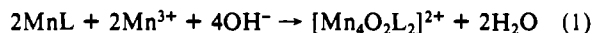


**Figure 1.** (a) View of MnL in MnL·MeOH. Selected bond distances (Å) and angles (deg) are as follows: Mn–O(1), 2.116 (8); Mn–O(2), 1.910 (9); Mn–O(3), 1.906 (8); Mn–N(2), 2.111 (10); Mn–N(3), 2.062 (10); Mn–N(4), 2.290 (10); O(1)–Mn–O(2), 88.1 (3); O(1)–Mn–O(3), 96.5 (3); O(1)–Mn–N(4), 172.4 (3); N(2)–Mn–N(3), 98.0 (4); N(2)–Mn–N(4), 103.0 (3). (b) View of the cation of  $[\text{Mn}_4\text{O}_2\text{L}_2](\text{PF}_6)_2 \cdot 4\text{MeCN}$  (four carbon atoms of each benzene ring excluded for clarity). Symmetry-equivalent atoms are not named or named with "a" added (e.g. Mn1, Mn1a). Selected bond distances (Å) and angles (deg) are as follows: Mn(1)–O(1), 1.916 (5); Mn(1)–O(2), 2.127 (6); Mn(1)–O(4), 1.909 (5); Mn(1)–N(1), 2.407 (8); Mn(1)–N(2), 1.997 (6); Mn(1)–N(3), 2.030 (7); Mn(2)–O(1), 2.301 (5); Mn(2)–O(3), 1.892 (5); Mn(2)–O(4), 1.916 (5); Mn(2)–N(4), 2.019 (7); Mn(2)–O(2A), 2.222 (5); Mn(2)–O(4A), 1.950 (5); Mn(1)–Mn(2), 3.000 (3); Mn(1)–Mn(2A), 3.042 (3); Mn(2)–Mn(2A), 2.906 (3); Mn(1)–O(4)–Mn(2), 103.3 (2); Mn(1)–O(4)–Mn(2A), 104.1 (2); O(4)–Mn(2)–O(4A), 82.5 (2); O(4)–Mn(1)–N(2), 170.7 (2); O(2)–Mn(1)–N(1), 162.0 (2); O(1)–Mn(1)–N(3), 172.6 (3); O(3)–Mn(2)–O(4), 166.7 (2); O(1)–Mn(2)–O(2A), 177.4 (2); O(3)–Mn(2)–N(4), 91.6 (2).

nearly quantitative yields.<sup>12</sup> The stoichiometry of the synthetic reaction is as follows:



The remarkably facile and efficient aggregation of **2** from **1** is a good indicator of how a flexible polypeptide backbone having side-chain donors (amine, carboxyl, phenol) could possibly organize

(12) MnL·MeOH was stirred with  $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$  in warm acetonitrile, and methanolic KOH was added ( $\text{MnL}:\text{Mn}^{3+}:\text{OH}^- = 1:1:2$ ) followed by solid  $\text{NH}_4\text{PF}_6$ . Upon concentration and cooling (5 °C), crystals of  $[\text{Mn}_4\text{O}_2\text{L}_2](\text{PF}_6)_2 \cdot 4\text{MeCN}$  deposited. When dried in air, the crystals rapidly lost MeCN, leaving  $[\text{Mn}_4\text{O}_2\text{L}_2](\text{PF}_6)_2$  as a powder (yield 93%). Anal. Calcd for  $[\text{Mn}_4\text{O}_2\text{L}_2](\text{PF}_6)_2$ : C, 44.66; H, 3.72; N, 7.71; Mn, 15.13. Found: C, 44.72; H, 3.70; N, 7.66; Mn, 15.10.

oxidic  $\text{Mn}_4$  ensembles<sup>6,7</sup> in PSII.

The structure<sup>13</sup> of  $[\text{Mn}_4\text{O}_2\text{L}_2]^{2+}$  is shown in Figure 1b. The cation is centrosymmetric. The coordination spheres are of two types,  $\text{MnN}_3\text{O}_3$  and  $\text{MnNO}_5$ —both axially elongated. The  $\mu_3$ -O atoms are displaced from the  $\text{Mn}_4$  plane by 0.858 Å in opposite directions. The shortest Mn···Mn contact is 2.906 (3) Å. The  $[\text{Mn}_4(\mu_3\text{-O})_2]^{2+}$  core, held by peripheral carboxylate bridging, is known in butterfly configuration<sup>1</sup> for  $z = 8$  and in centrosymmetric configuration<sup>1,2</sup> for  $z = 6$ . By contrast the core in **2** is phenolate bridged and is centrosymmetric with  $z = 8$ .

Complex **3** is antiferromagnetic; the magnetic moment decreases with decreasing temperature from 7.45  $\mu_B$  at 297 K to 5.00  $\mu_B$  at 10 K. No EPR signals are observed. In MeCN four quasi-reversible one-electron cyclic responses are seen corresponding to the oxidation-state interval  $\text{Mn}^{\text{IV}}_2\text{Mn}^{\text{III}}_2$  to  $\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2$  ( $E_{1/2}$  at Pt electrode, 298 K: 0.98, 0.82, 0.03, and –0.20 V versus SCE). Only two of the couples have  $E_{1/2}$  values above the water oxidation threshold. Complex **1** shows  $\text{Mn}^{\text{IV}}\text{--Mn}^{\text{III}}$  and  $\text{Mn}^{\text{III}}\text{--Mn}^{\text{II}}$  couples ( $E_{1/2}$ , 0.54 and –0.29 V).

In summary, flexible polydentate ligation is an excellent instrument for assembling the  $\text{Mn}_4$  moiety—a finding of considerable interest in the context of PSII. The centrosymmetric configuration is new for the  $\text{Mn}_4\text{O}_2^{8+}$  core, and so is phenolate bridging.

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**Supplementary Material Available:** For **1** and **2**, text giving details of structure determination and tables listing atomic coordinates (Tables I and VI), complete bond distances (Tables II and VII) and angles (Tables III and VIII), anisotropic thermal parameters (Tables IV and IX), and hydrogen atom positional parameters (Tables V and X) (13 pages); listings of observed and calculated structure factors for the above two complexes (16 pages). Ordering information is given on any current masthead page.

(13) A fresh crystal of  $[\text{Mn}_4\text{O}_2\text{L}_2](\text{PF}_6)_2 \cdot 4\text{MeCN}$  was covered with fast-setting epoxy to prevent solvent loss: space group  $P2_1/n$ , with  $a = 14.019$  (7) Å,  $b = 16.165$  (8) Å,  $c = 15.995$  (7) Å,  $\beta = 102.27$  (4)°,  $V = 3542$  (3) Å<sup>3</sup>,  $Z = 2$ , and  $\rho_{\text{calc}} = 1.52$  g cm<sup>–3</sup>. The structure was solved by direct methods with 3020 observed ( $I > 3\sigma(I)$ ) data collected at 23 °C, affording  $R = 6.81\%$ ,  $R_w = 7.50\%$ , and GOF = 1.77.

Department of Inorganic Chemistry      Swapan Kumar Chandra  
Indian Association for the Cultivation      Animesh Chakravorty\*  
of Science  
Calcutta 700032, India

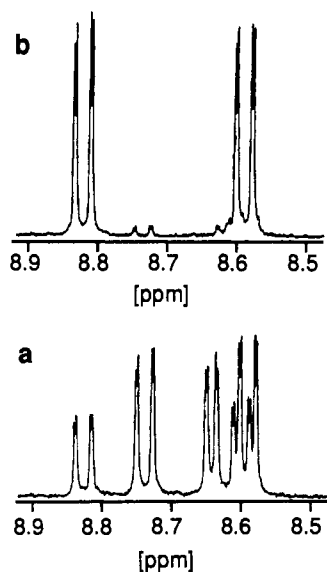
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### First Stereospecific Preparation of a Polynuclear Coordination Compound. Use of $\Lambda\text{-Ru}^{\text{II}}(\text{o-phen})_2$ as a Chiral Building Block

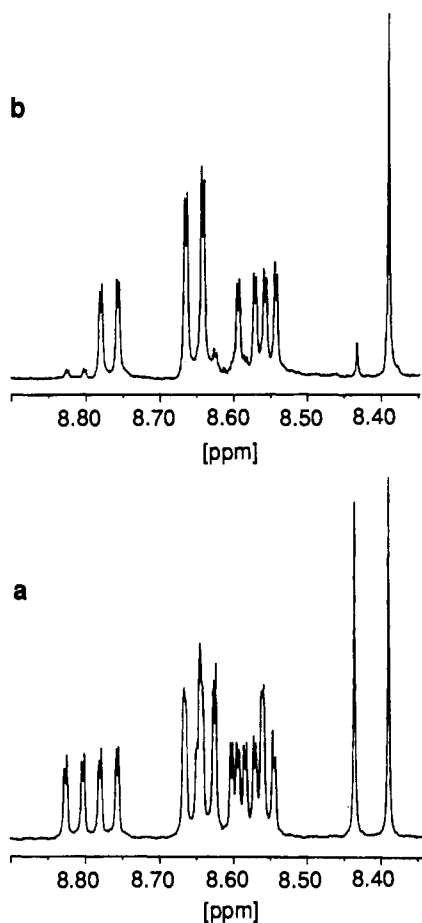
The resolution of  $\text{M}(\text{L}\text{L})_3$  and  $\text{M}(\text{L}\text{L})_2(\text{A})(\text{B})$  complexes (where  $\text{L}\text{L}$  are bidentate ligands) into optical isomers was one of the great achievements of Alfred Werner during the development of the coordination theory.<sup>1</sup> Although it is since clear, that octahedral coordination moieties of the above-mentioned type are chiral, stereoselective synthesis has not been developed in coordination chemistry in the same sense as in organic chemistry. Yet the chirality of the coordination centers is a major problem in the synthesis of polynuclear complexes. Recently, a method for separating enantiomers of complexes that are capable of forming dinuclear species was published.<sup>2</sup> The synthesis of dinuclear

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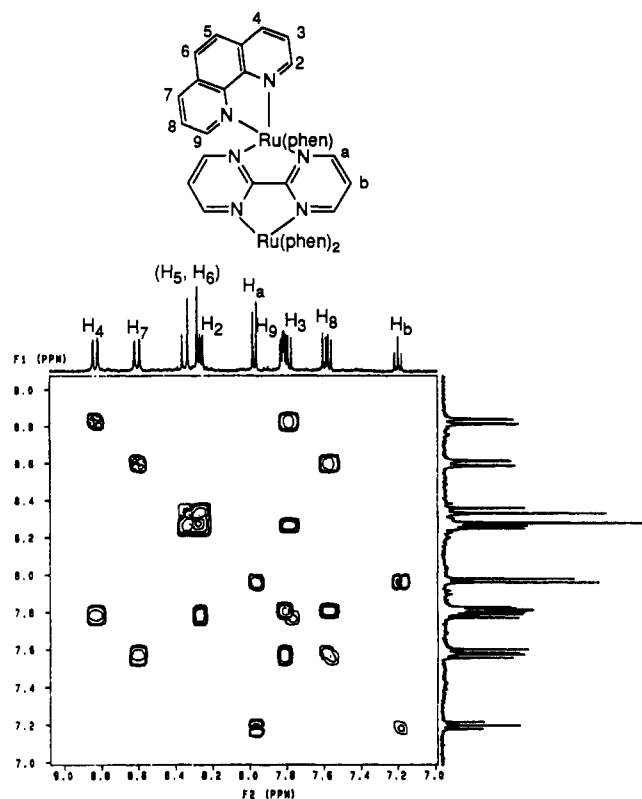
**Figure 1.** Parts of the  $^1\text{H}$  NMR spectra of the dinuclear species  $[(\text{Ru}(\text{o-phen})_2)_2\text{bpym}]^{4+}$  prepared from (a) *rac*- $\text{Ru}(\text{o-phen})_2\text{Cl}_2$  and from enantiomerically pure (b)  $\Delta$ - $[\text{Ru}(\text{o-phen})_2(\text{py})_2]^{2+}$ , respectively at 360 MHz in  $\text{CD}_3\text{CN}$ .  $T = 25^\circ\text{C}$ . The assignment of the signals emerges from the COSY spectrum given in Figure 3.



**Figure 2.** Parts of the  $^1\text{H}$  NMR spectra of the dinuclear species  $[(\text{Ru}(\text{o-phen})_2)_2(2,5\text{-dpp})]^{4+}$  prepared from (a) *rac*- $\text{Ru}(\text{o-phen})_2\text{Cl}_2$  and from enantiomerically pure (b)  $\Delta$ - $[\text{Ru}(\text{o-phen})_2(\text{py})_2]^{2+}$ , respectively at 360 MHz in  $\text{CD}_3\text{CN}$ .  $T = 25^\circ\text{C}$ . The singlets at 8.39 ppm (chiral form) and 8.44 ppm (meso form), are due to the protons in the central ring of the bridging ligand.

complexes using such chiral building blocks was not reported, however.

If a polynuclear complex contains  $N$  chiral coordination centers, a maximum of  $2^N$  isomers can be formed, if racemic building



**Figure 3.** COSY  $^1\text{H}$  NMR spectrum of  $\Delta, \Delta$ - $[(\text{Ru}(\text{o-phen})_2)_2\text{bpym}]^{4+}$  at 300 MHz in  $\text{CD}_3\text{CN}$ .  $T = 25^\circ\text{C}$ .

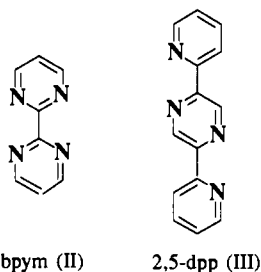
blocks are used. This number can be considerably smaller for symmetry reasons in actual cases, but there is always the problem of separation, identification, and purification of the mixture of isomers, having very similar properties. The use of a pure enantiomer as a building block in a stereoselective synthesis excludes completely the formation of isomers, facilitating enormously the task of characterization and purification of the polynuclear compound. Even dinuclear complexes with chiral coordination centers give rise to complicated isomer problems,<sup>3</sup> whereas polynuclear complexes give such a high number of isomers, that preparation of an isomerically pure substance becomes very unlikely.<sup>4</sup>

Dinuclear complexes with a symmetrical bridge and two identical coordination units yield a total of three isomers, namely one racemic mixture  $\Delta\Delta/\Delta\Delta$  and a meso form  $\Delta\Lambda$ , if racemic building blocks are used.<sup>3</sup> Likewise a trinuclear species, as, e.g., the one used for the study of intramolecular energy transfer,<sup>5</sup> forms four isomers (two racemic mixtures) in the case of three identical coordination units.

In order to avoid this general problem of molecular identity in multicenter coordination compounds, we started a general program for stereoselective syntheses of such species. In this communication we report on the first successful preparation<sup>6</sup> of isomerically pure dinuclear complexes using the chiral building block  $\Delta$ - $\text{Ru}(\text{o-phen})_2$ . The latter has been obtained by separating

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- (6)  $[(\text{Ru}(\text{o-phen})_2)_2\text{bpym}]^{4+}$  and  $[(\text{Ru}(\text{o-phen})_2)_2(2,5\text{-dpp})]^{4+}$  complexes were prepared by the reaction of  $\text{Ru}(\text{o-phen})_2\text{Cl}_2$  with the bridging ligand (BL = bpym; 2,5-dpp) in the standard fashion for  $[(\text{Ru}(\text{o-phen})_2\text{BL})_2]^{2+}$  and  $[(\text{Ru}(\text{o-phen})_2)_2(\text{BL})]^{4+}$  followed by isolation of the  $\text{PF}_6^-$  salt. Monomer and dimer were separated by silica gel TLC (eluate  $\text{H}_2\text{O}:\text{EtOH}:\text{NaCl} = 10:10:1$ ).  $\Delta, \Delta$ - $[(\text{Ru}(\text{o-phen})_2)_2\text{bpym}]^{4+}$  and  $\Delta, \Delta$ - $[(\text{Ru}(\text{o-phen})_2)_2(2,5\text{-dpp})]^{4+}$  were prepared in an analogous way, using  $\Delta$ - $[\text{Ru}(\text{o-phen})_2(\text{py})_2]^{2+}$  instead of  $\text{Ru}(\text{o-phen})_2\text{Cl}_2$ .

the complex  $[\text{Ru}(o\text{-phen})_2(\text{py})_2]^{2+}$  (I) into the optical isomers.<sup>7</sup> We followed the literature procedure with good results. Reactions of I with the two bridging ligands bpym (II) or 2,5-dpp (III) yield



bpym (II)

2,5-dpp (III)

dinuclear complexes  $[(\text{Ru}(o\text{-phen})_2)_2\text{bpym}]^{4+}$  and  $[(\text{Ru}(o\text{-phen})_2)_2(2,5\text{-dpp})]^{4+}$ , respectively. The 360-MHz  $^1\text{H}$  NMR spectra (Figure 1a and Figure 2a) are recorded from solutions obtained with  $\text{rac-Ru}(o\text{-phen})_2\text{Cl}_2$ , and the traces in Figure 1b and Figure 2b, from solutions obtained with  $\Delta\text{-}[\text{Ru}(o\text{-phen})_2(\text{py})_2]^{2+}$ , respectively. The spectra reveal clearly the stereospecific route of the reaction<sup>8</sup> leading to the dinuclear complexes.  $\Delta\text{-}$

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 (8) The relative abundance of the meso form and of the enantiomeric pair in the dinuclear complex is somewhat different if  $\text{rac-}[\text{Ru}(o\text{-phen})_2(\text{py})_2]^{2+}$  or  $\text{rac-Ru}(o\text{-phen})_2\text{Cl}_2$  is used for its synthesis. The exact course of the reaction in the formation of the dinuclear complexes is the subject of further investigations. The first results indicate retention of configuration if the two pyridine ligands in  $[\text{Ru}(o\text{-phen})_2(\text{py})_2]^{2+}$  are substituted by a dinuclear chelate. CD spectra indicate, e.g., clearly that the substitution of the two py ligands in  $\Delta\text{-}[\text{Ru}(o\text{-phen})_2(\text{py})_2]^{2+}$  by bpy yields  $\Delta\text{-}[\text{Ru}(o\text{-phen})_2(\text{bpy})]^{2+}$  with complete retention of configuration.

$\Delta\text{-}[(\text{Ru}(o\text{-phen})_2)_2\text{bpym}]^{4+}$  and  $\Delta\text{-}[(\text{Ru}(o\text{-phen})_2)_2(2,5\text{-dpp})]^{4+}$  are obtained in ca. 95% and 90% isomeric purity, respectively. Recrystallization yields further separation of the isomers. Full assignment of pure  $\Delta\text{-}[(\text{Ru}(o\text{-phen})_2)_2\text{bpym}]^{4+}$  has been given by COSY  $^1\text{H}$  NMR as illustrated in Figure 3. There are signals of 10 different protons present with the coupling constants values  $J_{23} = J_{89} = 5.2$  Hz,  $J_{24} = J_{79} = 1.2$  Hz,  $J_{34} = J_{78} = 8.3$  Hz,  $J_{56} = 9.0$  Hz, and  $J_{ab} = 5.7$  Hz. The spectrum of the dinuclear complex prepared from the racemic building block shows 20 different protons (10 from the  $\Delta\text{-}$  meso form).

The use of inert and enantiomerically pure building blocks for the synthesis of isomerically pure polynuclear complexes is a necessary prerequisite for the production of species with a well-defined identity. Such well-defined species are of interest in highly organized supramolecular structures containing several metal centers and also for studies of the interactions of metal complexes with biomolecules.

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Institute of Inorganic Chemistry  
 University of Fribourg  
 Pérolles, CH-1700 Fribourg, Switzerland

Xiao Hua  
 Alex von Zelewsky\*

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## Articles

Contribution from the Dipartimento di Chimica "G. Ciamician" dell'Università, Via Selmi 2, 40126 Bologna, Italy, and Groupe de Matériaux Inorganiques, Ecole Européenne des Hautes Etudes des Industries Chimiques de Strasbourg, 1 Rue Blaise Pascal, B.P. 296, 67008 Strasbourg Cedex, France

### Luminescent $\text{Eu}^{3+}$ , $\text{Tb}^{3+}$ , and $\text{Gd}^{3+}$ Complexes of a Branched-Triazacyclononane Ligand Containing Three 2,2'-Bipyridine Units

Luca Prodi,<sup>1a</sup> Mauro Maestri,<sup>1a</sup> Raymond Ziessel,<sup>\*1b</sup> and Vincenzo Balzani<sup>\*1a</sup>

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The  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ , and  $\text{Gd}^{3+}$  complexes of the branched-triazacyclononane ligand **1**, which contains three 2,2'-bipyridine coordinating units, have been prepared and their absorption spectra, luminescence spectra, luminescence decays, and transient absorption spectra and decays have been investigated. The three complexes show intense absorption bands at 243 nm ( $\epsilon \approx 14000 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 311 nm ( $\epsilon \approx 22000 \text{ M}^{-1} \text{ cm}^{-1}$ ), which are considerably red-shifted and weaker compared with the bands of the free ligand. The free ligand and the  $\text{Gd}^{3+}$  complex show ligand-centered (LC) fluorescence and phosphorescence, as well as triplet-triplet transient absorption. The transient absorption can also be observed for the  $\text{Tb}^{3+}$  complex but not for the  $\text{Eu}^{3+}$  complex. For the  $\text{Tb}^{3+}$  and the  $\text{Eu}^{3+}$  complexes excitation in the LC bands causes the characteristic luminescence of the lanthanide ion. The excitation spectra match closely the absorption spectra in the region of LC absorption. Measurements carried out in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  at 77 and 300 K show that, when coordinated to **1**, the metal ion is almost completely shielded from interaction with solvent molecules, in agreement with expectations based on molecular models. The emission lifetime at 77 K in  $\text{D}_2\text{O}$  for  $[\text{Tb}(\mathbf{1})]^{3+}$  is considerably shorter than that of analogous complexes. This may be due either to a high radiative rate constant or, more likely, to radiationless deactivation via coupling with the very close lying  $\text{CH}_2$  groups of the triazacyclononane ring. For  $[\text{Tb}(\mathbf{1})]^{3+}$  no temperature effect is observed on the luminescence decay, because of the relatively high energy gap between the luminescent  $^5\text{D}_4$  level and the upper lying  $^3\pi\pi^*$  LC level. For  $[\text{Eu}(\mathbf{1})]^{3+}$ , the lifetime in  $\text{D}_2\text{O}$  at 77 K is again rather short, and furthermore, it decreases with increasing temperature. The latter effect is presumably caused by an activated radiationless decay via a low-lying CT excited state, related to the presence of the aliphatic amine groups (intramolecular electron-transfer quenching). Because of its high luminescence quantum yield (0.37 in  $\text{H}_2\text{O}$  at 300 K),  $[\text{Tb}(\mathbf{1})]^{3+}$  can be an excellent luminescence label.

#### Introduction

Molecular species capable of exhibiting strong luminescence are quite interesting not only from a fundamental point of view but also because of their potential use for a variety of applications.

Some lanthanide ions possess strongly emissive and long-lived excited states but do not exhibit intense absorption bands.<sup>2</sup> Therefore, considerable effort is currently devoted to the design

(1) (a) Università di Bologna. (b) EHICS, Strasbourg.

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