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Studies of titanocene and zirconocene pyridine-2,6-*bis*-thiocarboxylates exhibiting partial desulfurization

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ABSTRACT

Attempts to synthesize bent metallocene complexes of pyridine-2,6-*bis*(thiocarboxylate), $Cp_2Ti(pdtc)$ and $Cp_2Zr(pdtc)$ yielded partially desulfurized products. In the case of $Cp_2Ti(IV)$ two types of products were obtained, in one case desulfurization was at one of the thiocarboxylate groups resulting in a carboxylate group while in the other case it was partial and from both the thiocarboxylate entities. In case of $Cp_2Zr(IV)$ similar partial desulfurization took place from both the thiocarboxylates. The complexes have been characterized by single crystal X-ray diffraction analysis. The ligands pyridine-2-carboxylate-6-thiocarboxylate, pyridine-2,6-dicarboxylate and pyridine-2,6-*bis*(thiocarboxylate) act as tridentate ligands. With both the metals binding of ligand is through the oxygen (and nitrogen) atoms leaving the sulfur free. Electronic absorption and emission spectra of the compounds have been studied experimentally and explained on the basis of DFT computations.

1. Introduction

Complexes of pyridine-2,6-dicarboxylate ligand have attracted a lot of attention [1–5]. The ligand exhibits quite a few different coordination modes leading to the formation of monomeric as well as polymeric complexes. Conversely, studies on the complexes of the corresponding thiocarboxylate [pyridine-2,6-*bis*(thiocarboxylate) (pdtc)] ligand are scanty. Though $pdtcH_2$ is a natural product, found in *Pseudomonas* bacteria [6] and have shown versatile ligational ability in its dianionic form with a few transition metal ions, yet its studies are limited largely to the complexes of Fe [7–9], Co [10,11], Ni [10,11] and Pd [12]. The complexes of Ni(II) and Pd(II) are dimeric (μ_2-S bridged) and undergo facile bridge cleavage reactions with a number of nucleophiles. $[Ni(pdtc)_2]^{2-,1-}$ were the first pair of structurally characterized Ni(II) and Ni(III) complexes with anionic sulfur ligands [11] which also threw light on factors that lead to unusually low values of redox potentials for this couple as found in [NiFe] hydrogenases. Pd(II) complexes show mesogenic behavior when suitably substituted [13]. A search of the literature revealed that other than the above mentioned late transition metals uranium is possibly the only metal whose complexes of pdtc have been synthesized and characterized crystallographically [14,15].

Continuing our studies on thiocarboxylate complexes [16–18] we here report the synthesis and characterization of the pdtc complexes of $Cp_2Ti(IV)$ and $Cp_2Zr(IV)$. The significance of the present study may be viewed not only in terms of the ligand's ability to stabilize uncommon oxidation state (Ni^{3+}) and unusual structural motifs [19] (e.g. Ni-SH) but also because of the fact that simple thiocarboxylates of these organometallic moieties have not been characterized yet (there is only one report on the synthesis of $Cp_2Ti(III)$ thiocarboxylate [20] and possibly no reports on corresponding $Cp_2M(IV)$ (M = Ti, Zr). Our attempts to isolate such complexes with thiobenzoate and thioacetate were unsuccessful. Notably, $Cp_2Ti(IV)$ carboxylates are known to be thermally unstable [21]).

2. Experimental

All the solvents were purified using standard methods. Pyridine-2,6-*bis*(thiocarboxylic) acid was synthesized using reported method [22].

IR spectra were recorded using Perkin-Elmer RX-1, FT-IR and Varian-3100 FTIR instruments. NMR spectra were obtained using a JEOL AL300 FT NMR spectrometer. Elemental analyses were performed using an Exeter model E-440 CHN analyser. CHS analysis of **4** was carried out at National Chemical Laboratory, Pune, India. Electronic absorption spectra were recorded using a Shimazdu UV-1700 PhermaSpec Spectorphotometer. Solid state emission spectra were recorded from VARIAN, CARY Eclipse Fluorescence spectrometer.

Single crystal X-ray data of compounds were collected on Xcalibur Oxford Diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). The SHELX program [23] was used

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for structure solution and refinement. Data collections for all the compounds were carried out at 293 K. Crystal data of complexes are given in Table 1. While refining the structure of **2** and **4** it was observed that the S atoms were disordered. On splitting them in two parts it became clear that the parts closer to C are oxygen. Further refinement was then made placing oxygen and sulfur atoms based on the distances from the carboxylate carbon (assuming that the sums of their occupancies equal to one).

2.1. Syntheses

2.1.1. Synthesis of [$Cp_2Ti(SCOPyCO_2)$] (**1**)

To a solution of pyridine-2,6-*bis*(thiocarboxylic) acid (0.200 g, 1.0 mmol) in methanol was added triethyl amine (0.202 g, 2.0 mmol) and stirred for 5 min then *bis*-cyclopentadienyltitanium dichloride (0.249 g, 1.0 mmol) was added with stirring. Precipitation occurred (yellow) just after addition. The reaction mixture was stirred further for an hour, the residue was then collected by filtration which was washed with methanol (two times) and dried under reduced pressure. The yellow residue was recrystallized from its chloroform solution by slow evaporation of the solvent. Yield: 0.254 g, (71%). *Anal.* Calc. for $C_{17}H_{13}O_3NSTi$: C, 56.84, H, 3.65, N, 3.90. Found: C, 56.57, H, 3.59, N, 3.93%. IR spectra (KBr, cm^{-1}): 1656 ν(CO), 1402 ν(CS). ^1H NMR ($CDCl_3$, ppm) 6.23 (10H of Cp, s), 8.24(1H, m, *J*(H, H) 7.2 Hz), 8.70(2H, m, *J*(H, H) 7.5 Hz) (Py). ^{13}C NMR ($CDCl_3$, ppm) 118.62 (Cp) 125.8, 126.3, 129.1, 142.7, 149.7 (Py), 167.0 (CO_2), 198.7 (COS).

2.1.2. Synthesis of [$Cp_2Ti(OCS)_2Py$] (**2**)

A method similar to that for the synthesis of **1** was applied for the synthesis of **2**, however, toluene was used as the solvent instead of methanol. Single crystals were grown from chloroform solution by slow evaporation of the solvent. IR spectra (KBr, cm^{-1}): 1658 ν(CO), 1405 ν(CS). ^1H NMR ($CDCl_3$, ppm) 6.20 (5H of Cp, s), 6.24 (5H of Cp, s), 8.09(^1H, d, *J*(H, H) 6.6 Hz), 8.42(1H, m, *J*(H, H) 7.8 Hz), 8.53 (1H, d, *J*(H, H) 7.5 Hz) (Py). ^{13}C NMR ($CDCl_3$, ppm) 118.5 (Cp), 118.7 (Cp), 128.1, 128.3, 128.6, 133.4, 134.3, 140.6 (Py), 186.1 (CO_2), 205.9 (COS).

2.1.3. Synthesis of [$Cp_2Ti(O_2C)_2Py$] (**3**)

When a chloroform solution of **1** with few drops of water was left for longer time (a week), yellow rectangular crystals of **3** were obtained.

2.1.4. Synthesis of [$Cp_2Zr(SCO)_2Py$] (**4**)

A similar procedure was followed as described for the synthesis of **1**, however, in place of Cp_2TiCl_2, Cp_2ZrCl_2 (0.292 g, 1.0 mmol) was used. The red orange, rectangular crystals were obtained from chloroform solution layered by petroleum ether (60–80 °C). Yield: 0.347 g (83%). *Anal.* Calc.: C, 50.75; H, 3.26; S, 7.81. Found: C, 50.35; H, 3.71; S, 7.54% (This fits with the partially desulfurized product, $C_{17}H_{13}O_2N(S/O)_2Zr$ in which 49% is thiocarboxylate and 51% has desulfurized to carboxylate moity). IR spectra (KBr, cm^{-1}): 1670 ν(CO), 1387 ν(CS). ^1H NMR ($CDCl_3$, ppm) 6.25 (5H of cp, s), 6.27 (5H of Cp, s), 8.26(^1H, m, *J*(H, H) 6.3 Hz), 8.30 (1H, m, *J*(H, H) 6.3 Hz), 8.70(1H, t, *J*(H, H) 8.7 Hz) (Py). ^{13}C NMR ($CDCl_3$, ppm) 114.4 (Cp), 114.4 (Cp), 125.5, 126.1, 128.0, 128.6, 142.9, 149.2 (Py), 165.3 (CO_2), 207.2 (COS).

2.2. Computational details

The energy optimized geometries of **1** and **4** were calculated using the B3LYP [24,25] exchange–correlation functional. The effective core potential (ECP) standard basis set LANL2DZ [26–28] was utilized for Ti and Zr atoms, where as the 6-31G** [29] basis set was used for C, H, O, N and S atoms. The energies and intensities of the 20 lowest-energy spin allowed electronic excitations were calculated by using TD-DFT at the same level of theory. The first static hyperpolarizabilty (β_0) for compounds **1** and **4** were calculated by using the finite field perturbation method by implementing the PCM model [30,31]. The solvent parameters were those of chloroform. X-ray coordinates were used for optimization of geometries. The optimized coordinates were used for the calculation of electronic excitations and hyperpolarizabilities. All the theoretical calculations were performed using the GAUSSIAN 03W set of programs [32]. Molecular orbital plots were generated by using the program MOLDEN [33].

3. Results and discussions

3.1. Syntheses and characterization

Complexes **1**, **3** and **4** were obtained by the reaction between Cp_2MCl_2 [M = Ti(IV) and Zr(IV)] and pyridine-2,6-*bis*(thiocarboxylic) acid in presence of triethyl amine in methanol as shown in Scheme 1.

Complex **1** was formed when desulfurization (possibly in the form of H_2S) of one of the thiocarboxylate groups occurred during the synthesis resulting in a carboxylate group. When a few drops of

Table 1
Crystal data and structure refinement of compounds.

	1	2	3	4
Empirical formula	$C_{17}H_{13}NO_3STi$	$C_{17}H_{13}NO_2E_2Ti$[a]	$C_{17}H_{13}NO_4Ti$	$C_{17}H_{13}NO_2E_2Zr$[a]
T (K)	293	293	293	293
Crystal system	orthorhombic	orthorhombic	monoclinic	orthorhombic
Space group	*Cmca*	$Pmn2_1$	$P2_1$	$Pmn2_1$
a (Å)	10.4723(8)	11.964(11)	8.0004(13)	11.948(5)
b (Å)	12.2097(6)	8.167(4)	7.7109(10)	8.280(5)
c (Å)	24.1589(15)	7.678(5)	11.5957(14)	7.847(5)
β (°)	90	90	95.946(12)	90
V (Å^3)	3089.0(3)	750.2(9)	711.49(17)	776.3(8)
Z	8	2	2	2
μ(Mo Kα) (mm^{-1})	0.703	0.657	0.622	0.805
Reflections collected/unique	4852/1894	2021/1432	3194/2215	2190/1148
R_{int}	0.0245	0.0444	0.0340	0.0201
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0640$, $wR_2 = 0.1635$	$R_1 = 0.0730$, $wR_2 = 0.1744$	$R_1 = 0.0850$, $wR_2 = 0.2254$	$R_1 = 0.0312$, $wR_2 = 0.0656$
R indices (all data)	$R_1 = 0.0931$, $wR_2 = 0.1807$	$R_1 = 0.1392$, $wR_2 = 0.2326$	$R_1 = 0.0925$, $wR_2 = 0.2351$	$R_1 = 0.0504$, $wR_2 = 0.0712$
Goodness-of-fit on F^2	0.854	0.982	1.062	1.023

[a] E = S partially substituted with O.