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STUDIES ON COORDINATION COMPOUNDS VII. CHROMATOGRAPHIC, THERMOANALYTICAL AND SPECTROSCOPIC STUDIES ON THERMAL DECOMPOSITION OF CADMIUM(II) AND LEAD(II) SALICYL-ALDOXIMATES

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On the basis of decomposition temperatures and infrared spectra, cadmium(II) and lead(II) bissalicylaldoximates were considered to have trans and cis structures, respectively.

In the first stage bis(salicylaldoximato)cadmium(II) decomposes thermally like bis(salicylaldoximato)lead(II), with one ligand molecule leaving, but the intermediate is unstable and immediately decomposes further. The oxidation of the end-product is a rapid, exothermic reaction, probably catalyzed by cadmium metal. The mass spectrum of $(C_7H_6O_2N)_2Cd$ *points to a different decomposition scheme than that elucidated through the pyrolysis decomposition products. This may be due to a catalytic effect of the ionization chamber. The thermal properties of* $(C_7H_5O_2N)Cd$ *support the preceding views.*

TG curves showed the decompositions of mono(salicyl-aldoximato)lead(II) and the intermediate of bis(salicyl-aldoximato) lead(II) to be similar. The mass spectra of the chelates confirmed the formation of the same polymer (m/e 222) in both decompositions. Only the mass spectrum of $(C_7H_5O_2N)Pb$ *exhibited the molecular peak m/e 343. The decomposition schemes of the lead(II) salicylaldoximates were therefore elucidated more exactly. The metallic lead seems not to catalyze the oxidation of the organic part.*

Rather scanty information on cadmium/II/ and lead/II/ salicyl-aldoximates is to be found in the literature. Ammann [1]

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mentioned that cadmium could not be precipitated as a salicylaldoximate from neutral aqueous solution. However, cadmium/II/ salicylaldoximate was precipitated from a sodium acetate-containing solution. According to Ammann [1] lead/II/ salicylaldoximate would not form at all. Some investigators have tried to extract salicylaldoximates with benzene or chloroform [2,3]. Dahl [2] concluded that lead/II/ salicylaldoximate was extracted completely from buffered aqueous solutions at pH 7.5 to 9. More than 90% of cadmium/II/ salicylaldoximate was not extracted until high pH.

Monosalicylaldoximates are virtually unknown in the literature. In one investigation, however, mono/salicylaldoximato/ zinc/II/ was formed when the reagent was used in 20% excess [4].

The thermal behaviour of several divalent metal salicylaldoximates has been studied by Duval [5], Lumme [6], Liptay et al. [7] and recently by Lumme and Korvola [8]. Duval [5] described the pyrolysis of lead/II/ salicylaldoximate and Lumme [6] also studied lead/II/ and cadmium/II/ salicylaldoximates thermogravimetrically, besides other salicylaldoximates, and showed that monosalicylaldoximates were formed as intermediates in the thermal decompositions of bissalicylaldoximates [6,8].

In the present work we have studied the thermogravimetric decomposition of cadmium/II/ and lead/II/ mono- and bissalicylaldoximates. The studied chelates were synthetized and their thermal decompositions were elucidated by analyses of the decomposition products and stable intermediates. Gas chromatograms and mass and infrared spectra were used for this. The elucidation of the cleavage products, however, is more uncertain than when a direct thermal balance - mass spectrometer system is used. The intermediates may react with the solvent or change in other ways before analysis.

EXPERIMENTAL

Reagents, syntheses and analyses of the compounds

Potentiometric titration curves of salicylaldoxime in aqueous potassium chloride [9] and alcohol solutions showed that ionization of the phenolic OH group takes place at approximately between pH 8 and 10 and that of the aldoxime group at pH 10 to 12. Therefore, the ligand was ionized to an extent of about 85% in each case with an exact quantity of sodium hydroxide solution.

Bis/salicylaldoximato/cadmium/II/. To 2.0 g /0.0143 mol/ of salicylaldoxime /pro analysi 98%/, Merck/, 122.46 ml of 0.1012 M NaOH /0.01239 mol/ was added with stirring. Then 1.4159 g /0.00614 mol/ of $CdCl_2 \cdot 2,5H_2O$ /99.1%, Noury-Baker, N.V./ dissolved in a little water was added. The chelate and bis/salicylaldoximato/cadmium/II/ precipitated immediately, and was filtered off, washed with water and dried for 3-4 days in a desiccator.

Bis/salicylaldoximato/lead/II/. $/C_7H_6O_2N/_2Pb$, was prepared in the same manner from 2.0 g of salicylaldoxime, 2.0534 g /0.00617 mol/ of $Pb/No_3/_2$ /pro analysi /99.5%/, Merck/ and 122.46 ml of 0.1012 M NaOH. The filtrate was weakly acidic /ph 5-6/.

Mono/salicylaldoximato/lead/II/ was prepared accordingly from 2.0 g of salicylaldoxime, 4.829 g /0.0145 mol/ of $Pb/NO_3/_2$ and 289.17 ml of 0.1009 M NaOH /0.02917 mol/.

Cadmium hydroxide is known to precipitate [10] from about pH 8-9, whereas the pH of a solution of totally ionized salicylaldoxime is above this. Therefore, mono/salicylaldoximato/cadmium/II/, $/C_7H_5O_2N/Cd$, was prepared by dissolving 1.3714 g /0.01 mol/ of salicylaldoxime in 20 ml of ethanol, adding 18.40 ml of 1.087 M NaOH /0.02 mol/ and then 2.2836 g /0.01 mol/ of $CdCl_2 \cdot 2.5H_2O$ in 20 ml of water. The solution was heated for one hour. 60 ml of conc. ammonia was added to dissolve any $Cd/OH/_2$ possibly formed. The mixture was evaporated to 1/3 of its volume, during which the ammonia escaped and the yellowish chelate precipitated and was handled as above.

The metal contents of cadmium/II/ and lead/II/ bissalicylaldoximates were determined electroanalytically [11]. The chelates were dissolved first in 6 M HNO_3, a small amount of 30% H_2O_2 being added if needed; the residual hydrogen peroxide was evaporated off and the solution was neturalized with NaOH. The analysis procedure was then followed.

The electroanalytical method was not suitable for the determination of the metal contents of the monosalicylaldoximates possibly done to the disturbing effect of the organic part of the chelates. Therefore, the metals were titrated complexometrically with EDTA [12]. The cadmium titration was performed at pH 10 with eriochrome black /Merck 3170/ as indicator and 0.01 N EDTA solution as titrant. The colour of the solution turned from violet to blue. For lead titration the buffer-indicator tablets Merck 8430 were used; 5 ml conc. ammonia was added and the sample was titrated with EDTA solution at pH 10 from wine-red to blue. The reproducibilities of the metal analyses for the bissalicylaldoximates were ± 0.15% /Cd/ and ± 0.03% /Pb/, and for the monosalicylaldoximates ± 0.10% /Cd/ and ± 0.33% /Pb/. The results are collected in Table 1.

The carbon, hydrogen and nitrogen contents of the chelates were determined by micro combustion analyses. These results are also shown in Table 1.

Table 1

Analytical data on the salicylaldoximates

Complex	M.w.	Found, %				Calculated, %			
		C	H	N	Metal	C	H	N	Metal
$(C_7H_6O_2N)_2Cd$	384.67	41.83	2.85	7.18	28.83	43.71	3.14	7.30	29.22
$(C_7H_6O_2N)_2Pb$	479.46	33.50	2.26	5.74	43.83	35.07	2.52	5.84	43.22
$(C_7H_5O_2N)Cd$	247.53	27.43	2.08	4.37	46.50	33.97	2.04	5.66	45.41
$(C_7H_5O_2N)Pb$	342.32	24.96	1.63	4.18	60.15	24.56	1.47	4.09	60.53

Apparatus and measurements

The TG apparatus was a Fisher TGA System Series 100A equipped with a Cahn electric balance, Model RG /connected to a high vacuum pump Speedivac, Model 2SC30/, a Cahn time derivative computer Mark II, which was calibrated with alcohol, and a

Watanabe Multicorder 1 mV three-pen recorder, Model MC 611, type H, with chart speed system S 10. For the DTG curve recording pen a self-made preamplifier should be used [13]. The temperature calibration was performed with an ice-water mixture. The balance calibration was adjusted so that a paper width of 25 cm corresponded to 10 mg. The TG and DTG curves were run on 8-10 mg of the compounds in Pt cups and in static air. The heating rate was 2.4 or 5.0 deg min^{-1}.

The DTA system was that described earlier [13] and was used to verify the endo- or exothermic nature of the thermal processes.

The mass spectra of the ligand and chelates were determined on solid samples through a direct inlet system on a Perkin-Elmer mass spectrometer, Model 2708. The temperature of the ionization chamber was kept at 100^{o} to avoid the thermal decomposition of the samples. The excitation energy varied from 40 to 60 eV. The heating was increased continuously and a spectrum was taken when the ionizing current showed the escape of the sample from the glass capillary holder. The mass spectra of the pyrolysis products were obtained by injection via the gas chromatograph of the mass spectrometer [14]. A stainless steel column 2 m in length filled with 3% OV-17 /methyl phenyl silicone in a ratio of 50:50 as the stationary phase and 100/120 mesh Varaport 30 as the solid support/ at 140^{o} and He /20 ml min^{-1}/ as carrying gas were used.

The pyrolyses of the chelates were performed using a modified Hamilton Multi-Purpose sampling [15] or a usual sand bath - cold finger system [14]. The pyrolysis products were dissolved in abs. ethanol and analyzed by taking gas chromatograms with a Perkin-Elmer gas chromatograph, Model 990, and the mass spectra with the mentioned mass spectrometer. In both cases an OV-17 column was used. Alcohol solutions of the solid decomposition products were analyzed gas chromatographically in the same way.

The IR spectra of the ligand and chelates were run on a Perkin-Elmer Model 457 grating infrared spectrophotometer at 4000-250 cm^{-1}. Potassium bromide disks were used, consisting of 1-2 mg of the sample per 200-300 mg of potassium bromide

/guaranteed reagent "Uvasol", E. Merck AG./ dried for 4-5 hours at 150^{o}. The mixture, weighed in to a ball-mill, was milled for 3-5 seconds in a vibrator /Wig L. Bug amalgamevibrator, Crescent Dental MFG., Co., U.S.A./. The tablet was then pressed from the powdered mixture in a hydraulic press /Perkin-Elmer accessories/ first at 0.5 to (1 to = 20 kp/cm^{2}), connected with a vacuum pump /Leybold Trivac S1/, and for the last 10 min at 10 to. As the reference a KBr tablet of equal thickness was used [13].

RESULTS AND DISCUSSION

A. TG data

The TG curves for salicylaldoxime and cadmium/II/ salicylaldoximates are shown in Figs. 1 and 2, respectively, and those for lead/II/ salicylaldoximates in Fig. 3. In the following discussion the results /weight loss percentages and temperatures/ for a heating rate of 5 deg min^{-1} are given first and those for 2.5 deg min^{-1} in brackets afterwards.

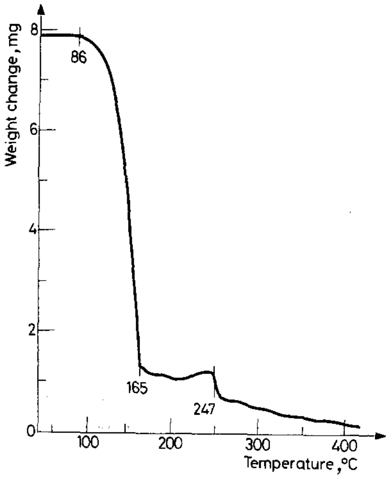

Fig. 1. TG curve of salicylaldoxime in static air atmosphere. Heating rate 5 deg min^{-1}.

1. *Salicylaldoxime*

The decomposition begins at about 86°, with simultaneous sublimation. The abrupt weight loss ends at about 165° and the residue begins to oxidize. The final decomposition occurs above 250° /Fig. 1/.

2. *Cadmium(II) salicylaldoximates*

Bis/salicylaldoximato/cadmium/II/ begins to decompose at 295° /260°/ when one salicylaldoxime molecule is left /curve 1, Fig. 2/. The theoretical weight loss is 35.7%, but the TG curve shows only 28% /29.6%/. This is obviously due to the decomposition of the evolved salicylaldoxime and all decomposition products have not left before the beginning of the evolution of the second salicylaldoxime ion. The infrared spectrum of the intermediate /Table 2/ points to this. In the reaction

$$(C_7H_6O_2N)_2Cd \longrightarrow (C_7H_6O_2N)(CN)Cd + C_6H_6O_2 \quad /1,2\text{-dihydroxybenzene}/$$

$$/\text{or } C_6H_6O + O/$$

the theoretical weight loss is 28.6%. However, not 1,2-dihydroxybenzene, but 1-hydroxybenzene was found in the mass spectrum.

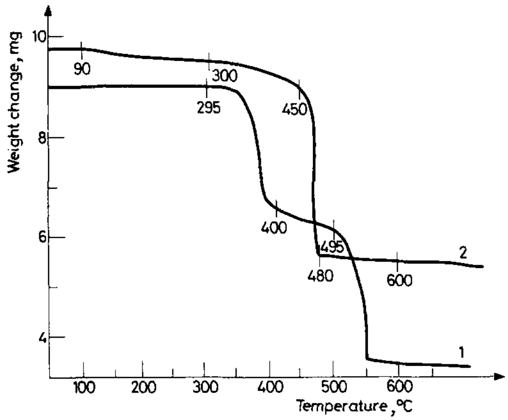

Fig. 2. TG curves of cadmium/II/ salicylaldoximates in static air atmosphere. Heating rate 5 deg min^{-1}. Curve: 1, $(C_7H_6O_2N)_2Cd$; 2, $(C_7H_5O_2N)Cd$.

The intermediate, primarily mono/salicylaldoximato/cadmium/II/, is not so stable as that of lead/II/, and decomposes immediately. A rapid decomposition continues at 495° /440°/. Cadmium obviously catalyzes the oxidation, in contrast to lead. The theoretical oxide level /CdO/ is 33.4%, and that found from the TG curve is 38.2% /35.9%/ at 600° /500°/. The results reasonably parallel the earlier ones obtained with a Chevenard thermobalance for 340 mg of the compound [6].

A slow decomposition of mono/salicylaldoximato/cadmium/II begins at 90° /60°/ and a rapid one at 450° /400°/. A value of 55.7% /53.2%/ is obtained for the oxide level above 650°, compared with the theoretical 51.9% /curve 2, Fig.2/.

The analogy of the TG curves shows that mono/salicylaldoxymato/cadmium/II/ is formed as an intermediate in the decomposition of bis/salicylaldoximato/cadmium/II/, although not so clearly as the formation of the mono salt from bis/salicylaldoximato/ lead/II/.

The DTG curves exhibited only peaks correspodong to the breaks in the TG curves of both cadmium/II/ salicylaldoximates. The DTA curves showed the processes to be exothermic.

3. Lead(II) salicylaldoximates

Bis/salicylaldoximato/lead/II/ decomposes between 200° and 255° to mono/salicylaldoximato/lead/II/:

$$(C_7H_6O_2N)_2Pb \longrightarrow (ON{=}CH{-}C_6H_4{-}O)Pb + C_7H_7O_2N$$

The weight loss is 24.1%, theoretically 28.6% /curve 1, Fig.3/. This intermediate was shown by IR spectrum to be indentical with the synthetized compound $(C_7H_5O_2N)Pb$. The weight loss between 353° and 370° was 2.7% /3.7%/, corresponding to the escape of one water molecule per two chelate molecules:

$$2\ (C_7H_5O_2N)Pb \longrightarrow (N{\equiv}C{-}C_6H_4{-}OPb)_2O + H_2O$$

The theoretical value is 2.6%. The further decomposition continues slowly from 438° and the oxide level /PbO/ is reached at 700° /600°/. The residue was 50.8% /47.3%/, theoretically 46.6%.

The results differ to some extent from those obtained with 350 mg samples of the chelate [6]. The main reasons for the observed differences /in the temperature ranges/ are obviously the reactions vessels used /Pt cup and porcelain crucible [6]/ and the sample amounts /8.7 and 350 mg [6]/.

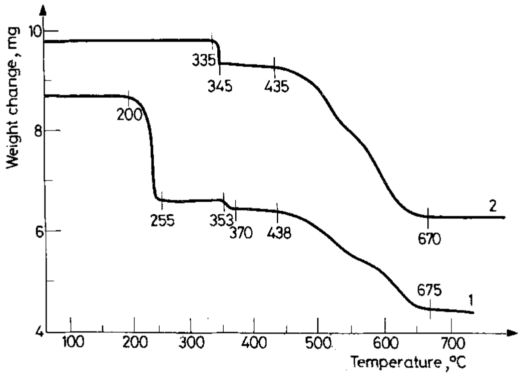

Fig. 3. TG curves of lead/II/ salicylaldoximates in static air atmosphere. Heating rate 5 deg $\min^{-1}$. Curve: 1, $(C_7H_6O_2N)_2Pb$; 2, $(C_7H_5O_2N)Pb$.

Mono/salicylaldoximato/lead/II/ decomposes abruptly at 335° /310°/ with a weight loss of 5.4% /3.3%/, corresponding to the escape of one water molecule and one oxygen atom per two chelate molecules /curve 2, Fig. 3/:

$$2\ (C_7H_5O_2N)Pb \longrightarrow (N \equiv C\text{-}C_6H_4\text{-}OPb)_2 + H_2O + 0.5\ O_2$$

The theoretical weight loss is 5.3%. The intermediate is stable between 345° and 435° and then decomposes slowly between 435° and 670° /600°/. The oxide level /PbO/ is 63.9%, theoretically 65.2%.

The DTG curves showed peaks corresponding to the weight losses indicated by the TG curves, the final decomposition process of mono/salicylaldoximato/lead/II/ in both cases /curves 1 and 2, Fig. 3/ occurring in two steps. The DTA curves implied that all processes are exothermic.

B. Gas chromatographic and mass spectrometric data

1. *Salicylaldoxime*

Mass spectra of salicylaldoxime were taken both via the solid inlet and through the gas chromatograph in alcohol solution. The spectra were identical and showed the same mass peaks as earlier [8]. The temperature-dependent loss of water from the molecular ion is the main process [8]. When the temperature of the inlet system is lowered, the cleavage of water diminishes [16]. Under the ionization chamber conditions the molecular ion of salicylaldoxime may probably undergo the McLafferty rearrangement [8,17] to some extent, when an amine would be the end-product.

Salicylaldoxime was also pyrolyzed in a sand bath - cold finger system up to 320° to get a more trustworthy basis for the explanation of the thermal behaviour of the metal salicylaldoximates. The pyrolysis products dissolved from the cold finger in alcohol were analyzed gas chromatographically. Mass spectra were taken for each of the 5 peaks shown by the gas chromatogram /Fig. 4/. Peak number 5 appeared to be due to sublimed salicylaldoxime itself; only a small amount of this is decomposed, but the proportion decomposed increases with temperature.

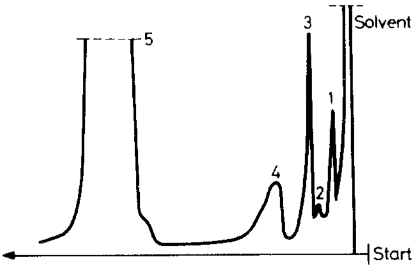

Fig. 4. Gas chromatogram of the condensed solid pyrolysis products of salicylaldoxime pyrolyzed to 320°. Column: stainless steel. Filling: OV-17. Own temp.: 140°. Carrier gas: He, 14 ml min^{-1}. H.W.D.: 200°.

The compound /m/e 210/ yielding peak number 1 could not be elucidated with certainty. The mass spectrum of peak number 2 showed it to be due to phenol. The mass spectra of peaks numbers 3 and 4 /salicylnitrile/ are presented in Fig. 5 and their cleavage schemes in Fig. 6 and in ref. [8]. The compound corresponding to peak number 3 in Fig. 4 is most probably formed

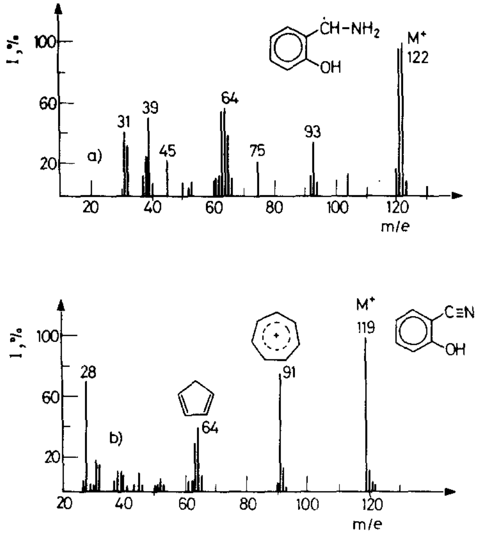

Fig. 5. Mass spectra of the compounds due to peaks numbers 3 and 4 /salicylonitrile/ in Fig. 4.

by the thermal loss of oxygen:

$$HO\text{-}N = CH - C_6H_4\text{-}OH \xrightarrow{-O} HN = CH - C_6H_4\text{-}OH$$

after which the cleavage scheme presented in Fig. 6 is possible.

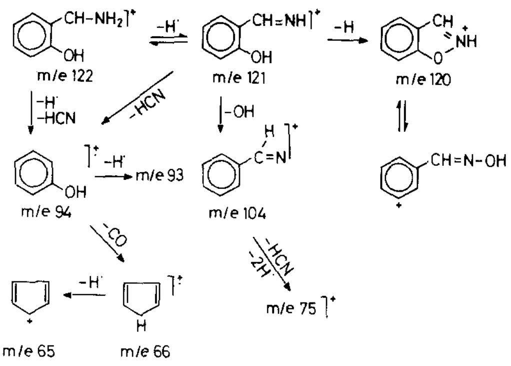

Fig. 6. Fragmentation scheme of the compound due to peak number 3 in Fig. 4.

The mass spectrum in Fig. 5, which differs from that presented for benzaldoxime [16], confirms that the compound in question is not benzaldoxime formed by the same process from salicylaldoxyme.

2. Chelates and intermediates

In spite of the use of low ionization energies and ionization chamber temperatures, a complete mass spectrum was obtained only for one of the chelates, mono/salicylaldoximato/lead/II/.

In the mass spectrum of bis/salicylaldoximato/cadmium/II/ the highest peak was observed at m/e 281. The compound contains one N atom and may be $N(CH_2-C_6H_3)_3$. This must be an adduct product of the ligands lost in the decomposition of $(C_7H_6O_2N)_2Cd$ and does not contain cadmium at all, because the peaks m/e 281-284 do not show the relative intensity relations /about 3:2:4:1/ corresponding to the relative abundances of the cadmium isotopes $^{112-114}Cd$ and ^{116}Cd. This is further confirmed by the peak m/e 207 and its neighbours. The initial part of the spectrum also shows salicylaldoxime (m/e 137) and its fragments (m/e 122, 119, 95) as cleavage products, but is additionally very complex, pointing in the above direction. The decomposition of $(C_7H_6O_2N)_2Cd$ in the ionization chamber tehrefore seems to differ from the described pyrolytic decomposition.

Mono/salicylaldoximato/cadmium/II/ also decomposed directly; the mass spectrum showed only the mass peaks of salicylaldoxime and is therefore not presented.

In the mass spectrum of bis/salicylaldoximato/lead/II/ /Fig. 7/, however, the mass peaks of the thermogravimetric decomposition products of the lead/II/ chelates were observed: the mass peaks of salicylonitrile (m/e 119) and phenol (m/e 94), the most stable products.

The mass spectrum of mono/salicylaldoximato/lead/II/ only showed the molecular ion peak at m/e 343 /Fig. 7/. The relationship between the relative intensities of the peaks m/e 341-343 is 1:1:2, corresponding to the relative abundance ratio of the lead isotopes $^{206-208}Pb$. The mass peaks of the suggested polymer m/e 222 and its possible degradation products are also seen in the spectrum. The early part of the spectrum includes mass peaks of salicylaldoxime fragments.

The mass spectrometric decomposition of the lead chelates corresponds well with the pyrolytic decomposition. However, the compounds with mass numbers m/e 122 and 210 found among the pyrolysis products are not observed in the mass spectra of the lead chelates.

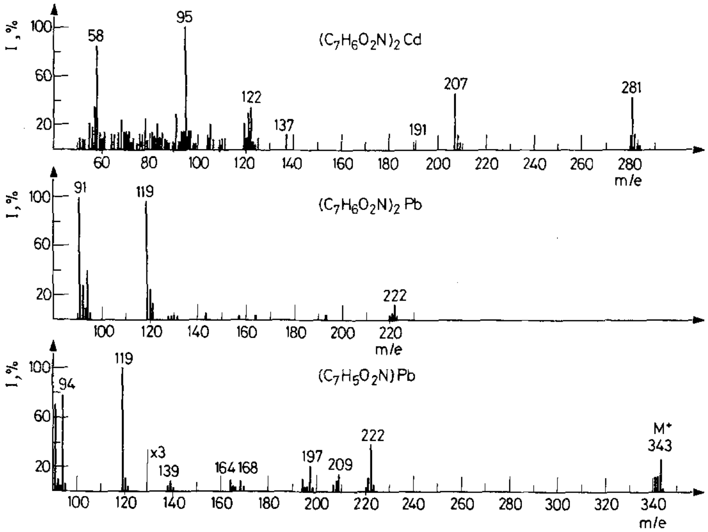

Fig. 7. Mass spectra of $(C_7H_6O_2N)_2Cd$, $(C_7H_6O_2N)_2Pb$ and $(C_7H_5O_2N)Pb$.

Bis/salicylaldoximato/cadmium/II/ was pyrolyzed up to the end-temperature of the escape of the first ligand molecule, 350° /curve 1, Fig. 2/. The pyrolysis products condensed on the cold finger were dissolved in alcohol and gave the gas chromatogram in Fig. 8.

The mass spectrum of peak number 1 of the gas chromatogram /Fig. 8/ revealed that the compound is the same as in the case of the lead chelate (m/e 210 in Figs. 11 and 12).

The mass spectrum of peak number 2 of the gas chromatogram /Fig. 8/ is seen in Fig. 9. The spectrum contains the peaks of phenol (m/e 94) and salicylonitrile (m/e 119), and two peaks at m/e 128 and 130, which remain unknown. The compounds must have been formed from fragments of salicylaldoxime.

Peak number 3 in Fig. 8 is due to the compound whose fragmentation is presented in Fig. 6. Salicylonitrile caused peak number 4. The amount of the compound due to peak number 5 was too low for a good mass spectrum. Salicylaldoxime initiated peak number 6 in Fig. 8.

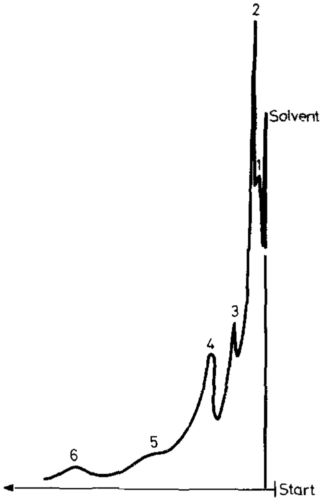

Fig. 8. Gas chromatogram of the condensed solid pyrolisis products of $(C_7H_6O_2N)_2Cd$ pyrolyzed to 350°. Drive conditions as in Fig. 4, except He 20 ml min^{-1} and H.W.D. 250°.

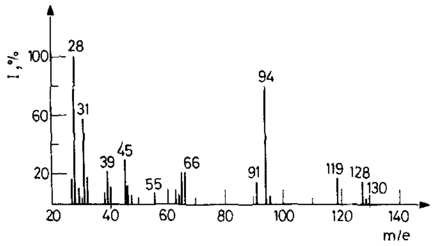

Fig. 9. Mass spectrum of the compound due to peak number 2 in Fig. 8.

As gaseous decomposition products of bis/salicylaldoximato/cadmium/II/, only CO_2 was found. Its amount remains almost constant to 200°, but increases abruptly to the end of the escape of the first salicylaldoxime molecule, then decreases, but after about 300° it increases steeply again, indicating the final oxidation of the chelate.

The compound with mass number m/e 130 was found as the only solid pyrolysis product of mono/salicylaldoximato/cadmium/II/.

As gaseous pyrolisis product again only CO_2 was observed, but at 200° the increase of the evolution pointed to the escape of possible impurities from the chelate. The final decomposition occurs above 300°, as expressed through the abrupt escape of CO_2.

A summary of the thermal and mass spectrometric decomposition processes of $(C_7H_6O_2N)_2Cd$ on the basis of the above results is presented in Fig. 10.

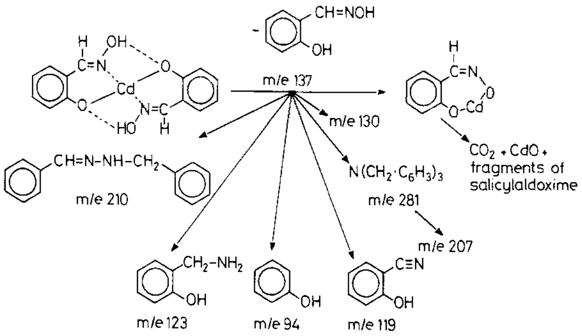

Fig. 10. Combined mass spectrometric and thermal decomposition scheme of $(C_7H_6O_2N)_2Cd$.

The pyrolisis of bis/salicylaldoximato/lead/II/ was performed to the end-temperature, 250°, of the loss of the first molecule of salicylaldoxime /curve 1, Fig. 3/. Mass spectra were taken from each peak of the gas chromatogram /Fig. 11/ of the alcohol solution of the solid pyrolisis products.

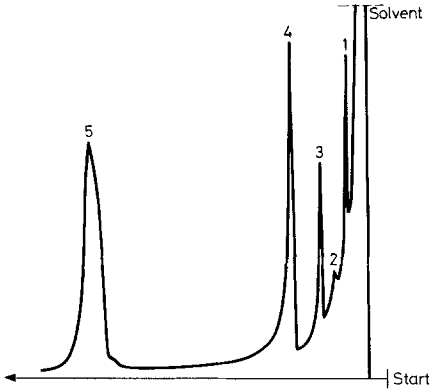

Fig. 11. Gas chromatogram of the condensed solid pyrolises products of $(C_7H_6O_2N)_2Pb$ pyrolyzed to 250°. Drive conditions as in Fig. 4, except own temp. 130°.

The compound producing peak number 1 /Fig. 11/ is obviously the same as that due to the first peak of the gas chromatogram /Fig. 4/ of the pyrolysis products of salicylaldoxime. The mass spectrum is given in Fig. 12, and its fragmentation scheme [18] in Fig. 13. The mass spectrum of peak number 2 in Fig. 11 showed it to arise from phenol. The mass spectra of the peaks numbered 3, 4 and 5 in Fig. 11 demonstrated that they are due to the compound m/e 121 /Figs 5 and 6/, salicylonitrile and salicylaldoxime, respectively.

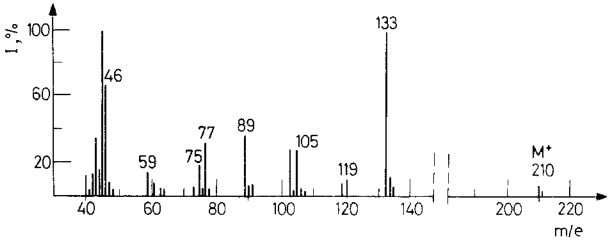

Fig. 12. Mass spectrum of the compound due to peak number 1 in Fig. 11.

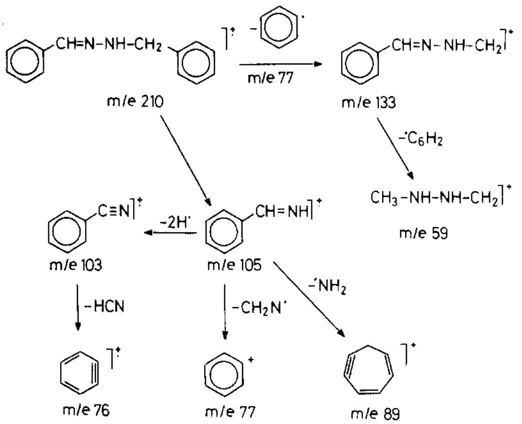

Fig. 13. Fragmentation scheme of the compound m/e 210.

From a comparison of the gas chromatograms in Figs. 4, 8 and 11 it is seen that among the evolved pyrolysis products of salicylaldoxime the ligand itself accounts for a predominant part, whereas in the case of the metal chelates its dominance is much lower. This stems from the higher pyrolysis temperatures of the latter.

The mass spectrum obtained via the solid inlet from the decomposition product evolved at 370° in the TG curve in Fig. 3 is given in Fig. 14. The compound is obviously a polymer formed through fusion of two salicylaldoximes, with molecular formula $C_{14}H_{10}N_2O$ (m/e 222). This compound is also observed in the mass spectra of both lead/II/ salicylaldoximates taken directly from the chelates via the solid inlet of the mass spectrometer. A further comparison of the mass spectra in Figs. 7 and 14 reveals that besides m/e 222 the spectra of the mono/salicylaldoximato/lead/II/ chelate and the polymer both include mass peaks at m/e 139, 164, 194 and 197. The peaks at m/e 91, 94 and 119 are observed in all spectra.

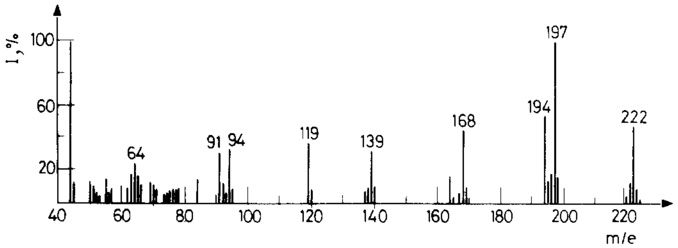

Fig. 14. Mass spectrum of the condensed solid decomposition product of $(C_7H_6O_2N)_2Pb$ at 375°. Product washed with alcohol, solid inlet.

Experiments showed that CO_2 begins to escape in greater amount from $(C_7H_6O_2N)_2Pb$ above 250°, suggesting that oxidation starts only during the process shown between 370° and 670° /curve 1, Fig. 3/ when the mentioned polymer also decomposes.

In the pyrolysis of mono/salicylaldoximato/lead/II/, phenol with m/e 94 appeared to be the only solid product on the cold finger. In this case too the abrupt evolution of CO_2 after 210° pointed to a similar end-decomposition as for bis/salicylaldoximato/lead/II/.

The combined decomposition scheme of bis/salicylaldoximato/lead/II/ may be presented on the basis of the preceding conclusions as given in Fig. 15.

C. Infrared spectra

The infrared spectra of the synthetized bis chelates in the spectral range 1650-350 cm^{-1} are given in Fig. 16. The observed absorption bands of the prepared compounds and isolated thermal decomposition intermediates with their suggested assignments are collected in Table 2. In the following the spectra are discussed, as divided into the ranges 4000-2000, 2000-900 and 900-250 cm^{-1}.

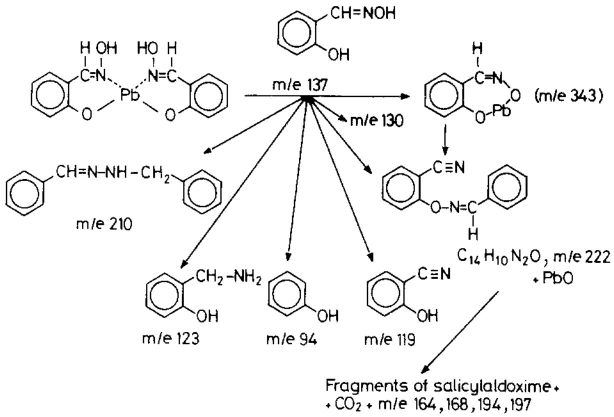

Fig. 15. Combined mass spectrometric and thermal decomposition scheme of $(C_7H_6O_2N)_2Pb$.

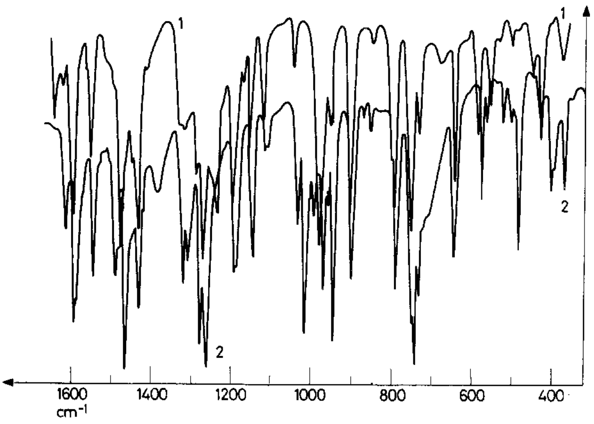

Fig. 16. IR spectra of $(C_7H_6O_2N)_2Cd$ and $(C_7H_6O_2N)_2Pb$ in the range 1650-350 cm^{-1}.

Curve: 1, $(C_7H_6O_2N)_2Cd$. The trans structure.

2, $(C_7H_6O_2N)_2Pb$. The cis structure.

Table 2

Infrared bands of salicylaldoxime, the synthetized salicylaldoximates and the thermal decomposition intermediates, and their assignments in the spectral range 4000-250 cm^{-1}

	Synthetized chelates				Intermediates		
$C_7H_7O_2N$	$(C_7H_6O_2N)_2Cd$	$(C_7H_6O_2N)_2Pb$	$(C_7H_5O_2N)Cd$	$(C_7H_5O_2N)Pb$	$(C_7H_5O_2N)Cd$ (400° C)	$(C_7H_5O_2N)Pb$ (370° C)	Assignment
cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	
	3502m						free OH
3420sh			3420wbr	3420vw,br	3400w	3430w,br	bond.OH
3380vs							str. OH
	3220w						str. CH
	3110w	3140w					-"-
	3060w	3050w	3050w	3060m	3060w	3055vw	-"-
	3005w	2980w	3010vw	3006m	3020sh	3015vw	-"-
	292oW	2880w		2960w	2930vw	2925vw	-"-
	2805w	2780w	2805vw				-"-
					2215w	2205s	str.C≡N
1950vw							def. CH
1910vw							-"-
1870vw							-"-
1790vw							-"-
	1645s				1630vw		str. C=C
							str. C=N
1615vs	1623w	1623s			1608vs		-"-
	1599vs	1599vs	1600vs	1598vs	1580vs	1595vs	-"- C=N-M
1573vs	1554vs	1552vs	1552s	1572vs			-"- C=C
				1538s	1546vs	1550m	-"-
1493vs	1478vs	1497vs					str. C=C
1470m	1447vw	1473vs	1468vs	1472vs	1472vs	1472vs	-"-
	1437vs	1437vs	1438vs	1433vs	1465vs	1447vs	str. C=N
1408vs	1410vw				1418m		str. OH

Table 2 /continued/

Synthetized chelates			Intermediates				
$C_7H_7O_2N$	$(C_7H_6O_2N)_2Cd$	$(C_7H_6O_2N)_2Pb$	$(C_7H_5O_2N)Cd$	$(C_7H_5O_2N)Pb$	$(C_7H_5O_2N)Cd$ (400° C)	$(C_7H_5O_2N)Pb$ (370° C)	Assign-ment
		1388m		1385vw	1390m	1378w	str. OH
			1353m	1340m			str. CO
		1327s					str. C-O
							str. M-O
1312w	1320w	1315m	1310sh	1317m	1310sh	1312s	-"-
1298vw	1290w	1282vs	1288s		1298vw		-"-
1288vs	1270vs	1268vs	1268vs	1281vs	1274vw	1270s	-"-
1260vs	1240s	1240sh	1242w	1248sh		1250w	str. OH
1235sh					1230vs		-"-
1212w	1200vs	1198vs	1205sh				benzene
1193m	1172w	1195vs	1191m	1190vs	1188vw	1180w	O-subst
1154s	1157s	1154vs	1152m	1153s	1147m	1153m	-"-
1113w	1127s	1122m	1120m	1122m		1103w	-"-
1037w	1046m	1042m	1040sh	1042m	1040vw	1032m	str. N-O
		1023vs					-"-
		1000m					-"-
990vs	981vs	974vs	980m,br	973vs			C=N-O
		963w					-"-
958s	953m	950vs	946w	947m			-"-
900vs	908vs	904vs	908vs	910vs	908w		C=N-O
		876w	870sh				-"-
858m	846w	857m	850sh	837w	863m	858s	-"-
787vs	795vs	797vs	811m		808w	815vw	-"-
			796m	796vs	796w		-"-
750m	753vs	751vs	758s	744vs	745vs	752s	str. CH
		742vs					-"-
738m	732s	737m	740s				-"-
718m		727vw		727vs	705vw	727w	-"-

Table 2 /continued/

	Synthetized chelates				Intermediates		
$C_7H_7O_2N$	$(C_7H_6O_2N)_2Cd$	$(C_7H_6O_2N)_2Pb$	$(C_7H_5O_2N)Cd$	$(C_7H_5O_2N)Pb$	$(C_7H_5O_2N)Cd$ (400° C)	$(C_7H_5O_2N)Pb$ (370° C)	Assignment
	673w				678m		str. CN
647vs	643vs	649vs	647m	647vs	655w	655w	C=N-O
	582s	582s	583m	582s	582m	570m	str. M-O
562w	553m	567m	550sh				str. M-N
	533vw	527m		540m	540w		str. M-O
	500w	506w	497m		495w	508w	-"-
490vw	485sh	487vs		487s			-"-
470s							str. C=C
							str. C=C
	447m				455vw		str. M-N
420vw	427s	432m	430sh			430w,br	str. M-O
		405s	412m	410s	400vw		-"-
	371m	371s		382s			-"-
	317w			308vw			-"-

Bond. = bonded, def. = deformation, str. = stretching, M = metal, o-subst. = ortho-substituted, br = broad, m = medium, sh = shoulder, s = strong, v = very, w = weak.

1. Synthetized chelates

Range 4000-2000 cm^{-1}

The OH stretching and CH vibrations of the benzene ring appear in this range /Table 2/. The broad OH stretching band at 3380 cm^{-1} indicates the inter- or intramolecular hydrogen bonding O...H-O- and N...H-O- of the ligands [19,20]. The hydrogen bond further causes a broadening and displacement of the band to lower frequency [19]. The OH stretching vibrations of the oxime group usually appear above 3500 cm^{-1} [21]. In the spectrum of $(C_7H_6O_2N)_2Cd$ an interesting stretching vibration band of the free OH group is seen at 3500 cm^{-1}. This shows that the cadmium chelate does not have as strong an intermolecular hydrogen bond O...H-O as the lead chelate, the spectrum of which does not contain the band at all.

The spectra of the monosalicylaldoximates in Table 2 show traces of OH vibrations, possibly due to moisture, at 3420 cm^{-1}. The CH stretching vibrations of the benzene ring [21a] appear in all spectra at 3000-3100 cm^{-1}. The CH vibrations of the carbon chain are probably just under 3000 cm^{-1} (Ref.[21a], p. 14).

Range 2000-900 cm^{-1}

This wavelength range contains the different C=N, C-O and N-O vibrations and the benzene ring vibrations. In the spectrum of salicylaldoxime /Table 2/ the C=N vibration [22] appears at 1615 cm^{-1} (Ref. [21], p.53) and the C=C vibration at 1573 cm^{-1} (Ref. [21a], p.79).

The IR spectrum of the product subliming at 220° from bis/salicylaldoximato/lead/II/ was in other respects similar to the present spectrum of salicylaldoxime and that of the Sadtler collection /Sadtler Catalog, IR spectrum No. 21072K /1971//, except that the OH band at 3400 cm^{-1} was weakened considerably and a sharp, medium band appeared at 1602 cm^{-1}, which is seen very strong in the spectra of all the salicylaldoximates /Table 2/. This points to dimerization of the sublimed salicylaldoxime through condensation via the oxime hydroxylic groups. Therefore, the band at about 1600 cm^{-1} may be assigned to the $>C = N-O-$ vibrations in the spectrum of the salicylaldoxime condensate, and to both $\rangle$C=N-O- and $\rangle$C=N-M- vibrations of the chelates.

A stronger and a weaker ring vibration are observed at 1493 and 1470 cm^{-1}, respectively (Ref. [21a], p.81). A strong band at 1410 cm^{-1} is due to the phenolic OH group. Bis/salicylaldoximato/lead/II/ has a medium band at this wavelength /1388 cm^{-1}/, but the others a weak or no band. The spectra of the chelates containing two ligands show no considerable transitions of the C=C and C=N bands. The bands of the spectra of the monosalicylaldoximates reveal a clear transition to lower frequencies.

The C-O stretching vibrations [22] appear at 1350-1200 cm^{-1}. This spectral range is interesting because it may be used to draw conclusions on the geometric isomerism of the chelates. The cis isomerism causes splitting of the band in this range [23]. A splitting of the 1312 and 1288 cm^{-1} bands of salicylaldoxime is observed in the spectrum of $(C_7H_6O_2N)_2Pb$ as very strong doublets at 1327, 1315 and 1282, 1268 cm^{-1}, respectively, but not for $(C_7H_6O_2N)_2Cd$ /Fig. 16 and Table 2/. This fact and the further bands at lower wavenumbers support the assumption that the salicylaldoxime ions are coordinated in cis positions to each other around the lead/II/ ion, whereas bis/salicylaldoximato/cadmium/II/ has the trans structure. This would also explain the strong intermolecular hydrogen bond in the lead/II/ chelate.

The bands between 1200 and 1050 cm^{-1} are due to the ortho--substituted benzene ring [19,24]. The N-O bond causes the bands in the range 1050-900 cm^{-1} (Ref. [24], p. 325). The band splittings in this range, strong triplets at 1042, 1023, 1000 and 974, 963, 950 cm^{-1}, in the spectrum of bis/salicylaldoximato/lead/II/ point again to the cis configuration [23].

Range 900-250 cm^{-1}

This range includes the bands of C-H vibrations of the benzene ring and those of metal-nitrogen and metal-oxygen bonds of the chelates. Salicylaldoxime and the chelates have both a very strong $\rangle$C=N-O band at 898-910 cm^{-1} and the C-H deformation vibrations of the benzene ring at about 800-700 cm^{-1} (Ref. [21a], pp. 74, 87). The strong band at 582 cm^{-1} in the spectra of all chelates must be due to the metal-oxygen bond [23]. The C=C vibrations of the benzene ring appear at 470 cm^{-1} for salicylaldoxime and around 490 cm^{-1} for the chelates (Ref. [24], p. 269). The strong band at 487 cm^{-1} in the spectra of the lead/II/ chelates is especially distinct.

The bands due to the metal-oxygen bond vibrations are probably at 430-370 cm^{-1} [23]. The band is split into a triplet for bis/salicylaldoximato/lead/II/ and into a doublet for the other salicylaldoximates. The triplet /432, 405, 371 cm^{-1}/ of bis/salicylaldoximato/lead/II/ again supports the cis configuration of the chelate [23].

The position of the metal-nitrogen bond vibration is uncertain, but the Cd-N stretching vibration band is probably at 553 cm^{-1} and that of the Pb-N stretching band at 567 cm^{-1}, if not in the group of the Pb-O vibration bands [19].

2. *Intermediates*

The thermal decomposition of $(C_7H_6O_2N)_2Cd$ differs from that of $(C_7H_6O_2N)_2Pb$ in so far as the monosalicylaldoximate was not confirmed as a pure intermediate at 400°, due to its higher instability /Table 2/. The infrared spectrum of the first intermediate formed in the thermal decomposition of $(C_7H_6O_2N)_2Pb$ at 255° verified it to be identical with the synthetized mono/salicylaldoximato/lead/II/ /Table 2/. The micro combustion analyses of the intermediate also confirmed the identity /$(C_7H_5O_2N\ Pb)$ /intermediate at 370°/. Found: C. 24.00; H, 1.47; N, 3.84. cf. Table 1/.

The spectrum of the intermediate obtained at 400° in the decomposition of bis/salicylaldoximato/cadmium/II/ differs almost entirely from that of the synthetized mono/salicylaldoximato/cadmium/II/ /Table 2/. It shows a weak cyanide band at 2215 cm^{-1}, pointing to some extent to the formation of a cadmium/II/ salicylaldoximate cyanide complex.

The spectra of the second intermediate /at 370°/ of bis-/salicylaldoximato/lead/II/ and of the intermediate at 357° of mono/salicylaldoximato/lead/II/ were similar, showing the strong $-C\equiv N$ band at 2205 cm^{-1}. Both intermediates indicate a nitrile bond /2205 cm^{-1}/ and C=N and Pb-O bonds. The vibrations of the benzene ring appear at normal places, 1472 and 1447 cm^{-1}. The C-O vibrations around 1300 cm^{-1} are seen as more weakly split. The N-O vibration at 1000 cm^{-1} has disappeared. The strong band at 858 cm^{-1} is assigned to the Pb-O bond and supports the presented alternatives of the compositions [25].

CONCLUSION

During the preparation of the chelates it was found that particularly cadmium/II/ forms chelates with difficulty. This is due to the weak ionization tendency of the aldoxime hydroxylic proton. Its ionization requires so high a pH that the metal may be precipitated as hydroxide. The IR spectra and TG curves of the chelates, however, showed the absence of metal hydroxides.

The decomposition temperatures shown by the TG curves, 295° for bis/salicylaldoximato/cadmium/II/ and 200° for bis-/salicylaldoximato/lead/II/, support the view that the former has the trans structure and the latter the cis structure, because the cis form is in general observed to be thermally less stable.

These conclusions on the structures of the chelates are also based on the nature of the infrared bands of the chelates, especially in the spectral ranges 1330-1260, 1050-1000, 910-780, 760-720 and 440-370 cm^{-1},

The difference in the configurations may in part be due to the different thermal decomposition behaviour of bis/salicylaldoximato/cadmium/II/ and lead/II/. The first decomposition period generally corresponds to the escape of one salicyalaldoxime molecule from the bissalicylaldoximates. This was confirmed in particular for bis/salicylaldoximato/lead/II/ by recognizing the decomposition products of the salicylaldoxime and lead/II/ chelate to be the same, the infrared spectra of the intermediate and synthetized mono/salicylaldoximato/lead/II/ to be identical, and from the micro combustion analyses results of the intermediate. For the second ligand escape various results were obtained by calculations from the TG curves. In this stage the lead/II/ salicylaldoximates were considered to decompose to some extent differently. This conclusion is supported by the IR and mass spectra of the intermediate at 370° in the TG curve. The mass spectra of the lead/II/ chelates include the mass peaks of a polymer, concluded to be $C_{14}H_{10}N_2O$ (m/e 222).

The mass spectrum of mono/salicylaldoximato/lead/II/ was the only one which showed the molecular ion peak (m/e 343) besides the mass peaks of the ligand. The decomposition scheme of the lead/II/ salicylaldoximates was therefore elucidated more thoroughly depending on the stability of mono/salicylaldoximato/lead/II/. Metallic lead seems not to catalyze the oxidation of the organic part, in contrast to cadmium.

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ZUSAMMENFASSUNG - Aufgrund der Zersetzungstemperatur und der Infrarotspektrum werden Cadmium(II)- und Blei(II)-bisalicylaldoximate als Verbindungen mit trans- bzw. cis-Struktur angesehen. Im ersten Schritt wird Bis(salicylaldoximato)-blei(II) unter Abspaltung eines Ligandmoleküls zersetzt, die Zwischenverbindung ist jedoch nicht stabil und zersetzt sich sofort weiter. Die Oxydation des Endproduktes ist eine schnelle exotherme, wahrscheinlich durch metallisches Cadmium katalysierte Reaktion. Das Massenspektrum von $(C_7H_6O_2N)_2Cd$ *weist auf ein Zersetzungsschema hin, das sich von dem aus den pyrolytischen Zersetzungsprodukten abgeleiteten unterscheidet. Dies ist möglicherweise auf einen katalytischen Effekt der Ionisa-*

tionskammer zurückzuführen. Die thermischen Eigenschaften von $(C_7H_5O_2N)Cd$ *unterstützen diese Auffassungen. Aus den TG-Kurven ist zu ersehen, dass die Zersetzungen von Mono(salicylaldoximato)-blei(II) und des Zwischenproduktes von Bis(salicylaldoximato)-blei(II) ähnlich sind. Massenspektren der Chelate bestätigen die Bildung des gleichen Polymers (m/e 222) bei der Zersetzung beider Verbindungen. Nur im Massenspektrum von* $(C_7H_5O_2N)Pb$ *tritt der Molekularpeak (m/e 343) auf. Die Zersetzungsschemata der Salicylaldoximate von Blei(II) sind deshalb genauer aufgeklärt. Metallisches Blei scheint die Oxydation der organischen Komponente nicht zu katalysieren.*

Резюме - На основании температур разложения и инфракрасных спектров бис-салицилальдоксимов двухвалентных кадмия и свинца сделано заключение, что оба комплекса имеют, соответственно, структуры с транс- и цис-конфигурацией. Первая стадия термического разложения кадмиевого комплекса подобна свинцовому и заключается в потере одной молекулы лиганда, но образующийся при этом промежуточный продукт неустойчив и сразу же разлагается. Окисление конечного продукта протекает быстро и, возможно, что эта экзотермическая реакция катализируется металлическим кадмием. Масс-спектр бис-салицилальдоксима кадмия указывает на процесс разложения, который отличается от того, что было установлено на основе пиролиза продуктов разложения. Это может быть обусловлено каталитическим влиянием ионизационной камеры. Термические свойства моносалицилальдоксима кадмия подтверждают предыдущие мнения. ТГ-кривые показали подобность разложения моносалицилальдоксима свинца и промежуточного продукта разложения бис-салицилальдоксима свинца. Масс-спектры обоих хелатов на образование при их разложении того же самого полимера с массовым числом 222. Только масс-спектр моносалицилальдоксима свинца показывает пик с массовым числом 343. Поэтому схемы разложения салицилальдоксимов свинца были определены более точно. Очевидно, что металлический свинец не катализирует окисление органической составляющей комплекса.