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CHARACTERIZATION, LUMINESCENT PROPERTIES, CRYSTAL STRUCTURE DETERMINATION, AND THERMAL PROPERTIES OF [Tl(Ph₂phen)Cl₃(DMSO)]**M. Ghadermazi**

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The new mixed-ligand complex of [Tl(Ph₂phen)Cl₃(DMSO)] (**1**) is obtained from the reaction of TlCl₃·4H₂O with 4,7-diphenyl-1,10-phenanthroline (Ph₂phen) in a methanol solution. Suitable crystals of **1** are obtained for the X-ray diffraction measurement by methanol diffusion into a DMSO solution. This complex is characterized by spectral methods (IR, UV-Vis, ¹H NMR, and luminescence), elemental analysis, thermal analysis (TG, DTA), and single crystal X-ray diffraction.

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INTRODUCTION

Thallium is a heavy element of group 13, which has two Tl⁺ and Tl³⁺ oxidation states. However, Tl⁺ is a stable ion and coordination compounds of both cations have been studied [1—4]. The thallium(III) cation with the spherical symmetry of electron shells (*d*¹⁰) is a hard acid [5]. Strongly bonded coordination compounds are formed by thallium(III) with hard donor atoms such as N and O atoms. Several thallium(III) complexes with N and O donor ligands were reported and characterized by spectroscopy and X-ray diffraction [6—13]. These complexes are of interest owing to their importance for applications in spectroscopy [6—9], crystallography [10—13], electronics and optics [13, 14], and nanomaterials [15].

4,7-Diphenyl-1,10-phenanthroline (Ph₂phen) is a good bidentate ligand, and numerous complexes have been prepared with Ph₂phen, such as those of gold [16], indium [17], mercury [18, 19], rhenium [20], ruthenium [21], copper [22], palladium [23], platinum [24], and europium [25]. Transition metal complexes of Ph₂phen are interesting owing to their importance for the application in stable single-layer light-emitting electrochemical cells (LEECs) [26, 27], luminescence and electroluminescence [25, 28], and the enhanced interaction of metal complexes with DNA [29, 30]. We report herein the synthesis, characterization, and crystal structure of a new thallium(III) mixed-ligand complex with chloride, dimethyl sulfoxide, and 4,7-diphenyl-1,10-phenanthroline.

EXPERIMENTAL

Materials and physical methods. 4,7-Diphenyl-1,10-phenanthroline and TlCl₃·4H₂O were purchased from Aldrich (Taufkirchen, Germany), and used as received. Other materials were purchased from Merck (Darmstadt, Germany) and used without further purification. Infrared spectra (4000—250 cm⁻¹) of solid samples were taken as 1 % dispersion in CsI pellets using a Shimadzu-470 spec-

trometer (Kyoto, Japan). NMR was recorded on a Bruker AC-300 spectrometer (Hüllhorst, Germany) for protons at 300.13 MHz in a DMSO- d_6 solvent. Elemental analysis was performed using a Heraeus CHN-O Rapid analyzer (Hanau, Germany). Melting point was obtained by a Kofler Heizbank Rechart type 7841 melting point apparatus (Bucharest, Romania). UV-Vis spectra were recorded on a Shimadzu 2100 spectrometer using a 1 cm path length cell in DMSO at room temperature (Kyoto, Japan). Luminescence spectra were recorded on a Perkin Elmer LS 45 using a 1 cm path length cell (Massachusetts, USA) and thermal behavior was measured by a STA 503 Bähr apparatus (Hüllhorst, Germany).

Synthesis of [Ti(Ph₂phen)Cl₃(DMSO)] (1). A solution of 4,7-diphenyl-1,10-phenanthroline (0.36 g, 1.10 mmol) in methanol (10 ml) was added to a solution of TiCl₃·4H₂O (0.42 g, 1.10 mmol) in methanol (10 ml) and the resulting colorless solution was stirred for 20 min at 40 °C. Suitable crystals for the X-ray diffraction measurement were obtained by methanol diffusion to a colorless solution of **1** in DMSO over two weeks (yield 0.60 g, 75.6 %, m.p. > 300 °C). IR (CsI, cm⁻¹): 3060 m, 2921 m, 2854 w, 1611 m, 1563 m, 1510 m, 1433 s, 1365 s, 1275 w, 1234 m, 1098 m, 1010 s, 941 m, 849 s, 759 s, 700 s, 626 w, 554 m, 491 w, 420 m, 339 m, 262 m. UV-Vis: λ_{max} (DMSO, nm), 315. Anal. calcd. (%): C 43.29, H 3.05, N 3.88. Found (%): C 43.01, H 3.03, N 3.85.

Single crystal X-ray diffraction analysis. The X-ray diffraction measurements were made on a Bruker APEX II CCD (Karlsruhe, Germany) area detector diffractometer at 298 K (MoK α radiation, graphite monochromator, $\lambda = 0.71073$ Å). The structure of **1** was solved by SHELX-97 and absorption correction was applied using the SADABS programs [31]. Data collection, cell refinement, and data reduction were performed by APEX II, SAINT, SHELXTL, PLATON, and MERCURY [31–34]. Crystal chemical information on the structure investigated was deposited with the Cambridge Structural Database under number CCDC 1033446, from where it can be obtained free on request at the following website: www.ccdc.cam.ac.uk/products/csd/faqs.

RESULTS AND DISCUSSION

Description of the molecular structure of [Ti(Ph₂phen)Cl₃(DMSO)] (1). Crystallographic data for **1** are given in Table 1, and the selected bond lengths and angles are presented in Table 2. The ORTEP view with the numbering schemes for compound **1** is shown in Fig. 1. This complex crystallized in the triclinic $P\bar{1}$ space group. In the crystal structure of complex **1**, the Ti^{III} atom is six-coordinated in a distorted octahedral configuration by two N atoms from the chelating 4,7-diphenyl-1,10-phenanthroline ligand, one O atom from dimethyl sulfoxide, and three Cl atoms. The Ti—N bond lengths are 2.392(8) and 2.394(8) Å, the Ti—O bond length is 2.391(8) Å, and Ti—Cl bond lengths are 2.465(3), 2.505(4), and 2.467(4) Å (Table 2). The Ti—N, Ti—O, and Ti—Cl bond distances are normal and comparable to those in related thallium(III) complexes [9, 13]. The phenanthroline ring is distorted from the planarity. The mean planes of rings $A(N1/C1—C3/C10/C24)$, $B(C10—C13/C23/C24)$, $C(N2/C13/C14/C21—C23)$, and $D(Ti1/N1/C23/C24/N2)$ make the following dihedral angles with each other: $A/B = 4.05^\circ$, $A/C = 2.74^\circ$, $A/D = 2.38^\circ$, $B/C = 1.50^\circ$, $B/D = 6.10^\circ$, and $C/D = 4.99^\circ$.

In the crystal structure of complex **1** (Fig. 2) the π — π interaction between the phenyl rings, $Cg4 \cdots Cg4^i$ (distance = 3.751(9) Å, symmetry code: $2-x, 3-y, 1-z$, where Cg4 are centroids of the ring (C5—C9)) and weak intermolecular bonds such as C—H...Cl and C—H...O

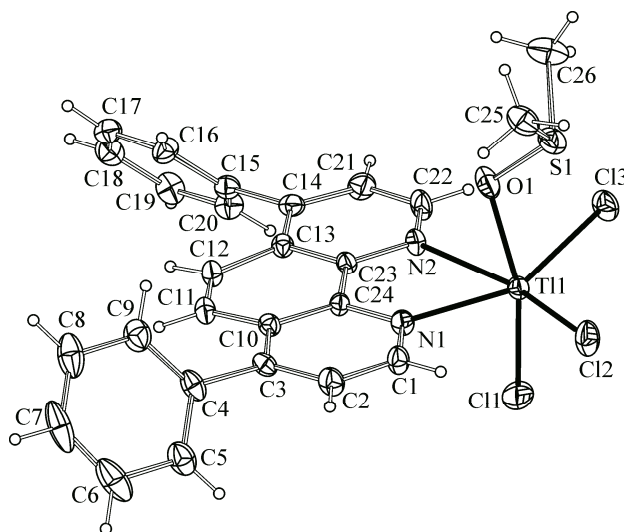


Fig. 1. Labeled diagram of **1**. Thermal ellipsoids are at 30 % probability level

Table 1

Crystallographic and structure refinement data for 1

Parameter	Value
Formula	C ₂₆ H ₂₂ Cl ₃ N ₂ OStI
Formula weight	721.26
Temperature, K	298(2)
Wavelength λ , Å	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a, b, c , Å	8.8112(5), 12.7297(7), 13.9412(8)
α, β, γ , deg.	111.667(4), 93.661(5), 104.342(4)
V , Å ³	1386.82(14)
Z	2
ρ_{calc} , g/cm ³	1.727
μ , mm ⁻¹	6.209
$F(000)$	696
Crystal size, mm	0.32×0.35×0.40
Range of data collection over θ , deg.	1.60—28.00
Intervals of reflection indices	$-11 \leq h \leq 11, -16 \leq k \leq 16, -17 \leq l \leq 18$
Measured / independent reflections	13939 / 6682 ($R_{\text{int}} = 0.095$)
Completeness over $\theta = 26.99$, %	99.7
R factors over $F^2 > 2\sigma(F^2)$	$R_1 = 0.0296, wR_2 = 0.0664$
R factors over all reflections	$R_1 = 0.0368, wR_2 = 0.0676$
S	0.961
Residual electron density (min / max), e/Å ³	0.533 / -0.445

Table 2

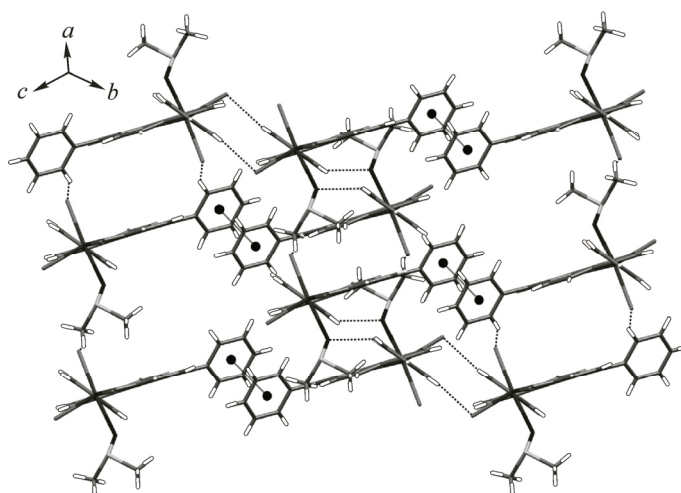
Bond distances (Å) and bond angles (deg.) for 1

Tl1—N1	2.392(8)	C11—Tl1—C12	101.38(12)	C12—Tl1—N2	159.2(2)
Tl1—N2	2.394(8)	C11—Tl1—C13	100.49(13)	C13—Tl1—O1	85.9(2)
Tl1—C11	2.504(4)	C11—Tl1—O1	166.2(2)	C13—Tl1—N1	156.02(19)
Tl1—C12	2.465(3)	C11—Tl1—N1	93.3(2)	C13—Tl1—N2	92.0(2)
Tl1—C13	2.467(4)	C11—Tl1—N2	86.6(2)	O1—Tl1—N1	76.8(3)
Tl1—O1	2.391(8)	C12—Tl1—C13	105.24(12)	O1—Tl1—N2	81.0(3)
		C12—Tl1—O1	88.5(2)	N1—Tl1—N2	69.2(2)
		C12—Tl1—N1	90.95(18)		

are effective in the stabilization of the crystal structure and the formation of the 3D supramolecular complex.

Spectroscopic characterization of [Tl(Ph₂phen)Cl₃(DMSO)] (1). IR absorption of **1** is listed in the EXPERIMENTAL section. The infrared spectrum of this complex shows several bands in the region of 3060—2854 cm⁻¹, which are assigned to the C—H stretching vibrations of the phenyl and pyridine rings and the DMSO methyl group. The bands observed in the range 1611—1365 cm⁻¹ are assigned to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$ vibrations. The medium to strong vibrations in the region 1098—554 cm⁻¹ are assigned to $\delta(\text{C}=\text{C}=\text{N})$ and $\delta(\text{C}=\text{C}=\text{C})$ deformation vibrations in the phenyl and pyridine rings [13, 17, 35—38]. In addition, a new signal at 941 cm⁻¹ is assigned to $\nu(\text{S}=\text{O})$ for the coordinated DMSO ligand [38]. The far IR spectrum of complex **1** was recorded between 420 and 262 cm⁻¹.

Fig. 2. Crystal packing diagram for **1**. Intermolecular C—H...Cl and C—H...O hydrogen bonds and π — π contacts are shown as dashed lines



Tl—N, Tl—O, and Tl—Cl stretching vibrations are seen at 420, 389, and 262 cm^{-1} , respectively [5, 6, 13].

The UV-Vis spectrum of the DMSO solution of complex **1** has a band at 286 nm, assigned to $\pi \rightarrow \pi^*$.

The ^1H NMR spectra of the free Ph₂phen ligand and complex **1** were measured in DMSO-*d*₆ at room temperature and the results are displayed in Fig. 3. As depicted in Fig. 3, the ^1H NMR spectrum of the free Ph₂phen ligand exhibited a singlet at 7.68 ppm for the phenyl groups, a doublet at 7.72 ppm for **Hb**, a singlet at 7.91 ppm for **Hc**, and a doublet at 9.16 ppm for **Ha**.

The ^1H NMR spectrum of complex **1** differs from that of the free Ph₂phen ligand. It exhibits hydrogen coupling with ^{203}Tl (29.5 %) and ^{205}Tl (70.5 %) isotopes with spin 1/2 nuclei [9, 13] and a slight deshielding of about 0.4 ppm, compared with the free Ph₂phen ligand. As seen in Fig. 3, **Ha** is split with $^{203,205}\text{Tl}$ and appears as a broad doublet with $^3J_{\text{TlH}} = 158.4$ Hz, centred at 9.56 ppm, and the splitting of **Hb** with thallium results in a doublet at around 8.31 ppm with $^4J_{\text{TlH}} = 48.0$ Hz. [9, 13] Furthermore, **Hc** appears at 8.14 ppm as a singlet.

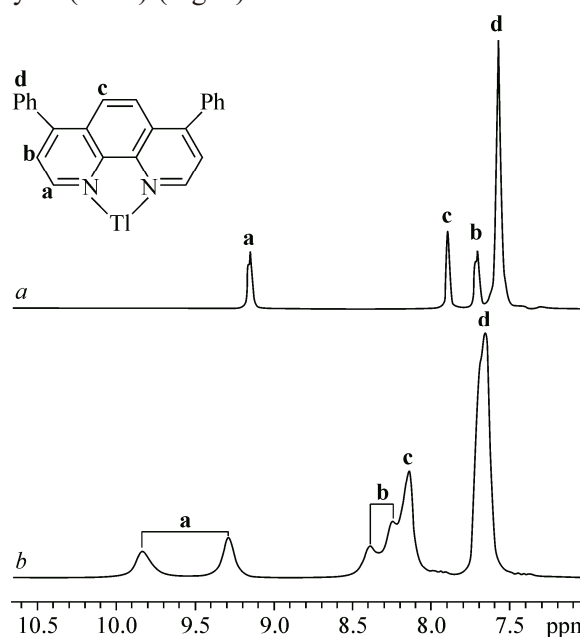
The luminescence emission spectra ($\lambda_{\text{ex}} = 340$ nm) of Ph₂phen and **1** were obtained in a DMSO solution at room temperature and the results are displayed in Fig. 4. As shown in this figure, the maximum emission of Ph₂phen at 376 nm is shifted to 382 nm in complex **1**, with a red shift after coordination to Tl(III) (6 nm red-shifted compared to the related emission band). Also, the luminescent emission of complex **1** is weaker than that of the free Ph₂phen ligand. The shapes of the luminescence emission spectra for Ph₂phen and **1** are similar, therefore, the emission properties of these compounds are believed to originate from $\pi^* \rightarrow \pi$ or $\pi^* \rightarrow n$ transitions in the Ph₂phen ligand [39—42].

Thermal studies of [Tl(Ph₂phen)Cl₃(DMSO)] (1**).** The thermal stability of **1** was determined on single crystal samples between 30—640 °C in the air atmosphere with a heating rate of 10 °/min by thermogravimetric (TG) and differential thermal analysis (DTA) (Fig. 5). The TGA curve shows that chemical decomposition starts at about 160 °C and ends around 610 °C with a weight loss of 70.2 % corresponding to the removal of one 4,7-diphenyl-1,10-phenanthroline ligand, three chloride and one dimethyl sulfoxide molecule (calcd. 68.3 %). The remaining weight of 29.8 % corresponds to 0.5Tl₂O₃ (calcd. 31.7 %) [43]. The DTA curve of **1** displays three distinct endothermic peaks at 155, 432, and 512 °C and two distinct exothermic peaks at 495 and 539 °C.

CONCLUSIONS

In this work, new mixed-ligand complex [Tl(Ph₂phen)Cl₃(DMSO)] (**1**) has been synthesized.

Fig. 3. Aromatic region of ^1H NMR spectra of Ph₂phen (a) and [Tl(Ph₂phen)Cl₃(DMSO)] (b) compounds in DMSO-*d*₆



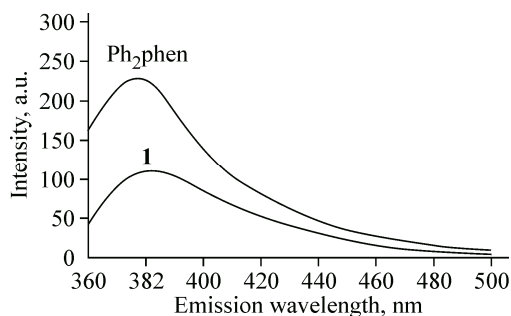


Fig. 4. Luminescence spectra of Ph₂phen (4.52×10^{-4} M) and [Ti(Ph₂phen)Cl₃(DMSO)] (**1**) (4.50×10^{-4} M) in DMSO at room temperature; excitation wavelength is 340 nm

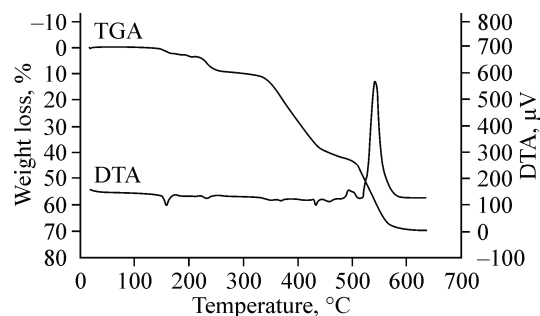


Fig. 5. Thermal behavior of **1**

This complex was fully characterized by spectroscopy methods and its structure was studied by the single crystal X-ray diffraction method. In this complex, the Ti^{III} atom is six-coordinated in a distorted octahedral configuration by two N atoms from the chelating 4,7-diphenyl-1,10-phenanthroline ligand, one O atom from dimethyl sulfoxide, and three Cl atoms. Also, the thermal stability of this complex was studied by thermal gravimetric (TG) and differential thermal analyses (DTA).

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