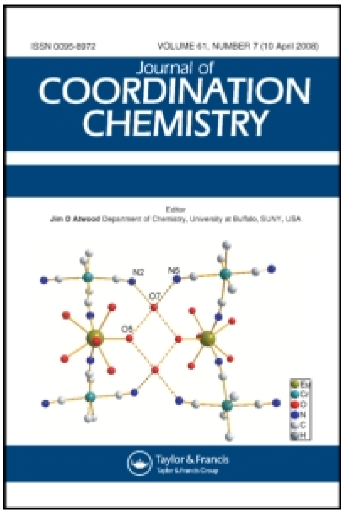

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CRYSTAL AND MOLECULAR STRUCTURE OF BIS(ISOTHIOCYANATO)TETRAKIS(PYRIDINE)-MAGNESIUM(II)

Janusz Lipkowski[a]; Dmitriy Soldatov[ab]
[a] Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland [b] Institute of Inorganic Chemistry SO RAN, Novosibirsk, Russie

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NOTE

CRYSTAL AND MOLECULAR STRUCTURE OF BIS(ISOTHIOCYANATO)TETRAKIS(PYRIDINE)-MAGNESIUM(II)

JANUSZ LIPKOWSKI and DMITRIY SOLDATOV#

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01 224 Warsaw, Poland

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$Mg(C_5H_5N)_4(NCS)_2$, $C_{22}H_{20}N_6S_2Mg$, is monoclinic, space group is $C2/c$, with $a = 12.379(4)$, $b = 13.093(5)$, $c = 15.060(6)$ Å, $\beta = 107.35(3)°$, $V = 2330(2)$ Å^3, $Z = 4$, $D_{calc} = 1.303$ g cm^{-3}, μ(CuKα) = 24.664 cm^{-1}, $F(000) = 952.0$. The structure consists of centrosymmetric monomeric units in which the Mg(II) cation is octahedrally coordinated to the N-atoms of four pyridines and two *trans*-coordinated isothiocyanate ligands. The structure is similar to those of $[M(C_5H_5N)_4(NCS)_2]$, where M = Fe, Co, Ni.

KEY WORDS: Magnesium(II), thiocyanate, pyridine, complex, structure, X-ray.

INTRODUCTION

In contrast to pyridine complexes of Ni, Co, Fe,[1-3] tetrapyridinates of magnesium and calcium halogenides were reported mostly as solvates with pyridine.[4-6] As was shown recently, isostructural solvates $[MgPy_4Br_2].2Py$*, $[CaPy_4Br_2].2Py$ and $[CaPy_4I_2].2Py$ are channel-type clathrates.[7] Being interested in the inclusion ability of such hosts, we undertook an X-ray study of the title compound in order to compare the molecular structure and crystal packing of this compound and other similar complexes.

EXPERIMENTAL

Preparation

Prismatic crystals of the title complex were obtained by recrystallization of magnesium thiocyanate from hot pyridine.[7] The product melts with decomposition at 239°C.

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* Py = pyridine.

\# On leave of absence from the Institute of Inorganic Chemistry SO RAN, 630090 Novosibirsk, Lavorentyeve 3, Russie

Structure Analysis

Because of the instability of the crystals in open air (gradual loss of pyridine), the X-ray study was performed using the crystal placed into a glass capillary and the intensity data collection was carried out at $-50°C$. An Enraf-Nonius CAD4 single-crystal diffratometer using Ni-filtered CuKα-radiation and a ω-2θ scan technique was used. The data were corrected for Lorentz and polarization effects; absorption was ignored.

The structure was solved by direct methods (SHELX-86[8] was used) in the monoclinic cell: $a = 12.379(4)$, $b = 13.093(5)$, $c = 15.060(6)$ Å, $\beta = 107.35(3)°$ and refined to $R = 0.048$. A summary of the experimental data is given in Table 1. Hydrogen atoms were included in final cycles at the calculated positions ($d_{C\text{-}H} = 1.08$Å) as "riding" on corresponding carbon atoms and with temperature factor fixed.

Fractional atomic coordinates, bond lengths and angles are listed in Table 2 to 5. Lists of cordinates of hydrogen atoms, thermal parameters and F_o/F_c tables are available upon request from J.L.

RESULTS AND DISCUSSION

The molecular structure of [MgPy$_4$(NCS)$_2$] is depicted in Fig. 1.[9] The molecule is centrosymmetric. The Mg(II) cation has a slightly distorted octahedral coordination by nitrogens of four pyridines and two *trans*-isothiocyanate groups. The Mg—N_{CS} and Mg—N_{Py} distances for two crystallographically independent pyridines are 2.109(2), and 2.239(2) and 2.248(3) Å, respectively. The thiocyanate ligand is linear and forms an angle equal to 155.9(2)° with the Mg—N_{CS} bond. The pyridine rings are planar to within 0.02Å, wth the Mg(II) cation deviating from the planes by +0.11 (ring I) and +0.08 (ring II) Å. The dihedral angles between the pyridine rings I and II and the equatorial plane of the complex (defined by four N_{Py}) are 55.7(1) and 65.2(1)°.

Table 1 Data collection and structure analysis parameters

Molecular formula	$C_{22}H_{20}N_6S_2Mg$
Molecular weight	456.9
Space group	$C2/c$
Unit cell (Å)	$a = 12.379(4)$
	$b = 13.093(5)$
	$c = 15.060(6)$
	$\beta = 107.35(3)°$
	$V = 2330(2)$Å^3
	$Z = 4$
Density (calc.) [g cm^{-3}]	1.303
Temperature [K]	223
Radiation	Nil-filtered CuKα
Absorption coefficient [cm^{-1}]	24.664
Crystal size [mm]	0.3 0.4 0.5
Number of reflections	
measured	2914
unique	2488
used in the structure analysis	1671 ($I > 3\sigma(I)$)
Final R value	0.048
Residual extrema in final difference map	$+0.27/-0.37$eÅ^{-3}

Table 2 Fractional atomic coordinates (×10^4) and *B*(eq) with e.s.d.s (in parentheses) for non-hydrogen atoms

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(eq)
Mg	2500(0)	2500(0)	5000(0)	2.77(3)
S	−776(1)	1453(1)	5830(1)	4.14(2)
N(1)	1108(2)	1704(2)	5199(2)	3.46(7)
N(2)	1342(2)	3799(2)	4384(2)	3.11(7)
N(3)	2113(2)	1868(2)	3551(2)	3.10(7)
C(1)	317(3)	1589(2)	5461(2)	2.90(9)
C(2)	256(3)	3626(3)	3887(3)	4.1(1)
C(3)	−496(3)	4408(3)	3531(3)	5.2(1)
C(4)	−151(4)	5400(3)	3686(3)	5.2(1)
C(5)	954(4)	5597(3)	4190(3)	4.8(1)
C(6)	1661(3)	4776(3)	4514(3)	3.9(1)
C(7)	2437(3)	2333(3)	2879(3)	3.7(1)
C(8)	2240(3)	1953(4)	2002(3)	4.5(1)
C(9)	1685(3)	1023(3)	1784(3)	4.4(1)
C(10)	1357(3)	531(3)	2445(3)	4.1(1)
C(11)	1563(3)	970(3)	3312(3)	3.5(1)

Table 3 Bond distances with e.s.d.s (in parentheses) (involving non-hydrogen atoms), Å

Mg—N(1)	2.109(2)	Mg—N(2)	2.239(2)
Mg—N(3)	2.248(3)	S—C(1)	1.619(4)
N(1)—C(1)	1.171(4)	N(2)—C(2)	1.347(4)
N(2)—C(6)	1.336(4)	N(3)—C(7)	1.340(5)
N(3)—C(11)	1.352(4)	C(2)—C(3)	1.381(5)
C(3)—C(4)	1.364(5)	C(4)—C(5)	1.378(6)
C(5)—C(6)	1.380(5)	C(7)—C(8)	1.363(6)
C(8)—C(9)	1.388(6)	C(9)—C(10(	1.347(6)
C(10)—C(11)	1.378(6)		

Table 4 Bond angles with e.s.d.s (in parentheses) (involving non-hydrogen atoms), degrees

N(2)—Mg—N(3)	87.3(1)
N(1)—Mg—N(3)	90.6(1)
N(1)—Mg—N(2)	89.1(1)
Mg—N(1)—C(1)	155.9(2)
Mg—N(2)—C(6)	122.8(2)
Mg—N(2)—C(2)	120.8(2)
C(2)—N(2)—C(6)	116.4(3)
Mg—N(3)—C(11)	121.6(2)
Mg—N(3)—C(7)	122.7(2)
C(7)—N(3)—C(11)	115.8(3)
S—C(1)—N(1)	178.9(2)
N(2)—C(2)—C(3)	122.5(3)
C(2)—C(3)—C(4)	119.9(4)
C(3)—C(4)—C(5)	118.8(3)
C(4)—C(5)—C(6)	118.0(4)
N(2)—C(6)—C(5)	124.4(3)
N(3)—C(7)—C(8)	123.9(3)
C(7)—C(8)—C(9)	118.8(3)
C(8)—C(9)—C(10)	118.8(3)
C(9)—C(10)—C(11)	119.2(3)
N(3)—C(11)—C(10)	123.5(3)

As calculations of interaction energy between ligands of such molecules show,[10] there is considerable steric strain for this type of conformation. In this case it results not only in distortions in the Mg—N_{Py} bond distances but also in the angle between these bonds changing from 90° (87.3(1)° for N_{PyI}—Mg—N_{PyII}). As a whole the geometry of the $[MgPy_4(NCS)_2]$ molecule is as for $[MPy_4(NCS)_2]$, where M=Fe, Co, Ni,[11–13] and seems to be defined by intramolecular interactions rather than by the nature and radius of the cation.

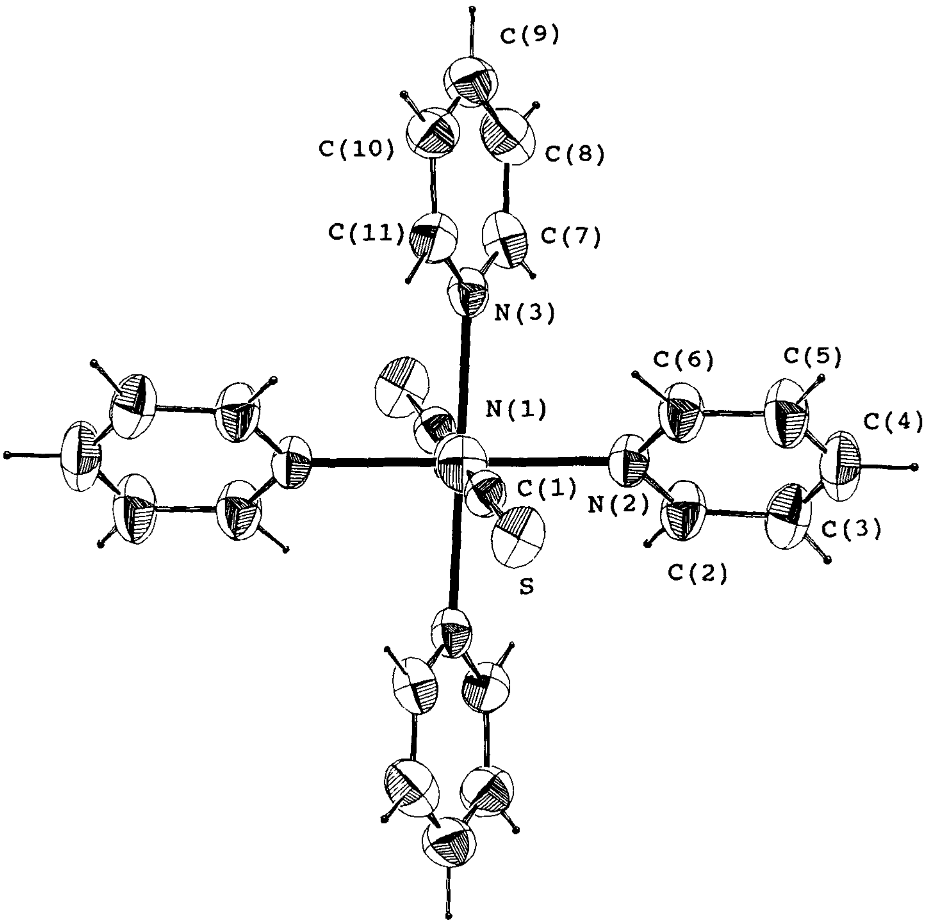

Figure 1 ORTEP[9] plot of the [MgPy$_4$(NCS)$_2$] molecule and the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and hydrogen atoms are depicted using arbitrary radii.

The crystal packing of the complex (Fig. 2) consists of monomeric units interacting with one another only by van der Waals forces. The space group and lattice constants are similar to those of analogous Fe, Co and Ni complexes. It is interesting to note that such similarity does not hold when the NCS anionic ligand is substituted with halogens, with the difference between tetrapyridinates of alkaline earth[14,4–6] and transition metal halogenates[1–3] increasing along with the radius of halogen anion, both in the geometry of the molecule and in the inclusion ability of the complexes.

Acknowledgements

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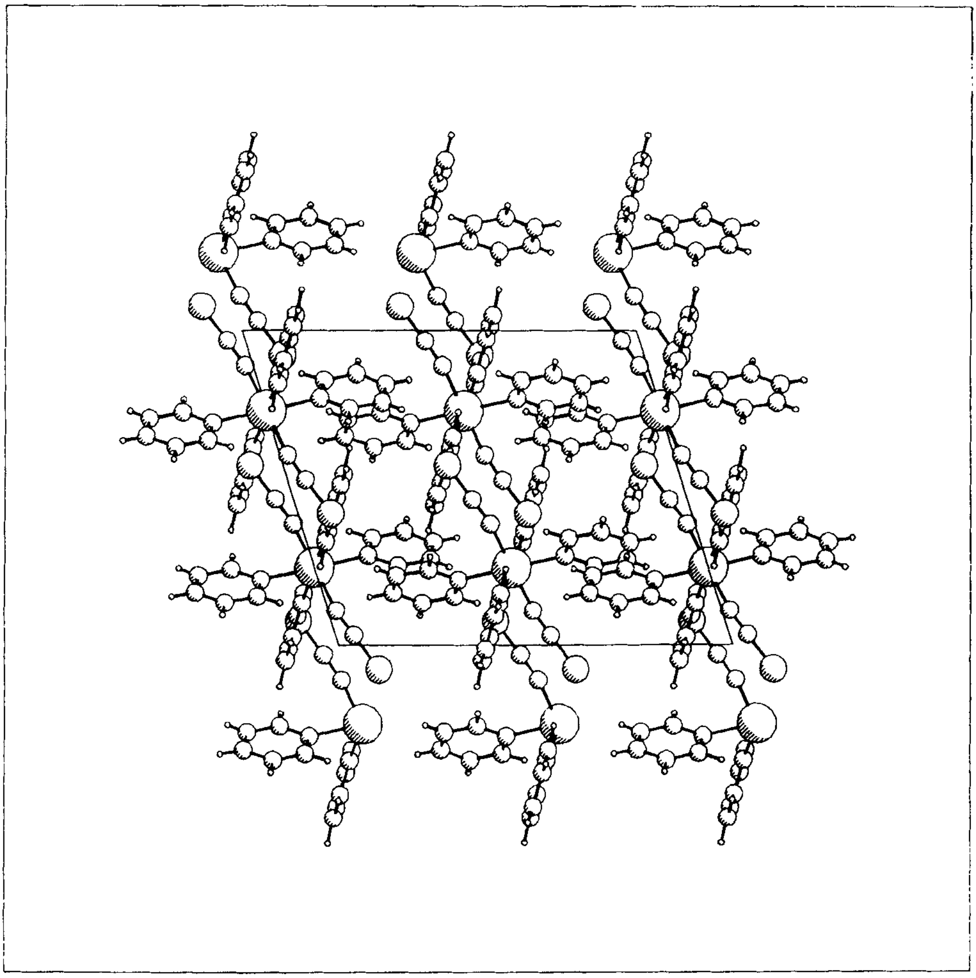

Figure 2 Molecular packing viewed along the **b** axis.

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