Eclética Química
ISSN: 0100-4670
atadorno@iq.unesp.br
Universidade Estadual Paulista Júlio de Mesquita Filho
Brasil

Ferenc, W.; Czapla, K.; Sarzy, J.

Magnetic, thermal and spectral characterization of 2,4- dimethoxybenzoates of Mn(II), Co(II) andCu(II)

Eclética Química, vol. 32, núm. 3, 2007, pp. 7-12
Universidade Estadual Paulista Júlio de Mesquita Filho
Araraquara, Brasil

ECLÉTICA Química

www.scielo.br/eq
www.ecletica.iq.unesp.br

Volume 32, número 3, 2007

Magnetic, thermal and spectral characterization of 2,4-dimethoxybenzoates of Mn(II), Co(II) andCu(II).

W.Ferenc[1*], *K.Czapla*[1] *and J.Sarzy*[2]
[1]*Faculty of Chemistry, Maria Curie-Skodowska University, Pl 20-031 Lublin, Poland*
[2]*Institute of Physics, Maria Curie-Skodowska University, Pl 20-031 Lublin, Poland*
**wetafer@hermes,umcs.lublin.pl*

Abstract: 2,4 - Dimethoxybenzoates of Mn(II), Co(II) and Cu(II) have been synthesized as hydrated or anyhydrous polycrystalline solids and characterized by elemental analysis, IR spectroscopy, magnetic studies and X-ray diffraction measurements. They possess the following colours: Mn(II) – white, Co(II) – pink and Cu(II) – blue. The carboxylate groups bind as monodentate, or a symmetrical bidentate bridging ligands and tridentate. The thermal stabilities were determined in air at 293-1173K. When heated the hydrated complexes dehydrate to from anhydous salts which are decomposed to the oxides of respective metals. The magnetic susceptibilites of the 2,4-dimethoxybenzoates were measured over the range 76-303 K and their magnetic moments were calculated. The results reveal the complexes of Mn(II), Co(II) to be high-spin complexes and that of Cu(II) to form dimer.

Keywords: 2,4-dimethoxybenzoates; magnetic properties of Mn(II), Cu(II), Co(II) and Nd(III); thermal stability; IR spectra.

Introduction

The preparation and investigations of 2,4- dimethoxybenzoates of Mn(II), Co(II) and Cu(II) are presented in this paper because, on one hand, the carboxylates play on important role in inorganic and bioinorganic chemistry, and then again many metal cations in a great number of various biological processes, especially six – membered ring system, are components of several vitamins and drugs [1,2]. Morover, carboxylates of d and 4f ion elements depending on their magnetic properties as magnets may by used in the modern branches of techniques and technology as electric materials, and they may have applications as precursors in superconducting ceramic and magnetic material productions.

According to literature survey compounds of various organic ligands also with dimethoxybenzoic acid have been studied. Therefore, there are papers that deal with their complexes with d and mainly 4f metal ion elements [3-13]. The complexes described in the above – mentioned papers were synthesized and characterized by elemental analysis, and IR spectra. Their thermagravimetric studied, X-ray diffraction and magnetic measurements were also presented.

2,4 – Dimethoxybenzoic acid is a crystalline solid sparingly soluble in water and its meltig point is 109° C [14,15]. It is used in various branches showing then different applications [16-19]; in biochemistry to form esters, in medicine and in pharmacy for the preparation of modern medicinies and in ion – exchange chromatography to analyse the new organic compounds. The compounds of 2,4 – dimethoxybenzoic acid are very little known. A survey of the literature shows that it is possible to find papers on its salts with some cations and on the investigations of some of their chemical properties. The salts of 2,4 – dimethoxybenzoic acid anion were obtained in the solid state only with lanthanide metal ions [20-23] and some of their properties were studied.

The 2,4 – dimethoxybenzoates of Mn(II0, Co(II) and Cu(II) have not been obtained. Therefore, the aim of this work was to prepare them as solids and to examine some of their physicochemical praperties including thermal stability in air during heating to 1173K, IR spectral characterization, X-ray powder investigations and magnetic behaviour in the range of 76-303K. Thermal stability investigations give information about the process of decompositions and the magnetic susceptibility measurements let study the kinds of the way of central ion cordination and the nature of bonding between central ions and ligands.

Experimental details

For the preparation of the complexes the following chlorides of d- block elements were used : $MnCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ (REAGENTS – Chemical Enterprise in Lublin (Poland)). The 2,4 – dimethoxybenzoic acid used for the prepartion was produced by Aldrich Chemical Company. In the experiments the solution of NH_3aq (25%) produced by Polish Chemical Reagents in Glivice (Poland) was also used.

The contents of carbon and hydrogen were determined by elemental analysis using a CHN 2400 Perkin-Elmer analyzer. The contents of M^{2+} metals were established by ASA method using ASA 880 spectrophotometr (Varian).

The IR spectra of complexes were recorded over the range of 4000-400 cm^{-1} using M-80 spectrophotometer (Zeiss, Jena). Samples for IR spectra measurements were prepared as KBr discs.

The X-ray diffraction patterns were taken on a HZG-4 (Zeiss, Jena) diffractometer using Ni - filtered CuK_α radiation. The measurements were made within the range 2θ = 4-80º by means of the Debye – Scherrer – Hull method.

Table 1. Elemental analysis data of Mn(II), Co(II) and Cu(II) 2,4-dimethoxybenzoates.

Complex $L=C_9H_9O_4^-$	C / %		H / %		M / %	
	calcd.	found	calcd.	found	calcd.	found
MnL_2	51.80	51.60	4.30	4.30	13.20	13.16
CoL_2	51.30	51.77	4.30	4.40	14.00	13.00
$CuL_2 \cdot H_2O$	48.70	48.57	4.50	4.52	14.30	14.31

Table 2. Frequencies of the absorption bands of COO^- and M-O group vibrations for 2,4-dimethoxybenzoates of Mn(II), Co(II), Cu(II) and Na(I) and that of CO for 2,4-dimethoxybenzoic acid (cm^{-1}).

Complex $L= C_9H_9O_4^-$	$\nu_{C=O}$	$\nu_{as\ COO^-}$	$\nu_{s\ COO^-}$	$\Delta\nu_{COO^-}$	ν_{M-O}
MnL_2	-	1620	1404	216	420
			1372	248	
CoL_2	-	1628	1408	220	420
$CuL_2 \cdot H_2O$	-	1608	1400	208	500
NaL	-	1604	1396	208	
HL	1670	-	-	-	-

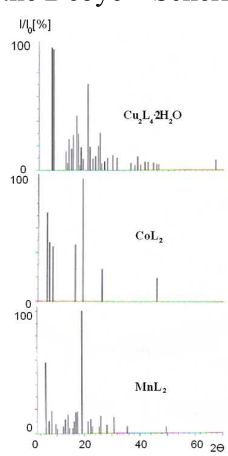

Figure 1. Dependence of I/I_o vs. 2θ for Mn(II), Co(II), and Cu(II) 2,4 dimethoxybenzoates.

The thermal stability and decomposition of the complexes were studied in air using a Setsys 16/18 (Setaram) TG, DTG i DTA instrument. The experiments were caried out under air flow in the temperature range of 297 – 1173K. Samples ranging between 5.00 mg and 5.07mg were heated in Al_2O_3 crucibles.

Table 3. Temperature range of thermal stbility of Mn(II), Co(II), and Cu(II) 2,4-dimethoxybenzoates in air.

Complex	ΔT^a / K	Mass loss / %		n^b	Final product of decomposition
L= $C_9H_9O_4^-$		calcd.	found		in solid state
$CuL_2 \cdot H_2O$	369.2 – 413.6	4.06	4.15	1	CuL_2
CuL_2	495 -731	82.08	75.53	-	CuO
CoL_2	509.8 – 776.2	82.43	78.02	-	Co_3O_4
MnL_2	458 - 820	81.1	76.36	-	Mn_2O_3

ÄT^a – temperature range of decomposition procesesses, n^b - numbert of water molecules lost in the dehydration process

Table 4. Magnetic data for the studied compounds of Mn(II), Co(II) and Cu(II).

MnL_2 L=$C_9H_9O_4^-$			CoL_2			$CuL_2 \cdot H_2O$		
T / K	$\chi_M \cdot 10^6$	μ_{eff} / MB	T / K	$\chi_M \cdot 10^6$	μ_{eff} / MB	T / K	$\chi_M \cdot 10^6$	μ_{eff} / MB
76	40058	4.94	76	29960	4.27	76	673	0.64
123	28522	5.30	123	19611	4.40	123	815	0.90
133	26468	5.31	133	18179	4.40	133	887	0.97
143	25113	5.36	143	17054	4.42	143	906	1.02
153	24018	5.43	153	15984	4.43	153	953	1.08
163	22551	5.43	163	15017	4.43	163	967	1.12
173	21388	5.44	173	14208	4.44	173	996	1.17
183	20316	5.46	183	13529	4.45	183	1005	1.21
193	19402	5.48	193	12860	4.46	193	1024	1.26
203	18589	5.50	203	12283	4.47	203	1039	1.30
213	17788	5.51	213	11707	4.47	213	1043	1.33
223	17043	5.52	223	11084	4.45	223	1043	1.37
233	16331	5.52	233	10721	4.47	233	1039	1.39
243	15688	5.53	243	10294	4.48	243	1039	1.42
253	15203	5.55	253	9959	4.49	253	1039	1.45
263	14774	5.58	263	9615	4.50	263	1034	1.48
273	14153	5.56	273	9531	4.56	273	1043	1.51
283	14187	5.67	283	9057	4.53	283	1029	1.53
293	13724	5.67	293	8787	4.54	293	1029	1.55
303	13363	5.69	303	8527	4.55	303	1020	1.57

Magnetic susceptibilities of polycrystalline samples of the studied 2,4-dimethoxybenzoates were investigated at 76 – 303K. The measurements were caried out using the Gouy method. Mass changes were obtained from Cahn RM-2 electrobalance. The calibrant employed was $Hg[Co(SCN)_4]$ for which the magnetic susceptibility of $8.08 \cdot 10^{-3} cm^3\ mol^{-1}$. Correctians for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants [24,25]. Magnetic moments were calculated according to the equation:

$$\mu_{eff} = 2.83\ (\chi_M T)^{1/2} \quad (1)$$

$$\mu_{eff} = 2.83\ (\chi_M T)^{1/2} \cdot 1.257 \cdot 10^{-6}\ m \cdot kg \cdot s^{-2}\ A^{-2} \quad (1^*)$$

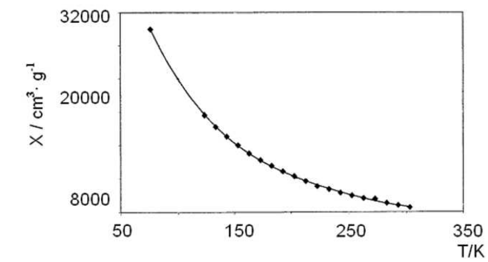

Figure 2. Dependence between magnetic susceptibility values vs. temperature for Co(II) complex.

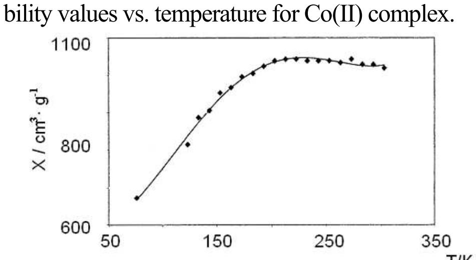

Figure 3. Relationship between magnetic susceptibility values vs. temperatures for Cu(II) 2,4-dimethoxybenzoate.

Complexes

The complexes of Mn(II), Co(II) and Cu(II) were prepared by adding the equivalent quantities of 0.1M ammonium 2,4 –dimethoxybenzoate (pH~ 5) to a hot solution containing the Mn(II), Co(II) and Cu(II) chlorides and crystallizing at 293K. The solids formed were filtered off, washed with hot water and methanol to remove ammonium ions, and dried at 303K to a constant mass.

Results and discussion

2,4- Dimetothoxybenzoates of Mn(II), Cu(II), Co(II) were synthesized as polycrystalline solids with a metal to ligand mole ratio of 1:2 and the general formula $M(C_9H_9O_4)_2 \cdot nH_2O$ for divalent ions, where M(II) = Cu, Co, Mn and n = 1 for Cu(II) n = 0 for Co(II) and Mn(II) (Table 1). Their colours are following: for Co – pink, Cu – blue, Mn – white. In Cu(II), Co(II) and Mn(II) compounds the d'!d electron transitions are those of the lowest energy and absorption occurs at relatively high wavelengths that depends on the nature of the metal ions.

The complexes were characterized by elemental analysis (Table 1). The compounds exihibit similar solid state IR spectra. Some of the results are presented in Table 2. The band at 1670 cm^{-1} originating from COOH group, presented in the spectrum of the acid, is replaced in the spectra complexes by two bands at 1628-1548 and 1408-1388 cm^{-1}, which can be ascribed to the asymmetric and symmetric vibrations of COO^- group, respectively [26-28]. The bands of C-H asymmetric and symmetric stretching vibrations of CH_3 groups are observed at 2950-2930 and 2850-2820 cm^{-1}, respectively. The bands of υ(C-C) ring vibrations appear at 1475-1440, 1175-1160, 920-900 and 830-780 cm^{-1}. The band with the maximum at 3310-3100cm^{-1} in the spectrum of 2,4-dimethoxybenzoate of Cu(II) is characteristic for υ(OH) vibration. The bands corresponding to metal-oxygen stretching appear at 500-420 cm^{-1}.

The Table 2 presents the values of the two band frequencies of asymmetrical and symmetrical vibrations for carboxylate group for 2,4- dimethoxybenzoates of Mn(II), Cu(II), Co(II) and Na(I). The difference, Δυ, between the frequencies $\upsilon_{as}(OCO^-)$ and $\upsilon_s(OCO^-)$ in the complexes are higher or lower (248;160 cm^{-1}) than that in the sodium salt (Δυ = 208 cm^{-1}). According to the spectroscopic cryteria [26,29,30] the carboxylate ions appear to be monodentate, bidentate bridging or chelating and tridentate groups. In the complex of Cu(II) the carboxylate group is bidentate bridging while in that of Co(II) it is tridentate or one is monodentate and second bidentate one. In the spectrum of Mn(II) compound two bands of symmetrical carboxylate group vibrations appear. Therefore these groups seem to be bidentate briding and monodentate ones.

From the X-ray diffraction patterns recorded for the 2,4 – diethoxybenzoates of Mn(II), Co(II) and Cu(II) it appears that they are crystalline of low symmetry and large size of the unit cells. They have different crystal structures (Fig.1).

The termal stability of Mn(II), Co(II), Cu(II) 2,4- dimethoxybenzoates was studied in air at 293-1273K (Table 3). During heating to 1273K the Cu(II) complex dehydrates in one step. In the temperature range of 369,2-413,6K it losses one water molecule and forms anhydrous salt. The loss of mass calculated from TG curve is equal to 4,15% and, the theoretical value is 4,06%. The anhydrous salt at 495-731K is decomposed to CuO that is a final product of complex decomposition. The intermediate compounds formed in this range of temperature may contain Cu and Cu_2O that being next oxidized to CuO. The residue mass calculated from TG curve is equal to 20.8%, while that theoretically calculated 18.69%. This discrepancy probably appears from the rest of Cu_2O in the final mass of complex decomposition, which was indicated by elemental analysis, IR spectra, and X-ray powder diffractogram. The mass loss calculeted from TG curve is equal to 79,2% (theoretical value is 81,31%). The dehydration process, in this case, is connected with an endothermic effect seen on DTA curve, while the combustion of the organic ligand is accompanied by exothermic one. Considering the temperature at which the dehydration process occurs and the way in which it proceeds, it is possible to assume that the water molecule is in the outer coordination sphere of the complex [32,33]. The anhydrous 2,4-dimethoxybenzoates of Mn(II), Co(II) in the temperature range of 458-909K are decomposed to the oxides Mn_2O_3, Co_3O_4, respectively. The mass losses calculated from TG curves being equal to 81,6-80%(theoretical values are 81,1-80,9%) correspond to their formations as the final products of complex decompositions. In the case of Co(II) complex the Co and Co_2O_3 are surely the intermediate products of complex decomposition. The final mass calculated from TG curve is equal 20.0% while the theoretically value is 19,1%. These worths correspond to the Co_3O_4 formation that was identified by IR spectra and X-ray powder diffractogram. The anhydrous 2,4 – dimethoxybenzoate of Mn(II) is directly decomposed to Mn_2O_3 that is the final product of complex decomposition. Its contains (found mass 18,4%) calculated from TG curve is in good accordance with Mn_2O_3 formation (theoretical value: 18,9%). It was identified by IR spectra and X-ray powder diffractogram.

The results indicate that the thermal decompositions of 2,4-dimethoxybenzoates of Mn(II), Cu(II), Co(II) in air proceed in the following ways:

$CuL_2 \cdot H_2O \rightarrow CuL_2 \rightarrow CuO$
$MnL_2 \rightarrow Mn_2O_3$
$CoL_2 \rightarrow Co_3O_4$ where $L = C_9H_9O_4^-$

The magnetic susceptibility of 2,4-dimethoxybenzoates of Mn(II), Cu(II), Co(II) was measured over the range of 76-303K (Table 4). The measured values for Mn(II), Co(II) obey the Curie-Weiss law, suggesting a weak ferromagnetic interaction (Fig. 2). The magnetic moment values experimentally determined at 76-303K for Mn(II), Co(II) compounds change from 4,94 MB to 5,69 MB for Mn(II) compound, from 4,27 MB to 4,55 MB for Co(II) complex. These magnetic moment data are very close to the spin - only values for the respective ions calculated from the equation $\mu_{eff} = [4S(S+1)]^{1/2}$ in the absence of the magnetic interaction for present spin-system. The magnetic moment values calculated at room temperature for Mn(II), Co(II) and Cu(II) ions are equal to 5.9 MB, 3.88MB and 1.73MB , respectively. For Mn(II), Co(II) and Cu(II) the magnetic moment values may be different, than the spin-only worth. In the case of Co(II) compound they are higher than the spin – only value. This difference between measured and caluculated data results from spin – orbital coupling [34]. For Mn(II) and Cu(II) complexes these values are lower. This is due to the fact that the vectors L and S are aligned by the strong field of the heavy atom in opposite directions and this diminishes the resultant magnetic moment. The experimental data suggest that compounds of Mn(II) and Co(II) seem high-spin complexes with probably weak ligand fields [35].

The magnetic susceptibility values of 2,4-dimethoxybenzoate of Cu(II) incrase with rising temperatures suggesting a weak antiferromagnetic interaction(Fig.4). The magnetic moment values experimentally determined change from 0,64 MB (at 76K) to 1,57 MB (at 303K). These values are lower than the d^9 spin-only magnetic moment $ì_{eff}$ = 1,73 MB. Such dependence is a typical behaviour for copper dimer (Table 4, Figs. 3) [35-38]. The magnetic moment values of the Cu(II) complex decrease from 1.57MB at 303K to 0.64MB at 76K, as a consequence of depopulation of the excited triplet (S = 1) state. It is well – known that the interaction between two S = ½ metal atoms in a dimer leads to two molecular states: a spin singlet (S = 0), and a triplet (S=1) separated by 2J. The interaction will be antiferromagnetic (J<0) if S=0 it is the ground state; on the contrary if S=1 the interaction will be ferromagnetic (J>0) [39-43]. The suggested formula for the Cu(II) complex is $Cu_2L_4(H_2O)_2$.

From the obtained results it appears that in 2,4-dimethoxybenzoates of Mn(II), Co(II) and Cu(II) the coordination numbers may be equal to 5 and 6 depending on the dentates of carboxylate group. The coordination numbers of individual ions could be estabilished on the basis of the complete crystal structure determination of monocrystals but they have not been obtained. Therefore according to the Cu(II) complex we can only suppose that each cooper(II) atom may show a fivefold coordination in the form of square pyramid with four oxygen atoms of the bridging 2,4-dimetoxybenzoate anions in the basal plane and one oxygen atom of water molecule at the apex [44]. In manganese(II) and cobalt(II) 2,4 - dimethoxybenzoates the ligands behave as tridentate groups. Cations are presumably in octahedral coordination.

Received 26 April 2007
Accepted 03 June 2007

References

[1] S.C. Mojumdar, D. Hudecová, and M. Melnik, Pol. J. Chem., 73 (1999) 759
[2] M. Mc Cann, J. F. Cronin, and M. Devereux, Polyhedron, 17 (1995) 2327
[3] W. Ferenc, and A. Walków-Dziewulska, Collect. Czech. Chem. Commun. 65(2) (2000) 179
[4] W. Ferenc, and A. Walków-Dziewulska, J. Therm. Anal. Cal., 61 (2000) 923
[5] W. Ferenc, and A. Walków-Dziewulska, J. Serb. Chem. Soc., 66 (2001) 543
[6] W. Ferenc, and A. Walków-Dziewulska, J. Therm. Anal. Cal., 71 (2002) 375
[7] W. Ferenc, A. Walków-Dziewulska, and S. Kuberski, Chem. Pap., 57 (2003) 375
[8] W. Ferenc, A. Walków-Dziewulska, and J. Chruœciel, J. Serb. Chem. Soc., 68 (2003)
[9] W. Ferenc, and A. Walków-Dziewulska, J. Therm. Anal. Cal., 74 (2003) 511
[10] W. Ferenc, A. Walków-Dziewulska, P. Sadowski, and Chruœciel J., J. Serb. Chem. Soc., 70 (2005) 833
[11] W. Ferenc, A. Walków-Dziewulska, and P. Sadowski, J. Therm. Anal. Cal., 82 (2005) 365
[12] W. Ferenc, A. Walków-Dziewulska, and J. Sarzyñski, J. Serb. Chem. Soc.,70 (2005) 1089
[13] W. Ferenc, A. Walków-Dziewulska, and P. Sadowski, Chem. Pap.59 (2005) 324
[14] Beilsteins Handbuch der organischen Chemie, Bd X Springer, Berlin, 1927
[15] Beilsteins Handbuch der organischen Chemie, Bd X Springer, Berlin, 1971
[16] Al-Afaleq, J. Eljazi, and A. Samar, Synth. Commun., 29 (1999) 1965
[17] R. P. Dunlap, N. W. Boaz, and A. J. Mura, U.S. US 5., 512, 589, 30Apr (1996)
[18] O. Cabaliero, and R. Cela, J. Microcolumn. Sep.,VI, 8 (1996) 231
[19] P. Barraclough, J. W. Black, and D. Cambridge, Eur. J. Med. Chem., 27 (1997) 207
[20] W. Ferenc, and A. Walków-Dziewulska, J. Serb. Chem. Soc., 65 (2000) 27
[21] W. Ferenc, and A. Walków-Dziewulska, J. Therm. Anal. Cal., 63 (2001) 865
[22] W. Ferenc, and A. Walków-Dziewulska, J. Serb. Chem. Soc., 65 (2000) 789
[23] W. Ferenc, and A. Walków-Dziewulska, J. Therm. Anal. Cal., 70 (2002) 949
[24] B. N. Figgis, and R. S. Nyholm, J. Chem. Soc. , 1958, 4190
[25] E. Kõnig, Magnetic Praperties of Coordination And Organometallic Transitian Metal Compounds, Berlin, 1966
[26] K. Nakamoto, Infrared and Ramana Spectra of Inorganic and Coordination Compounds, John-Wiley and Sons, New Jork, 1997
[27] A. K. Bridson, Inorganic Spectroscopic Methods, Oxford University Press, New York, 1998
[28] L. H. Harwood, and P. J. McCarthy, Spectroscopy and Structure of Metal Chelate Compounds, Wiley, New York, 1968
[29] R. C. Mehrotra, and R. Bohra, Metal Carboxylates, Academic Press, London, 1983
[30] B. S. Manhas, and A. K. Trikha, J. Indian. Chem. Soc., 59 (1982) 315
[31] Z. Bojarski, and E. £¹giewka, Structural X-Ray Analysis, Polish Scientific Publisher, Warsaw, 1988
[32] A.V. Nikolaev, V. A. Logvinienko, and L. S. Myachina, Thermal Analysis, Vol.2, Academic Press, New York, 1969
[33] B. Singh, B. V. Agarwala, P. L. Mourya, and A. K. Dey, J. Indian. Chem. Soc., 59 (1992) 1130
[34] K. Burger , Coordinatrion Chemistry: xperimental Methods, Akademia KiadO, Budapest, 1973
[35] J. Mroziñski, M. Janik, and T. Nowakowski, Zeszyty Naukowe Politechniki Œl¹skiej, 119 (1988) 125(in Polish)
[36] A. Earnshaw, Introduction to Magnetochemistry, Academic Press, London, 1956
[37] C. O'Connor, Progress in Inorganic Chemistry, Wiley, New York, 1982
[38] F. A. Keetle, Inorganic Physical Chemistry, Polish Scientific Publisher, Warsaw, 1999
[39] E. Kokot, and R. L. Martin, Inorg. Chem., 3 (1964) 1306
[40] B. N. Figgis, and R. L. Martin, J. Chem. Soc. (1956) 3837
[41] C. C. Hadjikostas, G. A. Katsoulos, M. P. Sigalas, C. A. Tsipis, and J. Mroziñski, Inorg. Chim .Acta., 167(1990) 165
[42] J. Casanova, G. Alznet, J. Latorre, and J. Borras, Inorg. Chem. 369 (1997) 2052
[43] O. Kahn, Angew.Chem.Int.Ed.Engl., 24(1985)834
[44] M. Klinga, M. Sundberg, M. Melnik and J. Mroziñski, J. Inorg. Chem. Acta.,162 (1989) 39