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Synthesis and photophysical properties of chiral, binuclear metal complexes

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Abstract

The synthesis of isomerically pure multicentred species is an important task for preparative chemists. Only stereochemically well-defined structures of polynuclear metal complexes lead to photophysical results that are clearly interpretable. We have developed several strategies to synthesise such compounds that have a predetermined chirality (Δ- or Λ-helix) at each metal center. The approximate local symmetry of the described metal complexes is D_3 (octahedral, tris-bidentate). The methods are the following: (a) resolving a racemic building block followed by substitution of the two labile monodentate ligands by a bidentate diimine

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ligand under total retention of configuration. (b) Synthesis of an optically pure precursor complex in which two chelating bipyridine ligands are bridged and each contain an optically active pinene unit. The remaining coordination sites are then replaced by a bidentate diimine ligand. (c) Use of ligands that have sterically demanding substituents perpendicular to the molecular plane. The use of such ligands leads direct to optically active compounds. Examples of these methods will be given, while considering their photophysical application.

Keywords: Optically active compound; Photophysical properties; Chiral complex; Binuclear metal complex

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1. Introduction

Chirality has been of interest in *inorganic chemistry* and especially in coordination chemistry since Alfred Werner [1]. Progress in many branches of *organic chemistry* was strongly connected with chirality and optical activity. In organic chemistry we often encounter long chains and also branched molecules with the possibility of one or more centers of chirality. Many properties of such molecules, e.g. those of a drug, depend on a well-defined stereochemistry. On the other hand, inorganic coordination compounds are more often metal complexes with only one center of chirality, and exhibit non-distinguishable properties between racemic and enantiomeric pure forms of the compounds. Enantioselective synthesis, i.e., the creation of one and only one helicity in a metal complex with local D_3 symmetry has been achieved only recently in rare cases [2]. This is somewhat surprising, in view of the enormous literature which exists on enantioselective synthesis in organic chemistry (leading to defined C-chirality centers). Chirality at the metal center is of great importance in homogeneous enantioselective catalysis, where great progress has been made recently [3]. All the reports published so far show, however, that a full control of the chirality at the metal center is difficult to achieve. With the mentioned development of metal-catalyzed enantioselective reactions and the synthesis of polynuclear metal complexes, we are in need of methods for the preparation of metal centers with well-defined stereochemistry.

2. General aspects of chirality and complex formation

The formation of polynuclear metal complexes leads to a mixture of different isomers. For example, the simple dinuclear complex $[(phen)_2Ru(bipyrimidine)Ru(phen)_2](PF_6)_4$ with two racemic metal centers gives an isomeric mixture of Δ,Δ:Δ,Λ:Λ,Λ-complexes in a ratio of approximately 1:2:1 (see Fig. 2). In general, the upper limit for the number N of isomers, which can be obtained during the formation of polynuclear complexes with n helical octahedral coordination units, is given by $N=2^n$. It is easy to see that the number of isomers increases enormously with the number of metal centers. In order to prepare isomerically pure compounds,

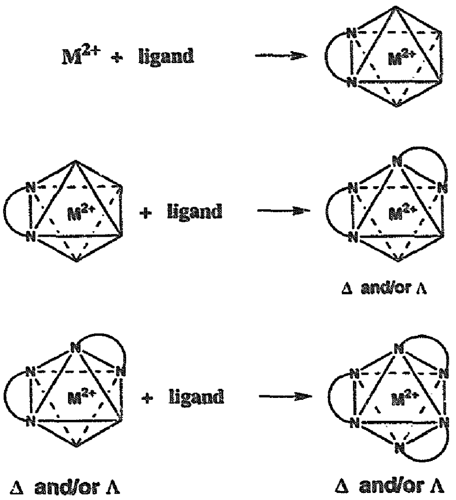


Fig. 1. The attachment of the second ligand determines the stereochemistry of the final octahedral metal complex.

it is important to control the stereochemistry at each metal center. Therefore, we must examine the complex formation with respect to their stereochemical behavior (see Fig. 1).

The attachment of the second ligand determines the stereochemistry of the final complex. The third ligand merely completes the coordination shell of the metal center without change of their helicity.

In Section 3, three different strategies for control of the stereochemistry during complex formation are presented.

3. Different strategies for the enantioselective synthesis of octahedral metal complexes

3.1. Method a

Resolving of an appropriate racemate of a building block, and using the enantiomerically pure precursor complex in suitable reactions to build up larger species, is a quite successful method [4]. Several isomerically pure dinuclear species have been synthesized in that way [5]. For example, with 2,2′-bipyrimidine, as a bridging ligand, all three isomers, the homochiral enantiomeric pair ΔΔ/ΛΛ and the heterochiral meso-form ΔΛ, were prepared in pure form (see Fig. 2).

A problem is the use of these building blocks for the preparation of PMDs, because the coordination centers can easily racemize in the excited state. An isomerically pure sample will, therefore, become a stereochemically undefined system after irradiation with light.

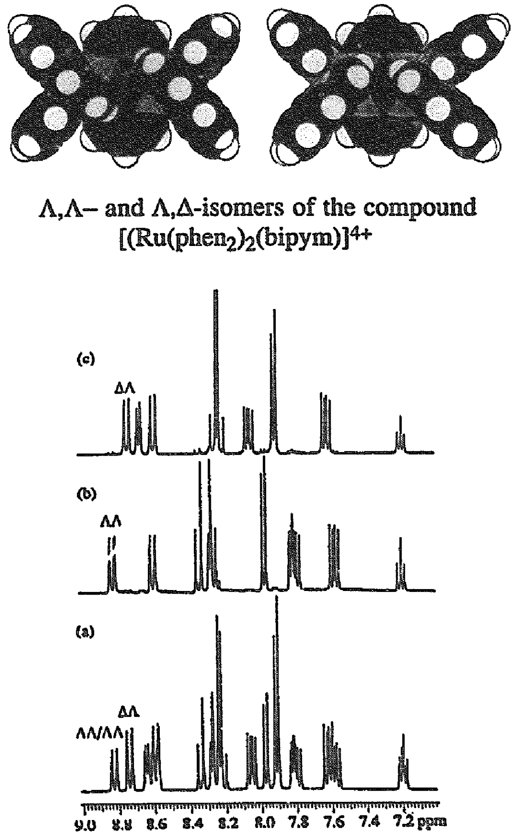


Fig. 2. The ^{1}H-NMR spectra shows clearly the applicability of method a. (a) Corresponds to the racemic mixture, (b) and (c) to the pure ΛΛ-, ΔΛ-form respectively of the compound [(Ru(phen)$_2$)$_2$(bipym)]$^{4+}$.

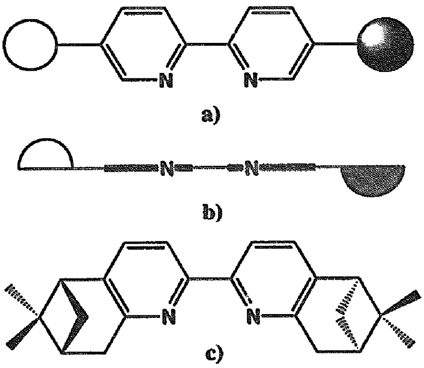
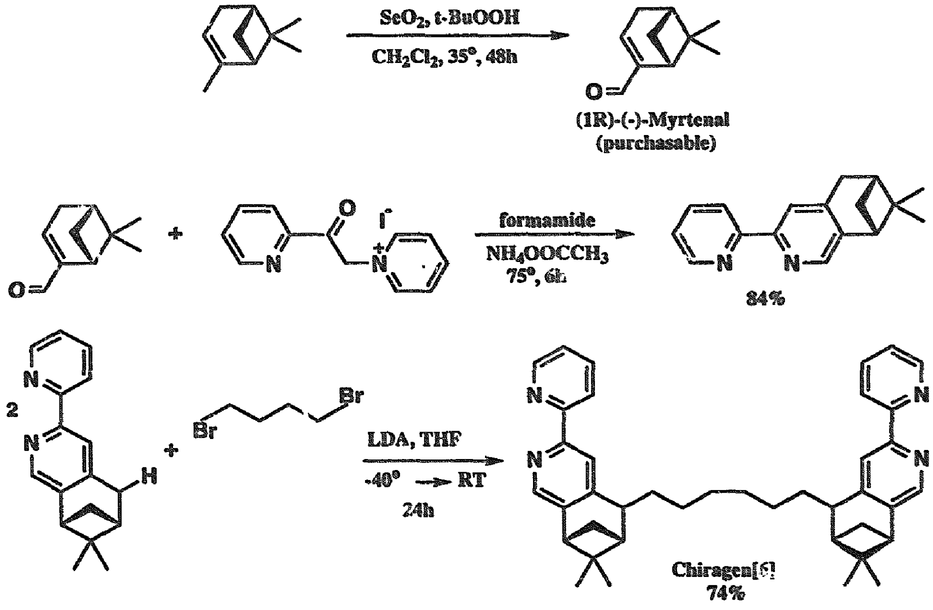


Fig. 3. Front view (a) and top view (b) of a substituted 2,2′-bipyridine ligand with bulky groups attached perpendicular to the molecular plane. (c) A real example of such ligands.

3.2. Method b

To avoid the problem of racemization, the second strategy is based on a precursor in which the two bidentate ligands are linked by a chiral connecting group. Starting from the chiral-pool molecule (+ or −)-α-pinene, which is available in high enantiomeric purity, 4,5-pinenebipyridine can be synthesized [6]. The stereospecific deprotonation and the subsequent alkylation lead to a bridged bis-bidentate ligand that forms, upon complexation with a metal, a pure stereoisomer [7]. The synthesis is depicted in Scheme 1.



Scheme 1.

Since these ligands predetermine the helical chirality (Δ/Λ) at the metal, we call them *chiragens*. Since pinene is available naturally in either of the enantiomeric forms, both helical configurations of the Ru complexes can be obtained, without the necessity to resolve a racemate.

3.3. Method c

The third method uses bidentate diimine ligands which have bulky substituents, perpendicularly attached to the molecular plane (see Fig. 3). This substituent induces a steric interaction that prefers only one of the two possible stereoisomers. Two examples of such substituted ligands are given in Fig. 4. An optical induction of 75% ee of one of the isomers was obtained after complexation of Fe(II) with the bis-4,5-pinenebipyridine ligand.

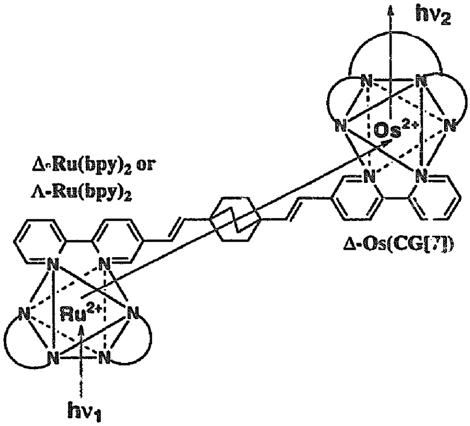


Fig. 4. A "supramolecular" binuclear metal complex as a model compound for energy- and/or electron transfer reactions.

4. Applications

To demonstrate the versatility of the application of the above mentioned methods, the following examples are given:

4.1. *Preparation of polynuclear compounds with well-defined stereochemistry*

The use of optically active building blocks, such as, for example (Δ or Λ)-$[M(L_1)_2X_2]^{2+}$ (method a) or (Δ or Λ)-$[M(\text{chiragen}[B])X_2]$ (method b), opens the possibility of synthesizing pure isomers of polynuclear metal complexes. Stereochemically well-defined compounds are important in the field of charge separation or energy transfer reaction on polynuclear complexes [8]. An example will be given.

To study the fundamental phenomenon of energy transfer processes we have mimicked that process by a model compound, depicted in Fig. 4.

The ruthenium complex acts as a sensitizer and reaches, after absorption of light, an excited state. The energy can be transferred to the osmium unity under simultaneous excitation of the osmium center. The osmium complex acts in this case as an internal quencher. Under emission of light the excited metal center loses its energy and falls back to the ground state. Because the wavelength of the emissions of the Ru- and the Os-centers, respectively, are different, that supramolecular, dinuclear compound is ideal for collecting data about energy- and/or electron-transfer reactions [9–11]. In the case that both metal centers have a well-defined chirality (Δ,Δ, Δ,Λ or Λ,Λ) the system opens a deeper insight into the energy transfer process. Irradiation of the Ru-center (in the Δ-form) with circular polarized light leads to an emission from the Os-center (in the Δ-form). The important photophysical information is the chirality of the emitted light (measured by the CPL properties). A change either of the chirality of the Ru-center or the Os-center gives supplementary information about the nature of the energy transfer process. At this moment the key compounds are being prepared and the photophysical measurements are under investigation.

4.2. Enantioselective catalysis on coordinatively unsaturated or labile optically active metal centers

Enantioselective catalysis, e.g., reductive alkylation of aldehydes [12], is feasible by using 4,5- or 5,6-bis-pinenebipyridine respectively, as chiral source in the labile nickel, zinc or copper complexes.

4.3. Compounds for non-linear optics

Optically active compounds that crystallize in non centro-symmetric space groups, are candidates for non-linear optical devices [13]. The easy access of compounds with the above-mentioned properties open a wide field for applications.

4.4. Optically active metal complexes for DNA intercalation reactions

Transition metal complexes that can interact with nucleic acids, have become the objective of intense research [14]. They define a new class of diagnostic and therapeutic substances. In particular, ruthenium compounds are known for intercalation with DNA. The emissive properties of this type of metal complexes can be exploited for identification and site-specific cleavage of DNA. Two different modes of interaction of metal complexes with DNA are known: intercalating interactions and groove-bound mode. The Δ-isomer of the compound $[Ru(phen)_3]^{2+}$ proceeds through the intercalation mode, while the Λ-isomer interacts through the groove-bound mode. With the presented methods, optically active emitting ruthenium complexes can be prepared, capable of intercalation reactions.

Acknowledgements

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References

[1] A. Werner, Ber. 44 (1911) 1887.
[2] A. Shanzer, J. Libman, R. Lazar and Y. Tor, Pure Appl. Chem., 61 (1989) 1529.
[3] R. Noyori, Science, 248 (1990) 1194.
[4] (a) X. Hua and A. von Zelewsky, Inorg. Chem., 30 (1991) 3796. (b) X. Hua, Ph.D. dissertation, University of Fribourg, Switzerland, 1993.
[5] X. Hua, Inorg. Chem., in press.
[6] P. Hayoz and A. von Zelewsky, Tetrahedron, 33 (1992) 5165.

[7] (a) P. Hayoz, Ph.D. dissertation, University of Fribourg, Switzerland, 1992. (b) P. Hayoz, A. von Zelewsky and H. Stoeckli-Evans, J. Am. Chem. Soc., 115 (1993) 5111.

[8] F. Vögtle, M. Frank, M. Nieger, P. Belser, A. von Zelewsky, V. Balzani, F. Barigelletti, L. De Cola and L. Flamigni, Angew. Chem. Int. Ed. Engl., 32 (1993) 1643.

[9] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, Coord. Chem. Rev., 84 (1988) 85.

[10] L. De Cola, V. Balzani, F. Barigelletti, L. Flamigni, P. Belser, A. von Zelewsky, M. Frank and F. Vögtle, J. Am. Chem. Soc., 32 (1993) 5228.

[11] P. Belser, Chimia, 48 (1994) 347.

[12] (a) K. Soai and S. Niwa, Chem. Rev., 92 (1992) 833. (b) C. Bolm, G. Schlingloff and K. Harms, Chem. Ber., 125 (1992) 1191. (c) A. Iuliano, D. Pini and P. Salvadori, Tetrahedron Asymmetry, 6 (1995) 739.

[13] D.J. Williams, Angew. Chem. Int. Ed. Engl., 23 (1984) 690.

[14] (a) J.K. Barton, Pure Appl. Chem., 61 (1989) 563. (b) R.M. Hartshorn and J.K. Barton, J. Am. Chem Soc., 114 (1992) 5919.