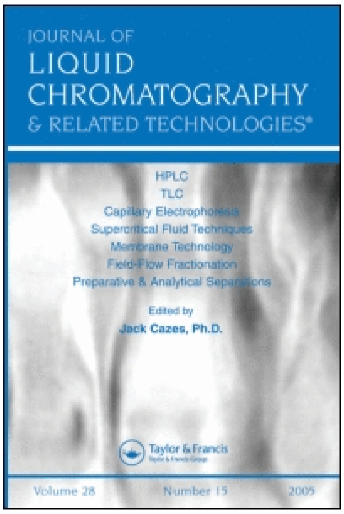

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G. Grassini-strazza[a]; M. Sinibaldi[a]; V. Carunchio[b]; A. Messina[b]
[a] CNR, Ist. di Cromatografia, Area della Ricerca di Roma, Stazione, C.P., Italy [b] Ist. di Chimica Analitica Università di Roma, Roma, Italy

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THIN LAYER CHROMATOGRAPHIC AND "IN SITU" SPECTROPHOTOMETRIC DETERMINATION OF PRODUCTS IN SOLID-SOLID THERMAL REACTION

G. Grassini-Strazza and M. Sinibaldi
CNR, Ist. di Cromatografia, Area della Ricerca di Roma
00016 Monterotondo Stazione, C.P.10 (Italy)
and
V. Carunchio and A. Messina
Ist. di Chimica Analitica Università di Roma
00185 Roma (Italy)

ABSTRACT

A method coupling thin layer chromatography and direct spectrophotometry is outlined. The visible spectra of the separated species were obtained by scanning, at constant intervals of wavelenght, the chromatographic plates in the reflectance mode. The method is applied to the determination of unknown products obtained in thermal solid-solid reactions between $[Co(bipy)_2(en)]Cl_3$ and NH_4Cl.

INTRODUCTION

In the thermal reactions of complexes in the solid state, further insight into the possible effect of the outer-sphere anion or of an added inorganic salt arises from the identification of the intermediate species formed before the decomposition process. Reflectance and/or IR spectra are frequently used for this purpose (1,2). However, these techniques proved to be very useful in the cases where only one species, having a spectrum very different from that of starting complex, was formed. In the other cases, owing to the overlap of the spectra of the reacting and produced compounds, it is difficult to discern whether two or more species are present. Chromatography appeared to be very suitable to separate all the species formed during the thermal reactions of some cobalt(III) complexes. In particular, evidence for stepwise ligand substitution was obtained by TLC (3), a technique providing the advantage of simplicity and allowing the simultaneous analysis of several samples. A further progress was to obtain the spectra of the chromatographically separated species "in situ" (4), instead of removing the zones with eluent. In solution, aquation and isomerization reactions may occurs, particularly in the cases where dichloro-species are formed as intermediate products; besides, the resulting solutions are often rather dilute to obtain significative spectra.

In the present paper the outlined method based on spectrophotometry "in situ" carried out after TLC separation is related in detail by reporting its application to the characterization of the products of the thermal reaction between $[Co(bipy)_2(en)]Cl_3$ and NH_4Cl (bipy= 2,2'-bipyridine; en=ethylenediamine).

EXPERIMENTAL

The complexes were prepared as described in the literature: cis -$[Co(bipy)_2Cl_2]Cl$ as reported by Jaeger et al. (5); $[Co(bipy)_3]Cl_3$ and $[Co(bipy)_2(en)]Cl_3$ as just outlined elsewhere(6).The procedure used for the thermal reaction was described in previous papers (3,4).NH_4Cl was used in a fifty-fold molar excess.

Thin Layer Chromatography

To achieve best separation conditions, very small samples volumes were used. Samples 0.1 - 0.2 μl) in 6N HCl-EtOH (1:5) solution (0.02M) were applied as a thin streak on 5x5 cm silica gel precoated plates (Merck , Darmstadt,West Germany).Ascending development to a height of about 2cm was performed in glass TLC tanks (7x3.5x7cm), by employing saturated aqueous LiCl-EtOH (1:2) as eluent. Before using,the plates were eluted first with 1M HCl-EtOH (1:5), then with H_2O-EtOH (1:5) in order to concentrate on the upper edge traces of iron,which interfere in the detection of cobalt(II) not complexed with 2,2'-bipyridine and/or ethylenediamine (thereafter indicates as Co(II)). The spots were detected by spraying with 20% ammonium sulphide solution.R_f values found: $Co(bipy)_3^{3+}$, near starting point; $Co(bipy)_2(en)^{3+}$,0.20; cis-$Co(bipy)_2Cl_2^+$,0.31. The spot corresponding to Co(II), which travels with the liquid front, is easily visible, owing to its blue colour. By spraying with ammonium sulphide it appears black.

Spectrophotometry

Owing to our specific goal,the slightly coloured separated compounds were not destroyed by a very sensitive detection reagent , as ammonium sulphide , but they were better visualized by sampling larger volumes (1-2 μl) of solution.Furthermore,instrumental procedure does not strictly agree with the optimized chromatographic conditions previously described. Samples had to be applied on the plates as round spots, providing to the light beam fall on the centre of the zone (higher concentration of solute). After the chromatographic separation, the spots were scanned directly on the plates with the KM-3 Chromatogram-Spectrophotometer (Carl Zeiss, West Germany) in the reflectance mode. The plates were scanned in a direction parallel to that of solvent flow . The spectrophotometer parameters were: $\Delta\lambda$, 10 nm; slit width, 0.1 mm; slit lenght, 3.5 mm; scanning speed, 50 mm min^{-1}.

Electrophoresis

High-voltage paper electrophoresis at 2000 volts was carried out in a Camag apparatus on Whatmann N°1 paper, using 0.25 M Na_2SO_4 as electrolyte (6,7).

RESULTS AND DISCUSSION

In order to obtain a rapid (about 15 minutes) and sharp separation, particular attention was paid to the chromatographic conditions. Thus some modifications were apported to conventional TLC and results comparable with those achieved by high-performance thin layer chromatography (HPTLC) were obtained. The conditions were as follow: 1) very small volumes (<0.5 µl), applied as a thin streak, of a solution of sample as dilute as compatible with detection limit. After development too, every single band resulted very narrow and a sharp separation between compounds having close R_f values, was achieved; 2) ascending development in small tanks. Saturation conditions were quickly attained and the results were well reproducible; 3) ascending development to a height of 2-2,5 centimeters only. The effect of the zone spreading seemed to be greatly reduced.

As regard to the spectrophotometry "in situ", preliminary experiments were performed in order to avoid, whenever possible, the difficulties reported for densitometric measurements of thin layer chromatograms of inorganic ions, as: problems arising from spraying the spots with chromogenic reagents; irregular shape of the spots after development; homogeneousness of the initial spot, depending on the quantity of accompanying salts present in the examined solution (8). The complexes under investigation are coloured ; they do not need to be visualized, as almost all inorganic ions, by chromogenic reagents whenever the concentration of the sample is sufficiently high. On the other hand, as the concentration increases, resolution is reduced. By employing 1-2 µl of 0.02 M solution good results were achieved. Besides the eluent did not modify the shape of the spots after development. In addition, the high concentration of LiCl and NH_4Cl present in the eluent and in the sample , respectively, did not trouble the spectrophotometric measurements.

The visible spectrum of the complexes was obtained, after development with the appropiate eluent, by scanning the chromatographic plates, in the reflectance mode in the range from 360 nm to 600 nm. As the apparatus gives readings at whatever established wavelenghts , we have performed the measurements at intervals of 10 nm . To obtain the spectrum of each separated species the peacks corresponding to each spot (identified by the R_f value) at the selected wavelenght were graphically joined. To verify the validity of the method , a mixture of pure samples of $[Co(bipy)_3]Cl_3$, $[Co(bipy)_2(en)]Cl_3$ and *cis*-$[Co(bipy)_2Cl_2]Cl$ was chromatographied and scanned: the results are reported in fig.1 . In addition in the same figure, the spectra of the three separated species were drawn;all the graphically obtained spectra (fig.2a) are similar to those reported in the literature (6,9,10), as it is evident in fig. 2b . The method was applied to characterize the products formed by heating for 4 hours at 165°C a mixture of $[Co(bipy)_2(en)]Cl_3$ and NH_4Cl. In the figure 3 the graphically obtained spectra were re

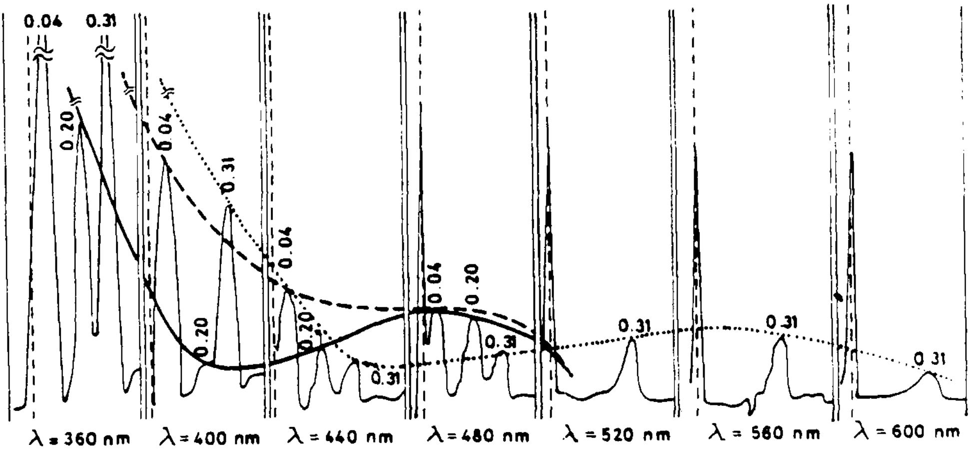

FIGURE 1. Scanning "in situ" in the reflectance mode and graphically obtained visible absorption spectra of a mixture of pure samples of $[Co(bipy)_3]Cl_3$ (R_f=0.04), $[Co(bipy)_2(en)]Cl_3$ (R=0.20), and cis-$[Co(bipy)_2Cl_2]Cl$ (R=0.31), after chromatographic separation of silica gel precoated plates.

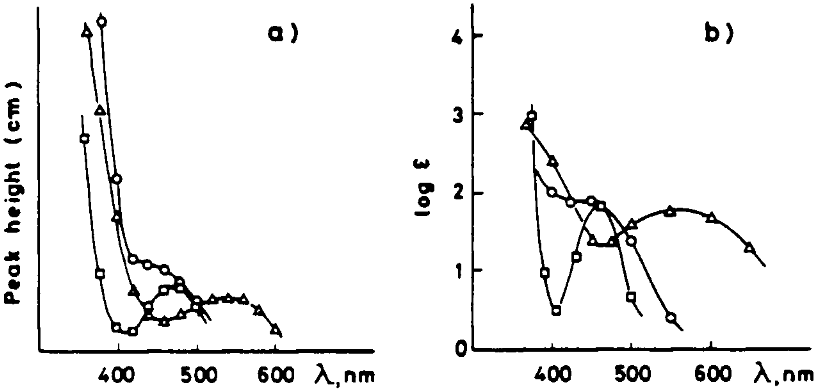

FIGURE 2: Visible absorption spectra of cis-$[Co(bipy)_2Cl_2]Cl$ (Δ——Δ), $[Co(bipy)_3]Cl_3$ (o——o) and $[Co(bipy)_2(en)]Cl_3$ (□——□): a) as obtained by scanning a TLC plate in the reflectance mode (cf. fig. 1); b) as reported in the literature (6, 9, 10).

ported. Three of these spectra compared well with the spectra reported in fig.2 . Thus the three species could be the starting complex , $Co(bipy)_2(en)^{3+}$ (R_f= 0.20) and two possible reactions products, cis- $Co(bipy)_2Cl_2{}^+$ (R_f=0.31) and $Co(bipy)_3{}^{3+}$ (R_f=0.04), respectively.The chromatographic and electrophoretic behaviour of these compounds supports this assignment. As regard to the product having R_f=0.44 we are not able to identify a species by means of the spectrum,even if its chromatographic behaviour suggests the presence of cobalt(II) complexes.Resuming,TLC showed that by heating at 165°C a mixture of $[Co(bipy)_2(en)]Cl_3$ and NH_4Cl,four main species are present after four hours. Three of these species were characterized by means of direct spectrophotometry . As regard to the thermal reaction,the data had shown that

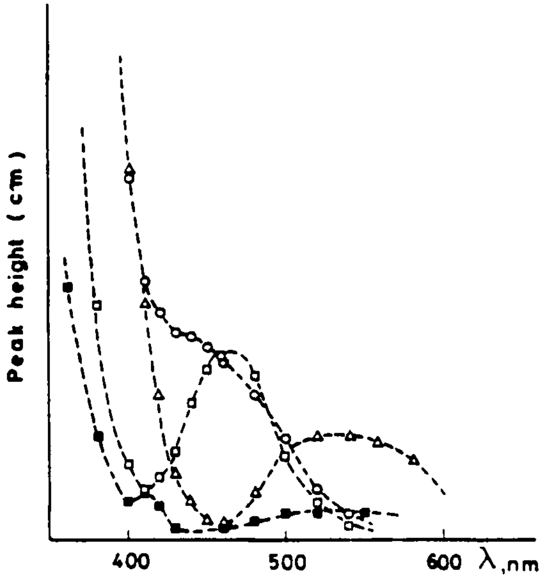

FIGURE 3

Visible absorption spectra of the reaction products of $[Co(bipy)_2(en)]Cl_3$ and NH_4Cl after 4 h isothermal heating at 165 °C, determined by scanning a TLC plate in the reflectance mode. (○---○) product with R_f=0.04; (□---□) product with R_f=0.21; (△---△) product with R_f=0.30; (■---■) product with R_f=0.44.

substitution of an ethylenediamine ligand by chloride occurred with the formation of an intermediate species, the cis- $Co(bipy)_2Cl_2^+$ as in the case of the corresponding reaction between $[Co(o\text{-}phen)_2(en)]Cl_3$ and NH_4Cl (4).

Concluding, the technique of spectrophotometry "in situ" , powerfully used in the quantitative analysis field, may be also, in our opinion, extended to the characterization of unknown product mixtures.

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