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STRUCTURAL AND THERMAL ANALYSIS OF PHOSPHORAMIDOTHIOATE, PHOSPHORODIAMIDOTHIOATE AND N,N′-DIPHENYLPHOSPHORODIAMIDOTHIOATE COMPLEXES OF Zn(II), Cd(II) AND Hg(II)

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A new series of complexes of Zn(II), Cd(II) and Hg(II) with phosphoramidothioate (PAT), phosphorodiamidothioate (PDAT) and N,N′-diphenylphosphorodiamidothioate (N,N′-DPDAT) ligands have been synthesized and studied. The structures of the new compounds are discussed on the basis of their spectroscopic and thermal data. Thermoanalytical studies of these compounds have shown a dependence of the thermal stability on the size of the metal cation; the PAT complexes have greater thermal stability than the others.

Although the ligands PAT, PDAT and N,N′-DPDAT have been known for many years [1–3], their coordination capacity has scarcely been examined and studies on their behaviour as ligands are rather limited. In a previous study [4] we reported results concerning the synthesis of some novel transition metal complexes of PAT and PDAT and the investigation of their bonding mode by quantum-chemical CNDO/2 calculations. As a continuation of our previous work on complexes of PAT and PDAT, we describe here the synthesis and the thermal investigation of a new series of Zn(II), Cd(II) and Hg(II) complexes with PAT, PDAT and N,N′-DPDAT. A literature survey reveals that little has been done on the thermal decomposition of this type of complexes. Examinations have been made of the thermal behaviour of ammonium phosphoramidothioate [3], as well as some calcium phosphoramidate salts [5] and some metal O,O-dialkylphosphorodithioates [6]. Therefore, it was also interesting to investigate the thermal properties of the compounds in question by applying TG and DTA techniques. Herein we report the preparation of nine new complexes and their IR and electronic spectra are also reported and discussed.

Experimental

a) Physical measurements

Infrared spectra were recorded in the 4000–250 cm^{-1} region on a Perkin–Elmer 467 spectrophotometer, using KBr pellets. Electronic spectra were obtained on a Perkin–Elmer Hitachi 200 spectrophotometer, in the solid state with Nujol mulls. The elemental analysis of C, H and N was performed on a Perkin–Elmer 240 elemental analyser. The metal determinations were carried out volumetrically by published methods [7]. The thermal decomposition was studied on a Mettler TA 2000 system at a heating rate of 6 deg/min, in the temperature region 25–1000° for $Zn_2(PO_2SNH_2)_2(H_2O)_3$, $Cd_2(PO_2SNH_2)_2(H_2O)_2$ and $Cd(POS(NH_2)_2)_2(H_2O)_4$, and in the region 25–650° for all the other complexes, using a sample mass of 20–40 mg and α-Al_2O_3 as reference. The measurements were performed in a dynamic atmosphere of nitrogen. The chart speed was maintained at 5 mm/min. All the samples were of the same particle size and were packed as uniformly as possible in a platinum crucible of appropriate size. The same platinum crucible was used throughout the experimental work.

b) Preparation of the complexes

The ligands PAT, PDAT and N,N'-DPDAT were prepared as described previously [1, 2]. Their complexes were prepared by the following general procedure.

Phosphoramidothioate complexes of Zn(II), Cd(II) and Hg(II)

To a solution of 2 mmol of hydrated metal chloride in water (20 ml), ammonium phosphoramidothioate (2.2 mmol), dissolved in water (20 ml), was added slowly under continuous magnetic stirring (2 h) at room temperature. A white residue (or pale-yellow for the Cd complexes) was formed, which was filtered off, washed successively with water, ethanol and diethyl ether and dried in vacuum above P_2O_5 for 48 h.

Phosphorodiamidothioate and N,N'-diphenylphosphorodiamidothioate complexes of Zn(II), Cd(II) and Hg(II)

A procedure similar to that described above was followed for the preparation of the PDAT and N,N'-DPDAT complexes, the differences being the use of 4.4 mmol for either the ammonium salt or the metal chloride. In order to complete the precipitation of the complexes, ethanol (40 ml) was added to the mother liquor.

Results and discussion

Zinc(II), cadmium(II) and mercury(II) halides react with aqueous solutions of the ammonium salts of the ligands PAT, PDAT and N,N'-DPDAT, to produce yellow or white complexes. All the studied compounds correspond to the general types $M_2L_4 \cdot xH_2O$ or $ML \cdot xH_2O$; the latter represents only the phosphoroamidothioate complexes. The compounds were found to be hydrated, and insoluble in water and common organic solvents, the latter suggesting polymeric structures. Due to their insolubility in common organic solvents, we have been unable to determine the extent of polymerization.

The assignments of the main IR bands shown in Table 1 were based on the data reported previously for the phosphorodiamidate salts [8, 9]. In the IR spectra the broad bands at 3400–3500 cm^{-1} and the appearance of a band in the vicinity of 840 cm^{-1} for some hydrated compounds demonstrates water coordinated to the metal [10, 11]. An additional band at 320 cm^{-1} was assigned to the presence of coordinated water [12]. The IR spectra data and the results of quantum-chemical CNDO/2 calculations on PAT and PDAT [4], indicated that oxygen and sulphur atoms are the donor sites of the ligands, with ν(P–O) and ν(P–S) stretching frequencies shifted by 20–30 cm^{-1} to lower wavenumbers from those for the free ligands. The bands in the 500–480 cm^{-1} and 330–295 cm^{-1} regions are attributed to ν(M–O) and n(M–S) stretching vibrations [13]. Therefore, all these vibrations can be useful as a guide to metal-oxygen and metal-sulphur bonding. This is almost in line with the IR data reported previously for similar compounds [14, 15]. Likewise, for the studied compounds the data suggest a distorted tetrahedral structure, the water molecules being linked directly to the metal atom.

The electronic spectra (Table 2) show bands which were attributed to a $\pi^* \leftarrow \pi$ transition. Analytical data and the positions of the characteristic IR bands are given in Table 1. Thermal decomposition curves are given in Figs 1–9, while the TG weight loss data and DTA peak temperatures are presented in Table 3. The TG and DTA curves reveal that the hydrated compounds decompose in two stages. The TG curves show that the first stage involves the loss of water for all the hydrated complexes. The second decomposition stage involves one or more steps, which appear as endothermic or exothermic peaks in the DTA curves. The residues left in the crucible consist of compounds incorporating the corresponding metal.

Table 1 Analytical Data and Relevant IR frequencies (cm^{-1}) for the new (PAT), (PDAT) and N,N'-DPDAT complexes of Zn(II), Cd(II) and Hg(II) with their assignments (KBr discs)

Compound	%C	%H	%N	%S	%M	ν(H_2O)	δ(H_2O)	ν(P–O)	ν(P–S)	ν(M–O)	ν(M–S)
$Zn_2(PO_2SNH_2)_2 \cdot (H_2O)_3$	—	2.48 (2.47)*	6.81 (6.88)	15.76 (15.72)	32.06 (31.95)	3440br**	830s	1100s 1100s	580s	500m	300m
$Zn_2[POS(NH_2)_2]_4 \cdot (H_2O)_4$	—	3.70 (3.73)	16.95 (17.30)	20.20 (19.81)	19.70 (20.20)	3400br	840s	1015vs	575s	480m	310m
$Zn_2[POS(NHC_6H_5)_2]_4 \cdot (H_2O)_4$	45.20 (45.90)	3.80 (4.49)	8.18 (8.91)	9.60 (10.21)	9.70 (10.41)	3420br	850s	1100s	570m	500m	305s
$Cd_2[PO_2SNH_2]_2 \cdot (H_2O)_2$	—	1.58 (1.66)	6.00 (5.79)	12.98 (13.24)	46.23 (46.54)	3400br	820s	1050s 1010s	590s	500m	325m
$Cd[POS(NH_2)_2]_2 \cdot (H_2O)_4$	—	3.72 (3.97)	12.99 (13.78)	15.08 (15.78)	26.88 (27.57)	3400br	840s	1030s	540sh	505m	330s
$Cd[POS(NHC_6H_5)_2]_2 \cdot (H_2O)_2$	41.90 (42.70)	4.30 (4.18)	7.60 (8.29)	8.80 (9.50)	15.80 (16.65)	3480br	850s	1080s	580m	500m	330s
$Hg_2[PO_2SNH_2]_2$	—	0.70 (0.64)	4.90 (4.49)	10.50 (10.28)	64.00 (64.36)	—	840s	1100s 1080s	585s	505m	290s
$Hg[POS(NH_2)_2]_2$	—	1.86 (1.89)	12.83 (13.24)	14.80 (15.17)	46.90 (47.46)	—	835m	1080s	585m	500w	295s
$Hg[POS(NHC_6H_5)_2]_2$	39.00 (39.64)	3.00 (3.32)	6.90 (7.70)	8.20 (8.81)	26.90 (27.58)	—	835vs	1100s	580m	510m	295vs

* Figures in parentheses are the calculated values

** vs = very strong, s = strong, m = medium, w = weak, br = broad

Table 2 Electronic spectra in Nujol mulls for the (PAT), (DPDAT) and N,N'-DPDAT complexes of Zn(II), Cd(II) and Hg(II)

Compound	Band I	Transition
$Zn_2(PO_2SNH_2)_2(H_2O)_3$	42.5*	$\pi^* \leftarrow \pi$
$Zn_2(POS(NH_2)_2)_4(H_2O)_4$	41.6	$\pi^* \leftarrow \pi$
$Zn_2(POS(NHC_6H_5)_2)_4(H_2O)_4$	37.0	$\pi^* \leftarrow \pi$
$Cd_2(PO_2SNH_2)_2(H_2O)_2$	40.0	$\pi^* \leftarrow \pi$
$Cd(POS(NH_2)_2)_2(H_2O)_4$	39.2	$\pi^* \leftarrow \pi$
$Cd(POS(NHC_6H_5)_2)_2(H_2O)_2$	37.7	$\pi^* \leftarrow \pi$
$Hg_2(PO_2SNH_2)_2$	43.4	$\pi^* \leftarrow \pi$
$Hg(POS(NH_2)_2)_2$	42.1	$\pi^* \leftarrow \pi$
$Hg(POS(NHC_6H_5)_2)_2$	40.8	$\pi^* \leftarrow \pi$

* $\tilde{\nu}$/kK

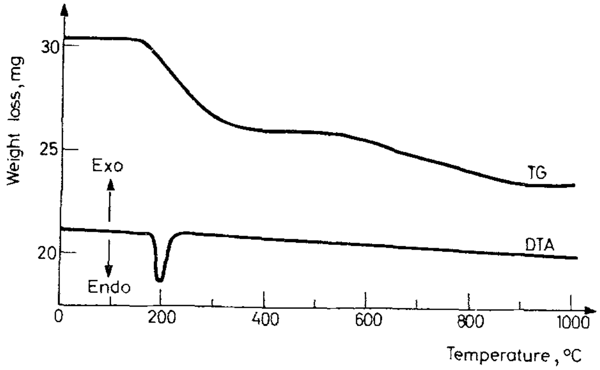

Fig. 1 Thermoanalytical curves for $Zn_2(PO_2SNH_2)(H_2O)_3$ in nitrogen

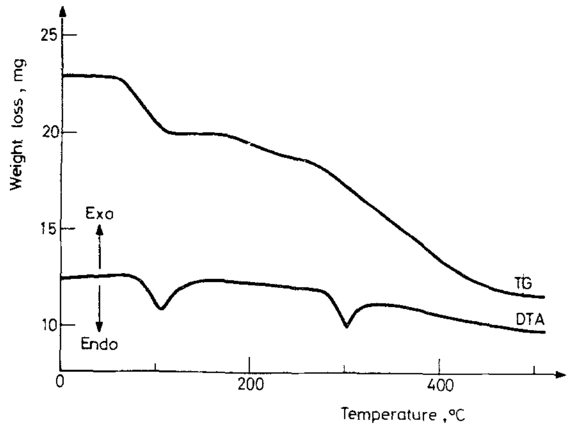

Fig. 2 Thermoanalytical curves for $Zn_2(POS(NH_2)_2)(H_2O)_4$ in nitrogen

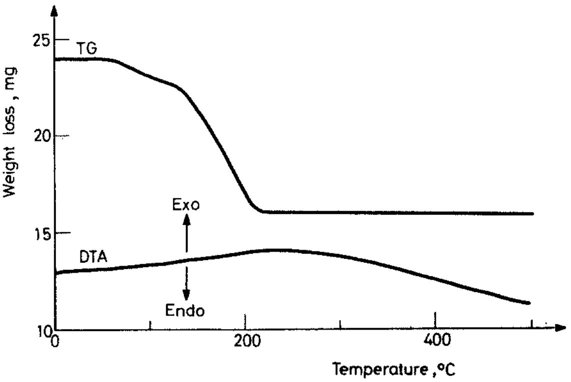

Fig. 3 Thermoanalytical curves for $Zn_2(POS(NHC_6H_5)_2)_4(H_2O)_4$ in nitrogen

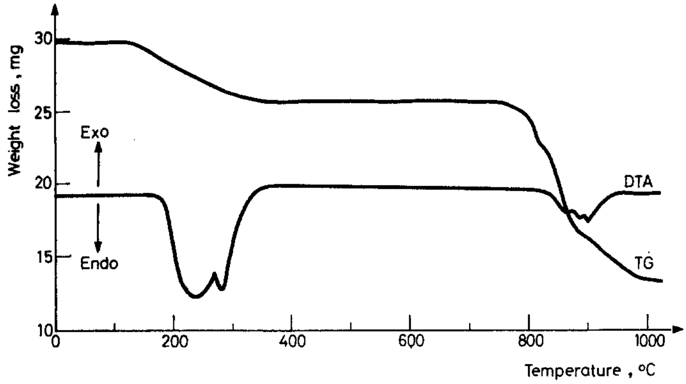

Fig. 4 Thermoanalytical curves for $Cd_2(PO_2SNH_2)_2(H_2O)_2$ in nitrogen

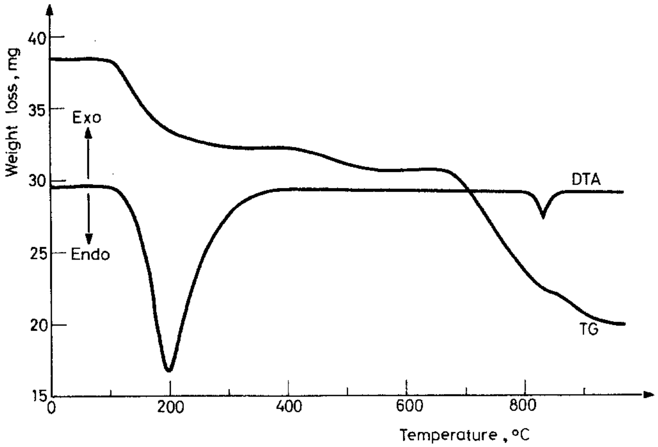

Fig. 5 Thermoanalytical curves for $Cd(POS(NH_2)_2)_2(H_2O)_4$ in nitrogen

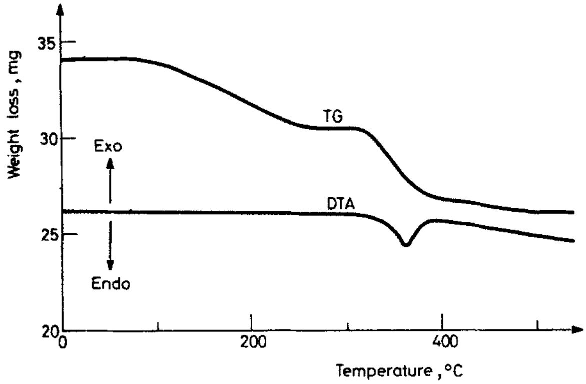

Fig. 6 Thermoanalytical curves for $Cd(POS(NHC_6H_5)_2)_2(H_2O)_2$ in nitrogen

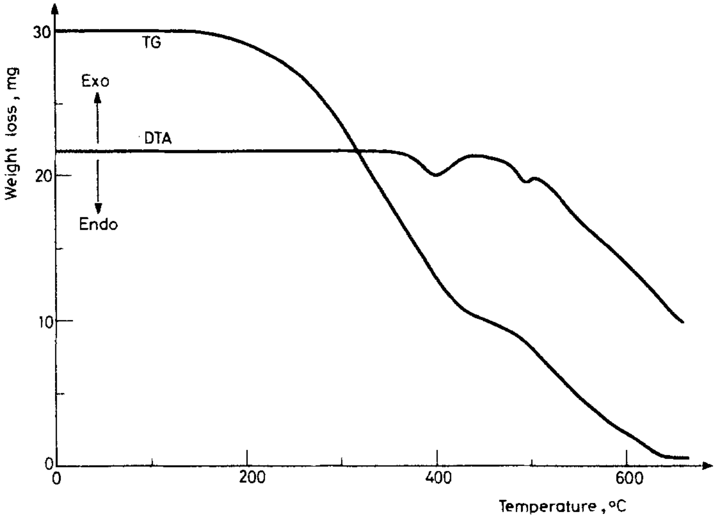

Fig. 7 Thermoanalytical curves for $Hg_2(PO_2SNH_2)_2$ in nitrogen

Characteristic features of the thermal decomposition of the studied complexes

(1) $Zn_2(PO_2SNH_2)_2(H_2O)_3$

The complex loses its water molecules in the temperature range 150–350°, and for this dehydration the DTA curve shows one endothermic peak (196°) (Fig. 1). The dehydrated complex is stable in the temperature range 350–550°. Subsequently, as the temperature is raised, the complex decomposes further and finally yields a residue of $(Zn_2(PO_2S)_2)$.

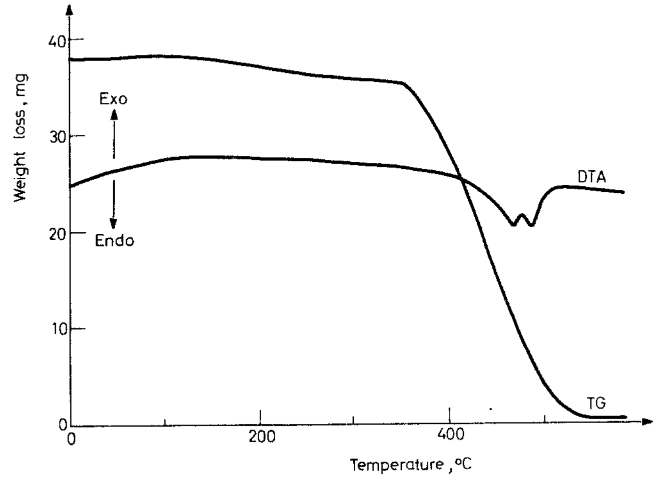

Fig. 8 Thermoanalytical curves for $Hg(POS(NH_2)_2)_2$ in nitrogen

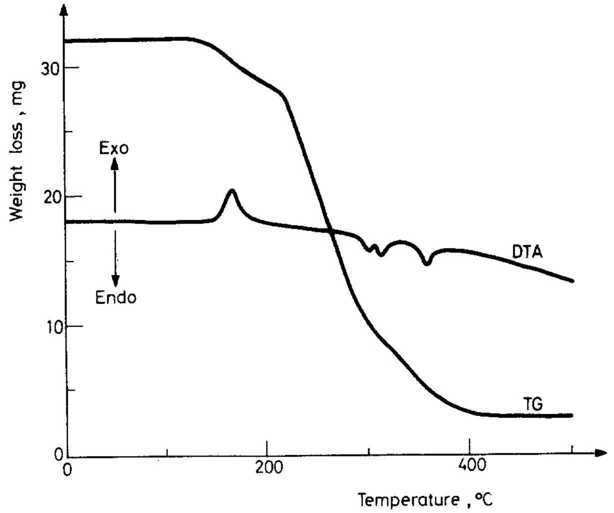

Fig. 9 Thermoanalytical curves for $Hg(POS(NHC_6H_5)_2)_2$ in nitrogen

(2) $Zn_2(POS(NH_2)_2)_4$

The water molecules being to come off in the temperature range 55–115°. Further decomposition of the complex occurs in two steps in the range 170–480°; the residue of the above decomposition is $Zn_2(PO_2S)_2$. The DTA curve shows two endothermic peaks, at 103° and 302°, corresponding to the first and the last step of the TG curve.

(3) $Zn_2(POS(NHC_6H_5)_2)_4(H_2O)_4$

The thermal decomposition of this complex takes place in the temperature range 60–210°. The first step involves dehydration (60–125°), in which the complex loses four water molecules. In the second stage, the dehydrated complex decomposes further and leaves $Zn_2(POS)_4(NHC_6H_5)_4$ as final residue.

(4) $Cd_2(PO_2SNH_2)_2(H_2O)_2$

Dehydration takes place in the temperature range 125–350° and the complex remains stable up to 750°. Its decomposition begins again in the range 750–1000°, yielding finally a residue of elemental Cd. The first stage of decomposition is endothermic in nature, as shown by two endothermic peaks, at 237° and 285°, in the DTA curve. The second stage is also endothermic, with three endothermic peaks in the DTA curve (860, 885 and 900°), with three inflexions in the TG curve for three decomposition stages.

(5) $Cd(POS)NH_2)_2)_2(H_2O)_4$

This complex loses water molecules in the temperature range 100–300°, and for this step of decomposition the DTA curve shows a strong endothermic peak (200°). In the second stage of decomposition (660–850°), another peak (at 837°) in the DTA curve indicates that this decomposition stage is also endothermic. The end-product is $CdPSO_2$.

(6) $Cd(POS(NHC_6H_5)_2)_2(H_2O)_2$

The thermal decomposition of this complex occurs in the temperature range 75–510°. The first step involves dehydration (75–256°). In the second stage of decomposition (315–510°), the dehydrated complex decomposes further in two steps, giving a final residue of $(Cd(POS)_2(NHC_6H_5)_3)$. The DTA curve exhibits one endothermic peak, at 365°, which shows that the complex undergoes an endothermic change.

(7) $Hg_2(PO_2SNH_2)_2$

When heated in a dynamic nitrogen atmosphere, this complex is stable up to 160°, and begins to decompose in three steps in the temperature range 160–635°. The decomposition processes are accompanied by two endothermic peaks, at 400° and 495°. Heating the sample above 635° leaves the crucible without residue.

(8) $Hg(POS(NH_2)_2)_2$

The thermal decomposition of this complex takes place in three decomposition steps in the temperature range 135–550°. For the final step, the DTA curve shows two endothermic peaks, at 470° and 488°. After heating of the sample over 550°, no residue was found.

Table 3 Thermoanalytical results (TG/DTA) of the (PAT), (PDAT) and (N,N'-DPDAT) complexes of Zn(II), Cd(II) and Hg(II) in nitrogen atmosphere

Complex	DTA results temperature peak, °C	Stage	TG results temperature range, °C	Mass loss %	Envolved moiety	
					formula	mass calcd. %
$Zn_2(PO_2SNH_2)_2(H_2O)_3$	196 (−)	1	150–350	14.0	$3H_2O$	13.27
		2	550–920	7.6	$2NH_2$	7.86
		residue	>920	85.2	$Zn_2PO_2S)_2$	78.64
$Zn_2(POS(NH_2)_2)_4(H_2O)_4$	103 (−)	1	55–115	11.4	$4H_2O$	11.2
		2	170–250	4.8	$2NH_2$	4.94
	302 (−)	3	250–480	31.5	$P_2S_2(NH_2)_6$	34.31
		residue	>500	51.2	$Zn_2(PO_2S)_2$	49.46
$Zn_2(POS(NHC_6H_5)_2)_4(H_2O)_4$						
		1	60–125	5.0	$4H_2O$	5.80
		2	125–210	28.0	$4NHC_6H_5$	29.34
		residue	>550	67.0	$Zn_2(POS)_4(NHC_6H_5)_4$	64.86
$Cd_2(PO_2SNH_2)_2(H_2O)_2$	237 (−), 285 (−)	1	125–130	14.4	$2H_2O+2NH_2$	14.07
		2	750–800	3.5	$1/2\ O_2$	3.31
		3	800–820	5.6	S	6.62
	860 (−), 885 (−)	4	820–895	20.0	P_2O_2	19.16
	900 (−)	5	895–1000	10.4	SO	9.93
		residue	>1000	46.1	2Cd	46.55
$Cd(POS(NH_2)_2)_2(H_2O)_4$	200 (−)	1	100–300	16.0	$4H_2O$	17.70
		2	400–550	4.0	NH_2	3.90
	837 (−)	3	660–850	22.4	$PS(NH_2)_2$	23.39
		4	850–930	5.6	NH_2	3.90
		residue	>930	51.5	$CdPSO_2$	50.96

$Cd(POS(NHC_6H_5)_2)_2(H_2O)_2$		1	75–256	4.7	$2H_2O$	5.34
	365 (−)	2	315–380	10.3	C_6H_5	11.42
		3	380–510	2.6	NH	2.22
		residue	> 510	82.4	$Cd(POS)_2(NHC_6H_5)_3$	80.96
$Hg_2(PO_2SNH_2)_2$		1	160–225	5.31	$2NH_2$	5.13
	400 (−)	2	225–438	59.8	$Hg(PSO)_2$	57.55
	495 (−)	3	438–635	34.7	HgO_2	37.32
		no residue	> 635			
$Hg(POS(NH_2)_2)_2$		1	135–235	3.67	NH_2	3.71
		2	235–355	3.15	NH_2	3.71
	470 (−), 488 (−)	3	355–550	92.18	$Hg(POS)_2$	92.58
		no residue	> 550			
$Hg(POS(NHC_6H_5)_2)_2$	168 (+)	1	130–217	13.25	NHC_6H_5	12.66
	302 (−), 311 (−)	2	217–320	60.41	$(POS)_2(C_6H_5NH)_3$	59.74
	356 (−)	3	320–400	16.33	Hg	27.60
		no residue	> 400			

(−): endothermic, (+): exothermic peak

(9) $Hg(POS(NHC_6H_5)_2)_2$

The complex is stable up to 130°. Its decomposition occurs in three steps. The DTA curve shows an exothermic peak at 168°, followed by three endothermic peaks, at 302, 311 and 356°, indicating that the last stage of decomposition is endothermic in nature. Heating of the sample above 400° leaves no final residue in the crucible.

Conclusions

The available experimental data allow us to suggest that the prepared complexes of Zn and some of the Cd and Hg(II) complexes are dimeric rather than monomeric, and hydrated, except these of Hg(II). The monomers show greater thermal stability, probably owing to the lower distortion of the tetrahedral structure and the smaller size of the Zn and Cd ions. The TG–DTA illustrate the greater thermal stability of the phosphoramidothioate complexes. The results of this study on the thermal decomposition of the studied complexes showed that thermal analysis can be useful for the determination of the number of molecules of water bound.

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Zusammenfassung — Komplexe von Zn(II), Cd(II) und Hg(II) mit Phosphoramidothioat (PAT), Phosphorodiamidothioat (PDAT) und N,N′-Diphenylphosphorodiamidothioat (N,N′-DPDAT) als Liganden wurden synthetisiert und untersucht. Die Strukturen der neuen Verbindungen werden basierend auf deren spektroskopischen und thermischen Daten diskutiert. Die thermoanalytische Untersuchung dieser Verbindungen hat eine Abhängigkeit der thermischen Stabilität von der Größe der Metallkationen ergeben, und zwar sind die PAT-Komplexe thermisch stabiler als die anderen.

Резюме — Синтезирована и изучена новая серия комплексов двухвалентных цинка, кадмия и ртути с такими лигандами как фосфорамидотиокислота, фосфордиамидотиокислота и N,N′-дифенилфосфордиамидотиокислота. Структура новых соединений обсуждена на основе ИК спектроскопических и термических данных. Термические исследования этих соединений показали зависимость их термоустойчивости от размера катиона. Комплексы с фосфорамидотиокислотой обладали наибольшей устойчивостью.