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THERMAL, SPECTROSCOPIC AND STRUCTURAL STUDIES OF ZINC(II) COMPLEX WITH NICOTINAMIDE

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The zinc(II) complex with nicotinamide (ncam) was prepared and investigated by single-crystal X-ray diffraction, infrared spectrum (FTIR), conductivity and thermal analysis techniques. The formula of complex is $[Zn(ncam)_2(H_2O)_4](NO_3)_2\cdot 2H_2O$. The nicotinamide molecule has three following donor sites: pyridine ring nitrogen, aminonitrogen and carbonyl group oxygen. In this monomeric complex, the Zn(II) ion is six-coordinated by two pyridine ring N atoms and four water O atoms in a slightly distorted octahedral arrangement. In the crystal structure, intermolecular O–H…O and N–H…O hydrogen bonds link the molecules to form a supramolecular structure. The complex is stable up to 323 and above 360 K it dehydrates in one step losing six water molecules. The dehydration proceeds in the range of 360–438 K, and its enthalpy value is equal to 62.6 ± 1.5 kJ mol^{-1}.

Keywords: *crystal structure, infrared spectroscopy, nicotinamide, thermal analysis, zinc complex*

Introduction

Nicotinamide (pyridine-3-carboxamide, 3-pyridinecarboxamide, vitamin B3) as a pyridine derivative is important bioligand occurring in the metabolic processes of human organism. It also dominates in plants and human tissues [1–3] showing the significant biological activity with a coenzyme called NAD (nicotinamide adenine dinucleotide) [4]. Nicotinamide as the amide form of niacin has the anti-flammatory properties and reveals pharmacological importance as a vital compound in drug industry [5–7].

Zinc is relatively abundant element in biological organisms, plays an essential role in the large number of enzymatic reactions [8–10]. Having the anti-bacterial and anti-viral activities, zinc and its compounds may be used as a therapeutic agent and anti-sicking agent playing a role in the prevention of pain crisis in sickle-cell disease and in the treatment of various sickness [10].

From the survey of the literature concerning the complexes of Zn(II) with nicotinamide and isonicotinamide it results that some of its compounds having various compositions were synthesized and investigated [2, 6, 10]. They were obtained as anhydrous compounds and for their preparation the Zn(II) chloride or iodide, as substracts, were used. The first of them contains the zinc(II) ion, chloride and nicotinamide, while the second one is composed of Zn(II) ion, iodide and nicotinamide, as well. The zinc(II) ion in these both complexes is coordinated by two chloride or iodide ions and two pyridine ring N atoms [2, 6].

The aim of this work was to obtain the Zn(II) complex with nicotinamide using for preparation $Zn(NO_3)_2\cdot 6H_2O$, to determine its structure and to study some of its properties.

Experimental

Synthesis of the complex

The complex of$[Zn(ncam)_2(H_2O)_4](NO_3)_2\cdot 2H_2O$ was prepared as solid by the direct synthesis of 0.1 mol dm^{-3} ethanol solutions of $Zn(NO_3)_2\cdot 6H_2O$ and nicotinamide, respectively, with the ratio of M(II):ligand=1:2. The colourless solution had been at first, stirred and heated to 303 K for 1 h and next it was slowly evaporated over covered using watch-glass. After two weeks of evaporation the single crystals suitable for the measurements were formed.

Methods

Infrared spectra for nicotinamide and its complex with Zn(II) were recorded over the range of 4000–400 cm^{-1} using FTIR 1725X Perkin Elmer spectrometer. The samples for the FTIR spectra measurements were prepared as KBr discs. The IR spectra were recorded to estimate the complex composition and to study the way of the metal-ion coordination.

Single-crystal diffraction data were measured at room temperature in the $\omega/2\theta$ mode on the Oxford Diffraction Xcalibur diffractometer using graph-

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ite-monochromated MoK_α radiation (λ=0.71073 Å). The stability of intensities was monitored by measurement of 3 standards every 100 reflections. Crystal structure was solved by direct methods using SHELXS97 [11] and refined by the full-matrix least-squares on F^2 using the SHELXL97 [12] program. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms of water molecules were located from a difference Fourier map and not refined. The remaining hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms, with U_{iso}(H)=1.2U_{eq}(C/N). Details of the crystal data, X-ray data collection and refinement are given in Table 1. The single-crystal X-ray measurements were carried out in order to define the symmetry of complex, its composition, the coordination number of central ion, to determine the position of water molecules and the parameters of elementary cell.

Table 1 Crystal data and structure refinement details for $[Zn(ncam)_2(H_2O)_4](NO_3)_2{\cdot}2(H_2O)$

Empirical formula	$C_{12}H_{24}N_6O_{14}Zn$
Formula mass	541.74
Temperature/K	295(2)
Crystal system	triclinic
Space group	P1
a/Å	7.0040(10)
b/Å	8.397(2)
c/Å	10.182(2)
α/°	100.11(2)
β/°	108.41(3)
γ/°	95.71(3)
V/Å^3	551.6(2)
Z	1
D_c/g cm^{-3}	1.631
Crystal size/mm	0.48×0.22×0.18
μ/mm^{-1}	1.194
F(000)	280
θ range/°	3.6–27.5
Index ranges	$-9\leq h\leq 9$; $-10\leq k\leq 10$; $-12\leq l\leq 13$
Completeness to θ=27.5	99.8%
Reflections collected	5028
Crystal decay/%	1.3
Data/parameters in refinement	5028/298
GOOF	1.04
R_1	0.0540
wR_2	0.1642
$\Delta\rho_{max}$; $\Delta\rho_{min}$/e Å^{-3}	1.18; –0.74

Thermal stability and decomposition of the complex was determined by Setaram Setsys 16/18 derivatograph, recording TG, DTG and DSC curves. The measurement was made at heating rate of 10 K min^{-1} with full scale. The sample (7.54 mg) was heated in ceramic crucible in air to 1273 K. The thermal stability of complex was studied for the determination of the intermediate and final products of its decomposition, to define the way of complex transformation with rising temperature in air atmosphere and to qualify the energetic effects connected with such processes as: dehydration, melting, polymorphic changes, crystallization, oxidation and reduction.

Molar conductance was measured with a PHYWE 13701.93 conductometer (10^{-3} M DMF solution was used). The aim of conductivity measurements was to determine the position of the nitrate(V) ions in the coordination sphere of analysed complex and to determine their location in the solid-state compound.

Results and discussion

Infrared spectroscopy

The nicotinamide and zinc(II) complex with nicotinamide were characterized by FTIR spectra (Table 2, Fig. 1). In the IR spectrum of complex the broad band with the value of maximum frequency at 3400 cm^{-1}, characteristic for ν_{O-H} vibrations confirms the presence of the water molecules [2, 11, 13, 14]. The strong band at 3382 cm^{-1} and the shoulder of band at 3190 cm^{-1} may be assigned to asymmetric and symmetric stretching vibrations of the NH_2 group, respectively. In the spectrum of nicotinamide the two strong bands at 3363 and 3153 cm^{-1} were attributed to $\nu_{as(NH_2)}$ and $\nu_{s(NH_2)}$, respectively. The observed fre-

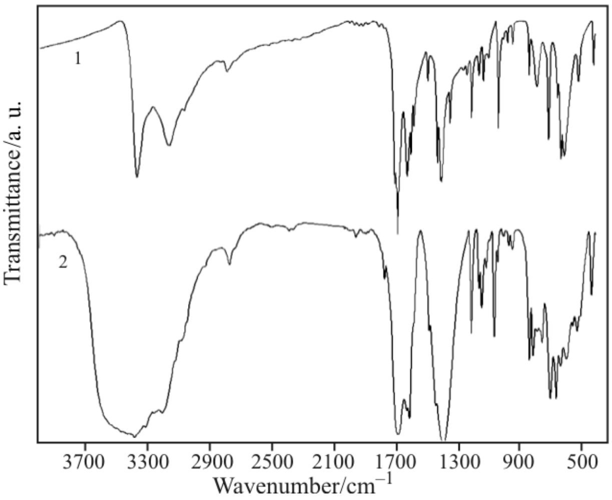

Fig. 1 FTIR spectra of 1 – nicotinamide and 2 – zinc(II) complex

quencies of stretching, wagging and rocking vibrations of NH_2 groups in the IR spectra of free ligand and its complex have practically the same value of their positions which may indicate that amino nitrogen is not involved in bonding with zinc(II) ion in the analysed complex [2, 6, 10, 14–19].

The strong bands of C=O bond observed at 1684 and 1682 cm^{-1} for nicotinamide and its complex, respectively, have the same values. Therefore it is possible to suggest that carbonyl oxygen of an amide does not participate in the coordination of the zinc(II) ion [2, 6, 10, 14–19].

The bands of pyridine ring vibrations in the IR spectrum of the free ligand occur in the ranges of 1593–1424, 1340–1231 and 1029–970 cm^{-1} while those in the spectrum of complex are in the ranges of

Table 2 Frequencies of the maxima of the absorption bands for ligand and its complex with Zn(II)

Frequencies/cm^{-1}		Assignment	Ref.
ligand	complex		
–	3400–3200 br	OH str	2, 13–15
3363 vs	3382 vs	NH_2 asym str	2, 6, 10, 14–17
3153 s	3190 sh	NH_2 sym str	2, 6, 10, 14–17
1699 sh	–	C=O str	2, 6, 10, 13–18
1684 vs	–	C=O str; C–H str	2, 6, 10, 13–18
–	1682 vs	C=O str; C–H str, N–O asym str	2, 6, 10, 13–18
1680 sh	–	C=O str	2, 6, 10, 13–18
1620 vs	1620 sh	NH_2 def	2, 6, 10, 15, 16
1593 m	1604 s	ring str (py)	2, 6, 10, 15
1575 m	–	ring str (py)	2, 6, 10, 15
1486 w	1477 vw	ring str (py)	2, 6, 10, 15
1424 m	1410 sh	ring str (py)	2, 6, 10, 15
1396 s	1384 vs	C–N str (am)	2, 6, 10, 15, 17
1340 m	–	ring str (py)	6, 10, 15
1231 w	–	ring str (py)	6, 10, 15
1202 m	–	CC str (py)	6, 10, 15, 16
–	1204 m	CC str (py), N–O sym str	6, 10, 15, 16
1154 w	1154 w	NH_2 rock	2, 6, 10, 15
1124 w	1136 m	C–$CONH_2$ (am)	2, 15
1092 vw	1107 vw	i. p. CH (py)	2, 10, 15
1029 s	1055 s	ring breat (py)	2, 10, 15
970 w	961 vw	ring str (py)	2, 6, 10, 15
936 w	938 w	o. p. C–H (py)	6, 10, 15
829 m	827 m	o. p. C–H (py)	6, 10, 15
–	805 m	N–O def	14–16
779 m	745 w	o. p. C–H (py)	10, 15
703 s	694 s	o. p. ring def	2, 6, 10, 15
–	654 s	NHv wag, N–O bend	2, 6, 10, 15, 16
646 w	–	NH_2 wag	2, 6, 10, 15, 16
624 s	626 w	i. p. ring def	10, 15
602 s	589 w	O=CN bend	2, 6, 10, 15
511 m	519 m	o. p. C–H (py)	6, 10, 15
–	426 m	M–N str	13, 15
412 m	–	o. p. ring def	6, 10, 15

where vs – very strong, s – strong, m – medium, w – weak, vw – very weak, sh – shoulder, br – broad, py – pyridine, am – amide, str – stretching, breat – breathing, def – deformation, rock – rocking, wag – wagging, asym – asymmetric, sym – symmetric, i.p. – in plane, o.p. – out of plane

1604–1410 and 1055–961 cm^{-1}. Their shifts to higher frequencies in the IR spectrum of zinc(II) complex suggest the coordination of nicotinamide through the pyridine ring nitrogen atom [2, 6, 10, 16]. The medium band at 426 cm^{-1} recorded in the spectrum of zinc(II) complex was assigned to M–N stretching [11, 13].

In the spectrum of the analysed complex the N–O bands of nitrate(V) groups with strong or medium intensity appear at 1682, 1204 and 805 cm^{-1} [2, 6, 10, 13–19].

Structure analysis

The single-crystal X-ray analysis reveals that the title complex has monomeric structure in which the only asymmetric unit of compound consists of one Zn(II) ion, being in the center of molecule, two nicotinamide ligands, four coordinated and two uncoordinated water molecules and two NO_3^- ions, as shown in Fig. 2. All ligands are monodentate. The geometry around the Zn(II) center (Table 3) can be described as slightly distorted octahedron. The basal plane contains four oxygen atoms of coordinated water molecules and its axial positions are occupied by heterocyclic nitrogen atoms of nicotinamide ligands. The Zn–O_w distances range from 2.083(6) to 2.108(6) Å, whereas the Zn–N_{py} bonds are 2.122(7) and 2.157(6) Å, respectively. These values match well with those found in the structures of $[Zn(ncam)_2(H_2O)_2(HCOO)_2]$, $[Zn(ncam)_2(H_2O)_4](C_6H_2N_3O_7)_2$ and in the similar type of complexes [20–23]. The structural parameters in pyridine rings and carboxamide groups of two ncam ligands in the above-mentioned compounds are similar and close, within experimental errors, to those for unsubstituted nicotinamide [24]. The pyridine rings are essentially planar (deviations from the planes ≤0.013 Å) and coplanar with carboxamide groups, as indicates the dihedral angles between their planes, being of 1.80° (molecule N1-C7) and 4.87° (molecule N11-C17).

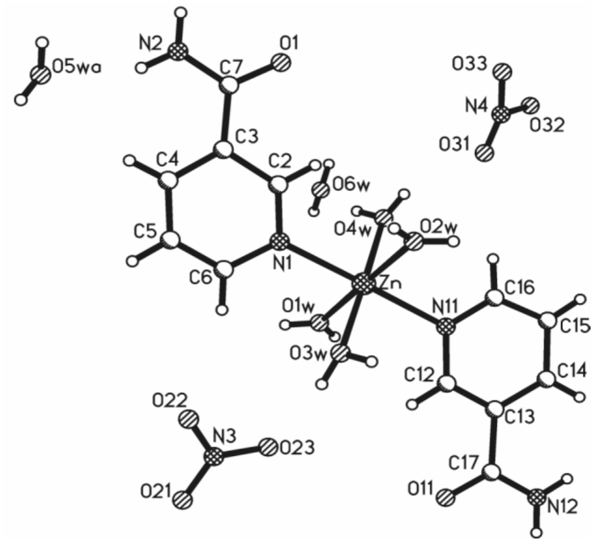

Fig. 2 The asymmetric unit of the complex with the atom labelling scheme

The crystal structure of the complex is stabilized by an extended network of strong, intermolecular N–H…O and O–H…O hydrogen bonds (Fig. 3). The donors in these interactions are amino nitrogen atoms N1, N11 and oxygen atoms of coordinated and uncoordinated water molecules; the acceptors are carbonyl oxygen atoms O1, O11 as well as O atoms of water molecules and nitrate ions. Apart from strong hydrogen bonds, there are also weak C–H…O and π…π intermolecular interactions, additionally stabilizing the three-dimensional supramolecular framework.

Thermal analysis

The thermal stability properties of zinc(II) complex was studied in air and its TG, DTG and DSC curves were registered (Fig. 4). It is stable up to 323 K after which during further heating it melts in the range of 323–350 K. Therefore on DSC curve the strong, peak appears while on the TG curve the plateau is re-

Table 3 Selected bond lengths Å and angles (°)

Zn-O(1w)	2.094(6)	Zn-O(4w)	2.100(8)
Zn-O(2w)	2.108(6)	Zn-N(1)	2.122(7)
Zn-O(3w)	2.083(6)	Zn-N(11)	2.157(6)
O(1w)-Zn-O(3w)	90.5(3)	O(3w)-Zn-N(1)	88.7(3)
O(1w)-Zn-O(4w)	88.7(3)	O(4w)-Zn-N(1)	90.2(3)
O(2w)-Zn-O(3w)	89.7(3)	O(1w)-Zn-N(11)	88.0(3)
O(2w)-Zn-O(4w)	91.1(3)	O(2w)-Zn-N(11)	91.1(3)
O(1w)-Zn-O(2w)	179.1(3)	O(3w)-Zn-N(11)	90.9(3)
O(3w)-Zn-O(4w)	178.7(3)	O(4w)-Zn-N(11)	90.2(3)
O(1w)-Zn-N(1)	91.0(3)	N(1)-Zn-N(11)	178.9(4)
O(2w)-Zn-N(1)	89.9(3)		

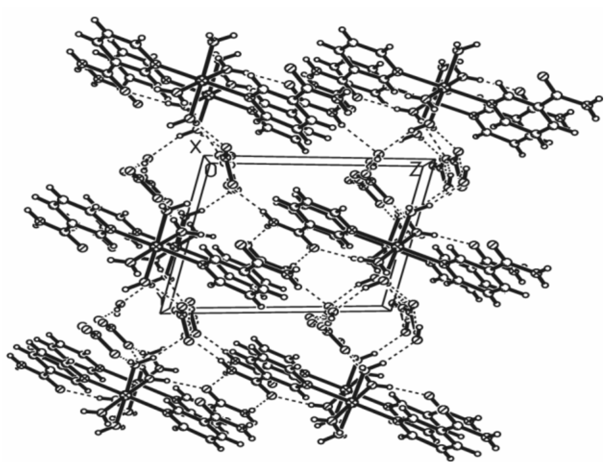

Fig. 3 Crystal packing along anaxis. Dashed lines indicate hydrogen bonds

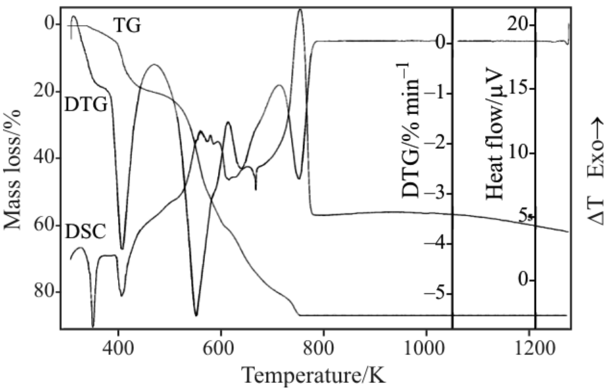

Fig. 4 TG, DTG and DSC curves of zinc(II) complex

corded. The maximum temperature value of the melting peak on DSC curve is equal to 346 K. The enthalpy value of melting heat of the sample in the above given temperature range is equal to 60.8±1.5 kJ mol^{-1}.

From the X-ray single crystal analysis it appears that the analysed complex forms hexahydrate in which four water molecules are coordination water whereas two the lattice one.

The dehydration process proceeds only in the one step therefore it is not possible to determine separately two dehydration temperature ranges for the water molecules located inside and outside of complex coordination spheres so we can get information only about the total dehydration process of this compound connected with the loss of all six water molecules. The one step of dehydration process makes impossible to calculate the energy bonding of water molecules positioned in those two complex coordination spheres.

The dehydration process of analysed compound proceeds in the range of 360–438 K. The loss of mass calculated in it from TG curve is equal to 19.7% which corresponds to release of six water molecules (theoretical value is 19.9%). During dehydration process the clear endothermic peak with the maximum at 405 K is seen on the DSC curve. The calculated value of enthalpy for this dehydration process is equal to 62.6±1.5 kJ mol^{-1} [25].

Having lost all water molecules the analysed complex forms the anhydrous compound that on further heating in the range of 503–766 K is ultimately decomposed to ZnO with the formation of some of unstable intermediate products being difficult for identification [26]. The loss of mass, in this case, determined from TG curve is equal to 84.4% and theoretically calculated is 84.9%. The thermal decomposition of complex may be illustrated by the following scheme:

$$[\text{Zn(ncam)}_2(\text{H}_2\text{O})_4](\text{NO}_3)_2\cdot2\text{H}_2\text{O}\xrightarrow{360-438\ \text{K}}[\text{Zn(ncam)}_2](\text{NO}_3)_2$$

$$[\text{Zn(ncam)}_2](\text{NO}_3)_2\xrightarrow{503-766\ \text{K}}\text{intermediate (unstable)}$$

$$\text{intermediate}\xrightarrow{700\ \text{K}}\text{ZnO}$$

From the thermal analysis data it appears that the number of water molecules is in good agreement with that defined by X-ray single crystal analysis.

Molar conductivity

Molar conductance value of DMF solution of zinc(II) complex is 167.3 Ω^{-1} cm^2 mol^{-1}. This value fall in the expected range for 1:2 electrolytes [27–29], indicating that the two nitrate(V) anions lie outside of the coordination sphere. It is also in a good agreement with the structural results.

Conclusions

The zinc(II) complex with nicotinamide was obtained as compound with the formula $[\text{Zn(ncam)}_2(\text{H}_2\text{O})_4](\text{NO}_3)_2\cdot2\text{H}_2\text{O}$. The FTIR spectrum and X-ray analysis of the complex demonstrated that Zn(II) ion is coordinated by pyridine ring whereas the carbonyl oxygen and amino nitrogen do not take part in its coordination. From structural studies and conductivity measurements it results that the two nitrate(V) anions lie outside of the coordination sphere.

Acknowledgements

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 682088. 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 T. Sismanoglu, Chin. Chem. Lett., 14 (2003) 1207.
2 H. Pasaoglu, S. Güven, Z. Heren and O. Büyükgüngör, J. Mol. Struct., 794 (2006) 270.
3 K. Shibata, Biosci. Biotechnol. Biochem., 58 (1994) 1729.
4 E. Akalin and S. Akyuz, Vib. Spectrosc., 42 (2006) 333.
5 M. Bechtel, M. Kademian and M. Zirwas, J. Drugs Derm., 2007 (case report).
6 S. Ide, A. Ata and S. Yurdakul, J. Mol. Struct., 605 (2002) 103.
7 S. S. Raj, H. K. Fun, P. S. Zhao, F. F. Jian, L. D. Lu, X. J. Yang and X. Wang, Acta Cryst., C56 (2000) 742.
8 K. Gyoryova, E. Szunyogova, J. Kovarova, D. Hudecova, D. Mudronova and E. Juhaszova, J. Therm. Anal. Cal., 72 (2003) 587.
9 V. Zeleak, M. Sabo, W. Massa and P. Llewellyn, Inorg. Chim. Acta, 357 (2004) 2049.
10 S. Bayari, A. Atac and S. Yurdakul, J. Mol. Struct., 655 (2003) 163.
11 G. M. Sheldrick, SHELXS97, Program for a Crystal Structure Solution, University of Göttingen, Göttingen 1997.
12 G. M. Sheldrick, SHELXL97, Program for the Refinement of a Crystal Structure from Diffraction Data, University of Göttingen, Göttingen 1997.
13 A. M. Donia, E. A. El-Boraey and M. F. El-Samalehy, J. Therm. Anal. Cal., 73 (2003) 987.
14 W. Zieliński and A. Rajca, Spectroscopic Methods and their Applications for the Organic Compound Identifications, Scientific and Technical Publisher, Warsaw 2000.
15 S. Konstantinović, B. Radovanović and A. Krkljes, J. Therm. Anal. Cal., 90 (2007) 525.
16 G. Socrates, Infrared and Raman Characteristic Group Frequencies, John Wiley & Sons, Chichester, 2001.
17 R. M. Silverstein, F. X. Webster and D. J. Kiemle, Spectroscopic Methods for Organic Compound Identifications, Polish Scientific Publisher, Warsaw 2007.
18 N. L. Alpert, W. E. Kaiser and H. A. Szymański, Infrared Spectroscopy, Polish Scientific Publisher, Warsaw 1974.
19 P. O. Käll, J. Grins, M. F and F. Söderlind, Polyhedron, 20 (2001) 2747.
20 L. Kh. Minacheva, T. S. Khodashova, M. A. Porai-Koshits, G. G. Sadikov, L. A. Butman, V. G. Sakharova and G. V. Tsintsadze, Koord. Khim., 5 (1979) 1889.
21 M.-H. Zeng, H. Liang, S.-M. Shi and K.-B. Yu, Jiegou Huaxue, 21 (2002) 651.
22 E. E. Castellano, O. E. Piro, B. S. Parajon-Costa and E. J. Baran, Z. Naturforsch., B: Chem. Sci., 57 (2002) 657.
23 I. Ucar, B. Karabulut, H. Pasaoglu, O. Buyukgungor and A. Bulut, J. Mol. Struct., 787 (2006) 38.
24 Y. Miwa, T. Mizuno, K. Tsuchida, T. Taga and Y. Iwata, Acta Cyst., B55 (1999) 78.
25 W. Ferenc, A. Dziewulska-Kułaczkowska, J. Sarzyński and B. Paszkowska, J. Therm. Anal. Cal., 91 (2008) 285.
26 D. Czakis-Sulikowska, A. Czylkowska, J. Radwańska-Doczekalska, R. Grodzki and E. Wojciechowska, J. Therm. Anal. Cal., 90 (2007) 557.
27 W. Geary, J. Coord. Chem. Rev., 7 (1971) 81.
28 A. M. Hamman, S.A. Ibrahim, M. A. El-Gahami and D. Fouad, J. Therm. Anal. Cal., 74 (2003) 801.
29 S. Chandra, L. K. Gupta and D. Jain, Spectrochim. Act., A 60 (2004) 2411.

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