

# Chemie in Freiburg Chimie à Fribourg

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## New Coordination Compounds for Photochemical Purposes and Beyond

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**Abstract.** A general account is given of the synthetic research carried out in the field of coordination chemistry in one group in the Institute of Inorganic Chemistry in Fribourg. With the goal of synthesizing artificial structures, which can function as photochemical molecular devices, several synthetic strategies for multicenter coordination species are mentioned. It is reported, that the molecules, which have been designed to form coordination compounds with predefined chiralities of the central metal, can also be used as ligands in enantioselective catalysis.

### 1. Introduction

Coordination chemistry has just passed its 100th anniversary. In an epoch-making publication [1] of 1893, Alfred Werner developed on 33 pages the foundations of coordination chemistry. In this publication, he introduced, for the first time, the octahedron and the square as molecular structural entities. Werner generalized therewith the structural ideas introduced by van't Hoff and Le Bel 20 years earlier

for the C-atom. Although coordination chemistry has seen an enormous development since Werner's time, the synthesis of more complicated coordination compounds became possible only since modern physical methods, especially NMR spectroscopy and X-ray crystallography, have been applicable in an interactive way with the chemist working in the laboratory. It can be predicted (and we hope that it will be true for the University in Fribourg, especially through the BENEFRIC cooper-

ation), that the synthetic chemist of the early 21st century will have the possibility to obtain detailed structural information about newly synthesized products, within a very short time, even if the molecules are highly complex [2].

The metallic elements are literally the entities of central interest in coordination chemistry. Given the enormous variability in coordination numbers and in oxidation states of metallic elements, the multitude of structures and functionalities of complex coordination species is virtually unlimited. Chemists have only begun to enter this, as yet largely untapped, world of artificial structures, which will be full of interesting [3][4] and, maybe, useful creatures.

### 2. Towards Photochemical Molecular Devices

One area where intricate coordination compounds may be of special importance are the so-called Photochemical Molecular Devices (PMDs) [5]. The natural photosynthetic system, on which all life on earth depends, contains transition-metal complexes in highly organized molecular

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structures. Coordination compounds with transition metals have much more diverse photophysical and photochemical properties, as compared to purely organic molecules, due to their open-shell electronic structures and their high spin-orbit coupling effects. The latter lead to a partial breakdown of selection rules, which is often a prerequisite for certain useful effects. A prominent example of a species with highly interesting photophysical and photochemical properties is the complex  $[\text{Ru}(\text{bpy})_3]^{2+}$ . In the last 15 years, this complex has become one of the most vigorously investigated molecular species. A primary goal of the synthetic group in the Institute of Inorganic Chemistry of the University of Fribourg was the preparation of Ru complexes with precisely pre-

defined light-absorption characteristics. The parent complex (Fig. 1) is bright orange, showing a metal-to-ligand charge-transfer absorption at 452 nm ( $\epsilon = 10^4 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ). Its excited state properties are quite unique, combining a relatively long life time (ca. 1  $\mu\text{s}$  at room temperature in solution) with very interesting redox potentials.

This complex has been investigated from many different points of view. Members of the Fribourg group, and other scientists around the world, have modified the complex using many other diimines, as well as other types of ligands. We have reviewed this development [6] with the group of V. Balzani, Bologna, Italy, with whom we have collaborated with since 1981.

Although  $[\text{Ru}(\text{bpy})_3]^{2+}$  undergoes a series of highly interesting reactions, and exercises several different functions, calling it a PMD would be an exaggeration. But it can be a building block for PMDs! Designating the trinuclear complex of (Fig. 2) a PMD, is no longer really an exaggeration.

A series of various multinuclear species of this kind was synthesized in Fribourg, where often ligands prepared in the group of F. Vögtle, University of Bonn, Germany, were used. These PMDs show interesting properties [7], which are often not just the sum of the properties of the building blocks. These properties are genuine supramolecular phenomena. 'The whole is more than the sum of its parts' is a basic truth, and is certainly applicable to these species.

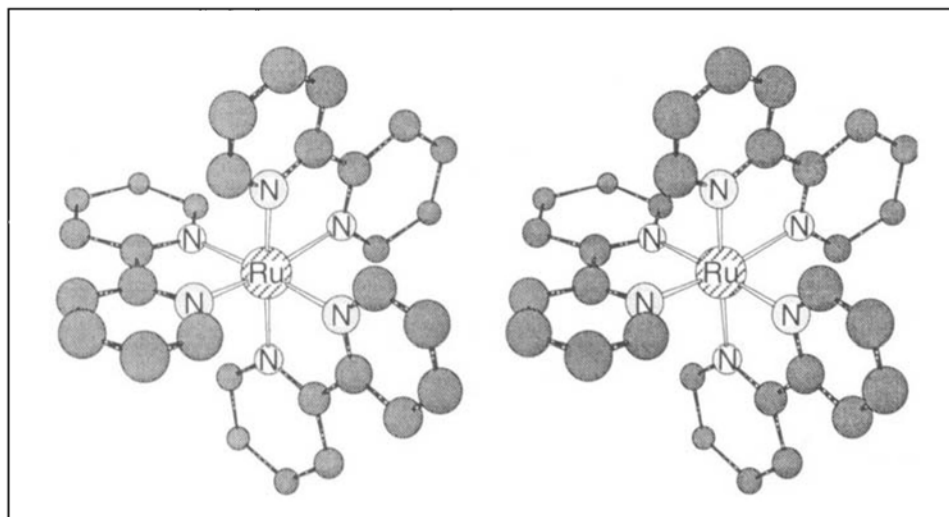


Fig. 1. Stereomodel of the triple helix of  $\Delta$ - $[\text{Ru}(\text{bpy})_3]^{2+}$  viewed along the threefold axis of the complex, which has  $D_3$ -symmetry (bpy = 2,2'-bipyridine)

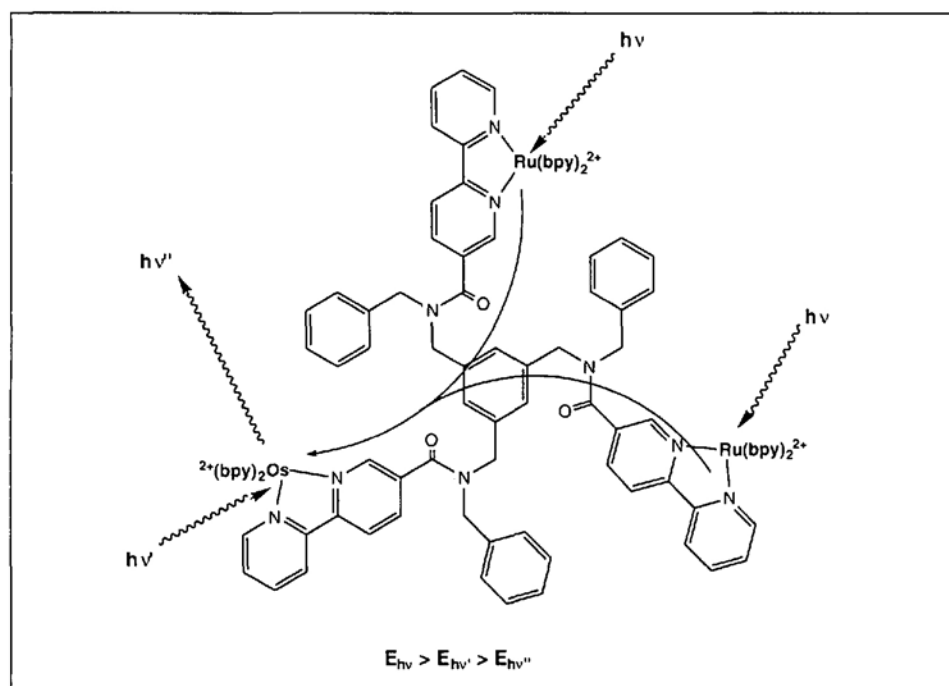


Fig. 2. A trinuclear complex, where the two Ru-centers can harvest photons. Through intramolecular energy transfer processes, emission is observed from the Os-center.

### 3. Why is Stereochemistry a Key Element for Large Structures

Even 20 years ago, the synthesis of coordination species, such as depicted in (Fig. 2), would have been extremely difficult, even though the glassware, chemicals, and basic laboratory equipment, have since changed very little. What has changed dramatically, as described above, is the possibility to 'see' what has been produced in a reaction step.

Building up such species, and 'looking' at them, mostly by NMR spectroscopy, we realized soon that there is a basic problem, the occurrence of isomers. The building blocks, namely the tris-bidentate complexes, are chiral entities ( $[\text{Ru}(\text{bpy})_3]^{2+}$  is a triple helix, either  $\Delta$  or  $\Lambda$ ). Unless enantiomerically pure building blocks are used, building complicated structures from chiral building blocks leads to mixtures of a large number of isomers (diastereoisomers and enantiomers). Such systems are characterized by a fuzzy stereochemistry, where a large number of very similar, yet non-identical molecules are present in a sample. The situation is comparable to the formation of proteins from amino acids. Nature has found a way to use enantiomerically pure building blocks, and so must we, the molecular engineers, try to build larger and larger artificial structures.

The synthesis of isomerically pure multicenter species has become one of the main goals of the synthetic group in Fribourg in recent years. Several strategies have been developed for this purpose, and we will shortly present two.

The first is quite straightforward, it consists of resolving a racemate of a build-

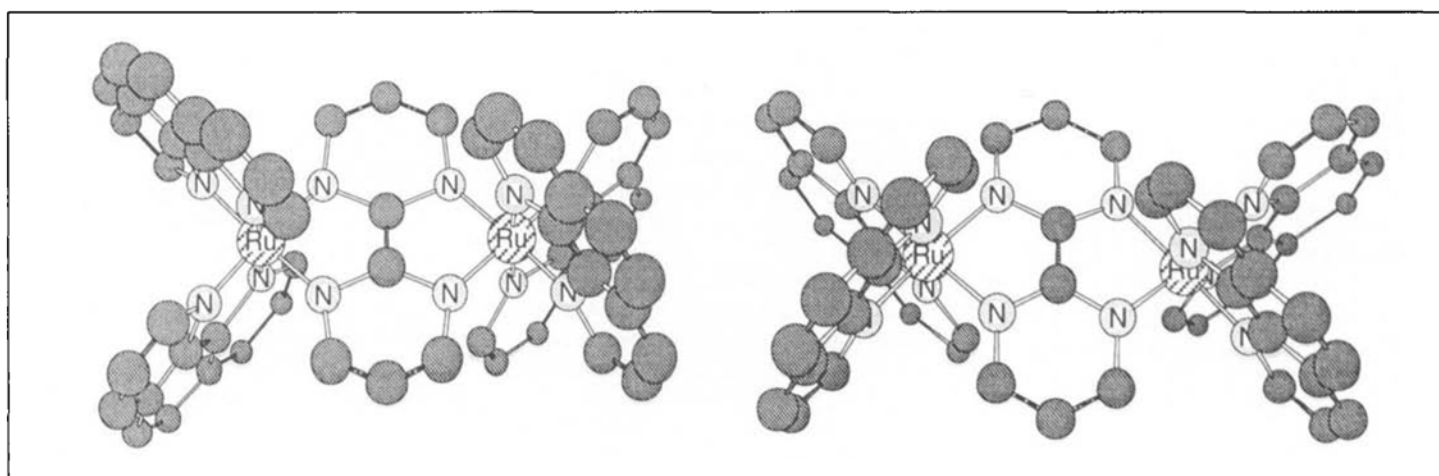


Fig. 3. The two diastereoisomers,  $\Lambda, \Lambda$ -[Ru(phen)<sub>2</sub>-bpym-Ru(phen)<sub>2</sub>]<sup>4+</sup> (left) and  $\Delta, \Lambda$ -[Ru(phen)<sub>2</sub>-bpym-Ru(phen)<sub>2</sub>]<sup>4+</sup> (right) (bpym = 2,2'-bipyrimidine)

ing block, and using the enantiomerically pure complex in suitable reactions to build up the larger species [8]. This method is actually quite successful, and several isomerically pure dinuclear species have been built in that way [9]. *E.g.* with 2,2'-bipyrimidine, as a bridging ligand, all three isomers, the homochiral enantiomeric pair  $\Delta\Delta/\Lambda\Lambda$  and the heterochiral *meso*-form  $\Delta\Lambda$ , were prepared in pure form. Two of them are depicted in (Fig. 3).

This approach will be also followed in the future for several multicenter systems, in order to obtain them in an isomerically pure form. A problem is the use of these building blocks in PMDs, because the coordination centers can racemize in the excited state. An isomerically pure sample, will, therefore, become a stereochemically fuzzy system after irradiation with light.

A second strategy was, therefore, developed, which should also avoid the problem of racemization. The general problem can be stated as follows: a coordination sphere with octahedral geometry (Fig. 4a) is sought, in which two *cis*-ligand positions (X) are easy to substitute and the four other positions are occupied by two bidentate chelates (L<sup>Λ</sup>L), which are chirally fixed. This configuration can be made rigid, if the two bidentate ligands are linked by a chiral connecting group (ch) (Fig. 4b), which predetermines the chirality at the octahedron.

Both configurations of (Fig. 4) have C<sub>2</sub>-symmetry. The synthesis of the type of ligand in Fig. 4b, was a real challenge in terms of organic synthesis. Because diimin-type ligands seem to be mandatory for use with photochemical devices, new derivatives of bipyridine had to be found. A family of ligands, the pinenebipyridines [10] was synthesized (Fig. 5).

Starting from these pinenebipyridines, bridged bis-bidentate ligands (Fig. 6) of

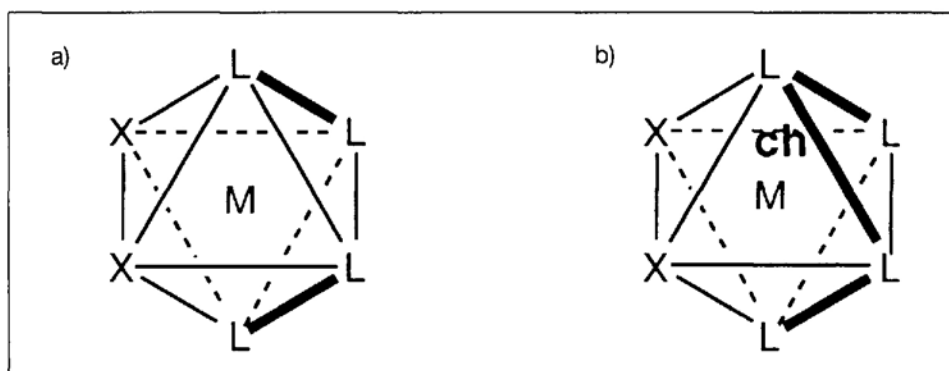


Fig. 4. Two complexes with two bidentate chelates. a)  $\Delta$ -[M(L<sup>Λ</sup>L)<sub>2</sub>X<sub>2</sub>], and b)  $\Delta$ -[M(L<sup>Λ</sup>L(ch)L<sup>Λ</sup>L)X<sub>2</sub>], where the chirality is predetermined by the chiral bridge ch.

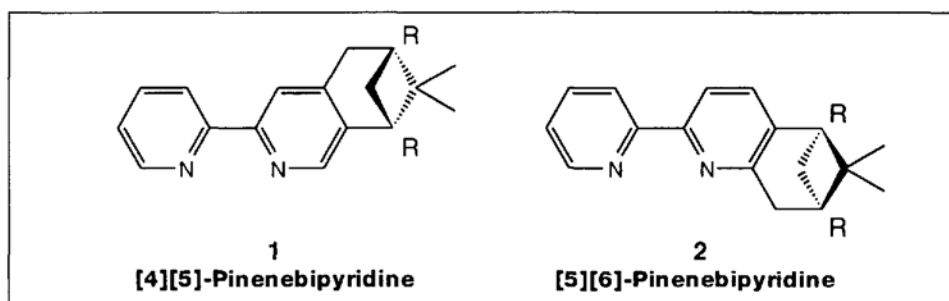


Fig. 5. Two 2,2'-bipyridine ligands available from chiral pool molecules in high enantiomeric purity

the type (L<sup>Λ</sup>L(ch)L<sup>Λ</sup>L) can be easily derived.

Since these ligands predetermine the helical chirality ( $\Delta/\Lambda$ ) at the metal, we call them *chiragens*. An example of a chiragen ligand and its Ru complex is [Ru(chiragen[6])(L<sup>Λ</sup>L)]<sup>2+</sup> (where (L<sup>Λ</sup>L) is any bidentate ligand). It has been completely characterized [11] for (L<sup>Λ</sup>L) = 4,4'-dimethyl-2,2'-bipyridine (Fig. 7). The NMR spectra and the X-ray analysis show a complex with C<sub>2</sub>-symmetry, having the helical chirality predetermined by the absolute configuration of the stereogenic C-centers in the pinene moieties of the ligand.

Since pinene is a chiral-pool molecule, available naturally in either of the enanti-

omeric forms, both helical configurations of the Ru complexes can be obtained, without the necessity to resolve a racemate. The enantiomeric purity of the metal complex is considerably higher, than that of the natural product used for the synthesis, because the heterochiral ligand ((*S*)- and (*R*)-configured, respectively, at the bridgeheads) cannot coordinate to one metal center for steric reasons [12]. For example, an *enantiomeric excess* (ee) of 90% in the starting material leads to an ee value of 99% in the final complex, thus showing considerable *chiral amplification*.

Several members of the chiragen ligand family – there is an almost unlimited number of derivatives accessible through

the synthetic procedure developed in our group – are now used for building up polynuclear complexes, which have a *well defined* and not a *fuzzy stereochemistry*.

#### 4. Beyond Photochemical Applications

Once the pinenepyrindines were available as compounds, it soon became clear that these ligands could serve other purposes as well (in fact, *P. Hayoz* who developed their synthesis thought of other applications from the beginning on). Especially promising are applications in the field of *enantioselective catalysis*, which is presently of great practical interest, because for any chiral artificial product (*e.g.* drugs), which comes into close contact with humans, the two enantiomers are considered to be different compounds. This point of view is certainly completely justified, since two enantiomers will, in general, behave quite differently in the non-racemic chiral environment provided by living systems.

Utilizing this process of development, we are now performing research in the

field of enantioselective catalysis, using metal complexes (*e.g.*  $Rh^{III}$  complexes with derivatives of pinenepyrindine ligands) for enantioselective hydrogenation and for other reactions yielding chiral molecules from prochiral starting materials.

I acknowledge with great pleasure the work of a number of 'doctorands' and a few post-doctorands, who have contributed enthusiastically to the development of the synthetic group in Fribourg, since my present colleague, *Peter Belser*, laid the foundation for this development with his Ph.D. thesis 1976–1979. Those, who have already left the institute are: *Laurent Chassot*, *Philippe Jolliet*, *Urs Maeder*, *Christine Deuschel Cornioley*, *Gabriel Gremaud*, *Pascal Hayoz*, *Roland Dux*, *Jürgen Nachbaur*, *Xiao Hua*, and *Paul Haag*. The members of the present group are: *Hans Ruedi Mürner*, *Eric Jandrasics*, *Michel Gianini*, *Véronique Monney*, *Marianne Riklin*, and *Philippe Collomb*. In the present essay, only an outline of the development was given, and all detailed results are reported in the theses of those mentioned above and in subsequent publications. Important contributions come also from people working in the 'background', especially *Liz Kohl*, who is running the NMR facility, and who provides an excellent literature search service by computer.

Prof. *Helen Stoeckli-Evans* at the University of Neuchâtel has been of enormous help, providing fast X-ray analyses of several key compounds. We are happy that this collaboration is now based on the official agreement BENEFRI between the three central Swiss Universities Bern, Neuchâtel, and Fribourg.

The development of the group has been strongly stimulated through the cooperation with the group of Prof. *Vincenzo Balzani* in Bologna. The definition of the aims of synthetic work takes place in many discussions with our Italian friends, who are so keen to build up the PMDs. More recently, this collaboration was extended in an almost all-European venture to the group of Prof. *Fritz Vögtle*, University of Bonn, who has a large knowledge and experience in building up complex organic molecular and supramolecular structures.

I also acknowledge the support of our own University, which has provided a fertile soil for

chemistry, first by the construction of the highly functional chemistry building 20 years ago and since, through an adequate basic laboratory equipment. The *Swiss National Science Foundation* has supported continuously our research, and *Ciba* has helped to fill those gaps, which often show up unexpectedly when a research group at a small University is running at the brink of its financial possibilities. I thank all these institutions for their generosity.

Finally, I want to thank my colleagues, who present their own research in this special issue of *Chimia*, for the excellent and stimulating environment and for their friendship.

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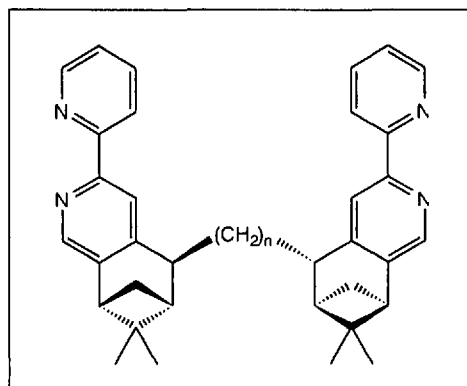


Fig. 6. *Chiragen[n]*,  $C_2$ -symmetric bis-bidentate ligand, which predetermines the helical chirality at the octahedral metal center

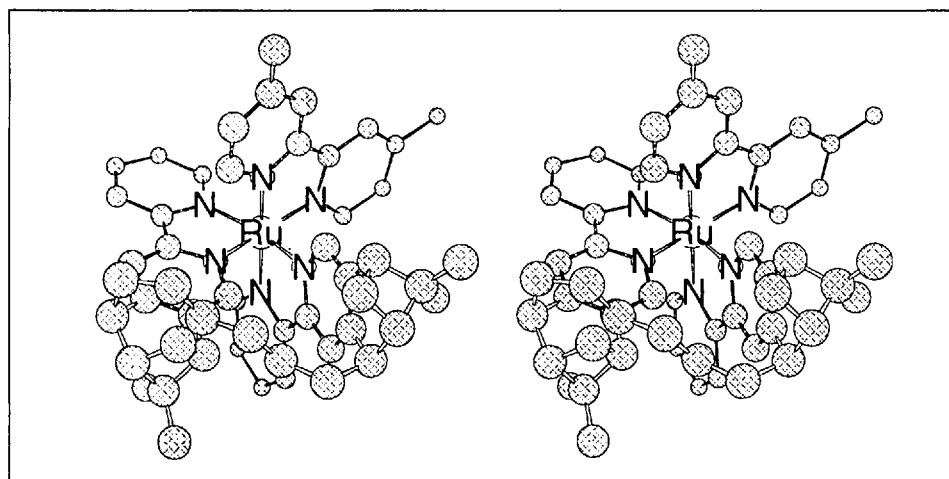


Fig. 7. Computer generated stereomodel of  $\Delta$ -[Ru(chiragen[6])(4,4'-DMbpy)] $^{2+}$

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