The Ligand 1,10-Phenanthroline-2,9-dicarbaldehyde Dioxime can Act Both as a Tridentate and as a Tetradentate Ligand − Synthesis, Characterization and Crystal Structures of its Transition Metal Complexes

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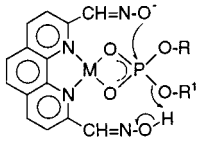
The polydentate ligand **L** has been prepared by treating 1,10-phenanthroline-2,9-dicarbaldehyde with hydroxylamine. This ligand and its complexes with Zn^{II}, Cu^{II}, Cd^{II}, Co^{II} and Ni^{II} were designed as potential agents for nucleic acid hydrolysis and have been characterized by elemental analysis, NMR spectroscopy, ES-MS and X-ray diffraction analysis. The ligand acts as a tridentate ligand in most cases, to form monomeric trigonal-bipyramidal, square-pyramidal or square-bipyramidal structures. In the case of metallation with cadmium nitrate it acts as a tetradentate ligand to give a pentagonal-bipyramidal structure. Dissociation of the oxime group to an oximate, which acts as an anionic bridging ligand, was observed in the case of metallation with zinc acetate thus giving rise to dimers and/or polymers.

Introduction

The metal-chelating properties of the 1,10-phenanthroline ligand and its derivatives have been utilized in a range of analytical reagents, as well as for the development of bioorganic probes.[1] In attempts to obtain hydrolytic chemical agents which are able to hydrolyze phosphodiester bonds in nucleic acids in the model of DNA or RNA nucleases,[2] we report here on the synthesis and the characterization of zinc, cadmium, copper, cobalt and nickel complexes of 1,10-phenanthroline-2,9-carbaldehyde dioxime. These complexes (metal cation) were designed to interact with the initial negatively charged phosphate, and to promote hydrolysis of the phosphodiester P−O bond through nucleophilic attack on the phosphorus atom by one oximate group, the other oxime group stabilizing the leaving oxygen atom (see hereafter for a possible schematic representation of the ternary system ligand/metal/phosphodiester: Scheme 1).[3−5] The oximate group has been chosen because it can effectively act as a nucleophile endowed with nucleolytic activity, as previously reported for free ligands such as pyridine-2-aldoxime[6] or simple inorganic complexes such as metallated complexes of 2-acetylpyridine oxime.[7] Although preliminary results on cleavage of nucleic acids models are rather deceiving, the interest for such structures lies also in the previously reported antitumor[8] and antimicrobial[9] activities of the phenanthrolinedicarbaldehyde derivative and/or of the corresponding dioxime ligand **L**. In the latter case, the activity might be related to the in vivo formation of metal chelates. In a related topic, the cytotoxic activity of tetradentate palladium complexes of phenanthroline-dimathanamines has been recently reported.[10]

The improved synthesis of the ligand 1,10-phenanthroline-2,9-dicarbaldehyde dioxime **L**, and the preparation and complete characterization of seven complexes of **L** are presented.



Scheme 1

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Synthesis and Characterization

The Ligand

The only reported method for the synthesis of 1,10-phenanthroline-2,9-dicarbaldehyde (Figure 1) involves the oxidation of the commercially available neocuproine by selenium dioxide in dioxane[11,12] or ethanol.[9] After completion of the reaction, the selenium separates as a yellow/red form which is difficult to filter, and some of it is retained in solution as a colloid. The elimination of selenium impurities is extremely difficult. This explains the fact that in the literature either the yield of the reaction is satisfactory (70%) but the product is analytically impure,[11] or the yields are not reported.[9,12] In addition, from an environmental viewpoint the replacement of SeO_2 by another oxidant is desir-

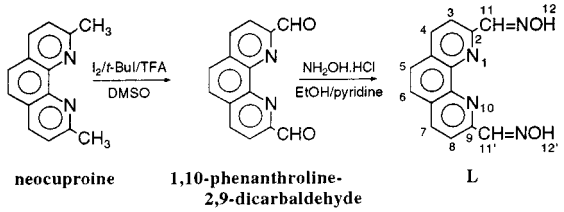

Figure 1. Synthesis of ligand **L**

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able. Therefore, in order to prepare 1,10-phenanthroline-2,9-dicarbaldehyde, we used the procedure initially described for the oxidation of methyl to formyl groups in heteroaromatic derivatives with iodine in dimethyl sulfoxide,[13] a method which was improved later by using *tert*-butyl iodide.[14] This procedure, applied to neocuproine, gave pure 1,10-phenanthroline-2,9-dicrbaldehyde in 48% yield as a hemihydrate in crystalline form. This dialdehyde derivative was then converted into the dioxime **L** according to the method previously reported.[11] Compound **L** has been fully characterized, including a crystallographic study which allowed for the determination of the *E* configuration of the two oxime groups, and for the observation of the co-existence of two different conformations (*s-cis* and *s-trans*) around the $C_{Ar}-C(=N-)$ single bond between the oxime group and the phenanthroline unit in the crystal (see below). In solution, these two conformations are probably in fast equilibrium since the NMR spectrum for **L** in DMSO corresponds to a symmetrical molecule.

Metal Complexes (Figure 2)

The formation of nearly all complexes, besides one, was achieved at room temp. under approximately stoichiometric conditions (metal ion/ligand molar ratio was in the range 0.64 to 1.3), after 2−30 min of reaction in DMF ([Zn**L**Cl_2 and [Cu**L**Cl_2)], DMSO ([Zn**L**$(AcO)]_n$)] or DMSO/H_2O ([Cd**L**Cl_2], [Co**L**Cl_2] and [Ni**L**(DMSO)Cl_2]). In all these cases, the reaction products were isolated as analytically pure species on spontaneous precipitation. Compound [Cd**L**(OH_2)(DMSO)$(NO_3)]^+$] was only prepared as crystals for X-ray diffraction analysis (see below). On the basis of elemental analyses, all complexes (whatever was the method of preparation), exhibited an unequivocal metal-to-ligand stoichiometry of 1:1. In some cases, one or two molecules of solvent were present (DMF, DMSO or water). Moreover, the CHN data showed that all complexes present existed as monomers, except [Zn**L**$(AcO)]_n$ which existed as dimer/polymer. The polymeric structure of this last compound was also confirmed by the NMR-spectroscopic data with

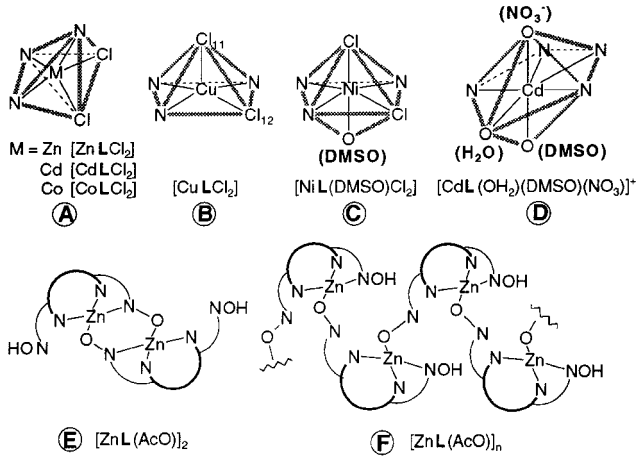

Figure 2. Proposed structures for complexes M−**L** (in structure **D**, one nitrate ion is outside the coordination sphere; in structure **E**/**F**, at least one acetate ion per metallated ligand is outside the coordination sphere)

the methyl resonance peak integrating for only one methyl group per metal unit and the other ligand in this case being an oximate bridging anion.

Data obtained by positive FAB-MS indicated that monocationic species corresponding to the complex having lost one proton $[\mathbf{L} + M - H^+]^+$ or retained one of the two anionic labile ligands $[\mathbf{L} + M + Cl^-]^+$, with an additional solvent molecule (water, DMSO), are usually observed. In addition, the redox-active copper complex gave some peaks corresponding to Cu^I monomeric $[\mathbf{L} + Cu^I]^+$ or dimeric species (dimer 2:1 $[2 \times \mathbf{L} + Cu^I]^+$). In ES-MS, only monocationic species were observed. They predominantly corresponded to the complex ligand/metal having lost one proton ($\mathbf{L} + M - H^+$) or retained one of the two anionic ligands ($\mathbf{L} + M + Cl^-$ or AcO^-). The presence of one or two solvent molecules could be observed, as well as in some cases, dehydration of the fragment (the aldoxime group giving possibly a nitrile function). In addition, we observed minor peaks, probably generated in the MS machine, corresponding to dimeric species of the type 2:1 (cases of $2 \times \mathbf{L} + Zn - H^+$, $2 \times \mathbf{L} + Cu^I$, $2 \times \mathbf{L} + Co^{III} - 2\,H^+$ and $2 \times \mathbf{L} + Ni^{II} - H^+$) or of the type 2:2 (cases of $2 \times \mathbf{L} + 2 \times Zn - 3\,H^+$, $2 \times \mathbf{L} + 2 \times Zn - 2\,H^+ + Cl^-$, $2 \times \mathbf{L} + 2 \times Zn - H^+ + 2\,Cl^-$, $2 \times \mathbf{L} + 2 \times Zn - 3\,H^+$, $2 \times \mathbf{L} + 2 \times Cu - 3\,H^+$ or $2 \times \mathbf{L} + 2 \times Cu - 2\,H^+ + Cl^-$, $2 \times \mathbf{L} + 2 \times Cd - H^+ + 2\,Cl^-$). The polymeric compound ([Zn**L**$(AcO)]_n$ not only gave peaks for the monomeric species $\mathbf{L} + Zn - H^+$ (with addition or loss of one water molecule) but also for dimers of the type 2:2 ($2 \times \mathbf{L} + 2 \times Zn - 3\,H^+$ or $2 \times \mathbf{L} + 2 \times Zn - 2\,H^+ + AcO^-$) or trimers of the type 3:3 ($3 \times \mathbf{L} + 3 \times Zn - 5\,H^+$), these latter polymeric fragments being the most abundant.

On complexation of cadmium chloride with ligand **L** (giving [Cd**L**Cl_2]), we observed changes in the ^1H NMR spectrum with a broadening of the peaks corresponding to 4-H/7-H and 11-H/11′-H (pattern at $\delta = 8.92$), and to 12-H/12′-H (massif at $\delta = 12.73$). The other signals remained sharp and well resolved. Increasing the temperature up to 60° C allowed for the resolution of the broad signal at $\delta = 8.92$ into one doublet at $\delta = 8.90$ (4-H/7-H) and one singlet at $\delta = 8.89$ (11-H/11′-H) and for the significant reduction of the width of the 12-H/12′-H signal. A similar behaviour was observed for complex [Cd**L**(OH_2)(DMSO)$(NO_3)]^+$. Although the crystalline structures of [Cd**L**Cl_2] and [Cd**L**(OH_2)(DMSO)$(NO_3)]^+$ are different (see below), these NMR-spectroscopic data support a common symmetrical structure in solution, with the ligand acting as a tetradentate ligand. With regard to the two zinc derivatives [Zn**L**Cl_2] and [Zn**L**$(AcO)]_n$, the ^1H NMR spectra were too complex and did not give any structural information, except for [Zn**L**$(AcO)]_n$ where the aromatic/aliphatic proton ratio supports a structure with only one acetate group per molecule.

Description of the Crystal Structures of L, [ZnLCl_2], [CuLCl_2], [CdLCl_2], [CdL(OH_2)(DMSO)$(NO_3)]^+$, [CoLCl_2] and [NiL(DMSO)Cl_2]

The molecular structure of **L**, as determined by X-ray analysis, is shown with its atom labelling scheme in Fig-

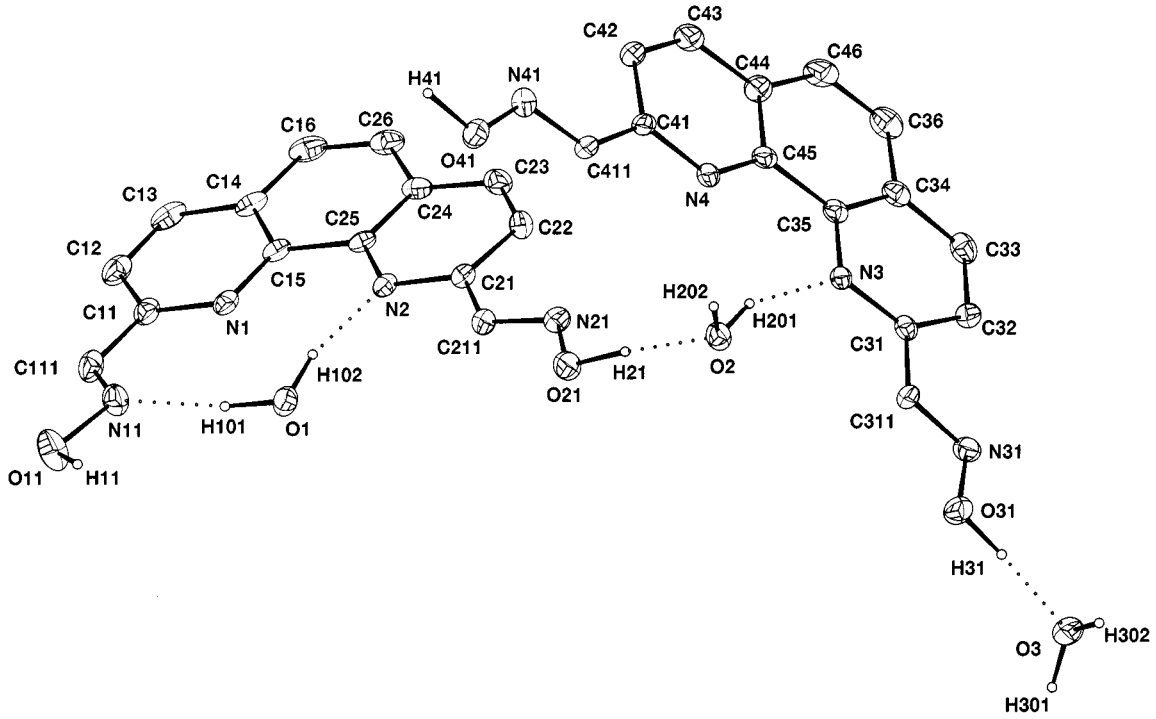

Figure 3. Molecular structure of **L** with atom labelling scheme illustrating the hydrogen bond between the two independent molecules (**La** and **Lb**) within the asymmetric unit; ellipsoids represent 30% probability; most of the hydrogen atoms have been omitted for clarity

ure 3. The asymmetric unit is composed of two independent molecules of the ligand and three water molecules. The two molecules **La** and **Lb** (Table 1) are linked by hydrogen bonds through one of the water molecule (O2). Moreover, each of these water molecules is engaged in hydrogen bonding with symmetrically related molecules **La** and **Lb**, thus developing a three-dimensional hydrogen bond network (Table 2). The two molecules **La** and **Lb** have an essentially planar conformation with the largest deviation from the plane being 0.168(5)Å at O(11) for molecule **La** and −0.083(5) Å at O(41) for **Lb**. The largest deviation is observed for molecule **La** where there are hydrogen-bond interactions with the water molecule (O1) (Figure 3). The C−N and C−C distances in the phenanthroline fragment (Table 1) are within the range observed in related molecules.[15] In both molecules **La** and **Lb**, the oxime groups have an *E* configuration. However, if in molecule **Lb** the conformation of both oxime groups is *s-trans* with respect to the N atoms of the phenanthroline fragment, then in molecule **La** these two groups show two different conformations, *s-cis* and *s-trans*, around the $C_{Ar}-C(=N)$ single bond. This difference in conformation is related to the occurrence of hydrogen bonds between the water molecule (O1) and the two N atoms, the N(11) of the oxime group and the N(2) of the phenanthroline fragment in molecule **La** (Table 2).

Table 1. Bond lengths [Å] for ligand **L**; esd values in parentheses refer to the last significant digit

Molecule **a**		Molecule **b**	
O(11)−N(11)	1.407(4)	O(31)−N(31)	1.425(4)
O(21)−N(21)	1.403(4)	O(41)−N(41)	1.416(5)
N(2)−C(21)	1.350(5)	N(3)−C(31)	1.335(5)
N(2)−C(25)	1.362(5)	N(3)−C(35)	1.365(5)
N(1)−C(11)	1.351(5)	N(4)−C(41)	1.345(5)
N(1)−C(15)	1.355(5)	N(4)−C(45)	1.363(5)
N(11)−C(111)	1.282(5)	N(31)−C(311)	1.278(5)
N(21)−C(211)	1.272(5)	N(41)−C(411)	1.270(5)
C(11)−C(12)	1.395(6)	C(31)−C(32)	1.407(6)
C(11)−C(111)	1.457(6)	C(31)−C(311)	1.469(5)
C(12)−C(13)	1.368(6)	C(32)−C(33)	1.359(6)
C(13)−C(14)	1.407(6)	C(33)−C(34)	1.406(6)
C(14)−C(15)	1.413(6)	C(34)−C(35)	1.413(6)
C(14)−C(16)	1.428(6)	C(34)−C(36)	1.426(6)
C(15)−C(25)	1.457(5)	C(35)−C(45)	1.455(5)
C(16)−C(26)	1.351(6)	C(36)−C(46)	1.341(6)
C(21)−C(22)	1.398(6)	C(41)−C(42)	1.409(6)
C(21)−C(211)	1.463(6)	C(41)−C(411)	1.456(6)
C(22)−C(23)	1.360(6)	C(42)−C(43)	1.355(6)
C(23)−C(24)	1.403(6)	C(43)−C(44)	1.413(6)
C(24)−C(25)	1.406(6)	C(44)−C(45)	1.409(5)
C(24)−C(26)	1.434(6)	C(44)−C(46)	1.430(6)

The crystallization of metal complexes, besides [Cd**L**Cl_2] (which was obtained by transmetallation of [Zn**L**Cl_2] in the presence of cadmium nitrate) and [Zn**L**(AcO)]$_n$ (unsuccessful crystallization attempts), was achieved at room temp. under approximately stoichiometric conditions (the metal/ligand ratio ranged from 1.3 to 1.9), after 2−7 days in DMSO or DMSO/H_2O. Since the three complexes [Zn**L**Cl_2], [Cd**L**Cl_2] and [Co**L**Cl_2] have closely related structures, only the molecular view of the cobalt complex [Co**L**Cl_2] with its atom labelling scheme is shown in Figure 4. The asymmetric unit also contains a DMSO solvent molecule which is hydrogen-bonded to the OH group of the

Table 2. Specified hydrogen bonds for ligand **L**

D−H [Å]	H···A [Å]	D···A [Å]	<(DHA) [°]	
1.04(3)	1.67(4)	2.664(5)	159(5)	O(11)−H(11)···O(1)[a]
1.03(3)	1.60(3)	2.620(4)	173(5)	O(21)−H(21)···O(2)
1.02(3)	1.66(3)	2.672(4)	173(5)	O(31)−H(31)···O(3)
1.02(3)	1.66(3)	2.670(4)	168(5)	O(41)−H(41)···O(1)[b]
1.00(3)	1.87(3)	2.860(5)	170(5)	O(1)−H(101)···N(11)
1.02(3)	1.82(3)	2.820(4)	166(5)	O(1)−H(102)···N(2)
0.99(3)	1.98(3)	2.915(4)	156(5)	O(2)−H(201)···N(3)
0.99(3)	2.39(5)	3.093(4)	127(4)	O(2)−H(201)···N(4)
1.00(3)	1.87(3)	2.870(4)	172(5)	O(2)−H(202)···O(31)[c]
1.01(3)	1.91(4)	2.842(4)	153(5)	O(3)−H(301)···O(21)[d]
1.01(3)	1.90(3)	2.845(4)	156(5)	O(3)−H(302)···O(41)[c]

[a] Symmetry transformations used to generate equivalent atoms: $-x-1, -y+2, -z+2$. − [b] $x+1, y, z$. − [c] $-x, -y+1, -z+2$. − [d] $-x-1, -y+1, -z+2$.

With regard to the complex [Cu**L**Cl_2 (Table 4), the asymmetric unit is composed of two molecules **a** and **b** of the complex and four DMSO solvent molecules which are each hydrogen-bonded to the OH groups. Although the metal atom is surrounded by the same ligands as in the previous complexes, the geometry around the metal center is best described as being a distorted square-pyramidal structure (Figure 2B and 5, Table 4); the N(1)−Cu(1)−Cl(12) angle increases to the mean value 151.8° (the corresponding N(1)−M−Cl(1) angles range from 121.2 to 127.7° for [Zn**L**Cl_2], [Cd**L**Cl_2] and [Co**L**Cl_2]), whereas the N(1)−Cu−Cl11) angle decreases to the mean value 99.7° (the corresponding angles range from 113.7 to 118.7° for [Zn**L**Cl_2], [Cd**L**Cl_2] and [Co**L**Cl_2]. Thus, in [Cu**L**Cl_2], the nitrogen atoms N(1), N(2), N(11) and the chrorine atom

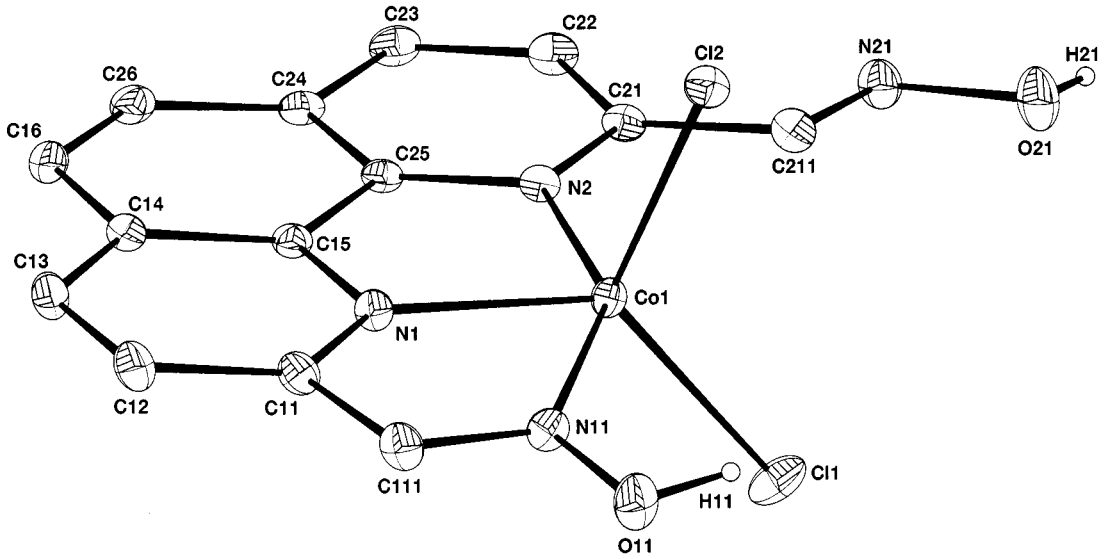

Figure 4. Molecular view of complex [Co**L**Cl_2 with atom labelling scheme; ellipsoids are drawn at 30% probability; hydrogen atoms have been omitted for clarity

coordinated oxime group. Such hydrogen bonding between the DMSO solvent and the complex occurs in all the related compounds. In these three complexes, the structure consists of a metal atom surrounded by one ligand **L** and two chlorine atoms in a distorted trigonal-bipyramidal geometry (Figure 2, **A** and Table 3). The axial positions are occupied by two nitrogen atoms N(2) and N(11) [N(2)−M−N(11) = 148.28(9)°, 138.03(15)° and 151.09(6)°, for the Zn, Cd and Co complexes, respectively]. The equatorial plane is made by the two chlorine atoms and the nitrogen atom N(1) of the phenanthroline fragment. The equatorial plane and the plane defined by the axial positions make a dihedral angle of 88.62(4)°. In the three complexes the metal center is coordinated to N(1), N(2) of the rigid 1,10-phenanthroline and to N(11) of the oxime group forming two fused five-membered rings with very acute N−M−N angles: N(1)−M−N(2) = 76.22(9)°, 69.58(15)° and 77.27(6)° and N(1)−M−N(11) = 72.07(9)°, 68.48(16)° and 73.94(6)°, for compounds [Zn**L**Cl_2], [Cd**L**Cl_2] and [Co**L**Cl_2], respectively.

Cl(12) form the basal plane, whereas Cl(11) occupies the apex position (Figure 2B). Applied to the five-coordinated structures [Cu**L**Cl_2), [Zn**L**Cl_2], [Cd**L**Cl_2] and [Co**L**Cl_2], the calculation of the geometric parameter $\tau = (\beta - \alpha)/60$ [α = N(1)−M−Cl (1 or 12), β = N(2)−M−N(11)] gives the values 0.03, 0.39, 0.28 and 0.42, respectively. Since τ is a parameter used as an index of the degree of trigonality,[16], these values support a tetragonal geometry for [Cu**L**Cl_2] (τ close to zero) and are in agreement with a structure intermediate between the perfectly tetragonal (τ = zero) and trigonal-bipyranidal (τ = 1) geometries for [Zn**L**Cl_2], [Cd**L**Cl_2] and [Co**L**Cl_2]. In [Cu**L**Cl_2], the Cu atom is 0.358 Å (mean value) above the best plane defined by the three N atoms and the Cl(12).. As in the previous three complexes, the metal center is coordinated to N(1) and N(2) of the rigid 1,10-phenanthroline and N(11) of one oxime group forming two fused five-membered rings with acute N−Cu−N angles: N(1)−Cu(1)−N(2) = 78.44(11)° for molecule **a** and 78.18(11)° for molecule **b**, N(1)−Cu(1)−

Table 3. Selected bond lengths [Å] and angles [°] for complexes [Zn**L**Cl_2], [Cd**L**Cl_2], and [Co**L**Cl_2]

	[Zn**L**Cl_2]	[Cd**L**Cl_2]	[Co**L**Cl_2]
Bond lengths			
M−N(1)	2.057(2)	2.292(4)	2.0193(16)
M−N(2)	2.275(3)	2.458(5)	2.2386(16)
M−Cl(2)	2.2553(9)	2.4367(14)	2.2529(8)
M−Cl(1)	2.2203(10)	2.4129(15)	2.2535(7)
M−N(11)	2.382(3)	2.470(5)	2.2726(17)
O(11)−N(11)	1.381(3)	1.380(6)	1.372(2)
O(21)−N(21)	1.388(3)	1.390(7)	1.387(2)
N(1)−C(11)	1.336(4)	1.331(7)	1.332(2)
N(1)−C(15)	1.355(4)	1.357(7)	1.349(2)
N(2)−C(21)	1.332(4)	1.328(7)	1.333(2)
N(2)−C(25)	1.358(4)	1.366(7)	1.358(2)
N(11)−C(111)	1.266(4)	1.281(7)	1.274(3)
N(21)−C(211)	1.272(4)	1.265(8)	1.268(3)
Angles [°]			
N(1)−M−N(2)	76.22(9)	69.58(15)	77.27/6)
N(1)−M−Cl(2)	118.70(7)	114.57(11)	113.70(5)
N(2)−M−Cl(2)	98.14(6)	97.33(10)	98.54(5)
N(1)−M−Cl(1)	123.20(7)	121.16(11)	127.72(5)
N(2)−M−Cl(1)	99.29(7)	95.27(11)	101.40(5)
Cl(2)−M−Cl(1)	117.99(4)	123.81(5)	118.06(3)
N(1)−M−N(11)	72.07(9)	68.48(16)	73.94(6)
N(2)−M−N(11)	148.28(9)	138.03(15)	151.09(6)
Cl(2)−M−N(11)	97.68(7)	101.21(10)	95.32(5)
Cl(1)−M−N(11)	97.25(7)	104.76(11)	94.16/5)

Table 4. Selected bond lengths [Å] and angles [°] for complex [Cu**L**Cl_2]

Molecule **a**		Molecule **b**	
Bond lengths			
Cu(1)−N(1)	1.949(3)	Cu(2)−N(3)	1.945(3)
Cu(1)−N(11)	2.132(3)	Cu(2)−N(31)	2.125(3)
Cu(1)−N(2)	2.193(3)	Cu(2)−N(4)	2.222(3)
Cu(1)−Cl(12)	2.2295(12)	Cu(2)−Cl(22)	2.2155(12)
Cu(1)−Cl(11)	2.4020(12)	Cu(2)−Cl(21)	2.4130(12)
O(11)−N(11)	1.361(3)	O(31)−N(31)	1.373(3)
O(21)−N(21)	1.385(4)	O(41)−N(41)	1.381(5)
N(1)−C(11)	1.336(4)	N(3)−C(31)	1.329(4)
N(1)−C(15)	1.346(4)	N(3)−C(35)	1.348(4)
N(2)−C(21)	1.334(4)	N(4)−C(41)	1.338(4)
N(2)−C(25)	1.359(4)	N(4)−C(45)	1.355(5)
N(11)−C(111)	1.277(4)	N(31)−C(311)	1.281(5)
N(21)−C(211)	1.279(5)	N(41)−C(411)	1.282(5)
Angles [°]			
N(1)−Cu(1)−N(11)	75.94(11)	N(3)−Cu(2)−N(31)	76.20(11)
N(1)−Cu(1)−N(2)	78.44(11)	N(3)−Cu(2)−N(4)	78.18(11)
N(11)−Cu(1)−N(2)	153.73(11)	N(31)−Cu(2)−N(4)	153.23(11)
N(1)−Cu(1)−Cl(12)	149.93(9)	N(3)−Cu(2)−Cl(22)	153.81(9)
N(11)−Cu(1)−Cl(12)	94.49(9)	N(31)−Cu(2)−Cl(22)	93.76(9)
N(2)−Cu(1)−Cl(12)	104.96(8)	N(4)−Cu(2)−Cl(22)	106.06(9)
N(1)−Cu(1)−Cl(11)	100.83(10)	N(3)−Cu(2)−Cl(21)	98.56(10)
N(11)−Cu(1)−Cl(11)	95.12(9)	N(31)−Cu(2)−Cl(21)	94.33(9)
N(2)−Cu(1)−Cl(11)	95.24(8))	N(4)−Cu(2)−Cl(21)	97.05(8)
Cl(12)−Cu(1)−Cl(11)	108.46(4)	Cl(22)−Cu(2)−Cl(21)	106.37(5)

N(11) = 75.94(11)° for molecule **a** and 76.20(11)° for molecule **b**.

A molecular view of complex [Ni**L**(DMSO)Cl_2] is shown in Figure 6 with its atom labelling scheme. The structure consists of a metal atom surrounded by one ligand **L**, two chlorine atoms and one DMSO linked by the O atom, in a distorted octahedral geometry. As in the previous complexes, the metal center is coordinated to N(1) and N(2) of the rigid 1,10-phenanthroline ligand and N(11) of one oxime group forming two fused five-membered rings (Table 3) with acute N−Ni(1)−N angles: N(1)−Ni(1)−N(2) = 77.53(17)° and N(1)−Ni(1)−N(11) = 74.68(17)°. These three nitrogen atoms occupy the equatorial plane which also contains the Cl(1) atom, whereas the axial positions are occupied by the second chlorine atom Cl(2) and the oxygen atom O(1) of the DMSO. All C, N and O atoms of the ligand, as well as the Cl(1) and Ni(1) atoms make an almost perfect plane, with the largest deviation from the plane being −0.13 Å at C(22). The hydrogen atom H(11) also belongs to this plane and there is a bonding interaction between it and Cl(1) [O(11)−H(11) = 1.015 Å; O(11)···Cl(1) = 3.097 Å; H(11)···Cl(1) = 2.256 Å; O(11)−H(11)···Cl(1) = 139.4°]. The atom H(21), which is out of the plane by 0.42 Å, is engaged in a bonding interaction with the atom O(1) of the [$-x + 3/2$, $y + 1/2$, z] symmetry-related molecule [O(21)−H(21) = 0.840 Å; O(21)···O(1) = 2.679 Å; H(21)···O(1) = 1.891 Å; O(21)−H(21)···O(1) = 155.5°], resulting in the formation of a two-dimensional hydrogen-bond network parallel to the *ab* plane.

A molecular view of complex [Cd**L**(OH_2)-$(DMSO)(NO_3)]^+$ is shown in Figure 6 with its atom labelling scheme. The cadmium atom presents a distorted pentagonal-bipyramidal geometry (Figure 2, **D**, Table 5); the equatorial plane is occupied by the four N atoms of ligand **L** and the oxygen atom of a water molecule, and the axial positions are occupied by two oxygen atoms belonging to a DMSO molecule and a nitrate anion. In this complex, the cadmium is coordinated to the four nitrogen atoms of the ligand resulting in the formation of three fused five-membered rings with very acute N−Cd−N angles, N(2)−Cd(1)−N(1) = 70.34(9)°, N(1)−Cd(1)−N(11) = 63.82(8)° and N(2)−Cd(1)−N(21) = 64.98(9)°. Of the four Cd−N distances, the two bonds connecting the metal center to the N atoms of the oxime groups are much longer, 2.720(3) and 2.780(3) Å, than the bonds involving the N atoms of the phenanthroline fragment, 2.341(3) and 2.369(2) Å. This lengthening may be a result of steric constraints. As a consequence of the coordination of the two nitrogen atoms N(11) and N(21), the two oximes have the same *s-cis* conformation around the C_{Ar}−C(=N) single bond. The unit also contains a free nitrate ion and a DMSO solvent molecule. The oxygen atom of DMSO and one of the oxygen atoms of the NO_3^- anion are connected, through hydrogen bonding, to the OH groups and also to the water molecule.

Since all these metal complexes have initially been designed as artificial nucleases with the potential ability to hydrolyze phosphomonoester and phosphodiester bonds, we performed some preliminary cleavage experiments using *p*-nitrophenyl phosphate as a substrate. As it is shown in Table 6, the hydrolytic activities of the zinc, copper, cobalt

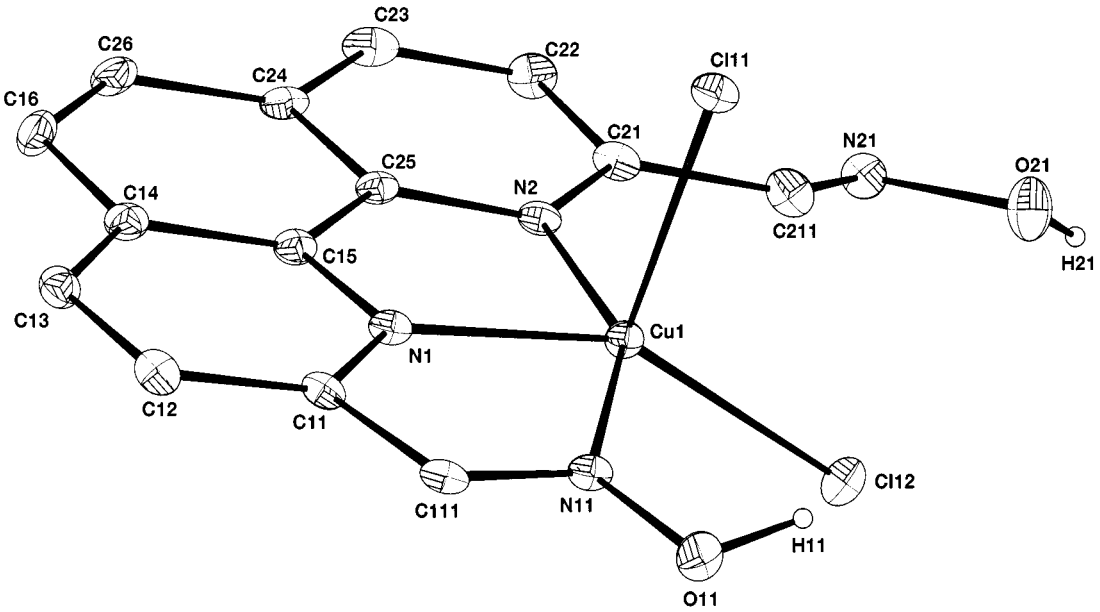

Figure 5. Molecular view of complex [Cu**L**Cl_2] with atom labelling scheme; ellipsoids are drawn at 30% probability; hydrogen atoms have been omitted for clarity

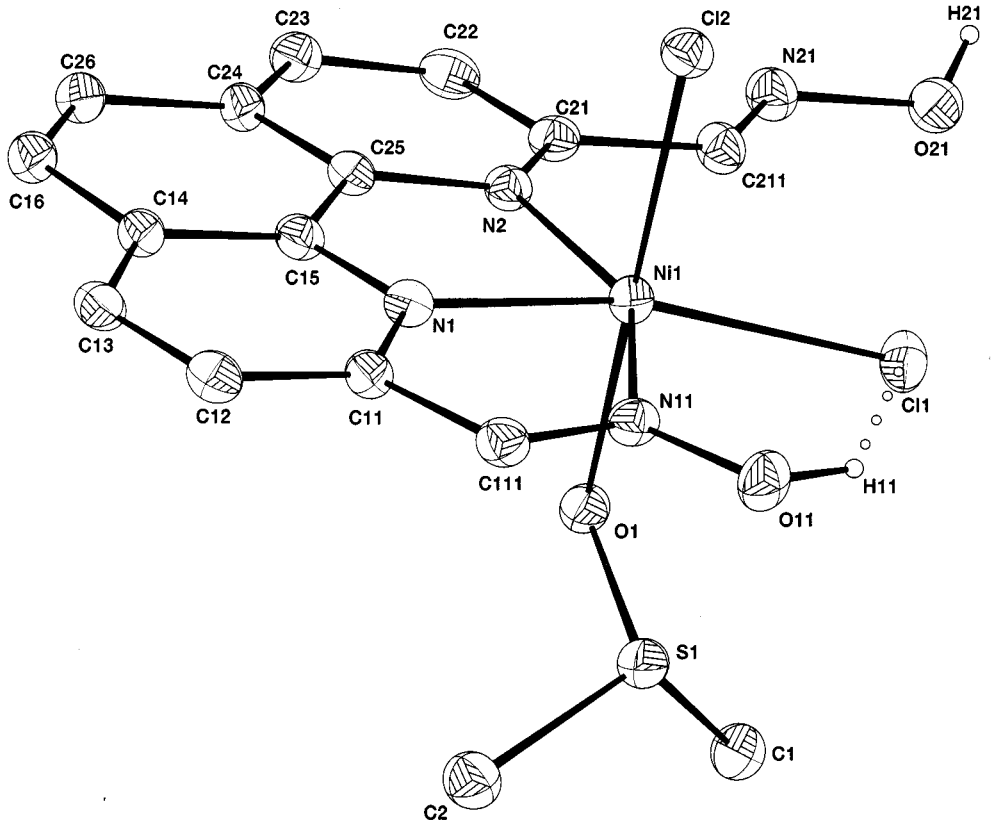

Figure 6. Molecular view of complex [Ni**L**(DMSO)Cl_2] with atom labelling scheme; ellipsoids are drawn at 30% probability; hydrogen atoms and non-coordinating lattice solvents molecules have been omitted

or nickel ions were not improved in the presence of ligand **L**. Moreover, the activity remained far below the activity of the lanthanide cerium salt alone, which is considered as one of the most reactive agents in the catalysis of DNA hydrolysis. It should be noted that in the case of cerium experiments, a slight but significant enhancement of its hydrolytic activity (+ 20 to + 80%) occurred in the presence of ligand **L**. This has also been observed during phosphodiester hy-

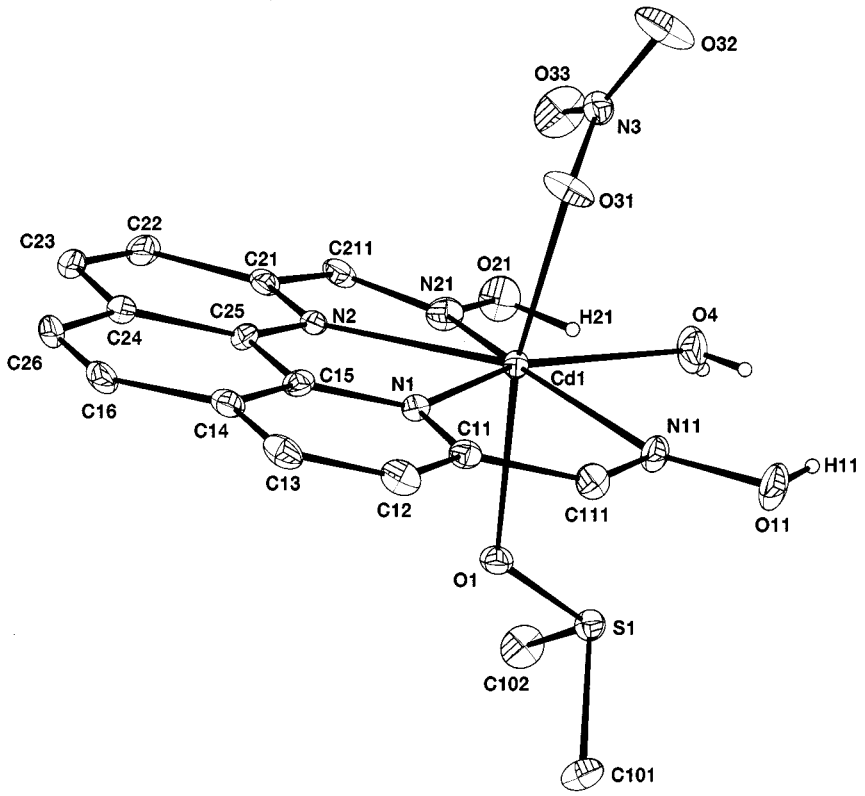

Figure 7. Molecular view of complex $[Cd\mathbf{L}(OH_2)(DMSO)(NO_3)]^+$ with atom labelling scheme; ellipsoids are drawn at 30% probability; hydrogen atoms and non coordinating anions have been omitted

Table 5. Selected bond lengths for complexes $[Cd\mathbf{L}(OH_2)(DMSO)(NO_3)]^+$ and $[Ni\mathbf{L}(DMSO)Cl_2]$

$[Cd\mathbf{L}(OH_2)(DMSO)(NO_3)]^+$		$[Ni\mathbf{L}(DMSO)Cl_2]$	
Cd(1)−O(4)	2.240(3)	Ni(1)−N(1)	2.008(4)
Cd(1)−O(1)	2.281(2)	Ni(1)−N(2)	2.216(4)
Cd(1)−O(31)	2.303(3)	Ni(1)−Cl(2)	2.351(2)
Cd(1)−N(2)	2.341(3)	Ni(1)−Cl(1)	2.394(2)
Cd(1)−N(1)	2.369(2)	Ni(1)−N(11)	2.131(4)
Cd(1)−N(21)	2.720(3)	Ni(1)−O(1)	2.131(4)
Cd(1)−N(11)	2.780(3)	O(11)−N(11)	1.373(6)
N(1)−C(11)	1.330(4)	O(21)−N(21)	1.402(6)
N(1)−C(15)	1.349(4)	N(1)−C(11)	1.337(7)
C(111)−N(11)	1.267(4)	N(1)−C(15)	1.337(8)
N(11)−O(11)	1.394(3)	N(2)−C(21)	1.320(7)
N(2)−C(21)	1.333(4)	N(2)−C(25)	1.384(7)
N(2)−C(25)	1.344(4)	N(11)−C(111)	1.289(7)
C(211)−N(21)	1.274(4)	N(21)−C(211)	1.282(7)
N(21)−O(21)	1.383(4)		
S(1)−O(1)	1.526(2)		
S(1)−C(101)	1.777(4)		
S(1)−C(102)	1.779(3)		
N(3)−O(32)	1.226(4)		
N(3)−O(33)	1.226(4)		
N(3)−O(31)	1.262(4)		

drolysis experiments using bis(*p*-nitrophenyl) phosphate as a substrate (data not shown).

Discussion

Previous studies[17] on complexes of the bidentate ligand 2,9-dimethyl-1,10-phenanthroline with Zn, Cu, Co and Ni have shown that these molecules possess a mirror plane which contains the metal and chlorine atoms and bisects the ligand molecule. The replacement of the two methyl groups by two oxime substituents introduces additional possibilities of chelation involving either the nitrogen or oxygen atoms of these groups. All the molecules presented here have provided unequivocal evidence for the structures of the 1:1 metal-ligand complexes. In all the complexes with chloro ligands, X-ray diffraction analyses showed a distorted trigonal-bipyramidal, a square-pyramidal or a square-bipyramidal structure involving the phenanthroline derivative as a tridentate ligand and coordination of the two chlorine atoms (Figure 2, **A**, **B** and **C**); the symmetry of the molecule was broken. However, as it was exemplified in two cases, the stereochemistry and the coordination number of the ligand may depend on the anion present.[18] Firstly, when ligand **L** was metallated with cadmium nitrate instead

Table 6. Hydrolysis of *p*-nitrophenyl phosphate (NPP) (expressed as mol-% conversion) by various metal ions and their complexes with and without ligand **L**

	Zn	Zn	Cu	Cu	Co	Ni	Ce	Ce
Run[a]	50 °C	80 °C	50 °C	80 °C	80 °C	80 °C	50 °C	80 °C
1 metal	−	20	−	25	18	−	85	100
2 metal + **L**	< 5	27	20	21	20	42	95	100

[a] Conditions: [NPP] = 500 μM; Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+} or Ce^{3+} cation 500 μM; metallated complex 500 μM (metal ion/**L**, 1:1); TRIS acetate buffer pH = 8 (50 mM) for 3 h at the indicated temperature.

of cadmium chloride, the crystal structure of $[Cd\mathbf{L}(OH_2)(DMSO)(NO_3)]^+$ appeared quite different from that of $[Cd\mathbf{L}Cl_2]$ (Figure 2, **D**). It showed a pentagonal-bipyramidal stereochemistry with the phenanthrolinedicarbaldehyde dioxime acting as a tetradentate ligand, whereas the three other ligands (H_2O, DMSO and one nitrato) contributed to the structure; the second nitrate ion was far away from the coordination sphere. In this molecule, the symmetry approaches C_{2v}, which is confirmed by the NMR-spectroscopic data. The second case is that of $([Zn\mathbf{L}(AcO)]_n$, obtained through metallation of **L** with zinc acetate. A polymer is probably formed, on the basis of elemental analysis, NMR and mass-spectrometric data. Figure 2 (**E** and **F**) shows two possible modes of connections for dimers or polymers. It is known that the oximate group can function as a bridge between two metal ions, through its deprotonated form, to afford bi- and trinuclear species[19] [in particular, see ref.[20] for an X-ray structure of a dimeric complex of 2,6-diacetylpyridine dioxime and Cu^{II} related to type **E** (Figure 2)]. It is probably the more acidic oximate group coordinated through the imine nitrogen atom on the metal center which is implicated in the coordination on the second metal ion through the deprotonated oxygen atom. This gives the proposed dimeric structure **E** that involves an almost planar six-membered ring (represented in Figure 2). Indeed, due to the linking effect involving the metal−ligand bond, the acid strength of the oxime group greatly increases, and depends on the nature of the metal ion.[21] As an example, the pK_a value of 2,6-diacetylpyridine dioxime is 10.2,[21] and that of the zinc complex is below 6[6b] and that of the copper(II) complex is 2.8.[22] So the oximate group can effectively compete with acetate as a ligand on the metal center (which is not the case when the anionic ligands are chloride ions), to give bridging coordination bonds resulting in the formation of dimeric or polymeric structures such as **E** and **F** in Figure 2. However, in the absence of an X-ray structure, we can neither exclude the "free" oxime ligand as a possible bridging group in the polymeric structure **F** (Figure 2), nor say if the acetate is within the coordination sphere (to give a five-coordinated structure as in $[Zn\mathbf{L}Cl_2]$ or outside (as a neutralizing charge).

All assignments of structures of complexes M−**L** were also confirmed by positive FAB-MS and ES-MS data. In addition, the ^1H NMR spectra of the diamagnetic zinc(II) and cadmium(II) complexes were recorded. The spectra of $[Zn\mathbf{L}Cl_2]$ (the broad peaks were not clearly resolved by an increase in temperature) and $[Zn\mathbf{L}(AcO)]_n$ (the complexity of NMR-spectroscopic patterns suggested a polymeric structure) did not afford further information on their structures in solution. The spectra of the cadmium complexes were more informative but rather atypical because of the coexistence of broad and sharp peaks for groups of protons of the same molecule. The exact nature of this unusual NMR spectrum (a similar case has been reported for cadmium complexes of 2,9-dihydrazino derivatives of 1,10-phenanthroline)[18] is debatable. A dynamic variation of coordination number of the cadmium(II) ions is a possible explanation. Equilibria between cadmium halide complexes are known,[23] and similar equilibria could be present here, ligand **L** acting either as a tridentate ligand (as in the crystal structure **A**, Figure 2) or a tetradentate ligand (as in crystal structure **D**, Figure 2), resulting in an asymmetrical or a symmetrical geometry of the complex, respectively. It was noteworthy that both complexes $[Cd\mathbf{L}Cl_2]$ and $[Cd\mathbf{L}(OH_2)(DMSO)(NO_3)]^+$ presented similar NMR profiles in solution (associating broad and sharp peaks), although the initial crystal structure was different. In both cases, the increase in temperature significantly reduced the width of the broad peaks to give signals corresponding to a symmetrical molecule (similar to that observed for the free ligand **L**). Therefore, in solution different species probably coexist.

We performed some preliminary experiments on the phosphomonoester bond cleavage with zinc, copper, cobalt and nickel acetate salts, both in the presence and absence of ligand **L**. No significant improvement of the catalytic activity of the metal cation in the presence of the ligand could be observed in these conditions. However, according to the present structural investigations on complexes M−**L**, the anions present in solution (introduced either as the counter ions of the metal cation or with the buffer) may play a crucial role in the structure of the various complexes in solution and, therefore, on their activity. Current investigations are focusing on defining the optimal conditions for use of these potential chemical nucleases as to expand the study to other metal complexes involving cerium or other lanthanides.

Conclusion

The attachment of an organic functional group to a metal-chelating ligand is an attractive way of developing the design of small metal complexes which are potentially able to hydrolyze the phosphodiester backbone of nucleic acids. In the present paper, we detailed the structure and the coordination geometry of an original series of metal complexes of a phenanthroline derivative bearing two aldoxime groups known for their highly nucleophilic properties. This series represents a range of complexes differing in the nature of the metal (Lewis acidity, size, etc.), the geometry of the crystal structure (trigonal-bipyramidal, square-pyramidal, square-bipyramidal and pentagonal-bipyramidal structures) or the conformational flexibility. These factors can affect the known in vivo biological interest of ligand **L** and its metal chelates and also their potential use as chemical nucleases in phosphodiester hydrolysis.[24]

Experimental Section

General: Commercially available reagents and all solvents were purchased from standard chemical suppliers and used without further purification. − ^1H NMR spectra were recorded with a Bruker AM 250 (250 MHz), [D_6]DMSO was used as a solvent δ_H = 2.62. − Elemental analyses were carried out by the "Service de Microana-

lyse du Laboratoire de Chimie de Coordination". − MS: Nermag R10−10, 70 eV (IE/DCI and FAB$^+$/*meta*-nitrobenzyl alcohol MNBA) or Perkin−Elmer SCIEX API 365 (electrospray) by the "Service de Spectrométrie de Masse de Chimie UPS−CNRS de Toulouse". For MS data, the indicated value for molecular or fragment peaks corresponded to the peak of higher intensity and are in agreement with calculated isotopic profiles. − UV/Vis: Hewlett−Packard 8452A diode array spectrophotometer, cuvettes of 1 cm pathlength. − IR: Perkin−Elmer 225 and 597. − Melting points were determined with a digital apparatus Electrothermal and are uncorrected.

1,10-Phenanthroline-2,9-dicarbaldehyde: Iodine was added (I_2, 7.02 g, 27.65 mmol, 2 equiv.) to a solution of neocuproine hemihydrate (2,9-dimethyl-1,10-phenanthroline, 3.0 g, 13.8 mmol, 1 equiv.) dissolved in DMSO (200 mL). The brown solution was stirred for 5 min at room temperature before 3.42 mL of 2-iodo-2-methylpropane (*t*BuI, 28.7 mmol, 2.07 equiv.) was added. Finally, trifluoroacetic acid (TFA, 3 mL, 38.94 mmol, 2.8 equiv.) was slowly added to the darkbrown solution by syringe and the mixture was stirred under reflux for 2 h (148 °C). After this, the solution was allowed to cool at room temperature. The excess of iodine was neutralized by slow addition of a solution of $Na_2S_2O_3$ (16 g/120 mL) and the dark precipitate formed was removed by filtration. 1,10-Phenanthroline-2,9-dicarbaldehyde was precipitated from the filtrate by addition of aqueous $NaHCO_3$ (10%) to pH = 4−5 and extracted with CH_2Cl_2. The organic phase was dried, concentrated and the residue was washed with ether to remove traces of DMSO. The crude product was recrystallized from acetone and dried under vacuum to give the pure compound (1.64 g, yield 48%). − M.p. 253 °C. − $C_{14}H_8N_2O_2$·1/2 H_2O (245): calcd. C 68.57, H 3.70, N 11.42; found C 68.84, H 3.62, N 11.55. − ^{1}H NMR ([D$_6$]DMSO): δ = 10.48 (d, ^4J = 0.8 Hz, 2 H, CHO), 8.93 (dd, ^4J = 0.8 Hz, ^3J = 8.2 Hz, 2 H, 8-H and 3-H), 8.44 (d, ^3J = 8.2 Hz, 2 H, 4-H and 7-H), 8.42 (s, 2 H, 5-H and 6-H), 3.43 (s, 1 H, 0.5 H_2O). − MS (EI); *m*/*z* (%): 236 (30) [M$^+$], 208 (100) [M − CO]$^+$, 180 (3) [M − 2CO]$^+$. − MS (DCI/NH_3); *m*/*z* (%): 254 (100) [M + NH_4]$^+$, 237 (37) [MH]$^+$. − IR (KBr): $\tilde{\nu}$ = 1701 cm^{-1} (C=O) vs, 1617 (C=C) s. − UV/Vis (DMSO 0.2% in H_2O): λ_{max} (lg ε) = 236 nm (4.58), 278 (4.47), 314 (3.99), 332 (3.93), 348 (3.72).

1,10-Phenanthroline-2,9-dicarbaldehyde Dioxime (L): A suspension of 1,10-phenanthroline-2,9-dicarbaldehyde (400 mg, 1.69 mmol, 1 equiv.) in 10 mL of absolute ethanol was stirred at 60 °C for 10 min. NH_2OH·HCl was then progressively added (622 mg, 8.8 mmol, 5.2 equiv.). The addition of about 400 mg of hydroxylamine dissolved the dialdehyde within a few minutes to give a brown solution, after which a brown precipitate was obtained (after the complete addition of NH_2OH·HCl). The reaction mixture, in 30 mL of absolute EtOH, was warmed to 80 °C and stirred for 20 min. The mixture was stirred at reflux (95 °C) for 2 h after the addition of pyridine (1.64 mL, 20.3 mmol, 12 equiv.). The reaction mixture was then allowed to cool at room temperature. After removal of the liquid phase, the precipitate was washed with 30 mL of water to eliminate the excess of NH_2OH·HCl, recrystallized from water/DMSO (55:45, v/v) and dried under vacuum (352 mg, yield 78%). − $C_{14}H_{10}N_4O_2$ (266). − M.p. 267 °C. − $C_{14}H_{10}N_4O_2$·1/2 H_2O 0.85 DMSO (341.3): calcd. C 55.20, H 4.71, N 16.40; found C 55.63, H 4.71, N 15.98. − ^{1}H NMR ([D$_6$]DMSO): δ = 12.07 (s, 2 H, NO*H*), 8.63 (d, ^3J = 8.2 Hz, 2 H, 3-H and 8-H), 8.53 (s, 2 H, C*H*(=NOH)), 8.29 (d, ^3J = 8.2 Hz, 2 H, 4-H and 7-H), 8.15 (s, 2 H, 5-H and 6-H). − MS (EI); *m*/*z* (%): 266 (30) [M$^+$], 248 (20) [M − H_2O]$^+$, 230 (18) [M − 2H_2O]$^+$. − IR (KBr): $\tilde{\nu}$ = 1615 cm^{-1} (C=N oxime) s. − UV/Vis (DMSO 0.2% in H_2O): λ_{max} (lgε) = 262 nm (4.33), 298 (4.35), 324 (4.00), 356 (3.40).

X-ray Diffraction Studies: Addition of a small amount of water in a concentrated solution of 1,10-phenanthroline-2,9-dicarbaldehyde dioxime in DMSO left at room temperature (25 °C), gave suitable yellow crystals for X-ray diffraction studies. Figure 3: ORTEP drawings of the ligand 1,10-phenanthroline-2,9-dicarbaldehyde dioxime hydrate. Selected bond lengths and angles are given in Table 1 and 2.

Dichloro(1,10-phenanthroline-2,9-dicarbaldehyde Dioxime)zinc [ZnLCl$_2$]: A solution of $ZnCl_2$ (12.8 mg, 94 μmol, final concentration 188 mM) in 100 μL of DMF was added to a brown solution of **L** (25 mg, 73 μmol, final concentration: 146 mM) in 400 μL of DMF. The expected complex, which precipitated immediately, was isolated by centrifugation and dried under vacuum to afford a brown powder (25 mg, 59.2 μmol, yield 81%). − $C_{14}H_{10}Cl_2N_4O_2Zn$ (402.5). − M.p > 360 °C. − $C_{14}H_{10}Cl_2N_4O_2Zn$·1/3DMF (422.2): calcd. C 42.20, H 2.91, N 14.22; found C 42.28, H 2.89, N 14.29. − ^{1}H NMR ([D$_6$]DMSO): δ = 12.90 (br, N*O*H*, N* = coordinated to Zn^{II}), 12.12 (br, NO*H*, N = free), 9.2−8.1 (8 H, 6 Ar−H + 2 H from C*H*=NOH), 8.07/3.0/2.85 (s, DMF). − MS (positive FAB, solution in DMSO); *m*/z (%): 329 (25) [**L** + Zn − H$^+$]$^+$, 365 (76) [**L** + Zn + Cl$^-$]$^+$, 443 (26) [**L** + Zn + Cl$^-$ + DMSO]$^+$. − MS (ES, solution in H_2O/DMSO); *m*/*z*: 310.9 [**L** + Zn − H$^+$ − H_2O]$^+$, 328.9 [**L** + Zn − H$^+$]$^+$, 346.9 [**L** + Zn − H$^+$ + H_2O]$^+$, 366.8 [**L** + Zn + Cl$^-$]$^+$, 595.1 (dimer 2:1 [2 × **L** + Zn − H$^+$]$^+$), 658.9 (dimer 2:2 [2 × **L** + 2 × Zn − 3H$^+$]$^+$), 695.0 (dimer 2:2 [2 × **L** + 2 × Zn − 2H$^+$ + Cl$^-$]$^+$, 733.0 (dimer 2:2 [2 × **L** + 2 × Zn − H$^+$ + 2Cl$^-$]$^+$, 737.0 (dimer 2:2 [2 × **L** + 2 × Zn − 3H$^+$ + DMSO]$^+$, 755.1 (dimer 2:2 [2 × **L** + 2 × Zn − 3H$^+$ + DMSO + H_2O]$^+$. − UV/Vis (DMSO 0.2% in H_2O): λ_{max} (lgε) = 262 nm (4.42), 298 (4.32), 320 (4.15), 356 (3.60), 382 (3.26).

X-ray Diffraction Studies: Crystals of [Zn**L**Cl$_2$] were obtained independently by addition of 500 μL of a DMSO solution of [$ZnCl_2$] (12.8 mg, 94 μmol, final concentration: 94 mM) to 1 mL of a brown DMSO solution of **L** (25 mg, 73 μmol, final concentration: 49 m^m). Under these conditions, the complex did not precipitate immediately and, by vapor diffusion of CH_2Cl_2, the solution afforded suitable yellow crystals after 2 d. Selected bond lengths and angles are given in Table 3.

(1,10-Phenanthroline-2,9-dicarbaldehyde Dioxime)zinc Bis(acetate) Monohydrate [ZnL(AcO)]$_n$: A solution of $Zn(OOCCH_3)_2$·2 H_2O (20.5 mg, 93 μmol, 25 mM final) in 2 mL of DMSO was added to a brown solution of **L** (50 mg, 146 μmol, final concentration: 38.9 mM) in 1.75 mL of DMSO. The mixture was stirred for 30 min at room temperature, the precipitate was then isolated by centrifugation and dried under vacuum to afford a bright yellow powder (40 mg, 85.5 μmol, yield 97%). − M.p. > 360 °C. − $C_{16}H_{12}N_4O_4Zn$·H_2O: calcd. C 47.14, H 3.46, N 13.74; found C 47.28, H 2.95, N 13.30. − ^{1}H NMR ([D$_6$]DMSO): δ = 12.50 (br, NOH), 9.2−8.1 (8 H, Ar−H + 2 H from C*H*=NOH), 1.85 (s, 3 H, CH_3COO), 8.07/3.0/2.85 (s, DMF). − MS (ES, solution in H_2O/MeOH); *m*/*z* (%): 310.9 [**L** + Zn − H$^+$ − H_2O]$^+$, 329.0 [**L** + Zn − H$^+$]$^+$, 347.0 [**L** + Zn − H$^+$ + H_2O]$^+$, 388.9 [**L** + Zn + AcO$^-$]$^+$, 595.1 (dimer 2:1 [2 × **L** + Zn − H$^+$]$^+$), 638.9 (dimer 2:2 [2 × **L** + 2 × Zn − 3H$^+$ − H_2O]$^+$), 656.7 (dimer 2:2 [2 × **L** + 2 × Zn − 3H$^+$]$^+$), 716.9 (dimer 2:2 [2 × **L** + 2 × Zn − 2H$^+$ + AcO$^-$]$^+$), 984.8 (trimer 3:3 [3 × **L** + 3×Zn − 5H$^+$]$^+$). − UV/Vis (DMSO 0.2% in H_2O): λ_{max} = 260 nm, 298, 324.

Dichloro(1,10-phenanthroline-2,9-dicarbaldehyde Dioxime)copper(II) [CuLCl$_2$]: A solution of $CuCl_2$ (12.6 mg, 94 μmol, final con-

centration 188 mM) in 100 μL of DMF was added to a brown solution of **L** (25 mg, 73 μmol, final concentration: 146 mM) in 400 μL of DMF. The expected complex, which precipitated immediately, was isolated by centrifugation and dried under vacuum to afford a greenish powder (26.5 mg, 66 μmol, yield 90%). − M.p. 300 °C (dec.). − $C_{14}H_{10}Cl_2CuN_4O_2$ (400.7): calcd. C 41.97, H 2.52, N 13.98; found C 42.22, H 2.02, N 13.88. − MS (positive FAB, solution in DMSO); *m/z* (%): 328 (46) [**L** + Cu^{II} − H^+]$^+$, 329 (100) [**L** + Cu^I]$^+$, 364 (35) [**L** + Cu^{II} + Cl^-]$^+$, 595 (20) [2 × **L** + Cu^I]$^+$. − MS (ES, solution in MeOH/H_2O); *m/z* (%): 267.1 [**L** + H^+], 285.0 [**L** + Cu^{II} − H^+ − (CH=NO)]$^+$, 309.8 [**L** + Cu^{II} − H^+ − H_2O]$^+$, 328.0 [**L** + Cu^{II} − H^+]$^+$, 594.1 (dimer 2:1 [2 × **L** + Cu^{II} − H^+]$^+$), 595.2 (dimer 2:1 [2 × **L** + Cu^I]$^+$), 654.9 (dimer 2:2 [2 × **L** + 2 × Cu^{II} − 3H^+]$^+$), 691.1 (dimer 2:2 [2 × **L** + 2 × Cu^{II} − 2H^+ + Cl^-]$^+$. − UV/Vis (DMSO 0.2% in H_2O): λ_{max} (lgε) = 272 nm (4.41), 324 (4.06), 370 (3.90).

X-ray Diffraction Studies: Crystals of [Cu**L**Cl_2] were obtained independently by addition of 40 μL of a DMSO solution of $CuCl_2$ (3.4 mg, 25 μmol, final concentration: 126 mM) to 160 μL of a brown DMSO solution of **L** (6.7 mg, 19.6 μmol, final concentration: 98 mM). In these conditions, the complex did not precipitate immediately, and by vapor diffusion of CH_2Cl_2, the solution afforded suitable orange red crystals after 5 d. Selected bond lengths and angles are given in Table 4.

Dichloro(1,10-phenanthroline-2,9-Dicarbaldehyde Dioxime)cadmium Bis(dimethylsulfoxide) [CdLCl_2]: 100 μL of an aqueous solution of $CdCl_2$ (17.2 mg, 94 μmol, final concentration 188 mM) was added to a brown solution of **L** (25 mg, 73 μmol, final concentration: 146 mM) in 400 μL of DMSO. The expected complex, which precipitated immediately, was isolated by centrifugation and dried under vacuum to afford a brown powder (24.5 mg, 40.5 μmol, yield 55%). − M.p. 300 °C − $C_{14}H_{10}CdCl_2N_4O_2$·2DMSO (605.3): calcd. C 35.68, H 3.63, N 9.25; found C 35.63, H 3.22, N 9.35. − ^{1}H NMR ([D_6]DMSO): δ = 12.73 (br. s, ca. 1.2 H, NO*H*), 8.92 (pattern, 4 H, 4-H, 7-H, 11-H and 11′-H), 8.42 (d, 2 H, ^3J = 8.3 Hz, 3-H and 8-H), 8.30 (s, 2 H, 5-H and 6-H), 2.66 (s, 12 H, 2DMSO) [recorded at 60° C, the broad signal at δ = 8.92 gave: δ = 8.90 (d, 2H, ^3J = 8.3 Hz, 4-H and 7-H), 8.89_5 (s, 2H, 11-H and 11′-H)]. − MS (positive FAB, solution in DMSO); *m/z* (%): 379 (23) [**L** + Cd^{II} − H^+]$^+$, 397 (18) [**L** + Cd^{II} − H^+ + H_2O]$^+$, 415 (100) [**L** + Cd^{II} + Cl^-]$^+$. − MS (ES, solution in H_2O + traces of DMSO); *m/z* (%): 267.0 [**L** + H^+], 378.9 [**L** + Cd^{II} − H^+], 397.0 [**L** + Cd^{II} − H^+ + H_2O]$^+$, 415.0 [**L** + Cd^{II} + Cl^-]$^+$, 475.0 [**L** + Cd^{II} − H^+ + H_2O + DMSO]$^+$, 790.9 (dimer 2:2 [2 × **L** + 2 × Cd^{II} − 2H^+ + Cl^-]$^+$), 924.9 (dimer 2:2 [2 × **L** + 2 × Cd^{II} − H^+ + 2Cl^- + DMSO + H_2O]$^+$), 984.9 (dimer 2:2 [2 × **L** + 2 × Cd^{II} − H^+ + 2Cl^- + 2DMSO]$^+$). − UV/Vis (DMSO 0.2% in H_2O): λ_{max} (lgε) = 236 nm (4.58), 260 (4.78), 264 (4.81), 322 (4.46), 350 (4.19).

X-ray Diffraction Studies: Crystals of compound [Cd**L**Cl_2] were obtained independently by adding 100 μL of an aqueous solution of $Cd(NO_3)_2$·$4H_2O$ (2.0 mg, 6.5 μmol, final concentration: 1.62 mM) to a solution of Zn**L**Cl_2 (2.0 mg, 4.9 μmol, final concentration: 1.2 mM) in 4 mL of a mixture of DMSO/H_2O (1:3), to induce the transmetallation. The solution was allowed to crystallize for 3 months (by slow solvent evaporation) at room temperature to afford yellow crystals suitable for X-ray analysis. Selected bond lengths and angles are given in Table 3.

Aqua(dimethylsulfoxide)(nitrato)(1,10-phenanthroline-2,9-dicarbaldehyde Dioxime)cadmium Nitrate [CdL(OH_2)(DMSO)(NO_3)]$^+$. − Analytical and X-ray Diffraction Studies: A solution of $Cd(NO_3)_2$·$4H_2O$ (29 mg, 94 μmol) in 100 μL of H_2O was added to a brown solution of **L** (25 mg, 73 μmol, final concentration: 146 mM) in 400 μL of DMSO. The expected complex did not precipitate immediately and, by vapor diffusion of CH_2Cl_2, the solution afforded suitable pale yellow crystals after 2 d. Figure 7: ORTEP drawing of the dinitrato(1,10-phenanthroline-2,9-dicarbaldehyde dioxime)cadmium complex. Selected bond lengths and angles are given in Table 5. − M.p. > 360 °C. − $C_{14}H_{10}CdN_6O_8$·DMSO·H_2O (598.8) − ^{1}H NMR ([D_6]DMSO): δ = 11.81 (br. s, ca. 1.5 H, NO*H*), 8.99 (pattern massif, 2 H, 4-H and 7-H), 8.67 (pattern massif, 2 H, 11-H and 11′-H), 8.37 (d, 2 H, ^3J = 8.0 Hz, 3-H and 8-H), 8.35 (s, 2 H, 5-H and 6-H), 2.60 (s, 6 H, DMSO) [recorded at 60° C, the broad signal at δ = 8.99 gave: δ = 8.96 (d, 2H, ^3J = 8.0 Hz, 4-H and 7-H), the broad signal at δ = 8.67 became a sharp singlet]. − MS (positive FAB, solution in DMSO/H_2O); *m/z* (%): 379 (61) [**L** + Cd − H^+]$^+$, 442 (100) [**L** + Cd + NO_3^-]$^+$, 457 (13) [**L** + Cd − H^+ + DMSO]$^+$, 520 (30) [**L** + Cd + NO_3^- + DMSO]$^+$, 598 (8) [**L** + Cd + NO_3^- + 2DMSO]$^+$, 818 (5) [2 × **L** + 2 × Cd + NO_3^- − 2H^+]$^+$. − MS (ES, solution in DMSO/H_2O); *m/z* (%): 379 [**L** + Cd − H^+]$^+$. − UV/Vis (DMSO 0.2% in H_2O): λ_{max} = 264 nm, 322, 348 (sh).

Dichloro(1,10-phenanthroline-2,9-dicarbaldehyde DioxDme)cobalt Mono(dimethyl sulfoxide) [CoLCl_2]: 100 μL of an aqueous solution of $CoCl_2$·$6H_2O$ (22.4 mg, 94 μmol, final concentration 188 mM) was added to a brown solution of **L** (25 mg, 73 μmol, final concentration: 146 mM) in 400 μL of DMSO. The expected complex, which precipitated after 30 min, was isolated by centrifugation and dried under vacuum to afford a brown powder (24.7 mg, 49.4 μmol, yield 68%). − M.p. > 360 °C. − $C_{14}H_{10}CoCl_2N_4O_2$·DMSO·0.2$CoCl_2$ (500.2): calcd. C 38.42, H 3.22, N 11.20; found C 38.31, H 2.74, N 11.27. − MS (ES, solution in DMSO/H_2O); *m/z* (%): 265.9 [**L**]$^+$, 305.9 [**L** + Co^{II} − H^+ − H_2O], 322.8 [**L** + Co^{III} − 2H^+], 323.8 [**L** + Co^{II} − H^+]$^+$, 589.0 (dimer 2:1 [2 × **L** + Co^{III} − 2H^+]$^+$). − UV/Vis (DMSO 0.2% in H_2O): λ_{max} (lgε) = 230 nm (4.51), 268 (4.67), 296 (4.44), 348 (4.16).

X-ray Diffraction Studies: Crystals of [Co**L**Cl_2] were obtained independently by addition of 40 μL of an aqueous solution of $CoCl_2$·$6H_2O$ (6 mg, 25 μmol, final concentration: 126 mM) to 160 μL of a brown DMSO solution of **L** (6.7 mg, 19.6 μmol, final concentration: 98 mM). Under these conditions, the complex did not precipitate immediately and, by vapour diffusion of CH_2Cl_2, the solution afforded suitable green/red dichroic crystals after 7 d. Figure 4: ORTEP drawing of the dichloro(1,10-phenanthroline-2,9-dicarbaldehyde dioxime)cobalt complex. Selected bond lengths and angles are collected in Table 3.

(Dichloro)(dimethylsulfoxide)(1,10-phenanthroline-2,9-dicarbaldehyde Dioxime)nickel Dihydrate Mono(dimethylsulfoxide) (NiL(DMSO)Cl_2): 100 μL of an aqueous solution of $NiCl_2$·$6H_2O$ (22.3 mg, 94 μmol, final concentration 188 mM) was added to a brown solution of **L** (25 mg, 73 μmol, final concentration: 146 mM) in 400 μL of DMSO. After concentrating the mixture to 350 μL, the expected complex precipitated and was isolated by centrifugation and dried under vacuum to afford a brown powder (37.2 mg, 63.3 μmol, yield 87%). − M.p. > 360 °C. − $C_{14}H_{10}Cl_2N_4NiO_2$·2DMSO·$2H_2O$ (588.1): calcd. C 36.76, H 4.46, N 9.53; found C 36.97, H 4.26, N 9.18. − MS (positive FAB, solution in DMSO/H_2O); *m/z* (%): 323 (100) [**L** + Ni − H^+]$^+$, 359 (8) [**L** + Ni + Cl^-]$^+$. − MS (ES, solution in DMSO/H_2O); *m/z* (%): 266.9 [**L** + H^+], 304.9 [**L** + Ni − H^+ − H_2O]$^+$, 322.9 [**L** + Ni − H^+]$^+$, 589.0 [2 × **L** + Ni − H^+]$^+$. − UV/Vis (DMSO 0.2% in H_2O): λ_{max} (lgε) = 260 nm (4.84), 316 (4.65), 364 (4.11).

Table 7. Crystal data for the ligand **L** and the complexes M-**L** (M-Zn, Ca, Cd, Cu and Ni)

Compound	**L**	[Zn**L**Cl_2]	[Cu**L**Cl_2]	[Cd**L**Cl_2]	[Co**L**Cl_2]	[Ni**L**(DMSO)Cl_2]	[Cd**L**(OH_2)(DMSO)(NO_3)]$^+$
Empirical formula	$C_{28}H_{26}N_8O_7$	$C_{36}H_{46}Cl_4N_8O_9S_4Zn$	$C_{36}H_{44}Cl_4Cu_2N_8O_8S_4$	$C_{18}H_{22}CdCl_2N_4O_4S_2$	$C_{16}H_{16}Cl_2CoN_4O_3S$	$C_{16}H_{16}Cl_2N_4NiO_2S$	$C_{18}H_{24}CdN_6O_{11}S_2$
Molecular mass	403.16	1135.59	1113.91	605.82	474.22	474.00	676.95
Crystal system	monoclinic	triclinic	triclinic	triclinic	monoclinic	orthorombic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	*Pbca*	$P\bar{1}$
a [Å]	7.5156(6)	11.4734(14)	9.100(2)	9.090(2)	15.872(3)	11.161(2)	9.274(5)
b [Å]	20.0795(15)	15.155(3)	16.396(3)	9.461(2)	7.517(2)	11.832(2)	9.951(5)
c [Å]	18.2339(14)	15.563(2)	16.890(3)	14.754(4)	15.563(2)	28.390(3)	14.769(5)
α [°]	90	99.268(16)	67.11(3)	103.06(3)	90	90	89.110(5)
β [°]	104.73(2)	97.949(14)	88.56(3)	92.37(3)	92.93(3)	90	78.440(5)
γ [°]	90	111.136(15)	80.77(3)	102.30(3)	90	90	75.520(5)
V [Å^3]	2751.5(4)	2433.8(6)	2289.6(8)	1202.4(5)	1942.6(7)	3749.0(8)	1292.0(10)
Z	4	2	2	2	4	8	2
F (000)	1224	1164	1140	608	964	1936	684
$\rho_{calcd.}$ [g cm^{-3}]	1.416	1.550	1.616	1.673	1.621	1.680	1.740
μ(Mo-K_α) [mm^{-1}]	0.105	1.434	1.403	1.336	1.291	1.457	1.074
No. of reflns. collected	17054	19251	20182	9592	17745	31110	12499
No. of unique reflns.	4297	7117	8339	3597	3715	3716	4655
Merging factor *R*(int)	0.1351	0.0326	0.0481	0.0662	0.0360	0.1282	0.0258
Data/restraints/parameters	4297/21/419	7117/188/619	8339/0/580	3597/85/296	3715/0/254	3716/0/251	4655/439/432
*R*1, *wR*2 [$I > 2\sigma(I)$]	0.0581, 0.1122	0.0323, 0.0802	0.0395, 0.0925	0.0481, 0.1297	0.0275, 0.0682	0.0551, 0.1343	0.0268, 0.0670
*R*1, *wR*2 (all data)	0.1381, 0.1370	0.0441, 0.0864	0.0658, 0.1047	0.0534, 0.1365	0.0350, 0.0716	0.0958, 0.1571	0.0307, 0.0765
$\Delta\rho_{min}/\Delta\rho_{max}$	−0.231/0.276	−0.442/0.488	−0.648/0.864	−1.286/0.834	−0.384/0.334	−0.903/0.491	−0.665/0.435
GOF	0.977	1.031	1.000	0.980	1.049	1.031	1.187

X-ray Diffraction Studies: Crystals of [Ni**L**(DMSO)Cl_2] were obtained independently by addition of 40 μL of a DMSO solution of $NiCl_2{\cdot}6H_2O$ (237.71) (6 mg, 25 μmol, final concentration: 126 mM) to 160 μL of a brown DMSO solution of **L** (6.7 mg, 19.6 μmol, final concentration: 98 mM). Under these conditions, the complex did not precipitate immediately and, by vapour diffusion of CH_2Cl_2, the solution afforded suitable green crystals after 5 d. Figure 6: ORTEP drawing of the dichloro(1,10-phenanthroline-2,9-dicarbaldehyde dioxime)nickel complex. Selected bond lengths and angles are collected in Table 3.

Crystal Structure Determination of the Ligand L and the Complexes [Zn$L$$Cl_2$], [Cu$L$$Cl_2$], [Cd$L$$Cl_2$], [Cd$L$$(OH_2)$(DMSO)$(NO_3)$]$^+$, [Co$L$$Cl_2$], and [Ni$L$(DMSO)$Cl_2$]: Data were collected with a Stoe IPDS (Imaging Plate Diffraction System) diffractometer equipped with an Oxford cryosystems Cooler Device. The final unit cell parameters were obtained by the least-squares refinement of 5000 reflections. Only statistical fluctuations were observed in the intensity monitors over the course of the data collections. All the structures were solved by direct methods (SIR92[25]) and refined by least-squares procedures on F^2. All H atoms attached to carbon atoms or to OH groups were introduced in calculations in idealised positions [d(CH) = 0.96 Å] and treated as riding models with isotropic thermal parameters, 20% higher than those of the carbon atoms to which they are attached. H atoms attached to water molecules were refined with an equivalent isotropic thermal parameter, the geometry of water molecules were restrained to have chemically reasonable dimensions. Some of the DMSO solvent molecules in [Zn$L$$Cl_2$], [Cd$L$$Cl_2$] and [Cd$L$$(OH_2)$(DMSO)$(NO_3)$]$^+$, and the free NO_3 in [Cd$L$$(OH_2)$(DMSO)$(NO_3)$]$^+$ are disordered. These disordered molecules were treated using the available tools in SHELXL-97. Least-squares refinements were carried out by minimising the function $\Sigma w(F_o^2 - F_c^2)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Models reached convergence with $R = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$ and $wR2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$, having the values listed in Table 1. Crystal data and data collection parameters are summarized in Table 7. The calculations were carried out with the SHELXL-97 program[26] running on a PC. Molecular view was realised with the help of CAMERON[27] Fractional atomic coordinates, anisotropic thermal parameters for nonhydrogen atoms and atomic coordinates for H atoms have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-134158−134163 and -139259. The ligand **L** and the complexes [Zn$L$$Cl_2$], [Cu$L$$Cl_2$], [Cd$L$$Cl_2$], [Co$L$$Cl_2$], [Ni$L$(DMSO)$Cl_2$], and [Cd$L$$(OH_2)$(DMSO)$(NO_3)$]$^+$ are referenced under the following denominations, respectively: **2**, **3**·Cl_2, **4**·Cl_2, **5**·Cl_2, **6**·Cl_2, **7**·Cl_2 and **5**·$(NO_3)_3$. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk

Hydrolysis of *p*-Nitrophenyl Phosphate (NPP) with Various Metal Ions and Their Complexes with L: NPP was incubated with various metal ions in the absence (run 1) or the presence (run 2) of ligand **L** in 50 mM TRIS acetate buffer (pH = 8) at 50 or 80 °C, for 3.0 h. NPP and the metal salts were introduced as aqueous solutions and ligand **L** as a DMSO solution. The final volume (1 mL) contained 5% DMSO. Metal salts were introduced as acetates except for cerium (sulfate). The reactions were followed by reversed-phase HPLC (C18 Nucleosil, 10 μm, 250×4.6 mm; elution with methanol/5 mM ammonium acetate (45:55), adjusted to pH = 5 with acetic acid; detection at 320 nm).

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