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## Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:

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### Hexapyridine Addition Compounds of Metal(II) Salts (Nickel and Magnesium Perchlorates, Magnesium Nitrate): Their Supramolecular Nature, and Anion Coordination of the Metal Cation [1]

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**To cite this Article** Soldatov, Dmitriy V. and Ripmeester, John A. (1998) 'Hexapyridine Addition Compounds of Metal(II) Salts (Nickel and Magnesium Perchlorates, Magnesium Nitrate): Their Supramolecular Nature, and Anion Coordination of the Metal Cation [1]', *Supramolecular Chemistry*, 9: 3, 175 – 181

**To link to this Article:** DOI: 10.1080/10610279808034984

**URL:** <http://dx.doi.org/10.1080/10610279808034984>

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# Hexapyridine Addition Compounds of Metal(II) Salts (Nickel and Magnesium Perchlorates, Magnesium Nitrate): Their Supramolecular Nature, and Anion Coordination of the Metal Cation [1]

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*(Received 22 December 1997)*

The X-ray structures of  $[\text{NiPy}_4(\text{ClO}_4)_2] \cdot 2\text{Py}$  (1),  $[\text{MgPy}_4(\text{ClO}_4)_2] \cdot 2\text{Py}$  (2), and  $[\text{MgPy}_4(\text{NO}_3)_2] \cdot 2\text{Py}$  (3) are presented. All three compounds are isostructural crystallizing in orthorhombic *Ccca* space group with 4 formula units per unit cell. For (1)  $a = 12.344(1)$ ,  $b = 16.104(1)$ ,  $c = 16.932(1)$  Å;  $V = 3366$  Å<sup>3</sup>;  $D_{\text{calc}} = 1.445$  g cm<sup>-3</sup>; final  $R = 0.074$  for 1418 observed data. For (2)  $a = 12.084(1)$ ,  $b = 16.465(1)$ ,  $c = 17.379(1)$  Å;  $V = 3458$  Å<sup>3</sup>;  $D_{\text{calc}} = 1.340$  g cm<sup>-3</sup>; final  $R = 0.053$  for 1782 observed data. For (3)  $a = 12.081(1)$ ,  $b = 15.146(1)$ ,  $c = 17.222(1)$  Å;  $V = 3151$  Å<sup>3</sup>;  $D_{\text{calc}} = 1.313$  g cm<sup>-3</sup>; final  $R = 0.063$  for 1153 observed data. The compounds consist of host complex molecules with two acido-groups and four pyridine ligands coordinated, and of guest pyridine species included in channels of molecular crystal framework. Coordination of poor acido-ligands in presence of non-bonded pyridine molecules is discussed and possible supramolecular nature of other  $M(\text{ClO}_4)_2 \cdot 6\text{Py}$  compounds is suggested.

*Keywords:* Werner clathrate, crystal structure, pyridine, guest-host chemistry, supramolecular compounds

## INTRODUCTION

Previously, many hexapyridine addition compounds of metal(II) salts were shown to be of a supramolecular nature, with four pyridines coordinated to the metal and two included in the crystal framework [2]. The clathrate nature of the compounds was shown recently by exchanging non-bonded pyridine [3] with other guest species. This allows these compounds to be classified as a novel group of Werner clathrates [4]. The important feature of this new family is the wide variability of the host complex constituents that maintain the structural similarity of the resulting  $[\text{MPy}_4\text{X}_2] \cdot 2\text{Py}$  clathrates:

Another feature is that the above compounds contain non-bonded pyridine, while acidic anions act as ligands to the metal cation. This is not a trivial fact because one could expect that pyridine would compete favourably for coordi-

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X = Br:  
 X = I:  
 X = N<sub>3</sub>:  
 X = NO<sub>2</sub>:  
 X = NO<sub>3</sub>:  
 X = NCO:  
 X = NCS:  
 X = HCOO:

M = Mg[5]; Ca[6]; Co, Ni[2]; Cu[7];  
 M = Ca[6]; Co, Ni[2]; Cu[8]; Cd[9];  
 M = Co, Ni[10];  
 M = Ni[11];  
 M = Mn[12]; Co[2]; Ni[2, 13]; Cu[2, 14]; Zn[2, 15]; Cd[2, 15b];  
 M = Mn, Fe, Co, Ni, Cu, Zn, Cd[16];  
 M = Ni[17];  
 M = Ni[2];

nation sites about the metal cation when "poor" ligands such as nitrate are involved. Nevertheless, an unequivocal conclusion from direct X-ray structural determinations [12–15] is that nitrate does coordinate as a monodentate ligand resulting in a structure similar to the others from the above list.

The problem becomes more significant when one attempts to predict the nature of dozens of other known (and still to come), but structurally uncharacterized "MX<sub>2</sub>\*6Py" compounds [2]. Among these, of special interest are the compounds of metal perchlorates, as the donating ability of the latter is considered to be extremely low. The "M(ClO<sub>4</sub>)<sub>2</sub>\*6Py" compounds form the largest series: M = Mg, Ca, Sr, Ba, Co, Ni, Zn, Cu, Cd, Hg [18]. Like other previously known "MX<sub>2</sub>\*6Py" compounds, those listed above containing perchlorate were considered to be hexapyridine complexes, [MPy<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>, with all of the pyridine coordinated with free perchlorate anions. This hypothesis seemed to be supported by IR studies [18k] as well as other observations. Meanwhile, only one structure from the series has been studied directly, that of [BaPy<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub>] [5b]. According to this study, all six pyridines and the perchlorates (acting as bidentate ligands) are coordinated to barium which therefore has ten-fold coordination; a similar situation is true of the [Ba(4-MePy)<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub>], [BaPy<sub>6</sub>I<sub>2</sub>] and [SrPy<sub>5</sub>Br<sub>2</sub>] compounds. This work did not shed light on the problem because cations of smaller size would hardly can be expected to have this kind of coordination.

To elucidate the problem further, an X-ray structural study of three compounds is reported. Two of these are hexapyridine compounds of

nickel and magnesium perchlorates where Ni represents a typical transition metal of the first row, and Mg is a main-group metal of small radius. The compound of magnesium nitrate, never reported before, is also included for comparison.

## EXPERIMENTAL SECTION

### Preparations

The clathrates are very hygroscopic, especially those of magnesium, and the compounds are unstable due to guest loss.

#### *Diperchloratotetrapyridinenickel(II)-pyridine (1:2) clathrate, [NiPy<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub>]\*2Py*

A mixture of Ni(ClO<sub>4</sub>)<sub>2</sub>\*6H<sub>2</sub>O (3.7 g; 10 mmol) and 2,2'-dimethoxypropane (20 ml) was refluxed for 1 hour until the color of the lower phase changed from green to brown. After cooling, a slight excess of pyridine (6 ml; 75 mmol) was carefully layered on top of the mixture which was protected from ambient moisture. After several days, suitable octahedral crystals grew on the upper side of the interface crust. If pyridine is added with mixing, the clathrate forms quickly and quantitatively as a fine crystalline product.

#### *Diperchloratotetrapyridinemagnesium(II)-pyridine (1:2) clathrate, [MgPy<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub>]\*2Py*

In a dry box Mg(ClO<sub>4</sub>)<sub>2</sub> (0.6 g; water content < 8%) was stirred with hot pyridine (40 ml). Slow

cooling resulted in several octahedral crystals of the clathrate.

**Dinitratotetrapyridinemagnesium(II)-pyridine (1:2) clathrate,  $[\text{MgPy}_4(\text{NO}_3)_2] \cdot 2\text{Py}$**

In a dry box, excess magnesium (turnings) was added to a solution of  $\text{AgNO}_3$  (1.7 g; 10 mmol) in methanol (20 ml). After 1 day, when a test for  $\text{Ag}^+$  became negative (no darkening of copper) the solution was filtered, mixed with excess of pyridine (25 ml), evaporated down to 20 ml and was allowed to cool slowly. The clathrate (2.6 g; 80 %) formed as parallelepiped like crystals.

**Crystallography**

In a dry pyridine atmosphere the crystals of the clathrates were mounted and sealed inside Lindemann glass capillary tubes. All experi-

ments were carried out at 20°C on a Siemens SMART CCD diffractometer equipped with graphite-monochromated  $\text{MoK}_\alpha$  radiation. The data collected were corrected for Lorentz and polarization effects and for absorption. A summary of the crystal data and experimental parameters is given in Table I.

The structures were solved and refined with the program SHELXTL [19], by using the heavy-atom (Ni-compound) or direct (Mg) methods, differential Fourier synthesis, full-matrix least squares, and anisotropic approximation for the non-hydrogen atoms. Hydrogen atoms were included in calculated positions ( $d_{\text{C-H}} = 0.93 \text{ \AA}$ ) as 'riding' on the corresponding carbon atoms and were refined isotropically with thermal factors 1.2 times greater than those for the adjacent carbon atoms. Guest pyridine nitrogen atoms were assigned by consideration of the thermal parameter and difference map residue behavior. Because of possible disordering of the

TABLE I Crystal data and experimental details

Compound	$[\text{NiPy}_4(\text{ClO}_4)_2] \cdot 2\text{Py}$	$[\text{MgPy}_4(\text{ClO}_4)_2] \cdot 2\text{Py}$	$[\text{MgPy}_4(\text{NO}_3)_2] \cdot 2\text{Py}$
Crystal habit	parallelepiped	octahedron	octahedron
Crystal color	light-blue	colorless	colorless
Crystal sizes, mm	0.3 0.4 0.5	0.5 0.5 0.5	0.4 0.4 0.4
Formula	$\text{C}_{30}\text{H}_{30}\text{Cl}_2\text{N}_6\text{NiO}_8$	$\text{C}_{30}\text{H}_{30}\text{Cl}_2\text{MgN}_6\text{O}_8$	$\text{C}_{30}\text{H}_{30}\text{MgN}_6\text{O}_6$
Formula unit mass	732.2	697.8	622.9
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	<i>Ccca</i>	<i>Ccca</i>	<i>Ccca</i>
Unit cell:			
<i>a</i> , Å	12.344(1)	12.084(1)	12.081(1)
<i>b</i> , Å	16.104(1)	16.465(1)	15.146(1)
<i>c</i> , Å	16.932(1)	17.379(1)	17.222(1)
<i>V</i> , Å <sup>3</sup>	3366(1)	3458(1)	3151(1)
<i>Z</i>	4	4	4
<i>F</i>	1512	1448	1304
<i>D</i> <sub>calc</sub> , g cm <sup>-3</sup>	1.445	1.340	1.313
$\mu(\text{MoK}_\alpha)$ , cm <sup>-1</sup>	7.92	2.62	1.12
$2\theta_{\text{max}}$ , deg.	60	60	60
<i>h, k, l</i> (min/max)	-15/16, -15/21, -22/22	-16/16, -22/12, -23/21	-16/14, -18/20, -9/23
Data:			
collected ( <i>R</i> <sub>int</sub> )	11719 (0.042)	21644 (0.022)	8804 (0.036)
unique	2185	2240	2036
unique-observed ( <i>I</i> > 2σ( <i>I</i> ))	1418	1782	1153
Refined parameters	133	133	124
<i>R</i> <sup>*</sup>	0.074	0.053	0.063
<i>R</i> <sub>w</sub> <sup>2</sup> ( <i>k</i> ; <i>m</i> ) <sup>**</sup>	0.133 (0.047; 3.00)	0.147 (0.065; 1.32)	0.151 (0.072; 0.67)
GOF	1.17	1.09	1.05
Res. density, eÅ <sup>3</sup>	-0.18/0.33	-0.27/0.38	-0.26/0.15

\*  $R = \sum |F_o| - |F_c| / \sum |F_o|$

\*\*  $R_w^2 = \sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)^2]$ ;  $w = 1 / [\sigma^2(F_o^2) + (kP)^2 + mP]$ , where  $P = (\max(F_o^2) + 2F_c^2) / 3$ .

nitrogen between position 1 and 4 (both lying on the crystallographic 2 axis) an attempt was made to refine the distribution. An occupancy of 75–90% was obtained for the main orientation but with low accuracy and no improvement in the refinement so that the disorder was disregarded. All positive data were involved in the final steps of the refinement. The biggest residual extrema on the difference map involved chlorine atoms in compounds containing perchlorate.

## RESULTS

All three compounds are isostructural and chemically similar. They are consistent with the formulations  $[\text{NiPy}_4(\text{ClO}_4)_2] \cdot 2\text{Py}$ ,  $[\text{MgPy}_4(\text{ClO}_4)_2] \cdot 2\text{Py}$ , and  $[\text{MgPy}_4(\text{NO}_3)_2] \cdot 2\text{Py}$  reflecting molecular crystal type and the presence of two kinds of molecules. No intermolecular contacts shorter than the sum of the van der Waals radii of the respective atoms are found. For this reason clathrate terminology will be used from now on. Fractional atomic coordinates are listed in Tables II–IV; Table V compares the host molecular geometries of the structures, and

TABLE II Final fractional atomic coordinates ( $\times 10^4$ ) and  $U(\text{eq}) = 1/3(U_{11} + U_{22} + U_{33})$  ( $\times 10^3 \text{ \AA}^2$ ) for  $[\text{NiPy}_4(\text{ClO}_4)_2] \cdot 2\text{Py}$

Atom	x	y	z	$U(\text{eq})$
Ni	0	2500	2500	46(1)
O(1)	1737(4)	2583(7)	2643(4)	65(2)
C1	2830(1)	2469(3)	2376(2)	61(1)
O(2)	2926(6)	1670(4)	2059(5)	107(2)
O(3)	3032(6)	3050(4)	1779(4)	114(3)
O(4)	3542(6)	2582(6)	3002(6)	191(7)
N(1)	0	1205(2)	2500	51(1)
C(11)	-727(3)	769(2)	2084(2)	55(1)
C(12)	-755(3)	-79(2)	2069(3)	66(1)
C(13)	0	-514(3)	2500	70(2)
N(2)	0	2500	1251(2)	54(1)
C(21)	735(4)	2083(3)	840(2)	65(1)
C(22)	771(4)	2072(3)	28(3)	83(1)
C(23)	0	2500	-382(4)	88(2)
N(1G)	2500	0	-493(5)	157(4)
C(11G)	1803(7)	-421(6)	-75(4)	161(3)
C(12G)	1731(6)	-433(5)	708(4)	148(3)
C(13G)	2500	0	1117(6)	141(4)

TABLE III Final fractional atomic coordinates ( $\times 10^4$ ) and  $U(\text{eq}) = 1/3(U_{11} + U_{22} + U_{33})$  ( $\times 10^3 \text{ \AA}^2$ ) for  $[\text{MgPy}_4(\text{ClO}_4)_2] \cdot 2\text{Py}$

Atom	x	y	z	$U(\text{eq})$
Mg	0	2500	2500	45(1)
O(1)	1706(2)	2569(6)	2600(5)	65(2)
C1	2857(1)	2478(2)	2384(2)	60(1)
O(2)	2986(4)	1702(2)	2061(3)	108(1)
O(3)	3090(4)	3055(2)	1811(3)	106(2)
O(4)	3509(4)	2584(5)	3035(3)	188(4)
N(1)	0	1165(1)	2500	49(1)
C(11)	-750(2)	738(1)	2099(1)	56(1)
C(12)	-778(2)	-98(1)	2087(1)	62(1)
C(13)	0	-526(2)	2500	65(1)
N(2)	0	2500	1213(1)	53(1)
C(21)	765(2)	2096(1)	811(1)	67(1)
C(22)	793(2)	2086(2)	20(1)	86(1)
C(23)	0	2500	-384(2)	87(1)
N(1G)	2500	0	-484(2)	134(2)
C(11G)	1755(3)	-393(3)	-92(2)	125(1)
C(12G)	1732(3)	-421(3)	686(2)	119(1)
C(13G)	2500	0	1080(2)	118(2)

TABLE IV Final fractional atomic coordinates ( $\times 10^4$ ) and  $U(\text{eq}) = 1/3(U_{11} + U_{22} + U_{33})$  ( $\times 10^3 \text{ \AA}^2$ ) for  $[\text{MgPy}_4(\text{NO}_3)_2] \cdot 2\text{Py}$

Atom	x	y	z	$U(\text{eq})$
Mg	0	2500	2500	55(1)
O(1)	1681(3)	2308(3)	2528(6)	75(2)
N	2627(3)	2539(4)	2438(4)	69(1)
O(2)	3008(6)	2732(5)	1819(4)	117(2)
O(3)	3296(6)	2605(5)	2951(5)	128(3)
N(1)	0	1041(2)	2500	59(1)
C(11)	-763(2)	577(2)	2106(1)	63(1)
C(12)	-787(2)	-333(2)	2090(1)	71(1)
C(13)	0	-802(3)	2500	71(1)
N(2)	0	2500	1186(1)	55(1)
C(21)	831(2)	2149(2)	776(1)	67(1)
C(22)	855(2)	2137(2)	-26(2)	76(1)
C(23)	0	2500	-430(2)	74(1)
N(1G)	2500	0	-494(2)	85(1)
C(11G)	1718(3)	-390(2)	-86(2)	89(1)
C(12G)	1688(3)	-414(2)	704(2)	93(1)
C(13G)	2500	0	1103(2)	93(1)

Figure 1 shows an ORTEP drawing with the atomic numbering scheme for  $[\text{NiPy}_4(\text{ClO}_4)_2] \cdot 2\text{Py}$ .

The host molecule (Fig. 1) has the metal cation in an octahedral environment, surrounded by two oxygens from two terminal acido-groups in a *trans*-configuration and four nitrogens from pyridine ligands in a propeller conformation. One-quarter of the formula unit is crystallogra-

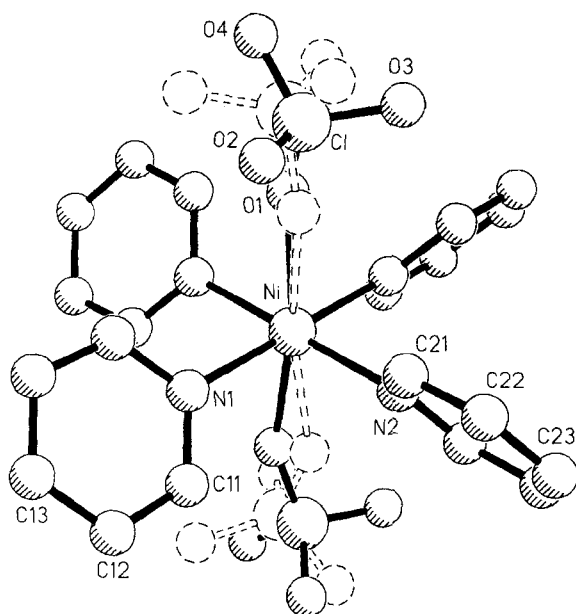


FIGURE 1 Host molecule (H-atoms are omitted) of  $[\text{NiPy}_4(\text{ClO}_4)_2] \cdot 2\text{Py}$  clathrate with atomic numbering scheme. Symmetrically equivalent positions for perchlorates are shown with dashes.

phically independent, the metal cation being located on a site of 222 crystallographic symmetry. The  $M-N_{\text{Py}}$  coordination bonds coincide with the two twofold axes in the equatorial plane of the complex while the anion ligands are disordered over two positions about the axial twofold axis. As one can see from Table V, the main differences among the structures concern distinct differences in coordination bond lengths and the angles of rotation of the ligands out of the equatorial plane.

Guest pyridine species are located in channels stretching along the  $a$ -axis direction (Fig. 2). As one can see from the figure, the anionic ligands as well as the guest species have high thermal parameters. The atomic thermal parameters of the guest pyridines are more than twice as large as those of the ligands in compounds with perchlorate while in  $[\text{MgPy}_4(\text{NO}_3)_2] \cdot 2\text{Py}$  they are comparatively low, suggesting a tighter guest accommodation.

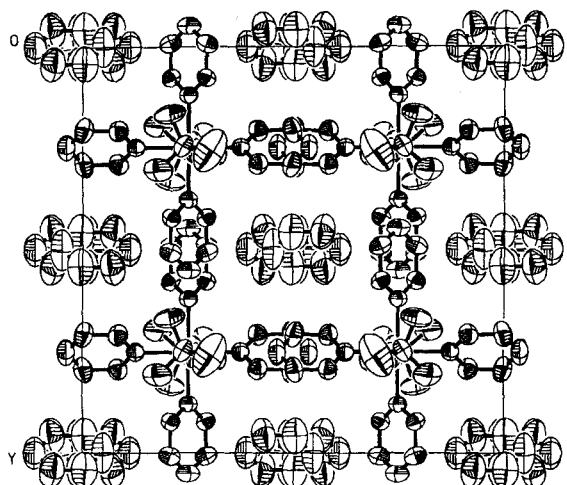


FIGURE 2 Projection of the  $[\text{NiPy}_4(\text{ClO}_4)_2] \cdot 2\text{Py}$  structure along the channel direction. The perchlorates' disorder is not shown and the H-atoms are omitted for clarity. The thermal ellipsoids are at 50% probability level.

## DISCUSSION

Contrary to expectations, the  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{Py}$  and  $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{Py}$  compounds turn out to be isostructural and isomorphous with known  $[\text{MPy}_4\text{X}_2] \cdot 2\text{Py}$  clathrates with only four of the six pyridine molecules coordinating. Taking into account the nearest interactions for Ni(II) and Mg(II) one can see that the structural type is determined by the size of the central atom rather than its chemical nature. This unexpected fact is illustrated as well by the comparison between  $[\text{MgPy}_4(\text{ClO}_4)_2] \cdot 2\text{Py}$  and  $[\text{BaPy}_6(\text{ClO}_4)_2]$ , where the metals of the same group form considerably different chemical and structural types. A similar situation is observed for  $[\text{MgPy}_4(\text{NO}_3)_2] \cdot 2\text{Py}$ , which is isomorphous with analogous compounds of typical transition metals Mn, Ni, Co, Cu and Zn, while  $\text{Ba}(\text{NO}_3)_2$  does not react with pyridine at all. Chemical differences are apparent as changes in coordination bond lengths:

TABLE V Geometry of the host molecules in the clathrates studied: selected bond lengths (Å), and bond-bond, bond-plane and interplane angles (°)

	[NiPy <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub> ] (M = Ni; X = Cl)	[MgPy <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub> ] (M = Mg; X = Cl)	[MgPy <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> ] (M = Mg; X = N)
BONDS			
M—N(1)	2.086(4)	2.197(2)	2.210(3)
M—N(2)	2.115(4)	2.237(2)	2.263(2)
M—O(1)	2.162(5)	2.072(3)	2.052(3)
X—O(1)	1.435(5)	1.449(4)	1.205(5)
X—O(2)	1.399(5)	1.404(4)	1.198(5)
X—O(3)	1.400(5)	1.406(3)	1.202(4)
X—O(4)	1.389(5)	1.389(3)	
ANGLES			
bond-bond			
M—O(1)—X	152.8(4)	158.2(5)	153.4(4)
bond-{plane}			
M—O(1)—{Eq}	7.4	5.9	8.2
{plane}—{plane}			
{NO <sub>3</sub> }—{Eq}			
{Py1}—{Eq}	51.7	52.6	53.5
{Py2}—{Eq}	53.8	54.4	61.8

{Eq} = {M, N(1), N(2)};

{Py1} = {N(1), C(11), C(12), C(13)};

{Py2} = {N(2), C(21), C(22), C(23)}.

Average	[MPy <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub> ]*2Py		[MPy <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> ]*2Py	
	Mg	Ni	Mg	Ni [13]
M—N <sub>Py<sub>6</sub></sub> , Å	2.22	2.10	2.24	2.11
M—O, Å	2.07	2.16	2.05	2.09

These data are consistent with Pearson's concept [20]: the 'hard' acceptor Mg(II) forms shorter bonds with 'hard' donor oxygen while for the 'softer' acceptor Ni(II) the situation is nearly opposite.

The question that is difficult to answer is why the less preferred perchlorate wins in competing with the stronger pyridine ligand for the fifth and sixth coordination sites about Ni(II) in [NiPy<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub>]\*2Py. The data obtained unequivocally suggest the coexistence of coordinated perchlorates and non-bonded pyridines in the structure. Possible explanations may involve the considerable intramolecular steric constraints when six pyridines coordinate to the central atom. Although such a mode of coordination is observed in some structures, this occurs either if no alternative ligands are present, as in

[FePy<sub>6</sub>]<sup>2+</sup>[Fe<sub>4</sub>(CO)<sub>13</sub>]<sup>2-</sup> [21a] (the cluster anions are too bulky and have low nucleophilicity due to extensive delocalization of the negative charge), or for metals of the 5-th and 6-th periods, as in [RuPy<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> [21b], [HgPy<sub>6</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> [21c], and the complexes of Sr and Ba mentioned above. At the same time, in the case of the metals of smaller radius, a supramolecular architecture with the small anionic ligands that are coordinated and pyridine species that are included appears to be preferable.

A further conclusion that can be extrapolated from this work is the probable supramolecular nature of other compounds of the type 'M(ClO<sub>4</sub>)<sub>2</sub>\*6Py', especially those of Ca, Co, Zn and Cu, and their structural similarity with those studied in this work.

#### Acknowledgment

This work was supported by the NATO Science Program (Research Visit Grant SRG 951535). We thank K. Udachin and G. Enright for helpful discussions.

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