

## Synthesis and thermal investigations of $[\text{Rh}(\text{bpy})_3]\text{X}_3$ ( $\text{bpy} = 2,2'$ -dipyridyl; $\text{X} = \text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$ , $\text{ReO}_4^-$ ) and $[\text{Rh}(\text{bpy})_3][\text{Cd}_n\text{X}_{2n+3}]$ ( $\text{X} = \text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$ ) type complexes

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### Abstract

New methods of synthesis of  $[\text{Rh}(\text{bpy})_3]\text{X}_3(\text{aq.})$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) have been developed, and rhodium(III) rhenate(VII), as well as tris(2,2'-dipyridyl) halogenocadmates, have been obtained. The quantitative composition of these compounds has been determined on the basis of chemical analysis and thermal and spectrophotometric investigations. A very weak outer-sphere interaction of various anionic counterions with chelate cations of  $[\text{Rh}(\text{bpy})_3]^{3+}$  type has been established in aqueous solution, in contrast to the interactions occurring in the solid state, as indicated by the results of thermal analysis.

### INTRODUCTION

Complex  $[\text{Rh}(\text{bpy})_3]^{3+}$  type cations can change their oxidation state in chemical reactions while maintaining constant composition, which enables the application of compounds containing these cations in investigations on electron transfer processes, which are significant, e.g., for solar energy conversion [1–3].

Our investigations aimed at the development of new methods of synthesis of  $[\text{Rh}(\text{bpy})_3]\text{X}_3$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) chelate complexes and at obtaining a similar compound, not yet described in the literature, with the perrhenate anion, as well as at isolation from solution of complex anions of  $[\text{Cd}_n\text{X}_{2n+3}]^{3-}$  type ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ) in a crystalline form, in order to determine the effect of various anionic counterions on the thermal stability of the rhodium(III) tris(2,2'-dipyridyl) cation.

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## EXPERIMENTAL

*Preparation and chemical analysis of  $[\text{Rh}(\text{bpy})_3]X_3$  and  $[\text{Rh}(\text{bpy})_3][\text{Cd}_n\text{X}_{2n+3}]$  type complexes*

To obtain  $[\text{Rh}(\text{bpy})_3]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$  [4,5], 7 g of hydrated rhodium(III) chloride, containing 41.66% of Rh and 46.94% of Cl, was dissolved in 180 cm<sup>3</sup> of water. Next, 30 cm<sup>3</sup> of ethanol, 75 cm<sup>3</sup> of dimethylformamide and 18 g of 2,2'-dipyridyl were added. The obtained solution was boiled under a reflux condenser for 1 h, and 180 cm<sup>3</sup> of the solvent mixture was then vaporized. The residue was filtered under vacuum. Next, 500 cm<sup>3</sup> of acetone was gradually added to the filtrate, with stirring, in order to precipitate hydrated rhodium(III) tris(2,2'-dipyridyl) chloride. The precipitate was filtered off, washed with acetone and dissolved in an ethanol–hydrochloric acid (1:1) mixture. Then the rhodium(III) tris(2,2'-dipyridyl) chloride solvated with hydrogen chloride and water was precipitated with acetone. To remove HCl, the preparation was dissolved in a water–ethanol (1:2) mixture, and a compound of composition  $[\text{Rh}(\text{bpy})_3]\text{Cl}_3 \cdot 5\text{H}_2\text{O}$  was precipitated. After filtering this off, the compound was washed with acetone and dried in air at room temperature.

$[\text{Rh}(\text{bpy})_3]\text{Br}_3 \cdot 4\text{H}_2\text{O}$  was obtained by precipitation with acetone from an aqueous solution of  $[\text{Rh}(\text{bpy})_3]\text{Cl}_3$  in the presence of hydrobromic acid.

$[\text{Rh}(\text{bpy})_3]\text{I}_3 \cdot 3\text{H}_2\text{O}$  was obtained as described in the literature [6].

Rhodium(III) tris(2,2'-dipyridyl) rhenate(VII) was synthesized from  $[\text{Rh}(\text{bpy})_3]\text{Cl}_3$  and  $\text{NH}_4\text{ReO}_4$  by crystallization in aqueous medium.

The  $[\text{Rh}(\text{bpy})_3][\text{Cd}_n\text{X}_{2n+3}]$  type chlorocadmates were obtained in ethanolic medium as a result of the reaction of  $[\text{Rh}(\text{bpy})_3]\text{Cl}_3$  with  $\text{CdCl}_2$ , while the respective bromo- and iodo-cadmates were synthesized in aqueous media from rhodium(III) tris(2,2'-dipyridyl) bromide and iodide and the respective cadmium halides because of the poor solubility of  $[\text{Rh}(\text{bpy})_3]\text{Br}_3$  and  $[\text{Rh}(\text{bpy})_3]\text{I}_3$  in ethanol.

All the preparations were dried in air at room temperature.

The halides and cadmium were determined gravimetrically in the form of  $\text{AgX}$  [7] and  $\text{CdS}$  [8], respectively; rhodium was determined spectrophotometrically [9]. The results of chemical analyses are listed in Table 1.

*Instruments*

Thermal analysis was carried out using a Q-1500 D derivatograph (MOM) and alundum crucibles;  $\text{Al}_2\text{O}_3$  served as the reference material. Atmosphere, static air; sample weight, 100 mg; heating rate, 10 °C min<sup>-1</sup>; final temperature, 1000 °C. The final products of thermal decomposition were heated at this temperature to constant mass and then analyzed by X-ray diffractometry using a DRON-2 diffractometer and Cu K<sub>α</sub> radiation.

TABLE 1  
Results of chemical analyses

No.	Complex	Rh (%)		Cd (%)		X (%)		C (%)		H (%)		N (%)	
		Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
1	[Rh(bpy) <sub>3</sub> ]Cl <sub>3</sub> ·5H <sub>2</sub> O	13.51	13.40	—	—	13.97	13.85	46.90	46.89	4.39	4.43	10.87	10.94
2	[Rh(bpy) <sub>3</sub> ] [Cd <sub>1.5</sub> Cl <sub>6</sub> ]·H <sub>2</sub> O	10.45	10.60	17.10	17.37	21.95	21.91	36.51	37.08	2.65	2.68	8.42	8.65
3	[Rh(bpy) <sub>3</sub> ] [Cd <sub>2</sub> Cl <sub>7</sub> ]	9.97	9.85	22.14	21.52	23.83	23.76	34.51	34.47	2.24	2.29	8.00	8.04
4	[Rh(bpy) <sub>3</sub> ] [Cd <sub>3</sub> Cl <sub>9</sub> ]·1.5H <sub>2</sub> O	8.35	8.20	26.87	27.01	24.89	25.42	28.35	28.69	2.03	2.15	6.50	6.69
5	[Rh(pby) <sub>3</sub> ]Br <sub>3</sub> ·4H <sub>2</sub> O	11.83	11.65	—	—	27.76	27.14	40.84	40.76	3.61	3.62	9.50	9.51
6	[Rh(bpy) <sub>3</sub> ] [Cd <sub>2</sub> Br <sub>7</sub> ]	7.59	7.59	15.75	16.58	41.31	41.26	26.57	26.55	1.65	1.77	6.10	6.19
7	[Rh(bpy) <sub>3</sub> ]I <sub>3</sub> ·3H <sub>2</sub> O	10.20	10.23	—	—	37.82	37.84	34.65	35.77	2.97	2.98	8.03	8.34
8	[Rh(bpy) <sub>3</sub> ] [Cd <sub>2</sub> I <sub>7</sub> ]	6.10	6.11	13.66	13.34	52.21	52.73	20.84	21.37	1.33	1.42	4.76	4.98
9	[Rh(bpy) <sub>3</sub> ] [ReO <sub>4</sub> ] <sub>3</sub> ·2.5H <sub>2</sub> O	7.47	7.53	—	—	—	—	26.32	26.33	2.15	2.12	6.06	6.14

Absorption spectra were recorded using a SPECORD UV-VIS spectrophotometer, while rhodium was determined using a SPEKOL 10 spectrophotometer.

## RESULTS AND DISCUSSION

The known methods of synthesis [10–13] and isolation from post-reaction mixtures of hydrated rhodium(III) tris(2,2'-dipyridyl) chloride are based on heating (ca. 270 °C) of soluble rhodium(III) chloride with 2,2'-dipyridyl (bpy), playing simultaneously the role of ligand and solvent, or heating of  $\text{RhCl}_3(\text{aq.})$  with bpy in 50% ethanol with the addition of a catalyst (e.g. *N*-ethylmorpholine).

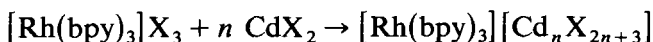
We did not manage to synthesize  $[\text{Rh}(\text{bpy})_3]\text{Cl}_3(\text{aq.})$  using *N*-ethylmorpholine as a catalyst, and the direct synthesis at ca. 270 °C is cumbersome due to the difficulties in purification of the crude preparation from dipyridyl decomposition products.

The above mentioned difficulties connected with the synthesis of  $[\text{Rh}(\text{bpy})_3]\text{Cl}_3$  led us to develop a new, relatively simple method of obtaining hydrated rhodium(III) tris(dipyridyl) chloride, which is the basic substrate for the synthesis of the complexes listed in the title.

$[\text{Rh}(\text{bpy})_3]\text{Br}_3 \cdot 4\text{H}_2\text{O}$  can be obtained according to literature data [11] in a reaction of  $\text{RhBr}_3(\text{aq.})$  with dipyridyl at 270 °C; however, this requires an application of the more expensive and less readily available rhodium(III) bromide. Because of this a new method has been developed of obtaining rhodium(III) tris(dipyridyl) bromide in a  $[\text{Rh}(\text{bpy})_3]\text{Cl}_3$ -water-hydrogen bromide-acetone system, in which the compound of interest is less soluble than  $[\text{Rh}(\text{bpy})_3]\text{Cl}_3$  and therefore precipitates from solution.

Rhodium(III) tris(dipyridyl) iodide and rhenate(VII) have been obtained by a double replacement reaction of  $[\text{Rh}(\text{bpy})_3]\text{Cl}_3$  with the respective salt in aqueous medium, owing to the poorer solubility of the compounds of interest compared with rhodium(III) tris(dipyridyl) chloride.

To obtain rhodium(III) tris(dipyridyl) halogenocadmates, reactions of  $[\text{Rh}(\text{bpy})_3]\text{X}_3$  with  $\text{CdX}_2$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ) have been carried out according to the equation



Attempts to isolate from solution the rhodium(III) dipyridyl complexes of  $[\text{Cd}_n\text{X}_{2n+2}]^{2-}$  type anions failed, in contrast to the similarly synthesized [14–16] ruthenium(II) dipyridyl complexes of composition  $[\text{Ru}(\text{bpy})_3][\text{Cd}_n\text{X}_{2n+2}]$ . It follows from this statement that the composition and charge of the halogenocadmata anions isolated from solution in the form of salts distinctly depend on the kind and charge of the cationic counterions and the nature of the halogen (Table 1), which is indicated by the higher value of  $n$  in the case of chlorocadmata compared with bromo- and iodo-cadmata.

TABLE 2

Results of thermal analysis

No.	Complex	Temperature range of dehydration (°C)	Temperature (°C)		Decomposition product (mg)	
			At beginning of decomposition	At end of decomposition	Calc.	Found
1	[Rh(bpy) <sub>3</sub> ]Cl <sub>3</sub> ·5H <sub>2</sub> O	60–220	220	740	16.5	16.4 Rh <sub>2</sub> O <sub>3</sub>
2	[Rh(bpy) <sub>3</sub> ][Cd <sub>1.5</sub> Cl <sub>6</sub> ]·H <sub>2</sub> O	40–180	230	760	13.1	14.9 Rh <sub>2</sub> O <sub>3</sub>
3	[Rh(bpy) <sub>3</sub> ][Cd <sub>2</sub> Cl <sub>7</sub> ]	–	340	790	12.2	14.5 Rh <sub>2</sub> O <sub>3</sub>
4	[Rh(bpy) <sub>3</sub> ][Cd <sub>3</sub> Cl <sub>9</sub> ]·1.5H <sub>2</sub> O	50–145	345	845	10.1	13.2
5	[Rh(bpy) <sub>3</sub> ]Br <sub>3</sub> ·4H <sub>2</sub> O	80–225	255	790	14.4	14.2 Rh <sub>2</sub> O <sub>3</sub>
6	[Rh(bpy) <sub>3</sub> ][Cd <sub>2</sub> Br <sub>7</sub> ]	–	370	760	9.4	11.8 Rh <sub>2</sub> O <sub>3</sub>
7	[Rh(bpy) <sub>3</sub> ] <sub>3</sub> ·3H <sub>2</sub> O	55–170	200	730	12.6	12.2 Rh <sub>2</sub> O <sub>3</sub>
8	[Rh(bpy) <sub>3</sub> ][Cd <sub>2</sub> I <sub>7</sub> ]	–	345	750	7.5	13.2 Rh <sub>2</sub> O <sub>3</sub>
9	[Rh(bpy) <sub>3</sub> ](ReO <sub>4</sub> ) <sub>3</sub> ·2.5H <sub>2</sub> O	50–150	410	740	9.3	9.3 Rh <sub>2</sub> O <sub>3</sub>

The compositions of all the complexes have been determined on the basis of the results of chemical analysis (Table 1), thermal investigations (Table 2 and Fig. 1A, B and C) and spectrophotometric investigations.

The location and shape of the bands in the UV spectra of the obtained compounds agree with literature data [17–24] concerning chelate cations of [Rh(bpy)<sub>3</sub>]<sup>3+</sup> composition, which proves a weak interaction of various counterions with rhodium(III) tris(dipyridyl) cations in solution and the existence of the above mentioned cations in an unchanged form in the obtained complexes. It also indicates that during the synthesis of halogenocadmates no abstraction of dipyridyl ligand from rhodium and complexing of cadmium in its halides occurred, which would disable the formation of the [Cd<sub>n</sub>X<sub>2n+3</sub>]<sup>3-</sup> type anions.

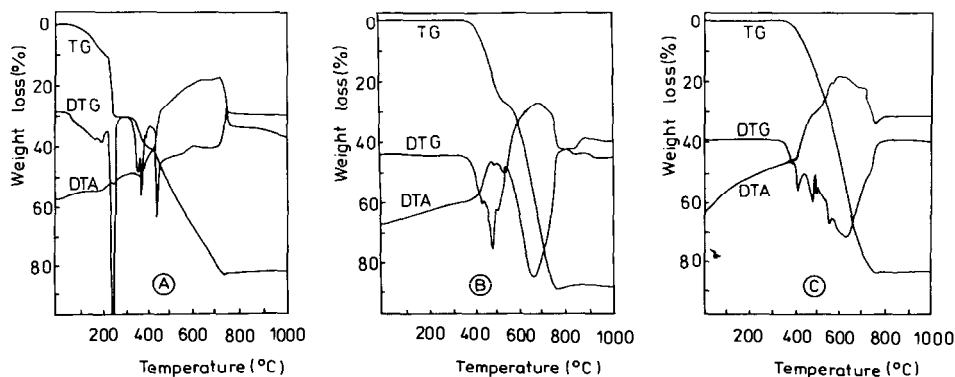


Fig. 1. Thermograms for (A) [Rh(bpy)<sub>3</sub>]Cl<sub>3</sub>·5H<sub>2</sub>O; (B) [Rh(bpy)<sub>3</sub>][Cd<sub>2</sub>Br<sub>7</sub>]; and (C) [Rh(bpy)<sub>3</sub>][Cd<sub>2</sub>Cl<sub>7</sub>].

To determine the effect of various anions on the thermal stability of complex  $[\text{Rh}(\text{bpy})_3]^{3+}$  cations, the obtained preparations were subjected to thermal investigations, the results of which indicate that they underwent dehydration without decomposition in the 40–225 °C temperature range.

It follows from the course of the DTA curves (Fig. 1A, B and C) that thermal decomposition of the examined complexes was always exothermic, due to incineration of organic components evolving during pyrolysis of the compounds. Final temperatures of these processes ranged from 730 ° to 845 °C. The course of the TG and DTG curves indicates that anhydrous rhodium(III) tris(dipyridyl) halides undergo decomposition with intramolecular rearrangement, resulting in evolution of dipyridyl, according to the equation



Further heating of the compound of composition  $[\text{Rh}(\text{bpy})_2\text{Cl}_2]\text{Cl}$  indicates the possibility of formation of  $[\text{Rh}(\text{bpy})_{1.5}\text{Cl}_3]$  as an intermediate before a final pyrolysis to free rhodium, which undergoes oxidation to  $\text{Rh}_2\text{O}_3$ .

Similarly, the final thermal decomposition product of the remaining halides is also metallic rhodium, which on further heating is easily oxidizable to  $\text{Rh}_2\text{O}_3$  containing traces of elementary rhodium (Table 2).

In the case of pyrolysis of rhodium(III) tris(dipyridyl) perrhenate, an alloy of composition  $\text{RhRe}_3$  is transiently formed at 670 °C. On further heating this oxidizes to  $\text{Re}_2\text{O}_7$ , which sublimates, and  $\text{Rh}_2\text{O}_3$ , which remains in the crucible.

The  $[\text{Rh}(\text{bpy})_3][\text{Cd}_n\text{X}_{2n+3}]$  type complexes in all cases undergo thermal decomposition with liberation of the majority of the contained cadmium. The final pyrolysis product is  $\text{Rh}_2\text{O}_3$  contaminated with an unknown phase containing rhodium and cadmium at unidentified stoichiometry. Attempts to identify the composition of the final product of thermal analysis of  $[\text{Rh}(\text{bpy})_3][\text{Cd}_3\text{Cl}_9]$  failed.

## CONCLUSIONS

The results of thermal analysis (Table 2) indicate that initial decomposition temperatures of anhydrous rhodium(III) tris(dipyridyl) chloride and chlorocadmates increase from 220 to 345 °C with an increase of the size of the anion. A similar increase of decomposition temperatures is observed in the rhodium(III) tris(dipyridyl) bromide and iodide series. This phenomenon indicates a stabilizing outer sphere effect [25–28] of anionic counterions on the thermal stability of the  $[\text{Rh}(\text{bpy})_3]^{3+}$  cation. It can be concluded, therefore, that the stability of the Rh–N bond in the compounds listed in the title depends in the solid state on the nature of the anionic counterion. A comparison of the results of our investigations with literature data [14,16]

allows us to conclude that the Rh–N bond in  $[\text{Rh}(\text{bpy})_3]^{3+}$  cations is weaker than the Ru–N bond in  $[\text{Ru}(\text{bpy})_3]^{2+}$  cations, but stronger than the M–N bond  $[\text{M} = \text{Mn}(\text{II}), \text{Fe}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II}) \text{ of } \text{Cd}(\text{II})]$  occurring in complex cations of a similar composition of  $[\text{M}(\text{bpy})_3]^{2+}$  type.

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