Journal of Thermal Analysis and Calorimetry, Vol. 58 (1999) 51-60

SYNTHESIS AND THERMAL STUDIES OF 2,4'-BIPYRIDYL COMPLEXES OF MANGANESE(II) SALTS

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(Received July 27, 1998; in revised form December 10, 1998)

Abstract

2,4'-Bipyridyl (2,4'-bipy or *L*) complexes of Mn(II) with the formulae $MnL_2X_2 \cdot 2H_2O$ (X^-=Cl, Br, NCS, NO_3), $MnLSO_4 \cdot 5H_2O$ and $MnL_4(ClO_4)_2 \cdot 2H_2O$ were synthesized and characterized via the IR spectra and magnetic, and conductivity measurements. The nature of the Mn(II)-ligand coordination is discussed. The thermal decompositions of these compounds were studied in air atmosphere. The mode of decomposition depends on the anion present, but the final product in all cases is Mn_3O_4. Some of the intermediates (MnL_2Cl_2, $MnLCl_2$, MnL_2Br_2, $MnL_2(NCS)_2$ and $MnLSO_4$) formed during the pyrolysis are isomeric with 2,2'-bipy and 4,4'-bipy complexes.

Keywords: IR spectra, manganese(II) complexes, thermal decomposition, 2,4'-bipyridyl complexes

Introduction

Coordination compounds of Mn(II) salts with 2,2'-bipyridyl (2,2'-bipy) and 4,4'-bipyridyl (4,4'-bipy) have been extensively investigated during many years [1–6]. However, complexes of Mn(II) salts with 2,4'-bipyridyl (2,4'-bipy or *L*) do not appear to have not been prepared and studied. This paper is a continuation of our earlier studies on coordination compounds of transition metal salts with 2,4'-bipy [7–9]. The present study reports the coordination compounds formed by the interactions of Mn(II) chloride, bromide, thiocyanate, nitrate and sulphate with the title ligand. It was of interest to examine the influence of anions with different coordination abilities on the thermal decompositions of the complexes with bipyridyl isomers. The compounds obtained were characterized by elemental and thermal analysis, and by IR spectroscopic, and magnetic and molar conductivity investigations. The thermal decompositions of these complexes (in the temperature range 20–1000°C) are reported and discussed.

Experimental

Preparation of compounds

All the 2,4'-bipy complexes with the various Mn(II) salts were prepared as described previously [9].

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1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
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Analyses

The compounds obtained were analysed after decomposition with dilute HNO_3. Manganese was determined chelatometrically, chloride, bromide and thiocyanate by the Volhard method and perchlorate by solvent extraction with ferroin. Sulphate was estimated gravimetrically as $BaSO_4$. C, H and N contents were determined by elemental analysis, with V_2O_5 as oxidizing agent. Analysis and identification of the solid intermediates of decomposition were performed by chemical analysis and X-ray diffraction. The intermediates (sinters) were prepared under conditions similar to those used in the thermal analysis. A sample of 100 mg was heated in a silite furnace at a heating rate of about $5^\circ C\ min^{-1}$ up to an appropriate temperature determined from the TG curves.

Materials and physical measurements

Thiocyanates of Mn(II) as hydrated products were prepared by the method described in the literature [7]. 2,4'-Bipy (*m.p.* $61^\circ C$) and $Mn(ClO_4)_2 \cdot H_2O$ were obtained from Aldrich; methanol (anhydroscan) from Lab-Scan; other chemicals were p.a. products from POCh-Gliwice. IR spectra in the region 400–4000 cm^{-1} were obtained on a Shimadzu model spectrophotometer (KBr pellets). Conductivity measurements were performed on an OK-102/1 conductivity meter equipped with an OK902 electrode at $25\pm0.05^\circ C$. The cell constant was determined by use of a standard aqueous solution of KCl. The molar conductivities (Λ_M) of the complexes were measured on $1.0 \cdot 10^{-3}$ mol dm^{-3} solutions in methanol. Thermal data (TG, DTA and DTG) and room-temperature magnetic moments were recorded as described earlier [8, 9].

Results and discussion

The analytical results on the compounds obtained are presented in Table 1, together with other characteristic data. The reactions between 2,4'-bipy and MnX_2 (except $Mn(ClO_4)_2$) afforded compounds of general formula $MnL_2X_2 \cdot 2H_2O$. The isolated compound $MnL_2(NCS)_2 \cdot 2H_2O$ was isomeric with the 4,4'-bipy complex [1]. The complexes of 2,4'-bipy with $MnSO_4$ and $Mn(ClO_4)_2$ were obtained at a metal to ligand ratio of 1:1 or 1:4, respectively. Diffractogram analysis indicated that the compounds isolated were crystalline solids. They were air-stable at room temperature. All the complexes dissolved fairly well in water and methanol, decomposed in aqueous acid and alkali and were insoluble in most organic solvents. The magnetic moments lay in the range 5.64–5.82 BM, indicating five unpaired electrons; hence, electron pairing or significant double pairing or significant double bonding does not occur (similarly as for $Mn(2\text{-bipy})_3Br_2$ [6]). The high molar conductivity of $MnL_4(ClO_4)_2 \cdot 2H_2O$ in MeOH corresponded to that of a 1:2 electrolyte, while $MnLSO_4 \cdot 5H_2O$ was characterized as a non-electrolyte [10]. The complexes $MnL_2Cl_2 \cdot 2H_2O$ and $MnL_2Br_2 \cdot 2H_2O$ behaved as 1:1 electrolytes (Λ_M values of 109 and 144 S cm^2 mol^{-1}, respectively). Bromides are usually more conducting than chloride derivatives, bromide being more labile [10, 11]. The other new complexes

Table 1 Analytical data, effective magnetic moments (μ_{eff}) and molar conductivity in methanol (Λ_M)

	Compound	Found (Calcd.)/%					Λ_M/ S cm^2 mol^{-1}	μ_{eff}/ BM
		Mn	C	N	H	*X*		
I	$MnL_2Cl_2 \cdot 2H_2O$	11.57 (11.58)	50.48 (50.65)	11.65 (11.81)	4.23 (4.25)	14.90 (14.95)	109.1	5.7
II	$MnL_2Br_2 \cdot 2H_2O$	9.73 (9.75)	42.68 (42.65)	10.06 (9.95)	3.62 (3.58)	27.73 (28.38)	144.4	5.7
III	$MnL_2(NCS)_2 \cdot 2H_2O$	10.47 (10.57)	50.50 (50.86)	17.27 (16.18)	3.90 (3.88)	22.50 (22.36)	74.2	5.6
IV	$MnL_2(NO_3)_2 \cdot 2H_2O$	10.74 (10.42)	45.79 (45.55)	15.72 (15.94)	3.76 (3.82)		49.0	5.8
V	$MnLSO_4 \cdot 5H_2O$	13.94 (13.83)	30.11 (30.23)	7.03 (7.05)	4.67 (4.57)	24.38 (24.18)	3.8	5.8
VI	$MnL_4(ClO_4)_2 \cdot 2H_2O$	5.86 (6.00)	52.48 (52.53)	12.37 (12.25)	3.82 (3.97)	21.67 (21.75)	190.9	5.8

displayed behaviour intermediate between those of non-electrolytes and 1:1 electrolytes. Higher than anticipated Λ_M values (*vide infra* IR) are usually due to the displacement of isothiocyanato or nitrato ligands by solvent molecules. Similar behaviour has previously been observed in metal complexes with other aromatic amines [12].

Infrared spectra

The principal features of the IR spectra of 2,4'-bipy and its complexes are presented in Table 2. The IR spectra of the 2,4'-bipy complexes with Mn(II) exhibited several absorption bands characteristic of CC, CN, CH and breathing frequencies of 2- and 4-substituted pyridine and were in good accord with previous observations on the complexes of 2,4'-bipy with other metal salts [8, 13]. As a result of the formation of compounds with Mn(II), the IR spectrum of 2,4'-bipy underwent a clear change only in the region of ring vibration modes for 4-substituted pyridine. The characteristic ring vibration modes for 4-substituted pyridine [14], i.e. ν(C=N) and ν_{ring} appearing at 1595 and 1405 cm^{-1} for the free ligand, were observed for these compounds at 1609–1614 cm^{-1} and 1405–1416 cm^{-1}, respectively. The breathing frequencies for 4-substituted pyridine, observed as a shoulder at 990 cm^{-1} for free 2,4'-bipy, were shifted by 23–25 cm^{-1} towards higher values for the complexes (bands with strong intensity). The IR spectra of the investigated complexes showed that 2,4'-bipy is bonded to a metal ion via the least hindered N(4') atom acting as a monodentate ligand [13].

The IR spectra of $MnL_2(NCS)_2 \cdot 2H_2O$ revealed the absorption band ν(CN) of the NCS group as a very strong, poorly resolved doublet at 2098 and 2086 cm^{-1}. The δ(NCS) and ν(CS) bands were identified at (cm^{-1}): 475 s and 866 vv, respectively.

Table 2 Principal IR bands (cm^{-1}) and their assignments in 2,4'-bipy and its complexes

Compound	ν(C=N) (4-sub)	ν(C=N) (2-sub)	ν ring (4-sub)	breathing (4-sub)
2,4'-bipy (L) [14]	1595 vs	1586 vs	1405 vs	990 sh
$MnL_2Cl_2{\cdot}2H_2O$	1609 vs	1591 s	1414 vs	1015 vs
$MnL_2Br_2{\cdot}2H_2O$	1609 vs	1591 vs	1414 vs	1015 vs
$MnL_2(NCS)_2{\cdot}2H_2O$	1609 vs	1583 vs	1412 s	1013 vs
$MnL_2(NO_3)_2{\cdot}2H_2O$	1611 vs	1590 s	1415 m	1014 s
$MnLSO_4{\cdot}5H_2O$	1611 vs	1590 m	1416 m	1015 m
$MnL_4(ClO_4)_2{\cdot}2H_2O$	1614 vs	1587 vs	1416 s	1013 m

v, m, s, sh – very, medium, strong, shoulder

The NCS^- group is an ambidentate ligand. The ν_{CN}(NCS) vibrations showed the Mn–thiocyanate bonding to be attained through the N-atom as in general for 3*d* transition elements [1, 15, 16]. The very small splitting of the CN stretching absorption band in the solid state suggests the octahedral configuration of the Mn complex [16]. $MnL_2(NCS)_2{\cdot}2H_2O$ was presumably neutral, as suggested by its IR spectrum, but exhibited an unexpectedly high Λ_M and was apparently partially dissociated in MeOH. Similar behaviour upon dissolution has been noted for neutral complexes of the type NiY_2X_2 (where Y=2,2'-bipy or phen and X=Cl, Br, I or NCS) and other complexes [17, 18].

The IR spectrum of $MnL_2(NO_3)_2{\cdot}2H_2O$ yielded absorption bands at (cm^{-1}): 1768 s, 1750 vw ($\nu_1+\nu_4$; $\Delta(\nu_1+\nu_4)=16\ cm^{-1}$), 990 s ($\nu_1$), 823 s ($\nu_2$), 1431 w, 1384 vs ($\nu_3$) and 746 m, due to monodentate nitrato groups [15, 19–21]. Coordination of this type is also observed in complexes of Mn(II) nitrate with other ligands [22–24].

The locations (cm^{-1}) of the ν_1 (989 m), ν_2 (468 m), ν_3 (1120 vs, br) and ν_4 (605 m) bands in the IR spectrum of $MnLSO_4{\cdot}5H_2O$ are generally diagnostic of the mode of coordination of the sulphate group [15, 25]. Coordination of this type is observed in many sulphato-Mn(II) complexes with other N-donors [26–28]. In the spectrum of $MnL_4(ClO_4)_2{\cdot}2H_2O$, the presence of a strong band at 1100 cm^{-1}, a weak peak at 982 cm^{-1} and a medium peak at 623 cm^{-1} was observed. Since such bands do not occur in the spectrum of free 2,4'-bipy, they were identified as the ν_3, ν_2 and ν_4 modes (respectively), consistent with T_d symmetry of the ionic perchlorate [15]. A strong, broad band in the water stretching region (ca. 3400–3500 cm^{-1}) and a medium (or weak) peak in the water bending region (at ca. 1645 cm^{-1}) were present in the IR spectra of all the new complexes.

Moreover, H_2O wagging vibrations for coordinated water were observed at (cm^{-1}): 547 s (1), 528 s (2), 559 m (3), 542 w (4), 530 m (5) and 547 w (6). The Mn–O stretching mode for coordinated water was masked by 2,4'-bipy.

Thermal analyses

The data obtained from the TG, DTG, DTA and DTA curves, supported by chemical analysis and the X-ray diffraction pattern investigations, are given in Table 3. The course of thermal decomposition depended strongly on the anion present. Since all of the complexes are hydrated, the first mass losses can be assigned to water evolution. The release of H_2O molecules takes place in well-defined steps, which can be clearly observed in the thermal curves (Figs 1–3). The thermal analysis

Table 3 Thermal analysis results on 2,4'-bipy complexes of Mn(II) salts in air

T_{range}/ °C	T_{peak} of DTA/ °C	Mass loss/%		Intermediates and products
		found	calcd.	
$MnL_2Cl_2 \cdot 2H_2O$				
70–105	88 endo	7.8	7.60	MnL_2Cl_2
180–288	282 endo	33.0	32.93	$MnLCl_2$
288–360	340 endo	16.5	16.47	$MnL_{0.5}Cl_2$
360–405	385 endo	17.0	16.47	$MnCl_2$
405–582	~540 endo br	10.0	9.89	Mn_2O_3
>900	920 endo		0.64	Mn_3O_4
$MnL_2Br_2 \cdot 2H_2O$				
90–130	120 endo	6.5	6.40	MnL_2Br_2
220–350	320, 340 endo	41.5	41.61	$MnL_{0.5}Br_2$[a]
350–400	390 endo	14.0	13.87	$MnBr_2$
445–560	540 exo	24.0	24.11	Mn_2O_3
>900	920 endo		0.48	Mn_3O_4
$MnL_2(NCS)_2 \cdot 2H_2O$				
100–225	190 endo	6.5	6.93	$MnL_2(NCS)_2$
240–350	295 endo 338 exo	45.0	45.1	$MnL_{0.5}(NCS)_2$
350–400	395 exo	20.0	19.08	$Mn(NCS)_2$+MnS (3:1)[b]
400–540	530 exo	7.0		mixture of $MnSO_4$, β-$MnSO_4$, traces of MnS and manganese oxides
760–920	900 endo	7.0	14.21	pure Mn_3O_4
$MnL_2(NO_3)_2 \cdot 2H_2O$				
92–130	118 endo	3.5	3.42	$MnL_2(NO_3)_2 \cdot H_2O$
140–180	165 endo	4.0	3.42	$MnL_2(NO_3)_2$
180–275	260 exo	72.5	73.19	$Mn(NO_3)_2$+MnO_2 (1:4)[b]
275–360	340 exo 420 exo	4.0	3.49	γ-MnO_2; γ-MnO_2→β-MnO_2
540–650	470 endo br	2.0	1.99	Mn_2O_3
>900			0.51	Mn_3O_4

Table 3 Continued

T_{range}/ °C	T_{peak} of DTA/ °C	Mass loss/%		Intermediates and products
		found	calcd.	
		$MnLSO_4·5H_2O$		
70–95	90 endo	9.0	9.60	$MnLSO_4·3H_2O$
105–148	130 endo	9.0	9.60	$MnLSO_4·H_2O$
148–180	170 endo	5.0	4.57	$MnLSO_4$
240–300	278 endo	11.0	9.82	$MnL_{0.75}SO_4$
300–360	340 endo	28.5	29.48	$MnSO_4$
760–940	920 endo	18.5	18.81	Mn_3O_4[c]

[a] by projecting minimum of DTG curve on o TG curve; [b] mole ratio; [c] via mixture of $MnSO_4$ and Mn_2O_3; br – broad

results demonstrate that the release of H_2O molecules is a one-step process for complexes (I)–(III), a two-step process for (VI) and a three-step process for (V). Dehydration is characterized by endothermic effects. The maximum rate of H_2O evolution (the temperature of the first peak in the DTA curve) decreases in the sequence

$$NCS>Br\approx NO_3>SO_4\approx Cl$$

The anhydrous complexes decomposed in various ways. However, chemical and X-ray analysis of the decomposition residues demonstrated that Mn_3O_4 was formed as the final product of decomposition of complexes (I)–(V), (Fig. 4a). Mn_3O_4 was

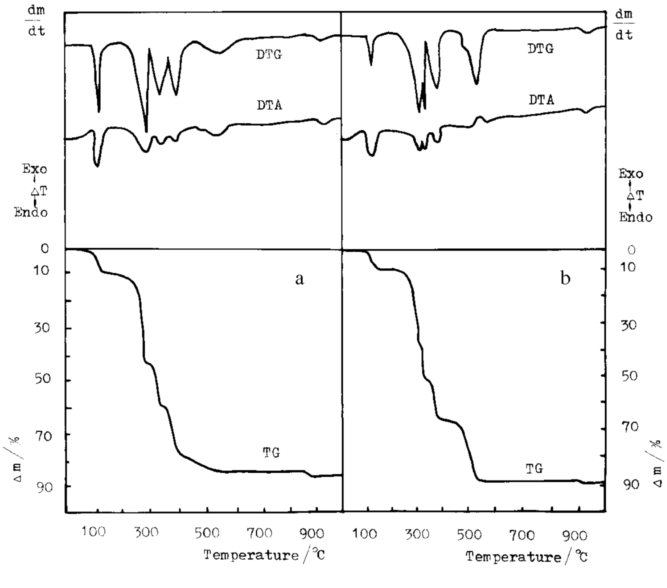

Fig. 1 Thermal analysis curves of a – $MnL_2Cl_2·2H_2O$ and b – $MnL_2Br_2·2H_2O$

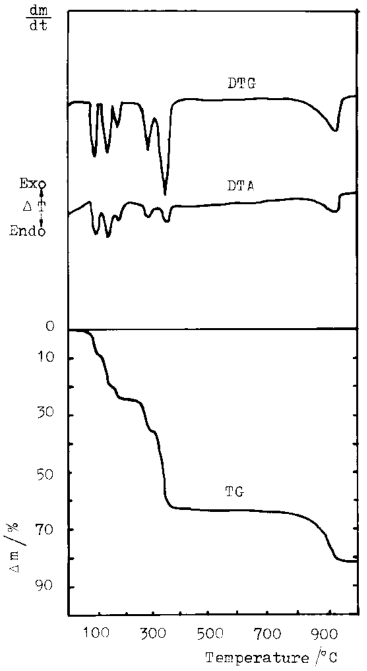

Fig. 2 Thermal curves of $MnLSO_4{\cdot}5H_2O$

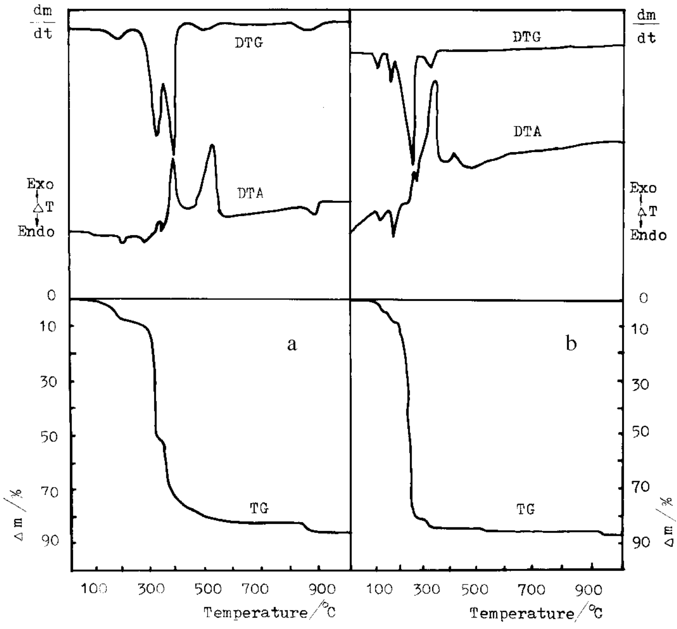

Fig. 3 Thermal curves of a – $MnL_2(NCS)_2{\cdot}2H_2O$ and b – $MnL_2(NO_3)_2{\cdot}2H_2O$

obtained via pure Mn_2O_3 for compounds (I), (II) and (IV) (Fig. 4b) or with an admixture of $MnSO_4$ for the remaining complexes. Most stable was $MnL_2(NCS)_2$, which started to lose 2,4'-bipy at 240°C, while least stable was $MnL_2(NO_3)_2$ (140°C). The 2,4'-bipy molecules were released in three steps for complex (I), and two steps for complexes (II), (III) and (V). During the partial deamination of these compounds, the following unstable compounds were detected from the thermolysis curves: $MnLCl_2$, $MnL_{0.5}Cl_2$, $MnL_{0.5}Br_2$ and $MnL_{0.75}SO_4$. The release of the last portion of 2,4'-bipy was accompanied by the formation of Mn(II) salts. $MnCl_2$ forms at 405°C (found: 25.7%; calcd.: 26.53%) and $MnBr_2$ at 400°C (found: 38.1%; calcd.: 38.13%). On increase of the temperature, these salts were oxidized to pure Mn_2O_3 (Fig. 2b). The dihalogenato complexes of Mn(II) with 1,10-phenanthroline also decomposed to Mn_2O_3, but at higher temperature [29].

In the DTA curve of complex (I), the exothermic effect characteristic of the oxidation process was not observed. Formation of Mn_3O_4 began at 900°C (this result agrees with the transformation temperatures reported by other authors [30, 31]).

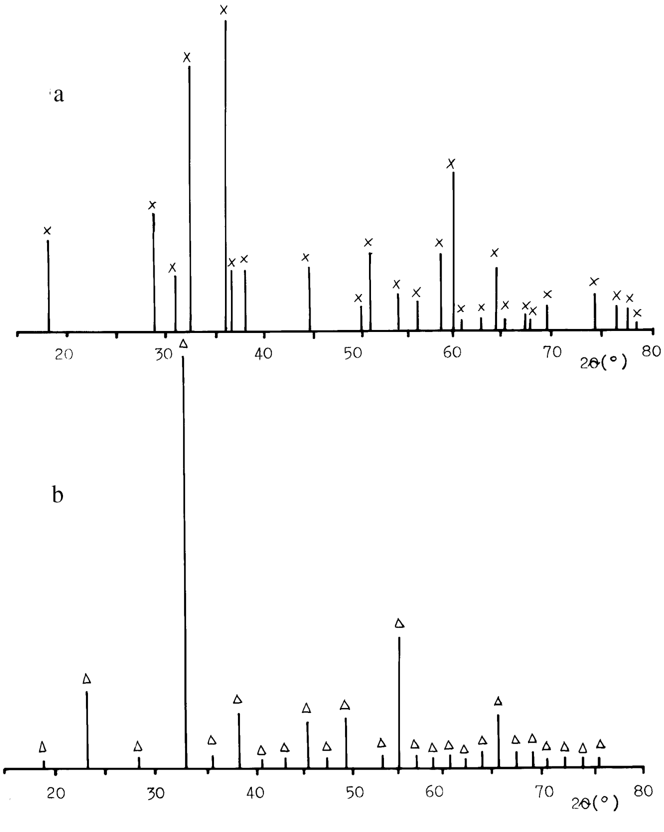

Fig. 4 X-ray diffraction patterns of decomposition products of complexes a – (I)–(V) heated up to 940°C; b – $MnL_2X_2{\cdot}2H_2O$ (X=Cl, Br, NO_3) heated up to 650°C; × – Mn_3O_4; Δ – Mn_2O_3 (The results were analysed by using the Powder Diffraction File, International Center of Diffraction Data, ICPDS-ICDD, 1990)

The intermediate compound $MnL_{0.75}SO_4$ began to decompose at about 300°C. A horizontal mass level was observed between 360 and 760°C, which corresponded to $MnSO_4$. On temperature elevation, $MnSO_4$ decomposed via Mn_2O_3 to Mn_3O_4. At 940°C, the only phase identified was Mn_3O_4. According to Erdey and Liptay [32], $MnSO_4$ also begins to decompose above 760°C, whereas other authors [33] report a temperature of 850°C.

The anhydrous complex $MnL_2(NCS)_2$ eliminated 1.5 moles of 2,4'-bipy (240–350°C) and $MnL_{0.5}(NCS)_2$ was formed. Upon further heating in the temperature range 350–400°C, the intermediate complex decomposed to a mixture of $Mn(NCS)_2$ and MnS (molar ratio 3:1). On increase of the temperature, simultaneous reactions proceeded. At 540°C, a mixture of $MnSO_4$ (with traces of MnS) and manganese oxides was formed. This is consistent with the conclusions of other authors [32, 34]. The horizontal level began above 540°C. The diffraction pattern of the sinter (prepared during the heating of compound (III) up to 650°C) indicated the presence only of $MnSO_4$, β-$MnSO_4$ and Mn_3O_4. Above 760°C, Mn(II) sulphate decomposed to Mn_3O_4 at 760–920°C, via a mixture containing Mn_2O_3 (the endothermic peak at 900°C). The final product of decomposition of $MnL_2(NCS)_2{\cdot}2H_2O$ at 920°C was pure Mn_3O_4 (found 15.0%; calcd.: 14.68%).

Deamination of $MnL_2(NO_3)_2$ accompanied by partial decomposition of $Mn(NO_3)_2$ to MnO_2 took place (the exothermic peak at 260°C). At 275°C two different phases existed: $Mn(NO_3)_2$ and MnO_2. Quantitative analysis data on the sample obtained in the thermal decomposition of $MnL_2(NO_3)_2{\cdot}2H_2O$ heated up to 275°C showed a molar ratio $Mn(NO_3)_2$:MnO_2=1:4. Some literature data [35, 36] report that a mixture of MnO_2 and $Mn(NO_3)_2$ is formed in the decomposition of $Mn(NO_3)_2{\cdot}6H_2O$. The composition of this mixture depends on the initial sample mass [35]. On temperature elevation, the remaining $Mn(NO_3)_2$ probably decomposed to γ-MnO_2. The corresponding exothermic peak in the DTA curve was very high (340°C). According to Hassan *et al.* [30], the phase transition γ-MnO_2 to β-MnO_2 is observed at ca 400°C. The exothermic peak at 420°C was assigned to the phase transition γ-MnO_2 to β-MnO_2. Between 540 and 650°C, β-MnO_2 was transformed to pure Mn_2O_3. Above 900°C, only diffraction lines characteristic of Mn_3O_4 were detected (Fig. 4a).

The intermediates MnL_2Cl_2, $MnLCl_2$, MnL_2Br_2, $MnL_2(NCS)_2$, $MnL_2(NO_3)_2$ and $MnLSO_4$ formed during the thermal decomposition are isomeric with the 2,2'-bipy [1, 37] or 4,4'-bipy [1, 38] complexes.

When heated in air, $MnL_4(ClO_4)_2{\cdot}2H_2O$ is explosive.

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This work was supported by the KBN, project no. 3T09A 002 12.

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