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

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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 (λ = 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). ^{1}H 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). ^{1}H NMR ($CDCl_3$, ppm) 6.20 (5H of Cp, s), 6.24 (5H of Cp, s), 8.09(^{1}H, 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). ^{1}H NMR ($CDCl_3$, ppm) 6.25 (5H of cp, s), 6.27 (5H of Cp, s), 8.26(^{1}H, 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

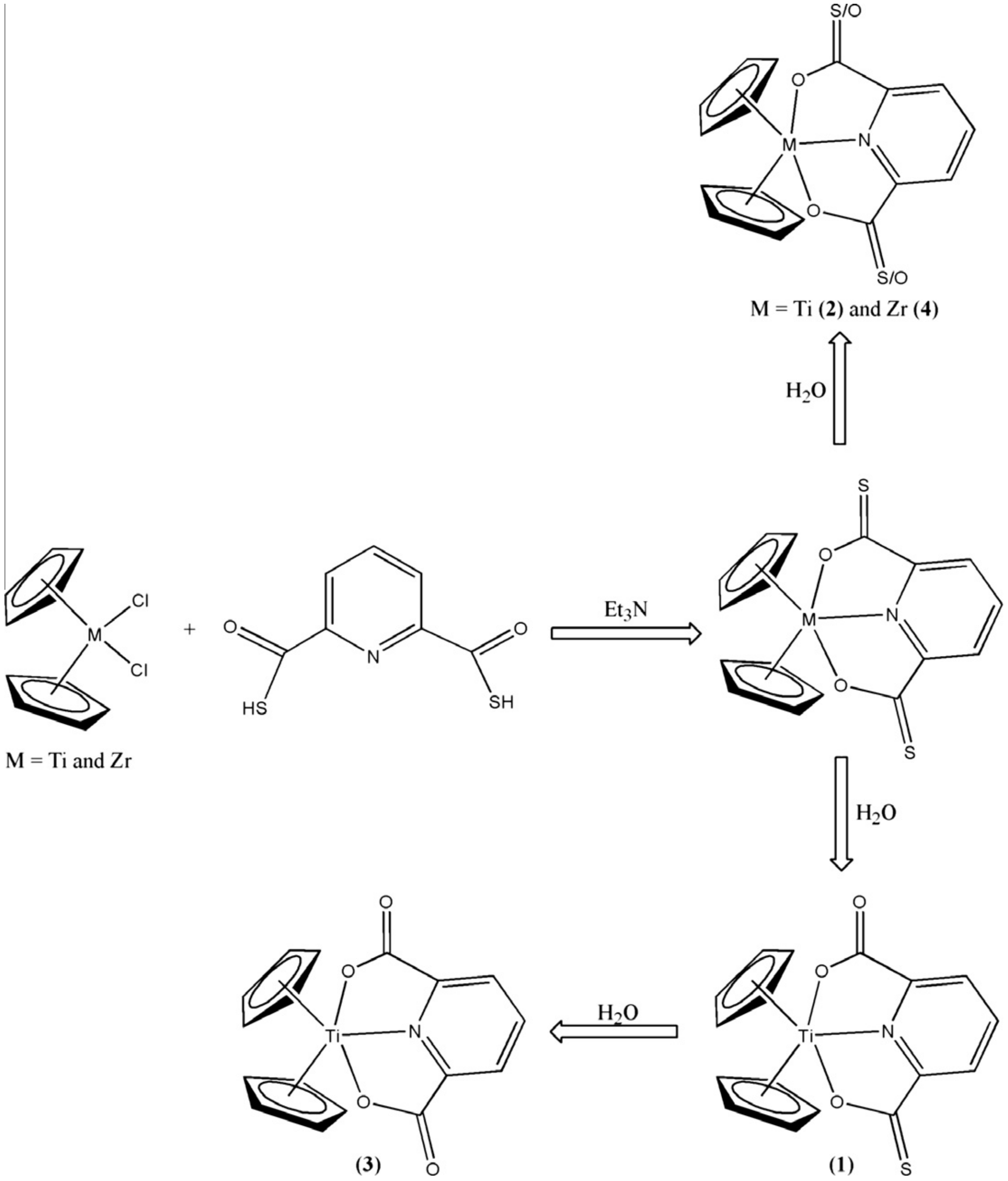
Complexes **1**, **3** and **4** were obtained by the reaction between Cp_2MCl_2 [M = Ti(IV) and Zr(IV)] and pyridine-2,6-*bis*(thiocarboxylic) acid in presence of triethyl amine in methanol as shown in Scheme 1.

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.



Scheme 1.

water were added to a chloroform solution of **1** complete desulfurization occurred and corresponding carboxylate complex **3** was obtained. Since the *bis*-thiocarboxylate derivative could not be isolated in methanol we attempted to isolate the same by carrying out the reaction in toluene which can be dehydrated much easily. However, the product obtained in this case contained Et_3NHCl which could not be separated completely by recrystalliztion. Crystals of complex **2** could, however, be selected under microscope and subjected to X-ray analysis. Desulfurization was also observed in the cases of complexes **2** and **4** but it was partial and from both the thiocarboxylate entities. Desulfurization of thiocarboxylate complexes is quite uncommon, however, we have recently reported [34] ready desulfurization of copper(II) thiocarboxylate complexes leading to the formation of the corresponding carboxylate complexes. This reactivity may be rationalized in view of the bonding modes of the ligands. As have been observed in the Cu(II) complexes bonding of the thiocarboxylate groups in both **1**, **2** and **4** is primarily through the oxygen atoms in contrast to possibly all other structurally characterized transition metal thiocarboxylate complexes (in which there is a strong M–S bonding).

It is however, interesting to note the difference between **1** and **2**/**4** in their desulfurization modes. While in **1** one of the thiocarboxylate undergoes complete desulfurization leaving the other group as such, **2** and **4** show partial desulfurization at both the thiocarboxylate groups. To the best of our knowledge **2** and **4** provide the first examples of metal complexes in which some of the molecules have changed from their original composition to a new one in the same lattice. A search of the literature revealed that such compositional change have earlier been reported only in the case of triphenylphosphine sulfide [35].

^1H and ^{13}C NMR spectra of the complexes were recorded to understand the nature of these in solution. In case of **1** a single sharp peak was observed due to the cyclopentadienyl protons. In addition there were two peaks with a proton ratio of 1:2, respectively due to the protons at C4 and C3+C5 of pyridine. The peaks appeared as multiplets since the environments at C2 and C6 are

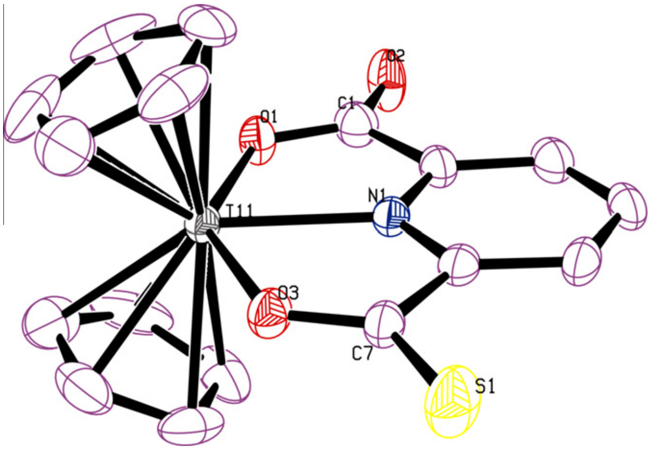


Fig. 1. Thermal ellipsoid plot of **1** (at 30% probability level. Hydrogen atoms are omitted for clarity). *Selected metric data:* Ti1–O1 2.122(4), Ti1–O3 2.145(4), Ti1–N1 2.191(4), Ti1–Cp 2.080, C7–S1 1.639(6), C7–O3 1.266(7), C1–O2 1.286(7), C1–O1 1.284(7), C1–C2 1.495(9), C7–C6 1.496(8); O1–Ti1–O3 141.48(16), O1–Ti1–N1 71.40(16), O3–Ti1–N1 70.08(16), Cp–Ti1–O1 98.57, Cp–Ti1–N1 114.72, Cp–Ti1–O3 97.29, Cp–Ti–Cp′ 130.52, O1–C1–O2 126.0(6), O3–C7–S1 125.5(5).

Table 2
Hydrogen bonding parameters.

Complex	D–H···A	H···A (Å)	D–H···A (°)	D···A (Å)	Symm. Op.
1	C–H5···S1	2.925	145.48	3.727	*x*, 1 − *y*, 1−*z*
	C–H3···O1	2.569	146.40	3.383	−*x*, −1/2 + *y*, 1.5 − *z*
	C–H12···O2	2.642	138.23	3.393	−*x*, −1/2 + *y*, 1.5 − *z*
4	C–H3···S1	2.826	122.94	3.422	1/2 + *x*, 2 − *y*, 1/2 + *z*
	C–H7···S1	2.766	122.56	3.359	1/2 − *x*, 1 − *y*, −1/2 + *z*

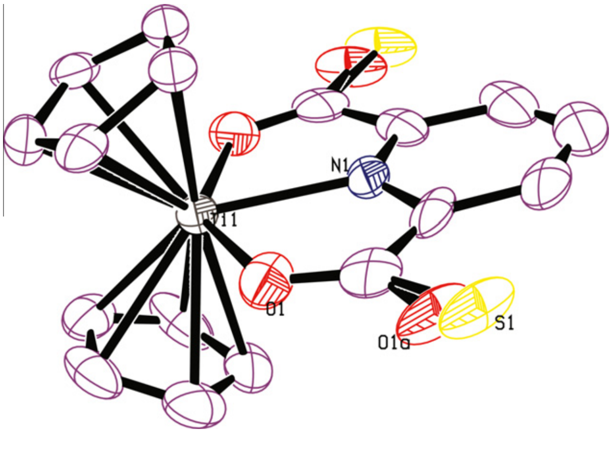


Fig. 2. Thermal ellipsoid plot of **2** (at 30% probability level. Hydrogen atoms are omitted for clarity). *Selected metric data:* Ti1–O1 2.154(8), Ti1–N1 2.184(12), Ti1–Cp 2.101, O1–C1 1.245(14), C1–S1 1.693(17), C1–C2 1.478(19); O1–Ti1–O1 143.3(5), O1–Ti1–N1 71.7(2), Cp–Ti1–O1 97.16, Cp–Ti1–N1 113.45, O1–C1–S1 142(3).

slightly different owing to the presence of CO_2 and COS groups, respectively. The ^{13}C NMR spectrum was also consistent with the ^{1}H NMR features. There were five signals due to the five carbon atoms of pyrindine indicating the chemical non-equivalence of C2/C6 and C3/C4. NMR spectral patterns of **2** and **4** are similar. In these cases two closely spaced singlets were observed due to the protons (and carbons in ^{13}C spectrum) of Cp groups which may arise due to the presence of both carboxylate and thiocarboxylate complexes in solution. The number of signals due to pyridine ring protons and carbons are also consistent in the respective spectra.

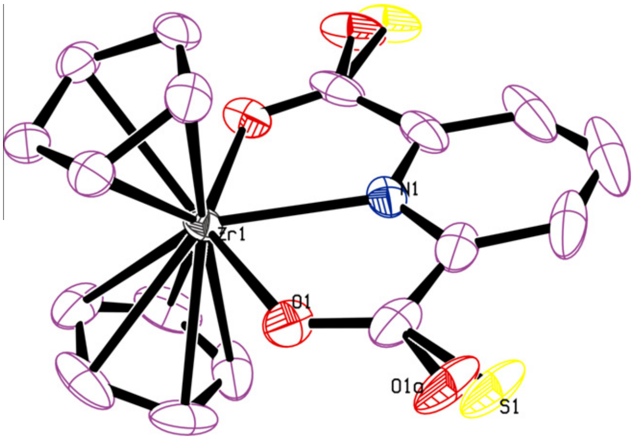


Fig. 3. Thermal ellipsoid plot of **4** (at 30% probability level. Hydrogen atoms are omitted for clarity). *Selected metric data:* Zr1–O1 2.186(6), Zr1–N1 2.278(13), Zr1–Cp 2.238, O1–C1 1.285(14), C1–S1 1.586(12), C1–C2 1.454(17); O1–Zr1–O1 136.9(4), O1–Zr1–N1 68.5(2), Cp–Zr1–O1 98.00, Cp–Zr1–N1 114.34, O1–C1–S1 137.7(13).

3.2. Crystal and molecular structures

Complex **1** was crystallized in orthorhombic system with space group *Cmca*. Molecular structure of complex **1** is depicted in Fig. 1. Ti(IV) is bonded to the two oxygen atoms, one from carboxylate and the other from thiocarboxylate groups and the nitrogen atom of pyridine ring. Thus in this complex the ligand behaves as a tridentate ONO donor-chelating one. The two centroids of two cyclopentadienyl groups occupied fourth and fifth coordination sites of the central titanium atom.

All the bond lengths are in their usual range. Geometry around titanium atom can be described as distorted trigonal bipyramidal with the two centroids of cyclopentadienyl rings and nitrogen atom of pyridine ring occupying the three equitorial sites and two oxygen atoms placed at axial positions. Bond angles Cp–Ti–N1 and Cp–Ti–Cp′ being 114.72° and 130.52° are slightly deviated from ideal angle of 120° whereas angle between O1–Ti–O3 (141.48°) is highly deviated from the ideal of axial positions. Notably, the S–M–S angles in Ni(II) and Pd(II) complexes vary in the range of 172–180°.

There are three types of intermolecular hydrogen bonds, one between a hydrogen of the pyridine ring and the sulfur atom of thiocarboxylate (C–H···S 2.925 Å), second one in between a hydrogen of pyridine and bonded oxygen of carboxylate group (C–H···O 2.570 Å) and another one in between hydrogen of cyclopentadienyl ring and oxygen of carboxylate (C–H···O 2.643 Å). The C–H···O/S distances and angles (Table 2) are quite comparable to those reported earlier [18,36,37]. CH···S interactions of two molecules are such that they form a couple of molecule facing each other. Besides these intermolecular hydrogen bondings a π–π interaction is also present between pyridine ring and cyclopentadienyl ring of two molecules with a centroid–centroid distance of 3.789 Å. Due to presence of these weak interactions molecules are arranged in the lattice forming a 3D network in a regular geometrical pattern (Figs. S1 and S2, Supporting information).

Complex **2** crystallized in orthorhombic system with space group *P*mn2$_1$. The molecule possesses a plane of symmetry bisecting the molecule through N1–Ti1. The molecular structure is depicted in Fig. 2. The overall geometry of the molecule is comparable to that of **1**.

As mentioned already partial desulfurization was noticed in cases of complexes **2** and **4**. In the case of **2** from single crystal X-ray diffraction studies it appeared that sulfur atoms in both

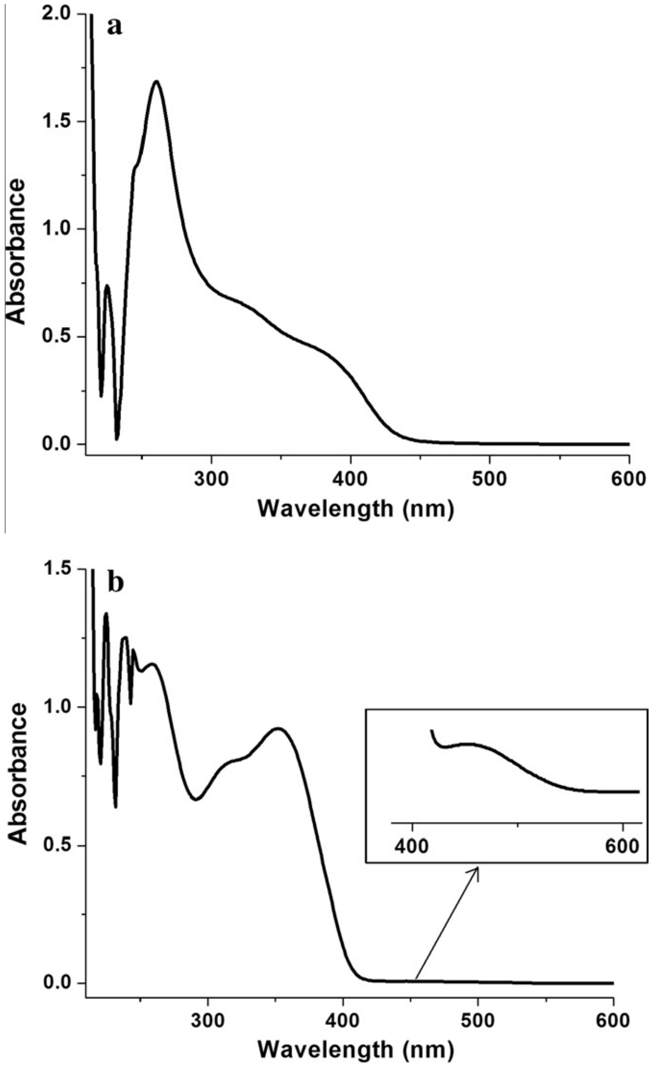


Fig. 4. Absorption spectra of (a) **1** (2×10^{-5} M) and (b) **4** (4×10^{-5} M).

the thiocarboxylate have 19% occupancy whereas in case of **4** (Fig. 3) sulfur atoms have 30% occupancy. Notably the elemental analyses also suggested partial desulfurization to the extent of 51% in the latter. Crystals obtained from different batches also showed similar composition. The molecular structures of **2** and **4** are quite similar.

There are two types of intermolecular hydrogen bonds in **4**, one between hydrogen of pyridine ring and sulfur and other in between hydrogen of cyclopentadienyl ring and sulfur (Table 2). Besides these hydrogen bonds a π–π interaction is also present between pyridine ring and cyclopentadienyl ring of two molecules with a centroid–centroid distance of 3.779 Å. Due to presence of these interactions molecules are arranged along *c*-axis forming a sheet (Fig. S3, Supporting information).

Complex **3** was crystallized in monoclinic system with space group $P2_1$ and crystal data are given in Table 1. Since the molecular structure has already been reported [38] earlier we refrain from giving any further details of it. However, the earlier reported structure was solved in the space group $P4_32_12$.

3.3. Electronic absorption spectra

Electronic absorption spectra of both **1** and **4** were recorded in chloroform solution. Complex **1** showed (Fig. 4a) strong absorption bands at 225, 260 nm and two broad peaks at 318 and 388 nm. Complex **4** showed (Fig. 4b) strong absorption bands at 225, 239, 246, 260, 311and 350 nm. Besides these another broad and weak band was observed at 462 nm. The higher energy bands may be assigned as inter- or intraligand charge transfer bands where as the lower energy bands are possibly due to ligand to metal or metal to ligand charge transfers.

For unambiguous assignment of the spectral bands TDDFT calculations have been carried out. Orbitals involved in selected transitions in **1** are shown in Fig. 5. Since **4** is a mixture containing both carboxylate and thiocarboxylate ligands we have carried out calculations for both and the orbitals involved in selected transitions are shown in Fig. 6a and b, respectively. From TDDFT calculations it's clear that higher energy band in both the cases of **1** and **4** are due to transitions of ligand to metal and interligand charge transfer transitions where as lower energy bands are due to inter/intraligand charge transfer transitions.

3.4. Emission spectra

Emission spectrum of complex **1** recorded in solid state (Fig. 7). It showed two strong emission bands at 408 and 528 nm when excited at 385 nm. Emission at 408 nm may be due to interligand charge transfers however comparatively lower energy emission band at 528 nm due to admixing of MLCT and ILCT. Conversely, **4** did not show any emission in this range.

3.5. Nonlinear optical properties

The nonlinear optical property of **1** and **4** (with thiocarboxylate form of ligand) was calculated by double numerical differentiation of energies (finite-field perturbation method).

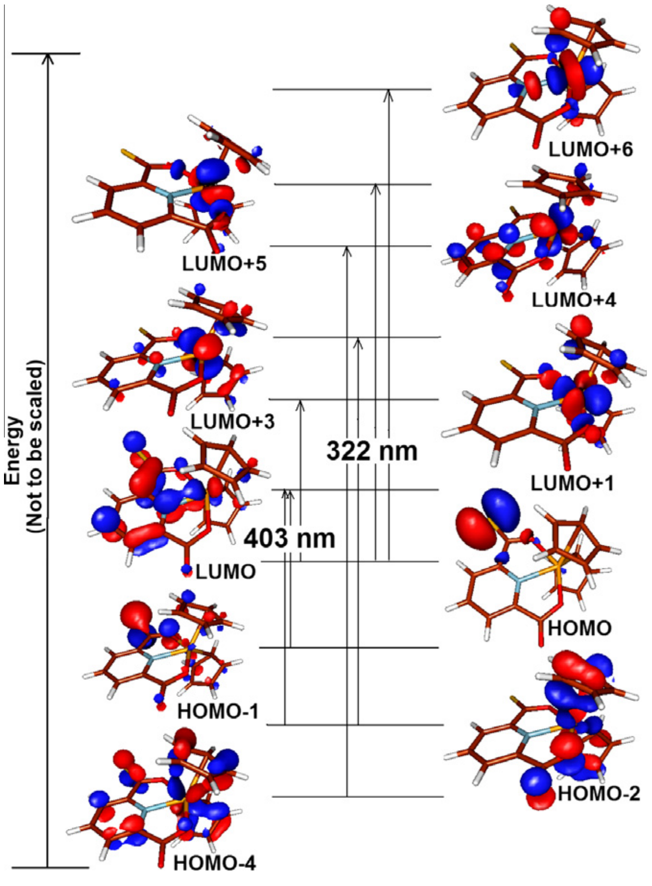


Fig. 5. Selected molecular orbitals for **1** (orbital contour value = 0.05).

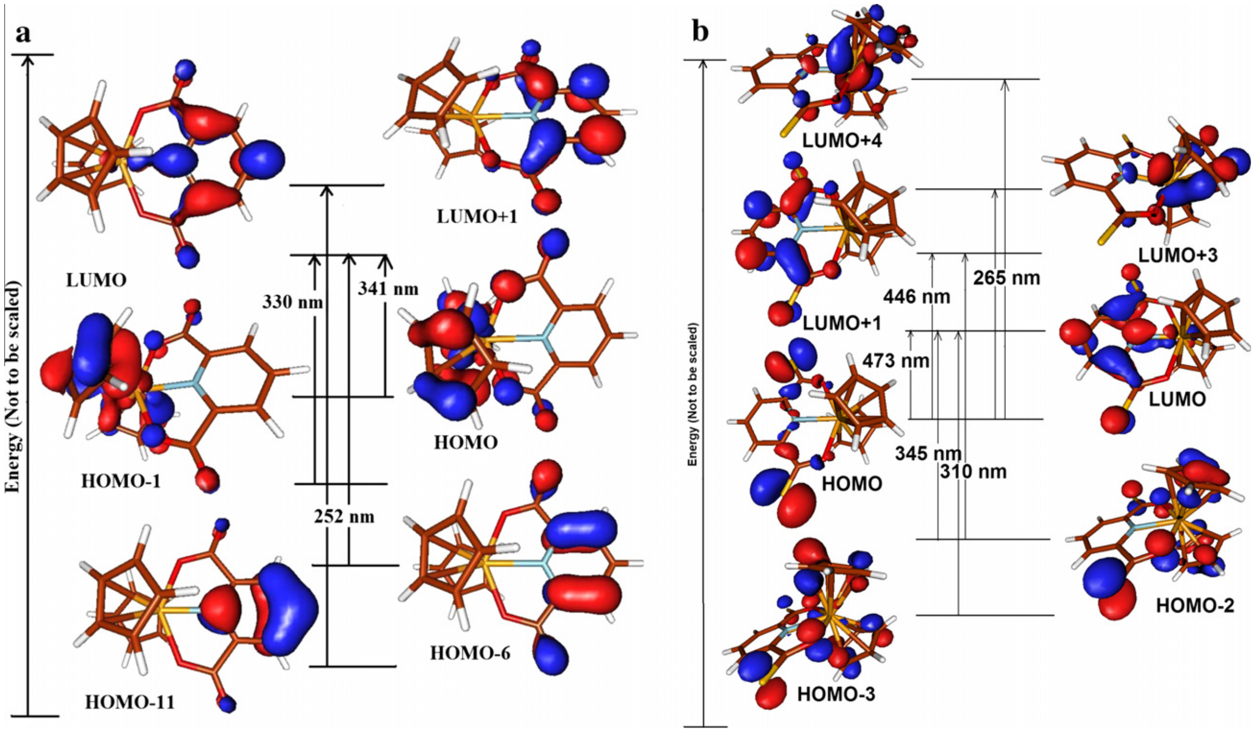


Fig. 6. Selected molecular orbitals for **4** (orbital contour value = 0.05). (a) In pure carboxylate form and (b) in pure thiocarboxylate form.

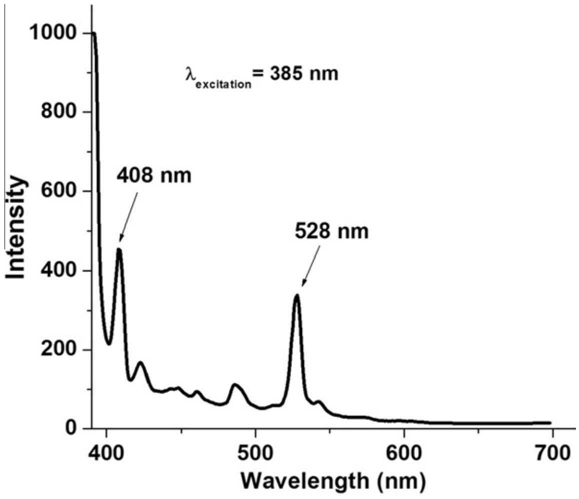


Fig. 7. Emission spectrum of **1** in solid state.

Table 3
Calculated dipole moments and hyperpolarizabilities of **1** and **4**.

System	μ	β_x	β_y	β_z	β_0
*p*NA	7.53	−13.70	0.03	0.04	13.72
1	0.74	79.01	1240.71	0.82	10.74
4	0.56	−1288.78	−2.99	2122.99	11.14

Hyperpolarizability is given by the coefficients in the Taylor series expansion of the energy in the external electric field [39]. If the external electric field is weak and homogeneous the expansion is (Eq. (1)).

$$E = E^0 - \mu_\alpha F_\alpha - 1/2\alpha_{\alpha\beta}F_\alpha F_\beta - 1/6\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma \tag{1}$$

In which E^0 is the energy of unperturbed molecules, F_α is the field of origin, and μ_α, $\alpha_{\alpha\beta}$, and $\beta_{\alpha\beta\gamma}$ are the components of dipole moment, polarizability, and first hyperpolarizability, respectively. The mean first hyperpolarizabilty is defined as shown in Eq. (2) [40].

$$\beta^0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \tag{2}$$

in which the β_x, β_y, and β_z components can be described by

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}, \quad \beta_y = \beta_{yyy} + \beta_{yxx} + \beta_{yzz}, \quad \text{and} \beta_z = \beta_{zzz} + \beta_{zxx} + \beta_{zyy}.$$

The solvent parameters used were those of chloroform. The β_0 value calculated for one molecule of **1** and **4** (considering sulfur containing pdtc ligand in the case of **4**) was found to be 10.74×10^{-30} and 11.14×10^{-30} esu, respectively in chloroform, which is less than *p*-nitroaniline (*p*NA, Table 3).

4. Conclusion

The organometallic complexes [$Cp_2Ti(SCOPyCO_2)$], [$Cp_2Ti(SCO)_2Py$] and [$Cp_2Zr(SCO)_2Py$] have been synthesized. Complex [$Cp_2Ti(SCOPyCO_2)$] 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. Similar desulfurization was also observed in the case of complexes [$Cp_2Ti(SCO)_2Py$] and [$Cp_2Zr(SCO)_2Py$] but it was partial and from both the thiocarboxylate entities. Bonding of the thiocarboxylate groups in both complexes is primarily through the oxygen atoms. Complexes [$Cp_2Ti(SCO)_2Py$] and [$Cp_2Zr(SCO)_2Py$] are the first example of a metal complex in which some of the molecules have changed from their original composition to a new one in the same lattice.

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Appendix A. Supplementary material

CCDC 826621, 890258, 861316 and 826620 contain the supplementary crystallographic data for complexes **1**–**4**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.11.014.

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