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Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:
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To cite this Article Lipkowski, Janusz and Soldatov, Dmitriy(1993) 'Crystal structure of bis(isothiocyanato)diaquabis(pyridine)-magnesium(II) solvate with pyridine 1:4', Supramolecular Chemistry, 3: 1, 43 — 46

To link to this Article: DOI: 10.1080/10610279308029837

URL: http://dx.doi.org/10.1080/10610279308029837

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SUPRAMOLECULAR CHEMISTRY, Vol. 3, pp. 43–46
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Crystal structure of bis(isothiocyanato)diaquabis(pyridine)-magnesium(II) solvate with pyridine 1:4

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(Received February 16, 1993)

Single crystal X-ray structure of solvate of $[MgPy_2(H_2O)_2(NCS)_2]$ (Py = Pyridine) complex with pyridine 1:4 at −50 °C is reported. It is monoclinc $P2_1/n$, with: $a = 9.530(5)$, $b = 12.495(4)$, $c = 15.592(5)$ Å, $\beta = 90.11(4)°$, $D_{calc.} = 1.165\ g{\cdot}cm^{-3}$, $Z = 2$. The number of data are 4215 (measured) and 1251 (unique-observed). The final R values are $R = 0.082$ (unit weights) and $R_w = 0.067$. In the centrosymmetric complex molecule the Mg(II) cation is octahedrally coordinated by four N and two O of the three pairs of trans-arranged ligands. Four solvating pyridine molecules form a second coordination sphere, with two pyridines connecting to each water ligand by means of hydrogen bonds.

INTRODUCTION

Recently, on studying clathration ability of the $[MgPy_4(NCS)_2]$* complex we obtained and reported the crystalline compound with mole ratio $Mg{:}Py{:}H_2O{:}NCS = 1{:}6{:}2{:}2$.[1] The chemical composition, RAMAN spectra and thermal properties suggested that the crystal structure would contain more than one type of pyridine moiety. It was supposed that this compound would be related to clathrates of $[MA_4X_2]$ complexes, where M is a transition metal cation(II), A is a neutral ligand such as substituted pyridine, and X is a univalent anionic ligand.[2] To answer these questions the single crystal X-ray study of the compound was undertaken.

RESULTS

The structure is monoclinic $P2_1/n$, with $a = 9.530(5)$, $b = 12.495(4)$, $c = 15.592(5)$ Å, $\beta = 90.11(4)°$, $D_{calc} = 1.165\ g{\cdot}cm^{-3}$, $Z = 2$. Fractional atomic coordinates, bond lengths and angles are listed in Tables 1–3.* In Figure 1 the atom numbering scheme and an ORTEP drawing of the complex and pyridine molecules are given.[3] The Mg(II) cation is octahedrally coordinated by two N atoms of the pyridine ligands, two N atoms of NCS-groups and two O atoms of the water ligands. The complex molecule being centrosymmetric, the three pairs of the ligands are each in trans-positions. The isothiocyanate ligand is linear and forms an angle equal to 172(1)° with the $Mg\text{-}N_{CS}$ bond. The distance $Mg\text{-}N_{CS}$ is 2.11(1) Å. The ring of the pyridine ligand is planar within 0.08 Å, with the Mg(II) cation deviating from the plane by 0.11 Å and the distance $Mg\text{-}N_{Py}$ being equal to 2.22(1) Å. The distance $Mg\text{-}O_{water}$ is 2.02(1) Å.

Four solvating pyridine molecules construct a second coordination sphere of the complex. Two crystallographically independent pyridines (A and B, respectively) are coordinated to water ligands by means of hydrogen bonds, with distances $O...N_{Py}$ being equal to 2.85(1) (for A) and 2.78(1) (for B) Å. Thus the structure consists of $[MgPy_2(H_2O)_2(NCS)_2]{\cdot}4Py$ monomeric units which interact with one another only by van der Waals forces. The rings of the solvate pyridine molecules are planar within 0.07 (for A) and 0.05 (for B) Å, with an angle between their planes being equal to 85.0(4)° and the angles between the ring planes of ligand pyridine and solvate ones equal to 90.5(5) and 95.0(5)° for A and B, respectively. Thus, the three pyridine rings lie approximately in three mutually-perpendicular planes.

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* Py = pyridine.

* Lists of coordinates of all hydrogen atoms, thermal parameters and Fo/Fc tables are available upon request.

Table 1 Fractional atomic coordinates (× 10**4) and B(eq) for the $[Mg(NCS)_2(H_2O)_2Py_2]·4Py$ structure

Atom	*X/A*	*Y/B*	*Z/C*	*B(eq)*
Complex:				
Mg	0	0	0	2.7(2)
S	2133(4)	3581(3)	−0025(3)	4.6(1)
C1	1500(12)	2356(10)	−0039(9)	2.8(3)
N1	1053(9)	1484(8)	−0057(7)	3.2(3)
O	0151(8)	−0147(7)	−1289(5)	3.1(3)
H1′	−0875(102)	−0451(72)	−1793(70)	
H2′	0572(95)	0195(79)	−1902(66)	
N2	2037(11)	−0841(9)	0136(7)	3.8(4)
C2	3116(15)	−0621(12)	−0409(10)	5.3(5)
C3	4365(17)	−1211(14)	−0334(12)	6.3(6)
C4	4507(17)	−1991(16)	0264(13)	7.9(8)
C5	3438(18)	−2181(14)	0843(12)	8.0(7)
C6	2206(14)	−1595(12)	0725(9)	5.3(5)
Pyridine A:				
N1A	2015(11)	0899(10)	7557(8)	3.9(4)
C1A	2031(15)	0663(12)	6740(11)	4.6(5)
C2A	2839(17)	1235(13)	6167(11)	6.8(7)
C3A	3597(15)	2072(13)	6422(11)	5.1(6)
C4A	3525(14)	2380(12)	7275(11)	4.7(5)
C5A	2732(15)	1764(12)	7833(11)	4.7(5)
Pyridine B:				
N1B	2883(12)	5842(10)	2730(8)	4.6(4)
C1B	2319(16)	5242(12)	2122(11)	5.8(5)
C2B	1018(17)	5450(13)	1742(12)	7.3(7)
C3B	0278(15)	6360(13)	2010(11)	6.2(5)
C4B	0833(15)	6984(13)	2618(9)	5.4(5)
C5B	2173(16)	6715(12)	2977(9)	5.0(6)

Table 2 Bond distances

Mg-N1	2.11(1)
Mg-O	2.024(8)
Mg-N2	2.22(1)
S-C1	1.65(1)
C1-N1	1.17(2)
O-H1′	1.3(1)
O-H2′	1.1(1)
N2-C2	1.36(2)
N2-C6	1.33(2)
C2-C3	1.40(2)
C3-C4	1.36(3)
C4-C5	1.38(3)
C5-C6	1.40(2)
N1A-C1A	1.31(2)
N1A-C5a	1.35(2)
C1A-C2a	1.38(2)
C2A-C3A	1.33(2)
C3A-C4A	1.39(2)
C4A-C5A	1.39(2)
N1B-C1B	1.32(2)
N1B-C5B	1.34(2)
C1B-C2b	1.40(2)
C2B-C3B	1.40(2)
C3B-C4B	1.34(2)
C4B-C5B	1.43(2)

Table 3 Bond angles

O-Mg-N2	90.7(4)
N1-Mg-N2	90.2(4)
N1-Mg-O	89.8(4)
S-C1-N1	179.0(1)
Mg-N1-C1	172.0(1)
Mg-O-H2′	147.0(5)
Mg-O-H1′	125.0(4)
H1′-O-H2′	82.0(7)
Mg-N2-C6	120.6(9)
Mg-N2-C2	120.4(9)
C2-N2-C6	119.0(1)
N2-C2-C3	119.0(1)
C2-C3-C4	121.0(2)
C3-C4-C5	120.0(2)
C4-C5-C6	116.0(2)
N2-C6-C5	124.0(1)
C1A-N1A-C5A	119.0(1)
N1A-C1A-C2A	121.0(1)
C1A-C2A-C3A	121.0(2)
C2A-C3A-C4A	118.0(1)
C3A-C4A-C5A	118.0(1)
N1A-C5A-C4A	121.0(1)
C1B-N1B-C5B	118.0(1)
N1B-C1B-C2B	124.0(1)
C1B-C2B-C3B	118.0(2)
C2B-C3B-C4B	119.0(2)
C3B-C4B-C5B	119.0(1)
N1B-C5B-C4B	122.0(1)

DISCUSSION

The solvate structure is significantly different from usual ‘clathrate’, ‘channel’ or ‘organic zeolite’ structural types. The large amount of solvating pyridine causes distinct separation of the $[MgPy_2(H_2O)_2(NCS)_2]$ molecules from one another (Fig 2); the complex species being surrounded, as illustrated in Fig 3, by pyridine moieties. The results of the X-ray investigation presented here together with the X-ray structure of $[MgPy_4(NCS)_2]^4$ allow the previously reported[1] experimental data on solvation equilibria in the system $Mg(NCS)_2/Py/H_2O$ to be rationalized. The equilibrium can be written as follows:

$$\underset{(I)}{[MgPy_4(NCS)_2]_{cryst}} + 2Py_{solv} + 2H_2O_{solv} \underset{>39°C}{\overset{\leq 39°C}{\rightleftarrows}} x\underset{(II)}{[MgPy_2(H_2O)_2(NCS)_2]\cdot 4Py_{cryst}} \qquad (1)$$

It may clearly be seen that there are two chemically non-equivalent pyridine species in the crystal structure. One is coordinated to the Mg(II) central cation while the other is hydrogen bonded to water which, in turn, is coordinated to Mg(II). The relative amounts of the two species are equal to 1:2. This result may be used

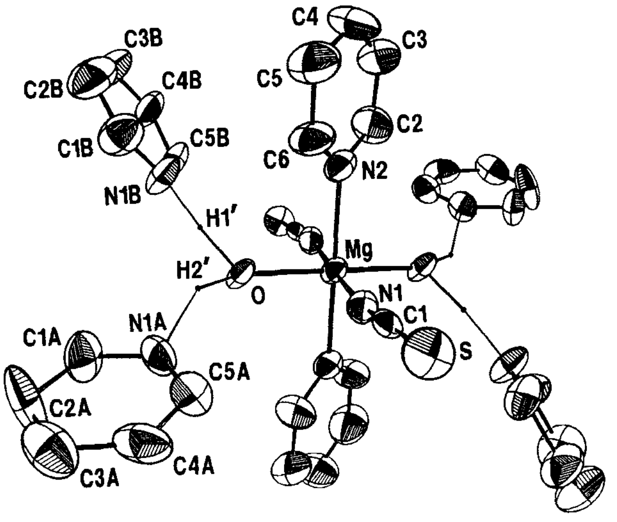

Figure 1 The atom numbering scheme and ORTEP plot of the [$MgPy_2(H_2O)_2(NCS)_2$]·4Py unit.

for interpretation of the IR spectral data listed in Table 4. The most striking feature is that the IR spectra of pyridine in the 1:4 solvate is qualitatively analogous to that measured in the supernatant fluid.

Rather interestingly, the solvate decomposes (both on TGA analysis or when left at room temperature in open air) according to the equation (2) below:

$$\underset{\text{(II)}}{[MgPy_2(H_2O)_2(NCS)_2]\cdot 4Py_{cryst}} \rightleftarrows$$

$$\times \underset{\text{(I)}}{[MgPy_4(NCS)_2]_{solid}} + 2Py_{gas} + 2H_2O_{gas} \qquad (2)$$

which is analogous to (1) in the reverse direction. It seems that water is rather weakly bonded in the complex, the solvate being thus stable in a rather narrow range of thermodynamic parameters.

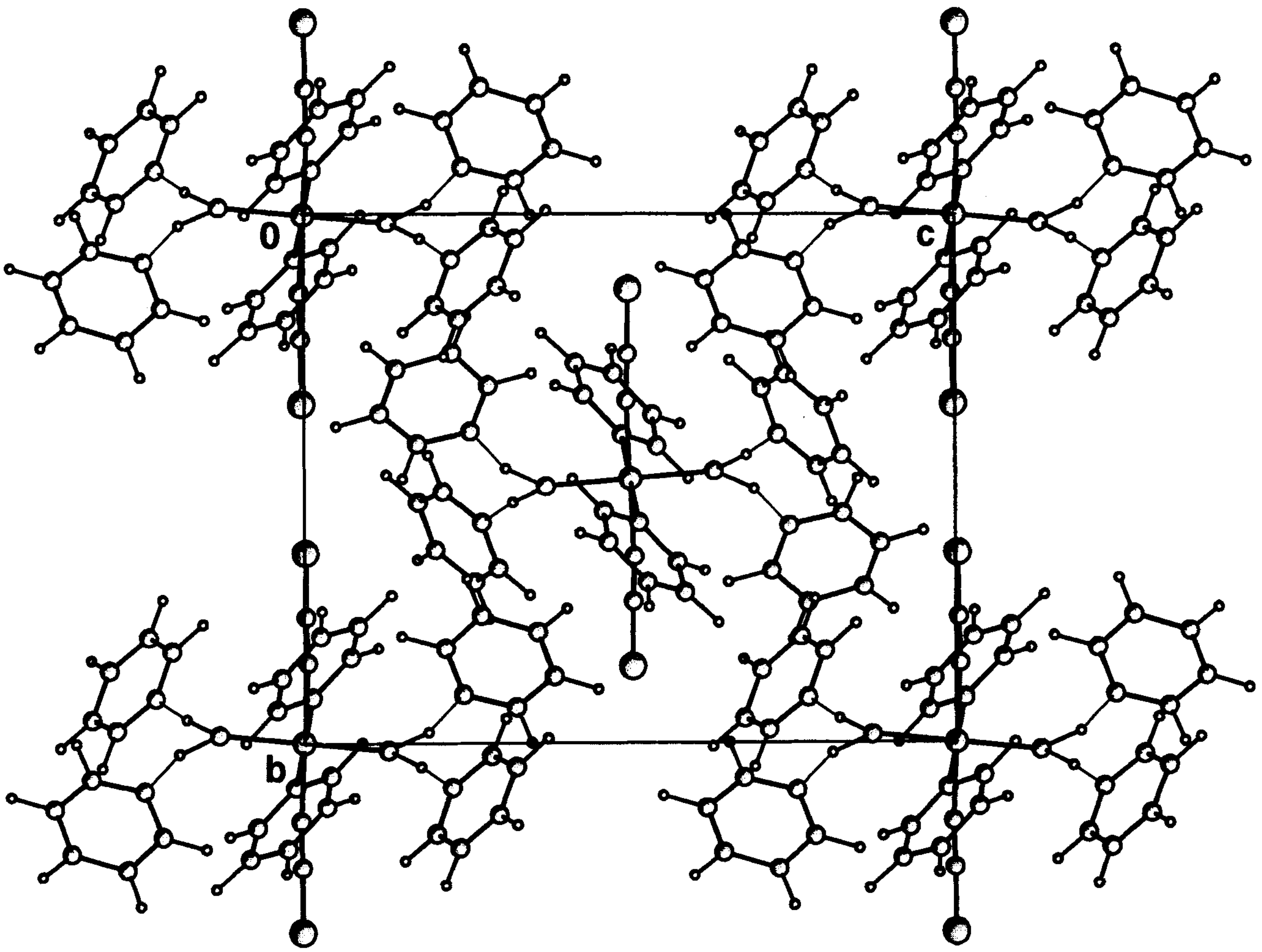

Figure 2 Molecular packing viewed along the x crystallographic axis.

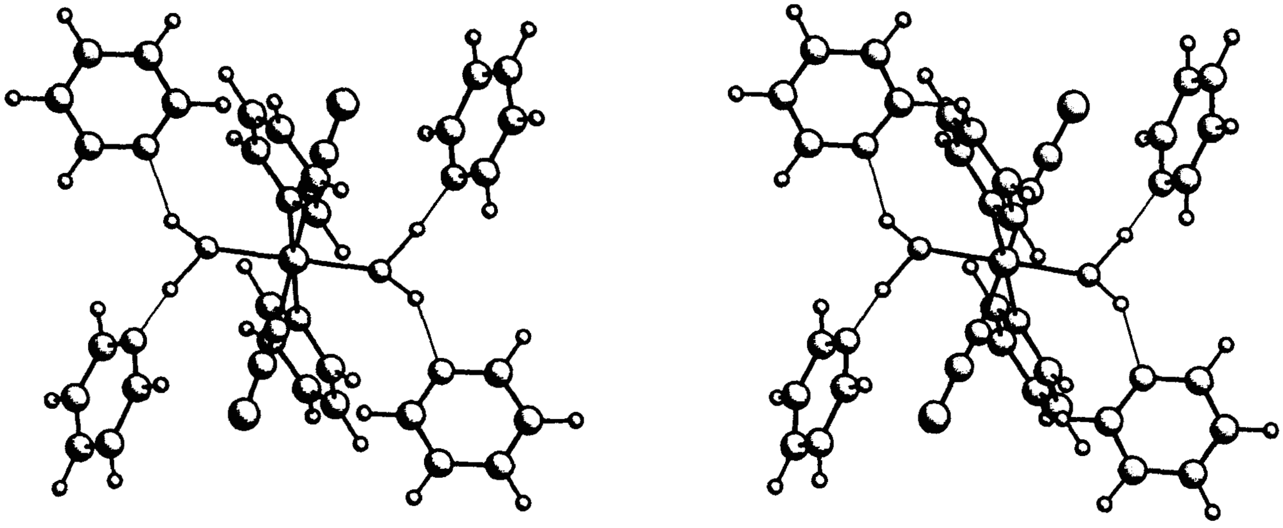

Figure 3 Stereoview of the $[MgPy_2(H_2O)_2(NCS)_2]\cdot 4Py$ unit.

Table 4 Wave numbers (cm^{-1}) of the four pyridine absorption bands dependant on the pyridine arrangement[a]

Py anhydrous	603m (601,^{b}603,^{c}605^d)	744s (740,^{e}744^b)	991m (988,^{b}990,^{e}992^d)	1581s (1580^{b,c,e})
Mixture $Py{:}H_2O = 2{:}1$ liquid	612m	749s	998s	1589s
$[MgPy_4(NCS)_2]$ (complex I) crystals	626s	759m	1008s	1572m
$[MgPy_2(H_2O)_2(NCS)_2]\cdot 4Py$ (solvate II) crystals	615w,625m	749m,758m	998s,1011m (1000,1010^d)	1573m,1591s
Mother liquid over solvate II	614m,627w	750m	1000s,1012w	1573m,1591s

[a] The positions of the other 8 bands of the pyridine not coordinated to the Mg(II) cation in the region 500–2000 cm^{-1} are the same for these samples within experimental error, 1–2 cm^{-1}.
Some literature data presented in brackets: Schader, B.; Meier, W. (Eds.), *Raman/IR Atlas of Organic Compounds*, Verlag Chemie GmbH, D-6940 Weinheim, 1975, Vol. 2, p. 17–01 (b); Szymanscki, H.A.; Erickson, R.E. *Infrared Hand Book*, IFI/Plenum, New York - Washington - London, 1970, Vol. 2, p. 1430 (c); the reference 1 in this work (d); Grasselli, J.G.; Ritchley, W.M. (Eds.), *Atlas of Spectral Data and Physical Constants for Organic Compounds, 2nd Edition*, CRC Press, Cleveland, Ohio 44128, 1975, Vol. IV, p 373 (e).

EXPERIMENTAL SECTION

The synthesis and purification methods of all the compounds and reagents used in the work were described in our previous paper.[1]

Because of the instability of the solvate crystals in open air, the X-ray study was performed using the crystal (0.4x0.4x0.6 mm) placed into a glass capillary and the intensity data collection at −50 °C. An Enraf-Nonius CAD4 single-crystal diffractometer, Ni-filtered CuKα-radiation, and the ω-2θ scan technique were used. 4215 reflections were measured, with there being 1251 unique-observed ($>3\sigma_I$). The data were corrected for Lorentz and polarization effects; absorption was ignored.

The structure was solved by direct methods (SHELX-86[5] was used) in the monoclinic cell and refined to $R=0.082$ ($R_w=0.067$, $w=4.5247/\sigma^2(F)$). Hydrogen atoms of the pyridines were included in final cycles as 'riding' on corresponding carbon atoms and with temperature factor fixed to free variable, while positions of the water hydrogens were found on difference map analysis. Residual extrema in the final difference map were as follows: maximum, +0.47; minimum, $-0.36\,e\cdot Å^{-3}$.

Infrared spectra were measured (as Nujol mulls in the case of solid samples) on a Perkin-Elmer Model 325 spectrometer.

ACKNOWLEDGMENT

This study was supported by the Institute grant no. 2 0242 91 01.

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