Notes

Bull. Korean Chem. Soc. **1996**, Vol. 17, No. 5   473

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Conformational Properties of Potassium 1,3-Dithiolan-2-ylidenemalonate

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A series of ylidenemalonates containing dithioether rings have been elucidated to be fascinating ligands by the authors: the ligands may be coordinated to a platinum atom *via* one of three distinct modes of O,O'-, O,S-, or S,S'-chelation depending on the dithioether ring size.[1,2] The variety of chelation modes could be explained in terms of the basicity of sulfur atoms. In our previous work on dimethyl 1,3-dithiolan-2-ylidenemalonate, an intramolecular sulfur-oxygen interaction was also shown to be governed by the basicity of sulfur atoms.[3] However, the crystal structure of the dimethyl 1,3-dithiolan-2-ylidenemalonate is not sufficient to discern its coordination mode as an anionic ligand. In order to scrutinize a relationship between the structure and the coordination mode of the anionic ligand, it is worthwhile to point out the crystal structure of its metal salt. Here is reported the structural properties of potassium 1,3-dithiolan-2-ylidenemalonate.

Experimental

Dimethyl 1,3-dithiolan-2-ylidenemalonate was prepared by the literature method.[4] Potassium hydroxide (1.68 g, 25 mmol) in 40 mL of 95% ethanol was added dropwise to dimethyl 1,3-dithiolan-2-ylidenemalonate (2.34 g, 10 mmol) in 40 mL of 95% ethanol, and then refluxed for 4 h. The precipitated crystalline potassium salt was obtained in quantitative yield. Elemental analysis: calculated for $C_6H_4O_4S_2K_2 \cdot CH_3OH$: C, 26.74; H, 2.56. Found: C, 26.69; H, 2.49. IR (KBr, cm^{-1}): v_{as} (C=O): 1587, 1550, v_s (C=O): 1382. ^{1}H NMR (D$_2$O, ppm): 3.49 (s). ^{13}C NMR (D$_2$O, ppm): 37.82, 125.27, 125.45, 179.90.

Elemental analysis was carried out at the Advaced Chemical Analysis Center, KIST. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 NMR spectrometer operating at 300 MHz (^{1}H) and 75.48 MHz (^{13}C) in pulse mode with Fourier transform. IR spectrum was measured as KBr pellet on a MIDAC model 101025 FT-IR spectrophotometer.

A crystal (0.15×0.30×0.35 mm) suitable for X-ray analysis obtained by recrystallization in a solvent pair of water/methanol (1:1) was sealed in a Lidemann glass capillary and mounted on an Enraf-Nonius CAD 4 diffractometer with graphite-monochromated molybdenum radiation. The unit-cell parameters were determined by least-squares refinement of 25 intense reflections ($15<2\theta<25$). Data were collected at ambient temperature [296(2) K] in $\omega/2\theta$ scan mode using variable rates, $\theta_{max}=25°$ for the range $0\leq h\leq 8$, $0\leq k\leq 14$, $0\leq l\leq 31$, and three standard reflections measured after every hour did not reveal any systematic variations in intensity. Maximum $\sin\theta/\lambda$ reached in intensity measurement was 0.59 Å^{-1}; 2743 measured intensities, 1599 unique, 1589 unique observed [$I>2\sigma(I)$]. Lorentz-polarization corrections but not absorption corrections were made. The crystal structure was determined by the conventional heavy atom method and Fourier techniques. All nonhydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions. Two carbon atoms (C(5), C(6)) were located in disordered positions; an occupancy factor of 0.5 was assigned according to the height of the Fourier synthesis. The maximum shift-to-e.s.d. in the final cycle of least squares was 0.137 for U$_{11}$ of disordered C(6). All calculations were performed on IBM PC 486 computer using *SHELXS*-5^a and *SHELXL*-93^b and atomic scattering factors for all nonhydrogen atoms were supplied by the *SHELXS*-86 system. Crystal pa-

474 *Bull. Korean Chem. Soc.* 1996, Vol. 17, No. 5

Notes

Table 1. Crystal Data and Structure Refinement for Potassium 1,3-Dithiolan-2-ylidenemalonate

Empirical formula	$C_6H_4O_4S_2K_2 \cdot CH_3OH$
Formula weight	314.45
Crystal system	monoclinic
Space group	*Pnaa* (No.56)
a	7.316(2) Å
b	12.550(2) Å
c	26.516(6) Å
V	2434.7(10) Å^3
Z	8
d_{cal}	1.716 mg/m^3
Absorption coefficient	1.121 mm^{-1}
F(000)	1280
θ	1.54 to 24.97 deg.
Index ranges	$0 \leq h \leq 8$, $0 \leq k \leq 14$, $0 \leq l \leq 31$
Reflections collected	1599
Refined parameters	164
Goodness-of-fit on F^2	1.062
Final R indices [$I>2\sigma$ (I)]	R1=0.0467, wR2=0.1262
R indices (all data)	R1=0.0469, wR2=0.1265
Largest diff. peak and hole	0.558 and −0.617 e. Å^{-3}

$R1=\sum||Fo|-|Fc||/\sum|Fo|$. $wR2=\{\sum w(Fo^2-Fc^2)^2/\sum wFo^4\}^{1/2}$, where $w=1/\{\sigma^2Fo^2+(aP)^2+bP\}$, where $P=\{Max(Fo^2, 0)+2Fc^2\}/3$ and a, b were determined by the program.
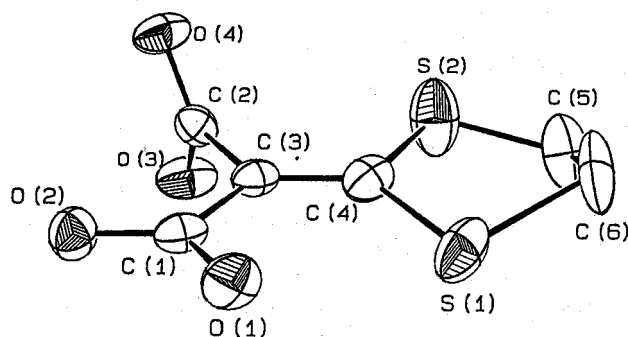
Figure 1. Drawing of potassium 1,3-dithiolan-2-ylidenemalonate (50% probability thermal ellipsoids) along with the atomic numbering scheme. Potassium and hydrogen atoms, and solvated methanol are omitted for clarity.

rameters and procedural information corresponding to data collection and structure refinement are given in Table 1.

Results and Discussion

The molecular geometry and atomic labeling scheme for the title compound are shown in Figure 1, and selected bond distances and angles are tabulated in Table 2. The carboxylate groups in the present compound exhibit a typical delocalization: C-O lengths of carboxylate groups are in the range of 1.248(5)-1.258(5) Å. An interesting feature is that the two carboxylate groups occupy mutually perpendicular position. The dihedral angle between the two groups (the planes of C(1), C(3), O(1), and O(2) and of C(2), C(3), O(3), and O(4))

Table 2. Bond Lengths (Å) and Angles (°) for Potassium 1,3-Dithiolan-2-ylidenemalonate

S(1)-C(4)	1.765(4)	S(1)-C(6)	1.93(2)
S(2)-C(5)	1.72(2)	S(2)-C(4)	1.749(5)
O(1)-C(1)	1.258(5)	O(2)-C(1)	1.254(5)
O(3)-C(2)	1.248(5)	O(4)-C(2)	1.254(5)
C(1)-C(3)	1.495(6)	C(2)-C(3)	1.506(5)
C(3)-C(4)	1.347(6)	C(5)-C(6)	1.56(3)
Os-Cs	1.376(7)*		
C(4)-S(1)-C(6)	94.4(8)	C(5)-S(2)-C(4)	101.9(6)
O(2)-C(1)-O(1)	124.8(4)	O(2)-C(1)-C(3)	117.2(4)
O(1)-C(1)-C(3)	118.0(4)	O(3)-C(2)-O(4)	125.2(4)
O(3)-C(2)-C(3)	117.3(4)	O(4)-C(2)-C(3)	117.5(3)
C(4)-C(3)-C(1)	123.5(4)	C(4)-C(3)-C(2)	119.9(4)
C(1)-C(3)-C(2)	116.6(3)	C(3)-C(4)-S(2)	121.3(3)
C(3)-C(4)-S(1)	124.8(3)	S(2)-C(4)-S(1)	113.8(3)
C(6)-C(5)-S(2)	109.4(12)	C(5)-C(6)-S(1)	107.4(11)

*Solvated methanol

is 83.6°, which is in striking contrast to the corresponding angles of 48.1° and 14.5° for dimethyl 1,3-dithiolan-2-ylidenemalonate[3] and diamineplatinum(II) analog,[1] respectively. The perpendicular conformation of the two carboxylate planes in the potassium salt may probably be ascribed to the dominant electrostatic repulsion between the two carboxylate groups of a strong ionic character. Such a perpendicular conformation of the two carboxylate planes seems to decrease significantly the contribution of the following resonance structures B or C compared with the coplanar conformation. The
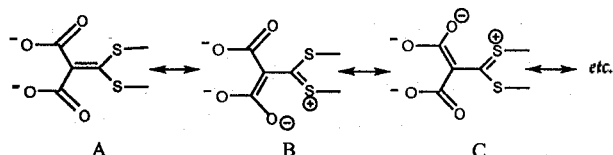
bond length of C=C may provide a concrete evidence on the contribution of the resonance structures. For instance, the length of C(3)-C(4) (1.347(6) Å) is prominently shorter than the corresponding lengths of dimethyl 1,3-dithiolan-2-ylidenemalonate (1.362(5) Å) and diamineplatinum(II) analog (1.374(9) Å), which exhibit significant contribution of the resonance structures B and C.[1,3] However, the double bond of the present compound is still slightly longer than the normal double bond (1.33 Å) due to the partial contribution of resonance forms B and C.[6] Furthermore, it is also noteworthy to point out that, for the coplanar carboxylate ion (C(1), O(1), and O(2)), the distance of S(1)⋯ O(1) (2.74 Å) discloses that an intramolecular sulfur-oxygen interaction still exists in the molecule. The longer bond lengths of C(4)-S(1) (1.765 (4) Å) and C(1)-O(1) (1.258(5) Å) than those of the corresponding C(4)-S(2) (1.749(5) Å) and C(2)-O(3) (1.248(5) Å), respectively, imply the presence of an intramolecular S⋯O interaction in the molecule. However, the strength of the interaction is drastically decreased relative to those of dimethyl 1,3-dithiolan-2-ylidenemalonate and diamineplatinum(II) analog as seen in Table 3. The strength of the intramolecular sulfur-

Notes

Bull. Korean Chem. Soc. 1996, Vol. 17, No. 5   475

Table 3. Structural Data of 1,3-Dithiolan-2-ylidenemalonate Analogs

Compound*	S···O distance (Å)	C=C distance (Å)	Dihedral angle(°) between two carboxylates	Ref.
K-salt	3.37 2.74	1.347(6)	83.6	This work
Me-ester	2.80 2.70	1.365(5)	48.1	3
Pt-complex	2.53 2.55	1.374(9)	14.5	1

*K-salt: Potassium 1,3-dithiolan-2-ylidenemalonate. Me-ester : Dimethyl 1,3-dithiolan-2-ylidenemalonate. Pt-complex : cis-Bis(cyclopropylamine)(1,3-dithiolan-2-ylidenemalonato)platinum(II)

oxygen interactions is linearly consistent with the trend of the dihedral angles between two carboxylates and the C=C bond lengths. Such prominent differences of the structural data among the compounds indicate that the presence of two anions strongly affects structural environment of these species of compounds.

In conclusion, the conformation of the two carboxylate groups of a dicarboxylate ligand seems to be dependent on their bonding nature, and for the title potassium salt, the characteristic properties such as perpendicular conformation of two carboxylates, C=C bond length, and S···O distance may be ascribed to domination of the electrostatic repulsion of the two adjacent anionic carboxylate groups in the molecular structure.

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Catalytic Redistribution/Dehydrocoupling of 2-Phenyl-1,3-disilapropane by Cp₂MCl₂/Red-Al System (M=Ti, Hf)

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Polysilanes with unusual optical and electronic properties due to σ-conjugation along the silicon backbone have been used for many special applications such as ceramic precursors, third-order NLO materials, deep-UV photoresists, photoconductors, and photoinitiators.[1] The conventional synthetic method to currently get high-molecular-weight polysilanes has been the Wurtz coupling reaction of dichlorosilanes using alkali metals, which is intolerant of some functional groups, lack of reproducibility, and have some limitations for controlling stereochemistry and molecular weight.

Harrod's recent discovery of group 4 metallocene-catalyzed dehydropolymerization led to great progress in poly(organosilane) synthesis.[2] A major handicap of the metallocene-catalyzed dehydrocoupling method is the production of low-molecular-weight polysilanes.[2,3] Intensive efforts have been made to increase the molecular weight of the polysilanes.[4~8]

Tilley *et al.* reported the dehydropolymerization of bis- and tris(silyl)arenes to produce highly cross-linked polysilanes.[4] We recently reported the dehydropolymerization of 2-phenyl-1,3-disilapropane, 1 to highly cross-linked polysilanes catalyzed by Cp₂MCl₂/*n*-BuLi (M=Ti, Hf).[9] We very recently described the catalytic redistribution of 1 by Red-Al.[10] Here we wish to report the catalytic dehydrocoupling of 1 by Cp₂MCl₂/Red-Al (M=Ti, Hf) yielding a low-molecular-weight polymer to compare with the dehydrocoupling of 1 by Cp₂MCl₂/*n*-BuLi (M=Ti, Hf).

Experimental Section

General Considerations. All reactions and manipulations were performed under prepurified nitrogen using Schlenk techniques. Dry, oxygen-free solvents were employed throughout. Glassware was flame-dried or oven-dried before use. Infrared spectra were obtained using a Perkin-Elmer 1600 series FT-IR or a Nicolet 520P FT-IR spectrometer. Proton NMR spectra were recorded on a Varian Gemini 300 spectrometer using CDCl₃/CHCl₃ as a reference at 7.24 ppm downfield from TMS. Gas chromatography (GC) analyses were performed using a Varian 3300 chromatograph equipped with a packed column (10% OV-101 on Chromosorb, W/AW-DMCS 1.5 m×1/8″ in. o.d.) in conjunction with a flame ionization detector. GC/MS data were obtained using a Hewlett-Packard 5890II chromatograph (HP-5, 5% phenyl-