A Few Examples of Cis Trans Isomerization in Complexes Involving the Oxamide Function

Jean-Pierre Costes [*]

Article

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Jean-Pierre Costes [1,2]

1 Laboratoire de Chimie de Coordination du CNRS, 205, route de Narbonne, BP 44099, Cedex 4,
   F-31077 Toulouse, France; jean-pierre.costes@lcc-toulouse.fr
2 Université de Toulouse ; UPS, INPT, Cedex 4, F-31077 Toulouse, France

Abstract: Synthesis of heterodinuclear 3d transition metal complexes in which two metal ions are introduced in equivalent coordination sites of a ligand is quite uncommon. We have previously shown that the application of the cis-trans isomerization of the oxamido group was able to furnish such a possibility. In the present paper we demonstrate that this synthetic pathway, relying on the possibility of changing the conformation (cis vs trans) of the oxamido group, can be extended to other ligands. Although we have not been able to structurally characterize these complexes, EPR and magnetic data do confirm the efficiency of this reaction pathway. We also demonstrate that the cis-trans isomerization of the oxamido group is not due to a particular property of the ion involved in the reaction. In fact, isomerization is governed by the basicity of the reaction medium. According to the reaction condition, it is possible to favor or not this phenomenon, and to increase the accessibility to a larger number of novel genuine complexes. But the oxophilic character of the lanthanide ions impedes this isomerization in 3d-4f complexes. The very weak magnetic interactions observed in these Cu-Gd complexes can be explained thanks to spin polarization.

Keywords: Coordination Chemistry; oxamide ligands; Magnetism; EPR; 3d-3d complexes; 3d-4f complexes

1. Introduction

The reaction of diamines with dicarboxylic acids or their derivatives yields condensation polymers called polyamides, molecules made of repetitive units linked by amide functions [1]. These polyamides (nylon for example) have known a huge industrial development, going from textiles to a lot of different applications [2,3]. A few decades ago, as we were interested in the syntheses of transition metal complexes with a limited number of metal atoms, we decided to prepare ligands involving a limited number of amide functions [4]. And we described synthetic processes able to give ligands possessing two amide functions only by use of diethyloxalate, a derivative of the simplest diacid molecule, oxalic acid, reacting it with diverse substituted diamine molecules (Scheme 1) [5–8]. Note that one amide function can be replaced by an oxamate or an acid function [9–11]. So, starting with a symmetrical ligand such as L^1H_4 with two equivalent coordination sites, we could isolate a mixed metal complex involving Cu^{II} and Ni^{II} ions, a result that was at first sight really unexpected [4]. It relies on the possible cis vs. trans conformation change of these oxamide ligands. In the present paper we demonstrate that this property is not limited to the L^1H_4 ligand, but that it can extended to other ligands. We also show that this conformation change can be avoided to yield again heteronuclear transition metal complexes or even heteronuclear transition metal-lanthanide complexes.
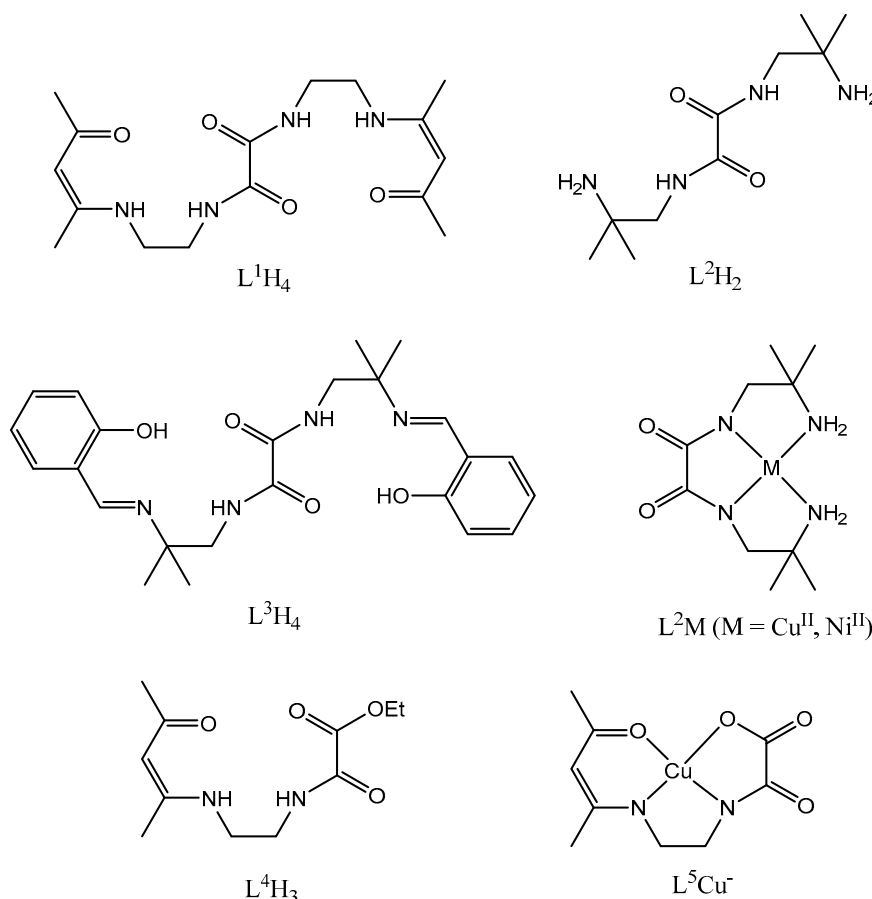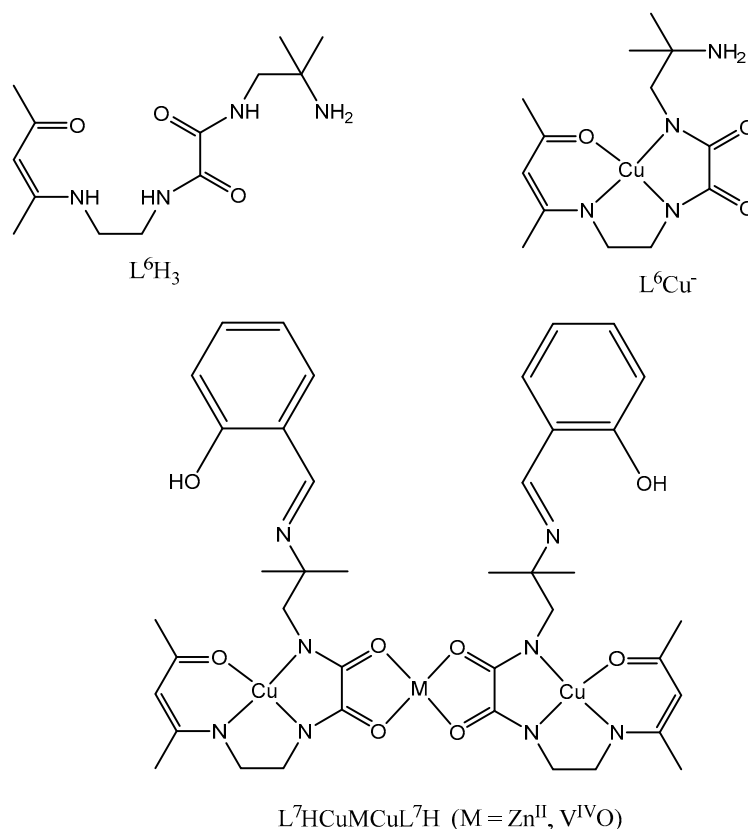
Scheme 1. Schematic representation of previously used ligands and complexes.

2. Results

2.1. 3d-3d Complexes

In previous work we showed that symmetrical oxamide ligands such as N-N'-bis(4-methyl-5-aza-3-hepten-2-on-7-yl) oxamide (L^1H_4, Scheme 1) or N-N'-bis[2,2-dimethyl-4-(2-hydroxyphenyl)-3-aza-3-buten] oxamide (L^3H_4, Scheme 1) are able to coordinate transition metal ions to yield neutral homodinuclear complexes such as CuL^1Cu, NiL^1Ni [4] or CuL^3Cu, NiL^3Ni, VOL^3VO [5], as demonstrated by the structural determination of the $[CuL^3Cu](H_2O)$ complex [7]. More surprisingly, thanks to the cis-trans isomerization of the oxamide function, the L^1H_4 can react with copper ions to give an anionic species formulated $(L^1HCuNa).2H_2O$. The EPR spectrum confirms that three nitrogen atoms are involved in the copper coordination sphere. In a following step this species acts as a ligand toward a nickel ion and yields the neutral heterodinuclear CuL^1Ni complex [4]. Note that the L^1H_4 ligand is prepared by reacting the half-unit ligand 7-amino-4-methyl-5-aza-3-hepten-2-one with diethyl oxalate in a 2:1 ratio while the reaction of this half-unit ligand with diethyl oxalate in a 1/3 ratio allows isolation of the L^4H_3 ligand (Scheme 1) [9]. The preparation of this L^3H_4 ligand necessitates a two-step reaction. The reaction of diethyl oxalate with 1,2-diamino-2-methylpropane in a 1:2 ratio first yields the L^2H_2 ligand while addition of salicylaldehyde to the aforementioned L^2H_2 ligand in a 2:1 ratio furnishes the L^3H_4 ligand [5]. According to the cis-trans isomerization of the oxamide function, it is possible to isolate L^2M complexes (M = Cu^{II}, Ni^{II}). The EPR spectrum of L^2Cu does confirm that the copper ion is bound to two pairs of inequivalent nitrogen atoms ($A_N = 15$ G and $A'_N = 8$ G) giving a superhyperfine structure of 13 lines in addition to the hyperfine structure ($A_{iso} = 95$ G, $g_{iso} = 2.08$) [8]. Addition of copper ions to this CuL^2 complex induces a trans isomerization of the oxamide ligand and formation of an infinite chain compound in which the copper ions are alternately bridged by the dideprotonated L^2 ligand and two nitrite anions, as demonstrated by the structural determination of the $[Cu(NO_2)_2CuL^2]_n$ compound [8].

In the present work we have built a new L^6H_3 ligand possessing two different coordination sites. In a first step the L^4H_3 ligand is reacted in a 1:1 ratio with 1,2-diamino-2-methylpropane, thus allowing isolation of the L^6H_3 ligand. Reaction of copper ions in a basic medium gives the anionic L^6Cu^- entity in which the copper ion presents a N_3O coordination sphere. Surprisingly, reaction with $Zn(sal)_2 \cdot 2H_2O$ or $VO(Sal)_2$ (sal = deprotonated salicylaldehyde) has not allowed to isolate the expected CuL^7Zn or CuL^7VO neutral complexes. From the analytical, FAB$^+$, magnetic data, it becomes clear that the isolated complexes correspond to the $(L^7HCu)_2Zn \cdot 2CH_3OH$ or $(L^7HCu)_2VO \cdot 2CH_3OH$ formulation, the phenol function remaining protonated. As an example the FAB$^+$ data for $(L^7HCu)_2Zn \cdot 2CH_3OH$ gives a first signal corresponding to the $[(CuL^7)_2Zn +1]^+$ cation with a maximum peak at m/z = 963 uma and a second one for the $[(CuL^7H)_2Zn + Na]^+$ cation at m/z = 985 uma. The theoretical and experimental isotopic patterns of these cations are in complete agreement (Figures S1 and S2). In order to explain such a behavior, we can expect that the free amine function reacts with the aldehyde function of the salicylaldehydato ligand coordinated to the Zn^{II} ion, which induces a decomplexation of the salicylaldehydato ligand coordinated to the Zn^{II} ion along with a concomitant protonation of the free phenol function by a proton coming from the reacting nitrogen atom. Then the oxygen atoms of the two oxamide functions that are in the vicinity of the Zn^{II} ion can enter into coordination with this ion. According to this observation, it appears that the Zn ion is not able to induce the cis-trans isomerization of the oxamide function. A similar observation is made for complex $(L^7HCu)_2VO \cdot 2CH_3OH$. The $\chi_M T$ product for this complex is constant and equal to 1.12 cm^{3}mol^{-1}K from 100 to 4 K (Figure S3). Such a value corresponding to three non interacting S = ½ ions does confirm that the vanadyl ion is again not able to induce the cis-trans isomerization of the oxamide function. Contrary to our previous results showing that Cu and Ni ions are able to induce the cis-trans isomerization [4,8], it seems that Zn and VO ions are not able to favor such an isomerization.

L^6H_3

L^6Cu^-

$L^7HCuMCuL^7H$ (M = Zn^{II}, V^{IV}O)

Scheme 2. Schematic representation of genuine ligands and complexes.

Reacting first the NiL^2 complex with salicylaldehyde in a basic medium, followed by addition of vanadyl ions allows isolation of the NiL^{3}VO complex in which the two 3d ions are coordinated to

the symmetrical ligand possessing two N_2O_2 coordination sites. As the Ni ion is diamagnetic, we observe a nice EPR spectrum with 8 lines at room temperature and in solution (CH_2Cl_2), characteristic of the vanadyl ion (Figure S4). In the present case we must conclude that the reaction of the amine functions with salicylaldehyde induces the cis-trans isomerization, thus yielding the L^3 ligand in which only one N_2O_2 coordination site is occupied by the Ni ion while the vanadyl ion is introduced in the other N_2O_2 coordination site to give the NiL^3VO compound. The eight lines EPR spectrum (Figure S4) confirms the isolation of a heterodinuclear complex, with absence of scrambling of the Ni and VO ions. Its magnetic behavior follows a Curie law with C equal to 0.40 $cm^3mol^{-1}K$. In order to understand the absence of scrambling, the reaction of the primary amine functions with the aldehyde functions must yield a $[NiL^3H]^-$ anionic species in a first stage, in which the Ni^{II} ion is coordinated to three nitrogen atoms and to the oxygen atom of a deprotonated phenol function. Then the cis-trans isomerization is favored by the basic medium, that allows the VO ion to enter into coordination in the newly formed N_2O_2 site, as in the case of the CuL^1Ni complex [4]. This result is surprising in view of our previous assertion in the above paragraph, where we were telling that the VO ion was not able to favor the cis-trans isomerization. We must conclude that the cis-trans isomerization is possible in a basic medium and is not observed in a neutral medium, whatever the concerned ions. So we again show that a symmetrical ligand possessing two identical N_2O_2 coordination sites allows formation of heterodinuclear complexes, what is quite surprising and original.
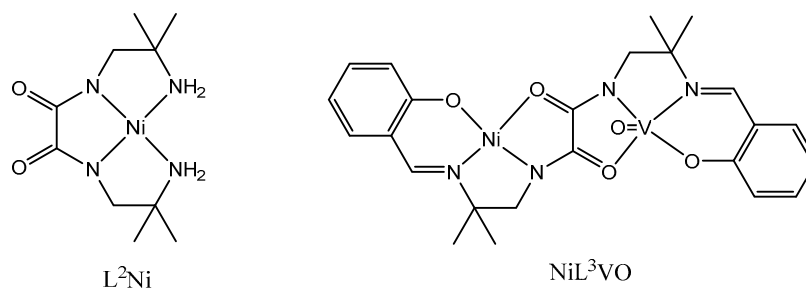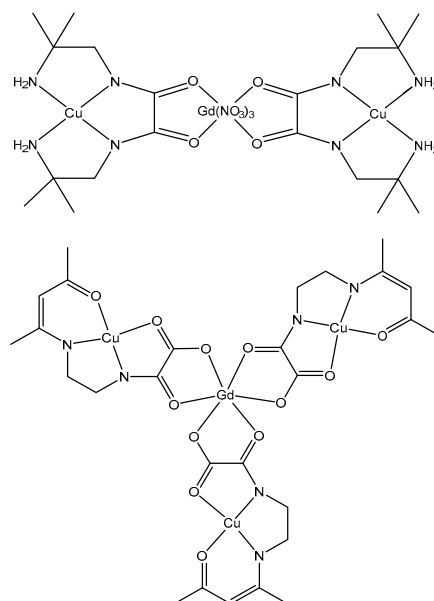

Scheme 3. Schematic representation of the starting and final complexes.

We have previously shown that the free L^3H_4 ligand reacts with vanadyl ions in basic medium to yield the VOL^3VO complex [5]. We have also demonstrated that the thermal dependence of the magnetic susceptibility follows a Curie law, with C = 0.69 $cm^3mol^{-1}K$, so that the magnetic interaction of the two vanadyl ions is absent or very weak. The EPR spectra (CH_2Cl_2 solution, 295 K) are more informative but they can be slightly different on going from a sample to another one, depending on the reaction time. It appears that two spectra are superimposed with a g parameter equal to 1.98, one with 8 lines and the other one with 15 lines, the 8 lines species appearing as a minor species giving shoulders in some lines of the main EPR spectrum after a prolongated heating, while the 8 lines species is favored before the thermal equilibrium is reached. (Figure S5). Such a result can be explained by the presence of two isomers, with a cis or trans arrangement of the V=O groups. The hyperfine splittings A are respectively equal to 94.6 x 10^{-4} cm^{-1} (8 lines spectrum) and 47.3 x 10^{-4} cm^{-1} (15 lines spectrum). From these data we can estimate the interaction parameters J. For the eight lines spectrum J must be lower than A, so that a J value lower than 10^{-3} cm^{-1} is expected, while for the fifteen lines spectrum the J parameter must be higher than A. It is expected to be comprised in between 10^{-3} and 10^{-2} cm^{-1}. These J values are very weak, in complete agreement with previous literature data [12]. In absence of structural determination, we can expect that the main compound should be the most symmetrical complex, with the apical VO groups in a trans arrangement. The previously published structural determination of the $[(terpy)Cu(ox)VO(ox)(H2O)]H2O$ complex indicates that the Cu and VO ions are linked by an oxalate bridge while a very weak Cu-VO magnetic interaction, expected to be ferromagnetic, is observed thanks to the magnetic study. Furthermore it is told that the magnetic susceptibility of the trinuclear $[(terpy)Cu(ox)VO(ox)(H2O)Cu(terpy](ClO_4) \cdot 2H2O$ complex follows a Curie law in the 4-100 K temperature domain, with a $\chi_M T$ value of 1.20 $cm^3mol^{-1}K$ [12]. This result does agree with our observation for the complex $(L^7HCu)_2VO\cdot2CH_3OH$ described above.

2.2. 3d-4f Complexes

It is possible to prepare 3d-4f entities by reaction of some of these mononuclear 3d complexes with lanthanide ions. So the L^2Cu complex reacts with gadolinium nitrate to yield a compound formulated $(L^2Cu)_2Gd(NO_3)_3 \cdot 5H_2O$ while the $[L^5Cu]^-$ anionic species gives a neutral complex formulated $(L^5Cu)_3Gd \cdot 5H_2O$. In these compounds, the oxophilic character of the Ln ions impedes any cis-trans isomerization. A look at the magnetic data is of interest. In the first complex the Gd ion is surrounded by two Cu ions and the $\chi_M T$ product is equal to 8.30 cm^{3}mol^{-1}K at 300 K. It remains constant till 10 K and then slightly decreases to 8.14 cm^{3}mol^{-1}K at 2K (Figure S6). In the second compound the Gd ion is surrounded by three Cu ions. The $\chi_M T$ product is equal to 9.15 cm^{3}mol^{-1}K at 300 K, does not change in the 20-300 K temperature domain while a slight increase at 9.80 cm^{3}mol^{-1}K is observed at very low temperature (Figure S7). We have previously shown that spin polarization is the mechanism that allows to understand the strength and sign of the magnetic Cu–Gd interactions in complexes assembling Cu and Gd ions [13]. When spin polarization is active an odd number of bridging atoms in between the ions bearing the spins favors a parallel alignment of the spins, whereas an even number of bridging atoms favors an antiparallel alignment. In the present complexes we have a mixture of even and odd numbers of atoms in the ligand bridging the metal ions, so that the resulting magnetic interaction is expected to be very weak. Furthermore we have to remember that the presence of singly occupied $3d_{x2-y2}$ orbitals is needed for the observation of ferromagnetic 3d-Gd interactions, the 3d ions with unoccupied $3d_{x2-y2}$ orbitals yielding antiferromagnetic 3d-Gd interactions [14]. In the trinuclear CuGdCu complex $(L^2Cu)_2Gd(NO_3)_3 \cdot 5H_2O$, the Cu and Gd ions are interacting through two three-atom OCN bridges and two four-atom OCCN bridges. It has been previously shown that such OCN bridges [13] and OCO bridges [15] give weak ferromagnetic interactions. Observation of a weak antiferromagnetic interaction in the trinuclear complex means that the interaction through the four-atom OCCN bridge overcomes the one coming from the three-atom OCN bridge. In the tetranuclear complex $(L^5Cu)_3Gd \cdot 5H_2O$, the Cu and Gd ions are interacting through two three-atom OCO and OCN bridges, and two four-atom OCCO and OCCN bridges. Observation of a weak ferromagnetic interaction implies that, according to the magnetic behavior of the trinuclear $(L^2Cu)_2Gd(NO_3)_3 \cdot 5H_2O$ complex, the magnetic interaction through the three-atom OCO bridges is slightly larger than the one coming from the four-atom bridges and becomes the predominant magnetic interaction. Eventually we can conclude that the magnetic behavior of these two complexes assembling Cu and Gd ions can be understood by the presence of an active spin polarization interaction. But we cannot forget that these interactions are very weak. Structural determinations of similar complexes along with theoretical calculations will be necessary to confirm such an assertion.

Scheme 4. Schematic representation of trinuclear and tetranuclear Cu-Gd complexes.

3. Discussion

Although we have not been able to structurally characterize these genuine complexes, EPR and magnetic data do confirm the efficiency of this reaction pathway. The example of the heterodinuclear NiL^3VO complex is quite informative. If scrambling was active, a mixture of NiL^3Ni and VOL^3VO complexes in a 1/1 ratio would be present. The magnetic data corresponding to such a mixture could agree with the data of the genuine NiL^3VO complex, as we demonstrate that the magnetic interaction in the dinuclear VOL^3VO complex is very weak and that de dinuclear NiL^3Ni complex is diamagnetic. On the contrary, the EPR data become informative. Observation of an eight-lines spectrum for the NiL^3VO complex does not agree with the fifteen-lines spectrum corresponding the VOL^3VO complex. This spectrographic result does confirm the existence of a genuine NiL^3VO entity. In addition the study of the homodinuclear VOL^3VO complex indicates that this entity is not unique, with the axial VO groups in a trans or cis conformation. The EPR study shows that the fifteen-lines species becomes the main product after a prolongated heating, so that we can expect that the most symmetrical species is the main species and that it corresponds to the trans conformation of the VO groups. It is not surprising to think that the eight-lines species corresponding to the cis conformation is favored before the thermal equilibrium is reached. The strength of the magnetic interaction in these two conformational VOL^3VO species can also be deduced from the EPR spectrum, thus confirming the weakness of these interactions.

We also demonstrate that the cis-trans isomerization of the oxamido group is not due to a particular property of the ion involved in the reaction. Indeed isomerization is governed by the basicity of the reaction medium. According to the reaction condition, it is possible to favor or not this phenomenon, and to increase the accessibility to a larger number of novel genuine complexes. In that case, the positive FAB mass spectra data are of prime interest for the complexes resulting from an absence of cis trans isomerization. Due to the isotopic pleiade of the 3d and 4f ions, the corresponding cationic signals give a direct information on the molecular mass of these species and the number of metal ions involved in a compound, at the exception of the solvent molecules (coordinated or not). This is the case for the neutral complexes $(L^7HCu)_2Zn \cdot 2CH_3OH$, $(L^7HCu)_2VO \cdot 2CH_3OH$, $(L^5Cu)_3Gd \cdot 5H_2O$ for which the main peaks appearing at 963, 966 and 983 uma, respectively, correspond to the $[(CuL^7H)_2Zn +1]^+$, $[(CuL^7H)_2VO +1]^+$ and $[(L^5Cu)_3Gd + 1]^+$ cationic species. For the $(L^2Cu)_2Gd(NO_3)_3 \cdot 5H_2O$ complex possessing three nitrato anions, the main signal appears at 866 uma, which corresponds to the $[(L^2Cu)_2Gd(NO_3)_2]^+$ formulation, with a loss of a nitrato anion. The magnetic data of these different entities do agree with these formulae and confirm the presence or absence of very weak magnetic interactions. Eventually the oxophilic character of the lanthanide ions limits the use of this synthetic pathway because it impedes this isomerization. As the magnetic interaction in 3d-4f complexes is dominated by spin polarization, very weak magnetic interactions can be expected in these complexes, due to the antagonist effects coming from the presence of even and odd numbers of bridging atoms in the ligand transmitting the interaction between the Cu and Gd ions.

4. Materials and Methods

2-methyl-1,2-diaminopropane, $Cu(Ac)_2 \cdot H_2O$, $Ni(Ac)_2 \cdot 4H_2O$, $Gd(NO_3)_3 \cdot 5H_2O$, (Aldrich) were used as purchased. The ligands L^1H_4 [4], L^4H_3 [9], L^2H_2 [5], L^3H_4 [5] and the complexes L^2Cu [5], VOL^3VO [5], $L^5CuNa \cdot 1.33H_2O$ [9] were prepared as previously described. High-grade solvents (dichloromethane, dimethylformamide, diethyl oxide, diisopropyl oxide, acetone, ethanol and methanol) were used for the syntheses of ligands and complexes.

4.1. Complexes

L^2Ni. To L^2H_2 (1 g, 4.35 mmol) in ethanol (20 cm^3) was first added an aqueous solution (5 cm^3) of NaOH (0.35 g, 8.7 mmol). Then, nickel acetate (1.08 g, 4.35 mmol) in water (10 cm^3) was added dropwise under stirring. Three hours later, the orange precipitate which appeared progressively was filtered off, washed with cold ethanol and diethyl ether and air-dried. Yield: 0.85 g (68%). Anal. Calcd for $C_{10}H_{20}N_4NiO_2$ (287.0): C, 41.85; H, 7.02 ; N, 19.52. Found : C, 41.52 ; H, 6.89 ; N, 19.23 %.

L⁶CuNa·2H₂O. A dichloromethane solution (30 mL) of L^4H_3 (1.7 g, 7.0 mmol) and 2-methyl-1,2-diaminopropane (0.62 g, 7.0 mmol) was stirred overnight. To the oil obtained by solvent evaporation was added ethanol (20 mL) with stirring, followed by a water solution (3 mL) of NaOH (0.84 g, 21.0 mmol) and then a dropwise addition of an ethanol solution (20 mL) of $Cu(ClO_4)_2·6H_2O$ (2.6 g, 7.0 mmol). The resulting solution was stirred for three hours and concentrated to 15mL. Addition of acetone (60 mL) induced formation of lilac precipitate that was filtered off, washed with acetone and dried. Yield : 0.85g (30 %). Anal. Calcd for $C_{13}H_{25}CuN_4NaO_5$ (403.5): C, 38.66; H, 6.24; N, 13.87. Found : C, 38.45 ; H, 6.16 ; N, 13.53.

(L⁷HCu)₂VO·2CH₃OH. A methanol solution (15 mL) containing L⁶CuNa·2H₂O (0.20 g, 0.5 mmol) and $VO(Sal)_2·H_2O$ (0.16 g, 0.5 mmol) was heated and stirred for 30 min. The resulting solution was cooled and evaporated. Addition of CH_2CL_2 (20 mL) give a solution that was filtered and concentrated to a few mL. Addition of isopropyl ether induced formation of a violet precipitate that was filtered off by suction and dried. Yield : 0.08 g (31 %). Anal. Calcd for $C_{42}H_{58}Cu_2N_8O_{11}V$ (1029.0): C, 49.02; H, 5.68 ; N, 10.89. Found : C, 48.60 ; H, 5.36 ; N, 10.65. FAB⁺ (DMSO, mnba): m/z = 966 (100), [L⁷HCu)₂VO + 1]⁺.

(L⁷HCu)₂Zn·2CH₃OH. A methanol solution (15 mL) containing L⁶CuNa·2H₂O (0.20 g, 0.5 mmol) and $Zn(Sal)_2·2H_2O$ (0.17 g, 0.5 mmol) was heated and stirred for 30 min. The resulting solution was cooled and evaporated. Addition of CH_2CL_2 (20 mL) give a solution that was filtered and concentrated to a few mL. Addition of isopropyl ether induced formation of a red precipitate that was filtered off by suction and dried. Yield : 0.09 g (35 %). Anal. Calcd for $C_{42}H_{58}Cu_2N_8O_{10}Zn$ (1027.5): C, 49.10; H, 5.69 ; N, 10.91. Found : C, 48.65 ; H, 5.32 ; N, 10.55. FAB⁺ (DMSO, mnba): m/z = 963 (87), [L⁷HCu)₂Zn + 1]⁺, 985 (55) [L⁷HCu)₂Zn + Na]⁺.

NiL³VO. A mixture of L²Ni (0.15 g, 0.5 mmol), sodium acetate (0.08 g, 1 mmol) in methanol (15 mL) was first stirred, followed by addition of $VO(Sal)_2·H_2O$ (0.16 g, 0.5 mmol) and then heated for thirty minutes and left to cool under stirring. The maroon precipitate that appeared was filtered off, washed with diethyl ether and dried . Yield : 0.12 g (41 %). Anal. Calcd for $C_{24}H_{28}N_4NiO_6V$ (578.1): C, 49.86; H, 4.88; N, 9.69. Found: C, 49.38; H, 4.86; N, 9.59.

(L²Cu)₂Gd(NO₃)₃·5H₂O. A mixture of L²Cu (0.15 g, 0.5 mmol) and $Gd(NO_3)_3·5H_2O$ (0.11 g, 0.25 mmol) in methanol (5 mL) was stirred for 1 hour. Addition of acetone (20 mL) and isopropylether (50 mL) induced formation of a violet precipitate that was filtered off, washed with acetone and diethyl ether. Yield: (0.23 g, 90 %). Anal. Calcd for $C_{20}H_{50}Cu_2GdN_{11}O_{18}$ (1017.0): C, 23.62 ; H, 4.96 ; N, 15.15. Found : C, 23.34 ; H, 4.76 ; N, 14.82. . FAB⁺ (DMSO, mnba): m/z = 866 (100), [(L²Cu)₂Gd(NO₃)₂]⁺.

(L⁵Cu)₃Gd·5H₂O. To L⁵CuNa·1.33H₂O (0.2 g, 0.62 mmol) in water (5 mL) was added with stirring $Gd(NO_3)_3·5H_2O$ (0.09 g, 0.20 mmol) dissolved in methanol (10 mL). The violet precipitate that appeared quickly was filtered off, washed with water, acetone and diethyl ether. Yield: (0.11 g, 50 %). Anal. Calcd for $C_{27}H_{43}Cu_3GdN_6O_{17}$ (1071.5): C, 30.26 ; H, 4.04 ; N, 7.84. Found : C, 30.04 ; H, 4.06 ; N, 7.76. FAB⁺ (DMSO, mnba): m/z = 983 (100), [(L⁵Cu)₃Gd + 1]⁺.

4.2. Physical Measurements

C, H, and N elemental analyses were carried out at the Laboratoire de Chimie de Coordination Microanalytical Laboratory in Toulouse, France. Mass spectra (FAB⁺) were recorded in dmf as solvent and 3-nitrobenzyl alcohol matrix with a Nermag R10–10 spectrometer. Magnetic data were obtained with a Quantum Design MPMS SQUID susceptometer. Magnetic susceptibility measurements were performed in the 2-300 K temperature range under a 0.1 T applied magnetic field, and diamagnetic corrections were applied by using Pascal's constants [16].

5. Conclusions

Synthesis of heterodinuclear 3d transition metal complexes in which two metal ions are introduced in equivalent coordination sites of a ligand is quite uncommon. In the present paper we shown that the application of the cis-trans isomerization of the oxamido group, that was observed previously, can be extended to other ligands. Although we have not been able to structurally characterize these genuine complexes, EPR and magnetic data do confirm the efficiency of this

reaction pathway. The EPR spectrum of the homodinuclear VOL^{3}VO complex does agree with the presence of two conformers, with a cis or trans arrangement of the axial VO groups. We also demonstrate that the cis-trans isomerization of the oxamido group is not due to a particular property of the 3d ion involved in the reaction. Indeed isomerization is governed by the basicity of the reaction medium. According to the reaction condition, it is possible to favor or not this phenomenon, and to increase the accessibility to a larger number of novel genuine complexes. But the oxophilic character of the lanthanide ions limits the use of this synthetic pathway because it impedes this isomerization in 3d-4f complexes. As the magnetic interaction in Cu-Gd complexes is dominated by spin polarization, very weak magnetic interactions can be expected in these complexes, due to the antagonist effects coming from the presence of even and odd numbers of bridging atoms in the ligand transmitting the interaction between the Cu and Gd ions.

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