Synthesis of Dissymmetric Schiff Base Ligands through Gadolinium(III) Coordination

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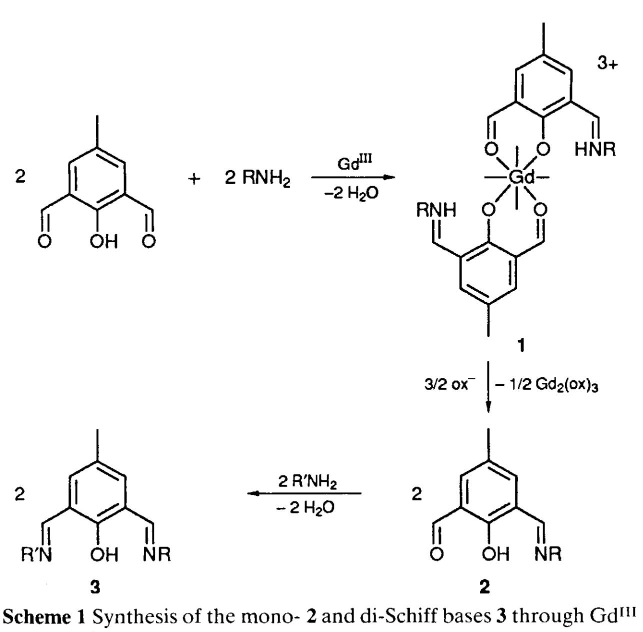
The reaction of the 2,6-diformyl-4-methylphenol with a primary amine in the presence of gadolinium(III) affords a complex in which gadolinium(III) is coordinated to two mono-Schiff bases through their carbonyl and phenolic oxygen atoms.

The selective functionalization of one out of several identical groups within the same molecule constitutes a challenge to synthetic chemists. Such an approach, however, is often required in designing dissymmetric polychelating ligands. An important class of molecules of this kind is that of the poly-Schiff bases, the archetype of which is the Robson ligand derived from 2,6-diformyl-4-methylphenol.[1] To the best of our knowledge, the only method available so far for synthesizing dissymmetric Robson-type ligands is that reported by Kida,[2] and subsequently used by Gagne,[3] then by Nag.[4,5] This method, however, directly leads to homo- or hetero-binuclear complexes; it does not allow the ligands themselves to be isolated.

We have found a completely different approach based upon the very high affinity of the trivalent rare earth elements for oxygen.[6,7] This approach is almost quantitative. It allows mono-Schiff bases of 2,6-diformyl-4-methylphenol to be obtained as well as dissymmetric di-Schiff bases. The synthesis pathway is shown in Scheme 1. The reaction of a primary amine RNH_2 with 2,6-diformyl-4-methylphenol in the presence of Gd^{III} affords the Gd^{III} complex **1** in which the rare earth is coordinated to two carbonyl and two phenolic oxygen atoms as well as water molecules completing the coordination sphere. In **1**, only one of the two carbonyl functions of the dialdehyde has reacted with the amine, the other one being efficiently protected by the Gd^{III} ion. The same reaction in the absence of Gd^{III} gives a mixture of mono- and di-Schiff bases. Subsequent treatment of a methanolic solution containing **1** with potassium oxalate dissolved in the minimum amount of water results in the mono-Schiff base **2**, and gadolinium(III) oxalate is precipitated. Dissymmetric di-Schiff bases may then be obtained by the reaction of a different primary amine $R'NH_2$ with **2**. The dissymmetric ligands **3** may be used to synthesize binuclear complexes in which the metal ions are in non-equivalent surroundings.[8]



Scheme 1 Synthesis of the mono- **2** and di-Schiff bases **3** through Gd^{III} coordination

Scheme 1 seems to be general. It has been optimized with RNH_2 = 2-(2-aminoethyl)pyridine, and $R'NH_2$ = *N,N*-dimethylethylenediamine; single crystals of $[\mathbf{1}(H_2O)_4](ClO_4)_2Cl \cdot 2.75H_2O$ have been isolated† as follows. To a 1 : 1 (40 ml) solvent mixture of dry acetonitrile and ethanol containing equimolar amounts (1 mmol) of 2,6-diformyl-4-methylphenol and 2-(2-aminoethyl)pyridine was added dropwise and under continuous stirring at room temperature a solution of gadolinium(III) perchlorate (0.5 mmol) and sodium chloride (0.75 mmol) in the same solvent mixture (20 ml). The yellow reaction mixture remained clear. Pale-yellow prismatic-like single crystals were obtained by slow diffusion of diethyl ether into a 1 : 3 mixture of the mother-solution and the pure solvent mixture. The molecular structure of $[\mathbf{1}(H_2O)_4]^{3+}$ is shown in Fig. 1. Gd^{III} is surrounded by eight oxygen atoms including four water molecules in a square antiprism fashion. The Gd–O distances range from 2.326(4) to 2.440(5) Å. Interestingly, the phenolic hydrogen atom has migrated towards the nitrogen atom of the imine group, affording an iminium function. The mono-Schiff base **2** and the dissymmetric bi-Schiff base **3** synthesized from this Gd^{III} complex have been characterized by their ^1H NMR spectroscopy in $CDCl_3$ solution.‡

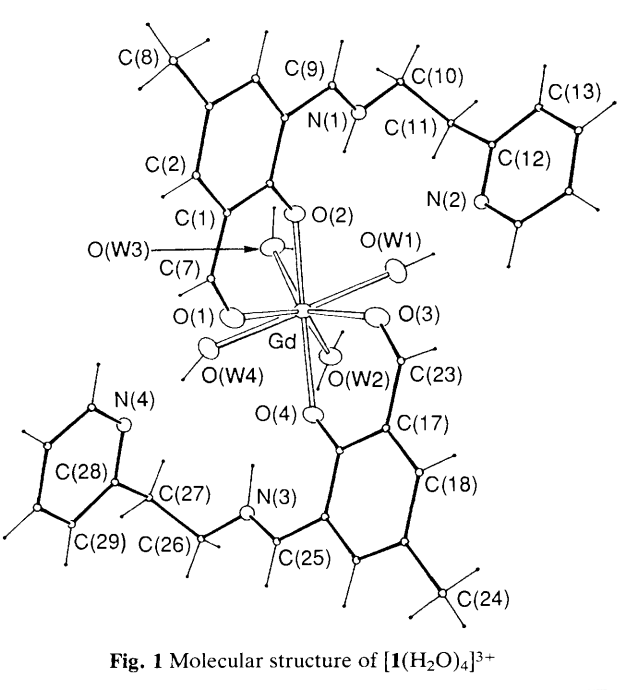


Fig. 1 Molecular structure of $[\mathbf{1}(H_2O)_4]^{3+}$

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† *Crystal data* for $[\mathbf{1}(H_2O)_4](ClO_4)_2Cl \cdot 2.75H_2O$: monoclinic, space group $P2_1/c$, $a = 18.079(4)$, $b = 14.560(3)$, $c = 16.409(3)$ Å, $\beta = 92.93(2)°$, $Z = 4$, $D_c = 1.66$ g cm^{-3}. 8192 reflections were collected, and 5511 with $I > 3\delta(I)$ were used. The structure was refined to $R = 0.048$, and $R_w = 0.076$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ For **2**: δ 2.2 (s, 3H), 3.2 (t, 2H), 4.1 (t, 2H), 7.2 (m, 3H), 7.6 (m, 2H), 8.3 (s, 1H), 8.6 (d, 1H), 10.5 (s, 1H) and 14.0 (s, 1H). For **3**: δ 2.2 (2s, 9H), 2.7 (t, 2H), 3.2 (t, 2H), 3.8 (t, 2H), 4.1 (t, 2H), 7.2 (m, 2H), 7.4 (s, 2H), 7.6 (m, 1H), 8.5 (s, 2H), 8.6 (d, 1H) and 13.8 (s, 1H).

E. B. thanks the EEC which financially supported his stay in Orsay.

Received, 10th January 1991; Com. 1/00124H

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