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THERMOANALYTICAL INVESTIGATIONS ON TRANSITION METAL 2,4-DICHLOROPHENOXYACETATES

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Solvates of metal 2,4-dichlorophenoxyacetates were investigated by means of DSC and simultaneous TG–DTA. The desolvation temperatures are influenced by the nature and quantity of the solvent molecules, both dependent on the nature of the metal cation and the solvent medium applied for the preparation of the salts.

Substituted phenoxyacetic acids, and especially 2,4-dichlorophenoxyacetic acid, are well known to be efficient herbicides. To complement investigations on the relations between structure and biological activity and the dependence of the macroscopic properties on the conditions of preparation, particularly of copper(II) 2,4-dichlorophenoxyacetate, $Cu(DCPA)_2$, recent publications reported studies on metal complexes of phenoxyacetic acids, mainly by means of IR and ESR spectroscopy.

The general structure of the metal salts of 2,4-dichlorophenoxyacetic acids is shown in Fig. 1. Recently, we found that the actual structure of the complex substituted metal phenoxyacetates depends on

— the nature and quantity of ligands *L* (here, the ligands are additionally bound solvent molecules) [2, 5];

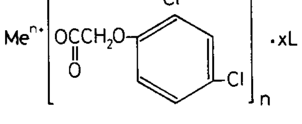

Fig. 1 Structure schema of metal 2,4-dichlorophenoxyacetates

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— the substituents on the aromatic ring [1, 3, 4];

— the thermal pretreatment [1, 3].

For example, we proved the existence of mono- and dinuclear complexes [6, 7]. The effects of ligands and heating were demonstrated by the colour of the compounds. Copper 2,4-dichlorophenoxyacetate freshly precipitated from aqueous solution is blue. The drying process causes a change to turquoise and finally to light-green. If the compound is precipitated from tetrahydrofuran solution, it exhibits and ultramarine colour. The precipitate obtained from a mixture of tetrahydrofuran and water is greenish in colour.

This work deals with the thermal properties of metal 2,4-dichlorophenoxyacetate solvates $M(DCPA)_2 \cdot L_x$ at temperatures below that of decomposition of the DCPA anion.

Experimental

The compositions of samples precipitated from different solutions, and the methods of investigation, are listed in Tables 1 and 2, respectively. Prior to thermal analysis, the samples were dried to constant weight at room temperature. Differential thermal analysis (DTA) and thermogravimetric (TG) investigations were performed simultaneously with a derivatograph. They were complemented by differential scanning calorimetric (DSC) and simultaneous evolved gas analytical

Table 1 Solvates obtained by precipitation from different media

Precipitating medium	Quantity and kind of ligands							
	Cu	Cu*	V	Cr	Mn	Fe(II)	Co	Ni
Water	5 H_2O		3 H_2O	3 H_2O	2 H_2O	2 H_2O	5 H_2O	4 H_2O
THF	5 THF	0.5 THF						
THF-water	1 THF				2 H_2O	—		
Ethanol-water	1 EtOH +4 H_2O				2 H_2O	2 H_2O		
Dioxane-water	1 Diox.		3 H_2O	—	2 H_2O	1 H_2O	5 H_2O	5 H_2O
DMF-water	3 H_2O +1 DMF				2 H_2O	1 H_2O +1 DMF		

Explanations: Cu* = preparation from anhydrous copper(II) sulphate; THF = tetrahydrofuran; DMF = N,N-dimethylformamide.

Table 2 Methods of investigation applied to the various samples

Precipitating medium	Metal		2,4-dichlorophenoxyacetates					
	Cu	Cu*	V	Cr	Mn	Fe(II)	Co	Ni
Water	2		2	2	2	2	2	2
THF	2	2						
THF-water	2				1	1		
Ethanol-water	2				1	1		
Dioxane-water	2		2	2	2	2	2	2
DMF-water	2				1	1		

Explanations: Cu* = preparation from anhydrous copper(II) sulphate; THF = tetrahydrofuran; DMF = N,N-dimethylformamide; 1 = DSC only; 2 = DSC and simultaneous TG–DTA.

Table 3 Conditions of measurement

	DSC	Simultaneous TG–DTA
Weight of sample	5 mg	100 mg
Heating rate	8 deg/min	3 deg/min
Temperature range	30–200°	25–300°
Crucible material	aluminium	platinum
cover	perforated lid	lid (not fixed)

(EGA) measurements, using a Perkin–Elmer DSC 1 b instrument with a built-in thermal conductivity detector (rinsing gas: dried N_2). The experimental conditions are listed in Table 3. If water was the sole ligand, its loss could be monitored quantitatively by EGA after calibration of the detector via the dehydrations of copper sulphate pentahydrate and of copper(II) acetate monohydrate.

The compositions of the compounds were checked by chemical elementary analysis.

Results and discussion

Copper 2,4-dichlorophenoxyacetate solvates

Figure 2 shows the DTA curves of compounds $Cu(DCPA)_2 \cdot L_x$ precipitated from different pure solvents and their mixtures. Without exception, all the thermal effects were endothermic. The weight losses taken from the simultaneously recorded TG curves (not reproduced here) and tabulated in Table 4 are considered in the interpretation of the DTA effects. The final temperatures of the TG steps

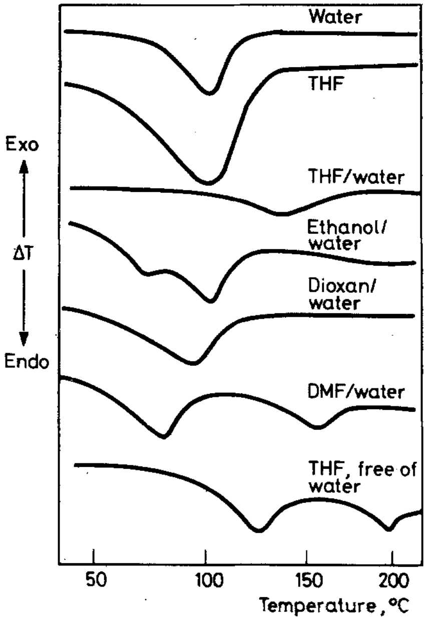

Fig. 2 DTA-curves of copper(II) 2,4-dichlorophenoxyacetates precipitated from different solvents

recorded in Table 4 are generally lower than the temperatures at which the DTA signals returned to their respective baselines. These deviations are methodologically due to the heat conduction through the sample and sample holder to the measuring thermocouple.

Table 4 Mass loss of copper(II) 2,4-dichlorophenoxyacetate solvates

Precipitating medium	Experimental, %	Temperature of mass loss, °C	Calculated, for %	mol	Elimination of solvent
Water	15	105	15.2	5	H_2O
THF	42	110	41.7	5	THF
THF-water	12	130	12.5	1	THF
Ethanol-water	10	80	10.3	1	EtOH
				+1	H_2O
	19	105	19.0	1	EtOH
				+4	H_2O
Dioxane-water	15	105	14.9	1	dioxane
DMF-water	9	80	8.6	3	H_2O
	20	105	20.2	3	H_2O
THF (anhydrous sample)	7	130	6.9	0.5	THF

From the thermoanalytical results, we draw the following conclusions:

The sample precipitated from aqueous solution loses 5 mol H_2O in two steps. 2 mol H_2O are liberated at as low as 60°. This is the reason why a trihydrate was found in former investigations, in which the samples were pre-dried at 60°.

The sample precipitated from THF solution gave the largest weight loss, caused by the literation of 5 mol THF. Due to its better resolution, the DSC curve exhibits two thermal effects, corresponding to the successive evolution of 3 and 2 mol THF, respectively.

The compound precipitated from a THF-water mixture loses 1 mol THF within a wide temperature range. This effect is observed as a shallow DTA peak.

A sample precipitated from an ethanol-water mixture exhibits two partially overlapping effects, which may be explained (in total) by the loss of 1 mol ethanol and 4 mol water. Within the first step 1 mol ethanol and 1 mol water are released, and within the second step the remaining 3 mol water.

A sample precipitated from a dioxane-water mixture released 1 mol dioxane. The binuclear nature of the dioxane complex was demonstrated previously [6].

From a mixture of the polar solvents water and N,N-dimethylformamide (DMF), we precipitated a complex $Cu(DCPA)_2 \cdot 3H_2O \cdot DMF$. Upon heating, this lost 3 mol H_2O at 60–80°, far below its boiling point, and 1 mol DMF at 100–160°. In our previous investigations, after drying at 60° we obtained a complex containing only 1 mol DMF as ligand.

The compound precipitated from a THF solution of anhydrous copper(II) sulphate is exceptional as it is white. The weight loss and endothermic effect between 80 and 150° are caused by the elimination of 0.5 mol THF. A second endothermic effect between 180 and 210° was not accompanied by any weight change. The explanation that this was due to melting of the compound was confirmed by observation through a hot-stage microscope. Quantitative evaluation of the DSC curve yielded a melting enthalpy of 23 kJ mol^{-1}. (All other copper(II) compounds melt immediately before their respective decompositions. The corresponding thermal effects were not separable, and melting enthalpies could not be determined.)

At the end of heating, all samples, as expected, had a light-green colour.

2,4-Dichlorophenylacetate hydrates of other metals

The DTA curves of the compounds $M(DCPA)_2 \cdot xH_2O$ ($M = VO^{2+}$, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}; and Ni^{2+}, Cu^{2+} for comparison), prepared from aqueous solution, ate shown in Fig. 3. Obviously, all these salts form hydrates. The different dehydration temperatures suggest that the water molecules are bound more or less strongly.

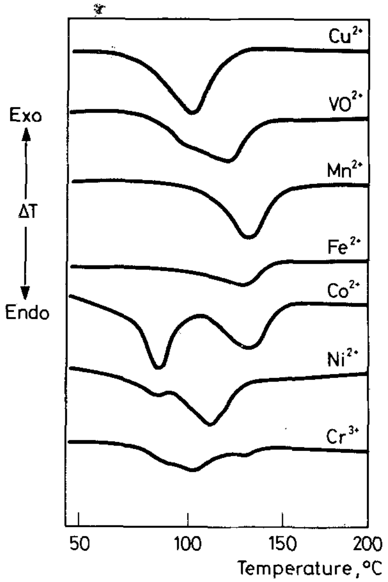

Fig. 3 DTA curves of different metal 2,4-dichlorophenoxyacetates precipitated from water

The vanadyl compound contains 3 mol H_2O. Upon heating, they are released in two poorly resolved steps. The dehydration enthalpy of 54 kJ per mol H_2O, clearly higher than the vaporization enthalpy (41 kJ mol^{-1}), points to the strength of the coordinate bond.

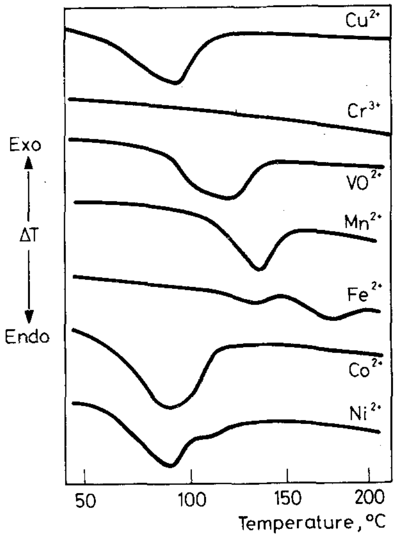

Fig. 4 DTA curves of different metal 2,4-dichlorophenoxyacetates precipitated from dioxan-water mixtures

Manganese(II) and iron(II) salts both exhibited one DTA effect. This is caused by the elimination of 2 mol H_2O. The two effects occur at the same temperature. Again, the enthalpy of dehydration was larger than 54 kJ per mol H_2O.

Both the cobalt and nickel salts show stepwise dehydration. $Co(DCPA)_2 \cdot 5H_2O$ releases 3 mol H_2O below, and 2 mol H_2O above 100°. $Ni(DCPA)_2 \cdot 4H_2O$ evolved 1 mol H_2O below, and 3 mol H_2O above 100°.

Chromium(III) 2,4-dichlorophenoxyacetate crystallized with 3 mol H_2O. The water is lost at relatively low temperatures. The following endothermic effect at 130° is not accompanied by a mass loss; its origin is not yet known.

Metal complexes prepared from a dioxane-water mixture

The metal complexes precipitated from dioxane-water mixtures contain water as a ligand, with the exception of the copper(II) salt, which binds 1 mol of dioxane (as mentioned above), and the Cr(III) complex. Their DTA curves are presented in Fig. 4.

Neither the DTA nor the TG curves of the chromium(III) compound exhibit any thermal effect within the investigated temperature range. Accordingly, we conclude that the compound does not contain any ligand.

For the vanadyl and manganese(II) salts, we observed the same endothermic effects and weight losses as for the samples precipitated from water. This behaviour points to identical compositions, and this was confirmed by chemical analysis.

The iron(II) salt contains 1 mol H_2O, which is evolved at around 130°. The endothermic effect at around 180° is not accompanied by a weight change.

The cobalt(II) compound again contains 5 mol H_2O, but they are released in a single step. The dehydration is finished at a lower temperature (80°) than that for the precipitate from aqueous solution (130°).

5 mol H_2O are gound to the nickel(II) salt. 4 of them are liberated below 100°.

For the latter two hydrates precipitated from water-dioxane mixtures, the dehydration temperature is lower than that for the hydrate obtained from purely aqueous solution. This behaviour suggests that the presence of dioxane in the precipitating medium lowers the binding strength of water molecules.

Further solvates of metal 2,4-dichlorophenoxyacetates

The results described above were obtained by means of simultaneous TG–DTA for the most part, and confirmed by DSC investigations. A number of further 2,4-dichlorophenoxyacetates (Table 2) were studied by DSC exclusively. Here, we mention only the manganese(II) salts were obtained from water and from all solvent mixtures. The endothermic effects of dehydration were identical for all samples, suggesting that there are no differences in water binding between these hydrates.

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Zusammenfassung — Solvate von Metall-2,4-dichlorphenoxyacetaten wurden durch DSC und simultane TG–DTA untersucht. Die Temperatur der Freisetzung der Solvatmoleküle wird von ihrer Art und Menge beeinflußt, die ihrerseits von der Natur des Metallkations und dem zur Präparation der Solvate angewandten Lösungsmittel abhängen.

Резюме — С помощью ДСК и совмещенного метода ТГ и ДТА изучены сольваты 2,4-дихлорфеноксиацетатов металлов. Температуры десольватации затрагиваются природой и количеством молекул растворителя, которые в свою очередь зависят от природы катиона металла и растворителя, использованного для получения солей.