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STRUCTURE-THERMAL BEHAVIOUR STUDIES ON THE SALICYLATO COMPLEX OF COBALT

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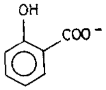
The salicylato complex of cobalt was synthesized and its structure established to be $[Co(sal)_2] \cdot 4\,H_2O$, where, sal =  , from elemental analysis, IR spectroscopy, magnetic susceptibility, cryoscopy and conductivity. The X-ray diffractogram of the complex has been given. Thermal decomposition has been studied in air by thermogravimetry (TG), differential thermal analysis and differential scanning calorimetry. TG shows three main steps of decomposition. The intermediates formed at various stages were collected and analysed. From the TG results and chemical analysis of the intermediates, a mechanism has been proposed for the thermal decomposition of the complex, leading to the oxide formation in the final stage.

Metal salicylates are a very important class of compounds and find application in many fields, e.g. as additives for controlling the burning rate behaviour of solid propellants [1] and in medicines [2]. Recently, these salicylates have been used as additives in polymer combustion processes [3]. In order to explain the mechanism of action of metal salicylates in various physicochemical processes, particularly in combustion, it is necessary to have a complete knowledge of the molecular structure and thermal behaviour of these compounds. From the above viewpoint, the present work has been carried out on cobalt salicylate.

Experimental

Preparation of the cobalt salicylate complex

Saturated solutions of $Co(NO_3)_2$ and sodium salicylate were mixed at room temperature, the ligand being in excess (1 : 3, 1 : 4, 1 : 5 molar ratios). The solutions were kept overnight to yield rose-red crystals of the salicylato complex. These were washed thoroughly and recrystallized from H_2O as rose-red crystals of the complex.

Analyses

a) *Estimation of Co.* Co was estimated volumetrically by titrating an aqueous solution of the complex against standard EDTA solution, using xylenol orange as indicator [4]. The percentage of Co was found to be 14.42.

b) *C and H analyses.* The C and H analyses were performed on a Coleman (U.S.A.) model 33 C—H analyzer. The percentages of C and H were found to be 36.01 and 4.48, respectively.

c) *Molecular weight determination.* The molecular weight was determined by cryoscopy, using a Beckmann thermometer. The molecular weight obtained was 131.

d) *Conductivity measurements.* The conductivity of the solution of the complex in H_2O ($\approx 10^{-3}$ M) was determined using a conventional conductivity bridge. The molar conductance was found to be 244.95 mho.

e) *X-ray diffractometry.* The X-ray diffractogram of the complex was taken on a Phillips X-ray diffractometer with a PW 1050/70 vertical goniometer, using MoKα radiation. The diffractogram is shown in Fig. 1. The cobalt salicylate X-ray diffractogram has not been reported in the literature.

f) *IR spectrum.* The IR spectrum of the complex was taken in KBr pellet, using a Carl-Zeiss Ur-10 infrared spectrophotometer.

g) *Magnetic susceptibility measurements.* The magnetic susceptibility of the complex was determined using a home-made Gouy balance, with a 'Mettler' single-pan balance of 0.00005 g accuracy and a holder arrangement for suspending

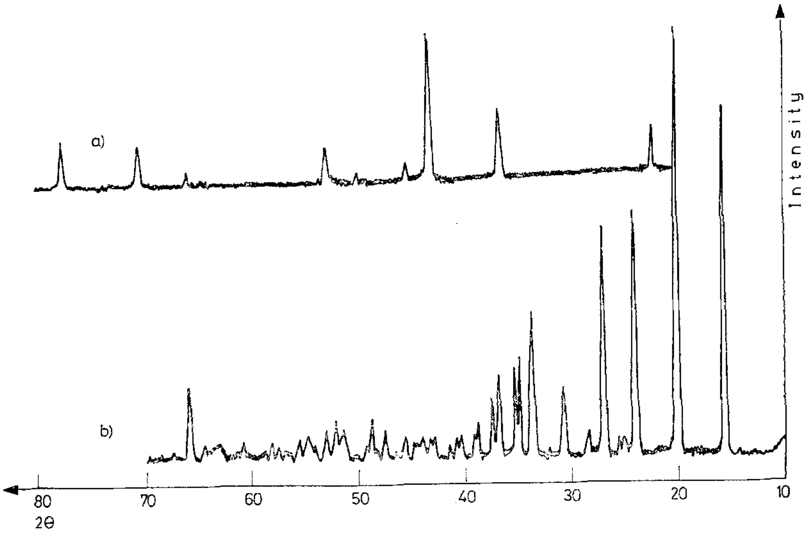


Fig. 1. X-Ray diffractograms of cobalt salicylate and its final decomposition product. A. Sample: final product of cobalt salicylate decomposition in air. Radiation CoKα(λ = = 1.7902 Å) Scan speed: 1° min^{-1}. B. Sample: Cobalt salicylate. Radiation: CoKα(λ = = 1.7902 Å). Scan speed: 2° min^{-1}

the Gouy tube. The length of the thread used for suspending the Gouy tube was so adjusted that the bottom of the tube was at the centre of the magnetic field. The well-powdered sample was packed uniformly in the tube and the length of the specimen thus packed was such that the top of the pack was above the magnetic field, i.e. in nil magnetic field. The weights of the sample in the presence and in the absence of the magnetic field were determined and the susceptibility was calculated. The molar paramagnetic susceptibility was found to be 5.02 BM.

h) *High-pressure liquid chromatography (HPLC).* The HPLC runs were made on a Waters Associates liquid chromatograph, using methanol + 2% water as the eluent. Cobalt salicylate was taken in a glass bucket and kept in a glass tube set in a furnace. The furnace temperature was maintained constant and the volatile products of decomposition at 200° and 400° were collected separately by absorbing in AR methanol. The mathanol solution was used in HPLC runs.

Thermal studies

The thermogravimetric analysis (TG) of the complex was carried out on a Stanton Redcroft model TG-750 thermobalance. Sample weight of about 7.0 mg was used in each run and the heating rate was 3° min^{-1}.

Differential thermal analysis (DTA) was done on a home-made assembly [5], using 85 mg of the sample. The T and ΔT outputs were recorded on a potentiometric recorder. The heating rate employed was 6°/min.

Differential scanning calorimetry (DSC) was performed on a Du Pont 990 model. 2–3 mg of the sample and a heating rate of 20°/min were used in each run.

Results and discussion

It was found by chemical analysis and X-ray diffractometry that the complexes obtained from the three compositions mentioned earlier (metal salt to ligand ratios of 1 : 3, 1 : 4 and 1 : 5) were identical.

The elemental analysis of the complex suggests that the formula is $CoC_{13}H_{19}O_{12}$. The C content showed the presence of two salicylate ions in the complex. The remaining atoms, H and O, must exist as H_2O. Hence, the tentative formula was assigned as $Co(C_7H_5O_3)_2 \cdot 4H_2O$.

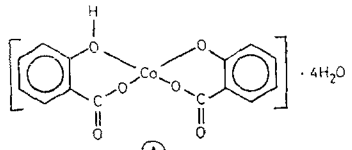
To determine whether the H_2O is coordinated or crystalline, information from the TG results was taken. The first step in the TG, which corresponds to the H_2O loss from the complex, is over at 97°. If the H_2O is coordinated, the weight loss would take place at a slightly higher temperature and hence the H_2O in the complex must be water of crystallization only. This is supported by the IR results, where the O–H stretching frequency suggests that the H_2O is crystalline H_2O.

That the salicylate is bidentate is shown by the fact that the phenolic O–H bending vibration is seen at 1345 cm^{-1}. If the phenolic O– is uncoordinated, the O–H bending vibration should occur at a slightly higher frequency.

The conductivity measurements show that the complex ionizes in H_2O to produce three ions (1 : 2 complex). This can be explained as due to the ionization of the phenolic –OH. This observation further explains the low molecular weight obtained by cryoscopy (131 instead of 405).

From the above observations, the structure of the complex may be assigned as

a)



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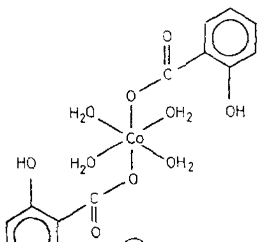
Recently, Gupta *et al.* [6] have studied the H-bonding in the salicylato complex of Co, and the structure of the complex is given as

b)



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where the complex is octahedral, the salicylate is monodentate and the H_2O is coordinated. However, our complex, though having the same molecular formula, is different from this one, as is clearly evident from the TG and IR data (discussed earlier). Thus, the structure of the complex obtained in the present investigation is A only and not B.

The TG of the complex shows that the decomposition occurs in three main stages (Fig. 2). The first stage corresponds to H_2O loss, which is accompanied

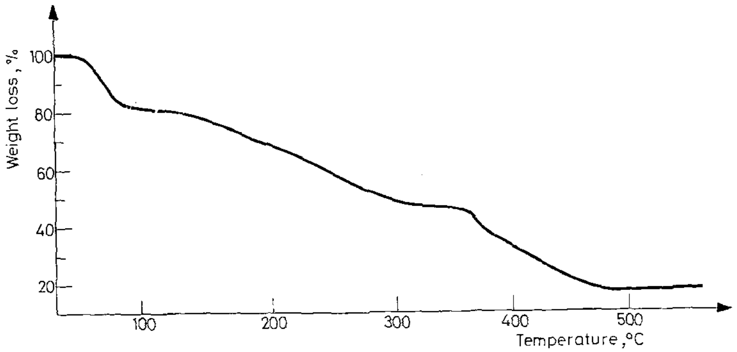
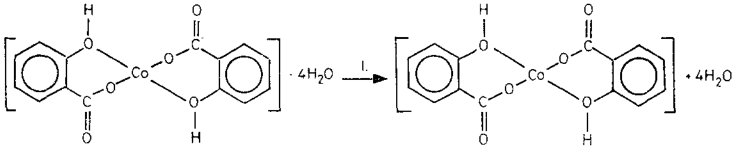


Fig. 2. TG trace of cobalt salicylate. Sample mass = 7 mg. Heating rate = 3° min^{-1}

by a colour change from rose-red to violet. The reaction can be given as

c)



In order to understand the nature of the intermediate formed during stage II, the furnace was maintained at 200° and the sample was taken in a glass bucket which was kept inside the tube as described earlier. The sample was heated to constant weights and the residue obtained (intermediate II_p) was analyzed chemically for the elements Co, C and H. The volatile products were taken in AR methanol and analysed by HPLC.

The smell of phenol was quite obvious and deposits of needle-like crystals were seen on the sides of the TG tube when the same decomposition was carried out in an open TG assembly [7]. These needles, which were suspected to be salicylic acid, were carefully collected (intermediate I) and subjected to DSC and IR analyses. The DSC and IR of pure salicylic acid were also performed and compared with those obtained for the volatile product. It was found that the two compounds

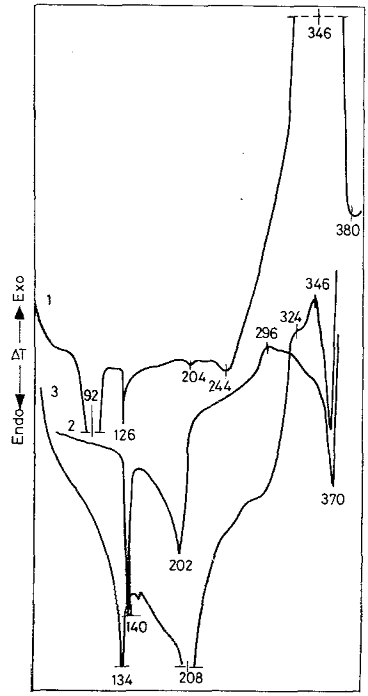
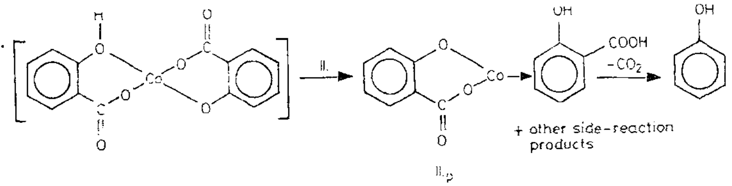


Fig. 3. DSC curves of various samples. 1) Co salicylate, 2) Salicylic acid (pure), 3) Volatile product from Co salicylate. Sample mass: 2—3 mg. Heating rate 20° min

were identical (Fig. 3). Thus, one of the volatile products in the 200° decomposition of Co salicylate is salicylic acid.

The elemental analysis of the intermediate II_p and the weight loss from the TG curve suggest that step II is nothing but the loss of one salicylate ion from the anhydrous complex. Hence, the reaction occurring in this step can be given as

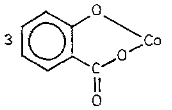
d)



The IR of the intermediate II_p in KBr lacks the O–H bending absorption at 1345 cm^{-1}, which gives further support to the structure (II_p) given above for the intermediate.

Step III seems to be the oxidation of the intermediate from step II to the oxide. The furnace mentioned earlier was maintained at 400° and the volatile products were collected and analysed by HPLC as before. Salicylic acid and phenol were formed in this step too. The chemical analysis, Ir and X-ray data show that the final product is Co_3O_4 (Fig. 1 and [8]). Thus, the reaction taking place here is

e)



$+ 2\,O_2 \rightarrow Co_3O_4 +$ other products

This mechanism receives complementary support from the DTA of the complex (Fig. 4). The first endotherm, with a peak temperature of 107°, corresponds to the H_2O loss. Immediately after this, there follows another broad endotherm, which ends at 298°. This process, when seen in conjunction with the TG of the complex, can easily be identified as the removal of the first salicylate ion from the

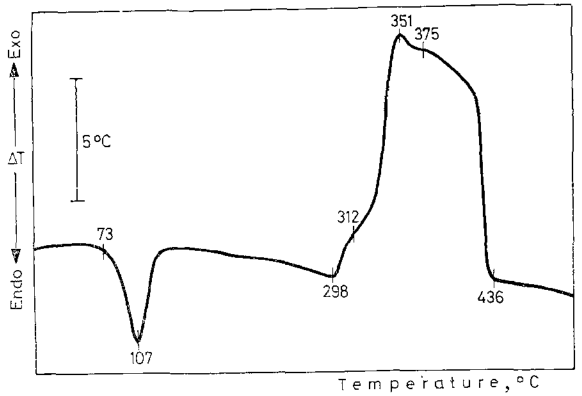


Fig. 4. DTA trace of Co salicylate. Sample mass = 85 mg. Heating rate = 6° min^{-1}

anhydrous complex to give II_p and salicylic acid, and this process should be endothermic. As soon as this process is over, a large exotherm is seen in the DTA, which is obviously the oxidation of II_p to give Co_3O_4. This oxidation should be highly exothermic. Thus, the DTA lends additional support to the mechanism proposed.

However, the decomposition seems to be quite complex when one considers the DSC of cobalt salicylate (Fig. 3). Apart from the three major peaks corresponding to the H_2O loss, the dissociation of the anhydrous complex and the oxidation of II_p, respectively, several other smaller peaks are observed, such as the endotherms at 126, 204 and 244°. These smaller endotherms are feebly visible in the DTA. These peaks are very small compared to the major peaks for which the mechanism has already been discussed above. These peaks are probably due to the various side-reactions occurring during the decomposition. The occurrence of such side-reactions is also revealed by the HPLC chromatograms (Fig. 5), where many other peaks are obtained than those for salicylic acid and phenol. Actually, the

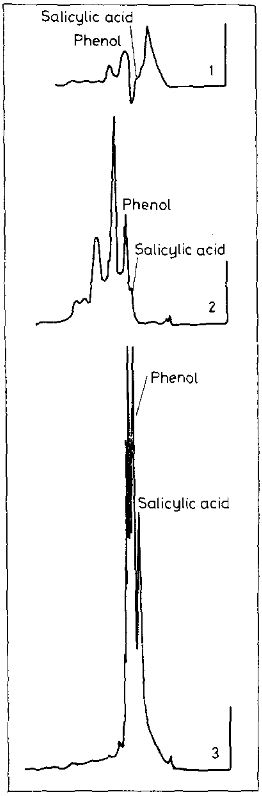


Fig. 5. HPLC chromatograms for cobalt salicylate decomposition. 1) Volatile products at 200°. 2) Volatile products for Co salicylate decomposition. 3) Synthetic mixtures containing phenol and salicylic acid. Eluent used: methanol +2% water

fact that one of the volatile products from 200° is a fluorescent material is seen from Fig. 5. The exact nature of these side-reactions, however, is not precisely known at present.

References

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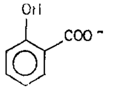
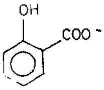
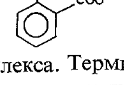
Résumé — On a effectué la synthèse du salicylate de cobalt complexe et établi sa structure $[Co(sal.)_2] \cdot 4H_2O$ où sal =  par analyse élémentaire, spectroscopie IR, susceptibilité magnétique, cryoscopie et conductivité. On donne le diffractogramme des rayons X du complexe. On a étudié la décomposition thermique dans l'air, par thermogravimétrie (TG), analyse thermique différentielle et analyse calorimétrique différentielle. La TG montre trois étapes principales de décomposition. On a prélevé et analysé les produits intermédiaires formés au cours des diverses étapes. A partir des résultats de la TG et de l'analyse chimique de ceux-ci, on propose un mécanisme pour la décomposition thermique du complexe qui conduit, lors de l'étape finale, à la formation d'oxyde.

Zusammenfassung — Der Salicylatkomplex von Kobalt wurde synthetisiert und seine Struktur als $[Co(sal.)_2] \cdot 4H_2O$ festgestellt, wobei  aus der Elementaranalyse, IR-Spektroskopie, der magnetischen Suszeptibilität, Kryoskopie und Leitfähigkeit bestimmt wurde. Das Röntgendiffraktogramm des Komplexes wird angegeben. Die thermische Zersetzung wurde in Luft durch Thermogravimetrie (TG), Differentialthermoanalyse und Differential-Scanning-Kalorimetrie untersucht. Die TG zeigt drei Hauptstufen der Zersetzung. Die sich in den einzelnen Stufen gebildeten Zwischenprodukte wurden gesammelt und analysiert. Aus den TG-Ergebnissen und der chemischen Analyse der Zwischenprodukte wurde ein Mechanismus der thermischen Zersetzung vorgeschlagen, der zur Oxibildung führt.

Резюме — Синтезирован салицилат кобальта и на основе элементарного анализа, ИК спектроскопии, криоскопии, измерений магнитной восприимчивости и проводимости этого комплекса, установили, что структура его должна соответствовать формуле $[Co(сал.)_2] \cdot 4H_2O$, где сал.  ионизованная салициловая кислота. Приведена дифрактограмма этого комплекса. Термическое разложение комплекса было изучено в атмосфере воздуха с помощью термогравиметрии (ТГ), термического анализа по производной и дифференциальной сканирующей калориметрии. ТГ измерения показали три главные стадии разложения. Промежуточные продукты, образующиеся на различных стадиях разложения, были собраны и подвергнуты анализу. На основе результатов ТГ исследований и химического анализа промежуточных продуктов, предложен механизм термического разложения комплекса, приводящего в конечной стадии к образованию окиси кобальта.