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On the Way towards New Materials: Metal Complexes as Building Blocks

Alex von Zelewsky* and Peter Belser

Abstract. Two related directions of materials research are described: *i*) The synthesis of photonic materials, based on transition-metal compounds mainly with ruthenium and osmium as the photoactive centers. The devices envisaged are antenna molecules, molecular wires, photon-activated switches, and molecules performing other logical functions. *ii*) The development of a strategy for the synthesis of complex coordination species suitable for molecular devices, based on modular synthons, where a special emphasis is put on the stereochemical aspect of the fragments employed. This strategy is based on a new family of chiral pyridine and bipyridine ligands that are useful for the construction of inert building blocks, as well as in self-assembly processes leading to highly organized systems.

Preface

Fed up with the quite sophisticated analysis of aesthetically very pleasing ESR spectra of metal complexes with free radicals as ligands [1], I looked for somewhat less esoteric applications of the knowledge acquired in coordination chemistry during the two decades since I had started my chemistry studies at the ETH in Zürich in 1955. In 1976, many of the basic facts of transition metal chemistry, as for instance their electronic spectra and their magnetic properties, were quite well understood. The times seemed right to get into *molecular engineering*, that means the design and production of new molecules, which might have useful properties. One possibility to go into molecular engineering in the field of coordination chemistry was and still is the synthesis of new ligands, mainly organic molecules that give, in combination with metallic elements, new materials. Obviously, for the synthesis of such ligands, a good knowledge of methods in synthetic organic chemistry is needed. It was fortunate that at this time a young man came to me asking whether I

would have a subject in synthetic chemistry for carrying out a Ph.D. thesis. This person had been an excellent student, and I knew that he had a very thorough formation, first in an apprenticeship as a 'laborant', then as a chemical engineer with practice in industry, and, finally, three years of university studies. I, therefore, did not hesitate to offer him a position in the institute. As a subject of the Ph.D. thesis, I proposed to *Peter Belser* the synthesis of metal complexes, especially with Ru^{II} as central metal, where the metal-to-ligand charge-transfer band could be tuned. Ru^{II} complexes had at this time just become a matter of central interest for electron-transfer reactions from the excited state. Three years later [2], *Peter Belser* had prepared 20 new ligands and 30 new complexes, and, indeed, the intense MLCT absorption band of the Ru complexes could be tuned to almost any wavelength in the visible region of the electromagnetic spectrum [3]. This was the beginning of a development which still goes on in our university. *Peter Belser* now has his own research group, but we still collaborate very closely, and both of us have many contacts with several groups in other countries. Our aim is still the design of molecules that finally lead to materials, and I'm glad that I can describe in this article together with my colleague *Peter Belser* the development of more than 20 years of research in our groups and its present state.

Alex von Zelewsky

1. Tuning of the Excited-State Properties

Modified π -System Sensitizers

The cation tris(2,2'-bipyridine)ruthenium(II) is one of the most used mediators in photoinduced energy or electron-transfer processes. A unique combination of chemical stability, reversible redox properties, excited-state reactivity, and lifetime, combined with easily detectable emission of light, are the most attractive properties of the parent complex [Ru(bpy)₃]²⁺ and of many other members of the large family of ruthenium(II)-diimine complexes [4]. The absorption maximum of the MLCT (metal-to-ligand charge transfer) band of [Ru(bpy)₃]²⁺ lies at 450 nm ($\epsilon = 14\,600\text{ M}^{-1}\text{cm}^{-1}$). As shown in *Fig. 1*, it is a relatively narrow absorption band. As one of the main interests of [Ru(bpy)₃]²⁺ is its application as sensitizer in solar-energy conversion [5], a narrow absorption is a drawback, because only a small part of the solar radiation can be seized. Tuning of the absorption behavior is therefore one of the prerequisites for applications of such complexes. Tuning can be achieved either by introduction of different substituents or through a change of the size of the π -system of the 2,2'-bipyridine ligand (bpy) [6].

The substituents have a direct influence on the electron density at the N-atom by an inductive and/or mesomeric effect. Directly correlated with the electron density on the N-atoms is also the π -backbonding capability of the ligand. Both effects are manifested in the photophysical properties of the Ru complexes. The chemical character of the substituents (electron donor or electron acceptor) determines directly the energy of the MLCT transition and therefore the position of the absorption band (see the *Table*). The substitution position at the pyridine ring influences the MLCT transition, too. A further important photophysical property is the absorption intensity (ϵ). It depends on the overlap between the two orbitals that are involved in the charge-transfer transition. A lengthening of the Ru–N bond for sterical reasons induces a weaker absorption. An example of such a behavior is the metal complex [Ru(6,6'-dm-bpy)₃]²⁺. The two methyl substituents in the 6- and 6'-position of the bpy ligand are sterically stressed, and the Ru–N bond length is therefore longer as in the case of [Ru(bpy)₃]²⁺. As indicated in the *Table*, the ϵ value drops from $14\,600\text{ M}^{-1}\text{cm}^{-1}$ to a value of $7\,440\text{ M}^{-1}\text{cm}^{-1}$.

An interesting example for an extension of the π -system is given by the metal-

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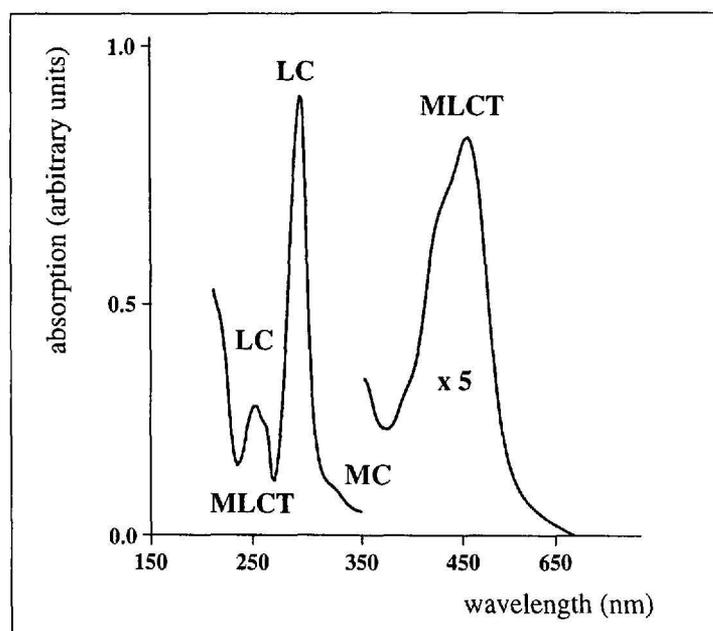


Fig. 1. Absorption spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$. MLCT corresponds to a metal-to-ligand charge-transfer transition, MC to metal-centered transition and LC to a ligand-centered transition.

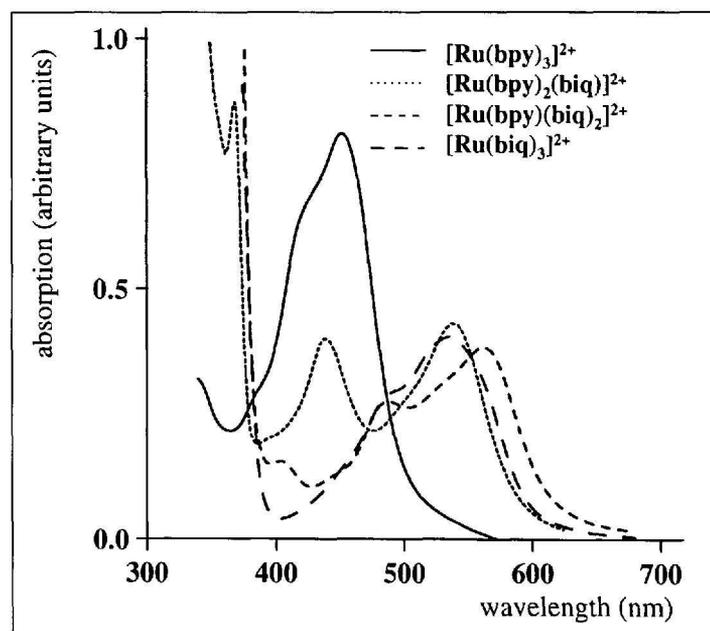


Fig. 2. Absorption spectra of $[\text{Ru}(\text{bpy})_{3-n}(\text{biq})_n]^{2+}$ ($n = 0, 1, 2, 3$)

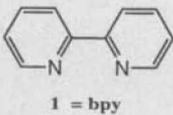
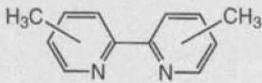
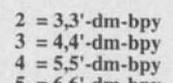
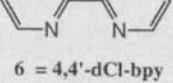
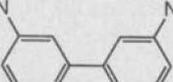
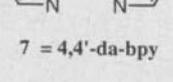
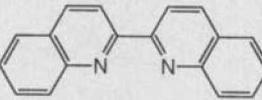
complex family $[\text{Ru}(\text{bpy})_{3-n}(\text{biq})_n]^{2+}$ ($n = 0, 1, 2, 3$), in which biq corresponds to the ligand 2,2'-biquinoline. We can observe two well-separated MLCT transitions (see Fig. 2). In a first approximation, their origin can be attributed to the two transitions $\text{Ru} \Rightarrow \text{bpy}$ and $\text{Ru} \Rightarrow \text{biq}$.

2. Towards Stable Photosensitizers

One of the drawbacks using $[\text{Ru}(\text{bpy})_3]^{2+}$ as photosensitizer is its quite substantial photodecomposition during the irradiation process. Once the molecule is in the triplet excited state, a low-lying LF state is thermally accessible (weakening of the Ru–N bonds of the bipyridine ligand), and this leads to a substitution of one bipyridine ligand by solvent molecules. To overcome this difficulty, we have designed a closed-cage Ru^{II} complex with a tris(diimine) ligand sphere. First attempts failed to build up the desired compound by a separate ligand synthesis and following incorporation of the metal center into the free ligand (see Scheme 1) [7]. Steric hindrance and the free rotation of the bipyridine moieties around the amide bonds gave only polymeric material.

A second approach in which a template synthesis was applied has given the caged Ru complex. A Ru^{II} complex with three bipyridine ligands that are functionalized (acid-chloride function) at the 5,5'-positions has the right geometry to cap two faces of the octahedron by 1,3,5-tris[*N*-benzyl(aminomethyl)]benzene moieties. Only high dilution technique combined

Table. Absorption Maxima and Extinction Coefficients of Ruthenium-tris-Diimine Complexes

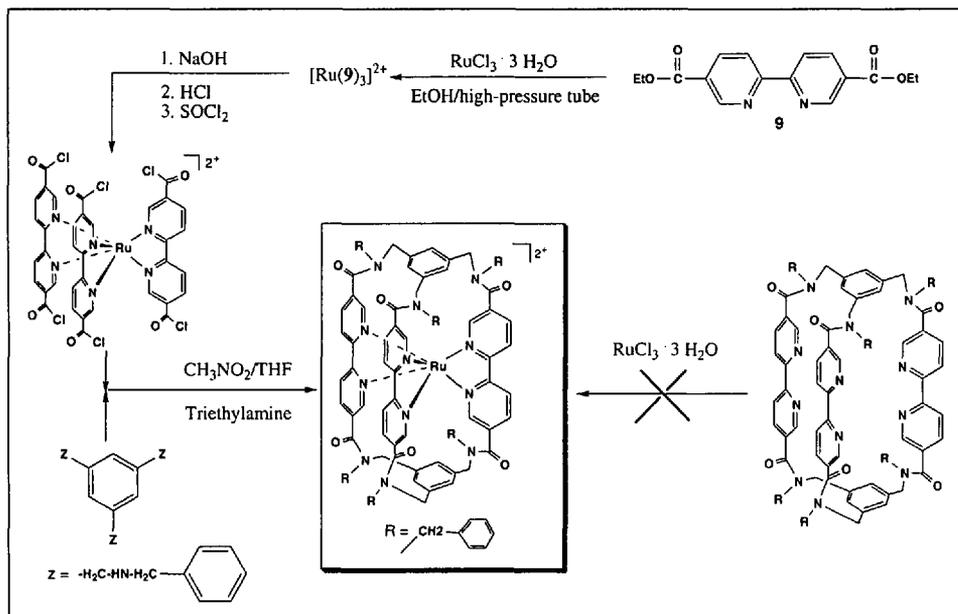
Complex	λ_{max} [nm]	ϵ
 1 = bpy	452	14 600
 2 = 3,3'-dm-bpy	456	11 000
 3 = 4,4'-dm-bpy	459	17 000
 4 = 5,5'-dm-bpy	440	14 700
 5 = 6,6'-dm-bpy	446	7 440
 6 = 4,4'-dCl-bpy	462	17 000
 7 = 4,4'-da-bpy	504	10 500
 8 = biq	526, 439	8 710, 8 060
$[\text{Ru}(\text{bpy})_2(\text{biq})]^{2+}$	547, 481	8 550, 6 590
$[\text{Ru}(\text{biq})_3]^{2+}$	524	9 000

with a precise stoichiometric addition of the two reactants has given the desired compound.

The photophysical properties of the new caged Ru complex are interesting (see Fig. 3). The UV/VIS absorption spectrum shows an absorption (MLCT transition) at 455 nm ($\epsilon = 10\,300 \text{ M}^{-1}\text{cm}^{-1}$), which is very close to that of $[\text{Ru}(\text{bpy})_3]^{2+}$.

The C=O groups of the six amide functions are expected to influence strongly the absorption signal (bathochromic shift). This effect is reduced in the cage complex by their orthogonal orientation with respect to the aromatic pyridine rings of bpy. The orthogonal orientation of the bipyridine–C=O fragments was deduced from molecular models, which demonstrate the

Scheme 1



rigidity of the cage. The rigidity of the metal complex is also mirrored in the emission intensity at room temperature. The closed-cage Ru^{II} complex shows an emission intensity twice that of the parent [Ru(bpy)₃]²⁺ compound [8].

The electrochemical property of the closed-cage Ru^{II} complex (see Fig. 3) indicate that [*Ru(cage)]²⁺ is a stronger oxidizing agent than the corresponding [*Ru(bpy)₃]²⁺. Therefore, the potential difference in a charge, separated state must be more pronounced concerning the reference system of [Ru(bpy)₃]²⁺.

The most promising result was found during photochemical experiments. Irradiation of [Ru(cage)]²⁺ (in a CH₂Cl₂ solution) during weeks has given no detectable decomposition. The observed increase in stability against photodecomposition is higher than 10⁴ [9].

Another interesting result was found during the study of the so-called 'half-cage' compounds (see Fig. 4). The compound [Ru(10)]²⁺ that was synthesized with the same rigid cap as the [Ru(cage)]²⁺ complex, shows the same stability concerning photodecomposition as the two-fold capped cage compound. The compounds [Ru(11)]²⁺ and [Ru(12)]²⁺ with more flexible caps give photosubstitution and photoracemization reactions. Thus, a rigid cap on one side of the complex is sufficient to prevent photodecomposition reactions.

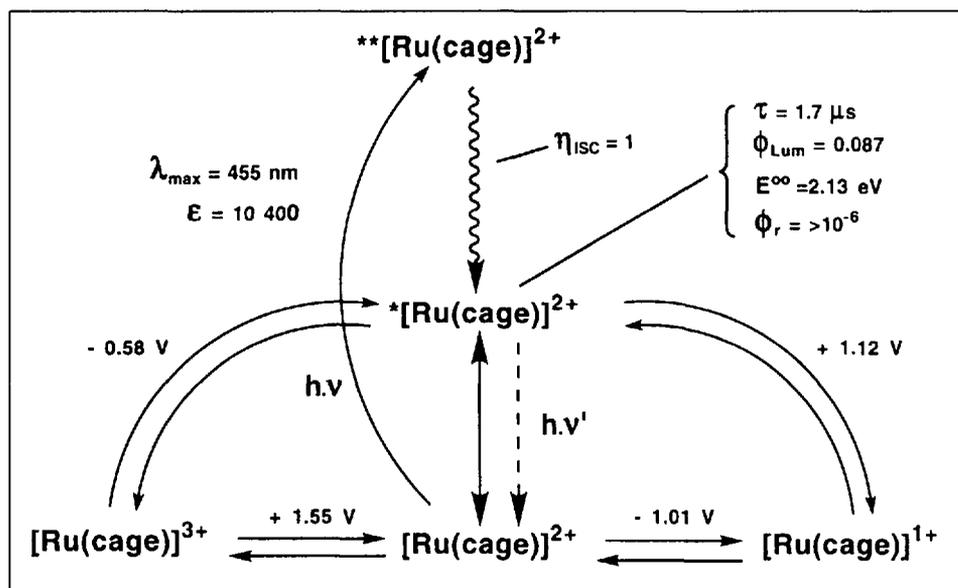


Fig. 3. Molecular quantities of [Ru(cage)]²⁺ relevant for energy- and electron-transfer processes. **[Ru(cage)]²⁺ indicates spin-allowed excited states and *[Ru(cage)]²⁺ indicates the lowest spin-forbidden excited state.

3. Bridged Dinuclear Complexes

The extension from mononuclear metal complexes to bridged dinuclear compounds gives the opportunity to study energy, and/or electron-transfer processes.

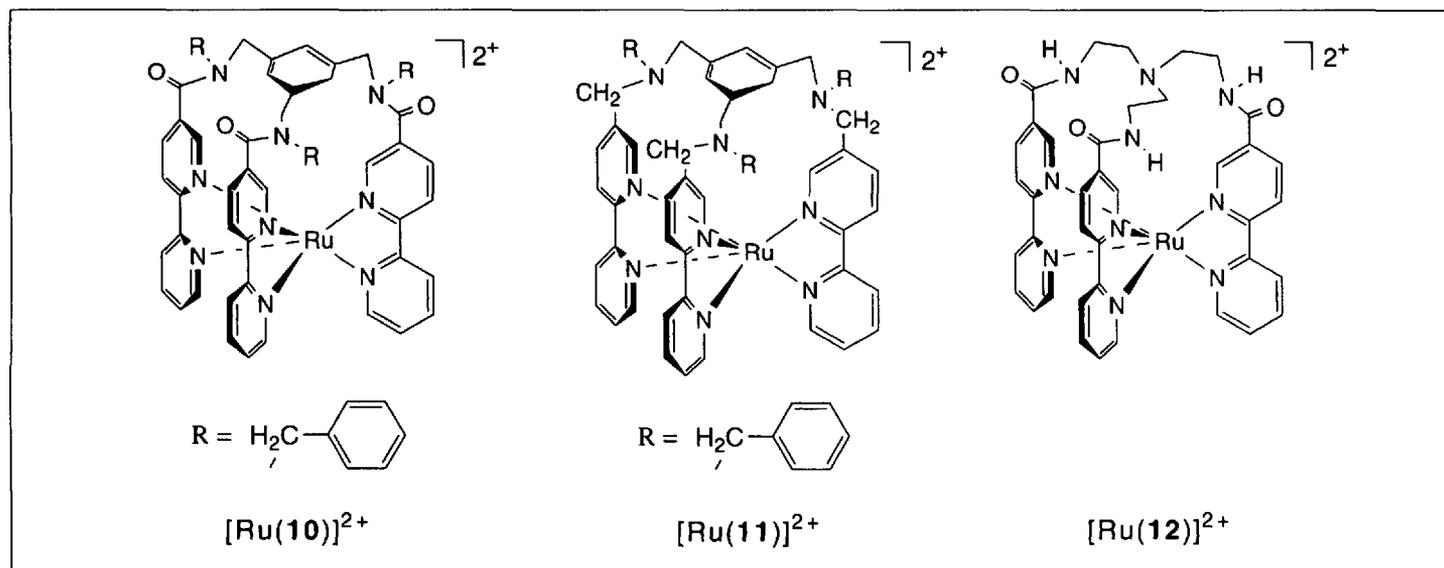


Fig. 4. The 'half-cage' complexes [Ru(10)]²⁺, [Ru(11)]²⁺, and [Ru(12)]²⁺

Advancement in this field requires the availability of molecular components (building blocks) having well-defined structures and properties. Such molecular components are metal-based units linked together by a bridging ligand (see Fig. 5). The bridging ligand itself is often based on a spacer condensed with two chelating sites (ligands of the type bipyridine, phenanthroline, or terpyridine).

To link spacers together to a spacer chain is a further requirement for such a component. Another important point of such bridged metal complexes is their degree of spatial organization. Species where the active units are linked by non-rigid bridges are of little interest, because practical applications require vectorial energy or electron transfer over long distances. Furthermore, if the geometry of such so-called 'molecular devices' is not strictly defined, the results obtained cannot be compared with the predictions of energy- and electron-transfer theories.

The following factors play an important role in the design of new bridging ligands: *i*) The two chelating sites contribute to the determination of the spectroscopic and redox properties of the metal-based units; *ii*) The spacer and its connection to the chelating ligands determines the geometrical structure of the molecular device; *iii*) The chemical nature of the spacer (insulator or conjugated π -system) is important for the electronic communication between the two metal-based components.

In consideration of the above-mentioned arguments, we have developed a series of rigid rod-like bridging ligands and their corresponding dinuclear metal complexes and studied the intercomponent energy and electron-transfer processes (see also Fig. 6) [10]. The most interesting compound in the series is the mixed-metal complex with an adamantane spacer ($\text{Ru}^{\text{II}}(\text{PAP})\text{Os}^{\text{II}}$) [11]. Spectroscopic and electrochemical measurements show that the two metal-based units are electronically weakly coupled. Both metal centers have luminescence bands that are well separated. After irradiation into the MLCT band of the Ru^{II} -based unit, a strongly quenched emission (compared to $\text{Ru}^{\text{II}}(\text{PAP})\text{Os}^{\text{II}}$, with a shorter lifetime of the excited state) with a corresponding sensitization of the Os^{II} -based luminescence can be observed. The results show that in $\text{Ru}^{\text{II}}(\text{PAP})\text{Os}^{\text{II}}$, an intercomponent energy-transfer process takes place (see Fig. 6). To develop the enhanced emission from the Os^{II} unit, a certain time for energy moving through the bridging ligand is needed. The rise time is easily observable

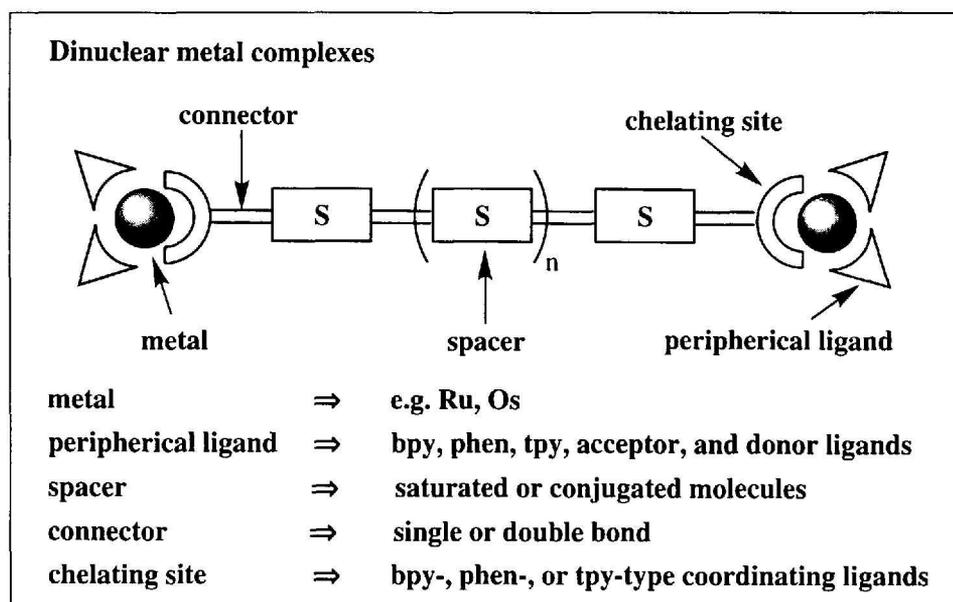


Fig. 5. Schematic representation for bridged dinuclear metal complexes

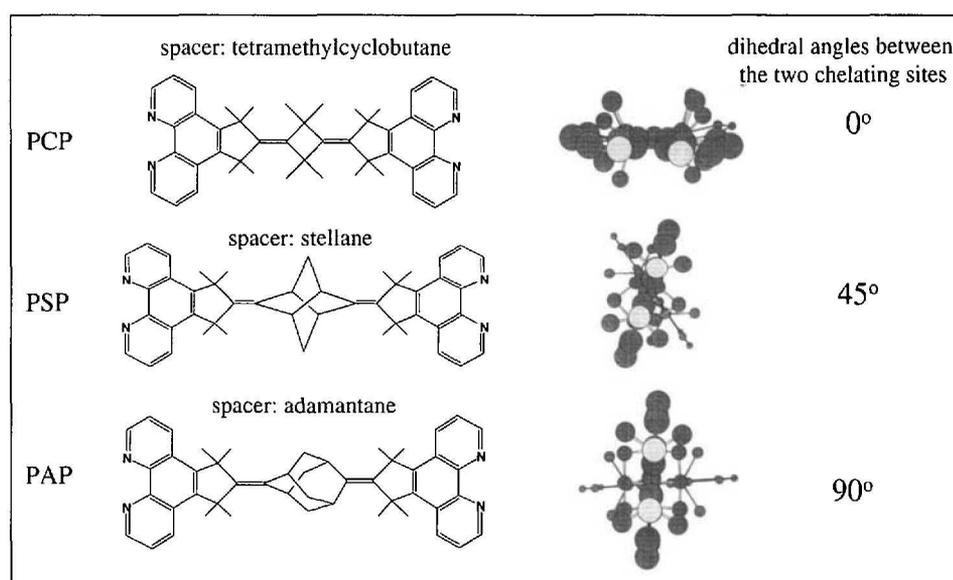


Fig. 6. Rigid rod-like bridging ligands with their Chem3D representation. The preparation of the bridging ligand PSP is in progress.

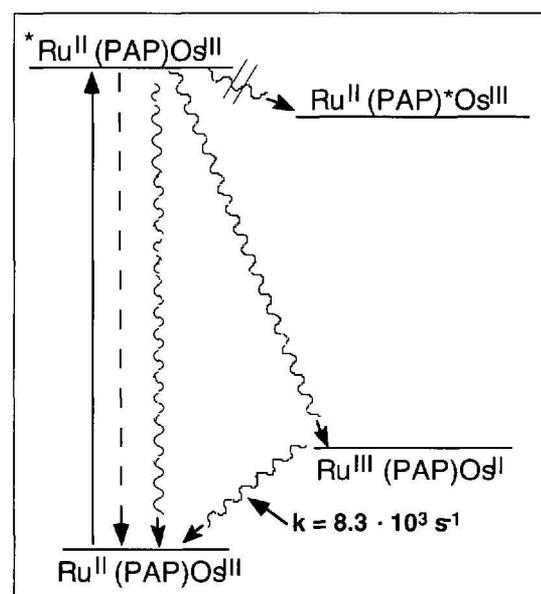


Fig. 7. Energy-level diagram showing the photoinduced electron-transfer deactivation process in $[\text{Ru}^{\text{II}}(\text{PAP})\text{Os}^{\text{III}}]^{5+}$. Full line, excitation; dotted line, luminescence; wavy line, radiationless decay.

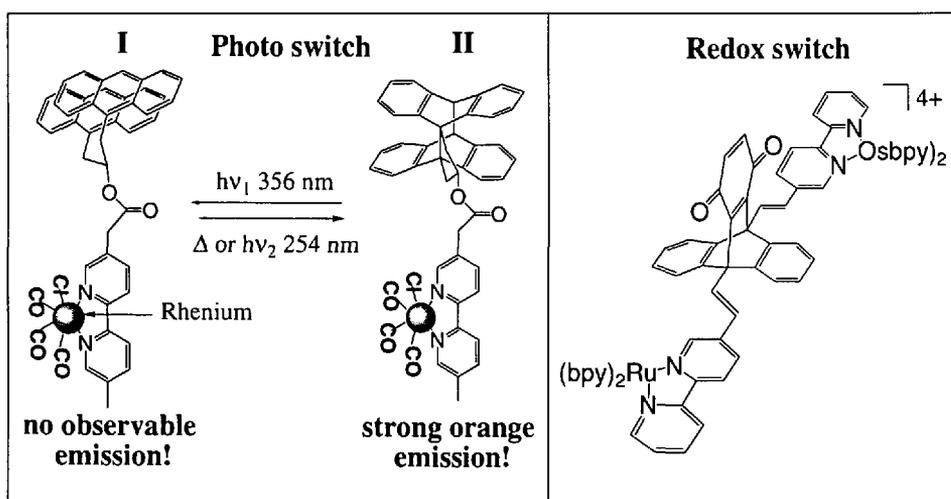


Fig. 8. Examples for photo and redox switches

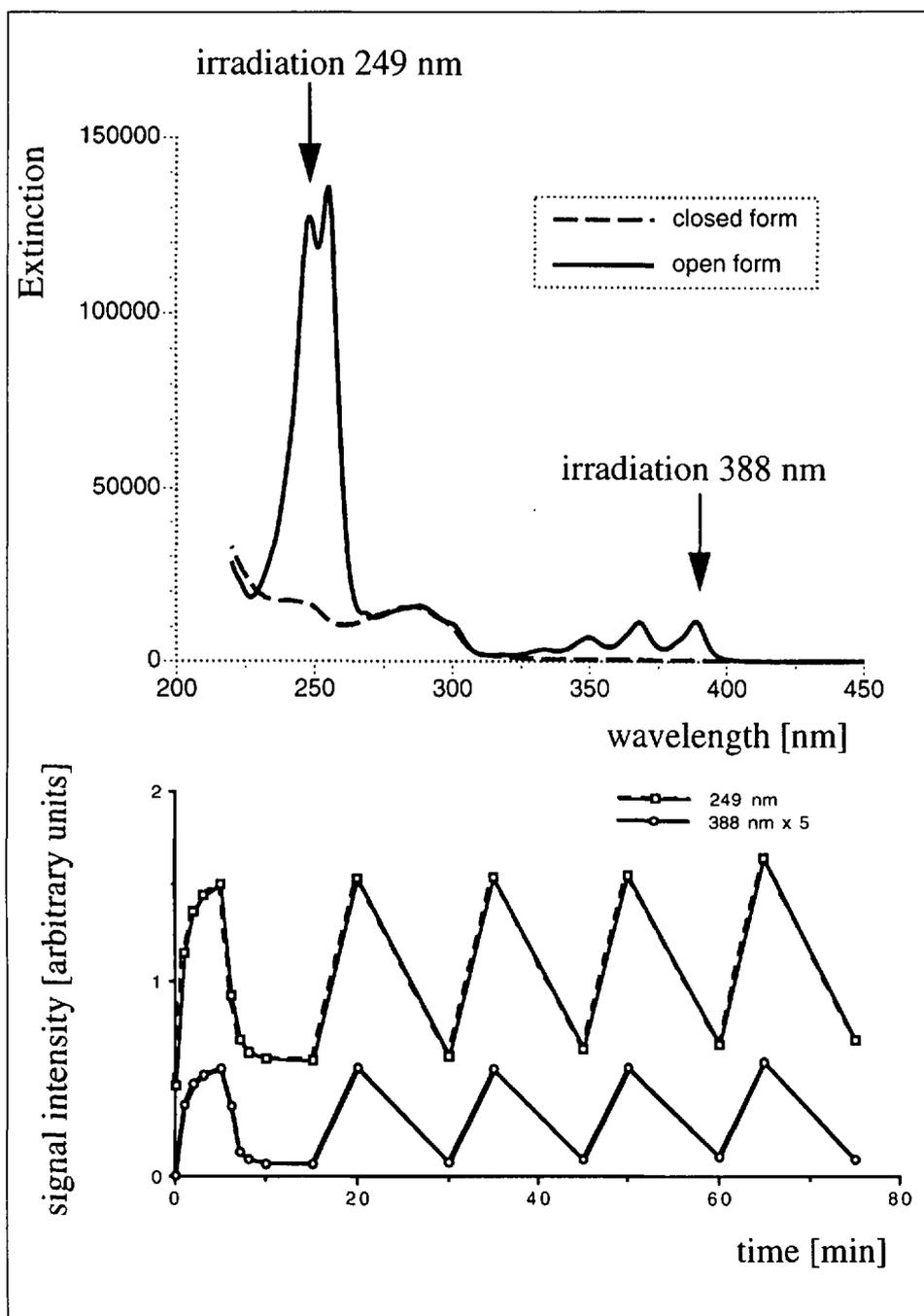


Fig. 9. Reversible ON/OFF response by irradiation either at 388 nm or 249 nm into the photo switch (see Fig. 8)

by an exponential increase of the emission signal in a pulsed-laser flash-photolysis experiment.

Selective oxidation of the Os^{II} center in $Ru^{II}(PAP)Os^{II}$ into Os^{III} converts the emissive Os unit into a non-emissive one. Such a system is ideal for a study of electron-transfer processes. The Os^{III} unit acts as a quencher for the Ru^{II} -based excited state. The quenching process leads to the formation of the $Ru^{III}(PAP)Os^{II}$ intervalence-transfer product (see Fig. 7). The $Ru^{III}(PAP)Os^{II}$ species decays then to the ground-state isomer $Ru^{II}PAPOs^{III}$ with a rate constant of $8.3 \cdot 10^3 \text{ s}^{-1}$. That means that the lifetime of such a rigid bridged dinuclear metal complex (in the intervalence-transfer state) is 0.12 millisecond!

4. Polypyridine Ligands for Molecular Devices

Functional units of molecular dimensions, like switches, diodes, molecular wires, and sensors have become a matter of intense research. *Molecular devices* has become the general term (sometimes debated) to designate such engineered molecular systems. Technological applications may still be quite far away, but the trend is clearly set, and it would be not too surprising, if molecular devices would revolutionized several fields of technology in the next century.

The previously discussed polypyridine ligands and their metal complexes are useful components for the design and the preparative realization of such molecular devices. Recently, we have developed a molecular photonic switch and a redox switch that are capable to perform the logic operation YES/NO [12]. The switches work on the basis of photoinduced energy-transfer (PET) processes. Irradiation triggers transformations, that is either an intramolecular cyclization (see Fig. 8) or a change from a quinone to a semiquinone structure.

The photo switch consists of two separate subunits: the switch (two anthracene units) and the detector (rhenium complex). The two parallel, stacked anthracene units dimerize by irradiation with light of 356 nm wavelength. A 254-nm irradiation opens the chemical bonds of the dimerized product. The two anthracene moieties are formed. The state of the switch is indicated by the Re complex. The intense emission from the Re unit is strongly quenched when the anthracene molecules are present (see I, Fig. 9). After cyclization at 254 nm irradiation, II is formed, and an orange emission can be

observed. The irradiation process on the switching part is reversible. Fig. 9 gives an impression of the switching process observed at two different wavelengths (UV/VIS spectrum).

The second described molecular device is a redox switch (see Fig. 8). The quinone/triptycene spacer acts as an electron trap. No emission can be observed from the osmium-metal-based unit. After reduction of the quinone spacer into the semiquinone form, the bridge is accessible for an electron-transfer process. A PET-induced emission is then observable. Another interesting feature is the pH dependence of the redox potential of the quinone/semiquinone redox couple. Therefore, the PET process can be also triggered by pH change.

The interest in exploring the field of molecular devices is strongly increasing. An application of molecular devices is for the moment obviously speculative. A possible use of such photochemically active molecules lies in the (holographic) data storage [13]. Compounds that can write and read data by irradiation with light of different wavelengths are interesting. Our photo switches should be able to function as RAM (Random Access Memory) when they are dispersed in a polymeric matrix. An important point for further applications is the response time and the reversibility for such molecular changes.

5. Stereochemically Well-Defined Building Blocks

If a molecular material with engineered function is to be synthesized, a modular approach is highly desirable. This strategy has been known and developed since a relatively long time in organic chemistry. The concept and the use of synthons [14] has contributed strongly to molecular engineering in organic chemistry. An important feature of a synthon is its stereochemical aspect, which allows the construction of stereochemically well-defined species of much larger molecular dimensions. Neither were synthons developed systematically in coordination chemistry, nor was the stereochemical concept of such structural elements given due attention until quite recently. Until ca. 1980 (and in many cases even in recent reports), many coordination compounds have been described in the literature, which contain several stereoisomers, yet their existence was not even mentioned. During the last two decades, however, several groups started to use coordination compounds for highly imaginative molecular engineering pur-

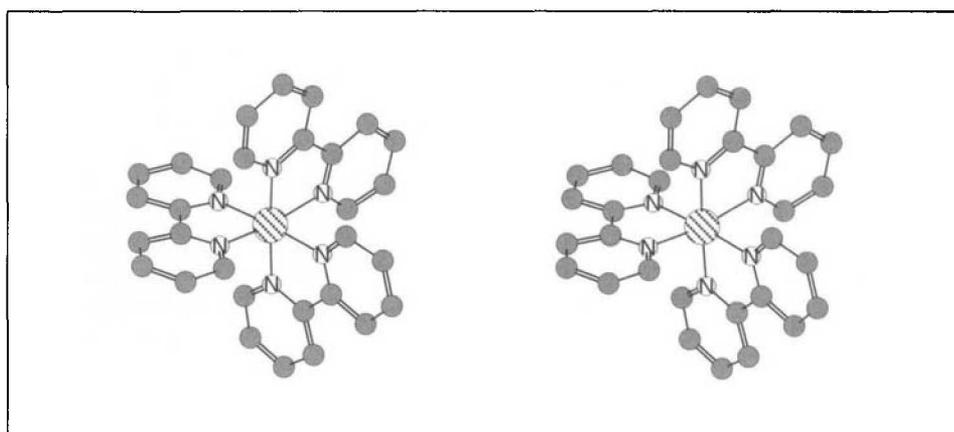


Fig. 10. A stereoview of a complex $[M(bpy)_3]$ showing its helical chirality. This pair can be viewed either as a right-handed (Δ in parallel view) or as a left-handed (Λ in cross-eyed view) helix. See [16].

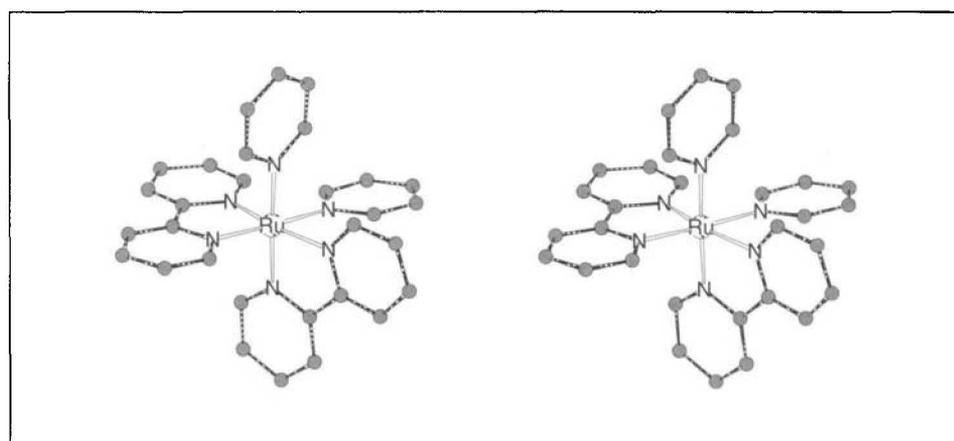


Fig. 11. Stereopair (Δ in parallel view, Λ in cross-eyed view) of the building block $[Ru(bpy)_2(py)_2]^{2+}$ containing the synthon $[\Delta\text{- or } \Lambda\text{-}Ru(bpy)_2]$

poses [15]. The molecules described in Sects. 1–4 of this article, represent examples where a conventional approach to synthesize coordination units leads to severe stereochemical problems. Every tris-bidentate coordination center of octahedral coordination geometry represents an element of chirality with inherently two possible configurations (Fig. 10).

A simple dinuclear species comprising two tris-bidentate metal centers therefore yields a mixture of three stereoisomers, namely one enantiomeric pair of homochiral molecules and an overall achiral 'meso-form'. These $\Delta\Delta$, $\Lambda\Lambda$, and $\Delta\Lambda$ -isomers are normally obtained in a statistical ratio of 1:1:2. In order to avoid the difficulty of obtaining stereoisomeric mixtures, we developed two strategies for the synthesis of isomerically pure multicenter coordination compounds.

The first method is very straightforward and it applies principles that have been known since Alfred Werner's times. As a first step, a mononuclear bis-bidentate complex is synthesized as a racemate. The two enantiomers are then separated by formation of diastereoisomeric salts.

As already shown by Alfred Werner [17], in many such cases, substitution reactions can be carried out at the metal under retention of configuration. A method, fairly generally applicable in the large field of Ru-diimine complexes, that have shown to be one of the most interesting types of species in the field of photonic materials, was developed in the Ph.D. thesis of Xiao Hua [18]. The complex $[Ru(bpy)_2(py)_2]^{2+}$ (Fig. 11) can easily be separated into its enantiomers by benzoyl tartrate, and it is an excellent building block for polynuclear Ru complexes.

$[Ru(bpy)_2(py)_2]^{2+}$ contains the chiral synthon $[cis\text{-OC-6-Ru}(bpy)_2]$ in an enantiomerically pure form (OC-6 is the official IUPAC designation of an octahedral coordination geometry [19]), which retains its configuration under rather harsh conditions (but not always, see below), and it is therefore a useful building block in many cases [20]. This method is now used by several laboratories for the production of stereochemically well-defined polynuclear Ru complexes. There are, however, clearly two drawbacks of this building block: firstly, a resolution of a

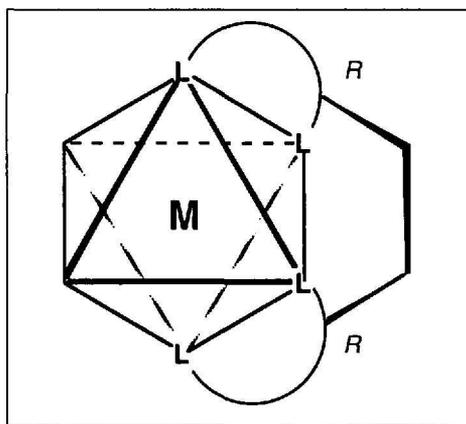


Fig. 12. A C_2 -symmetric synthon for an octahedral coordination center with predetermined chirality

racemate is necessary and, therefore, only a maximum yield of 50% is possible. Even this theoretical limit cannot be reached, because there are inevitable losses in the separation procedures. Secondly, even though the enantiomerically pure building block $[Ru(bpy)_2(py)_2]^{2+}$ is thermally quite stable, the building block itself and the configurationally predetermined tris-dimin centers constructed from it undergo racemization with a relatively high quantum yield under irradiation, even with visible light. Because of these limitations, a second, completely new strategy was developed.

In this strategy, a general design for a ligand was set up, where two bidentate

chelating units would be connected by a chiral bridge, in such a way as to predetermine the helical chirality of the two chelating units around the metal completely (Fig. 12).

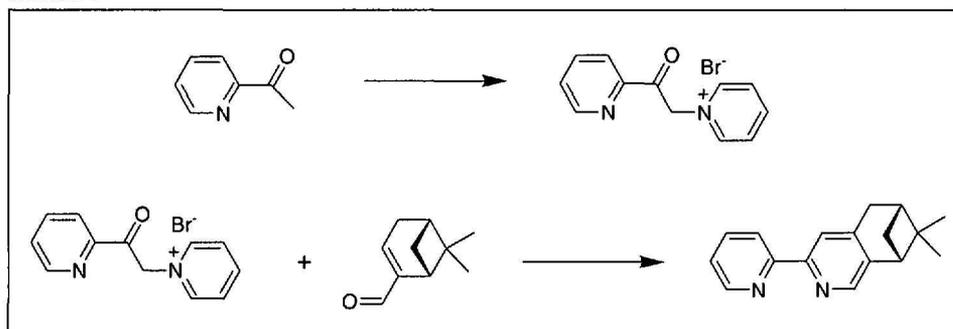
This strategic concept was proposed to *Pascal Hayoz*, who started his Ph.D. work in April 1990 in our institute as a subject for his thesis. About one year later, *Hayoz* found an elegant solution to the problem through the synthesis of the pinene-fused bipyridine ligands (Scheme 2).

An important feature of these bipyridine derivatives is the reactivity of the methylene groups of the pinene moiety. Deprotonation with strong bases takes place with a high stereoselectivity, which allows for the connection of two ligands via a bridge that is chirally anchored at the two bidentate ligands. Through this reactivity, two or even more such ligand units can be linked through various types of bridges (Scheme 3).

We call these ligands, where the four donor atoms are predisposed so that only one of the two configurations (Δ or Λ) at the metal center can be formed through diastereoselectivity, CHIRAGEN ligands. They generate chirality at the metal center. The origin of this chirality lies in the natural process through which the particular pinene molecules used for the ligand preparation was synthesized somewhere out in the woods in a pine tree [21]. A first example of a completely diastereoselective formation of a complex using a CHIRAGEN ligand was demonstrated by *Hayoz* with a simple alkane bridge of six methylene groups that yielded a Ru complex with completely predetermined configuration (Fig. 13).

This complex contains the synthon $[cis-OC-6-Ru(CHIRAGEN[6])]$. In the past five years, a large number of new ligands containing the pinene moiety or other groups derived from terpene molecules (up to now 88 different completely characterized molecular species) have been synthesized in our laboratories. All of them are based on the original synthetic concept proposed by *Hayoz*. Through variation of the bridge, ligands could be produced that put lower steric strain on the metal complexes formed, therewith improving the yields [22]. One of these ligands, CHIRAGEN[m-xy], yields a particularly useful building block (in our laboratory jargon the *Mürner* building block) (Fig. 14). With such a building block and a CHIRAGEN ligand that has as a bridge between the two bpy units another bpy group, a trinuclear compound could be synthesized that contains in total 27 elements of chirality (see Fig. 15) [23].

Scheme 2



Scheme 3

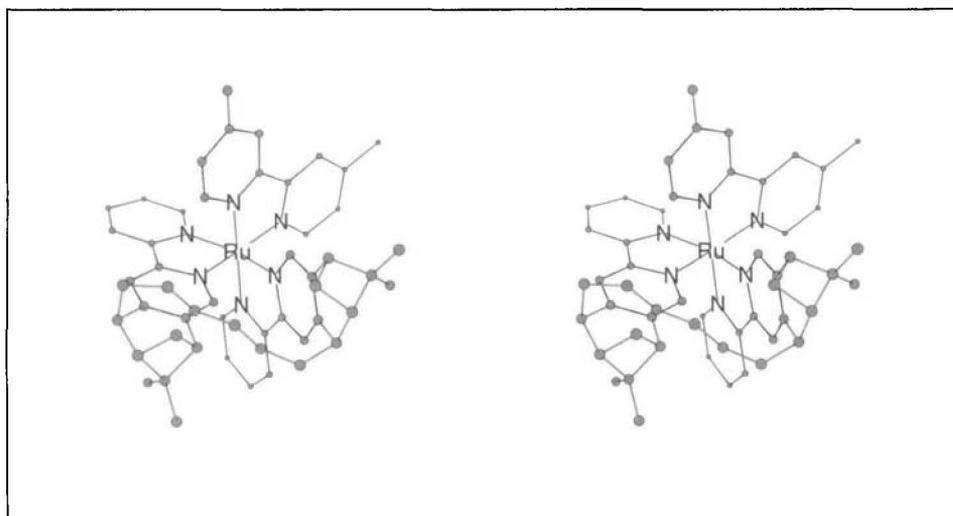
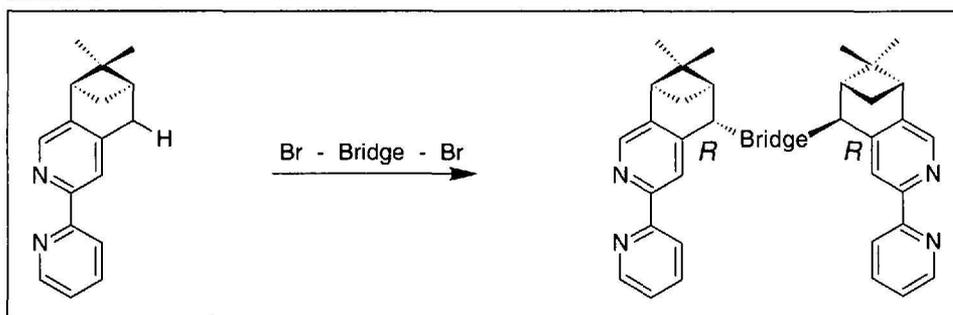


Fig. 13. Stereopair of the complex $[Ru(CHIRAGEN[6])(4,4'-dm-bpy)]^{2+}$

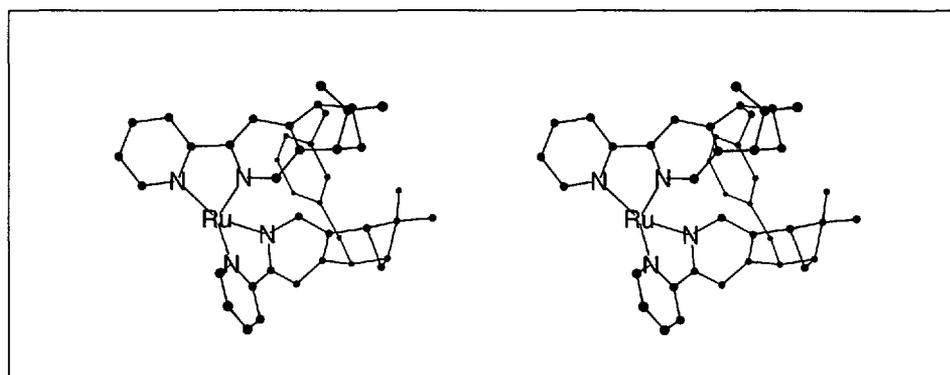


Fig. 14. Stereoview of the synthon containing the CHIRAGEN[m-xyl] ligand. The building block used is generally the *cis*-dichloro complex.

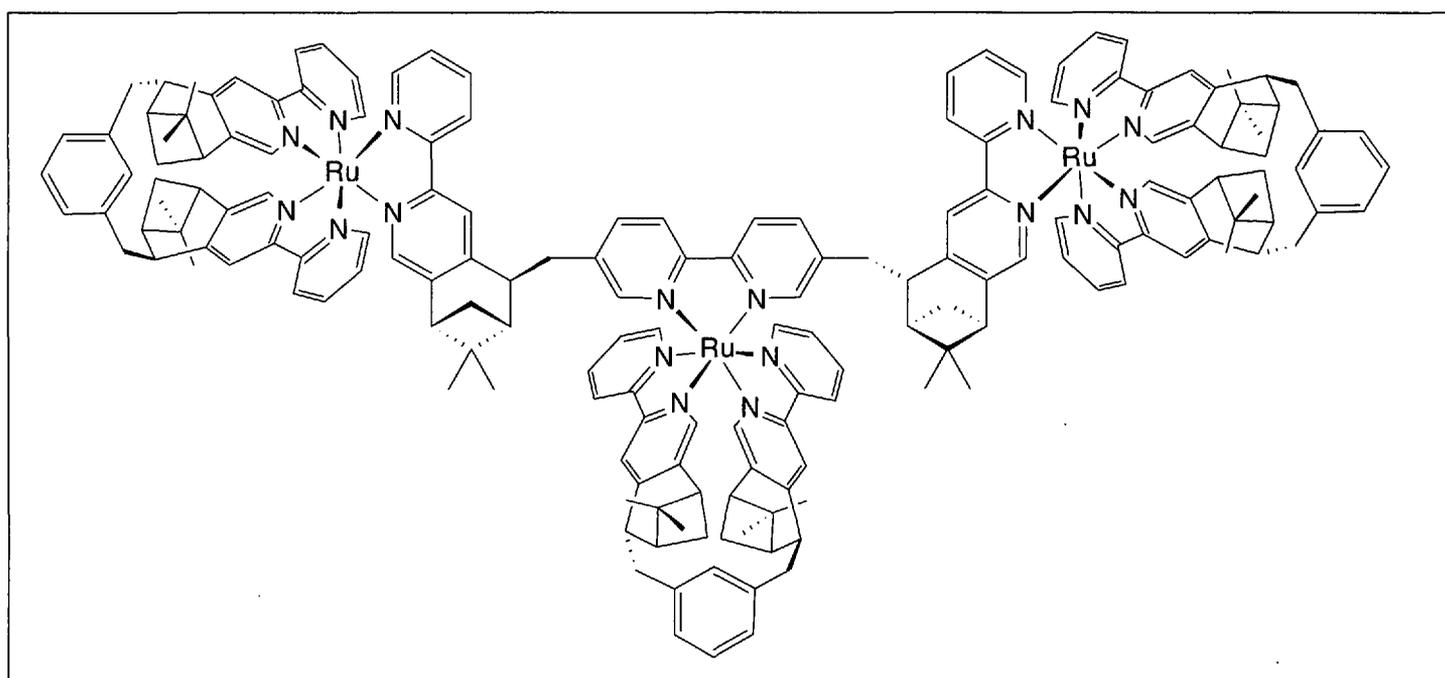


Fig. 15. Trinuclear complex $[Ru(CHIRAGEN[m-xyl])_3(CHIRAGEN[bpy])]$, comprising 27 elements of chirality

The stereochemistry of the complex is completely determined by the use of myrthenal, which is the molecule carrying originally the chiral information. Presently, ligands of this type are used in the preparation of several new compounds, and we are participating in a European Network Program (Pisa, Bruxelles, Strasbourg, Dublin, Bologna, and Fribourg): 'From Molecules to Materials: a Concerted Approach to Nanometer-Sized Oligometallic Complexes with Predetermined Configurations and Functions', where we contribute with our stereochemically well-defined building blocks to the construction of new molecules that constitute materials with new functionalities.

6. Chiral Ligands for Self-Assembled Species

The ligands discussed in Sect. 5, especially the CHIRAGEN ligands, yield a wealth of new coordination compounds

through more or less conventional methods of synthesis. A new promising trend in chemistry in general, and especially also in coordination chemistry, is the synthesis of materials through spontaneous self-assembly. In a spontaneous self-assembly, relatively complicated molecular structures are formed out of a given mixture of constituting molecular building blocks, that represent a sufficient thermodynamic preference in order to achieve a high selectivity. Very often, interesting structures formed in spontaneous self-assembly are chiral objects. No enantioselectivity is possible, (at least not in a non-chiral environment) when the building blocks themselves do not carry any chiral information. Therefore, at least one racemate, and in some cases several diastereomerically different racemates, will be formed in spontaneous self-assembly reactions leading to chiral structures starting from achiral material. Since pyridine- and bipyridine-type ligands are important for the self-assembly in various systems containing

metal ions, we employed our CHIRAGEN-type ligands also in the field of the spontaneous self-assembly reactions. Indeed, complete stereoselectivity has been found in several cases [24]. The most interesting self-assembled species, a circular hexagonal complex comprising a total of 78 atoms has been obtained starting from a CHIRAGEN molecule derived from 5,6-pineno-bpy (Fig. 16). This structure is a hexanuclear, monostranded chirally completely predetermined helicate.

The 5,6-pineno bpy ligands are much more prone to build up metal complexes with tetrahedral (T-4) centers as opposed to the octahedral OC-6 centers for 4,5-pineno-bpy. The large number of CHIRAGEN-type ligands, combined with the numerous metal centers that can be considered for spontaneous self-assembly reactions, leads to an extremely large number of systems to be examined in view of possible interesting applications of these molecular ingredients. In a coming chapter of research, the hitherto more intuitive

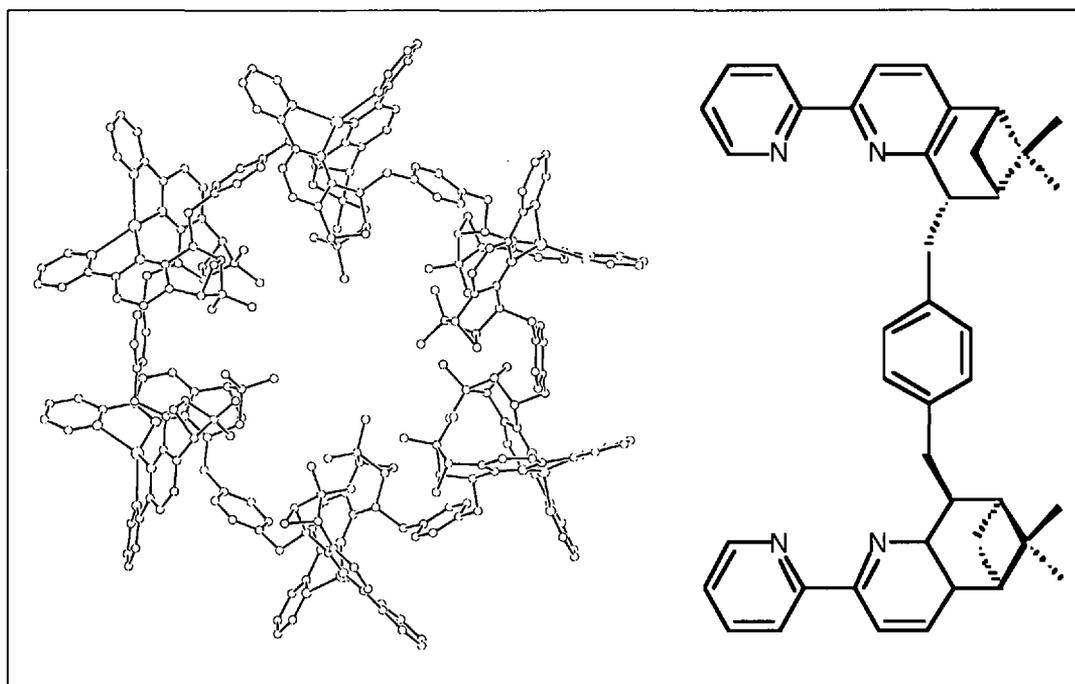


Fig. 16. A CHIRAGEN ligand (L = 5,6-CHIRAGEN[p-xy]) (right) and its hexanuclear, circular, mono-stranded helicate M_6L_6 , where $M = Ag^+$ or Cu^+

approach for selecting such systems will be replaced by a more systematic screening, comprising systematic molecular modeling. However, the latter method is still of somewhat limited usefulness, since our systems are very large and comprise metal ions for which molecular modeling is always a difficult task.

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