A Novel Synthetic Strategy toward Soluble, Well-Defined Ruthenium(II) Coordination Polymers

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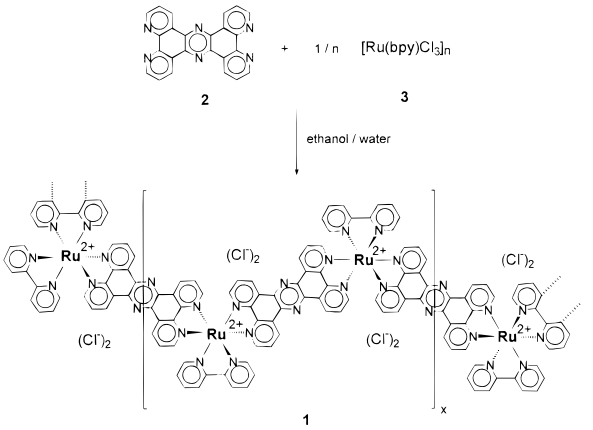
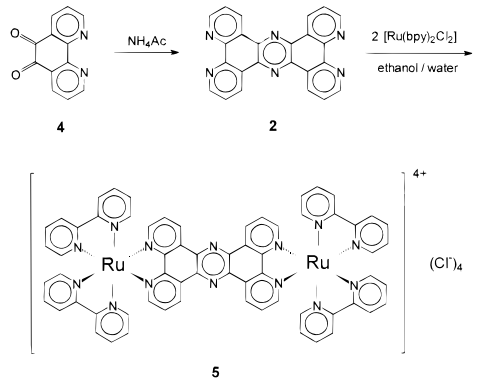
Polynuclear coordination compounds composed of transition metal complexes of ruthenium(II) and intrinsically rigid heteroaromatic chelating ligands are of considerable interest because they may perform useful functions in several fields, such as information recording and conversion of light into chemical energy.[1] The overwhelming majority of polynuclear ruthenium complexes available today, however, either contain only a very small number of metal atoms or, if the number is larger, are constitutionally not well-defined and/or hardly soluble.[2,3] Therefore, improved coordination polymers and, for their preparation, novel synthetic strategies have to be developed to make available soluble, well-defined products. In order to achieve solubility, which is the basic requirement for polymer characterization and processability, one possibility may consist in the preparation of unbranched coordination polymers having nonrodlike main chains. Through the synthesis of the novel coordination polymer **1** via the synthetic route shown in eq 1, we can now prove that this strategy indeed opens up an elegant pathway to constitutionally well-defined ruthenium(II) coordination polymers which are readily soluble not only in a variety of organic solvents but also in pure water.



1 (1)

The strategy used here is based upon the conversion of a bis-bidentate chelating ligand such as **2** and a "metal monomer" like **3**, which already contains one mono-bidentate chelating ligand. On condition that no exchange of ligands occurs between the individual ruthenium complexes, unbranched coordination polymers such as **1** should be available in which the bis-bidentate chelating ligands and the octahedrally coordinated ruthenium(II) centers form the polymer main chain, whereas the 2,2'-bipyridine (bpy) ligands occupy the two remaining coordination positions of each octahedron. By this strategy, readily soluble macromolecules of statistically coiled main-chain conformation may be formed, in contrast to the rodlike ruthenium coordination polymers described recently.[3]

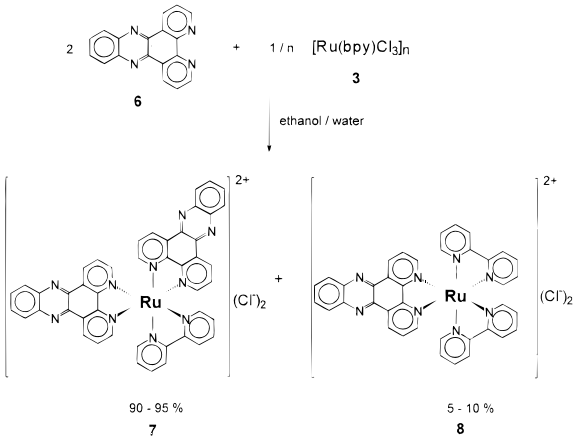
The synthesis of the still unknown[4] tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]phenazine (tppz) (**2**), the required monomer for the synthesis of **1**, was performed in analogy to the well-established syntheses of tetrakis-(α-pyridyl)pyrazine derivatives by treating 1,10-phenanthroline-5,6-quinone (**4**)[5] in a melt of ammonium acetate at 180 °C (eq 2A).[6] **2** can easily be purified by a single



(2A)

recrystallization from chloroform and was obtained in 20% yield and high purity (>98%, ^{1}H NMR). The structure of **2** was proven by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and the preparation of the dinuclear complex **5** (eq 2A). Through the synthesis of this model complex, which occurs nearly quantitatively and without any detectable side reaction by heating **2** in the presence of 2 equiv of $[Ru(bpy)_2Cl_2]$, it could also be shown that **2** is a suitable monomer for the synthesis of polymer **1**: representative ^{1}H (Figure 1A) and ^{13}C NMR spectra (Figure 2A) of the obtained raw product show solely the absorptions of the dinuclear complex **5**:[7] neither unchanged starting materials nor complexes in which the phenazine nitrogen atoms of **2** participate could be detected. While the first finding confirms the formation of high-molecular-weight polymers **1**, the latter excludes cross-linking during the planned polymer synthesis. Ligand exchange was not observed, either.

$[Ru(bpy)Cl_3]_n$ (**3**), on the other hand, was chosen here as the metal monomer counterpart for the synthesis of polymer **1**. It was prepared from equimolar amounts of 2,2'-bipyridine and $RuCl_3$.[8] Its ability to act as a monomer was checked first in model conversions with dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dpp) (**6**) (eq 2B). It



(2B)

could be shown that the obtained products were composed of about 90−95% of the expected complex **7**. However, 5−10% of $[Ru(dpp)(bpy)_2](PF_6)_2$ (**8**) was found in all products as well. In some accompanying experiments, it could be shown that product **8** is neither formed by a ligand exchange process nor from free $[Ru(bpy)_2Cl_2]$ which might already be present in compound **3**. On the contrary, **8** is formed from the metal monomer $[Ru(bpy)Cl_3]_n$ (**3**) itself, which exhibits a polymeric constitution.[9] Obviously, defect structures or

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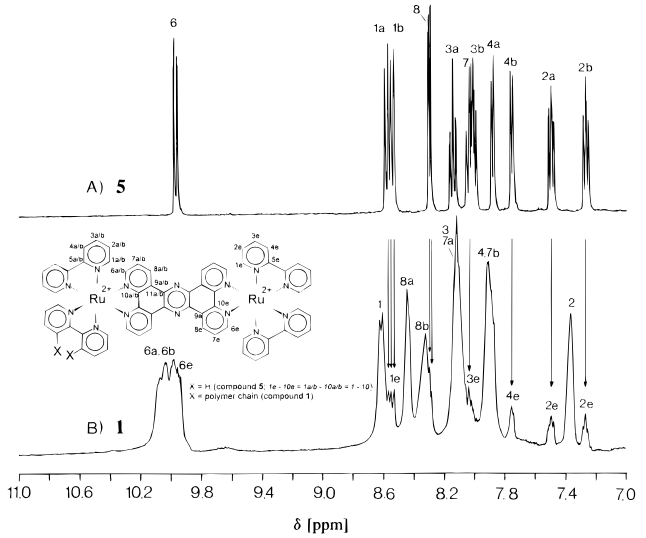

Figure 1. ^{1}H NMR spectra of model complex **5** (A) and polymer **1** (B), recorded at 400 MHz in CD_3CN at room temperature; for indices a, b, and e, see text.

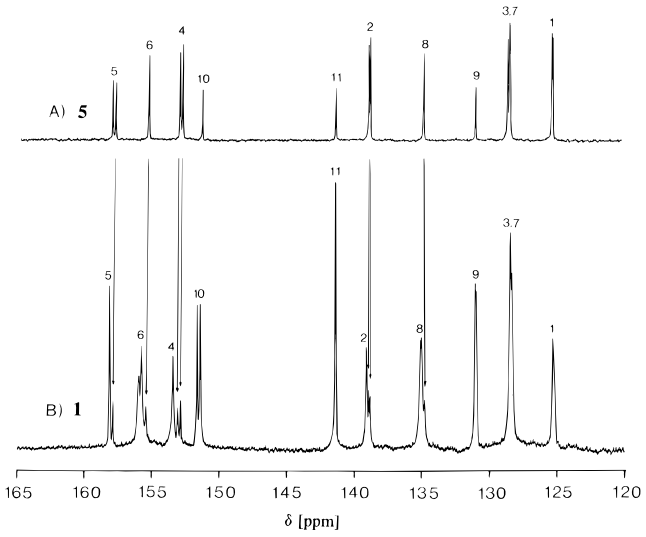

Figure 2. Aromatic region of the ^{13}C NMR spectra of model complex **5** (A) and polymer **1** (B), recorded at 100 MHz in CD_3-CN at room temperature.

end groups of this "monomer" contain some ruthenium centers which are already coordinated by two 2,2'-bipyridine ligands. Consequently, it is impossible to avoid this contamination which leads to the formation of complex **8**, and it was also impossible to suppress it by varying the methods for preparing **3**. On the other hand, no further side reactions were found in these model investigations, and the ruthenium complexes which bear two bpy ligands instead of one can only act as end groups in a polymer synthesis according to eq 1. Thus, polymers **1** were synthesized using tppz (**2**) and metal monomer **3** (eq 1): by refluxing equimolar amounts of **2** and **3** in a mixture of ethanol and water, a dark red-brown, homogeneous solution was obtained. From this solution, polymer **1** was precipitated quantitatively by adding an aqueous solution of NH_4PF_6. Alternatively, polymer **1** could be precipitated as the chloride by adding an excess of acetone directly into the reaction mixture. The obtained black solid readily and completely redissolved in water or ethanol (as the chloride) or in acetonitrile (as the hexafluorophosphate) and could thus be analyzed with high resolution NMR spectroscopy. Figure 1B shows the ^{1}H NMR spectrum of the obtained polymer **1**.

By comparing this spectrum with that of model complex **5** (Figure 1A), all the observed absorptions can

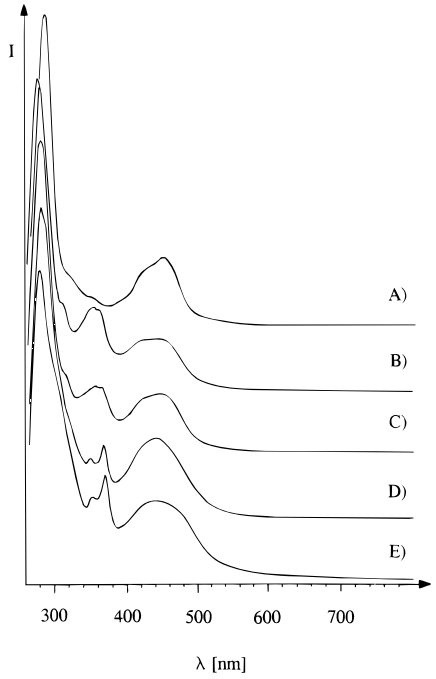

Figure 3. UV−vis spectra of complexes $[Ru(bpy)_3](PF_6)_2$ (A), **7** (B), **8** (C), **5** (D), and polymer **1** (E), recorded in acetonitrile at room temperature.

be assigned either to the inner-chain repeat units of polymer **1** or to its well-defined end groups, all of which bear two bpy ligands (index e, Figure 1B). Fortunately, some of the protons of these terminal bpy ligands absorb well-separated from the corresponding protons of the inner-chain repeat units. This feature opens up a possibility of determining the degree of polymerization of **1** with the aid of NMR end-group analysis. Comparison of the intensities of the absorptions of the H2 protons of the inner-chain repeat units ($\delta = 7.38$) with those of the absorptions of the terminal protons H2e ($\delta = 7.27$ and 7.49 respectively) results in number-average degrees of polymerization P_n of 11−15 (M_n = 11 000−15 000), depending on the quality of monomer **3** used. This evaluation is considered to be reliable since, on the one hand, the polymer was precipitated quantitatively from the reaction mixture and then redissolved completely. On the other hand, there are no additional absorptions detectable in the NMR spectra besides those which are assigned unambiguously to polymer **1**. Consequently, no additional end groups need be considered in this evaluation. Also, the ^{13}C NMR spectra support the structure of polymer **1**, since only the expected absorptions of the chain repeating units and those of the end groups were found here as well (Figure 2B).

The coordination of the ruthenium centers in polymer **1** with two different kinds of chelating ligands lowers the symmetry of the octahedral complexes.[10] As a result, two distinct resonance frequencies were found for each tppz proton and each tppz carbon atom of the inner-chain tppz ligands (indices a and b, Figure 1B).[11] For the end groups, on the other hand, all absorptions of the bpy ligands are doubled in the ^{1}H as well as in the ^{13}C NMR spectra (indices a and b, Figure 1A). This feature represents an additional proof of structure for the constitutionally homogeneous polymer **1**.

Figure 3 shows the UV−vis absorption spectra of $[Ru(bpy)_3](PF_6)_2$ (A), complexes **7** (B) and **8** (C), the dinuclear model complex **5** (D), and polymer **1** (E). At wavelengths below 400 nm, the absorptions of the ligand-centered (LC) $\pi^* \leftarrow \pi$ transitions were observed as intense signals: absorptions at 280−290 nm were

assigned to the 2,2'-bipyridine ligands and absorptions at 350−370 nm to the dipyridophenazine (B and C) and tetrapyridophenazine (D and E) ligands, respectively. Above 400 nm, absorptions were observed which correspond to metal−ligand charge-transfer (MLCT) transitions. As could be shown earlier for other ruthenium complexes, the wavelengths of all these absorptions are mainly determined by the ligands which are grouped around an individual metal complex.[1,2] The same applies to the results of the electrochemical investigations (acetonitrile, $N(C_4H_9)_4ClO_4$, room temperature, *vs* SCE). While $[Ru(bpy)_3](PF_6)_2$ exhibits a half-wave potential of $E_{1/2}^{ox} = 1.29$ V for the metal-localized first oxidation, the corresponding oxidation process was found to occur at $E_{1/2}^{ox} = 1.38$ V in the dinuclear complex **5**. Finally, polymer **1** shows a half-wave potential for this oxidation process of $E_{1/2}^{ox} = 1.43$ V. Thus, absorption spectra as well as electrochemical data show that the ruthenium centers of the multinuclear complexes (**5** and **1**) can be considered to be nearly independent of one another: π-electron delocalization and metal−metal interactions seem to be rather weak. This finding is in agreement with observations made with many other coordination compounds of similar constitution.

In conclusion, the synthetic strategy presented here proved to be appropriate to the synthesis of soluble, constitutionally well-defined ruthenium(II) coordination polymers **1** of well-known degree of polymerization. The excellent solubility of **1** in water and ethanol (Cl^- as counterion) or acetonitrile (PF_6^- as counterion) seems to be a result of, most probably, the statistically coiled conformation of the polymer main chain, which is associated with the chirality of the $[Ru(bpy)_3]$ motif and which prevents an energetically advantageous organization of chain segments in the solid state.[11] Thus, the introduction of, for example, chemically and thermally labile, solubilizing side chains is not required.[12] A further increase in the degree of polymerization of **1** by replacing monomer **3**, the broadening of the concept to the synthesis of other coordination polymers, and a profound analysis of the chain topology and the properties of coordination polymer **1** are presently being carried out and will form the subject of a subsequent paper.

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Supporting Information Available: Description of the synthetic procedures and lists of the NMR chemical shifts of compounds **1**, **2**, **5**, and **7** (2 pages). Ordering information is given on any current masthead page.

References and Notes

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(7) Three different enantiomeric pairs are possible for compound **5** because of the chirality of the $[Ru(bpy)_3]$ motif: the ΔΔ, ΔΛ, and ΛΛ configurations. Despite the fact that NMR spectroscopy seems to point toward the existence of only one of these isomers in the product, nevertheless, the formation of a racemic mixture containing all three enantiomeric pairs is more probable because (a) the spatial distance between the two ruthenium centers is very large (>10 Å) and thus presumably too large to cause significant differences between the NMR chemical shifts of the respective stereoisomers, (b) all crystallization conditions tested so far only led to microcrystalline powders of compound **5**, and (c) neither a chiral building block is used in the synthesis [see, for example: (a) Rutherford, T. J.; Quagliotto, M. G.; Keene, F. R. *Inorg. Chem.* **1995**, *34*, 3857. (b) Hua, X.; von Zelewsky, A. *Inorg. Chem.* **1991**, *30*, 3796] nor sterical demands force the formation of only one configuration of **5** [see, for example: Hayoz, P.; von Zelewsky, A.; Stoeckli-Evans, H. *J. Am. Chem. Soc.* **1993**, *115*, 5111].

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(11) As already discussed above for compound **5** (see ref 7), NMR spectroscopy is not appropriate, obviously, to distinguish between different sequences of enantiomeric centers along the main chain of polymer **1**. Nevertheless, here as well we assume the formation of irregular sequences of both enantiomers within the polymer chains during the polymerization process, causing the postulated statistically coiled chain topology. In addition to the arguments given in ref 7, wide-angle X-ray scattering experiments show polymer **1** to be nearly amorphous in the solid state. Furthermore, trial small-angle X-ray scattering measurements point toward a rather small radius of gyration of polymer **1**. These two observations additionally support the coiled shape of **1**; a detailed study of the chain topology of polymer **1** will form the subject of a subsequent paper.

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