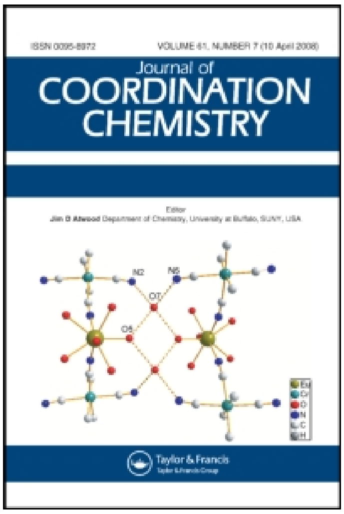


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Crystal structure, spectroscopic and thermal studies of anhydrous potassium 2,6-dihydroxybenzoate

Alina Kula[a]; Liliana Mazur[a]; Zofia RzĄczyńska[a]
[a] Faculty of Chemistry, Department of General and Coordination Chemistry, Maria Curie-Skłodowska University, 20-031 Lublin, Poland

To cite this Article Kula, Alina , Mazur, Liliana and RzĄczyńska, Zofia(2008) 'Crystal structure, spectroscopic and thermal studies of anhydrous potassium 2,6-dihydroxybenzoate', Journal of Coordination Chemistry, 61: 11, 1751 — 1758
To link to this Article: DOI: 10.1080/00958970701746667
URL: http://dx.doi.org/10.1080/00958970701746667

Journal of Coordination Chemistry
Vol. 61, No. 11, 10 June 2008, 1751–1758

Crystal structure, spectroscopic and thermal studies of anhydrous potassium 2,6-dihydroxybenzoate

ALINA KULA, LILIANA MAZUR and ZOFIA RZĄCZYŃSKA*

Faculty of Chemistry, Department of General and Coordination Chemistry,
Maria Curie-Skłodowska University, 20-031 Lublin, Poland

(*Received 25 June 2007; in final form 12 July 2007*)

The crystal structure, infrared spectrum and thermal stability of the potassium salt of 2,6-dihydroxybenzoic acid have been studied. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 3.847(1)$ Å, $b = 15.099(5)$ Å, $c = 13.248(4)$ Å, $\beta = 98.35(2)°$ and $Z = 4$. The compound of the general formula KL is a three-dimensional polymer, in which K ions are bridged by coordinated organic ligands by oxygen atoms of carboxylate and hydroxy groups. The anhydrous compound decomposes at 230°C. The IR spectrum of the potassium salt is discussed.

Keywords: Potassium 2,6-dihydroxybenzoate; Potassium γ-resorcylate; X-ray structure; IR spectrum; Thermal analysis

1. Introduction

2,6-Dihydroxybenzoic acid (γ-resorcylic acid) crystallizes in the orthorhombic $Pna2_1$ [1] or monoclinic $P2_1/c$ [2] space group as an anhydrous compound or in the orthorhombic *Pnma* space group as a monohydrate [1]; the acid has the possibility of interesting intra- and intermolecular hydrogen bonds [1]. The carboxylic group of the γ-resorcylic acid molecule in the crystal of the anhydrous orthorhombic form is in an *anti* conformation as a result of the intramolecular hydrogen bond with one hydroxyl group of acid, acting as a proton acceptor. Simultaneously, this hydroxyl group forms an intermolecular hydrogen bond as the proton donor. The second hydroxyl group takes part in the intramolecular hydrogen bonding as a proton donor. The molecules are linked by intermolecular hydrogen bonds. Inter- and intramolecular hydrogen bonds form chains with alternating σ- and π-bond cooperativity.

The structure of the monohydrate may be considered to be either disordered γ-resorcylic acid monohydrate or hydronium γ-resorcylate in which complete proton transfer from the carboxylic acid to the water has occurred [1]. As in the anhydrous form, the carboxylic group is in an *anti* conformation and acts as a donor in the formation of an intramolecular hydrogen bond. The hydroxylic groups, the water molecules and the carboxylic groups form, as in the anhydrous acid, an infinite

---

*Corresponding author. Email: rzacz@hermes.umcs.lublin.pl

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970701746667

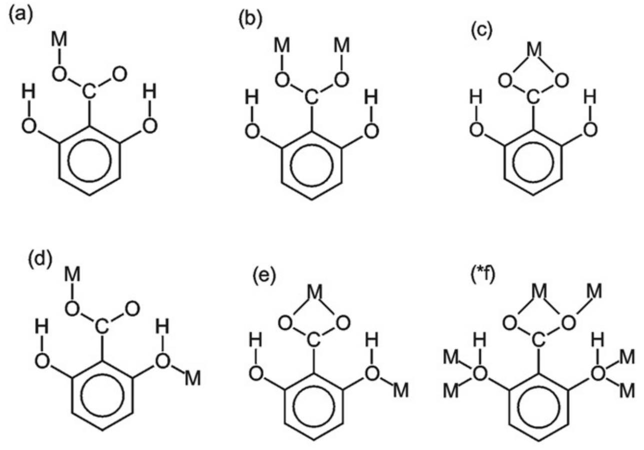
hydrogen-bonded chain with mixed σ- and π-bond cooperativity. In the monoclinic form of acid the carboxylic group is in the *syn* conformation [2].

Interaction of γ-resorcylic acid, as a hydroxybenzoic acid, with common metal ions is of particular interest for basic understanding of metal complexation in the environment. In the soil, organic matter consists of polymeric molecules referred to as humic and fulvic acids, whose cores contain aromatic nuclei bearing as the main substituents, carboxylic and phenolic groups [3]. Hydroxybenzoic acids are simple models, appropriate to investigate the ligand behavior of soil organic matter.

2,6-Dihydroxybenzoic acid is one of dihydroxybenzoic acids, forming metal complexes, which are representatives of humic and fulvic substances. As a ligand it may form up to eight-coordinate complexes. The first donor group, the carboxylate, has a great diversity in metal ion coordination and in the majority of the structures coordinates monodentate, bidentate chelating [4], bidentate bridging [5, 6] or rarely, tridentate chelating-bridging [7, 8] (scheme 1). Each of the hydroxyl groups of 2,6-dihydroxybenzoic acid has the possibility to form two coordination bonds. In most metal complexes of 2,6-dihydroxybenzoic acid, the metal-ligand coordination occurs by the oxygen atoms of carboxylic groups only, with phenolic OH groups not taking part in metal ion coordination. Examples include lanthanide and actinide complexes [4, 9, 10] as well as transition metal complexes [3, 5, 6, 11]. Among known structures, metal coordination through the phenolic group occurs in lead(II) [12] and copper(II) [3, 11] complexes with 2,6-dihydroxybenzoic acid.

Previously, we described 2,6-dihydroxybenzoates of the lanthanides(III) from La(III) to Lu(III) and Y(III), their preparation, solubility in water, spectral properties, dehydration process and thermal decomposition in air [4, 13–15] and structures of the isomorphic Tb(III) and Ho(III) complexes. In the structure of these hydrated complexes the metal ions are coordinated by oxygen atoms of the carboxylate groups and molecules of water. Phenolic OH groups take part in forming intramolecular hydrogen bonds only [4].

This study reports the crystal structure of the potassium salt of 2,6-dihydroxybenzoic acid as a continuation of the studies of the structural, spectral and thermal properties of the metal complexes of benzoic acid derivatives.



Scheme 1. Coordination fashions of 2,6-dihydroxybenzoate ligand (*discovered for the first time in this work).

2. Experimental

2.1. *Preparation of the potassium salt of 2,6-dihydroxybenzoic acid*

1 g (6.49 mmol) of 2,6-dihydroxybenzoic acid was dissolved in 20 mL deionized water. Then 13 mL of 0.5 mol L^{-1} KOH (0.364 g, 6.5 mmol) aqueous solution was added with stirring for 1 h at room temperature. After three weeks colorless, plate-shaped single crystals, suitable for X-ray diffraction were obtained.

2.2. *X-ray crystallography*

The single-crystal diffraction data were collected at room temperature in the $\omega/2\theta$ mode on an Oxford Diffraction Xcalibur diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The stability of intensities was monitored by measurement of 3 standards every 100 reflections. The crystal structure was solved by direct methods using SHELXS97 [16] and refined by the full-matrix least-squares on F^2 using SHELXL97 [17]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms of hydroxyl groups were located from a difference Fourier map and refined with isotropic displacement parameters. The remaining hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms, with $U_{iso}(H) = 1.2\ U_{eq}(C)$. Details of the crystal data, X-ray data collection and refinement are given in table 1. Selected interatomic geometric parameters are listed in table 2.

Table 1. Crystal data and experimental parameters for potassium 2,6-dihydroxybenzoate.

Empirical formula	$C_7H_5KO_4$
Formula weight	192.21
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	3.847(1)
b (Å)	15.099(5)
c (Å)	13.248(4)
β (°)	98.35(2)
V (Å^3)	761.4(4)
Z	4
D_c (g cm^{-3})	1.677
Crystal size (mm)	0.40 × 0.30 × 0.21
μ (mm^{-1})	0.664
F(000)	392
θ range (°)	4.1–30.1
Index ranges	$-5 \le h \le 5$; $-21 \le k \le 0$; $-2 \le l \le 18$
Reflections collected	2271
Completeness to $\theta = 30.1°$ (%)	96.1
Crystal decay (%)	1.4
Data/parameters in refinement	2237/115
GOOF	0.960
R_1	0.0895
wR_2	0.1741
$\Delta\rho_{max}$; $\Delta\rho_{min}$ (e Å^{-3})	0.55; −0.37

2.3. *IR spectra*

The IR spectra of 2,6-dihydroxybenzoic acid and the potassium salt were recorded in the range of 4000–400 $\mathrm{cm^{-1}}$, using a Perkin-Elmer 1725X FTIR spectrometer. The samples were prepared as KBr discs.

2.4. *Thermal stability*

The thermal stability of the potassium salt in air was determined using a Setsys 16/18 TG, DTG, DTA instrument. The sample (6.6 mg) was heated in an Al_2O_3 crucible at 293–973 K in air flow with a heating rate of 5 $\mathrm{K\,min^{-1}}$. The products of decomposition were calculated from the TG curve.

3. Results and discussion

3.1. *Crystal structure*

The crystal structure of the anhydrous potassium salt of 2,6-dihydroxybenzoic acid (**1**) $\{K[C_6H_3(OH)_2COO]\}_n$ was determined by single-crystal X-ray diffraction. The compound in the crystalline state is a three-dimensional polymer, in which the asymmetric unit consists of a potassium cation and 2,6-dihydroxybenzoate anion pair. In the structure the metal ions are surrounded by six 2,6-dihydroxybenzoate ligands and

Table 2. Selected bond lengths (Å) and angles (°) for potassium 2,6-dihydroxybenzoate.

K–O(1)	2.988(4)	O(1)–C(1)	1.280(7)
K–O(2)	2.780(4)	O(2)–C(1)	1.259(6)
K–O(2)$^{(a)}$	2.763(4)	C(1)–C(1f)	1.483(7)
K–O(4)$^{(b)}$	2.778(4)	C(2f)–O(3)	1.358(6)
K–O(3)$^{(c)}$	2.802(4)	C(6f)–O(4)	1.360(6)
K–O(3)$^{(d)}$	2.883(4)		
K–O(4)$^{(e)}$	2.901(4)		
O(2)–K–O(1)	45.2(1)	O(2)$^{(a)}$–K–O(1)	75.2(1)
O(2)$^{(a)}$–K–O(4)$^{(b)}$	163.9(1)	O(4)$^{(b)}$–K–O(1)	93.7(1)
O(2)$^{(a)}$–K–O(2)	87.9(1)	O(3)$^{(c)}$–K–O(1)	106.8(1)
O(4)$^{(b)}$–K–O(2)	92.4(1)	O(3)$^{(d)}$–K–O(1)	135.7(1)
O(2)$^{(a)}$–K–O(3)$^{(c)}$	117.7(1)	O(4)$^{(e)}$–K–O(1)	119.6(1)
O(4)$^{(b)}$–K–O(3)$^{(c)}$	76.3(1)	C(1)–O(1)–K	87.5(3)
O(2)–K–O(3)$^{(c)}$	62.7(1)	C(1)–O(2)–K	97.6(3)
O(2)$^{(a)}$–K–O(3)$^{(d)}$	61.9(1)	C(1)–O(2)–K$^{(f)}$	123.5(3)
O(4)$^{(b)}$–K–O(3)$^{(d)}$	130.6(1)	C(6f)–O(4)–K$^{(g)}$	127.0(3)
O(2)–K–O(3)$^{(d)}$	118.9(1)	C(6f)–O(4)–K$^{(f)}$	93.9(3)
O(3)$^{(c)}$–K–O(3)$^{(d)}$	85.2(1)	C(2f)–O(3)–K$^{(c)}$	144.1(3)
O(2)$^{(a)}$–K–O(4)$^{(e)}$	90.2(1)	C(2f)–O(3)–K$^{(d)}$	116.5(3)
O(4)$^{(b)}$–K–O(4)$^{(e)}$	85.3(1)		
O(2)–K–O(4)$^{(e)}$	164.5(1)	O(2)–C(1)–O(1)	122.4(5)
O(3)$^{(c)}$–K–O(4)$^{(e)}$	130.9(1)	O(2)–C(1)–C(1f)	119.3(6)
O(3)$^{(d)}$–K–O(4)$^{(e)}$	73.2(1)	O(1)–C(1)–C(1f)	118.4(5)

Symmetry codes: (a) $x+1, y, z$; (b) $x-1/2, -y+3/2, z-1/2$; (c) $-x-1, -y+2, -z$; (d) $-x, -y+2, -z$; (e) $x+1/2, -y+3/2, z-1/2$; (f) $x-1, y, z$; (g) $x-1/2, -y+3/2, z+1/2$.

coordinate with seven oxygen atoms, three of which are from carboxylate and four from hydroxylic groups (figures 1 and 2). The coordination polyhedron around the potassium ion can be described as a distorted, monocapped trigonal prism. The O2, O3c, O4b and O2a, O3d, O4e oxygen atoms (symmetry codes as in table 2) construct the top and bottom, parallel to one another, basal planes of the prism. The hydroxyl and carboxyl oxygen atoms of four 2,6-dihydroxybenzoate ligands form the equatorial plane (O2/O2a/O4e/O4b) of the polyhedron, while the O3c, O3d and O1 atoms are in

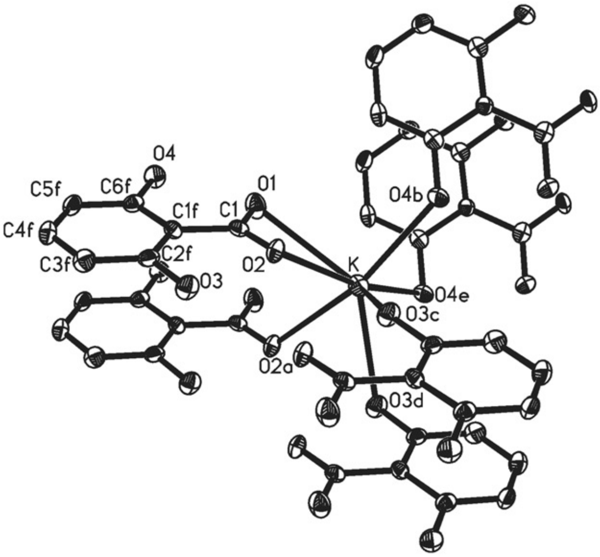


Figure 1. The coordination environment around the potassium center for the title complex. The displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. The symmetry codes are as in table 2.

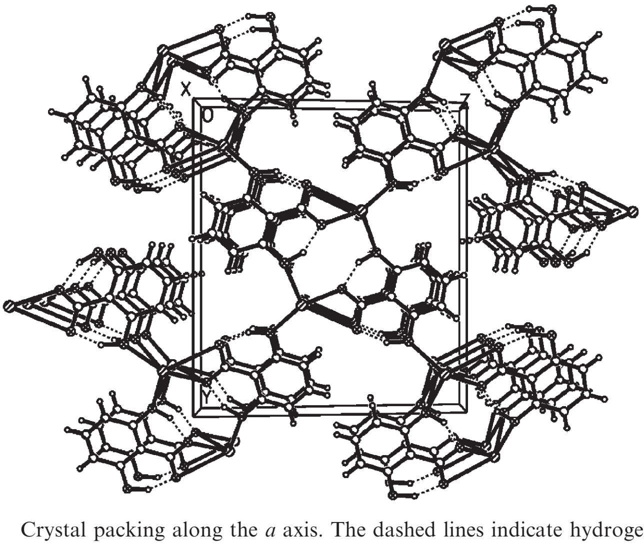


Figure 2. Crystal packing along the *a* axis. The dashed lines indicate hydrogen bonds.

pseudo-axial positions. The central K^+ is located at 0.382(3) Å below the least-square O2/O2a/O4e/O4b plane, whereas the capping atom O(1) extends 1.967(3) Å beyond this plane. The O1–K–O3c and O1–K–O3d angles are 106.8(1) and 135.7(1)°. All of the O–K–O angles of the equatorial plane deviate from ideal values of 90 and 180° (table 2).

The K–$O_{carboxyl}$ bonds of the title complex range from 2.763(4) to 2.988(4) Å and K–$O_{hydroxyl}$ bonds are from 2.778(4) to 2.901(4) Å, which compare quite well with the mean values determined from the Cambridge Structural Database (2.82 Å for K–$O_{carboxyl}$ bond and 2.74 Å for K–$O_{hydroxyl}$ bond [18]).

In the title complex 2,6-dihydroxybenzoate shows a new (reported for the first time in this work) coordination mode (scheme 1(f)). The carboxylate groups in **1** are tridentate: two oxygen atoms chelate potassium ion and one of them (O2) additionally bridges the neighboring metal ions. At the same time each of the phenolic groups bridges two metal centers.

The bond distances and angles within the 2,6-dihydroxybenzoate ligand have the expected values. The small difference in the C–O distances of the COO^- group [1.259(6) and 1.280(7) Å] probably originates from different coordination modes. The 2,6-dihydroxybenzoate ions, as a whole, are essentially planar with an rms deviation of 0.02 Å. The dihedral angle between the benzene ring plane and the carboxylate group is 3.49(1)°.

Each of the phenolic groups coordinate two potassium ions and simultaneously forms a hydrogen bond with the oxygen atom of carboxylate group of the same ligand. Very short, [$D \cdots A = 2.523(7)$ and 2.506(6) Å], quite linear, strong, intramolecular hydrogen bonds are formed (table 3).

Among the weak interactions in this structure there are long, weak hydrogen bonds in which C(5f)–H(5f) is the proton donor to the O(1) of the carboxylate group. The distance $D \cdots A$ is 3.510(6) Å. These hydrogen bonds do not influence the complex stability. The stability of the structure is due to the bridging covalent mode of the organic ligand. The complete list of hydrogen bonds and their geometric parameters is given in table 3.

3.2. *IR spectra*

The IR spectrum of free 2,6-dihydroxybenzoic acid shows a strong absorption band of carboxylic group –COOH at 1664 cm^{-1}. The characteristic absorption bands of the hydroxylic groups are at 1469, 1422, 1275 and 812 cm^{-1} [19, 20]. The absorption band at 1469 cm^{-1} may overlap the aromatic $\nu(C–C)_{ar}$ bands in this region. In the IR spectrum of the potassium salt, the band of the carboxylic group is absent, due to formation of COO^-. The asymmetric absorption, $\nu_{as}(COO^-)$, at 1606 cm^{-1} and the

Table 3. Hydrogen bond geometry.

$D–H \cdots A$	D–H (Å)	$H \cdots A$ (Å)	$D \cdots A$ (Å)	∠$D–H \cdots A$ (°)
$O(3)–H(3) \cdots O(2)$	0.85(7)	1.701	2.523(7)	163
$O(4)–H(4) \cdots O(1)$	0.84(6)	1.772	2.506(6)	145
$C(5f)–H(5f) \cdots O(1)^{(a)}$	0.93	2.604	3.510(6)	165

Symmetry code: (a) $x + 1/2, -y + 3/2, z + 1/2$.

symmetric absorption, $\nu_s(COO^-)$, at 1391 cm^{-1} can be observed. The presence of ν_{as} and ν_s indicates that the carboxylic group is deprotonated. Moreover, the bands $\beta_{sym}(COO^-)$ and $\gamma_{sym}(COO^-)$ at 851 and 582 cm^{-1} appear. The IR spectrum is not sufficient to determine the mode of carboxylic group coordination.

A distinctive band νCOH at 1275 cm^{-1} in the IR spectrum of the free acid is shifted insignificantly to higher frequency (about 9 cm^{-1}) in the potassium salt. The other δOH bands at 1422 and 812 cm^{-1} are shifted to higher frequencies (about 14 cm^{-1}), too. Shifting absorption bands of hydroxyl group may result from OH coordination.

In the IR spectrum of the investigated compound broad absorption bands appear due to strong hydrogen bonds with characteristic peaks at 3456, 3049, 3017, 2665, 2363, 1940 and 1827 cm^{-1}. The band corresponding to K–O (oxygen atoms from carboxylate group) is below 400 cm^{-1} [21, 22].

3.3. *Thermal analysis*

Potassium 2,6-dihydroxybenzoate is stable at room temperature. Upon heating, the decomposition process begins at 210°C. The TG curve shows a loss of mass of 14.6% from 210 to 250°C which is connected with partial decarboxylation of organic ligand. In the DTA curve the endothermic effect is observed at 225°C. In the temperature range 250–310°C further decomposition of the compound takes place. 2,6-Dihydroxybenzoic ligand decomposes by releasing a molecule of resorcinol (1,3-dihydroxybenzene), as observed for decomposition of lead(II) complex. At 310°C complex of decarboxylated ligand with potassium ion is formed (1 : 1 molar ratio) [12]. This may be confirmed by the TG curve which shows 23% loss of mass (theoretical 22.4%). At 680°C the TG and DTG curves show a plateau and K_2CO_3 is formed.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 612002. Copies of the data can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.uk).

References

[1] M. Gdaniec, M. Gilski. *Acta Cryst.*, **C50**, 1622 (1994).
[2] L.R. MacGillivray, M.J. Zaworotko. *J. Chem. Cryst.*, **24**, 703 (1994).
[3] F. Cariati, L. Erre, G. Micera, A. Panzanelli, G. Ciani, G. Sironi. *Inorg. Chim. Acta*, **80**, 57 (1983).
[4] T. Głowiak, W. Brzyska, A. Kula, Z. Rzączyńska. *J. Coord. Chem.*, **48**, 477 (1999).
[5] G. Smith, C.H.L. Kennard, T.C.W. Mak. *Z. Kristallogr.*, **184**, 275 (1988).
[6] T.C.W. Mak, G. Smith, C.H.L. Kennard. *Z. Kristallogr.*, **207**, 33 (1993).
[7] Z. Rzączyńska, A. Bartyzel, T. Głowiak. *Polyhedron*, **22**, 2595 (2003).
[8] Z. Rzączyńska, A. Bartyzel, E. Olszewska, W. Sawka-Dobrowolska. *Polyhedron*, **25**, 687 (2006).
[9] P.C.R. Soares-Santos, H.I.S. Nogueira, F.A.A. Paz, R. Sa Ferreira, L.D. Carlos, J. Klinowski, T. Trinidade. *Eur. J. Inorg. Chem.*, **19**, 3609 (2003).

[10] G. Micera, L. Strinna Erre, F. Cariati, D.A. Clemente, A. Marzotto, G. Ciani. *Inorg. Chim. Acta*, **109**, 135 (1985).
[11] G. Micera, P. Pin, L. Strinna Erre, F. Cariati. *Thermochim. Acta*, **84**, 175 (1985).
[12] T. Głowiak, H. Kozłowski, E.L. Strinna Erre, G. Micera, B. Gulinati. *Inorg. Chim. Acta*, **202**, 43 (1992).
[13] W. Brzyska, Z. Rzączyńska, A. Kula, M. Jaroniec. *Polish J. Chem.*, **72**, 2087 (1998).
[14] W. Brzyska, Z. Rzączyńska, A. Kula, J. Jaroniec. *Polish J. Chem.*, **72**, 2524 (1998).
[15] M. Sikorska-Iwan, Z. Rzączyńska, A. Kula, M. Jaroniec. *J. Therm. Anal. Calorim.*, **66**, 841 (2001).
[16] G.M. Sheldrick. *SHELXS97*, *Program for a Crystal Structure Solution*, University of Göttingen, Göttingen (1997).
[17] G.M. Sheldrick. *SHELXL97*, *Program for the Refinement of a Crystal Structure from Diffraction Data*, University of Göttingen, Göttingen (1997).
[18] F.H. Allen. *Acta Cryst.*, **B58**, 380 (2002).
[19] L.J. Bellamy. *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London (1975).
[20] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, Toronto (1997).
[21] K. Nakamoto, P.J. McCarthy. *Spectroscopy and Structure of Metal Chelate Compounds*, Wiley, New York (1986).
[22] G. Varsanyi. *Assignments for Vibrational Spectra for Seven Hundred Benzene Derivatives*, Wiley, New York (1974).