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The Application of High-performance Liquid Chromatography in the Investigation of Reactions Involving Ruthenium(II)bis(bipyridyl) Compounds

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The chemical properties of ruthenium polypyridyl compounds have been studied in great detail in the last few years [1–10]. Both synthetic and photochemical studies have been carried out mostly using spectroscopic or electrochemical techniques. These detection methods are however not sensitive to the presence of small amounts of impurities. Problems are encountered also in the synthesis and the photochemical studies of compounds of the type $[Ru(bipy)_2XY]^{n+}$ (bipy = 1,2′-bipyridyl) where the simultaneous formation of more than one reaction product can hinder the spectroscopic study of the reactions, and in the study of coordination isomers where the spectroscopic properties of the isomers are similar.

A technique ideally suited to study such potentially complicated systems in high-performance liquid chromatography (HPLC). Although this technique has been used extensively in organic and analytical chemistry, its application to inorganic chemistry has been limited [11–13] and indeed only few applications in ruthenium chemistry have been reported, only dealing with tris(bipyridyl) type compounds [14–18]. To our knowledge there are no reports of the use of HPLC in the study of ruthenium bis(bipy) compounds of the type $[Ru(bipy)_2XY]^{n+}$. In order to be able to follow photochemical reactions and also to simplify the control of the synthesis of such compounds we have developed an HPLC method based on a cation exchange column. In this work two applications of this HPLC system are reported. Firstly the photochemical behaviour of the compound $[Ru(bipy)_2(viz)_2](PF_6)_2$ in acetonitrile/0.01 M LiCl is investigated (viz = *N*-vinylimidazole). Using this HPLC method we have also established the presence of two coordination isomers of the compound $[Ru(bipy)_2(HL_1)](PF_6)_2$ (HL_1 is 3-(pyridin-2-yl)-1*H*-1,2,4-triazole).

Experimental

Materials

The ruthenium bis(bipyridyl) compounds were prepared by literature methods [19–21]. All solvents used for photochemistry as well as chromatography were of HPLC grade. All other chemicals used were Analar grade and used without further purification.

Equipment

High-performance liquid chromatography was carried out using a Waters 990 Photodiode array HPLC system in conjunction with a NEC APC III computer, a Waters pump model 6000 A, a 20 μl injector loop and a μ Partisil SCX radial PAK cartridge. The detection wavelength used was 280 nm. The chromatrography was carried out using acetonitrile/water (80/20) containing 0.08 M $LiClO_4$ as a mobile phase. Flow rate used varied from 1.5 to 4.0 ml/min depending on the nature of the compounds investigated. Photochemical experiments were carried out using a high pressure mercury lamp, and a glass filter to cut out ultraviolet radiation.

Results and Discussion

In the search for a suitable HPLC method a number of stationary phases were investigated. The first studies were carried out using C_{18}, CN and ODS columns. It was however observed that with these columns it was possible to separate species with a different charge, but separation between species with the same overall charge was less efficient. To be useful the method should however be able to separate different bis(bipy) compounds having the same overall charge but different ligands. Such a separation was obtained using a method, based on an SCX cation exchange column, similar to the one reported by O'Laughlin for the separation of tris(bipy) compounds of different transition metals [16]. For compounds of the type $[Ru(bipy)_2XY]^{n+}$, the singly charged compounds, such as $[Ru(bipy)_2(viz)Cl]^+$, elute in general before the compounds with a 2+ charge (note however the rather short retention time for the bis(viz) compound). Also the peaks of the singly charged species are sharper than those obtained for the doubly charged complexes. For the latter a certain amount of tailing is observed. This tailing can be reduced by increasing the flow rate and/or the lithium salt concentration in the mobile phase. In experiments where both types of compounds were present in the reaction mixture, the best results were obtained when the flow rate was increased with time. So for example for the first 4 min a flow rate of 2.0 ml/min is maintained, then the flow rate is changed to 4.0 ml/min over a 1-min interval. In this manner shorter retention times and sharper peaks were obtained for the doubly charged species while the separation of the singly charged compounds remained good.

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A series of chromatograms taken during the photolysis of $[Ru(bipy)_2(viz)_2]^{2+}$ (retention time 3.14 min, absorption maxima 480 and 330 nm, peak 1 in Fig. 1) in CH_3CN/0.01 M LiCl is shown in Fig. 1. When the photolysis of the bis(imidazole) compound in acetonitrile/0.01 M LiCl is followed using UV–Vis spectroscopy, no isosbestic points are observed and a complicated reaction pattern is therefore expected. This is confirmed by the HPLC results, which show the formation of at least 5 different species during the photolysis of $[Ru(bipy)_2(viz)_2]^{2+}$ (see peaks 2–6 in Fig. 1). Based on the photodiode array analysis of the chromatograms we can conclude that the species $[Ru(bipy)_2(viz)Cl]^+$ (retention time 2.87 min, absorption maxima 515 and 360 nm, peak 2), $[Ru(bipy)_2(viz)(CH_3CN)]^{2+}$ (retention time 3.88 min, absorption maximum 455 nm, peak 3) and $[Ru(bipy)_2(CH_3CN)Cl]^+$ (retention time 3.60 min, absorption maxima 475 and 340 nm, peak 4) are formed. The formation of $Ru(bipy)_2Cl_2$ was not observed. The nature of the products was confirmed by comparison of the absorption spectra obtained with those of authentic samples [22] and by additional photochemical experiments of $[Ru(bipy)_2(viz)_2]^{2+}$ and $[Ru(bipy)_2(viz)Cl](PF_6)$ in acetonitrile. The chromatograms in Fig. 1 suggest that during the first part of the experiment $[Ru(bipy)_2(viz)Cl]^+$ and $[Ru(bipy)_2(viz)(CH_3CN)]^{2+}$ are formed simultaneously as in reactions 1 and 2:

$$[Ru(bipy)_2(viz)_2]^{2+} \xrightarrow[h\nu]{CH_3CN} [Ru(bipy)_2(viz)(CH_3CN)]^{2+} + viz \qquad (1)$$

$$[Ru(bipy)_2(viz)_2]^{2+} \xrightarrow[h\nu]{Cl^-} [Ru(bipy)_2(viz)Cl]^{+} + viz \qquad (2)$$

Upon further photolysis $[Ru(bipy)_2(CH_3CN)Cl]^+$ (retention time 3.60 min, absorption maxima 475 and 340 nm) is formed as the main product. Figure 1 shows that two more products are obtained with retention times of 4.29 and 5.14 min (peaks 5 and 6). The nature of these products, that have their lowest absorption maximum at respectively 495 and 445 nm, is at present not known. So with this technique we are able to detect intermediates and at the same time quantify their relative concentrations in reactions where a spectroscopic investigation would be very difficult. It has to be remembered, however, that the species detected are those that exist on the column and are dependent on the mobile phase. Preliminary results obtained for the HPLC analysis of the photolysis of $[Ru(bipy)_2(viz)Cl]^+$ in methanol

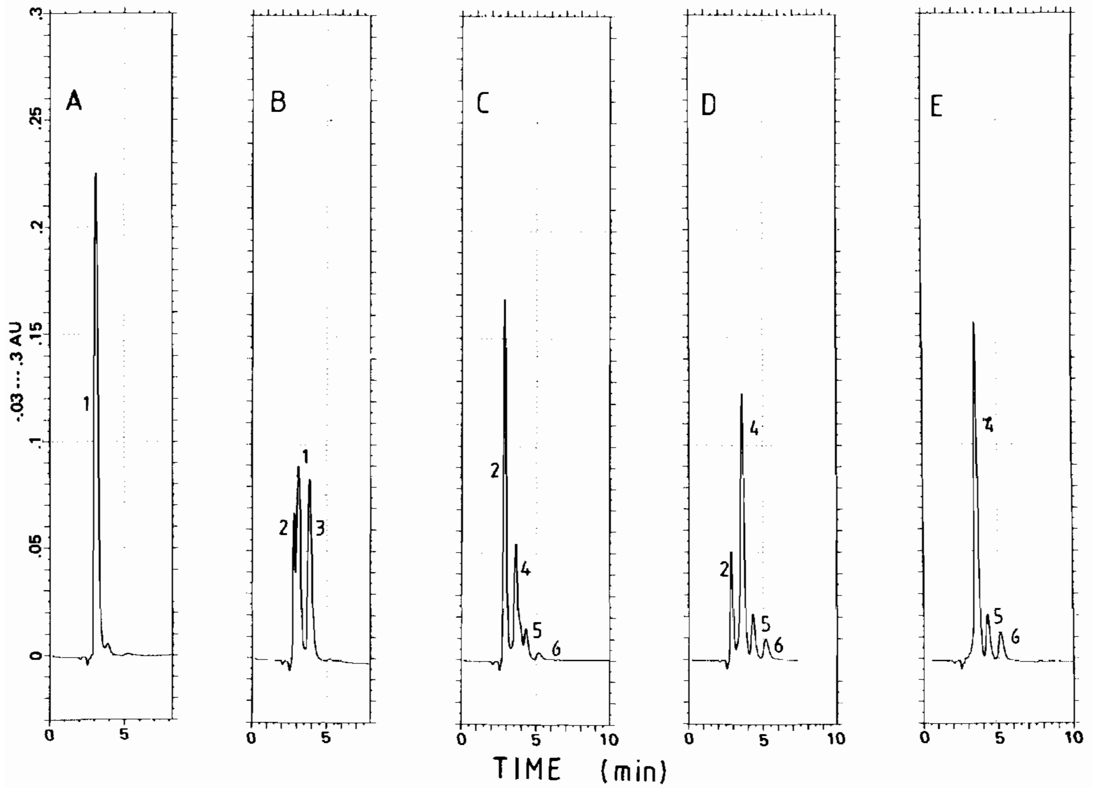

Fig. 1. Chromatograms taken during the photolysis of $[Ru(bipy)_2(viz)_2](PF_6)_2$ in CH_3CN/0.1 M LiCl. Irradiation times: A, 0 s; B, 20 s; C, 130 s; D, 350 s; E, 1200 s. Flow rate 1.5 ml/min.

suggest that the photoproduct $[Ru(bipy)_2(viz)H_2O]^{2+}$ is stable but that $[Ru(bipy)_2(H_2O)Cl]^+$ rapidly exchanges water for acetonitrile when injected onto the column. It has to be take into account therefore that when photochemical experiments are carried out in solvents other than CH_3CN, ligand exchange processes may occur on the column.

In the second application of the HPLC method the possible presence of coordination isomers for ruthenium bis(bipy) compounds of 3-(pyridin-2-yl)-1*H*-1,2,4-triazole (HL_1) and 5-methyl-3-(pyridin-2-yl)-1*H*-1,2,4-triazole (HL_2) (see Fig. 2) was investigated. For these ligands there are two possible coordination modes, as coordination can take place through N^1 and $N^{2'}$ or through N^1 and $N^{4'}$. Spectroscopic evidence suggests the first type of bond for HL_2, while for HL_1 no unambiguous assignment could be made [21]. The HPLC traces obtained for $[Ru(bipy)_2(HL_1)](PF_6)_2$ (1) and $[Ru(bipy)_2(HL_2)](PF_6)_2$ (2) are given in Fig. 3. It is worthwhile pointing out that the absorption spectra obtained (absorption maximum for both compounds about 470 nm), using the photodiode array detector, suggest that in both complexes the pyridyl triazole ligands deprotonate while on the column.

Figure 3A shows the presence of two species, having the same absorption spectrum, for compound 1 in a 1:1 ratio. This ratio suggests that there is no preference for coordination at $N^{2'}$ or $N^{4'}$. No indication for the presence of these coordination isomers was obtained from spectroscopic techniques. For compound 2 only one major peak is obtained (see Fig. 3B). This is as expected as for steric reasons coordination at $N^{4'}$ is not favoured. Coordination through $N^{2'}$ is further confirmed by the NMR spectrum of the compound [21].

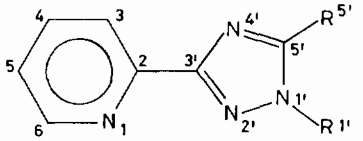

Fig. 2. $R^{1'} = R^{5'} = H, HL_1$. $R^{1'} = H, R^{5'} = CH_3, HL_2$.

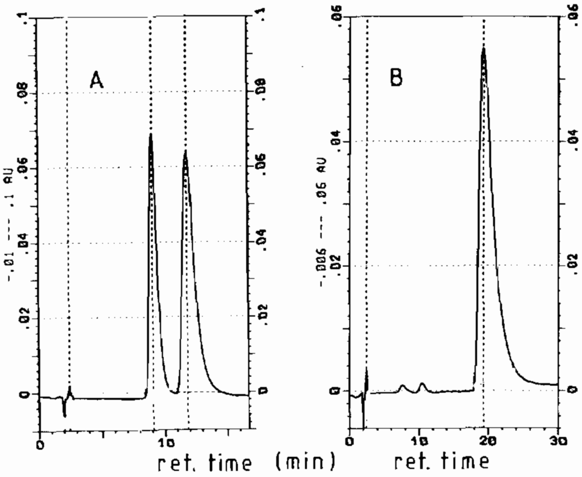

Fig. 3. Chromtograms of the compounds $[Ru(bipy)_2(HL_1)](PF_6)_2$ (A) and $[Ru(bipy)_2(HL_2)](PF_6)_2$ (B). Flow rate 2.0 ml/min.

Conclusions

The results reported here show that the HPLC method described, based on a cation exchange column, can be very useful for the study of the photochemical properties of ruthenium compounds. Following these reactions with HPLC clearly has an advantage over the use of the more traditional spectroscopic methods. With only minor modifications we have also used this method successfully to optimise reaction conditions for a range of ruthenium compounds. When HPLC is used in combination with a photodiode array detector, the species formed can be identified very easily. Also the detection of coordination isomers is greatly facilitated by this method. One has however to take into account the possibility of changes of the ligand compositions of the species injected on the column because of their interaction with the mobile phase. Our results show that ligand exchange processes do occur in some cases and also that deprotonation of ligands can take place. This in itself however yields useful information about the stability of the compounds concerned.

Acknowledgements

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