H - and ^{13}C -NMR data contributed to the identification and characterization of the compound. Proton 'b' gives a singlet at 3.65 and 3.84 ppm for potassium methyl xanthate and its Pd complex, respectively. Carbon 'b' resonances are shifted to lower field in the Pd complex (206 ppm), as compared to those of ligand (202 ppm), thus indicating that the sulfurs take part in coordination to the palladium metal.

X-ray analysis

An ORTEP¹⁷ drawing of the [Pd(Me-Xanthate)₂] with the atom-numbering scheme is given in Figure 2. The Pd(II) atom is in distorted square planar geometry surrounded by 2 chelating xanthate anions. In this way the ligand behaves as a bidentate species and chelates the tin atom by means of sulfur atoms.^{10,11} Four sulfur atoms and one Pd atom are almost coplanar. Because of the 4-membered chelate ring, the S3-Pd1-S2 angle has

been compressed to 75.45(4)°. The remaining S-Pd-S bond angles are 177.97(4)° and 104.77(5)°. The crystal data and the selected bond lengths and angles are given in Tables 1 and 2, respectively.

The S4-C2 and S5-C2 bond distances tend to average, indicating a partial double bond character. This suggests a pronounced electronic delocalization in OCS₂ moiety. The unit cell packing (Figure 3) of the complex shows that molecules are parallel to each other and the 2 methyl groups are in trans position.

Table 1. Crystal data and structure refinement.

Empirical formula	C ₄ H ₆ O ₂ PdS ₄
Formula weight	320.73
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 6.3307(14) Å α = 90 (3)° b = 13.876(7) Å β = 97.59(17)° c = 10.835(2) Å γ = 90 (3)°
Volume	943.4(6) Å ³
Z	4
Density (calculated)	2.258 Mg/m ³
Absorption coefficient	2.799 mm ⁻¹
F(000)	624
Crystal size	0.03 × 0.01 × 0.012 mm
Theta range for data collection	3.79 to 22.90°
Index ranges	-5 ≤ h ≤ 6, -13 ≤ k ≤ 14, -11 ≤ l ≤ 11
Reflections collected	4539
Independent reflections	1122 [R(int) = 0.0193]
Completeness 2 theta = 22.90°	87.0%
Max. and min. transmission	0.1662 and 0.1662
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1122 / 0 / 107
Goodness-of-fit on F ²	1.103
Final R indices [I > 2sigma(I)]	R ₁ = 0.0233, wR ₂ = 0.0572
R indices (all data)	R ₁ = 0.0326, wR ₂ = 0.0596
Largest diff. peak and hole	0.315 and -0.352 e.Å ⁻³

Conclusion

[Pd(Me-Xanthate)₂] was synthesized by the reaction of palladium(II) chloride, CS₂, and methanol. Elemental analysis showed good agreement between the calculated and observed % of C, H, and S. NMR data revealed that potassium methyl xanthate exhibits 4-coordinated geometry in solution. In solid state, the palladium

Table 2. Selected bond lengths (Å) and bond angles (°).

Bond Lengths (Å)		Bond Angles (°)	
Pd1-S3	2.325(12)	S3-Pd1-S2	75.45(4)
Pd1-S5	2.331(13)	S3-Pd1-S5	177.97(4)
Pd1-S2	2.333(13)	S5-Pd1-S2	104.77(5)
Pd1-S4	2.337(13)	S3-Pd1-S4	104.35(4)
S2-C1	1.693(4)	S5-Pd1-S4	75.31(4)
S3-C1	1.693(5)	S2-Pd1-S4	176.60(4)
S4-C2	1.689(4)	C1-S2-Pd1	84.77(16)
S5-C2	1.689(5)	C1-O2-C4	118.7(4)

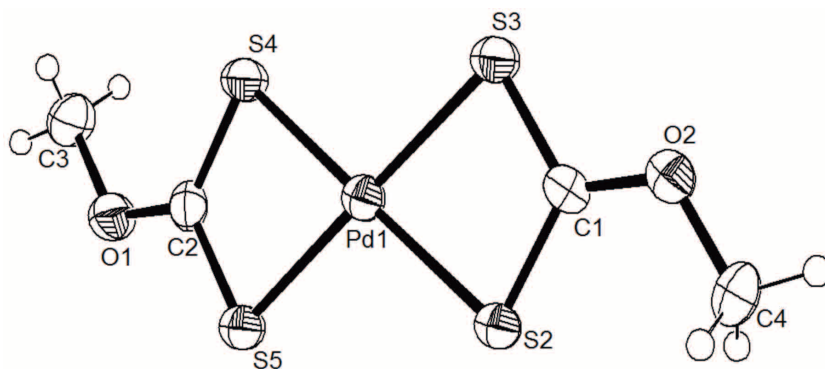


Figure 2. An ORTEP¹⁷ drawing of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability level.

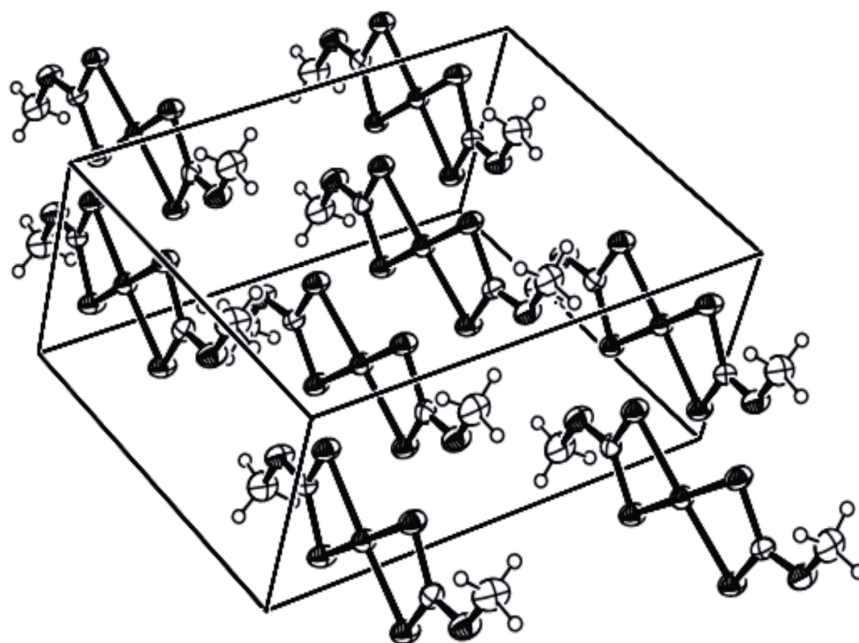


Figure 3. A packing diagram of [Pd(Me-Xanthate)₂].

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atom is coordinated to the sulfur atoms of the xanthate ligand and the complex exhibits distorted square planar geometry.

Supplementary material

Crystallographic data for the complex have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 673281. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CBZ 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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