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PREPARATION OF TRANSITION METAL COMPLEXES OF STRONGLY BASIC LIGANDS BY THERMAL DECOMPOSITION

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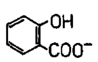
SUMMARY

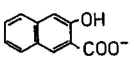
The usual stoichiometry of metal salicylates, 2-oxy-3-naphtholates, anthranilates and salicylaldoximates is $M^{2+}(HL^-)_2.xH_2O$. Heating such a solid in an inert atmosphere causes proton transfer between the two HL^--ligands and the following reaction takes place: $M(HL)_2(s) \longrightarrow ML(s) + H_2L(g)$. The new complex ML(s) (e.g. zincsalicylate) reacts with solid or dissolved monoprotic ligands HL' (e.g. 8-hydroxyquinoline) to form the mixed complex (e.g. zinc-salicylate-oxyquinolate) in excellent yield.

PREPARATIVE THERMAL DECOMPOSITION

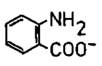
If transition metal salicylates (1) are precipitated in neutral or weakly acidic solution the stoichiometry of the precipitate is $M^{2+}(Hsal^-)_2.xH_2O$. $M^{2+}Sal^{2-}$ can not be prepared in aqueous solution, because the phenol group is too weak an acid (pK = 13.4) and therefore metal hydroxide will precipitate rather than metal salicylate. By analogy 2-oxy-3-naphtholat(2), anthranilate(3) and salicylaldoximate(4) will form $M(HL)_2.xH_2O$ and not ML.



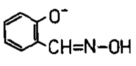
(1)
$Hsal^-$



(2)
$Hnapht^-$



(3)
$Hanthran^-$



(4)
$Hsalox^-$

But ML can be prepared by heating $M(HL)_2.xH_2O$ in a flow of argon. The general scheme of the reaction A

$$M(HL)_2.xH_2O(s) \longrightarrow M(HL)_2(s) + H_2O(g) \longrightarrow ML(s) + HL(g) \qquad (A)$$

is illustrated by the formation of zinc salicylate, fig. 1.

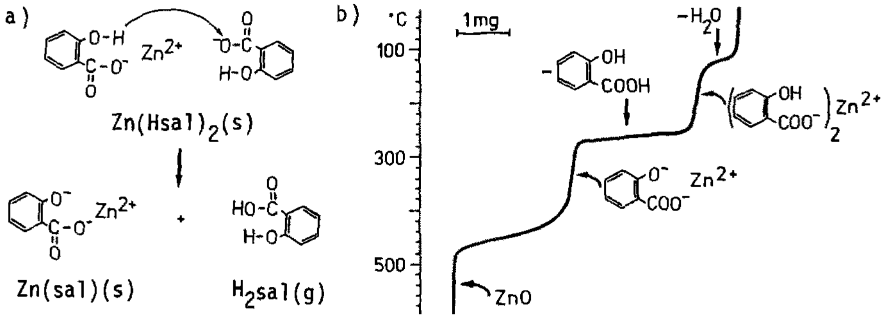


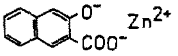
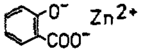
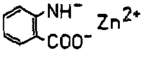
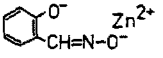
Fig. 1 Thermal decomposition of $Zn(Hsal)_2.2H_2O$ yielding Zn(sal).
a) Reaction scheme b) Thermogravimetric trace

The thermal decomposition of $Ni(Hsal)_2.4H_2O$ (ref. 1), $Fe(Hsal)_2.2H_2O$ (ref. 2), $M(Hanthran)_2$ (M = Ni, Cu, Zn (ref. 3)) and of $M(Hsalox)_2$ (M = Co, Ni, Cu (ref. 4)) has been studied before, and our extension of these studies confirms the previous results.

By thermogravimetry we observed that the following compounds behaved as described in reaction (A): $M(Hsal)_2$ (M = Mn, Co, Ni, Zn, Ca, Mg); $Zn(Hnapht)_2$; $M(Hanthran)_2$ (M = Zn, Cd); $M(Hsalox)_2$ (M = Zn, Cd). Particular emphasis was on the zinc complexes where it was confirmed by masspectrometry for all four ligands that $H_2L(g)$ was the main species leaving the complex at around 200 - 300°C and where ZnL was prepared on a preparative scale allowing elemental analysis of the product (table 1).

TABLE 1

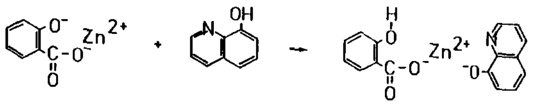
Elemental analysis of ZnL.

								
	calc.	found	calc.	found	calc.	found	calc.	found
Zn	32.44	32.07	26.0	25.7	32.6	31.1	32.6	33.7
C	41.68	40.71	52.5	52.6	41.9	41.7	41.9	41.0
H	1.98	1.96	2.38	2.28	2.49	2.43	2.49	2.52
N	-		-		6.98	6.94	6.98	6.27

IR spectroscopy showed that the O-H streching vibration at 3100 - 3600 cm^{-1} disappeared when $Zn(HL)_2$ was converted into ZnL. $Zn(Hanthran)_2$ has two bands in this region of interest, one at 3300 cm^{-1} and one at 3140 cm^{-1}. In Zn(anthran) the one at 3140 cm^{-1} has disappeared while the other one is shifted to 3290 cm^{-1}.

PREPARATION OF MIXED COMPLEXES

The complexes ML are solids with inherently very basic properties. They should therefore react with a ligand HL' having an acidic proton to form M(HL)(L'). Indeed, when a suspension of Zn(sal) was stirred over night at 70°C in a toluene solution of oxyquinoline the complex Zn(Hsal)(oxyquinolate) was formed.



By analogy, when reacting Zn(anthran) with oxyquinoline in toluene we obtained Zn(Hanthran)(oxyquinolate) and heating a tablet of a stoichiometric mixture of Zn(anthran) and 2-aminophenol for 15 hours to 160°C yielded Zn(Hanthran)(2-aminophenolate). By X-ray powder diffraction (fig. 2) it was verified that the products were not merely a mixture of $Zn(HL)_2$ and $Zn(L')_2$ but Zn(HL)(L'). A further proof of the formation of Zn(HL)(L') consists of treating the product with a solvent which dissolves $Zn(L')_2$ as well as HL' but not Zn(HL)(L'). E.g. chloroform is a good solvent for oxyquinoline and $Zn(oxyquinolate)_2$ but the product of the reaction of Zn(sal) with oxyquinoline i.e. Zn(Hsal)(oxyquinolate) is only sparingly soluble in chloroform.

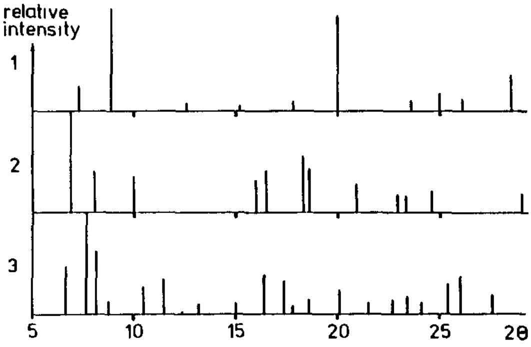


Fig. 2 X-ray powder diagrams. 1: Zn(Hsal)(oxyquinolate) 2: $Zn(oxyquinolate)_2$ 3: $Zn(Hsal)_2$.

The sequence of reactions

$$\begin{aligned} M(HL)_2(s) &\longrightarrow ML(s) + HL(g) \\ ML(s) + HL' &\longrightarrow M(HL)(L')(s) \end{aligned}$$

seems to be attractive for the preparation of many complexes containing two different ligands.

ACKNOWLEDGEMENT

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REFERENCES

1 K. Kishore and R. Nagarayan, Thermochim. Acta, 67 (1983) 351-60.
2 P. Kokkonen, L.H.J. Lajunen, A. Jaakkola and H. Ruotsalainen, Thermochim. Acta, 79 (1984) 289-298.
3 G. D'Aszenzo, A.D. Magri, E. Cardarelli and G. De Angelis, Thermochim. Acta, 13 (1975) 461-66.
4 P. Lumme and M.L. Korvola, Thermochim. Acta, 13 (1975) 419-39.