# Configuration of Octahedral Metal Compounds − Equilibrium, Crystal and Molecular Structure of Nickel(II) Complexes of Linear $N_2O_4$, $N_4S_2$ or $N_6$ Donors Set Atoms Ligands

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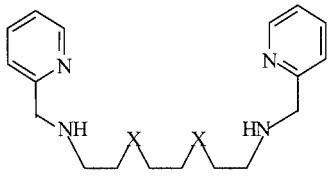
Two new nickel(II) complexes of symmetric hexadentate mixed-ligand N,O [1,12-bis(2-pyridyl)-5,8-dioxa-2,11-diazadodecane (pydado)] and N,S [1,12-bis(2-pyridyl)-5,8-dithia-2,11-diazadodecane (pydadt)] donor atoms have been synthesised as perchlorate salts and characterised by X-ray crystallography and ligand-field spectroscopy. In both complexes the $Ni^{2+}$ ion is hexacoordinate. The cation $[Ni(pydado)]^{2+}$ is pseudo-octahedral with the two pyridyl groups in *trans* position; all Ni–N and Ni–O bond lengths are practically equivalent. In $[Ni(pydadt)]^{2+}$ complex, however, the size of the thioether sulfur atoms imposes a $C_{2v}$ symmetry; the pyridyl groups and the sulfur atoms are in *trans* positions and all Ni–N bond lengths are equivalent. The comparison of these structures with those of octahedral cobalt, copper and zinc complexes with the same ligands shows that their configurations depend not only on the nature of the two central donor atoms of the ligand, but also on the nature of the metallic ion. In aqueous solution, the stability constants of the $Ni^{II}$ chelates with these two ligands, determined by potentiometry, show the formation of $[Ni(LH)]^{3+}$ and $[NiL]^{2+}$ species in all cases. The chelating power of the pydadt ligand is slightly greater than that of pydado.


## Introduction

The bioinorganic chemistry of the transition metal complexes has become increasingly important since the discovery that metal ions are found at the active site of several very important classes of metalloenzymes.[1] The catalytic activity of these compounds depends on the nature of the donors atoms of the ligand[2] and the configuration of the complex.[3] In this case, considerable interest has developed in nickel complexes with mixed-donor ligands in order to elucidate the relationship between the donor atoms of the ligand and the geometry around the metal ion.[4]

Nickel(II) complexes of linear ether or thioether ligands with different numbers of oxygen or sulfur donor atoms and a heterocyclic nitrogen have attracted attention recently.[5] In order to elucidate the effects of the distinctive structural features of the ligands on the properties of the resulting complexes, we described earlier the coordination complexes of cobalt, copper and zinc with three linear hexadentate ligands [1,12-bis(2-pyridyl)-2,5,8,11-tetraazadodecane (pytrien), 1,12-bis(2-pyridyl)-5,8-dioxa-2,11-diazadodecane (pydado) and 1,12-bis(2-pyridyl)-5,8-dithia-2,11-diazadodecane (pydadt)].[6,7] These ligands contain ether oxygen or thioether donors as well as aliphatic and aromatic nitrogen donors in the their ligand framework (Scheme 1).




X = O (pydado)
X = S (pydadt)
X = NH (pytrien)

Scheme 1

As a continuation of our interest in the study of complexes that model the active sites in metalloproteins and to better understand the physicochemical properties of such complexes, especially the stereochemistry of the metallic centre, we present here the thermodynamic constants of the metal chelates formed by these ligands in aqueous solution as well as the syntheses of the nickel(II) complexes. Their configuration has been investigated by crystal structures and compared to those described earlier.[6−8]

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## Results and Discussion

### Synthesis

The violet nickel(II) complex of pydado was synthesised by the treatment of an aqueous solution of the ligand hydrochloride salt with tetramethylammonium hydroxide and one equivalent of nickel(II) perchlorate hexahydrate. The pink nickel(II) compound of pydadt was obtained by treating an ethanolic suspension of the ligand hydrochloride salt and four equivalents of sodium acetate with nickel(II) perchlorate hexahydrate. The two complexes were obtained as perchlorate salts, as confirmed by the presence of a strong band at 1090 $cm^{-1}$ in the IR spectra. The chromatography studies of each nickel(II) complexes indicate the presence of only one diastereoisomer. Crystals suitable for structure determination were obtained by recrystallisation from water (compound **1**) or from a water/ethanol (1:2, v/v) mixture (compound **2**) by slow evaporation of the solvent at room temperature.

### Solution Equilibria: Metal Chelate Formation Constants

The ligand equilibrium constants of the ligands pytrien,[9] and pydado and pydadt were determined previously.[7] The thermodynamic constants for the two ligands studied are listed in Table 1.

Table 1. Protonation constants ($\log K^n_H$), stability constants ($\log\beta$) and deprotonation constants ($\log K$) for $Ni^{2+}$ complexes of pydado and pydadt (I = 1 M $KNO_3$ and 20 °C)[a]

| | Ligands[b] | | | | Complexes | | |
|---|---|---|---|---|---|---|---|
| | $\log K^1_H$ | $\log K^2_H$ | $\log K^3_H$ | $\log K^4_H$ | $\log\beta_{110}$ | $\log\beta_{111}$ | $\log K$ |
| pydado | 8.63(3) | 7.76(4) | 2.36(4) | 1.5(6) | 12.85(1) | 15.38(7) | 2.53 |
| pydadt | 8.32(5) | 7.58(4) | 2.40(6) | 1.6(5) | 13.88(2) | 16.24(5) | 2.36 |

[a] Values in parentheses represent 1σ standard deviation for the last significant digit. [b] From ref.[7]

Complexation of $Ni^{2+}$ with pydado and pydadt occurs below pH 3. The NiL species with these two ligands are completely formed at pH 5.5 (pydado) and pH 4.5 (pydadt). The protonated metal chelate Ni(HL) is formed in small amounts: a maximum of 10% of the analytical $Ni^{2+}$ concentration with pydadt at pH 2.6, and a third, along with $Ni^{2+}$ and NiL species, with pydado at pH 3.1.

The stability constants $\beta = |MHL^{3+}|/|M^{2+}||L||H^+|$ for the equilibrium in Equation (1) for nickel(II) complexes of pydado and pydadt appear in Table 1. The stability constants of the complex with pydado are smaller than those with pydadt. These results are in good agreement with those described by Martell and co-workers[10] in the coordination of pyridyl ligands possessing ether (O) or thioether (S) donor atoms. A thioether donor coordinates more strongly to divalent transition metals than an ether donor. The preference of these metals to bind to the softer thioether may be also explained by the larger size of the sulfur atom, allowing it to approach the metal ion more closely, with less contraction of the ligand backbone.[11] The stability constants for the nickel(II) complex with pytrien are higher than those with pydado and pydadt; this is in agreement with the chelating power of nitrogen atom with regard to ether oxygen or thioether sulfur atoms.

$$M^{2+} + L + H^+ \rightleftarrows M(HL)^{3+} \quad (1)$$

The chelate protonation constants for the equilibrium in Equation (2), defined as $K = [MHL^{3+}]/[ML^{2+}][H^+]$, also appear in Table 1.

$$ML^{2+} + H^+ \rightleftarrows MHL^{3+} \quad (2)$$

The protonation constant of $[NiL]^{2+}$ (L = pydado and pydadt) is close to the protonation constant $K^3_H$. Therefor, the $K$ values do not allow the determination of the protonated nitrogen atom.

### X-ray Diffraction Studies

The structures of complexes $[Ni(pydado)](ClO_4)_2\cdot H_2O$ (**1**) and $[Ni(pydadt)](ClO_4)_2$ (**2**) were determined by single-crystal X-ray diffraction. Pertinent crystallographic and refinement details are reported in Table 2.

Table 2. X-ray experimental data for compounds **1** and **2**

| | **1** | **2** |
|---|---|---|
| Formula | $C_{18}H_{28}Cl_2N_4NiO_{11}$ | $C_{18}H_{26}Cl_2N_4NiO_8S_2$ |
| $M$ | 606.06 | 620.17 |
| Crystal system | triclinic | monoclinic |
| Space group | $P\bar{1}$ | $P2_1/c$ |
| $a$ (Å) | 9.3915(5) | 11.6381(2) |
| $b$ (Å) | 11.444(5) | 17.4104(4) |
| $c$ (Å) | 12.4039(5) | 24.8793(5) |
| α (deg) | 93.656(5) | 90 |
| β (deg) | 98.551(5) | 94.987(5) |
| γ (deg) | 108.023(5) | 90 |
| $V$ (Å$^3$) | 1245.1(2) | 5022.1(3) |
| $T$ (K) | 173 | 294 |
| $Z$ | 2 | 8 |
| μ(Mo-$K\alpha$) ($mm^{-1}$) | 1.058 | 1.203 |
| F000 | 1288 | 628 |
| Reflections measured | 8140 | 11871 |
| Unique reflections collected | 3164 | 7083 |
| $wR(F^2)$ | 0.074 | 0.066 |
| $R1$ [$I > 3\sigma(I)$] | 0.053 | 0.041 |
| $R_{int}$ | 0.04 | 0.04 |

### [Ni(pydado)][$ClO_4$]$_2\cdot H_2O$ (1)

The molecular structure of this complex consists of $[Ni(pydado)]^{2+}$ cations and $ClO_4^-$ anions. The two perchlorate anions are both ordered, with Cl−O bond lengths (average, 1.399 Å) and O−Cl−O bond angles (average 110.9°) similar to those reported earlier.[6,7] A view of the cation with the labelling scheme is shown in Figure 1.

Principal bond lengths and angles are listed in Table 3. The nickel(II) centre is coordinated by two aromatic nitrogens [N(1) and N(4)], two secondary amine nitrogens [(N2) and N(3)] and two ether oxygens [O(1) and O(2)]. Though several isomers can be obtained with a linear hexadentate ligand, the one observed here has the pyridine nitrogen atoms in the *trans* positions; the same isomer have been found for a zinc(II) complex.[7]

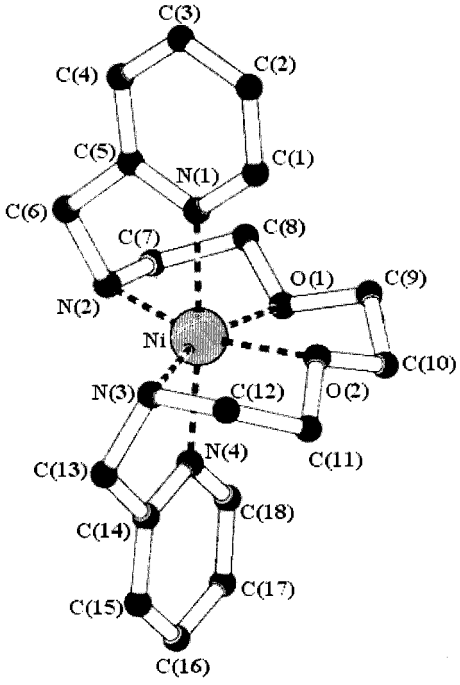



Figure 1. A PLUTON projection of the cation $[Ni(pydado)]^{2+}$ and the atom labelling-scheme; hydrogen atoms are omitted for clarity

The N(1)−Ni−N(4), N(2)−Ni−O(2) and N(3)−Ni−O(1) bond angles are 175.3(1)°, 159.8(1)° and 160.2(2)°, respectively. All nickel-donor atom bond lengths are slightly different [$Ni-N_{amine}$ (average 2.076 Å), $Ni-O_{ether}$ (average 2.084 Å) and $Ni-N_{pyridyl}$ (average 2.090 Å)]. Thus, the coordination geometry around the nickel atom is described as a slightly distorted octahedron, which is occupied by N(2), O(1), O(2) and N(3) at the equatorial sites and N(1) and N(4) at the axial sites. The two oxygen donor atoms are practically in the equatorial plane [N(1)−Ni−O(1): 92.8° and N(1)−Ni−O(2): 90.4°], whereas the two secondary amine nitrogen atoms are located below and above this plane, respectively [N(1)−Ni−N(2): 80.4° and N(1)−Ni−N(3): 96.9°].

Compared to the $[Zn(pydado)]^{2+}$ complex described earlier,[7] all metal-donor atom bond lengths in the nickel complex are smaller than those in the zinc complex, which is consistent with the larger radius of $Zn^{II}$. Conversely, the five chelate bond angles of 79.4(1)−83.3(2)° [average 81.4°] subtended by the ligand at the nickel atom are larger than their analogues of 74.1(1)−81.2(2)° [average 77.7°] in the zinc complex, in agreement with a smaller distortion in the nickel compound.

Table 3. Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

| Complex **1** | | | |
|---|---|---|---|
| Ni−N(1) | 2.088 (4) | Ni−N(4) | 2.092(4) |
| Ni−N(2) | 2.078(4) | Ni−O(1) | 2.085(3) |
| Ni−N(3) | 2.074(4) | Ni−O(2) | 2.083(3) |
| N(1)−Ni−N(2) | 80.4(2) | N(2)−Ni−O(2) | 159.8(1) |
| N(1)−Ni−N(3) | 96.9(2) | N(3)−Ni−O(1) | 160.2(2) |
| N(1)−Ni−N(4) | 175.3(1) | N(3)−Ni−O(2) | 83.3(2) |
| N(1)−Ni−O(1) | 92.8(1) | N(3)−Ni−N(4) | 80.7(2) |
| N(1)−Ni−O(2) | 90.4(1) | O(1)−Ni−O(2) | 79.4(1) |
| N(2)−Ni−N(3) | 115.4(2) | N(4)−Ni−O(1) | 90.7(1) |
| N(2)−Ni−N(4) | 97.0(2) | N(4)−Ni−O(2) | 93.3(1) |
| N(2)−Ni−O(1) | 83.2(1) | | |
| **Complex 2** | | | |
| Ni(1)−S(1) | 2.469(1) | Ni (2)−S(3) | 2.440(1) |
| Ni (1)−S(2) | 2.470(1) | Ni (2)−S(4) | 2.463(1) |
| Ni (1)−N(1) | 2.087(3) | Ni (2)−N(5) | 2.098(3) |
| Ni (1)−N(2) | 2.083(3) | Ni (2)−N(6) | 2.099(3) |
| Ni (1)−N(3) | 2.079(3) | Ni (2)−N(7) | 2.104(3) |
| Ni (1)−N(4) | 2.091(3) | Ni (2)−N(8) | 2.101(3) |
| N(1)−Ni(1)−N(2) | 79.7(1) | N(5)−Ni(2)−N(6) | 79.6(1) |
| N(1)−Ni(1)−N(3) | 99.1(1) | N(5)−Ni(2)−N(7) | 100.0(1) |
| N(1)−Ni(1)−N(4) | 94.4(1) | N(5)−Ni(2)−N(8) | 90.1(1) |
| N(1)−Ni(1)−S(1) | 165.06(9) | N(5)−Ni(2)−S(3) | 164.5(1) |
| N(1)−Ni(1)−S(2) | 90.44(8) | N(5)−Ni(2)−S(4) | 94.14(9) |
| N(2)−Ni(1)−N(3) | 178.8(1) | N(6)−Ni(2)−N(7) | 179.1(1) |
| N(2)−Ni(1)−N(4) | 98.5(1) | N(6)−Ni(2)−N(8) | 101.0(1) |
| N(2)−Ni(1)−S(1) | 86.46(9) | N(6)−Ni(2)−S(3) | 85.0(1) |
| N(2)−Ni(1)−S(2) | 94.85(9) | N(6)−Ni(2)−S(4) | 94.57(9) |
| N(3)−Ni(1)−N(4) | 81.3(1) | N(7)−Ni(2)−N(8) | 79.9(1) |
| N(3)−Ni(1)−S(1) | 94.8(1) | N(7)−Ni(2)−S(3) | 95.42(9) |
| N(3)−Ni(1)−S(2) | 85.37(9) | N(7)−Ni(2)−S(4) | 84.61(9) |
| N(4)−Ni(1)−S(1) | 93.07(9) | N(8)−Ni(2)−S(3) | 94.09(9) |
| N(4)−Ni(1)−S(2) | 166.39(9) | N(8)−Ni(2)−S(4) | 164.40(9) |
| S(1)− Ni(1)−S(2) | 85.18(4) | S(3)−Ni(2)−S(4) | 85.73(4) |

The crystal structure of complex **1** shows two, three-centre bifurcated H-bonds[12] between each secondary amine hydrogen and two oxygen atoms of each perchlorate anion [H(01)···O(4): 2.558 Å, H(01)···O(6): 2.416 Å and H(02)···O(7): 3.501 Å, H(02) ··O(9): 2.125 Å]. In the lattice of this complex, the intermolecular distances between the oxygen atom of the water of crystallisation and two oxygen atoms of one of the two perchlorate anions [O(11)···O(3): 3.217 Å and O(11)···O(5): 3.372 Å] are less than the sum of their van der Waals radii. This suggests that these species are also involved in hydrogen bonding interactions.

**$[Ni(pydadt)][ClO_4]_2$ (2)**

Compound **2** crystallises in a triclinic system with eight molecules in the unit cell. In the crystal lattice, the two enantiomeric isomers of the $[Ni(pydadt)]^{2+}$ cations are present in equal parts, giving a racemate. Three of the four $ClO_4^-$ anions are ordered, whereas the fourth, in which each oxygen atom occupies two sets of positions, is disordered. Each perchlorate anion forms a two-centre chelate H-bond[12] between one oxygen atom and each of two secondary amine hydrogens (O···HN, average 2.132 Å). A per-

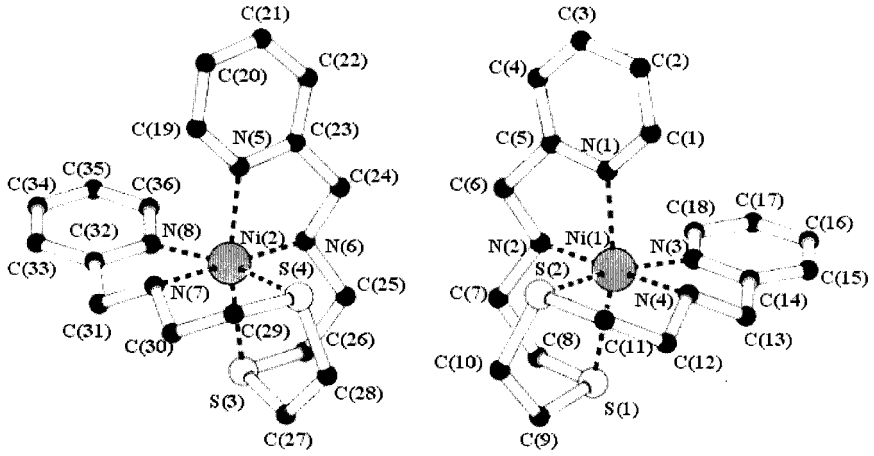



Figure 2. A PLUTON projection of the two enantiomeric cations of $[Ni(pydadt)]^{2+}$ and the atom labelling-scheme; hydrogen atoms are omitted for clarity

spective drawing of the two enantiomers cations with atom labelling is illustrated in Figure 2, relevant bond lengths and angles are given in Table 3.

The molecular structure of complex **2** shows that each $[Ni(pydadt)]^{2+}$ cation is hexacoordinate, with the two aromatic nitrogen atoms in the *cis* positions, whereas the two amino nitrogen atoms are in the *trans* positions. In each enantiomer, the bond lengths of the same donor atoms (N or S), while not always exact, are quite close [Ni(1)−N: average 2.085 Å; Ni(1)−S: 2.470 Å; Ni(2)−N: average, 2.101 Å], with the exception of the isomer labelled Ni(2), where the two Ni−S bond lengths are different [Ni(2)−S(3): 2.440 Å and Ni(2)−S(4): 2.463 Å]. In addition, the variation of the Ni−N and Ni−S bond lengths is opposite in the two enantiomers: the Ni(1)−N bond lengths are slightly shorter than Ni(2)−N (−0.016 Å), while the Ni(1)−S bonds are slightly longer than Ni(2)−S (average +0.018 Å). The $N_{py}-Ni-S$ (average 165°) and $N_{amino}-Ni-N_{amino}$ (average 179°) bond angles, which are practically the same in the two enantiomers, are not very close to those of an ideal octahedral geometry. According to the result obtained from ligand field spectroscopy (see below), complex **2** has $C_{2v}$ symmetry.

### Absorption Spectra

The electronic spectra of the two nickel(II) compounds (**1** and **2**) in the solid state are no different to those obtained in aqueous solution. The absorption spectra for these compounds exhibit essentially similar patterns in the 250−500 nm region, with two strong bands possibly due to intraligand[13] and charge-transfer transitions.

In the visible region, $[Ni(pydado)](ClO_4)_2$ (**1**) displays two bands at 890 nm and 560 nm. These two bands arise from $^3A_{2g}\rightarrow{}^3T_{2g}$ and $^3A_{2g}\rightarrow{}^3T_{1g}(^3F)$ transitions. The third band at higher energy is completely obscured by a metal-ligand charge transfer. These observations are consistent with an octahedral geometry around the $Ni^{2+}$ ion. The ligand-field parameters were calculated using the energy levels given by Lever: 10 Dq = 11230 $cm^{-1}$, Racah parameter $B$ = 860 $cm^{-1}$. These parameters, and those of the octahedral $[Ni(pytrien)](ClO_4)_2$ complex (10 Dq = 12360 $cm^{-1}$, $B$ = 826 $cm^{-1}$),[8] are in agreement with $NiN_4O_2$ and $NiN_6$ chromophores, respectively.

The spectrum of $[Ni(pydadt)](ClO_4)_2$ (**2**) shows two more-intense absorption bands centred around 890 nm and 540 nm. Each band present shoulders, which indicates a lowering of the symmetry around the $Ni^{2+}$ ion. These two absorption envelopes could be cleanly resolved into just three (10360 $cm^{-1}$, 11560 $cm^{-1}$ and 12050 $cm^{-1}$) and two (16950 $cm^{-1}$ and 18800 $cm^{-1}$) Gaussian components, respectively. The corresponding energy levels[14a] for these transitions are given in Figure 3; they are in agreement with those calculated for a $C_{2v}$ symmetry,[14b] and described by Meredith and Palmer[15] for a $[Ni(histidine)_2(OH_2)_2]$ complex.

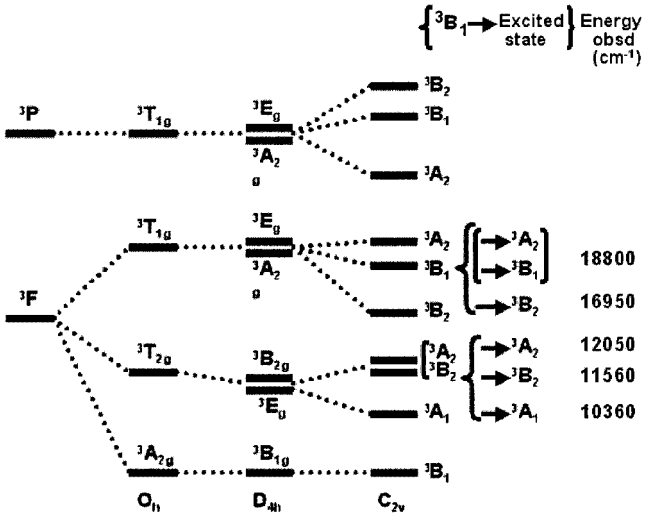


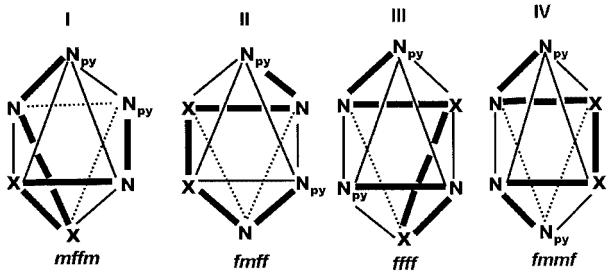

Figure 3. Observed energy levels[15] for $[Ni(pydadt)](ClO_4)_2$ with free ion and high symmetry

### Configuration of the Octahedral Complexes

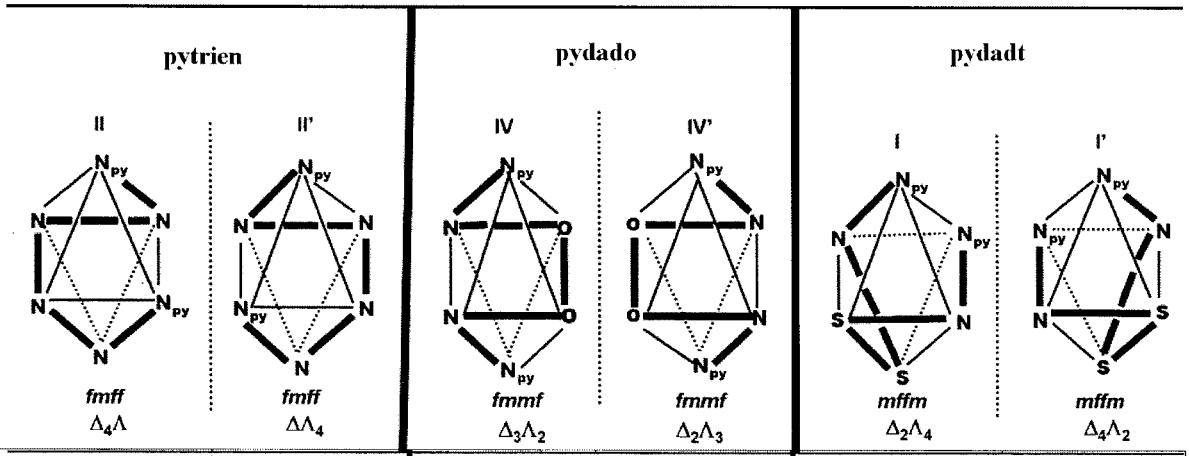
We have studied the coordination of first-row transition metals (cobalt, nickel, copper and zinc) with the linear hexadentate ligands pytrien,[6] pydado[7] and pydadt,[7] which possess two central N, O and S donors, respectively. These ligands, with three different donor atoms, are of the type A B C C B A, in which A represents a pyridyl nitrogen atom, B a secondary amine nitrogen atom and C the central heteroatom (N, O or S). Disregarding isomerism due to the fact that the secondary amine nitrogen donor can became stereogenic, and the non-planarity of the chelate rings formed upon complexation, there are many possibilities of ligand arrangement, meaning that there are four pairs of enantiomers possible with these $A_2B_2C_2$ donor sets. Generally, only one pair of enantiomers, which were resolved, was observed, indicating a stereoselectivity introduced by the different ligating atoms.[16]

All possible diastereoisomers of our complexes with linear hexadentate ligands are shown in Scheme 2. When dealing with this kind of octahedral compound, the α (or β)-*cis* or *cis-trans-cis* types of nomenclature are not adequate to describe the geometry of the complex, as they do not differentiate between the wrapping of the ligand around the metal ion in all the isomers; for example, the two configurations I and III (Scheme 2) are both *cis-trans-cis*. Therefore the extension of the Saito method,[17] introduced by Hartshorn and House,[18] was used to describe the configuration of the octahedral complexes obtained with these three linear hexadentate ligands; for each sequence of three donor atoms, the descriptors m and f indicate meridional and facial ligand segments, respectively. Consequently, each isomer of octahedral complexes with a linear hexadentate ligand can be described with four characters, with pairs of enantiomers having the same labelling.




Scheme 2

The X-ray crystal structures of the cobalt, nickel, copper and zinc complexes with the three hexadentate ligands show that the four compounds isolated with each ligand crystallise in the same diastereoisomer as the four described above. $[M(pytrien)]^{n+}$ ($n$ = 3 for Co and $n$ = 2 for Ni, Cu and Zn), $[M(pydado)]^{2+}$ and $[M(pydadt)]^{2+}$ have the configuration II, IV and I, respectively (Figure 4). As the only difference between these ligands is the two central heteroatoms, the stereoselectivity of these complexes is introduced by the central ligating atoms. In the crystal lattice, $[Cu(pydado)]^{2+}$ or $[Ni(pydadt)]^{2+}$ are racemates, whereas the others complexes have only one of the two enantiomers for the corresponding configurations. With each ligand, disregarding the




| AC_NH [a] | *R R S S* | *S S R R* | *S S* | *R R* | *R R* | *S S* |
|---|---|---|---|---|---|---|
| Cobalt | $[Co(pytrien)]^{3+}$ | - | - | $[Co(pydado)]^{2+}$ [b] | [b]$[Co(pydadt)]^{2+}$ | - |
| Nickel | $[Ni(pytrien)]^{2+}$ [c] | - | $[Ni(pydado)]^{2+}$ | - | $[Ni(pydadt)]^{2+}$ | $[Ni(pydadt)]^{2+}$ |
| Copper | $[Cu(pytrien)]^{2+}$ | - | Racemic distorted tetrahedral | | Powder form | |
| Zinc | - | $[Zn(pytrien)]^{2+}$ | $[Zn(pydado)]^{2+}$ | - | - | $[Zn(pydadt)]^{2+}$ |

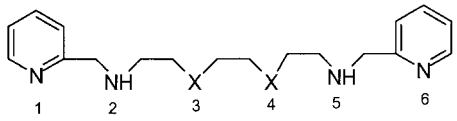
[a] Absolute configuration of the secondary amine nitrogen atoms. [b] Ref.[8] [c] Ref.[24]

Figure 4. The configurations of cobalt, nickel, copper and zinc complexes with pytrien, pydado and pydadt ligands

nature of the metal ion, the cobalt and zinc compounds are always enantiomers, while the nickel complexes have either the enantiomeric configuration of the cobalt or the zinc complex.

A comparison of all octahedral metal complexes of pytrien and pydado shows that the donor atoms 5 and 6 (Scheme 3) are reversed in the octahedron. The absolute configuration of the stereogenic amine nitrogen atom 2 is retained for the two cobalt (*R*) and the two zinc (*S*) complexes, whereas it is inverted in the nickel compounds.




Scheme 3

The large size of the sulfur donor atoms of the pydadt ligand does not allow the facial coordination of the heteroatoms 1, 2 and 3 (Scheme 3) around the metal ion. Therefore, an mffm configuration is imposed for all $[M(pydadt)]^{2+}$ cations, so that the bulky pyridyl groups and the larger thioether sulfur atoms are in *trans* positions.

## Conclusion

The equilibrium constants of the $Ni^{II}$ chelates with pydado and pydadt determined by potentiometry show the formation of $[NiLH]^{3+}$ and $[NiL]^{2+}$ species in all cases; $[NiLH]^{3+}$species are present in small amounts around pH 3, while $[NiL]^{2+}$ are fully formed in neutral medium. The stability constants of the $[Ni(pydadt]^{2+}$ species are slightly greater than those of $[Ni(pydado]^{2+}$, in agreement with analogous ligands described by Martell and co-workers.[10,11] Comparison of the thermodynamic constants of these nickel(II) complexes and the other $M^{II}$ complexes (M = cobalt, copper and zinc) of the same ligands,[7] shows that the values of the stability constants follow the Irving−Williams series.

X-ray crystallographic studies show that the Ni−N and Ni−O bond lengths in $[Ni(pydado]^{2+}$ cation are practically identical, and this is in good agreement with the electronic spectrum, which is easily interpreted in $O_h$ symmetry. However, the presence of the thioether sulfur atoms in the $[Ni(pydadt]^{2+}$ complex, in which the Ni−S bond lengths are always longer than Ni−N (+0.376 Å), leads to a large distortion around the nickel ion, with the bulky pyridyl groups and sulfur donor atoms in *trans* positions. This distortion is corroborated with the nature of the electronic spectrum of $[Ni(pydadt]^{2+}$ complex, characteristic for $C_{2v}$ symmetry.

The crystal structures of some octahedral first-row transition metal complexes with these kinds of symmetrical linear hexadentate ligands show clearly that the two central heteroatom donors introduce a stereoselectivity of the complexes obtained and therefore dictate their configuration. Conversely, the central metal ion imposes their conformation; for example, cobalt and zinc always have an inverse conformation.

## Experimental Section

**Chemicals and Starting Materials:** All solvents were purified by conventional procedures[20] and distilled prior to use. Chemicals commercially available (Aldrich) were used as supplied without further purification. The ligands, 1,12-bis(2-pyridyl)-5,8-dioxa-2,11-diazadodecane (pydado) and 1,12-bis(2-pyridyl)-5,8-dithia-2,11-diazadodecane (pydadt) were obtained as tetrahydrochloride salts from the condensation of 2-pyridine carboxaldehyde and triethylene dioxa(or dithia)diamine, as described previously.[7]

***CAUTION:*** *Although we have experienced no problems while handling any of the perchlorate substances described herein, readers are advised to handle these compounds as potentially explosive compounds.*

Elemental analyses (C, H and N) were carried out on a Perkin−Elmer 2400 C, H, N element analyser in our university. The metal analysis was performed on an ICP AES Liberty Series II Varian apparatus. Magnetic susceptibilities were determined at room temperature (20 °C) using $HgCo(SCN)_4$ as a calibrant; diamagnetic susceptibility corrections were calculated from Pascal's constants.[21]

**Potentiometry:** All chemicals used were of analytical grade. $HNO_3$ and KOH were purchased from Prolabo. $KNO_3$ and $Ni(NO_3)_2{\cdot}3H_2O$ were purchased from Fluka. The metal ion solutions were prepared (ca. 0.01 M) and standardised with $Na_2H_2edta{\cdot}2H_2O$. All measurements were performed in a thermoregulated cell at (20.0 ± 0.1) °C, under $N_2$ to prevent absorption of $CO_2$, as described previously.[7]

The measurement apparatus consist of a microprocessor burette (Metrohm Dosimat 665) and a pH meter (Metrohm 713) equipped with a combined pH glass electrode (Metrohm AG 9101) linked to a PC. The stability constants were calculated and refined with the computer program PROTAF.[22]

**Spectroscopy:** The UV/Vis. spectra were recorded on a Perkin−Elmer Lambda 6 spectrophotometer. Gaussian deconvolution of visible absorption spectra were performed using an application developed under "QUATTRO PRO" by J. Rimbault in our laboratory. IR spectra were obtained in KBr pellet.

**$[Ni(pydado)](ClO_4)_2{\cdot}H_2O$ (1):** A solution of tetramethylammonium hydroxide 0.5 M was added dropwise to an aqueous solution (30 mL) of pydado·4HCl (0.49 g, 1 mmol) and nickel(II) perchlorate hexahydrate (0.36 g, 1 mmol) to adjust the pH to around 8. Slow evaporation of the solvents at room temperature yielded violet crystals, suitable for X-ray diffraction studies, after two months. Yield: ca. 75%; m.p. 255 °C. $C_{18}H_{28}Cl_2N_4NiO_{11}$: calcd. C 35.7, H 4.6, N 9.2, Ni 9.7; found C 35.8, H 4.3, N 9.3, Ni 9.5. $\chi_M = 4310 \times 10^{-6}$ uem cgs, $\mu_{eff} = 3.18\ \mu_B$. UV/Vis ($H_2O$): $\lambda_{max}$ (ε) = 890 nm (12 $mol^{-1}{\cdot}L{\cdot}cm^{-1}$), 560 (13).

**$[Ni(pydadt)](ClO_4)_2$ (2):** A mixture of sodium acetate trihydrate (0.54 g, 4 mmol) and the ligand pydadt·4HCl (0.54 g, 1 mmol) in absolute ethanol (30 mL) was stirred, whilst boiling, for 10 min in a water bath. The mixture was then cooled and the sodium chloride that precipitated was filtered. Nickel perchlorate hexahydrate

(0.36 g, 1 mmol) in absolute ethanol (20 mL) was added dropwise to the filtrate and the solution was stirred for 2 h at room temperature. The mauve powder formed was filtered off and washed with ethanol. Recrystallisation from water/ethanol (1:5) gave pink crystals suitable for X-ray diffraction after three weeks. Yield: ca. 70%; m.p. 270 °C. $C_{18}H_{26}Cl_2N_4NiO_8S_2$: calcd. C 34.9, H 4.2, N 9.0, Ni 9.5; found C 34.7, H 3.9, N 8.9, Ni 9.1. $\chi_M = 4550 \times 10^{-6}$ uem cgs, $\mu_{eff} = 3.27\ \mu_B$. UV/Vis ($H_2O$): $\lambda_{max}$ ($\varepsilon$) = 965 nm sh, 890 (40 $mol^{-1}\cdot L\cdot cm^{-1}$), 830 sh; 570 sh, 540 (23).

**Crystal Structure Determinations:** The crystal data were collected on a Kappa CCD diffractometer using monochromatic Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073Å). The structures were solved by direct methods. After refinement of the non-hydrogen atoms, Fourier difference maps revealed maxima of residual electron density close to positions expected for hydrogen atoms. Hydrogen atoms were introduced as fixed contributors at calculated positions [C−H = 0.95 Å; B(H) = 1.3 Beq]. Final difference maps revealed no significant maxima. All calculations were performed with the Nonius OpenMoleN package.[23] Neutral-atom scattering factor and anomalous dispersion coefficients were taken from a standard source.[24] Molecular drawings were produced with the PLUTON software package.[25]

CCDC-213876 [for Ni(pydado)]$(ClO_4)_2\cdot H_2O$] and -213877 [for Ni(pydadt)]$(ClO_4)_2$] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] [1a] J. C. Noveronn, M. M. Olmstead, P. K. Mascharak, *J. Am. Chem. Soc.* **1999**, *121*, 3553. [1b] B. A. Brennan, G. Alms, M. J. Nelson, L. T. Durney, R. C. Scarrow, *J. Am. Chem. Soc.* **1996**, *118*, 9194. [1c] J. R. Lancaster Jr., *The Bioinorganic Chemistry of Nickel* (Ed.: J. R. Lancaster), VCH Publishers, New York, **1988**. [1d] R. Cammack, *The Bioinorganic Chemistry of Nickel* (Ed.: J. R. Lancaster), VCH Publishers, New York, **1989**; chapter 8. [1e] R. H. Holm, P. Kennepohl, E. I. Solomon, *Chem. Rev.* **1996**, *96*, 2239, and references cited therein.

[2] [2a] J. Xia, J. Dong, S. Wang, R. A. Scott, P. A. Lindahl, *J. Am. Chem. Soc.* **1995**, *117*, 7065. [2b] R. Cammack, C. Bagyanka, K. Kovacs, *Eur. J. Biochem.* **1989**, *182*, 357. [2c] S. L. Tan, J. A. Fox, N. Kojima, C. T. Walsh, W. H. Orme-Johnson, *J. Am. Chem. Soc.* **1984**, *106*, 3064.

[3] [3a] M. K. Eidsness, R. A. Scott, B. C. Prickril, D. V. DerVartanian, J. LeGall, I. Moura, J. J. G. Moura, H. D. Peck Jr., *Proc. Natl. Acad. Sci., U. S. A.* **1989**, *86*, 147. [3b] M. K. Eidsness, R. J. Sullivan, R. A. Scott, *The Bioinorganic Chemistry of Nickel* (Ed.: J. R. Lancaster), VCH Publishers, New York, **1989**; chapter 4.

[4] [4a] N. Goswami, D. Eichhorn, *Inorg. Chem.* **1999**, *38*, 4329. [4b] E. Pereira, L. Gomes, D. B. Castro, *J. Chem. Soc., Dalton Trans.* **1998**, 629. [4c] E. Bouwman, R. K. Henderson, A. K. Powell, J. Reedijk, *J. Chem. Soc., Dalton Trans.* **1998**, 3495. [4d] T. Pandiyan, C. Duran de Bazua, M. Soriano-Garcia, *Fresenius' J. Anal. Chem.* **1996**, *354*, 636. [4e] M. Palaniandavar, T. Pandiyan, M. Lakshiminarayanan, H. Manohar, *J. Chem. Soc., Dalton Trans.* **1995**, 445.

[5] [5a] C. P. Kulatilleke, S. N. Goldie, M. J. Hegg, L. A. Ochrymowycz, D. B. Rorabacher, *Inorg. Chem.* **2000**, *39*, 1444. [5b] C. R. Lucas, S. Liu, *J. Chem. Soc., Dalton Trans.* **1994**, 185. [5e] B. Adhikary, S. Liu, C. R. Lucas, *Inorg. Chem.* **1993**, *32*, 5957.

[6] C. Jubert, A. Mohamadou, E. Guillon, J. P. Barbier, *Polyhedron* **2000**, *19*, 1447.

[7] C. Jubert, A. Mohamadou, J. Marrot, J. P. Barbier, *J. Chem. Soc., Dalton Trans.* **2001**, 1230.

[8] C. Jubert, PhD Thesis, University of Reims, **2001**; p. 105.

[9] [9a] S. D. Kim, J. K. Kim, W. S. Jung, *Bull. Kor. Chem. Soc.* **1996**, *17*, 80. [9b] S. D. Kim, J. K. Kim, W. S. Jung, *Polyhedron* **1998**, *17*, 1223.

[10] [10a] S. A. Bedell, J. H. Timmons, A. E. Martell, I. Murase, *Inorg. Chem.* **1982**, *21*, 1525. [10b] W. R. Harris, I. Murase, J. H. Timmons, A. E. Martell, *Inorg. Chem.* **1978**, *17*, 889. [10c] J. H. Timmons, W. R. Harris, I. Murase, A. E. Martell, *Inorg. Chem.* **1978**, *17*, 2192.

[11] R. G. Lacoste, A. E. Martell, *Inorg. Chem.* **1964**, *3*, 881.

[12] H. R. Hoveyda, V. Karunaratne, C. J. Nichols, S. J. Rettig, A. K. W. Stephens, C. Orvig, *Can. J. Chem.* **1998**, *76*, 414.

[13] [13a] M. Ray, S. Mukherjee, R. N. Mukherjee, *J. Chem. Soc., Dalton Trans.* **1990**, 3635. [13b] M. Ray, R. N. Mukherjee, *Polyhedron* **1992**, *11*, 2929.

[14] [14a] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, Oxford, New York, Tokyo, 2nd ed., **1984**, p. 126. [14b] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, Oxford, New York, Tokyo, 2nd ed., **1984**, p. 517.

[15] P. L. Meredith, T. A. Palmer, *Inorg. Chem.* **1971**, *10*, 1049.

[16] J. C. Bailar Jr., *Coord. Chem. Rev.* **1990**, *100*, 1.

[17] Y. Saito, *Top. Stereochem.* **1978**, *10*, 95.

[18] R. M. Hartshorn, D. A. House, *J. Chem. Soc., Dalton Trans.* **1998**, 2577.

[19] N. Arulsamy, J. Glerup, A. Hazell, D. J. Hodgson, C. J. Mc Kenzie, H. Toftlund, *Inorg. Chem.* **1994**, *33*, 3023.

[20] D. Perrin, W. L. F. Armarego, R. D. Perrin, *Purification of Laboratory Chemicals*, Pergamon, Oxford, 3rd ed., **1988**.

[21] A. Earnshaw, *Introduction to Magnetochemistry*, Academic Press, London, **1968**, p. 5.

[22] [22a] R. Fournaise, C. Petitfaux, *Talanta* **1987**, *34*, 385. [22b] R. Fournaise, C. Petitfaux, *Analusis* **1990**, *18*, 242.

[23] *OpenMoleN, Interactive Structure Solutions*, Nonius B. V., Delft, The Netherlands, **1997**.

[24] D. T. Cromer and J. T. Waber, *International Tables for X-ray Crystallography*, **1974**, IV, The Kyonoch Press, Birmingham, Table 2.2b and Table 2.3.1.

[25] A. L. Spek, *WINPL98, Interactive Molecular Graphics and Calculations Program for Windows*, University of Utrecht, The Netherlands, **2000**.

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