Diastereoisomeric Forms of Ligand-bridged Dimetallic Diruthenium(II) and Ruthenium(II)–Osmium(II) Species containing Bidentate Polypyridyl Ligands

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A new general synthetic route is reported for dinuclear species of the type $[(L_t)_2RuL_bRu(L_t')_2]^{4+}$ or $[(L_t)_2RuL_bOs(L_t')_2]^{4+}$ (L_t, L_t' = bidentate polypyridyl ligands, $L_t \neq L_t'$; L_b = bridging ligand), together with the chromatographic separation and characterization of the diastereoisomeric pairs of the dimers.

There is considerable interest in polymetallic 'supramolecular' assemblies containing chromophoric centres, for which polypyridyl complexes of ruthenium, osmium and rhenium have been primary targets because of the capacity for controlled variation of their ground and excited state properties, redox potentials, and electron and energy transfer characteristics.[1]

An important issue which has received little attention in these studies is that of stereoisomerism within the molecular assemblies. Even in the simplest case of a symmetrical dinuclear complex with a symmetrical bridge, *viz.* $[(bipy)_2Ru(bipym)Ru(bipy)_2]^{4+}$ (bipy = 2,2'-bipyridine; bipym = 2,2'-bipyrimidine), there will be *meso* (ΔΛ) and *rac* (ΔΔ/ΛΛ) diastereoisomeric forms. The presence of different ligands on the two centres, an unsymmetrical bridge, or higher nuclearity in the assembly rapidly increase the isomeric complexity.

We reported recently the development of a general synthetic methodology for mononuclear tris(heteroleptic) ruthenium complexes of bidentate polypyridyl ligands.[2] The present communication reports the extension of this scheme to a general synthetic method for dinuclear species of the type $[(L_t)RuL_bRu(L_t')_2]^{4+}$ (L_t, L_t' = bidentate polypyridyl ligands where $L_t \neq L_t'$; L_b = bridging ligand), together with the chromatographic separation and NMR characterization of the diastereoisomeric pairs.

A variety of monomeric precursors of the general types $[Ru(L_t)_2(CO)_2]^{2+}$ and $[Ru(L_t')_2L_b]^{2+}$ may be synthesized as outlined previously.[2] Heating $[Ru(L_t)_2(CO)_2]^{2+}$ with a three-fold excess of trimethylamine *N*-oxide in acetone or methoxyethanol (*ca.* 50 cm^3 per 20 mg of the dicarbonyl species) at reflux for 3 h in the presence of a 20% excess of $[Ru(L_t')_2L_b]^{2+}$ realizes the corresponding dimer $[(L_t)_2RuL_bRu(L_t')_2]^{4+}$. Following ion-exchange chromatography (SP-Sephadex C-25 cation exchanger, 0.5 mol dm^{-3} NaCl eluent), products were isolated as the PF_6^- salts and recrystallized (acetone–diethyl ether): overall yields of the products were approximately 35%. For dimeric species containing Os centres, *i.e.* $[(L_t)_2RuL_bOs(L_t')_2]^{4+}$, two alternative synthetic schemes were utilized, either $[Ru(L_t)_2L_b]^{2+}$ was treated with $[Os(L_t')_2Cl_2]$ [3] (by refluxing equimolar amounts in aqueous methanol solution, *ca.* 50 cm^3 per 20 mg of the ruthenium species), or $[Os(L_t')_2L_b]^{2+}$ {prepared by refluxing $[Os(L_t')_2Cl_2]$ with a four-fold excess of L_b in aqueous methanol} was treated with $[Ru(L_t)_2(CO)_2]^{2+}$ under the same conditions as for the analogous decarbonylation synthesis of the diruthenium species. In the present work, we have synthesized and characterized the dimeric complexes $[(bipy)_2Ru(bipym)Ru(phen)_2]^{4+}$, $[(bipy)_2Ru(bpypz)Ru(phen)_2]^{4+}$, $[(phen)_2Ru(bipym)Ru(tmbipy)_2]^{4+}$, $[(tmbipy)_2Ru(bipym)Ru(bipy)_2]^{4+}$, $[(bipy)_2Os(bipym)Ru(phen)_2]^{4+}$ and $[(bipy)_2Os(bipym)Ru(tmbipy)_2]^{4+}$ [phen = 1,10-phenanthroline; tmbipy = 4,4',5,5'-tetramethyl-2,2'-bipyridine; bpypz = 2,3-bis(2-pyridyl)pyrazine].

For all these dimeric species, there are two diastereoisomeric forms, each comprising an enantiomeric pair. The two stereoisomers may be represented schematically as shown in Fig. 1. A significant difference in the relative ligand orientations may be discerned in the two diastereoisomeric pairs: the polypyridyl ligands 'above' and 'below' the plane of the bridging ligand (Fig. 1) are approximately parallel in the ΔΔ/ΛΛ form, whereas they are perpendicular in the ΛΔ/ΔΛ stereoisomer.

In earlier work, Hua and von Zelewsky[4] have reported the stereoselective synthesis of similar dinuclear species using chiral monomers as precursors: while this represents a definitive solution to the problem of the stereoisomerism in such dimers, it requires that the precursors must be resolved on an individual basis. We have found that the two diastereoisomeric pairs may be separated by ion-exchange chromatography (SP-Sephadex C25 cation exchanger, 0.25 mol dm^{-3} sodium toluene-*p*-sulfonate as eluent), presumably based on the differential association of the aromatic anion with the alternative relative orientations of the heterocyclic ligands in the two forms. The method appears quite general and we have separated the diastereoisomers for the six dimeric species listed above. Variation of the bridging ligand L_b (symmetric bipym or unsymmetric bpypz) and metals (homonuclear Ru–Ru or heteronuclear Ru–Os) has little effect on the separation, although the efficacy of the procedure (and therefore the length of column required) is substantially influenced by the identity

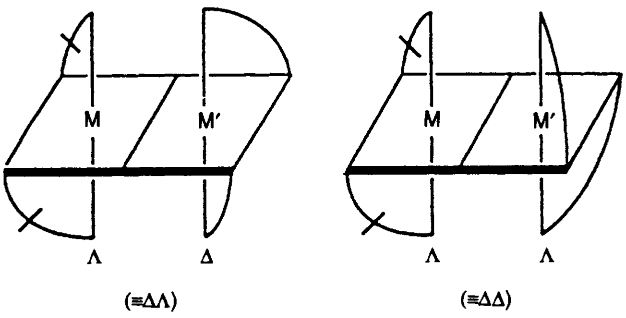


Fig. 1 Schematic view of the orientation of the non-bridging bidentate ligands in the two diastereoisomeric pairs of the general dinuclear species $[(L_t)_2ML_bM'(L_t')_2]^{4+}$ (the L_t and L_t' chelate rings are differentiated by hatch marks)

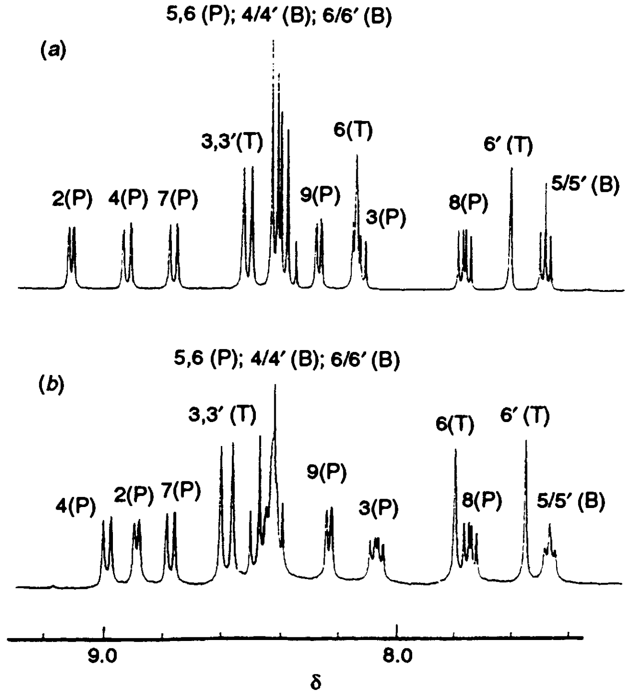
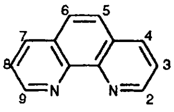
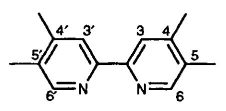


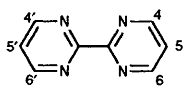
Fig. 2 Proton NMR spectra (300 MHz, 25 °C, [$^2H_6$]acetone) of (*a*) ΛΔ (≡ΔΛ) and (*b*) ΔΔ (≡ΛΛ)-[$(phen)_2Ru(bipym)Ru(tmbipy)_2]^{4+}$; protons of phen, bipym and tmbipy are indicated by P, B and T respectively



phen



tmbipy



bipym

of the terminal ligands. For the systems reported, the two diastereoisomers were observed to form in comparable amounts; there was no indication of substantial stereospecificity induced by differential steric interactions in the two forms.

Proton NMR studies have been undertaken for the separated stereoisomers, and are reported below for the representative example [$(phen)_2Ru(bipym)Ru(tmbipy)_2]^{4+}$: the 300 MHz ^1H NMR spectra of the separated diastereoisomeric pairs of this dinuclear species are shown in Fig. 2. Full assignment of the observed resonances for both diastereoisomers has been obtained by decoupling experiments, and connectivity confirmed by heteronuclear multiple-bond correlation (HMBC) and heteronuclear multiple-quantum coherence (HMQC) two-dimensional NMR techniques. In both stereoisomeric forms, the two non-bridging ligands on each metal centre are related by a two-fold axis of symmetry, although the two ends of each individual ligand are in non-equivalent environments. Based on the conventional numbering sequences for the three ligands involved (see above), and adopting the convention that the numbering sequence in the phen ligand starts in the ring *cis* to both the ligating atoms of the bridge (and that the non-primed numbers in the tmbipy ligand also refer to the pyridine ring in that ligand *cis* to both ligating atoms of the bridge), the assignments are as indicated in Fig. 2. The stereochemistry of the two diastereoisomeric pairs has also been deduced from the NMR studies.

The most significant differences between the two spectra are the shifts in the resonances for the protons attached to the 2 position of the phen ligands, and to the 6 position of tmbipy (*i.e.* the protons in those ligands adjacent to a pyridyl ring co-ordinated to the other metal centre). In both cases, these protons in ΔΔ/ΛΛ-[$(phen)_2Ru(bipym)Ru(tmbipy)_2]^{4+}$ are shielded (relative to the ΛΔ/ΔΛ form) by the ring current associated with that adjacent pyridyl ring.

We are currently undertaking photophysical studies on the separated diastereoisomers to assess the effect of the stereochemistry on the electronic communication between the two metal centres. Those studies, and full details of the present synthesis and characterization of the diastereoisomeric dinuclear species, will be reported subsequently.

Acknowledgements

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