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2,2′:6′,2″-Terpyridine – An Introduction, a Short Historic Overview, and Fundamental Aspects*

1.1 Introduction

Modern terpyridine chemistry brings together three worlds – coordination chemistry (from an inorganic chemist's perspective), organic chemistry, and supramolecular chemistry. The latter field was pioneered by Cram, Lehn, and Pedersen, who demonstrated the selectiveness of host–guest chemistry with the examples of crown ethers, spherands, cryptands, and related macrocyclic systems. The significance of this work was acknowledged when the *Nobel Prize in Chemistry* 1987 was awarded to these three researchers [1–3]. Since then, supramolecular chemistry has evolved tremendously and represents one of the most active fields of current research. Lehn described supramolecular chemistry as the "chemistry beyond the molecule," which is "based on organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces" [4]. Supramolecular chemistry relies on three fundamental processes, *e.g.*, self-recognition, self-assembly, and self-sorting, which enable one to prepare advanced structures on the basis of mainly non-covalent interactions (*e.g.*, van-der-Waals forces, hydrogen bonding, and ionic or coordinative interactions). As detailed elsewhere [5], such interactions are intrinsically weaker when compared to traditional covalent bonds and feature a certain degree of reversibility. Nature itself has set the benchmarks for functional supramolecular systems, and most biological processes, such as protein functions or enzyme catalysis, rely on sophisticated combinations of inter- and intramolecular non-covalent interactions [6]. The same also holds true for data storage and transfer in animate beings. In this respect, DNA is the most notable example, where self-recognition of complementary base pairs *via* hydrogen bonding (*H*-bonding) results in the self-assembly of the famous double-helical structure. Examples from nature have inspired researchers worldwide to assemble functional supramolecular systems for various purposes: molecular machines, *i.e.*, molecules, which might undergo controllable movements upon stimulus (*e.g.*, by energy), represent one notable application. Feringa, Sauvage,

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Terpyridines: Multifaceted Ligands for Diverse Applications, First Edition.
Ulrich S. Schubert, Andreas Winter, and George R. Newkome.

and Stoddart received the *Nobel Prize in Chemistry* 2016 for their distinguished contributions to this field [7–9].

Metal-to-ligand coordination is widely used in modern supramolecular chemistry. Unlike van-der-Waals forces or hydrophobic-hydrophilic interactions, the interaction between metal centers and organic ligands is rather strong (40–120 kJ mol^{-1}) and highly directional [10]. These properties enable one to construct advanced metallo-supramolecular polymers [11–16], dendrimers [17–20], 2D/3D nanostructures [21–25] or coordination nanosheets (CONASHs) [26, 27] *via* cautious choice of metal ions and organic ligands. Among others, complexes derived from chelating *N*-heteroaromatic ligands, in particular based on pyridine derivatives [*i.e.*, 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), and 2,2′:6′,2″-terpyridine (tpy)], have found widespread use in metallo-supramolecular applications. As detailed in Section 1.2, the provable discovery of terpyridine dates back to the studies by Morgan and Burstall in the 1930s [28]. For the following decades, up to the 1980s, terpyridine chemistry remained a niche topic with only sporadic reports on the formation of complexes with transition metals or main-group elements being published [29]. This, however, changed when the remarkable photophysical [30–34], electrochemical [33, 35], electrochromic [36, 37], magnetic [38], pharmaceutical [39–42], and catalytic properties [25, 43, 44] of tpy complexes were discovered. These properties have been utilized by numerous research groups to assemble functional materials and devices for various fields of application [29]. The ongoing intense research is reflected by the enormous number of scientific publications per year (*i.e.*, journal articles and reviews), which deal with terpyridine or its complexes regarding synthesis, properties, and applications (March 2025: *ca.* 10.8 k hits in SciFinder^{n} for a substructure search; Figure 1.1). Moreover, the tpy substructure is mentioned in more than 3000 patents.

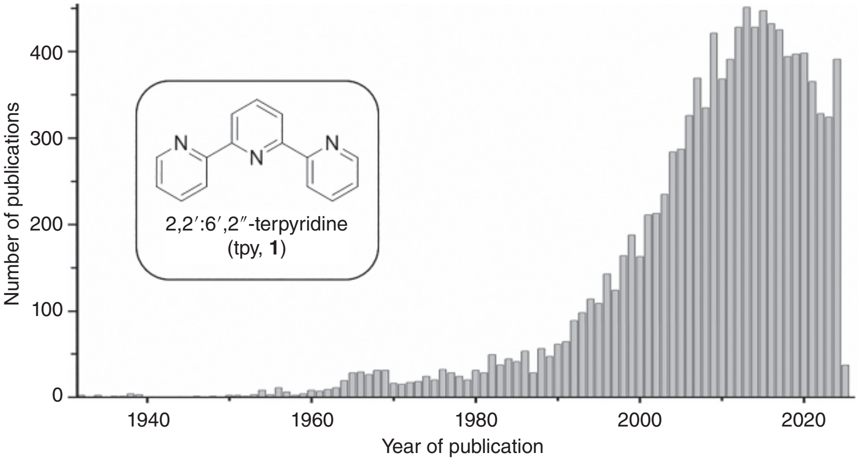


Figure 1.1 Histogram of the number of scientific publications containing the substructure of 2,2′:6′,2″-terpyridine (tpy, **1**); only journal articles and reviews were counted (SciFinder^{n} search performed on March 1st, 2025).

Before turning to the utilization of terpyridine and its complexes in the various applications, the reader is invited to step back and have a look at the ligand's early history. Subsequently, the fundamental aspects of terpyridine chemistry, such as structure and bonding as well as synthesis, will be discussed.

1.2 The Discovery of 2,2′:6′,2″-Terpyridine – A Story Often (But not Fully) Told

In 1925, the *Department of Scientific and Industrial Research* (DSIR) opened the *Chemical Research Laboratory* (CRL) at their campus in Teddington, United Kingdom (Figure 1.2a) [49]. There, research was focused on diverse topics, which were believed to meet the public interests (thus, filling the gap between academic research and industry). The laboratory, whose title was changed to the *National Chemical Laboratory* (NCL) in 1958, operated until 1965, when it was merged into the *National Physical Laboratory*. Morgan joined the CRL in 1925 and was appointed as the executive director only two years later; he remained in this position until his retirement in 1938 (Figure 1.2b). During this period, he established three main research schemes, which were devoted to organic reactions under high pressure, synthetic ion-exchange resins, and the exploration of low-temperature fractions of coal tar, as feedstock for organic fine chemicals [46, 49]. Against this background, Morgan and Burstall, his long-term co-worker whom he already knew as a student from his time at the University of Birmingham, performed the dehydrogenation

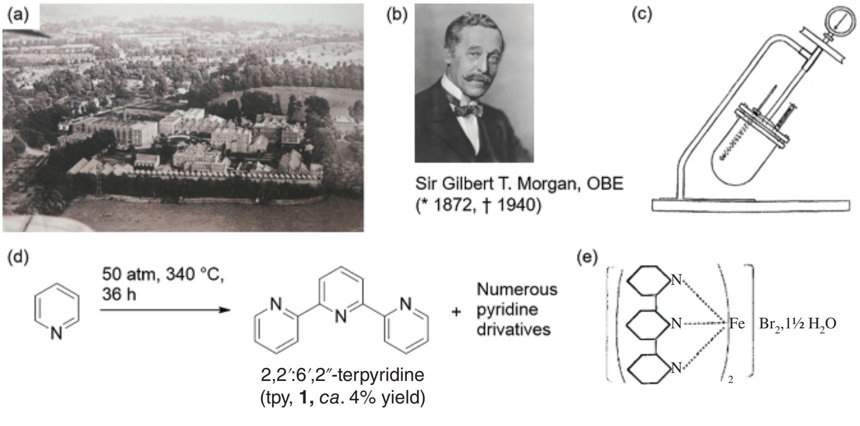


Figure 1.2 (a) Where it all began: Aerial photograph from 1919 showing the Teddington research campus, where the *Chemical Research Laboratory* was later also located [45] / Grace's Guide Ltd / CC BY-SA 4.0. (b) Photograph of Sir Gilbert T. Morgan [46] / with permission of Royal Society of Chemistry; regrettably, a photograph of Francis H. Burstall (1903–1955) could not be provided [47]. (c) Illustration of an in-house-built rotating autoclave, which was used for the high-pressure reactions [48] / with permission of John Wiley & Sons. (d) Schematic representation of the original tpy synthesis. Adapted from [28]. (e) Schematic representation of the proposed structure of $[Fe(tpy)_2]^{2+}$ [28] / with permission of Royal Society of Chemistry.

of pyridine using $FeCl_3$, as the oxidant, in an autoclave (*i.e.*, 50 atm at 340 °C; Figure 1.2c,d) [28]. Under these forcing reaction conditions, 2,2′:6′,2″-terpyridine (tpy, **1**) was formed, even though in very low yield, along with *ca*. 20 other pyridine derivatives, including various constitutional isomers of tpy (the in-total 48 constitutional tpy-like isomers are summarized in Appendix A [50, 51]). Notably, Morgan and Burstall also reported the first transition-metal complex, presumably purple-colored $[Fe(tpy)_2]^{2+}$ (Figure 1.2e) [28]. Thus, the capability of tpy to serve as a (presumed) tridentate ligand for metal-ion complexation was already recognized in this primary study. In subsequent years, these authors intensified their research on this topic and reported diverse complexes of **1** [52–54]. These results also found entrance into the inorganic chemistry textbook, which these authors published in the late 1930s [55]. However, after Morgan's retirement and the outbreak of World War II, research in Teddington on this topic was discontinued. In Morgan's perception, the discovery of tpy represented a notable, although not outstanding, result of his scientific work, which counted *ca*. 350 publications [48]. Burstall, who spent his whole working life at the CRL, continued working in NCL's radiochemical group until his death in 1956 (the chromatographic separation of actinoid-metal ions was his last research topic) [47]. Until 1960, other groups of researchers were already paying attention to important properties of tpy complexes in solution, such as their kinetic stability [56, 57] and the kinetics of ligand-exchange processes [58] as well as electrochemical [59, 60] and photophysical aspects [61]. Likewise, the scope of tpy complexation was extended toward other metal cations (*e.g.*, Cu^{I} [62] or In^{III} [63]). Interestingly, the first study also dealing with the biological activity of tpy was performed in that period of time [64], far before the emergence of tpy complexes, as potential metallodrugs (see Chapter 4). These contributions led to intensified research on tpy complexes, which then geared up by the mid-1960s (Figure 1.1).

Undoubtedly, Morgan and Burstall have to be credited for the verifiable discovery of tpy; accordingly, these authors are commonly regarded as the "fathers" of terpyridine chemistry. The oxidative coupling of pyridine under similar reaction conditions was already reported by Hein and Retter beforehand [65]. However, these authors obtained 2,2′-bipyridine (bpy) in reasonable yield (*ca*. 50%); whereas the nature of the presumptive by-products was not communicated (if they were analyzed at all). Thus, Constable and Housecroft raised the question whether 1932 was the molecule's actual year of birth [66]. These authors pointed to earlier work by the Austrian chemist and inventor Blau (Figure 1.3a), whose name is commonly associated with the discovery of bpy in the late 1880s. This researcher obtained bpy from the dry-distillation of Cu^{II} pyridine-2-carboxylate (Figure 1.3b) [68, 70]. Admittedly, Blau was not the first who performed the dry-distillation of picolinate salts [71], but he paid attention to a by-product, which he named "tetrapyridyl" [70]. This compound had a similar elemental constitution as bpy and revealed the characteristic purple coloration upon treatment with a Fe^{II} salt. Thus, one might speculate that Blau's "tetrapyridyl" was indeed tpy [66]. However, these experiments were performed when coordination chemistry was far from being understood – Werner established the ground-breaking theory of coordination chemistry only a few years later [72] – and further evidence for this assumption is

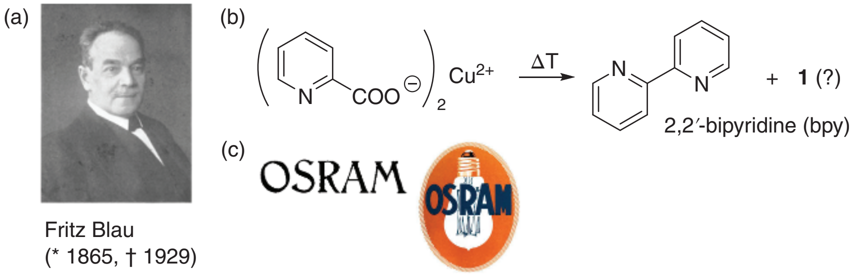


Figure 1.3 (a) Photographs of Fritz Blau. Reproduced with permission from [67] / with permission of Springer Nature. (b) Schematic representation of Blau's bpy synthesis, where tpy might have been formed as a by-product. Adapted from [68]. (c) Representation of OSRAM's original word logo and picture mark, which were registered in 1906 and 1919, respectively [69] / OSRAM SYLVANIA Inc.

not at hand. Blau concluded his scientific career after achieving his habilitation. His last scientific work, which dealt with bpy complexes, was published in 1899 [73]; his first patent on the "manufacture of electric glow lamps," was published in 1901 [74]. By that time, Blau was already involved in the advisory board of the *Elektrische Glühlampenfabrik* "*Watt*" and he eventually joined the *Auergesellschaft* in 1902. Later, he became the lead scientist of the *OSRAM GmbH* and was one of the inventors of the OSRAM™ light bulb [67]. The neology of the famous trade and company name *OSRAM*, as a frankenword of osmium and wolfram, is often ascribed to him (Figure 1.3c) [69]. As his focus of interest had shifted, studies on the coordination behavior of bpy or tpy were discontinued by this author. To the best of our knowledge, terpyridine was not mentioned further in the available literature until Morgan's and Burstall's experiments in Teddington (*vide supra*).

In the 21st century, science has become increasingly influenced by computers and artificial intelligence (AI), which play an important role in today's research. Computational chemistry (*i.e.*, calculations and simulations), automatization, and machine learning (ML) have brought significant progress that goes far beyond humans' learning and handling capabilities [75–80]. Looking back on those days where tpy chemistry started feels like looking at a world of difference, where scientific discovery was still often equalized with serendipity.

1.3 Terpyridine and Its Complexes – Nomenclature, Structure, and Bonding

Ambiguity in nomenclature represents one complicating factor regarding the identification of early contributions in the field of terpyridine chemistry. Burstall coined the generic term "polypyridyl" ligands for "bases, in which two or more pyridine rings are linked (but not fused) together" [54]. The various constitutional isomers of bpy and tpy are the simplest representatives of this ligand family. However, the term "polypyridyl" might already lead to the first misunderstanding. For a polymer chemist, a polypyridine is a rigid, π-conjugated

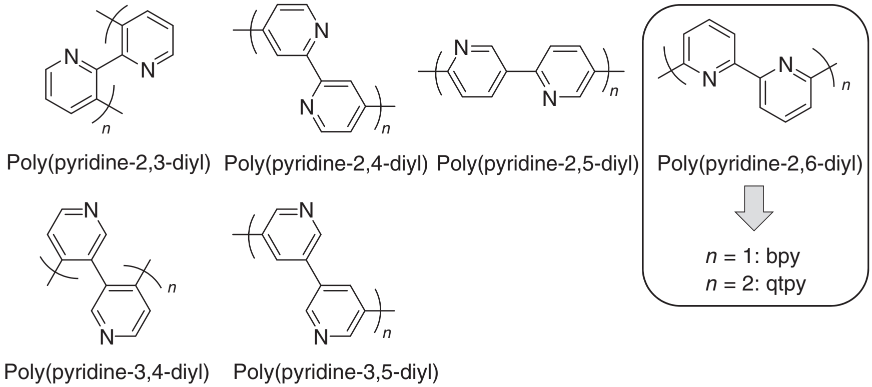
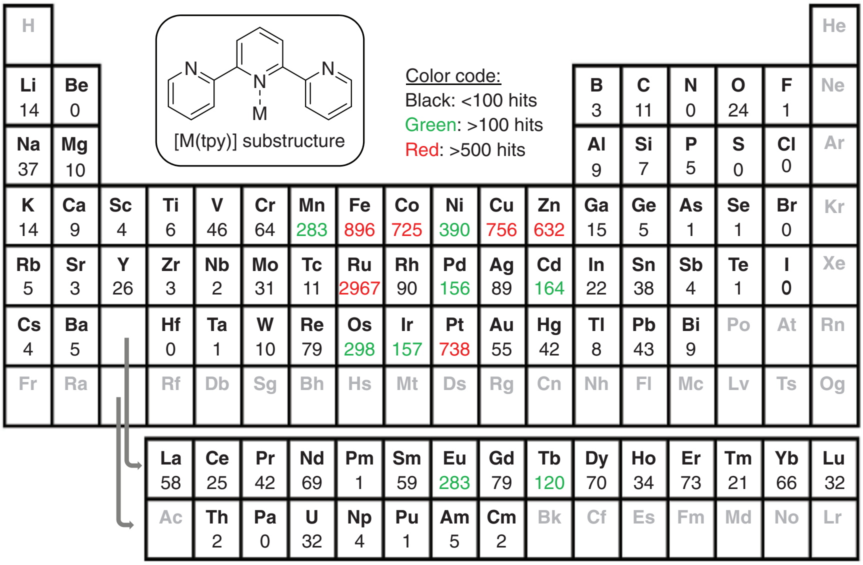


Figure 1.4 Schematic representation of the various regioregular "polypyridines."

chain of pyridine rings; one might distinguish between various regioregular isomers – poly(pyridine-2,3-diyl), poly(pyridine-2,4-diyl), poly(pyridine-2,5-diyl), poly(pyridine-2,6-diyl), poly(pyridine-3,4-diyl), and poly(pyridine-3,5-diyl) – as well as irregular ones with mixed substitution patterns (Figure 1.4). From this perspective, bpy, tpy, and 2,2′:6′,2″:6″,2‴-quaterpyridine (qtpy) represent the shortest oligomers of poly(pyridine-2,6-diyl) with two, three, or four pyridine rings, respectively. From these polymers, poly(pyridine-2,5-diyl) (PPy) and poly(pyridine-2,6-diyl) (PmPy) have been studied to a significant extent [81, 82]. However, the discussion of these conjugated polymers goes well beyond the scope of this Chapter; their utilization, as multidentate ligands, has – to the best of our knowledge – not yet been envisaged. Nonetheless, the generic term "polypyridyl" is commonly used throughout the scientific literature. On the contrary, Constable *et al.* prefer the more practical term "oligopyridine" in order to distinguish the short oligomers (up to the sexipyridine), which exhibit a defined coordination chemistry, from the "real" polypyridine polymers [83–85].

What about the nomenclature of the tpy ligand itself? Starting from the initial report from 1932, many names have been used for this molecule in a highly inconsistent fashion. The long list of alternative names includes tripyridyl, terpyridyl, tripyridine, 2,2′,2″-terpyridine, 2,6-dipyridin-2-yl-pyridine, *etc.* Similarly, various other abbreviations have been (and actually are still) used (*e.g.*, terpy, trpy, *etc.*). According to IUPAC recommendations from 2014 (IUPAC: International Union of Pure and Applied Chemistry) [86], one should prefer the systematic name 1^2,2^2:2^6,3^2-terpyridine over 2,2′:6′,2″-terpyridine, which was listed as the preferred IUPAC name (PIN) in IUPAC's "Blue Book" of 1979 [87]. However, this alteration, which circumvents the use of multiple primers, is hardly recognized by the scientific community and the "traditional" notation is widely retained (and remains accepted by IUPAC). In order to be consistent with the majority of the available literature and following our habit also to do so, 2,2′:6′,2″-terpyridine, abbreviated as tpy, is uniformly used in this Book. By doing so, all the other "terpyridinic" constitutional isomers, which are depicted in Appendix A, are largely left out of consideration. From these, the 3,2′:6″,3″- and 4,2′:6′,4″- isomers have found



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Rb 5	Sr 3	Y 26	Zr 3	Nb 2	Mo 31	Tc 11	Ru 2967	Rh 90	Pd 156	Ag 89	Cd 164	In 22	Sn 38	Sb 4	Te 1	I 0	Xe
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			Ac	Th 2	Pa 0	U 32	Np 4	Pu 1	Am 5	Cm 2	Bk	Cf	Es	Fm	Md	No	Lr

Figure 1.5 The periodic table of elements. For each element, the figure denotes the number of journal articles in which compounds with the "M(tpy)" substructure were mentioned. (SciFinder^{n} research performed on 1st December 2024).

application, as directing ligands, for the formation of coordination polymers based on transition-metal ions; in these assemblies, the central pyridine rings of the ligands typically do not participate in coordination [88–91]. Klein *et al.* identified in total of 21 isomers which could basically serve as tridentate ligands, *i.e.*, binding involves all three rings of the ligand framework (Appendix A). In this respect, one has to further consider the phenomenon of "rollover cyclometallation," which gives rise to a range of potential binding motifs: N^N^N, C^N^N, N^C^N, C^C^N, C^N^C, and C^C^C [51]. According to this notation, tpy represents a neutral N^N^N ligand, which uses its three *N*-atoms for coordination; whereas in the C^C^C motif, all three centers are formally carbanions. Using divalent group-10 metal ions, complexes with some of these binding motifs were recently reported [51]. The research, which deals with the coordination chemistry of tpy's constitutional isomers, is discussed in Chapter 2.

Starting from the very first tpy complex, *i.e.*, the $[\mathrm{Fe(tpy)_2}]^{2+}$ *bis*-complex [28], a massive wave of complexes containing ions of main-group elements, transition metals as well as lanthanide or actinide metals has been reported over the last decades. The plethora of structures ranges from mononuclear complexes and dyads/triads to polynuclear assemblies. Figure 1.5 provides an overview of the number of scientific publications per element. Notably, for almost every element – excluding the noble gases and highly radioactive, mostly synthetic elements – examples for complexes (or compounds, to be more general) can be found.

At least in the case of the alkaline-metal, some of the early transition-metal (*e.g.*, $\mathrm{Sc^{III}}$, $\mathrm{Ti^{IV}}$, $\mathrm{Zr^{IV}}$) and the actinide ions [*e.g.*, $\mathrm{U(O)_2}^{\mathrm{VI}}$, $\mathrm{Am^{III}}$, $\mathrm{Cm^{III}}$], a practical use

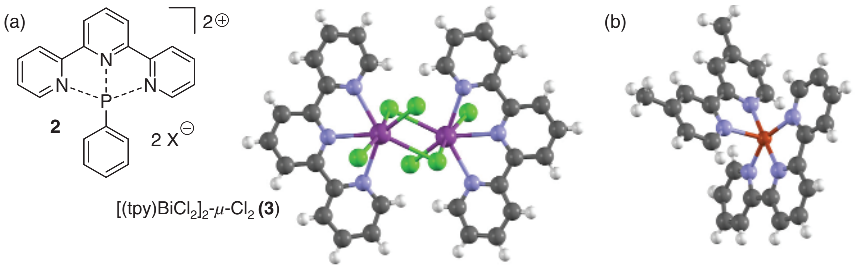

Figure 1.6 (a) Left: Schematic representation of the formal P^{III} complex **2** (X = TfO^- or PF_6^-); right: Solid-state structure of the dinuclear Bi^{III} complex **3** (solvent molecules were omitted for clarity). Adapted from [95, 97]. (b) Solid state structure of the pentagonal $[Cu(tpy)(dmbpy)]^{2+}$ complex (dmbpy: 4,4-bpy; counterions and solvent molecules were omitted for clarity). Adapted from [98].

of the complexes might be doubted – these compounds rather represent chemical oddities. Regarding the latter, the use of chelating *N*-donor ligands, including tpy, for the selective actinide extraction from nuclear fuel solutions has at least been considered [92]. However, ligands, which contained 1,3,5-triazine moieties, were by far more selective than tpy-based ones and have even been tested under "real" process conditions [93]. At least for some of the main-group elements, assemblies with notable properties have been reported. In this respect, the air-stable organo-catalyst **2**, which contains a formal P^{III} ion [94–96], as well as the Bi^{III}-containing solid-state emitters, such as **3**, are worth mentioning (Figure 1.6a) [97, 99]. Overall, the field of terpyridine chemistry with the main-group elements appears to be less explored and not even fully understood. Besides our recent review on this topic [29], the only systematic survey dates back to 1986 [85]. An overview of this often disregarded topic is presented in Chapter 3. On the other hand, the late transition-metal ions and some rare-earth-metal ions (*i.e.*, Eu^{III}) have attracted enormous interest. This holds particularly true for the ions with d^6 (*e.g.*, Fe^{II}, Ru^{II}, Os^{II}, Ir^{III}), d^8 (*e.g.*, Ni^{II} and Pt^{II}) or d^{10} electron configuration (*e.g.*, Zn^{II}).

According to the bond theories in coordination chemistry [100], which basically go back to Werner's visionary ideas [72], the coordination geometry of a complex will strongly depend on the nature of the employed metal ion. The (distorted) octahedral geometry represents the most common motif, which prevails *inter alia* for all d^6-configured ions. In the case of tpy, the coordination sphere of such ions can be saturated either by two tpy ligands or one tpy ligand and additional (ancillary) ligands. Accordingly, Morgan and Burstall already assumed a pseudo-octahedral geometry for their *bis*-complexes with Fe^{II} or Ru^{II} ions [53]. These authors further concluded that, for geometric constraints, the *mer*-isomer should be favored over the *cis*-*fac* and *trans*-*fac* ones (*mer*: meridional, *fac*: facial; Figure 1.7). Based on today's knowledge, tpy ligands are not able to form *fac*-isomers at all; these isomers are only accessible for more flexible ligands, such as the related 2,6-di(quinolin-8-yl)pyridine (dqp, see Section 1.6). Besides the octahedral geometry, other coordination environments are also possible: trigonal-bipyramidal (*e.g.*, with Cu^{II} centers; Figure 1.6b) [98] and square-planar complexes (*e.g.*, with Pd^{II}, Pt^{II}, or Au^{III} centers) with tpy ligands are known [39]. Moreover, rare-earth-metal ions can – due to their f-orbitals – reach

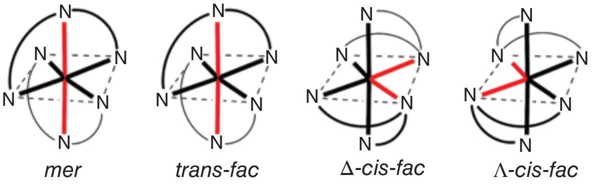

Figure 1.7 Schematic representation of the possible configurations, which might occur in *bis*-tridentate complexes of octahedral geometry [101] / with permission of Royal Society of Chemistry.

coordination numbers of up to nine and, thus, form complexes with three tridentate ligands, such as tpy [102, 103]. Such a behavior, *i.e.*, formation of complexes with similarly high coordination numbers, can also be observed for the heavy Pb^{II} and Bi^{III} ions (*e.g.*, complex $[Pb(tpy)_3]^{2+}$) [29]. The enormous structural diversity, in particular for all the heteroleptic complexes, reveals that the prediction of a certain coordination geometry is difficult. To address this issue, Moore *et al.* presented a tabulated overview of the coordination geometries of transition-metal ions, thereby taking the various oxidation states, coordination numbers, and geometries of the respective elements into account [104]. This qualitative analysis provides comprehensive guidance to appraise the complex geometry. Such *a priori* considerations can be supported by a cautious evaluation of the manifold of solid-state structures, which are accessible from the Cambridge Crystallographic Data Centre (CCDC) [105].

Which are the most recognized tpy complexes in view of practical use? From the unmanageable variety of structures, three examples are highlighted (Figure 1.8). Firstly, Ru^{II} complex **4**, Grätzel's "black dye," is a prominent sensitizer (*i.e.*, light absorber) in dye-sensitized solar cells (DSSCs) [106]. This topic, the utilization of tpy ligands in the context of photovoltaics, is discussed in Chapter 6. Secondly, tpy complexes, such as Meyer's Ru^{II} complex **5** [107], are utilized as catalysts in the context of artificial photosynthesis, *i.e.*, the (electrochemical) splitting of water [43]. This notable aspect of terpyridine chemistry is covered in Chapter 8. Thirdly, Jennette, Lippard *et al.* found that Pt^{II} complexes, such as **6**, were capable of intercalating into the DNA [108]; thus, complexes of this type are considered alternatives to the well-known metallodrug cisplatin (see Chapter 4) [109].

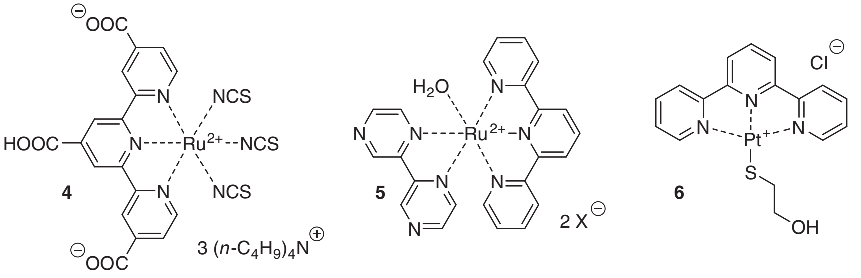

Figure 1.8 Schematic representation of Grätzel's "black dye" **4**. Meyer's water-oxidation catalyst **5** (X = Cl^- or PF_6^-), and Lippard's DNA intercalator **6**.

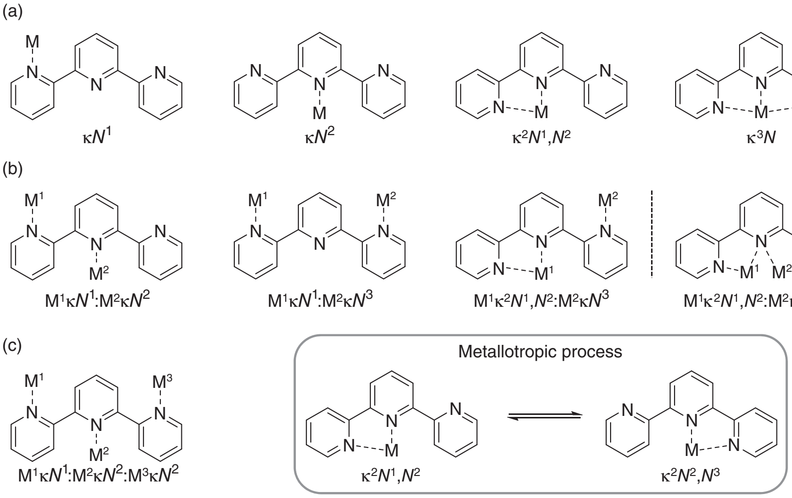

Figure 1.9 Schematic representation of the various coordination modes, which might occur in metal-terpyridine complexes; the respective “kappa notation,” according to IUPAC’s recommendations, is also given. (a) Mononuclear species, (b) binuclear species, and (c) trinuclear species. In the case of (b) and (c), the metal (*i.e.*, M^1, M^2, and M^3) might be the same or different. Adapted from [84].

Even though the previous considerations might suggest that tpy might always act as a tridentate ligand, the coordination behavior of this ligand is by far more complicated. In order to distinguish between the various possible binding modes, IUPAC recommends one to consequently follow the so-called “kappa notation” (Figure 1.9) [110]. Accordingly, tridentate binding of a tpy ligand to a metal center *via* its three *N*-atoms corresponds to the κ^3N mode.

Utilization of all three *N*-atoms might also give rise to other assemblies – binuclear as well as trinuclear ones (the respective notations are $M^1\kappa^2N^1,N^2{:}M^2\kappa N^3$ and $M^1\kappa N^1{:}M^2\kappa N^2{:}M^3\kappa N^3$). In addition to these, a range of nonclassical complexes has been reported, in which the tpy ligands are coordinated in hypodentate fashion (*i.e.*, not all *N*-atoms are used.) [83, 111]. Such complexes correspond to the mononuclear κN^1, κN^2, and κ^2N^1,N^2 as well as binuclear $M^1\kappa N^1{:}M^2\kappa N^2$ and $M^1\kappa N^1{:}M^2\kappa N^3$ modes. The chelate effect, which is addressed later in this section, can be overcome if the *mer*-configuration of a tpy ligand is disabled for geometric constraints or pre-saturation of the metal’s coordination sphere. Bidentate coordination (*i.e.*, in the κ^2N^1,N^2 mode) has been found in some Re^{I}, Ru^{II}, and Ir^{III} complexes – representatively, complex $Re(tpy)(CO)_3Cl$ (**7**) is depicted in Figure 1.10 [112]. Such complexes often exhibit a metallotropic rearrangement, in which the κ^2N^1,N^2 and κ^2N^2,N^3 motifs are rapidly interconverted (as shown in Figure 1.9, the outer pyridine rings switch between an active and a passive role); it is commonly believed that species of higher coordination numbers are involved in this process [83]. Schatzschneider *et al.* reported one notable example of a complex in which the unreckoned monodentate κN^1-type coordination of tpy was observed (Figure 1.10) [113]. In this case, the azido ligand, as a strong σ- and π-donor, was

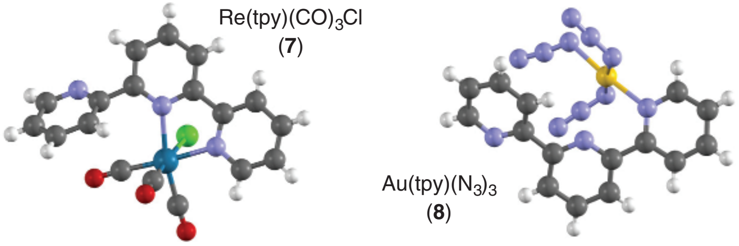

Figure 1.10 Solid-state structures of Re^I complex **7** and Au^{III} complex **8** (solvent molecules were omitted for clarity). Adapted from [112, 113].

even able to repel two initially coordinated pyridine rings in course of the synthesis [*i.e.*, square-planar $Au(tpy)(N_3)_3$ (**8**) was obtained instead of $Au(tpy)(N_3)$]. It has to be emphasized that the tridentate κ^3N mode is only possible for **1**; whereas bidentate coordination *via* the $M^1\kappa^2N^1,N^2$ mode is also possible for numerous of its constitutional isomers, which possess a bpy-like substructure (Appendix A) [114]. The coordination chemistry of those ligands (with mainly transition-metal ions) is comparatively less explored and will be discussed briefly in Chapter 2.

In some respect, tpy protonation can be compared to its complexation by metal ions. ^1H-NMR titration studies and single crystal X-ray diffraction (XRD) analysis revealed that the bidentate $M^1\kappa^2N^1,N^2$ mode was also favored in the singly protonated $[tpyH]^+$ state [115, 116]. Whereas, doubly protonated $[tpyH_2]^{2+}$ featured an unique fixation of the two protons, which both interacted with the *N*-atom of the central pyridine rings and each with an *N*-atom of one of the outer pyridine moieties [116, 117]. Such a binding, which formally corresponds to an $M^1\kappa^2N^1,N^2{:}M^2\kappa N^2,N^3$ mode, is, for steric constraints, hardly possible for binuclear metal-tpy complexes.

When talking about the coordination of tpy ligands to a metal center, one has to take the occurrence of steric repulsion into account. Steric repulsion between the ligand's protons in 3/3″-position on the one hand and 3′/5′-position on the other comes into play as soon as the molecule rotates into the *cis*,*cis*-conformation, which is the premise for coordination in the tridentate κ^3N mode (Figure 1.11a). Computational studies revealed that electronic repulsion of the inward-pointing *N*-atoms further destabilizes the all-*cis*-isomer. For the *trans*,*trans*-conformer, repulsive forces are minimized; thus, this isomer is highly favored in the absence of metal ions [117]. A comprehensive and differentiated analysis was provided by Batista, Hazari *et al.*, who computed the entire energy surface of tpy reflecting the rotation of its outer rings (Figure 1.12) [120]. According to these authors, the *cis*,*trans*-configuration is energetically disfavored by *ca.* $31.4\,kJ\,mol^{-1}$ when compared to the all-*trans*-configuration, as the global energetic minimum. Notably, the conformational change to reach the thermodynamically least favorable all-*cis*-conformation is energetically even more uphill: The rotation of the second pyridine ring requires *ca.* $46.0\,kJ\,mol^{-1}$, thus *ca.* $14.6\,kJ\,mol^{-1}$ more than for the rotation of the first pyridine ring. The predicted preference for the all-*trans*-configuration has been verified experimentally at the example of