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PREPARATION AND THERMAL DECOMPOSITION OF HALOGENOMETALATES. PART I. TRIS(2,2′-DIPYRIDYL)RUTHENIUM(II) HALOGENOCADMATES

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ABSTRACT

Halogenometalates having the composition $[Ru(bpy)_3][Cd_nX_{2n+2}]$ were obtained The maximum value of n equals 5 for chlorocadmates, and 2 for bromo- and iodocadmates Analysis of electron spectra revealed the presence of the $[Ru(bpy)_3]^{2+}$ cation in the complexes obtained Thermolysis of these compounds is generally single-stage, and is accompanied by a strong exothermic effect resulting from combustion of the decomposition products Decomposition temperatures depend on the type and size of the halogenocadmate anions, the analysis of which enabled the determination of the structure of tris(dipyridyl)ruthenium(II) hexahalogenodicadmates

INTRODUCTION

Cadmium halides react with halides of some metals and ammonium halides forming numerous compounds containing halogenocadmate anions [1–8], e g $[CdX_3]^-$, $[CdX_4]^{2-}$, $[Cd_2X_6]^{2-}$, $[CdX_5]^{3-}$ and $[CdX_6]^{4-}$, where X = Cl, Br or I The papers of Seifert and coworkers [9–14] indicate the possibility of the existence of more complex anions, such as $[Cd_5Cl_{12}]^{2-}$ and $[Cd_5Cl_{11}]^-$

A search for isolation methods of the anions from solutions in the form of crystalline compounds containing a suitable counterion constitutes a separate problem Of great help is the hypothesis of Basolo [15] (solid metal complexes are stabilized by large counter-ions, preferably ions of the same but opposite charge), published in a monograph on stabilization and isolation of complex ions in crystalline form from solutions The pertinence of this hypothesis in the case of chloropolycadmate anions has been recently confirmed by Murzubraimow and Toktomamatow [16] Using monoprotonated semicarbazide as a counter-ion, they managed to obtain (CH_6N_3S)-$[Cd_3Cl_8]$

We considered the possibility of using a large $[Ru(bpy)_3]^{2+}$ cation as a counter-ion suitable in the light of Basolo's hypothesis for stabilization [3,15,17,18] for the isolation of salts containing halogenocadmate anions

In spite of extensive research on conversion of solar energy using a complex $[Ru(bpy)_3]^{2+}$ cation [13–22] and a large number of papers on halogenocadmates, no data are reported on their compounds On the other hand, there are a few reports on thermolysis [23] of the discussed halogenocadmates and cadmium compounds with complex cations containing a metal [6] acting as a counter-ion

EXPERIMENTAL

Materials

Hydrated tris(dipyridyl)ruthenium(II) halides were obtained by methods reported previously [24,25] All the reagents used were analytically pure

Preparation and chemical analysis of $[Ru(bpy)_3][Cd_nX_{2n+2}]$ *type halogenocadmates*

In order to obtain the afore-mentioned complexes, hydrated tris(dipyridyl)ruthenium(II) halides were dissolved in hot ethanol, the process being followed by addition of hot ethanol solutions of suitable cadmium halides, with the molar ratio of Ru Cd being equal to 1 n ($n = 1$–10) Isolated precipitates were heated in the mother liquor to boiling, and subsequently filtered and washed with hot ethanol The preparations obtained were dried in air at room temperature

Halides and cadmium in the discussed compounds were determined gravimetrically in the form of AgX and $CdNH_4PO_4$ H_2O [26], respectively Ruthenium was determined spectrophotometrically at $\lambda_{max} = 452$ nm The

TABLE 1

Results of analyses

No	Complex	Ru (%)		Cd (%)	
		Found	Calcd	Found	Calcd
1	$[Ru(bpy)_3][CdCl_4]$	12 2	12 27	14 33	13 64
2	$[Ru(bpy)_3][Cd_2Cl_6]$	9 60	10 04	22 03	22 32
3	$[Ru(bpy)_3][Cd_3Cl_8]$ 2 $5H_2O$	7 89	8 18	27 93	27 29
4	$[Ru(bpy)_3][Cd_4Cl_{10}]$ $3H_2O$	7 03	7 08	30 70	31 49
5	$[Ru(bpy)_3][Cd_5Cl_{12}]$ $4H_2O$	6 37	6 20	33 65	34 50
6	$[Ru(bpy)_3][CdBr_4]$	10 00	10 09	11 40	11 22
7	$[Ru(bpy)_3][Cd_2Br_6]$	7 72	7 93	17 86	17 65
8	$[Ru(bpy)_3][CdI_4]$	8 58	8 50	9 76	9 45
9	$[Ru(bpy)_3][Cd_2I_6]$	6 27	6 49	14 67	14 45

[1] X = Halogen

C, H, N analyses were performed on a Carlo Erba elemental analyser Model 1106

Instruments

Thermal analysis was carried out using a MOM derivatograph and alundum crucibles Al_2O_3 served as a reference material atmosphere, air, sample weight, 100 mg, heating rate, 10 K min^{-1}, sensitivity of DTA, 1/10, DTG, 1/10, TG, 100, final temperature, 900 °C

The final products of thermal decomposition which remained in the crucibles were analysed by X-ray radiography using a DRON-2 diffractometer and Cu K_α radiation

Absorption spectra and determination of ruthenium were carried out using a SPECOL-10 spectrophotometer

RESULTS AND DISCUSSION

The afore-mentioned complexes were obtained as a result of the reaction of tris(2,2′-dipyridyl)ruthenium(II) halides with cadmium(II) halides in ethanol, according to the following equation

$$[Ru(bpy)_3]X_2 + nCdX_2 \rightarrow [Ru(bpy)_3][Cd_nX_{2n+2}]$$

where the maximum value of n equals 5 for chlorocadmate complexes and 2 for bromo- and iodocadmates The same reagents react in water according to the following equation

$$[Ru(bpy)_3]X_2 + CdX_2 \rightarrow [Ru(bpy)_3][CdX_4]$$

whereas iodides additionally form hexaiododicadmates, as they do in ethanol

X (%) [a]		C (%)		H (%)		N (%)	
Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
17 04	17 21	43 14	43 74	2 87	2 94	10 27	10 20
21 06	21 12	36 36	35 78	2 34	2 40	7 17	8 34
23 60	22 96	30 30	29 16	2 25	2 37	6 64	6 80
24 95	24 83	25 93	25 24	1 81	2 12	4 60	5 89
25 77	26 11	23 28	22 12	1 60	1 98	3 25	5 16
32 17	31 91	32 75	35 97	2 16	2 39	8 39	8 39
37 16	37 64	28 28	28 29	1 88	1 88	6 91	6 59
42 44	42 67	30 20	30 26	2 0	2 02	6 96	7 06
49 26	48 94	23 17	23 16	1 56	1 55	6 18	5 40

TABLE 2

Results of thermal analysis

No	Complex	Temperatures (° C) and character of peaks in DTA [a]		Temperature (° C)		Decomposition product (mg)	
		Exothermic	Endothermic	At the beginning of decomposition	At the end of decomposition	Calcd	Found
1	$[Ru(bpy)_3][CdCl_4]$	385w, 545s	–	370	680	16 15	15 8 RuO_2
2	$[Ru(bpy)_3][Cd_2Cl_6]$	550s	380w	400	730	13 21	13 4 RuO_2
3	$[Ru(bpy)_3][Cd_3Cl_8]$ 2 $5H_2O$	615s	355w	440	760	10 77	10 8 RuO_2
4	$[Ru(bpy)_3][Cd_4Cl_{10}]$ $3H_2O$	610s, 760w	355w	465	760	9 32	9 2 RuO_2
5	$[Ru(bpy)_3][Cd_5Cl_{12}]$ $4H_2O$	570s, 750w	355w	485	760	8 16	7 9 RuO_2
6	$[Ru(bpy)_3][CdBr_4]$	395w, 560s	–	380	710	13 3	13 3 RuO_2
7	$[Ru(bpy)_3][Cd_2Br_6]$	505w, 610s	390w	420	720	10 45	10 6 RuO_2
8	$[Ru(bpy)_3][CdI_4]$	400w, 460w, 580s	–	370	720	17 94	17 8 Ru Cd
9	$[Ru(bpy)_3][Cd_2I_6]$	450w, 560s	360vw	420	630	20 94	20 8 Ru Cd_2

[a] Key vw, very weak, w, weak, s, strong

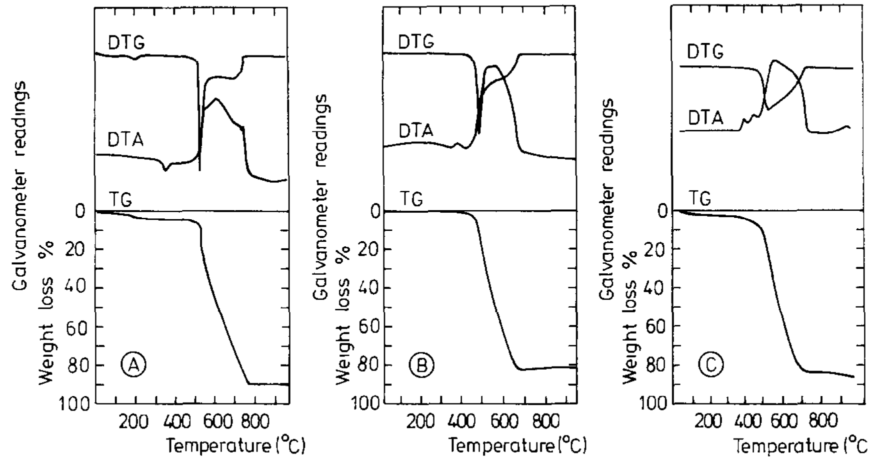


Fig 1 Thermograms for (A) $[Ru(bpy)_3][Cd_3Cl_8]$ 2 $5H_2O$, (B) $[Ru(bpy)_3][CdCl_4]$ and (C) $[Ru(bpy)_3][CdI_4]$

The results of analysis of the compounds obtained are listed in Table 1 According to literature data [27,28], cadmium(II) forms, with dipyridyl, complexes of the composition $[Cd(bpy)_n]^{2+}$, where $n = 1$–3 The possibility of formation of $[Ru(bpy)_3]X_2$ with CdX_2 had to be taken into account due to the possibility of detachment of dipyridyl from ruthenium In order to elucidate this problem, the orange compounds obtained were analysed spectrophotometrically The measured electron spectra were almost the same as those of tris(dipyridyl)ruthenium(II) halides ($\lambda_{max} = 450$–452 nm MLCT) and were consistent with literature data [29–31] It follows from the above considerations that the Ru–N bond in the $[Ru(bpy)_3]^{2+}$ cation does not undergo destruction during synthesis of the above compounds, which also allows for the application of spectrophotometry to the determination of ruthenium and of the correct formulae of the obtained complexes These complexes are sparingly soluble in ethanol, while in water their solubility decreases with the increase of the halogen radius They do not undergo decomposition during storage in air, but they do reveal a slight hygroscopic character

The results of thermal analysis are listed in Table 2 and illustrated in Figs 1a, 1b and 1c

It follows from the analysis of the TG curves (Fig 1a) that the water-containing compounds obtained start to dehydrate at 50 °C The final temperatures of dehydration are 220, 200 and 210 °C for $[Ru(bpy)_3][Cd_3Cl_8]$ 2 $5H_2O$, $[Ru(bpy)_3][Cd_4Cl_{10}]$ $3H_2O$ and $[Ru(bpy)_3][Cd_5Cl_{12}]$ $4H_2O$, respectively

The thermograms (DTA curves) of the investigated halogenopolycadmates reveal the presence of endothermal peaks prior to decomposition temperature, related to melting points of the obtained compounds Their values are listed in Table 2 and illustrated in Fig 1a

The data contained in Table 2 indicate that decomposition temperatures of the complexes investigated depend on the size and kind of halogenocadmate anions The phenomenon results from different energies of the cadmium–halogen bond, which is confirmed by the values of the bond force constants [32] determined for the $[CdX_4]^{2-}$-type anion and equal to 1 41, 1 19 and 0 98 N cm^{-1} for Cd–Cl, Cd–Br and Cd–I, respectively The above values indicate that decomposition temperatures cannot be compared for all the complexes obtained On the other hand, a distinct increase of thermal stability is observed with an increase of the size of the respective anions in separate series of tris(dipyridyl)ruthenium(II) chloro-, bromo- and iodocadmates

DTA curves of tris(dipyridyl)ruthenium(II) tetrahalogenocadmates and hexaiododicadmates reveal the presence of characteristic exothermal peaks following directly after the initial decomposition temperatures Their presence probably indicates that the initial stages of decomposition are of a complex nature, are multistage in character and are accompanied by formation of intermediates, which can undergo phase transitions The peaks discussed are accompanied by small mass losses (TG curves), while no changes are observed on the DTG curves (Figs 1b, 1c)

Further decomposition is single-stage, similar to the rest of the investigated compounds, and the strong exothermic effect is related to combustion of the volatile substances formed (Figs 1a, 1b and 1c)

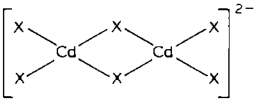
Ruthenium(IV) oxide is the final product of decomposition in the case of chloro- and bromocadmates, while a ruthenium–cadmium alloy with a Ru–Cd or $Ru-Cd_2$ composition is formed as a result of decomposition of iodocadmates The residue was analysed by X-ray analysis Apart from the afore-mentioned compound, RuO_2 was reduced with hydrogen at 500–600 ° C and the resultant ruthenium was identified

CONCLUSIONS

It seems that isolation of $[Cd_nX_{2n+2}]^{2-}$ complex anions from alcoholic solutions was possible by application of suitable $[Ru(bpy)_3]^{2+}$ counter-ions, which stabilize the above-mentioned anions [3,15,17,18]

The increase in decomposition temperatures observed in a given series of the obtained compounds highlights the increase of the size of the complex anions and their stabilizing effect on thermal stability of the investigated compounds $[Ru(bpy)_3]X_2$ compounds (X = F, Cl, Br or I) reveal similar behaviour, their decomposition temperatures also increase with an increase of the ionic radius of the halide ions [24,33–35], which is consistent with Basolo's considerations

The formulae of the compounds obtained with composition $[Ru(bpy)_3][Cd_2X_6]$ can be also written as $[Ru(bpy)_3][CdX_3]_2$, however, if such is the case their decomposition temperatures should be lower than that of $[Ru(bpy)_3][CdX_4]$ because of the smaller size of $[CdX_3]^-$ anions Therefore, it seems more probable that $[Cd_2X_6]^{2-}$ anions occur in the compounds examined Their structure has been established [2,4,5] and can be presented in the following manner



It follows from our investigations and literature data that the composition and structure of halogenocadmate anions depends on the conditions of synthesis, size and kind of cations, and stoichiometric ratios of the reagents, as well as radius and electronegativity of the X substituent

The electronic structure of a compound of a type similar to that presented in this paper has been recently discussed by Canadell and Eisenstein [36] On the basis of theoretical calculations they have found that an optimum number of valence electrons per MX_2 molecule is 16 and that the X substituent should be characterized by large electronegativity and small size These expectations are fully confirmed by the results obtained—chloropolycadmate anions with a maximum value of n equals 5 can be obtained when $X = Cl$, while, when $X = Br$ or I, the maximum value of n equals 2

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