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LETTER

# New organometallic dithiooxalate compound. Synthesis and structure of $[Cp_2ZrCl]_2(dto)$

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The coordination chemistry of dithiooxalate (dto) has been studied with most of the transition metals. Noticeably lacking are dto complexes with the Group 4 metals. Only one Group 4 complex ($Zr(dto)_4{}^{4-}$) has been mentioned in the literature [1]. This factor, plus the lack of coordination compounds with dithiooxalate attached to organometallic fragments, led to the investigation of the reactivity of dto toward $d^0$ $Cp_2MCl_2$ species, where $Cp = C_5H_5{}^-$. To date, there are only two organometallic–dto complexes known: $Mn_2(CO)_{10}dto$ [2] and $Cs_4[Re_2(CO)_6(dto)_3]$ [3]. Herein, we report the synthesis and structural characterization of a new organometallic dto complex, $[Cp_2ZrCl]_2(dto)$ (**1**).

## Experimental

### *Synthesis of $[Cp_2ZrCl]_2(dto)$ (1)*

Under $N_2$, 0.2724 g (0.932 mmol) $Cp_2ZrCl_2$ and 0.3681 g (1.86 mmol) $K_2dto$ were dissolved in 50 ml of $CH_2Cl_2$. The solution was stirred for 24 h and then filtered to remove excess dto. Addition of pentane to the filtrate gave a yellow microcrystalline material. Yield = 0.1437 g, 48.67%. *Anal.* Calc. for $Zr_2S_2Cl_2O_2C_{22}H_{20}$: C, 41.71; H, 3.16; S, 10.11. Found: C, 41.35; H, 3.21; S, 10.13%. m.p. = 232 °C d, $^1H$ NMR (200 MHz, δ, ppm, in $CDCl_3$): 6.28 (s, Cp). $^{13}C$ NMR (50 MHz, δ, ppm, in $d_6$-DMSO): 132.9 (d, $J(C\text{–}H) = 57.5$ Hz, Cp). IR (Nujol mull, NaCl plates): 3107.72(m), 1377.35(s), 1022.40(m), 922.09(m), 814.06(s), 721.47(m) $cm^{-1}$.

### *X-ray structure determination*

Crystals of **1** were grown by the slow diffusion of pentane into a $CH_2Cl_2$ solution**. Intensity data were collected with an Enraf-Nonius CAD-4 diffractometer using a $\theta$–$2\theta$ scan technique. Intensities of 4082 unique reflections (3054 reflections with $F^2 > 3\sigma(F^2)$) were measured by using a graphite-monochromated Mo Kα radiation. Lorentz, polarization and absorption corrections were applied. The structure was solved by Patterson and Fourier techniques and refined with full matrix least-squares methods (Enraf-Nonius SDP). Final $R = 0.029$, $R_w = 0.035$ ($w^{-1} = \{\sigma^2(I) + pI^2\}/4F^2$; $p = 0.04$; 271 parameters).

## Results and discussion

The synthesis of **1** from the direct reaction of $Cp_2ZrCl_2$ and $K_2dto$ in $CH_2Cl_2$ under $N_2$ gave a moderate yield of the yellow microcrystalline product. The electronic spectrum of **1** in $CH_2Cl_2$ shows absorptions at 371 (1240) and 271 (sh) nm. $[Cp_2ZrCl]_2(dto)$ is electrochemically inactive between 1.0 and −1.0 V in either $CH_2Cl_2$ or $CH_3CN$ solution. Final fractional coordinates and thermal factors for non-H atoms are given in Table 1.

The crystal structure of **1** has two independent half-complexes in the asymmetric unit, with each lying on a crystallographic center of symmetry located midway between the C atoms of the dto ligand. Each Zr is five coordinate, bound to two Cp ligands, a chlorine, an oxygen and a sulfur atom of the dto ligand. This coordination number has been seen previously for $Cp_2ZrCl$(carboxylate) complexes [4]. The geometry about the Zr atoms is a distorted trigonal bipyramid. The Cp–Zr–Cp angles are 128.5 and 129.4° for Zr(1) and Zr(2), respectively. The Cp–Zr–S angles range from 111.1–119.1° with the sum of the angles about the $Cp_2ZrS$ moiety adding to within 0.5° of 360° for both complexes. The O–Zr–Cl angles are distorted from linearity with the angles equal to 141.6° for Zr(1) and 141.4° for Zr(2). The $ZrCl(\mu\text{-dto})ZrCl$ fragment is planar (see Fig. 1). The Zr–S distances of 2.695(1) and 2.698(1) Å for Zr(1)–S(1) and Zr(2)–S(2), respectively, are in the order of the longer Zr–S distance (2.689(1) Å) in $Zr(SOCNEt_2)_4$, though they are considerably

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**1, $Zr_2S_2Cl_2O_2C_{22}H_{20}$; space group $P\bar{1}$, $a = 7.885(1)$, $b = 12.946(2)$, $c = 13.044(2)$ Å, $\alpha = 64.20(1)$, $\beta = 88.48(1)$, $\gamma = 76.67(1)°$, $V = 1825(3)$ Å$^3$, 293 K, $Z = 2$, $D_{calc} = 1.90$ g $cm^{-3}$, $\mu = 13.0$ $cm^{-1}$.

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TABLE 1. Final fractional coordinates and $B_{eq}$ thermal factors for non-H atoms[a]

| | $x$ | $y$ | $z$ | $B_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| Zr(1) | 0.82881(5) | 0.27709(3) | 0.53171(3) | 2.193(8) |
| Zr(2) | 0.42893(5) | 0.24778(3) | 0.03645(3) | 1.987(8) |
| Cl(1) | 0.7234(2) | 0.09319(9) | 0.5654(1) | 4.45(3) |
| Cl(2) | 0.5538(1) | 0.77328(8) | 0.14792(8) | 3.37(2) |
| S(1) | 0.4767(1) | 0.33142(9) | 0.5219(1) | 3.19(3) |
| S(2) | 0.4733(2) | 0.56461(8) | 0.12584(8) | 2.97(2) |
| O(1) | 0.7274(3) | 0.4693(2) | 0.4987(2) | 2.79(7) |
| O(2) | 0.4487(4) | 0.3759(2) | 0.1075(2) | 3.09(7) |
| C(1) | 0.8621(6) | 0.4139(4) | 0.3267(3) | 3.3(1) |
| C(2) | 1.0271(6) | 0.3686(4) | 0.3850(4) | 3.7(1) |
| C(3) | 1.0765(6) | 0.2483(5) | 0.4142(4) | 4.7(1) |
| C(4) | 0.9402(7) | 0.2174(4) | 0.3768(4) | 4.4(1) |
| C(5) | 0.8054(6) | 0.3209(4) | 0.3234(3) | 3.6(1) |
| C(6) | 1.0145(6) | 0.3074(4) | 0.6628(4) | 4.2(1) |
| C(7) | 0.8595(7) | 0.2909(5) | 0.7163(4) | 5.0(1) |
| C(8) | 0.8505(6) | 0.1750(5) | 0.7461(4) | 4.5(1) |
| C(9) | 1.0005(6) | 0.1202(4) | 0.7140(4) | 4.0(1) |
| C(10) | 1.1027(6) | 0.2007(4) | o.6648(4) | 3.9(1) |
| C(11) | 0.6180(6) | 0.1284(4) | 0.2200(4) | 3.5(1) |
| C(12) | 0.7297(5) | 0.1811(3) | 0.1368(4) | 3.2(1) |
| C(13) | 0.7414(5) | 0.1333(4) | 0.0602(4) | 3.3(1) |
| C(14) | 0.6396(6) | 0.0509(3) | 0.0941(4) | 3.6(1) |
| C(15) | 0.5661(6) | 0.0470(4) | 0.1932(4) | 4.0(1) |
| C(16) | 0.1811(6) | 0.1908(5) | 0.1549(4) | 4.3(1) |
| C(17) | 0.1440(6) | 0.3103(4) | 0.1125(4) | 4.7(1) |
| C(18) | 0.1105(6) | 0.3583(5) | −0.0057(5) | 5.6(2) |
| C(19) | 0.1205(6) | 0.2681(6) | −0.0321(4) | 6.3(2) |
| C(20) | 0.1685(6) | 0.1634(4) | 0.0657(5) | 5.6(1) |
| C(21) | 0.5755(5) | 0.5282(3) | 0.4949(3) | 2.37(9) |
| C(22) | 0.4781(5) | 0.4758(3) | 0.0621(3) | 2.50(9) |

[a] e.s.d.s in parentheses are in the units of the least-significant digit. $B_{eq} = \frac{4}{3}\Sigma_i \Sigma_j b_{ij}(\mathbf{a}_i \cdot \mathbf{a}_j)$.

longer than the short Zr–S distance of 2.669(1) Å [5]. The average Zr–S distance in $[Zr(S_2C_6H_4)_3]^{2-}$ is 2.543 Å [6]. In $[Cp_2Zr(SC_6H_5)]_2O$, the Zr–S distances are also short (2.542(2) and 2.554(2) Å) [7]. The Zr–O distances in **1** are 2.277(3) and 2.258(3) Å. The Zr–O distances in $Zr(SOCNEt_2)_4$ are 2.200(2) and 2.180(2) Å [5]. In the structure of $(Cp_2ZrS)_2$ [8], the planar $Zr_2S_2$ core forms a nearly perfect square with Zr–S distances of 2.490(3) and 2.482(3) Å. These distances are described as being extremely short. The Zr–S–Zr angle is 90.4(1)° and the S–Zr–S angle is 89.6(1)° in this compound. The distances in the $Zr_2S_2$ core in the $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZrS]_2$ complex [9] is similar to that found in $(Cp_2ZrS)_2$. The longer Zr–S and Zr–O bonds in **1** may be attributable to the $\pi$-interactions in the dto ligand which may cause a weakening of the Zr–dto bonds.

The varied modes of ligation of the dto ligand include S,S′-, O,O′- and O,S-binding possibilities. Examples of each have been documented, as well as the bridging of two metals by the dto ligand. If

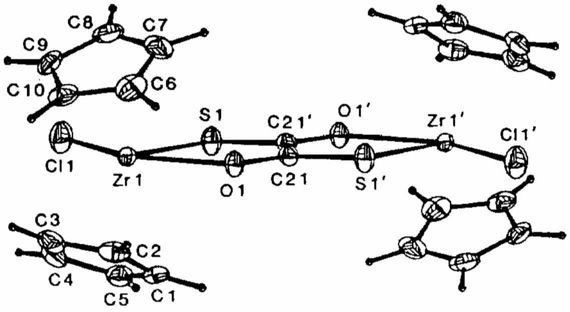

Fig. 1. Structure of one asymmetric unit of $[Cp_2ZrCl]_2(dto)$ showing atom labeling scheme. Selected bond lengths (Å) and angles (°): Zr(1)–O(1) 2.277(3), Zr(1)–S(1) 2.698(1), Zr(1)–Cl(1) 2.557(1), C(21)–S(1) 1.683(4), C(21)–O(1) 1.252(4), C(21)–C(21)′ 1.510(7), Zr(2)–O(2) 2.258(3), Zr(2)–S(2) 2.698(1), Zr(2)–Cl(2) 2.532(1), C(22)–S(2) 1.680(4), C(22)–O(2) 1.242(5), C(22)–C(22)′ 1.524(8), Cl(1)–Zr(1)–S(1) 71.34(4), S(1)–Zr(1)–O(1) 70.31(7), Cl(2)–Zr(2)–S(2) 71.09(4), S(2)–Zr(2)–O(2) 70.52(7), S(1)–C(21)–O(1) 125.(3), S(1)–C(21)–C(21)′ 116.1(4), O(1)–C(21)–C(21)′ 118.9(4), S(2)–C(22)–O(2) 125.6(3), S(2)–C(22)–C(22)′ 116.2(4), O(2)–C(22)–C(22)′ 118.3(4).

dto is bridging two homologous metals, the form of chelation if O,S for both metals [10–12]. Comparison of the dto bridge in $In_2(dto)_5{}^{4-}$ [10] and $[(P\varnothing_3)_2Ag]_2(dto)$ [12] to **1** shows close similarities. For both half molecules of **1**, the C–S (1.683(4); 1.680(4) Å) and C–O (1.252(4); 1.242(4) Å) bond lengths are comparatively short, indicating possible $\pi$-bonding between the atoms. Subsequently, the C–C distances are representative of a C–C single bond distance (C(21)–C(21)′, 1.501(7) Å; C(22)–C(22)′, 1.524(8) Å). The C–C distance is 1.561(11) and 1.545(16) Å for the In and Ag compounds, respectively. The C–S (Ag, 1.717(8); In, 1.705(11) Å) and C–O (Ag, 1.213(9); In, 1.238(14) Å) distances compare favorably with **1**. The O–Zr–S angles are 70.31(7) and 70.52(7)° for Zr(1) and Zr(2), respectively. The O–M–S angle is 73.8(1)° when M = Ag and 74.01(22)° when M = In.

Further investigations into the reactivity of **1** and the characterization of other $Cp_2MCl_2$ (M = Hf, Mo, V, Nb)–dto reaction products are currently underway.

## Supplemental material

A listing of general temperature factor expressions ($U$), hydrogen atom coordinates, bond distances and angles (6 pages) and tables of calculated and observed structure factors (27 pages) are available from the authors upon request.

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