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SYNTHESIS, FEATURES AND THERMAL DECOMPOSITION OF HEXACHLOROSTANNATES AND HEXACHLOROPLATINATES OF TRIS(2,2'-DIPYRIDYL)METAL(II) AND TRIS(1,10-PHENANTHROLINE)METAL(II) (METAL = Ru, Fe, Ni)

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Several complex salts of general formula $[M^{II}(dipy)_3]M^{IV}Cl_6$ or $[M^{II}(phen)_3]M^{IV}Cl_6$ (where M^{II} = Ru, Fe, Ni and M^{IV} = Sn, Pt) were synthetized and subjected to thermal analyses. Heating of these derivatives leads to the release of organic fragments and chlorine, which are often involved in oxidation processes. The residues comprise metal oxides or pure metals (e.g. Pt). Differences in the structures and features of the ligand molecules, revealed on the basis of quantum-chemistry calculations, account qualitatively for the differences in behaviour and stability of the complex compounds studied.

Keywords: complexes

Introduction

The octahedral ions MX_6^{2-} (where M = metal(IV) and X = halogen) form salts with divalent cations. Rough thermochemical evaluations based on the Hess law and Kapustinskii-Yatsimirskii relationship reveal that the dimensions of known divalent ions (M^{II}) are too small for them to form stable salts of the type $M^{II}MX_6$ [1–3]. However, complex salts containing divalent ions can be formed if one increases their dimensions by attaching ligand molecules. In this work we attempted to prepare salts containing $PtCl_6^{2-}$ or $SnCl_6^{2-}$ as anions and complex cations formed from the divalent metal ions Ru(II), Fe(II) and Ni(II) and two ligands: 2,2'-dipyridyl and 1,10-phenanthroline. Furthermore,

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the thermal behaviour of the compounds synthesized was studied. Lastly, we made an effort to explain why dipyridyl forms complex salts more easily than phenanthroline. For this purpose comparative thermoanalytical investigations were carried out on the ligand molecules and their hydrochlorides. A quantum-chemistry method (AMI) was also employed to predict structures and some features of the ligands and their mono- and diprotonated forms.

The investigations undertaken were mainly of a cognitive character. It is worth mentioning, however, that ruthenium(II) complexes find application as a cyclic medium in systems for solar energy conversion [4, 5].

Materials and methods

Hexachloroplatinates and hexachlorostannates of complex cations were prepared by mixing aqueous solutions of the appropriate acids (H_2PtCl_6 and H_2SnCl_6) with nearly stoichiometric amounts of aqueous solutions of chloride salts of complex cations [6]. The latter salts were prepared by methods described in the literature [7–9].

Thermal analyses were performed on an OD-103 derivatograph, with α–Al_2O_3 as reference in a dynamic atmosphere of nitrogen (conditions: $m = 100$ mg, heating rate = 5 deg/min). The method of evaluation of the heat of reaction has been described elsewhere [10].

Quantum-chemistry calculations were carried out at the level of the AMI method [11], using the MOPAC program package [12].

Results and discussion

An example of the results of thermoanalytical investigations is shown in Fig. 1, whereas data concerning the thermal behaviour of all the compounds are compiled in Tables 1 and 2.

The thermal processes proceeding in the hexachlorometallates upon dynamic heating exhibit a complex nature (Fig. 1A and B; Table 1). In the salts containing $[Ru(dipy)_3]^{2+}$ or $[Ru(phen)_3]^{2+}$ strong exothermic effects originating from the oxidation (or chlorination) of organic fragments are observed. The residues after heating up to 1100 K consist of pure metals (Pt) or their oxides with traces of carbonization products. The complex shapes of the thermoanalytical curves, and also the relatively high temperatures of the onset of decomposition ($T_{0.01}$), exclude the possibility of elimination of ligand molecules in the primary step. It is more feasible that chlorine is initially released, which participates in secondary chlorination (exothermic) processes. If the exothermicity of these latter processes exceeds the endothermicity of the thermal decomposition reactions, the resulting exothermic effect is seen in the DTA curves. Such behaviour is exhibited by the complex salts of ruthenium(II). If the second of the above-mentioned effects is the more pronounced, the overall process is endothermic in certain temperature ranges. This latter behaviour characterizes the decomposition of the complex Fe and Ni salts.

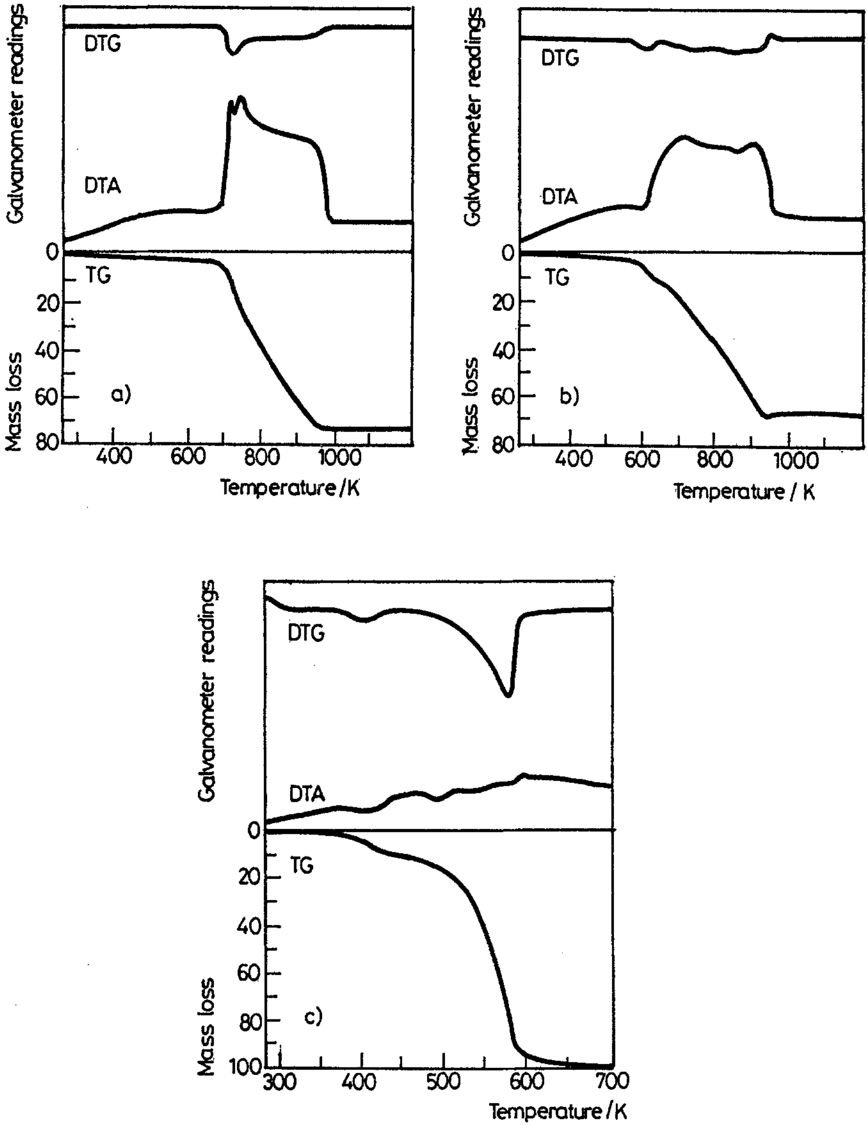

Fig. 1 Thermal analyses of $[Ru(phen)_3]SnCl_6$ (A), $[Ru(dipy)_3]PtCl_6$ (B) and $(Phen{\cdot}HCl){\cdot}H_2O$ (C)

Complementary thermoanalytical investigations were also carried out for dipyridyl and phenanthroline and their hydrochlorides (Fig. 1C; Table 2). These permitted evaluation of the heats of the thermal processes, which are also given in Table 2.

Table 1 Thermal characteristics of complex hexachlorometallate salts[a]

Substance	Temperetures of peaks / K			T_α / K	
	DTG	DTA		$T_{0.01}$	$T_{0.99}$
		endo	exo		
[Ru(dipy)$_3$]SnCl$_6$	705 s		700 s, 735 s	680	
[Ru(phen)$_3$]SnCl$_6$	745 s		760 w, 805 s	715	
	1085 w(+)		1080 s		
[Fe(dipy)$_3$]SnCl$_6$	545 m, 585 w	540 w, 590 w			
	695 s, 870 w	670 m, 825 w	725 m, 868 m		
[Ni(dipy)$_3$]SnCl$_6$	665 w	665 m			
	705 s	705 m	1035 m		
[Ru(dipy)$_3$]PtCl$_6$	625 m, 740 m	600 w	725 s	565	995
	885 m, 925 m		855 m		
	955 w(+)		925 s		
[Fe(phen)$_3$]PtCl$_6$	640 s	605 m	640 s	585	775

[a] *w* = weak, *m* = medium, *s* = strong; T_α = temperature at which degree of conversion is equal to α (i.e. $T_{0.01} = T_{\alpha=0.01}$); (+) denotes an increase in weight of the sample.

2,2'-Dipyridyl and 1,10-phenanthroline are bidentate ligands. Each of them also exhibits two proton acceptor sites. The AMI method reveals that the affinity for the attachment of the first proton (in kJ/mol) is equal to 933.7 and 951.3, but for the attachment of the second, is only 558.7 and 551.6, for dipyridyl and phenanthroline, respectively. This explains why only the monochloride salts are stable for both cases.

1,10-Phenanthroline (Fig. 2A) is planar, containing a conjugated system of three aromatic rings. In contrast, in 2, 2'-dipyridyl (Fig. 2B) the two aromatic rings can rotate almost freely with respect to one other. Owing to the *peri* interactions between the lone electron pairs on the nitrogen atoms, the lowest-energy structure of the latter compound is non-planar. This facilitates the dipyridyl molecule in adjustment of its structure to the dimensions of the coordinating M^{II} atoms, as well as to the structure and dimensions of

Table 2 Thermoanalytical and thermochemical data for 2,2'-dipyridyl, 1,10-phenanthroline and their hydrochlorides

Substance	Process	Thermoamalytical data						Thermochemical data[b]	
		Peak temperature[a] / K				Temperature[a] / K			
		DTG	DTA			$T_{0.1}$	$T_{0.8}$	ΔH_r / kJ·mol^{-1}	T_v / K
		T_p	T_σ	T_m	T_p (endo)				
2,2'-dipy	melting			353				25.0*	
	volatilization	474			474	415	469	61.8	476
2,2'-phen·H_2O	dehydration	383			383	341	381	55.5	387
	melting			403				37.0*	
	volatilization	585			585	517	580	81.9	588
2,2'-dipy·HCl	melting, phase transition		409, 419	450					
	dissociative volatilization	483			481	435	483	150.8	491
(2,2'-phen·HCl)·H_2O	dehydration	409			409	383	421	68.5	425
	melting, phase transition		486		498				
	dissociative volatilization	586			588	509	585	136.7	595

[a] T_m = Temperature of melting; for meanings of other symbol, see Table 1.

[b] Values with an asterisk were estimated and others were evaluated on the basis of the van't Hoff equation: $\ln\alpha = -\frac{\Delta H_r}{\Delta nRT} - \frac{\Delta H_r}{\Delta nRT_v}$ (where ΔH_r is the enthalpy change for the process; R is the gas constant; T_v is the temperature at which the pressure of gaseoue products reaches atmospheric pressure; and Δn is the number of moles of gaseous products) [10]

the $M^{IV}Cl_6^{2-}$ ions in the crystal lattice. These facts explain why it is much easier to synthesize complexes with the latter ligand [13].

Another feature differentiating the two ligands is revealed by examination of the net atomic charges (Fig. 2). It can be seen that the negative charge in 1,10-phenanthroline is concentrated more on the carbon than on the nitrogen atoms, whereas in 2,2'-dipyridyl it is also situated on the two nitrogen atoms. This means that the former ligand exhibits mainly a π-type donor character, whereas the latter also has an n-type donor character. n-Donors usually form more stable complexes, which implies that dipyridyl should have a better ability to form complexes than phenanthroline.

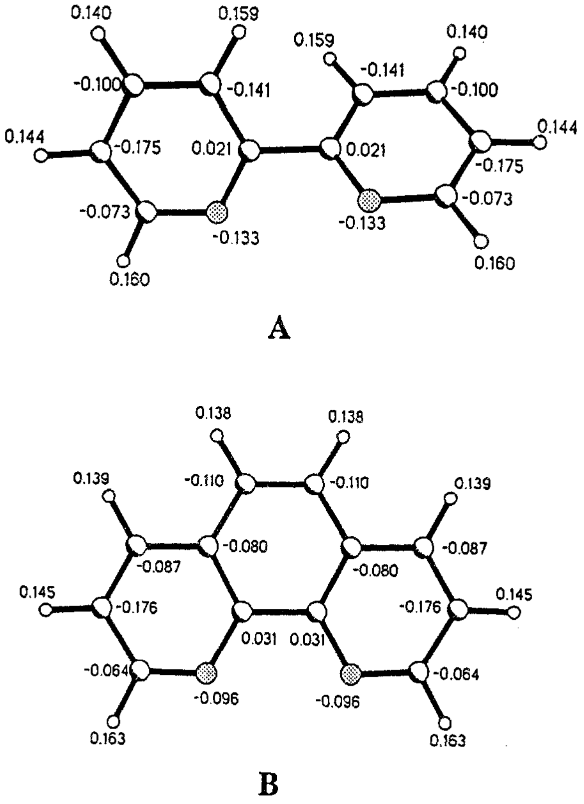

Fig. 2 Lowest-energy structures of 2,2'-dipyridyl (A) and 1,10-phenanthroline (B),

The compounds examined in this work exhibit similar features to other complex salts containing $[M^{II}(phen)_3]^{2+}$ or $[M^{II}(dipy)_3]^{2+}$ that were studied earlier [14, 15]. The present work extends our knowledge on this group of compounds and promotes an understanding of the role played by the ligand molecules in their stability and thermal reactivity.

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Zusammenfassung — Einige Komplexsalze der allgemeinen Formel $[M^{II}(dipy)_3]M^{IV}Cl_6$ und $[M^{II}(phen)_3]M^{IV}Cl_6$ (mit M^{II}=Ru,,Fe,Ni und M^{IV}=Sn,Pt) wurden hergestellt und einer Thermoanalyse unterzogen. Durch Erhitzen dieser Derivate werden organische Fragmente und Chlor freigesetzt, welche oft an Oxidationsprozessen teilnehmen. Die Reste bestehen aus Metalloxiden oder aus reinem Metall (z.B. Pt). Mit Hilfe quantenchemischer Berechnungen ermittelte Unterschiede in der Struktur und den Eigenschaften der Ligandenmoleküle können die Unterschiede in Verhalten und Stabilität der Komplexverbindungen erklärt werden.