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Oxophily of Gadolinium(III) and Synthesis of Dissymmetric Di(Schiff bases) and Dissymmetric Dinuclear Compounds. Crystal Structure of $[Cu_2L'(OH)](ClO_4)_2{\cdot}H_2O$ with L′ = 2-[*N*-(2-pyridylethyl)formimidoyl]-6-[*N*-((dimethylamino)propyl)formimidoyl]phenolato

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The strong oxophilic character of the Gd(III) ion has been utilized to protect one of the carbonyl functions of 2,6-diformyl-4-methylphenol, which has allowed to synthesize quantitatively mono(Schiff bases), then dissymmetric di(Schiff bases). The synthetic process is as follows: the reaction of 2,6-diformyl-4-methylphenol with a primary amine RNH_2 in the presence of Gd(III) affords a complex in which Gd(III) is coordinated to two mono(Schiff bases) through their carbonyl and phenolic oxygen atoms. The mono(Schiff base) may be isolated by precipitation of Gd(III) in the form of gadolinium(III) oxalate. The reaction of another primary amine, $R'NH_2$, on this mono(Schiff base) affords a dissymmetric di(Schiff base), from which dissymmetric dinuclear compounds can be synthesized. For example, this reaction has been carried out with RNH_2 = 2-(2-aminoethyl)pyridine and $R'NH_2$ = *N,N*-dimethylpropylenediamine. The mono(Schiff base) 2-formyl-6-(*N*-(2-pyridylethyl)formimidoyl)-4-methylphenol (HL) and the di(Schiff base) 2-[*N*-(2-pyridylethyl)formimidoyl]-6-[*N*-((dimethylamino)propyl)formimidoyl]-4-methylphenol (HL′) have been unambiguously characterized from their ^1H NMR spectra. The copper(II) dinuclear compound $[CuL'(OH)](ClO_4)_2{\cdot}H_2O$ obtained from this di(Schiff base) has been synthesized, and its crystal structure has been solved. This compound crystallizes in the monoclinic system, space group $P2_1/n$. The lattice parameters are a = 13.439(10) Å, b = 14.153(6) Å, c = 14.734(13) Å, β = 92.73(7)°, and Z = 4.

Introduction

The selective functionalization of one out of several identical functions within the same molecule and the design of dissymmetric dinuclear species constitute a challenge for synthetic chemists. This challenge is first intellectual; it is obviously more difficult to design a dissymmetric dinuclear compound than a symmetric one. It is also stimulated by the fact that this dissymmetry is often found in metallo-biosites. This is for instance the case for both oxygen carriers, hemerythrin and hemocyanin. The active site of the former protein is an iron pair; in the desoxy form, one of the iron atoms is pentacoordinated, and the other one is hexacoordinated.[2-4] As for the latter protein, it contains a copper pair, the nonsymmetric nature of which has been revealed by X-ray diffraction on the desoxy form.[5,6]

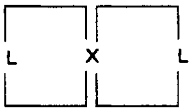
Several approaches have been proposed so far to design dissymmetric dinuclear species. To date, these approaches can be classified into two main categories.

(1) The first is the use of complexes as ligands. The typical reaction may be symbolized as

$$LMX + M'L' \rightarrow LMXM'L'$$

where M and M′ are metal ions, L and L′ are peripheral ligands, and X is a potentially bridging ligand which is terminal in the LMX mononuclear precursor. Among the numerous examples of compounds obtained in that way, we may mention the M(salen)-$M'(hfa)_2$ species, where salen is *N,N′*-ethylenebis(salicylideneaminato) and hfa is hexafluoroacetylacetonato,[7-10] and the dinuclear copper(II) compounds LCuXCuL′ (L ≠ L′) where X is a bisbidentate ligand like oxalato. In those compounds the magnitude of the intramolecular interaction may be tuned by the nature of the L and L′ peripheral ligands.[11,12]

(2) The second is the use of binucleating ligands of the type



where X stands for the bridging part, and L and L′ stand for the peripheral ligands. The LX and L′X cavities can be occupied by like or unlike metal ions. In the former case, the dissymmetry for L ≠ L′ only concerns the surroundings of the metals; in the latter case, it concerns the metal themselves.[13-16] These binucleating ligands are extremely numerous, and a large variety of synthetic approaches have been used to prepare them. Two of these approaches are more particularly relevant to the work

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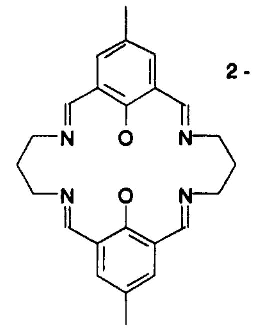
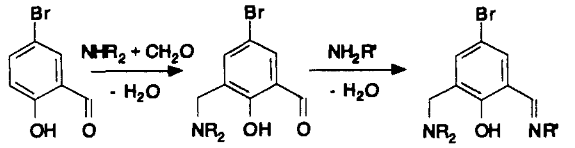
reported in this paper, namely (i) the stepwise synthesis of heterodinuclear compounds incorporating the Robson ligand[17]



performed by Kida,[18] Gagné,[19,20] and then Nag,[21,22] where what is remarkable in Gagné's work[19] is that the dissymmetry of the final compound is achieved despite the perfect symmetry of the binucleating ligand and of the 2,6-formyl-4-methylphenol used as starting compound; and (ii) the step-wise introduction of two different pendant arms into the 2- and 6-positions of a 4-substituted phenol by Fenton, Latour and co-workers.[23] These authors started from the 4-bromosalicylaldehyde and introduced first a methyleneamine group on the unsubstituted 2-position through the Mannich reaction[24,25] and then a imine function on the 6-position by reaction of a primary amine with the carbonyl function, according to



It may be noted here that the starting phenol was already nonsymmetric, in contrast with Gagné's work.

In this paper, we describe a totally novel method to introduce two different primary amines as pendant groups on 2,6-diformyl-4-methylphenol. This method, which seems quite general, is based on the efficient protection of one of the two aldehyde functions of 2,6-diformyl-4-methylphenol by trivalent rare earths owing to their strong oxophilic character.[26,27] We will successively describe the synthesis of the mono(Schiff base) 2-formyl-6-(*N*-(2-pyridylethyl)formimidoyl)-4-methylphenol (HL), of the di(Schiff base) 2-[*N*-(2-pyridylethyl)formimidoyl]-6-[*N*-((dimethylamino)propyl)formimidoyl]-4-methylphenol (HL′), and of the copper(II) dinuclear compound $[CuL'(OH)](ClO_4)_2{\cdot}H_2O$ obtained from this di(Schiff base). The crystal structure of this copper(II) compound will be reported, and the potentialities of our method will be discussed.

Experimental Section

Synthesis. The synthesis of the Gd(III) mononuclear compound $[Gd(HL)_2(H_2O)_2)_4](ClO_4)_3{\cdot}4H_2O$ ((**1**)Gd) was described in the preceding paper of this issue.[27] The free mono(Schiff base) HL was prepared as follows: 1 mmol of (**1**)Gd dissolved in 30 mL of methanol was treated with a slight excess of potassium oxalate dissolved in a minimum amount of water. The gadolinium(III) oxalate immediately precipitated. It was filtered off, and the mono(Schiff base) HL was extracted twice with diethyl ether from the filtrate. After the extract was dried over Na_2SO_4, the diethyl ether was removed under reduced pressure, and HL crystallized in a vacuum desiccator. The yield is almost quantitative. We checked that HL may be obtained from another rare earth ion like Ne(III), Sm(III), or Eu(III), and from another salt of the Gd(III) mononuclear cation $[Gd(HL)_2(H_2O)_4]^{3+}$ like the nitrate or the triflate.

Table I. Crystal Data for $[CuL'(OH)](ClO_4)_2{\cdot}H_2O$

formula	$[Cu_2(ON_4C_{21}H_{27})$-$(OH)(OH_2)$-$(ClO_4)]^+(ClO_4^-)$	*Z*	4
fw	712.5	μ(Mo Kα), cm^{-1}	17.8
space group	$P2_1/n$	d_{calcd}, g cm^{-3}	1.69
a, Å	13.439(10)	*T*, °C	20
b, Å	14.153(6)	abs cor by	Difabs
c, Å	14.734(13)	R^a	0.040
β, deg	92.73(7)	R_w (unit weight)[b]	0.043
V, $Å^3$	2799(9)		

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_c)^2]^{1/2}$.

Table II. Fractional Atomic Coordinates with Esd's for $[CuL'(OH)](ClO_4)_2{\cdot}H_2O$

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq},[a] $Å^2$
Cu(1)	0.23586(8)	0.66748(9)	0.48569(7)	0.0381
Cu(2)	0.22366(9)	0.82974(9)	0.61770(8)	0.0386
O(1)	0.1878(5)	0.6942(4)	0.6064(4)	0.0365
O(2)	0.2732(5)	0.7957(4)	0.5013(4)	0.0395
O(3)	0.3734(5)	0.8098(6)	0.7049(5)	0.0642
N(1)	0.2847(6)	0.6556(6)	0.3608(5)	0.0422
N(2)	0.2048(6)	0.5350(5)	0.4954(5)	0.0363
N(3)	0.1523(6)	0.8401(6)	0.7302(5)	0.0425
N(4)	0.2373(6)	0.9714(6)	0.5951(5)	0.0426
C(1)	0.1153(7)	0.6462(7)	0.6456(6)	0.0341
C(2)	0.0914(7)	0.5529(7)	0.6188(6)	0.0368
C(3)	0.0215(7)	0.5039(7)	0.6664(7)	0.0427
C(4)	−0.0249(7)	0.5406(7)	0.7415(7)	0.0459
C(5)	−0.0958(9)	0.4834(8)	0.7948(8)	0.0571
C(6)	0.0006(7)	0.6315(7)	0.7665(6)	0.0398
C(7)	0.0695(7)	0.6848(7)	0.7224(6)	0.0374
C(8)	0.0935(7)	0.7761(7)	0.7600(6)	0.0422
C(9)	0.1705(9)	0.9208(8)	0.7892(7)	0.0543
C(10)	0.1591(8)	1.0149(7)	0.7411(8)	0.0569
C(11)	0.2395(7)	1.0332(7)	0.6763(7)	0.0467
C(12)	0.332(1)	0.9923(8)	0.5473(9)	0.0686
C(13)	0.1534(9)	0.9987(8)	0.5316(8)	0.0649
C(14)	0.2642(8)	0.7259(8)	0.3033(7)	0.0516
C(15)	0.2958(8)	0.7234(9)	0.2150(8)	0.0573
C(16)	0.350(1)	0.649(1)	0.1879(8)	0.0674
C(17)	0.3664(9)	0.576(1)	0.245(1)	0.0686
C(18)	0.3330(7)	0.5798(8)	0.3342(7)	0.0448
C(19)	0.3466(8)	0.5014(8)	0.4000(8)	0.0544
C(20)	0.2473(8)	0.4653(7)	0.4345(7)	0.0483
C(21)	0.1396(7)	0.5014(7)	0.5489(7)	0.0379
Cl(1)	0.0010(2)	0.7763(2)	0.4264(2)	0.0519
O(4)	0.0665(5)	0.6968(5)	0.4197(5)	0.0553
O(6)	−0.0982(6)	0.7472(7)	0.3980(6)	0.0820
O(5)	0.0068(6)	0.8113(6)	0.5162(5)	0.0742
O(7)	0.0323(6)	0.8479(6)	0.3675(6)	0.0839
Cl(2)	0.5441(2)	0.7372(2)	0.5260(2)	0.0635
O(8)	0.4917(6)	0.8194(6)	0.4982(6)	0.0762
O(9)	0.5046(9)	0.6601(6)	0.4795(7)	0.1125
O(10)	0.5499(9)	0.7266(8)	0.6197(5)	0.1098
O(11)	0.6447(6)	0.7461(9)	0.4981(8)	0.1321

[a] $U_{eq} = (U_1U_2U_3)^{1/3}$.

The dissymmetrical Schiff base HL′ was synthesized as follows: 1 mmol of HL and 1 mmol of *N*,*N*-dimethylpropylenediamine were dissolved in 20 mL of methanol. The mixture was stirred for a few minutes, and then the methanol was completely removed under reduced pressure. HL′ was then obtained as an orange oil. Both HL and HL′ were characterized by their ^1H-NMR spectra in $CDCl_3$ solution, as discussed below.

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Table III. Interatomic Distances (Å) and Bond Angles (deg) for $[CuL'(OH)](ClO_4)_2 \cdot H_2O$

Cu(1)–Cu(2)	3.019(2)		
Cu(1)–O(1)	1.958(6)	Cu(2)–O(1)	1.983(6)
Cu(1)–O(2)	1.894(6)	Cu(2)–O(2)	1.930(6)
Cu(1)–N(1)	1.990(8)	Cu(2)–N(3)	1.959(8)
Cu(1)–N(2)	1.928(8)	Cu(2)–N(4)	2.042(8)
Cu(1)–O(4)	2.467(7)	Cu(2)–O(3)	2.352(7)
		Cu(2)–O(5)	3.223(8)
N(1)–C(14)	1.33(1)	N(3)–C(8)	1.29(1)
N(1)–C(18)	1.32(1)	N(3)–C(9)	1.45(1)
N(2)–C(20)	1.47(1)	N(4)–C(11)	1.48(1)
N(2)–C(21)	1.30(1)	N(4)–C(12)	1.51(1)
		N(4)–C(13)	1.48(1)
O(1)–C(1)	1.34(1)	C(7)–C(8)	1.44(1)
C(1)–C(2)	1.41(1)	C(9)–C(10)	1.51(2)
C(1)–C(7)	1.42(1)	C(10)–C(11)	1.50(1)
C(2)–C(3)	1.38(1)	C(14)–C(15)	1.39(1)
C(2)–C(21)	1.44(1)	C(15)–C(16)	1.35(2)
C(3)–C(4)	1.40(1)	C(16)–C(17)	1.35(2)
C(4)–C(5)	1.50(1)	C(17)–C(18)	1.41(2)
C(4)–C(6)	1.38(1)	C(18)–C(19)	1.48(2)
C(6)–C(7)	1.38(1)	C(19)–C(20)	1.54(1)
Cl(1)–O(4)	1.435(7)	Cl(2)–O(8)	1.410(6)
Cl(1)–O(5)	1.412(8)	Cl(2)–O(9)	1.381(7)
Cl(1)–O(6)	1.438(8)	Cl(2)–O(10)	1.387(7)
Cl(1)–O(7)	1.410(8)	Cl(2)–O(11)	1.437(7)
O(1)–Cu(1)–O(2)	78.5(2)	O(1)–Cu(2)–O(2)	77.1(3)
O(1)–Cu(1)–N(1)	173.7(3)	O(1)–Cu(2)–N(3)	91.0(3)
O(1)–Cu(1)–N(2)	92.2(3)	O(1)–Cu(2)–N(4)	163.7(3)
O(2)–Cu(1)–N(1)	95.5(3)	O(2)–Cu(2)–N(3)	166.8(3)
O(2)–Cu(1)–N(2)	168.5(3)	O(2)–Cu(2)–N(4)	93.6(3)
N(1)–Cu(1)–N(2)	93.9(4)	N(3)–Cu(2)–N(4)	96.6(3)
O(1)–Cu(1)–O(4)	89.3(3)	O(1)–Cu(2)–O(3)	97.3(3)
O(2)–Cu(1)–O(4)	96.9(3)	O(2)–Cu(2)–O(3)	97.7(3)
N(1)–Cu(1)–O(4)	89.3(3)	N(3)–Cu(2)–O(3)	89.3(3)
N(2)–Cu(1)–O(4)	89.6(3)	N(4)–Cu(2)–O(3)	97.2(3)
		O(3)–Cu(2)–O(5)	167.2(3)
		O(1)–Cu(2)–O(5)	70.9(2)
		O(2)–Cu(2)–O(5)	84.8(2)
		N(3)–Cu(2)–O(5)	86.0(3)
		N(4)–Cu(2)–O(5)	95.2(3)
Cu(1)–O(1)–Cu(2)	100.0(3)	Cu(2)–N(3)–C(8)	124.5(7)
Cu(1)–O(1)–C(1)	124.8(5)	Cu(2)–N(3)–C(9)	119.4(7)
Cu(2)–O(1)–C(1)	129.2(5)	C(8)–N(3)–C(9)	115.9(8)
Cu(1)–O(2)–Cu(2)	104.3(3)		
Cu(1)–N(1)–C(14)	117.4(7)	Cu(2)–N(4)–C(11)	116.6(6)
Cu(1)–N(1)–C(18)	122.0(7)	Cu(2)–N(4)–C(12)	110.6(6)
C(14)–N(1)–C(18)	120.5(9)	Cu(2)–N(4)–C(13)	106.7(6)
		C(11)–N(4)–C(12)	106.1(8)
Cu(1)–N(2)–C(20)	121.1(7)	C(11)–N(4)–C(13)	110.0(8)
Cu(1)–N(2)–C(21)	123.9(7)	C(12)–N(4)–C(13)	106.6(9)
C(20)–N(2)–C(21)	114.8(8)		
O(1)–C(1)–C(2)	121.0(8)	N(3)–C(8)–C(7)	129.0(9)
O(1)–C(1)–C(7)	119.9(8)	N(3)–C(9)–C(10)	113.7(9)
C(2)–C(1)–C(7)	118.7(9)	C(9)–C(10)–C(11)	113.0(9)
C(1)–C(2)–C(3)	118.5(9)	N(4)–C(11)–C(10)	115.2(8)
C(1)–C(2)–C(21)	124.7(9)	N(1)–C(14)–C(15)	121.1(11)
C(3)–C(2)–C(21)	116.6(9)	C(14)–C(15)–C(16)	119.3(12)
C(2)–C(3)–C(4)	123.7(9)	C(15)–C(16)–C(17)	119.3(11)
C(3)–C(4)–C(5)	122.2(10)	C(16)–C(17)–C(18)	120.2(12)
C(3)–C(4)–C(6)	116.4(9)	N(1)–C(18)–C(19)	119.3(11)
C(5)–C(4)–C(6)	121.4(10)	N(1)–C(18)–C(19)	117.4(9)
C(4)–C(6)–C(7)	123.4(9)	C(17)–C(18)–C(19)	123.2(11)
C(1)–C(7)–C(6)	119.2(9)	C(18)–C(19)–C(20)	112.6(9)
C(1)–C(7)–C(8)	123.7(9)	N(2)–C(20)–C(19)	110.4(8)
C(6)–C(7)–C(8)	117.0(9)	N(2)–C(21)–C(2)	126.1(9)
O(4)–Cl(1)–O(5)	109.4(5)	O(8)–Cl(2)–O(9)	109.4(6)
O(4)–Cl(1)–O(6)	108.6(5)	O(8)–Cl(2)–O(10)	112.4(6)
O(4)–Cl(1)–O(7)	108.6(5)	O(8)–Cl(2)–O(11)	108.0(6)
O(5)–Cl(1)–O(6)	112.4(5)	O(9)–Cl(2)–O(10)	114.2(8)
O(5)–Cl(1)–O(7)	108.6(6)	O(9)–Cl(2)–O(11)	105.8(8)
O(6)–Cl(1)–O(7)	109.1(6)	O(10)–Cl(2)–O(11)	106.5(7)

Finally the dissymmetrical copper(II) dinuclear compound $[Cu_2L'(OH)](ClO_4)_2 \cdot H_2O$ was prepared as follows: First 1 mmol of HL′ was dissolved in 30 mL of methanol. A 2-mmol sample of Cu(II) perchlorate dissolved in 10 mL of methanol was then added. Single crystals of $[Cu_2L'(OH)](ClO_4) \cdot H_2O$ were obtained by slow diffusion of diethyloxide into the methanolic solution. Anal. Calcd for $C_{21}H_{24}N_4O_{11}Cl_2Cu_2$: C, 35.40; H, 4.24; N, 7.86; Cl, 9.95; Cu, 17.84. Found: C, 35.46; H, 4.12; N, 7.42; Cl, 9.64; Cu, 17.75.

Caution! No problems were encountered during the preparation of the perchlorato derivative described above. However, suitable care and precautions must be taken when handling such potentially explosive compounds.

Crystallographic Data Collection and Structure Determination. A selected crystal was set up on an Enraf Nonius CAD4F diffractometer. Unit cell dimensions and the crystal orientation matrix together with their estimated standard deviations were obtained from least-squares refinements of the setting angles of 25 reflections. Two standard reflections were monitored periodically; no intensity decay was observed. Corrections were made for Lorentz and polarization effects. Empirical absorption corrections were applied (Difabs).[28] Crystallographic data and other pertinent informations are summarized in Table I. Computations were performed by using the program CRYSTALS[29] adapted on a MicroVax II. Atomic form factors for neutral Cu, Cl, O, C, N, and H were taken from ref 30. Anomalous dispersion was taken into account. Structure was solved by interpretation of Patterson maps which clearly indicated Cu atoms positions. All remaining non-hydrogen atoms were found by successive electron density map calculations. Their atomic coordinates were refined with anisotropic temperature factors. At this stage, hydrogen atoms were located on a difference electron density map; their coordinates were refined with an overall isotropic temperature factor. Least-squares refinements were carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The models reached convergence with R and R_w having the values listed in Table I. The criteria for a satisfactory complete analysis were the ratios of the rms shift to standard deviation being less than 0.2 and no significant features in the final difference map. Atomic coordinates are given in Table II. Selected bond distances and bond angles are given in Table III.

^{1}H NMR Spectra. They were recorded with an AC 250 Bruker spectrometer.

Synthetic Approach

The basic idea of our synthetic approach is to take advantage of the well-known oxophily of trivalent rare earth metals. This oxophily allows to protect one of the two carbonyl functions of a diformyl derivative. The reaction of 2,6-diformyl-4-methylphenol with 1 equiv of a primary amine RNH_2 in the absence of any metal ion affords a mixture containing the starting phenol, the mono(Schiff base), and the di(Schiff base). The mono(Schiff base) HL can be isolated, but the procedure is rather tedious and the yield is low. If the reaction takes place in the presence of $^1/_2$ equiv of Gd(III), the formation of the $[GdL_2(H_2O)_4]^{3+}$ complex is quantitative. Interestingly, even in the presence of an excess of primary amine there is no formation of di(Schiff base) in a detectable amount. The free mono(Schiff base) HL can be easily isolated by extraction of Gd(III) in the form of insoluble gadolinium(III) oxalate. The yield in mono(Schiff base) is then almost quantitative. Moreover, the rare earth is not lost; indeed, it is straightforward to transform gadolinium(III) oxalate into Gd_2O_3 and then into gadolinium(III) perchlorate, which can be used again for a subsequent synthesis.

From HL, any dissymmetric di(Schiff base) can be prepared, again with a very high yield, by reaction of another primary amine $R'NH_2$. Let us note here that a dissymmetric di(Schiff base) of the type

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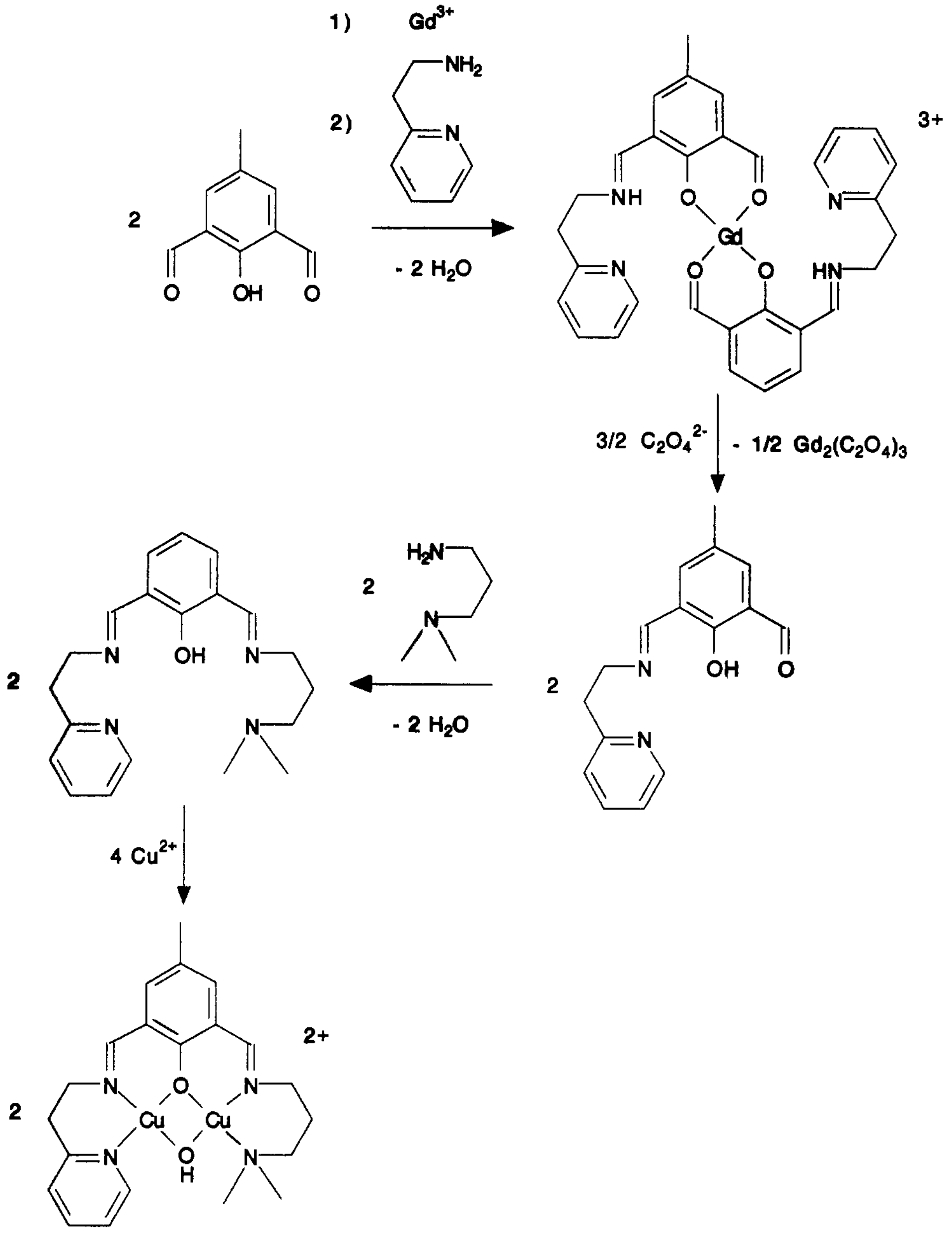
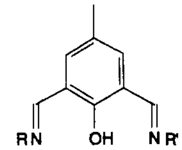


Figure 1. Scheme for the synthesis of the mono(Schiff base) HL, the dissymmetric di(Schiff base) HL′, and the dinuclear compound $[Cu_2L'(OH)](ClO_4)_2 \cdot H_2O$.



in principle may be prepared in either way, by introducing first RNH_2 and then $R'NH_2$ or the reverse. Practically, one method may be more convenient: the case when one of the two possible mono(Schiff bases) is solid at room temperature and therefore can be more easily handled.

In this work, the two pendant groups we introduced into 2,6-diformyl-4-methylphenol have two coordinating nitrogen atoms. Our goal was to synthesize and solve the crystal structure of a dissymmetric dinuclear entity, in order to illustrate our approach in a more striking fashion. Moreover, it was important to verify whether a dissymmetric di(Schiff base) in the presence of a metal ion did not reorganize, affording two symmetric dinuclear entities. In some cases, such a reorganization seems to occur, at least in part. This point would deserve to be investigated in a more thorough manner.

Figure 1 shows the synthetic route leading to HL, HL′, and the copper(II) dinuclear compound. Table IV gives the ^1H-NMR assignments for the mono-Schill base HL, and Table V for the di(Schiff base) HL′.

Description of the Structure of $[Cu_2L'(OH)](ClO_4)_2 \cdot H_2O$

The asymmetric unit together with the atom-numbering scheme is shown in Figure 2. This unit contains a dinuclear cation $[Cu_2L(OH)]^{2+}$ together with two perchlorate groups and a water molecule. As expected, the dinuclear cation is dissymmetric, with a 2-ethylpyridine group on one side, and a dimethylpropylamine group on the other side. The copper atoms within the binuclear entity are bridged by the phenolic oxygen atom O(1) and the hydroxo group O(2)H. The Cu(1), Cu(2), O(1), and O(2) bridging network is almost planar; atomic deviations from the least-squares plane are less than 0.018 Å. The Cu–O–Cu bridging angles are equal to 100.0(3)° on the phenolato side and 104.3(3)° on the hydroxo side. The sum of the three angles around O(1) is 354.0°. The Cu(1)–Cu(2) separation is equal to 3.019(2) Å. The Cu–O bond lengths range from 1.894(6) to 1.983(6) Å, and the Cu–N bond lengths range from 1.928(8) to

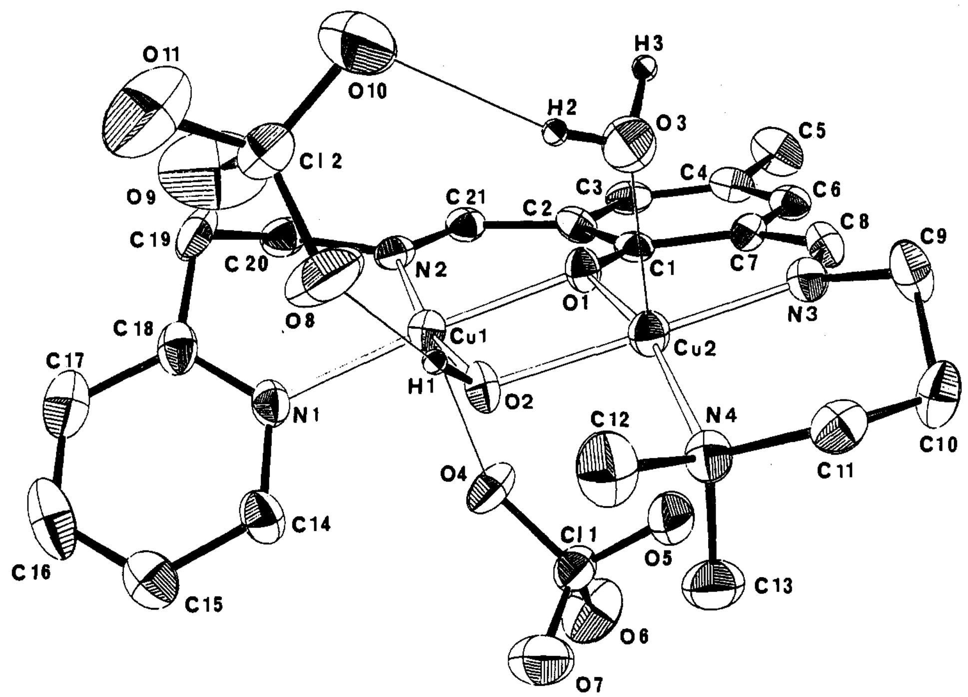
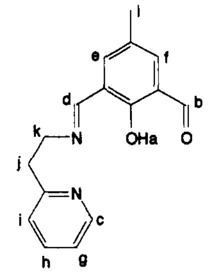


Figure 2. Perspective view along with the numbering scheme for $[Cu_2L'(OH)](ClO_4)_2 \cdot H_2O$.

Table IV. ^{1}H-NMR Assignments for the Mono(Schiff base) HL Dissolved in $CDCl_3$[a]



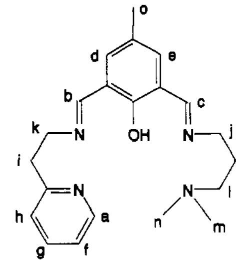
H	δ	H	δ
H_a	14.1 (s br, 1H)	H_g, H_h, H_i	7.2 (m, 3H)
H_b	10.5 (s, 1H)	H_k	4.1 (t, 2H)
H_c	8.6 (d, 1H)	H_j	3.2 (t, 2H)
H_d	8.3 (s, 1H)	H_l	2.2 (s, 3H)
H_e, H_f	7.6 (m, 2H)		

[a] The standard in TMS.

2.042(8) Å. All bond length and angle values are in the range found in symmetrical di(μ-phenolato)-,[31] di(μ-hydroxo)-,[32] or (μ-phenolato)(μ-hydroxo)copper(II)[33-37] dinuclear compounds.

Both copper atoms are in square pyramidal surroundings. The apical position around Cu(1) is occupied by the O(4) atom of a perchlorate group, with a Cu(1)–O(4) bond length of 2.467(7) Å. The average deviation of N(I), N(2), O(1), and O(2) atoms around Cu(1) from their least-squares plane is ±0.076 Å. Cu(1) is slightly pulled out from this basal plane in the direction of the perchlorate group by 0.040 Å. The apical position around Cu(2) is occupied by a water molecule, with a Cu(2)–O(3) bond length of 2.352(7) Å. The average deviation of N(3), N(4), O(1), and O(2) around Cu(2) from their least-squares plane is ±0.69 Å, and the displacement of Cu(2) with respect to the basal plane in the direction of the apical water molecule is 0.182 Å, which is in line with the fact that the Cu(2)–OH_2 interaction is stronger than the Cu(1)–$OClO_3$ interaction. The dihedral angle between the two basal planes is equal to 172.2°. The apical ligands are situated on either side of the $[Cu_2L'(OH)]$ plane.

Table V. ^{1}H-NMR Assignments for the Di(Schiff base) HL′ Dissolved in $CDCl_3$[a]



H	δ	H	δ
H_a, H_b, H_c	8.6 (m, 3H)	H_i	3.2 (t, 2H)
H_d, H_e	7.6 (m, 2H)	H_l	2.4 (t, 2H)
H_f, H_g, H_h	7.2 (m, 3H)	H_m, H_n, H_o	2.2 (2s, 9H)
H_k	4.1 (t, 2H)	H_p	1.9 (m, 2H)
H_j	3.7 (t, 2H)		

[a] The standard is DMS.

Two neighboring dinuclear units are linked together through hydrogen bonds involving hydrogen atom H(3) of the water molecule and oxygen atom O(6) of the ligated perchlorate group related by the n-glide plane ($^1/_2 + x$, $^3/_2 - y$, $^1/_2 + z$). This builds an infinite chain parallel to the diagonal of the (a,c) plane. The second perchlorate group may be considered as noncoordinated. It builds two hydrogen bonds: the first one between its O(8) oxygen atom and the H(1) atom of the bridging hydroxo group, and the second one between its O(10) oxygen atom and the H(2) atom of the water molecule.

Conclusion

The method used to synthesize dissymmetric Schiff bases described in this paper seems to be of general applicability. We

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tested it with several couples of primary amines, and we have not yet found any exceptions. Furthermore, the yields in both mono- and di(Schiff bases) are high, often quantitative. The trivalent rare earth which protects a carbonyl function during the first stage of the synthetic process must be used in stoichiometric amount, i.e. one rare earth metal ion for two molecules of diformylphenol. This rare earth ion, however, is very easily recovered, and therefore can be reutilized in a subsequent synthesis. In principle, there are two ways to design a given di(Schiff base) according to the order in which the primary amines are introduced. Sometimes, however, one way is more convenient than the other. This is so for the di(Schiff base) HL′ reported in this work. In other respects, the imine functions can be reduced with sodium borohydride, which affords methyleneamine pendant groups.

From the di(Schiff base) HL′ we have prepared the dissymmetric copper(II) dinuclear species $[Cu_2L'(OH)](ClO_4)_2\cdot H_2O$. To our knowledge, all other dinuclear compounds derived from 2,6-diformyl-4-methylphenol and incorporating an exogenous bridge were symmetric,[33-37] even if in some cases the two metal sites were not crystallographically equivalent. The structure of $[Cu_2L'(OH)](ClO_4)_2\cdot H_2O$ in itself is not exceptional; it reflects the dissymmetry of the ligand which it arises from. This structure, however, confirms, if it were necessary, the dissymmetry of HL′.

We hope that the method described in this paper will be of interest to many chemists. We intend to explore further all the potentialities in synthetic chemistry arising from the oxophilic character of the trivalent rare earths.

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Supplementary Material Available: Tables listing crystal data collection and refinement conditions, anisotropic thermal factors, atomic coordinates for hydrogen atoms, bond distances and bond angles involving hydrogen atoms, and important least-squares planes (5 pages). Ordering information is given on any current masthead page.