



Terpyridine Metal Complexes as Building Blocks for Supramolecular Assemblies and Polymers: Thermal Stabilities and Thin Film Preparation

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Abstract. 5,5''-Dimethyl-2,2':6',2''-terpyridine complexes with various transition metal ions like Zn(II), Co(II), Mn(II) and Hg(II) were investigated concerning their thermal properties. A significant dependency of the thermal stability (5% weight loss) of the complexes depending on the kind of metal ion used could be observed ranging from 315 to 390 °C. Furthermore, self-assembled thin films of such metallo-supramolecular Hg(II) complexes were prepared and characterized by synchrotron based X-ray reflectivity and fluorescence techniques.

Key words: terpyridine, metal complexes, thermal stability, thin film preparation, supramolecular systems.

1. Introduction

Terpyridine metal complexes have been extensively studied in the last century in view of their electronic and redox properties, e.g., in the direction of applications in photocatalysis or energy conversion [1]. Hundreds of complexes with transition metal ions like cobalt, copper, iron, chromium, nickel or ruthenium have been synthesized with various counter ions and investigated [2]. However, most studies have been limited to systems involving unsubstituted terpyridine ligands and counter ions like bromo, iodo or perchlorate – the very useful 5,5''-dimethyl substituted terpyridine and the interesting hexafluorophosphate counter ion were only described in a very few cases [3]. Furthermore, no consistent data concerning the thermal stability of such complexes could be found. We have been interested in the use of 5,5''-disubstituted terpyridines as building blocks for functional polymers as well as in the application of fused terpyridine moieties for the construction of extended metallo-supramolecular coordination arrays [4]. With this application in mind, terpyridine metal complexes represent ideal model systems. In this work we

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report the thermal stabilities of these complexes. Furthermore, we used one system for the preparation of stable thin films by layer-by-layer adsorption methods [5].

2. Experimental

2.1. MATERIALS

Diethylether was distilled under argon from sodium. Reagent solutions were added against an N₂ counterstream. Solvents were removed with a rotary evaporator *in vacuo*. ¹H and ¹³C NMR spectra were recorded on a Bruker AC 300 in CDCl₃ or CD₃CN at 300 and 75 MHz, respectively. The chemical shifts were calibrated to the residual solvent peak or TMS. Melting points were measured on a digital Mettler FP-5/FP-51 apparatus. The thermogravimetric analysis (TGA) measurements were done using a Polymer Laboratories Simultaneous Thermal Analyzer STA 1500, heating rate 10 K/min in synthetic air.

2.2. SYNTHESIS

5,5''-Dimethyl-2,2':6',2''-terpyridine (2,6-di(5'-methylpyrid-2'-yl)pyridine) (1)

Terpyridine **1** was synthesized according to published procedures and using a new synthetic strategy with organotin intermediates and Stille type coupling procedures [6]. M.p. 174–175 °C. Elemental Analysis: Calc. for C₁₇H₁₅N₃: C, 78.13, H, 5.79, N, 16.08. Found: C, 77.92, H, 5.73, N, 16.07.

Bis(5,5''-dimethyl-2,2':6',2''-terpyridine) manganese(II) hexafluorophosphate (2)

Synthesized from 5,5''-dimethyl-2,2':6',2''-terpyridine **1** in methanol using manganese(II) acetate in 96% yield as a yellow crystalline solid [7]. Elemental Analysis: Calc. for C₃₄H₃₀F₁₂MnN₆P₂: C, 47.03, H, 3.46, N, 9.68. Found: C, 46.75, H, 3.51, N, 9.64.

Bis(5,5''-dimethyl-2,2':6',2''-terpyridine) mercury(II) hexafluorophosphate (3)

Synthesized from **1** in methanol using mercury(II) acetate in 85% yield as white crystalline solid [7]. Elemental Analysis: Calc. for C₃₄H₃₀F₁₂HgN₆P₂: C, 40.27, H, 2.96, N, 8.29. Found: C, 40.09, H, 3.06, N, 8.26.

Bis(5,5''-dimethyl-2,2':6',2''-terpyridine) cobalt(II) hexafluorophosphate (4)

Synthesized from **1** in methanol-water using cobalt(II) acetate tetrahydrate in 96% yield as a brown crystalline solid [7]. Elemental Analysis: Calc. for C₃₄H₃₀N₆CoF₁₂P₂: C, 44.19, H, 2.71, N, 10.31. Found: C, 46.59, H, 3.71, N, 9.32.

Bis(5,5''-dimethyl-2,2':6',2''-terpyridine) zinc(II) hexafluorophosphate (5)

Synthesized from **1** in methanol with zinc(II) acetate dihydrate in 87% yield of a white crystalline solid [7]. Elemental Analysis: Calc. for C₃₄H₃₀F₁₂N₆P₂Zn: C, 46.52, H, 3.42, N, 9.57. Found: C, 46.07, H, 3.58, N, 9.48.

2.3. LAYER-BY-LAYER SELF-ASSEMBLY

Specially prepared silicon substrates were subsequently treated with solutions of poly(ethylene imine) (PEI), poly(styrene sulfonate) (PSS) and the metal complexes [8]. X-ray experiments were carried out at the D4 bending magnet station of the storage ring DORIS at HASYLAB/DESY (monochromatic X-ray beam of 12.5 keV). The surface diffuse scattering (nonspecular scattering) has been measured both in the plane of incidence and out of the plane of incidence. The X-ray fluorescence under grazing angles was recorded simultaneously with the reflectivity measurements [8].

3. Results and Discussion

For the potential application of metallo-supramolecular systems in new functional materials the thermal stability of such building blocks is of great importance. In view of an extension of isolated terpyridine metal complexes to more interesting metal containing polymers or thin films we choose the 5,5''-dimethyl-2,2':6',2''-terpyridine **1** as the basic heterocyclic unit due to the easy latter functionalization, e.g., using radical bromination methods (Figure 1). It is known for a long time that such terpyridine ligands form very stable complexes with various transition metal ions (the schematic complexation and a model of the obtained complex is shown in Figure 1) [7]. However, we could not find consistent data concerning the thermal stability of such complexes and about the influence of the metal ions. Therefore we decided to systematically investigate the thermal behavior of selected ligands and metal complexes in view of their thermal stability (5% weight loss). We first compared our central ligand **1** (5,5''-dimethyl-terpyridine) with the commercially available 2,2':6',2''-terpyridine (Figure 2). The unsubstituted ligand was less stable than the dimethyl substituted ligand **1** as shown in Figure 2 (5% weight loss at 225 °C compared to 245 °C). The same tendency was seen also in the melting temperatures (93 °C compared to 175 °C [7]). The introduction of methyl groups into the 5-position of the terminal pyridine moieties improved therefore the thermal stability of the ligands. Studies in the direction of introducing longer chains are currently in progress. In a second step we investigated the thermal behavior of some selected 5,5''-dimethyl-terpyridine metal complexes. We prepared the corresponding Mn(II), Hg(II), Co(II) and Zn(II) complexes (Figure 1). The results of the thermogravimetric analysis revealed a significant influence of the metal ion used on the thermal stability of the resulting metal complex. The Mn(II) complex showed already a weight loss of 5% at 315 °C, whereas the corresponding Zn(II) was stable up to 390 °C. The Co(II) and the Hg(II) complex were found to decompose at 371 °C and 336 °C, respectively. These findings are rather important in two respects: First, the influence of the used substituents and metal ions should be taken into consideration when designing new metallo-supramolecular materials. Second, the very specific thermal stability of the different complexes could be maybe used

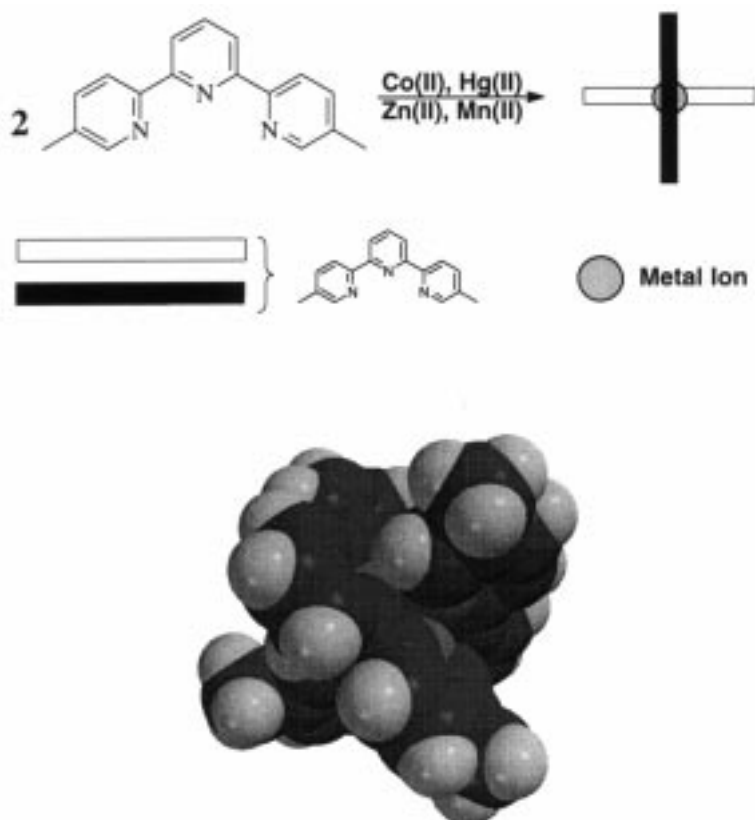


Figure 1. Top: Schematic representation of the 5,5''-dimethyl-terpyridine **1** leading to the formation of the [1 × 1] complexes. Bottom: Space filling model of the [1 × 1] Co(II) complex (MacSpartan 1997, level MM2).

Table I. Thermal stability (5% weight loss) of the investigated ligands and complexes (measured in synthetic air)

	Terpyridine ligands		[1 × 1] Terpyridine complexes			
	Unfunctionalized	5,5''-dimethyl 1	Mn	Hg	Co	Zn
<i>T</i> (°C)	225	245	315	336	371	390

for the construction of temperature sensitive systems. The results are summarized in Table I.

Besides the design and synthesis of such “*isolated*” systems we were interested in the ordered and stable arrangement of [1 × 1] metal complexes on surfaces or within thin films. For this purpose we used self-assembly into thin monomolecular films by adsorption onto polyelectrolyte covered substrates [5]. We prepared a

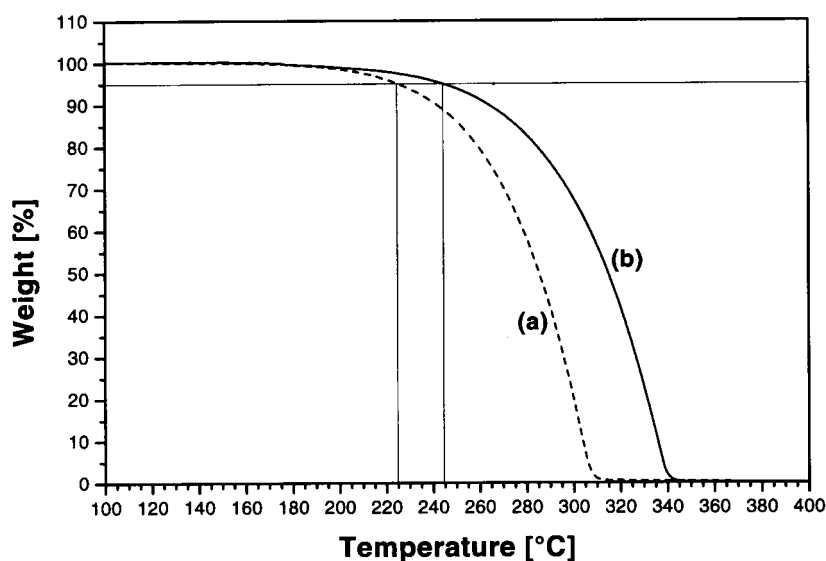


Figure 2. Thermogravimetric analysis (TGA) of the commercially available unsubstituted 2,2':6',2''-terpyridine (a) and the 5,5''-dimethyl-terpyridine **1** (b).

thin cushion of polyelectrolytes onto a silicon substrate (successive adsorption of poly(ethylene imine) and poly(styrene sulfonate) layers) followed by a top layer of the $[1 \times 1]$ Hg(II) complexes (Figure 4, experimental details see [8]). X-ray reflectivity measurements indicated clearly the successful adsorption of the complexes expressed by the differences in the oscillation amplitude of curves (a) and (b) reflecting the increased density contrasts and interfacial widths (Figure 5). Furthermore, the pronounced fringes of (b) indicate a very well defined interface for the adsorbed complexes. Simultaneous the X-ray fluorescence of the $[1 \times 1]$ Hg(II) complex adsorbed on the surface has been measured (Figure 6). The characteristic fluorescence energies (L_{α} for Hg) provide the most direct proof of the complex adsorption.

4. Conclusion

The present results demonstrate the significant influence of the substituents and metal ions on the thermal stability of the terpyridine metal complexes. The Zn(II) complexes showed the highest stability, whereas the corresponding Mn(II) complexes were 75 °C less stable. The introduction of methyl groups improved the thermal stability of the ligands as well. Furthermore, self-assembled thin films of the Hg(II) complexes were prepared using layer-by-layer adsorption and characterized by synchrotron based X-ray reflectivity and fluorescence techniques. This findings could open new entries for the construction of novel functional metallo-supramolecular materials with special thermal properties.

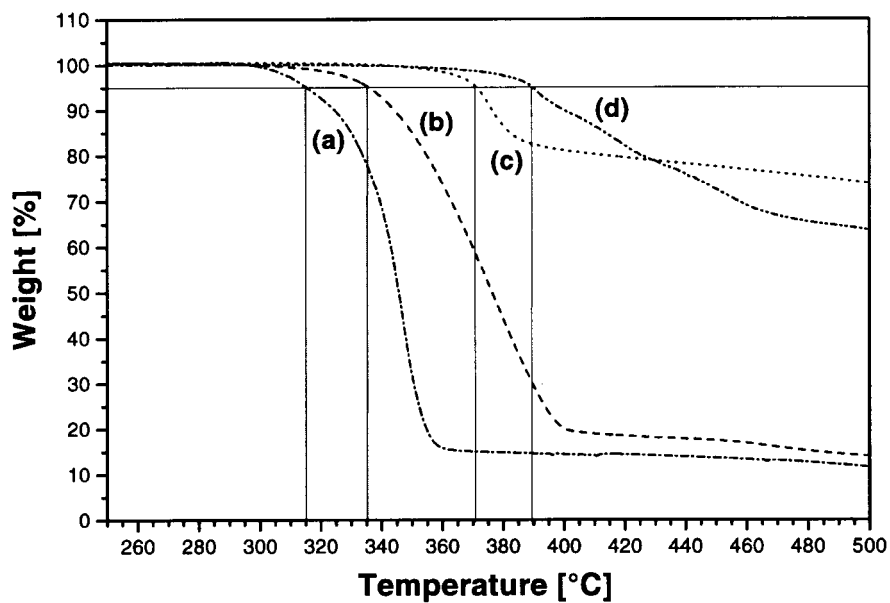


Figure 3. Thermogravimetric analysis (TGA) of the 5,5''-dimethyl-terpyridine metal complexes: (a) [1 × 1] Mn(II); (b) [1 × 1] Hg(II); (c) [1 × 1] Co(II); (d) [1 × 1] Zn(II).

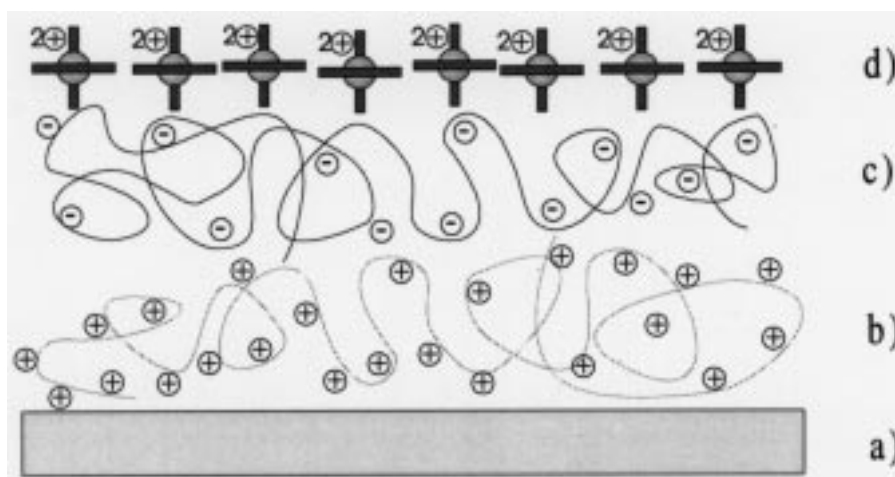


Figure 4. Schematic drawing illustrating the build-up of the complex layers: (a) silicon substrate (Si); (b) poly(ethylene imine) (PEI); (c) poly(styrene-4-sulfonate) (PSS); (d) [1 × 1] metal grids. The filled circles refer to the metal ions.

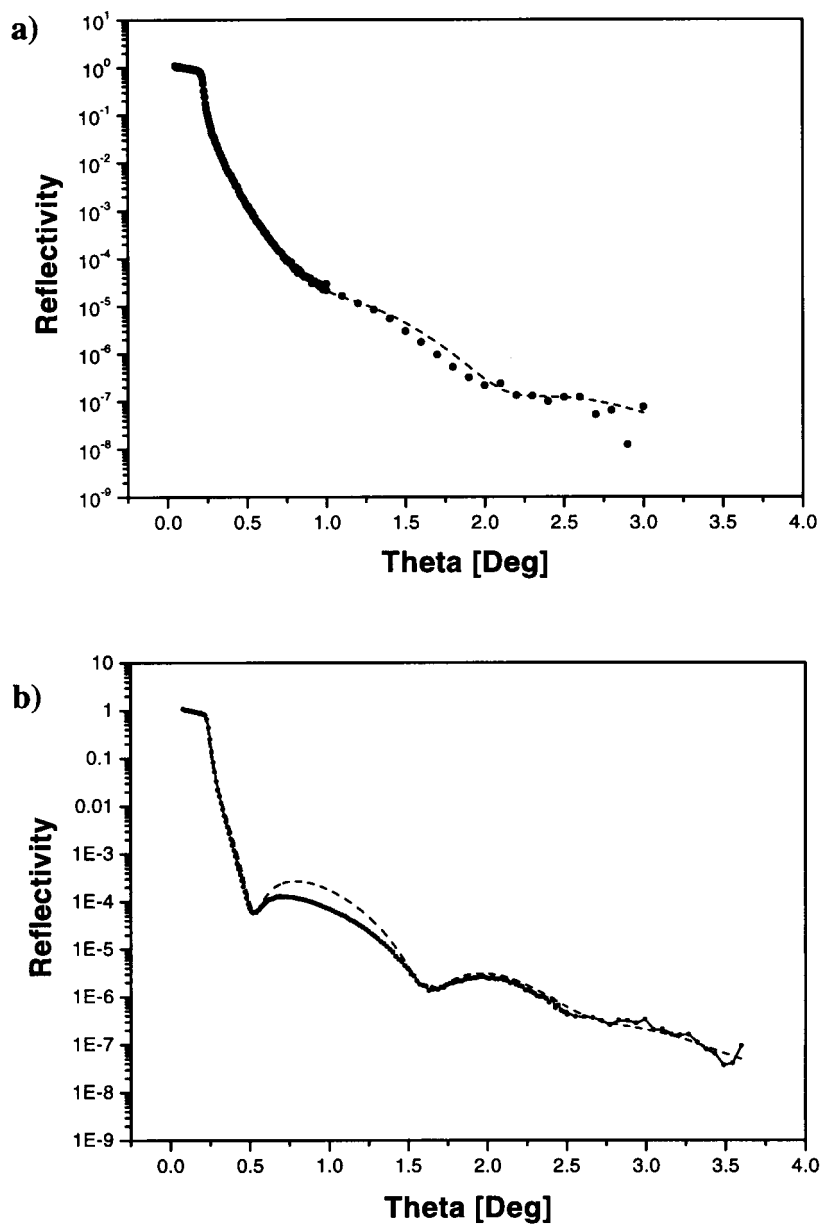


Figure 5. Typical X-ray reflectivity profiles $R(q_z)$ of the self-assembled films: (a) films composed of the polyelectrolyte layers PSS/PEI/Si without any metal complexes; (b) films with $[1 \times 1]$ Hg complexes adsorbed on top. The curves reflect the laterally averaged density profiles of the film along the interface normal. The total film thickness can be derived directly from the spacing of the minima (dashed lines: simulation [8]).

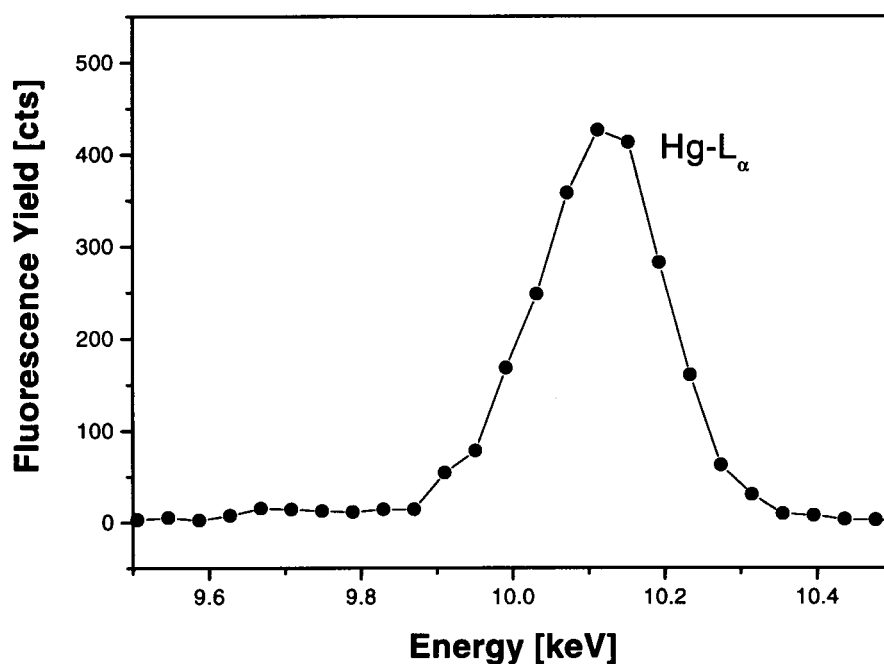


Figure 6. X-ray fluorescence spectra of monomolecular layer of $[1 \times 1]$ Hg complexes.

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