

## THE EFFECT OF OUTER SPHERE CATIONS ON THE THERMAL STABILITY OF NITRITOCUPRATES(II)

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Thermal analyses by Derivatograph were made for salts of the general formula  $M_2^I M^{II} [Cu(NO_2)_6]$  where  $M^I = K^+, Rb^+$  or  $Cs^+$ ; and  $M^{II} = Ca^{2+}, Sr^{2+}, Ba^{2+}$  or  $Pb^{2+}$ . From the results and the chemical and diffractometric analysis of sinters of chosen salts, the mechanism of thermal decomposition was established. Some conclusions concerning the effects of outer sphere cations on the thermal stabilities of these salts are also drawn.

The effects of outer sphere ions on the properties of crystalline complex compounds have not been sufficiently investigated, whereas there are comparatively numerous publications referring to the effects of these ions on the stabilities of complexes in solution.

The thermal stabilities of ammoniates and hydrates formed the object of extensive studies by Biltz et al. [1, 2]. The stability of the complex cation was found to increase with the volume of the outer sphere anion. The thermal stabilities of chloraurates  $R[AuCl_4]$  were investigated by Paravano and Malquori [3]. These authors found that the stability decreases with increasing strength of the polarizing field of the cation R. The effect of the radius of the outer sphere cation on the temperature of thermal dissociation was also studied for hexacyanoferrates(II) [4]. Duval [5] has presented a thermogravimetric curve for potassium lead nitritocuprate(II). There are no literature data on thermal investigations of other nitritocuprates(II).

### Experimental

#### *Materials*

#### *Preparation of nitritocuprates*

Salts of the formula  $K_2 M^{II} [Cu(NO_2)_6]$ , where  $M^{II} = Pb^{2+}$  or  $Sr^{2+}$ , were crystallized from aqueous solutions containing copper nitrate, strontium or lead nitrate, and potassium nitrite in a molar ratio 1 : 1 : 6.

The compounds  $M_2^I Pb [Cu(NO_2)_6]$ , where  $M^I = Rb^+$  or  $Cs^+$ , were crystallized from aqueous solutions containing  $Cu(NO_2)_2$ ,  $Pb(NO_3)_2$  and  $M^I NO_2$  in a molar ratio 1 : 1 : 4.

The remaining complex salts of the discussed group were crystallized from aqueous solutions containing  $\text{Cu}(\text{NO}_2)_2$ ,  $\text{M}^{\text{II}}(\text{NO}_2)_2$  and  $\text{M}^{\text{I}}\text{NO}_2$  in a molar ratio 1 : 1 : 2.

Solutions of copper, rubidium and caesium nitrites were prepared in exchange reactions of the respective sulphates with barium nitrite; strontium and calcium nitrites were prepared in exchange reactions of the respective chlorides with silver nitrite. For all preparations, reagents "pure for analysis", produced by "POCh", Gliwice, were used. Concentrations of the stock solutions were as follows:  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Cu}(\text{NO}_2)_2 \sim 3.5$  molar,  $\text{Pb}(\text{NO}_3)_2 \sim 1$  molar,  $\text{M}^{\text{II}}(\text{NO}_2)_2$  ( $\text{M}^{\text{II}} = \text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  or  $\text{Ba}^{2+}$ )  $\sim 3$  molar, and  $\text{M}^{\text{I}}\text{NO}_2$  ( $\text{M}^{\text{I}} = \text{K}^+$ ,  $\text{Rb}^+$  or  $\text{Cs}^+$ )  $\sim 15$  molar.

The salts were crystallized at about  $0^\circ$  for 1 to 240 hours. The crystals were filtered and dried on filter paper at room temperature.

### Methods

#### Analysis of the salts

The nitrite content of each compound was determined by titration with potassium permanganate after Wilcox [7]. Copper in compounds not containing lead was determined by direct titration with EDTA in the presence of murexide as

Table 1  
Composition of nitritocuprates(II)

No	Compound formula	Content, %					
		$\text{Ca}^{2+}$		$\text{Cu}^{2+}$		$\text{NO}_2^-$	
		calcd.	detrmd.	calcd.	detrmd.	calcd.	detrmd.
1.	$\text{K}_2\text{Ca}[\text{Cu}(\text{NO}_2)_6]$	8.75	8.81	13.88	13.73	60.27	60.86
2.	$\text{Rb}_2\text{Ca}[\text{Cu}(\text{NO}_2)_6]$	7.28	7.15	11.54	11.46	50.12	49.99
3.	$\text{Cs}_2\text{Ca}[\text{Cu}(\text{NO}_2)_6]$	6.21	6.26	9.84	9.72	42.76	42.28
		$\text{Sr}^{2+}$					
4.	$\text{K}_2\text{Sr}[\text{Cu}(\text{NO}_2)_6]$	17.33	17.27	12.58	12.64	54.61	54.56
5.	$\text{Rb}_2\text{Sr}[\text{Cu}(\text{NO}_2)_6]$	14.65	14.50	10.63	10.52	46.14	46.35
6.	$\text{Cs}_2\text{Sr}[\text{Cu}(\text{NO}_2)_6]$	12.64	12.58	9.17	9.15	39.83	39.81
		$\text{Ba}^{2+}$					
7.	$\text{K}_2\text{Ba}[\text{Cu}(\text{NO}_2)_6]$	24.74	24.39	11.45	11.48	49.73	49.72
8.	$\text{Rb}_2\text{Ba}[\text{Cu}(\text{NO}_2)_6]$	21.20	20.96	9.81	9.76	42.60	42.17
9.	$\text{Cs}_2\text{Ba}[\text{Cu}(\text{NO}_2)_6]$	18.49	18.63	8.56	8.64	37.16	37.48
		$\text{Pb}^{2+}$					
10.	$\text{K}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$	33.15	33.19	10.17	10.20	44.16	43.79
11.	$\text{Rb}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$	28.86	28.80	8.85	8.70	38.46	37.88
12.	$\text{Cs}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$	25.49	25.54	7.82	7.84	33.97	33.85

indicator. In compounds containing both copper and lead, the total content of the two metals was determined by titration with EDTA in the presence of murexide. In a separate sample, lead was titrated with EDTA in the presence of eriochrome black, after copper had been masked with potassium cyanide [8].

Barium [9] and strontium [10] were determined gravimetrically as sulphates. Calcium was determined with EDTA in the presence of murexide as indicator, after masking of the copper with cyanide [8].

### *Thermal investigations*

The thermal investigations of nitritocuprates were made with a Derivatograph (MOM Budapest, type OD 102) on 60 mg samples in the temperature range from 20 to 1200°. The heating rate was 6°/min.  $\alpha$ - $\text{Al}_2\text{O}_3$  was used as reference material. Calibration of the DTA curve was carried out using Barshad's method [11].

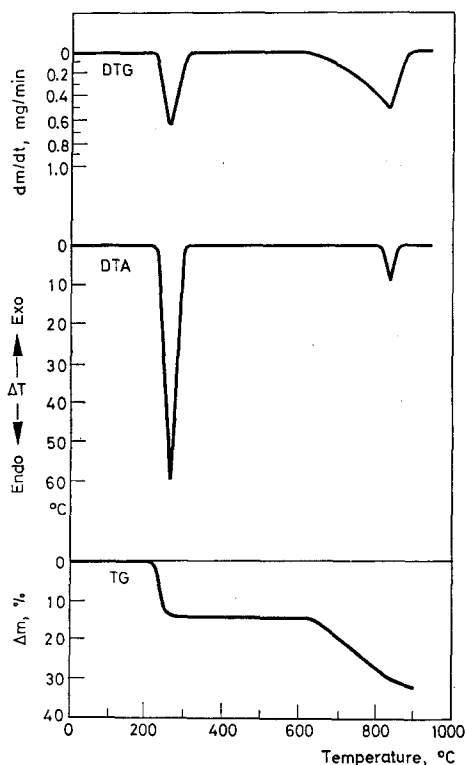


Fig. 1. TG, DTG and DTA curves of  $\text{Cs}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$

### Diffraction analysis

The diffractometric analysis of sinters was made in a DRON-1 diffractometer with Cu  $K\alpha$  radiation and a nickel filter. The intensity of reflections was measured with a scintillation counter (conjugation Q/2Q). The diffraction curves were recorded with an automatic recorder for  $2^\circ$  angles from  $2^\circ$  to  $70^\circ$ .

### Results

Typical thermal curves are shown in Fig. 1 for  $\text{Cs}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$  and in Fig. 2 for  $\text{Cs}_2\text{Sr}[\text{Cu}(\text{NO}_2)_6]$ .

It is evident from all three curves in Fig. 1 that two thermal reactions take place in the investigated temperature range, both endothermic and accompanied by loss of mass. The first begins at  $220^\circ$ , attains its highest rate at  $260^\circ$  and ends at  $310^\circ$ ; the second begins at about  $600^\circ$ , attains its highest rate at  $830^\circ$  and ends at  $880^\circ$ .

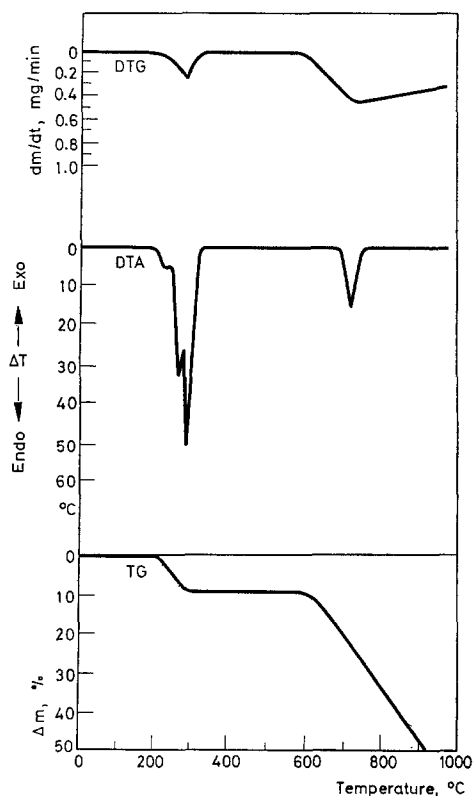


Fig. 2. TG, DTG and DTA curves of  $\text{Cs}_2\text{Sr}[\text{Cu}(\text{NO}_2)_6]$

Thermogravimetric curves of alkali metal and alkaline earth metal nitritocuprates differ from that of  $\text{Cs}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$  in showing large losses of mass in the second decomposition stage. The decomposition temperatures of the complex salts investigated are given in Table 2.

Table 2  
DTG peak temperatures for nitritocuprates(II)

No	Compound formula	T, °C	No	Compound formula	T, °C
1.	$\text{K}_2\text{Ca}[\text{Cu}(\text{NO}_2)_6]$	202	7.	$\text{K}_2\text{Ba}[\text{Cu}(\text{NO}_2)_6]$	210
2.	$\text{Rb}_2\text{Ca}[\text{Cu}(\text{NO}_2)_6]$	223	8.	$\text{Rb}_2\text{Ba}[\text{Cu}(\text{NO}_2)_6]$	238
3.	$\text{Cs}_2\text{Ca}[\text{Cu}(\text{NO}_2)_6]$	238	9.	$\text{Cs}_2\text{Ba}[\text{Cu}(\text{NO}_2)_6]$	258
4.	$\text{K}_2\text{Sr}[\text{Cu}(\text{NO}_2)_6]$	260	10.	$\text{K}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$	220
5.	$\text{Rb}_2\text{Sr}[\text{Cu}(\text{NO}_2)_6]$	280	11.	$\text{Rb}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$	240
6.	$\text{Cs}_2\text{Sr}[\text{Cu}(\text{NO}_2)_6]$	285	12.	$\text{Cs}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$	260

### Analysis of sinters

#### Chemical analysis

In order to elucidate the course of thermal decomposition and the products, sinters of the investigated salts were prepared under conditions similar to those applied in thermal investigations (heating rate 5–6°/min). Heating was stopped at the final transformation temperature. The correct preparation of the sinter was controlled by determining the loss of mass.

For the analysis of sinters (Table 3) the same classical methods were used as for the analysis of the salts.

Nitrates were determined by the method of Ulsch [12]. No nitrites were found in the sinters.

Table 3  
Results of analysis of sinters of nitritocuprates(II)

Initial compound formula	Content in the sinter					
	$\text{Pb}^{2+}$		$\text{Cu}^{2+}$		$\text{NO}_3^-$	
	%	mole	%	mole	%	mole
$\text{Cs}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$ (300°)	29.80	0.1438	9.23	0.1452	17.73	0.2859
	$\text{Pb}^{2+} : \text{Cu}^{2+} : \text{NO}_3^- = 1.00 : 1.01 : 1.99$					
$\text{Cs}_2\text{Sr}[\text{Cu}(\text{NO}_2)_6]$ (300°)	13.85	0.1580	10.20	0.1605	29.53	0.4727
	$\text{Sr}^{2+} : \text{Cu}^{2+} : \text{NO}_3^- = 1.00 : 1.02 : 2.99$					

Fig. 3 shows the diffractograms of  $\text{Cs}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$  and its sinters obtained at  $300^\circ$  and  $900^\circ$ .

Table 4 gives the interplanar distances  $d$  determined from the diffractogram of the sinter obtained at  $300^\circ$ .

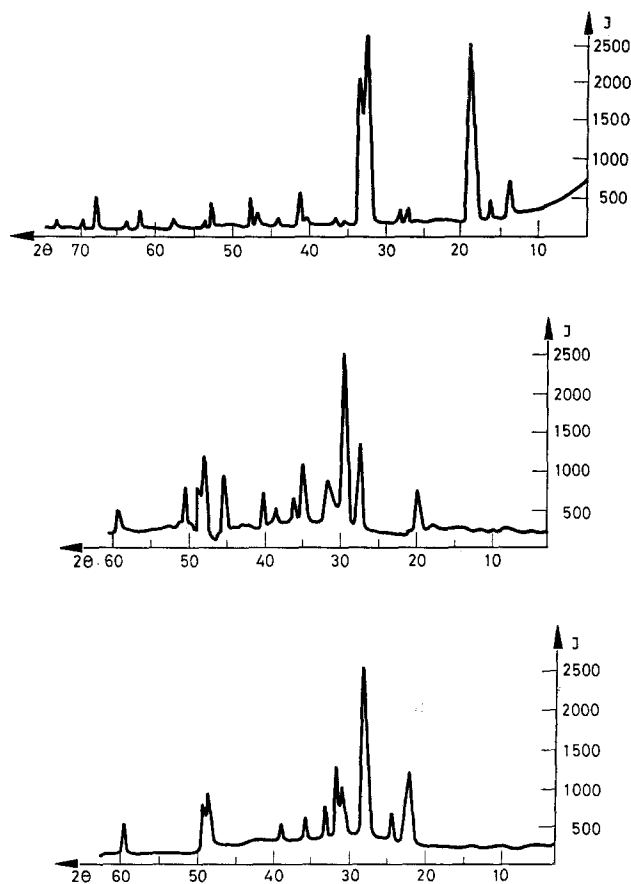


Fig. 3. Diffractogram of  $\text{Cs}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$  a) before sintering, b) after sintering at  $300^\circ$ , c) after sintering at  $900^\circ$

The presence of  $\text{CsNO}_3$ ,  $\text{PbO}$  and  $\text{CuO}$  was detected in this sinter, and of  $\text{Cs}_2\text{O}$ ,  $\text{PbO}$  and  $\text{CuO}$  in that obtained at  $900^\circ$ . Table 5 gives values of interplanar distances determined from a diffractogram of the caesium strontium nitritocuprate sinter obtained at  $300^\circ$ .  $\text{CsNO}_3$ ,  $\text{SrO}$ ,  $\text{Sr}(\text{NO}_3)_2$  and  $\text{CuO}$  were identified in this sinter.

Table 4

Values of interplanar distances determined from the diffractogram of  $\text{Cs}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$  sinter ( $300^\circ$ )

$2\theta$	$\theta$	d/n	Ident. No	Subst.
19.95	9.97	4.45	4.45	$\text{CsNO}_3$ IV
28.30	14.15	3.15	3.15	$\text{CsNO}_3$ I
28.60	14.30	3.12	3.11	PbO I
31.80	15.90	2.81	2.80	PbO II
34.90	17.45	2.57	2.57	$\text{CsNO}_3$ V
35.70	17.85	2.51	2.51	CuO I
38.90	19.45	2.31	2.31	CuO II
40.50	20.25	2.23	2.23	$\text{CsNO}_3$ IV
45.60	22.80	1.99	1.99	$\text{CsNO}_3$ II
48.80	24.40	1.86	1.85	CuO III
			1.86	PbO III
50.25	25.12	1.81	1.82	$\text{CsNO}_3$ II
59.50	29.75	1.55	1.55	PbO IV

Table 5

Values of interplanar distances determined from the diffractogram of  $\text{Cs}_2\text{Sr}[\text{Cu}(\text{NO}_2)_6]$  sinter ( $300^\circ$ )

$2\theta$	$\theta$	d/n	Ident. No	Subst.
19.70	9.85	4.51	4.50	$\text{Sr}(\text{NO}_3)_2$ I
19.90	9.95	4.46	4.45	$\text{CsNO}_3$ IV
28.40	14.20	3.14	3.15	$\text{CsNO}_3$ I
30.00	15.00	2.97	2.97	SrO I
34.90	17.45	2.57	2.58	SrO III
35.70	17.85	2.51	2.51	CuO I
38.40	19.20	2.34	2.35	$\text{Sr}(\text{NO}_3)_2$ II
38.90	19.45	2.31	2.31	CuO II
40.50	20.25	2.23	2.24	$\text{Sr}(\text{NO}_3)_2$ III
45.60	22.80	1.99	1.99	$\text{CsNO}_3$ II
48.80	24.40	1.86	1.85	CuO III
50.25	25.12	1.82	1.82	SrO II
53.50	26.75	1.71	1.70	CuO IV

### Discussion

The equations of thermal decompositions of the investigated nitritocuprates were established by comparing the results of chemical and diffractometric analysis of sinters with mass losses from the thermogravimetric curves and preparations of sinters.

The diffractogram of the lead caesium nitritocuprates(II) sinter showed the presence of  $\text{CsNO}_3$ ,  $\text{PbO}$  and  $\text{CuO}$ . According to the chemical analysis, the molar ratio  $\text{Pb} : \text{Cu} : \text{NO}_3$  was  $1 : 1 : 2$ . The mass loss after heating up to  $300^\circ$  was 14.16%, while that during the preparation of the sinter was 14.9%. Hence, the reaction of thermal decomposition of  $\text{Cs}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$  may be represented by the equation:



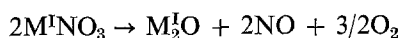
Analogous equations were found for the decompositions of the rubidium and potassium salts (see Table 6, left upper part).

Table 6

Losses of mass during the thermal decomposition of nitritocuprates(II)

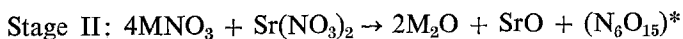
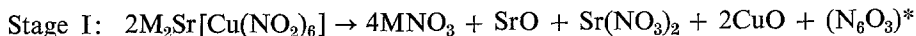
Compound formula	Loss of mass in %					
	I stage			II stage		
	Determined derivatographically	Determined in sinter	Calculated from equation	Determined derivatographically	Determined in sinter	Calculated from equation
$\text{K}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$	19.16	19.30	19.20	25.77	25.55	21.37
$\text{Rb}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$	15.83	15.95	16.72	18.81	19.45	18.07
$\text{Cs}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$	14.16	14.90	14.76	28.13	29.58	15.59
$\text{K}_2\text{Sr}[\text{Cu}(\text{NO}_2)_6]$	13.33	12.73	13.06	30.93	31.24	32.06
$\text{Rb}_2\text{Sr}[\text{Cu}(\text{NO}_2)_6]$	10.83	10.61	11.04	28.77	28.31	27.08
$\text{Cs}_2\text{Sr}[\text{Cu}(\text{NO}_2)_6]$	9.16	9.63	9.52	32.11	33.06	23.38

In a similar way, the second stage of the process can be represented as decomposition of the alkali nitrate:



The respective mass loss data can be found in the 5th, 6th and 7th columns of Table 6. It can be seen that the agreement is best for the potassium salt and somewhat poorer for that of rubidium, whereas the experimental mass loss of  $\text{Cs}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$  is much higher than that calculated from the above equation. This discrepancy is probably caused by decomposition of  $\text{Cs}_2\text{O}$  to peroxide and metal, and evaporation of the latter [11].

From the data in Table 6 the following equations can be deduced for the decomposition of alkali metal strontium nitritocuprates:



\* The composition of the volatile products was not studied. In the reactions the overall formula of the gaseous products following from the loss of mass is given.



The influence of outer sphere ions on the decomposition temperature of nitritocuprates can be illustrated best by plotting the decomposition temperature against the radius difference  $2r_{M^I} - r_{M^{II}}$  (Figs 4 and 5).

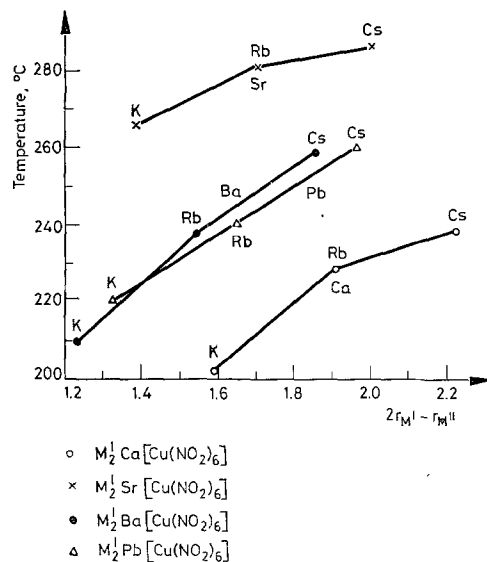


Fig. 4. The dependence of thermal decomposition temperatures for nitritocuprates (II) on the difference of radii of outer sphere cations. Change of  $M^I$  cation

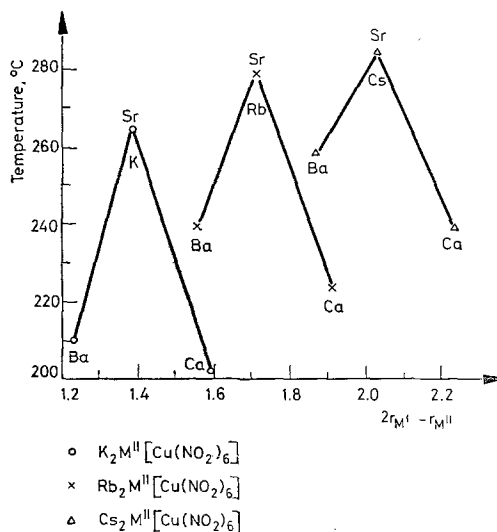


Fig. 5. The dependence of thermal decomposition temperatures for nitritocuprates (II) on the difference of radii of outer sphere cations. Change of  $M^{II}$  cation

The thermal stabilities of the salts increase with increasing radius of the monovalent cation in the sequence:



where  $M^I = Ca^{2+}, Sr^{2+}, Ba^{2+}$  or  $Pb^{2+}$ .

The differences between the decomposition temperatures in the series of lead salts are:

$$T_{Rb-K} = 20^\circ;$$

$$T_{Cs-Rb} = 20^\circ.$$

The higher stabilities of the heavier alkali metal salts can be inferred from their crystal structures. Calculations were made of the distances between the copper atom and the outer surface of the alkali metal ion, represented as a sphere with an ionic radius corresponding to the coordination number 6. The following values were obtained:

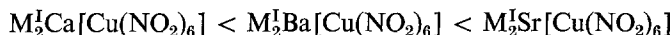
$$K_2Pb[Cu(NO_2)_6]: \quad 3.25 \text{ \AA},$$

$$Rb_2Pb[Cu(NO_2)_6]: \quad 3.13 \text{ \AA},$$

$$Cs_2Pb[Cu(NO_2)_6]: \quad 3.02 \text{ \AA}.$$

Hence, it follows that the ionic bond between the complex anion and the alkali metal cation is weakest for potassium and strongest for caesium (shortest distance). This result is consistent with the higher decomposition temperature of the latter.

A very distinct effect of the alkaline earth metal cation in the outer sphere on the stabilities of nitritocuprates is also observed. Most stable are the strontium salts; the stabilities of the barium and calcium salts are much lower and not very far apart:



where  $M^I = K^+, Rb^+$  or  $Cs^+$ .

The respective differences of the decomposition temperatures are:

	$T_{Sr-Ca}$	$T_{Sr-Ba}$
in the potassium salt series	58°	50°
in the rubidium salt series	57°	42°
in the caesium salt series	47°	20°

Substitution of lead for strontium is followed by a considerable lowering of the thermal stability, probably owing to the stronger polarising action of the lead ion. Nevertheless, the lead salts are still more stable than those of barium and calcium.

The effects of divalent cations on the stabilities of nitritocuprates can not be deduced by geometric considerations. Conclusions as to their sequence will not be possible before the respective energetic calculations are performed.

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RÉSUMÉ — Le mécanisme de la décomposition thermique des sels de formule générale  $M_2^I M^{II}$   $[\text{Cu}(\text{NO}_2)_6]$  où  $M^I = \text{K}^+, \text{Rb}^+, \text{Cs}^+$  et  $M^{II} = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Pb}^{2+}$  a été établi à partir des données thermiques obtenues à l'aide d'un Derivatograph, ainsi que par des analyses thermiques et diffractométriques sur les produits frittés. L'effet des cations de la couche externe sur la stabilité thermique de ces sels est discuté.

ZUSAMMENFASSUNG — Es wurden thermische Analysen mit einem Derivatographen für die Salze der allgemeinen Formel  $M_2^I M^{II}$   $[\text{Cu}(\text{NO}_2)_6]$  durchgeführt [ $M^I = \text{K}^+, \text{Rb}^+, \text{Cs}^+$ ;  $M^{II} = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Pb}^{2+}$ ]. Aus den Ergebnissen dieser sowie der chemischen und diffraktometrischen Analysen der Sinterprodukte der jeweiligen Salze wurde der Mechanismus ihrer chemischen Zersetzung ermittelt. Einige Folgerungen bezüglich der Wirkung von Kationen der äusseren Sphäre auf die thermische Stabilität konnten ebenfalls gemacht werden.

Резюме — С помощью дериватографа проведен термический анализ солей общей формулы  $M_2^I M^{II}[\text{Cu}(\text{NO}_2)_6]$ , где  $M^I = \text{K}^+, \text{Rb}^+, \text{Cs}^+$ ;  $M^{II} = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Pb}^{2+}$ . Исходя из полученных результатов, а также при помощи химического и диффрактометрического анализа шлаков взятых солей, установлен механизм термического разложения. Выведены некоторые заключения, касающиеся влияния катионов во внешней сфере на термическую стабильность исследованных солей.