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CHROMATOGRAPHIC STUDY OF THERMAL REACTIONS OF *cis*- AND *trans*-[Coen$_2$(OCOC$_6$H$_4$X)$_2$]NO$_3$ COMPLEXES IN THE SOLID PHASE*

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ABSTRACT

Thermal reactions of some *cis*- and *trans*-[Coen$_2$(OCOC$_6$H$_4$X)$_2$]NO$_3$ complexes mixed with ammonium or sodium chloride, nitrate and sulphate are reported. Reflectance spectra have shown a *cis* to *trans* thermal isomerization and, in the presence of NH$_4$Cl, the formation of *trans*-[Coen$_2$Cl$_2$]Y as final product. For the *cis*-isomers, the most interesting result is the chromatographic evidence of a stepwise reaction, resulting in the replacement of one carboxylato ligand by chloride and the formation of an intermediate species, characterized as *trans*-[Coen$_2$(OCOC$_6$H$_4$X)Cl]Y. These intermediate species, are hardly detectable in the corresponding reactions of the *trans*-isomers. These results may mean that in the *trans*-carboxylato compounds the reaction rate of the second step is higher than that of the first, while the reverse can be supposed in the corresponding reaction of the *cis*-isomers.

INTRODUCTION

Inter- and intra-molecular thermal reactions of transition metal complexes in the solid state have been the subject of a number of investigations[1–8]. In particular, for several cobalt(III) complexes, with four nitrogen coordinating ligand, *trans* preferred reactions are observed in the presence of both NH$_4^+$ and NO$_3^-$ ions[3,5] by heating a mixture of the compounds and inorganic salts. Although in several cases multistep reactions occur[7], relatively little attention has been paid to the reaction intermediates, which remain often unidentified.

In order to study the course of a reaction in the solid state, reflectance spectroscopy proved to be a suitable technique[3,5,8], in the same way as spectrophotometry was used for reactions in solution. However in both cases, because of the possible

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Abbreviations used:
en = ethylenediamine; Y = anion; *cis*-db or *cis*-dibenzoato = *cis*-[Coen$_2$(OCOC$_6$H$_5$)$_2$]Y; id. for *trans* isomer; *trans*-dcl or *trans*-dichloro = *trans*-[Coen$_2$Cl$_2$]Y; *trans*-clb or *trans*-chlorobenzoato = *trans*-[Coen$_2$(OCOC$_6$H$_5$)Cl]Y.

overlap of the spectra of the reacting and produced species, it is not always possible to discern whether two or more species are present. Chromatography appears to be very suitable to provide further information on the compounds formed during the heating and on stepwise ligand substitution, in the light of our goals in choosing this technique for previous investigations in solution[9,10].

The present study was undertaken to examine the formation of intermediate species during some solid–solid thermal reactions. We report here the reactions of *cis*- and *trans*-$[Coen_2(OCOC_6H_5)_2]NO_3$ in the presence of various ammonium or sodium salts. For these compounds, *cis* to *trans* thermal isomerization was observed in the absence of added salts[11], so that the prevailing isomeric form would be the same also in the presence of both NH_4^+ and NO_3^- ions, which for some other complexes give rise to *trans* preferred reaction[3,5]. In addition, some *cis*- and *trans*- ring substituted dibenzoato complexes, $[Coen_2(OCOC_6H_4X)_2]NO_3$ ($X = p\text{-}CH_3$, $p\text{-}OCH_3$, $p\text{-}Cl$) were studied.

EXPERIMENTAL

Preparation of complexes

The complexes were prepared as described in the literature, the *trans*- and *cis*-forms of $Coen_2Cl_2^+$ as perchlorate, according to Bailar[15]; the two forms of $Coen_2(OCOC_6H_5)_2^+$ and the corresponding benzoato-ring substituted, as nitrate, according to Aprile et al.[16]; the *trans*-$Coen_2(OCOC_6H_5)Cl^+$, as perchlorate, after Dasgupta et al.[17].

Operative conditions

Thermal reactions have been performed by employing 10–50 mg of each complex or of a mixture of complex and inorganic salts (1:10 ratio by weight). Thin sample beds, prepared by gentle grinding in a mortar, have been heated isothermally at 135 ± 1 °C, in static air in an oven. Reflectance spectra are recorded at room temperature on samples heated for a convenient time and allowed to equilibrate in a dessicator for 30 min. A Beckman Model DB-GT spectrophotometer equipped with reflectance accessory has been used to obtain the reflectance spectra of the samples. Magnesium oxide plates have been used as the reflectance references.

Separation of products has been achieved by TLC on precoated silica gel plates, Merck (Darmstadt, G.F.R.) 60, using methanol–96% ethanol–25% aqueous ammonium acetate–1 N acetic acid in methanol (70:30:5:0,3)[13] as mobile phase. The mixture of complexes and inorganic salts, after heating, has been treated with 5–10 ml of acetone, then filtered, and the residue has been dissolved in 2–5 ml of $MeOH–H_2O$(9:1). Portions (0.5–1 μl) of both solutions have been applied to the plates, and development has been carried out in Desaga chambers, the mobile phase being placed there 18 h before development. The chromatography was carried out at -25°C[14]. Ascending development to a height of 8 cm was normally complete in 45–50 min. The spots were detected by spraying with ammonium sulphide solution.

RESULTS AND DISCUSSION

cis- and trans-$[Coen_2(OCOC_6H_5)_2]NO_3$

As observed by LeMay[6], preliminary studies showed that several factors affect the rate of thermal reactions, as the sample-bed thickness and the presence of moisture. Since our purpose was essentially to put in evidence the intermediate species, the extent of substitution reaction of *cis-* and *trans-*$[Coen_2(OCOC_6H_5)_2]NO_3$ was determined by comparison of the reflectance spectra and the chromatographic results of the samples heated in the presence of inorganic salts with that of the sample heated without salts from the same batch.

A mixture of the complexes under investigation and ammonium or sodium chlorides, nitrates and sulphates have been heated isothermally at 135°C. We have chosen this temperature because the compounds decompose at 200°C and isomerization process of *cis*-dibenzoato occurs only at temperatures above 100–110°C[11]; chromatography has shown that decomposition at 135°C appears to be negligible, even after several hours of heating. Samples are removed at a known time and the extent of reaction followed by reflectance spectroscopy and chromatography.

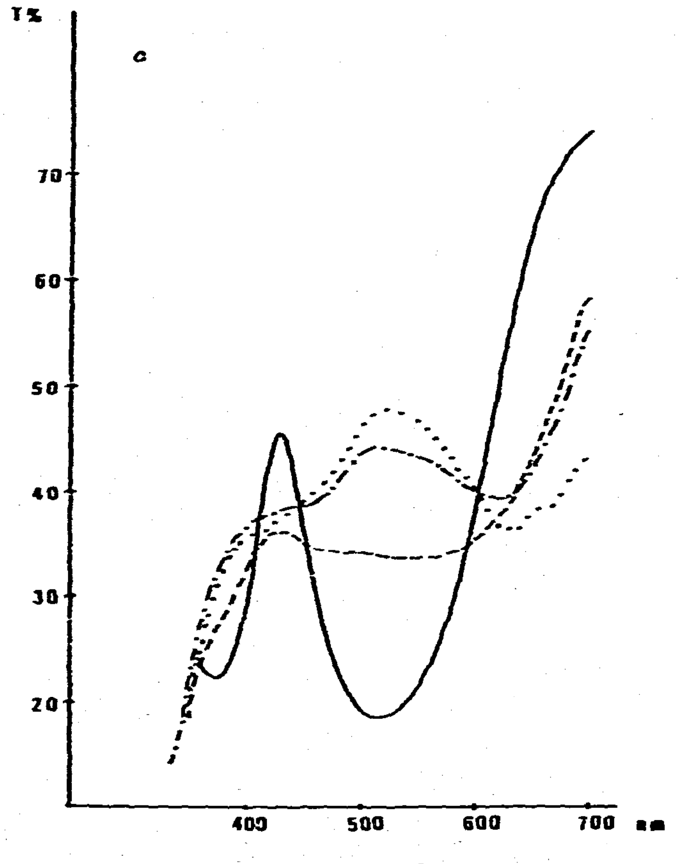

Fig. 1. (See legend at the bottom of p. 88.)

For both isomers, when the experiment is conducted in the presence of NH_4Cl, a green colour has developped slowly and after 120 min the reaction seems to be complete. Changes in reflectance spectra, recorded at room temperature and at various stages of reaction, are reported in Fig. 1. As illustrated in the figure, the spectra of the samples heated for 120 min show an absorption maximum and a shoulder at about 620 and 400 nm, respectively, and a reflectance peak at about 530 nm. The main bands correspond to that of *trans*-[Coen$_2$Cl$_2$]Y, showing that substitution and isomerization reactions occur. Furthermore, spectral changes during the heating show that probably more than one species are present. Chromatography appeared to be suitable for their separation. Numerous and different types of chromatographic experiments have been tried, because of various factors which have to be taken into consideration, such as the fast aquation and/or isomerization of the complexes under investigation, interactions of the complexes with the developing solvent mixtures and/or the adsorbent, weak solubility of *trans*-[Coen$_2$Cl$_2$]Y in organic solvents, interactions between the added inorganic salts and the developing solvent. TLC has given the best result. As pointed out, wide differences in behaviour

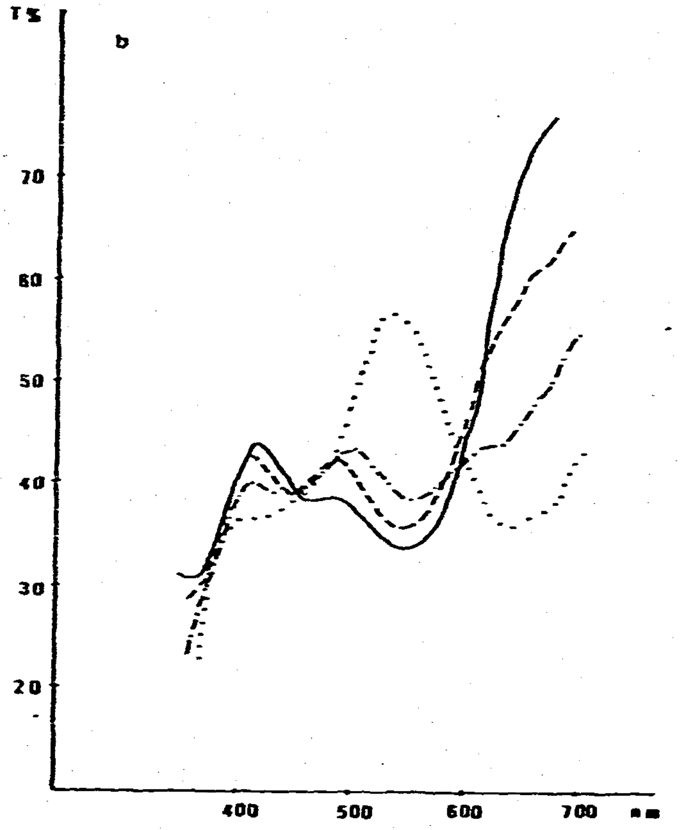

Fig. 1. Change in reflectance spectra during heating at 135°C of (a) *cis*-[Coen$_2$(OCOC$_6$H$_5$)$_2$]NO$_3$ + NH$_4$Cl; (b) *trans*-[Coen$_2$(OCOC$_6$H$_5$)$_2$NO$_3$] + NH$_4$Cl. The reaction time is 0 (———), 20 (– – –), 40 (–·–·–·) and 120 (······) min.

of cobalt(III) complexes are encountered when using pre-coated silica gel thin layers obtained from various sources[12]. We have obtained R_f values reproducible to ±0.03 employing a convenient thin layer. The solvent mixture was that reported by Seiler for the separation of some other cobalt(III) complexes[13]. The temperature of $-25°$ was chosen because of the good results achieved at low temperatures in the chromatographic separation of some inorganic compounds[14]. To obtain good chromatographic results even for the reaction mixture of complexes and inorganic salts, these samples are first dissolved in acetone and, after removal of the acetone, the residue, consisting mainly of *trans*-$[Coen_2Cl_2]Y$ and NH_4Cl, was dissolved in MeOH–H_2O (9:1). Preliminary experiments showed, indeed, that in our operative conditions, the complexes under investigation are inert in acetone and the very low quantity of NH_4Cl present in these solutions does not interfere in the successive chromatographic separation, as in the case of methanol or ethanol employed as solvent.

Figures 2a and 2b depict the typical thin-layer chromatograms of the reaction products of the *cis*-dibenzoato and of the same complex in mixture with NH_4Cl, both heated at 135°C for convenient times. Figures 3a and 3b show the reaction products of the corresponding reaction for the *trans*-isomer.

As shown in Fig. 2a, the *cis*- complex is thermally converted to the corresponding *trans*-isomer. After 24 h, the *trans*- compound is the main product, but it is contaminated with a very small quantity of some other materials, among which we have identified cobalt(II) species.

In the chromatograms illustrated in Fig. 2b, two separations are reported for each time of heating of the mixture of the complex and ammonium chloride, corresponding to the solutions in acetone and in methanol, respectively: the chromatographic results of the first solutions provide the disappearance of the starting complex, the *cis*-dibenzoate and the formation of other products, whereas that of the second solution show the progressive appearance of the final product, the *trans*-$[Coen_2Cl_2]Y$. For the sake of comparison, some blanks, run on unheated samples, are reported in Fig. 2b: a mixture of *cis*-dibenzoato, *trans*-dibenzoato and *trans*-dichloro and cobalt(II). As shown in the same figure development of the mixture heated for 20 min resulted in four spots, one of which does not correspond to the blanks. Three were identified as *trans*-dibenzoato, *trans*-dichloro and *cis*-dibenzoato.

The quantity of the unidentified product decreases with reaction time and it disappears in the sample heated for 60 min. This decrease and disappearance in relation to reaction time suggests the unknown compound to be an intermediate species and by its chromatographic behaviour it seems to be a +1 charged, *trans*-isomer. On the basis of these facts, the unknown species has been preliminary characterized as *trans*-$[Coen_2(OCOC_6H_5)Cl]Y$, probably produced by substitution of a carboxylato ligand by chloride. To confirm this hypothesis, TLC has been carried out on a blank of *trans*-$[Coen_2(OCOC_6H_5)Cl]ClO_4$. The R_f value of this species is the same as that of the product evidenced by chromatography, as shown in Fig. 2b.

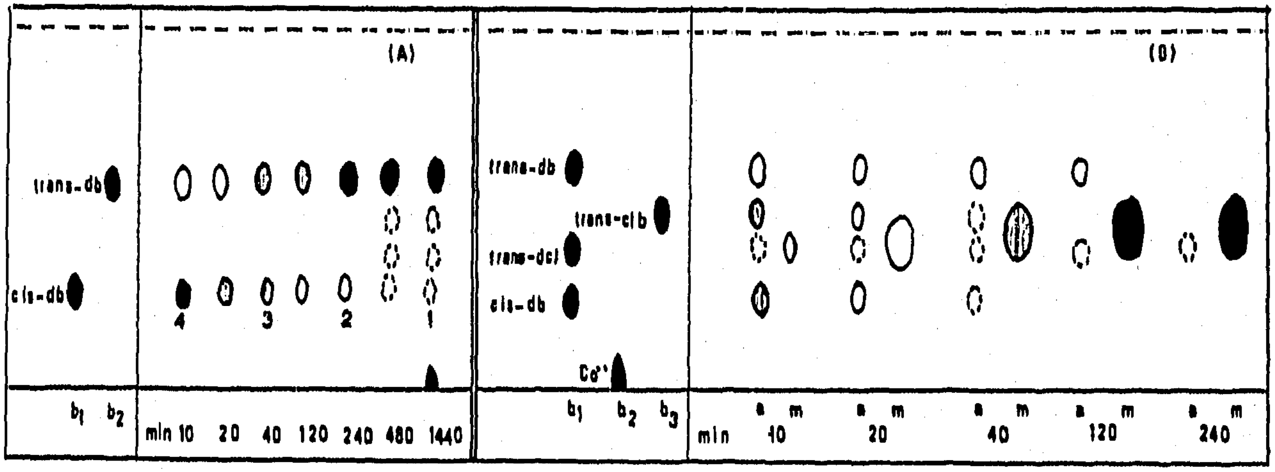

Fig. 2. TLC of the reaction products of *cis*-[Coen$_2$(OCOC$_6$H$_5$)$_2$]NO$_3$ (A) and of the same complex mixed with NH$_4$Cl (B), heated at 135°C for various times. b$_1$, b$_2$, b$_3$ = blanks. a = Solution in acetone; m = solution in methanol–H$_2$O (9:1). The numbers 1, 2, 3, 4 indicate the intensity of the spot from left to right: very weak; well visible; strong; very strong.

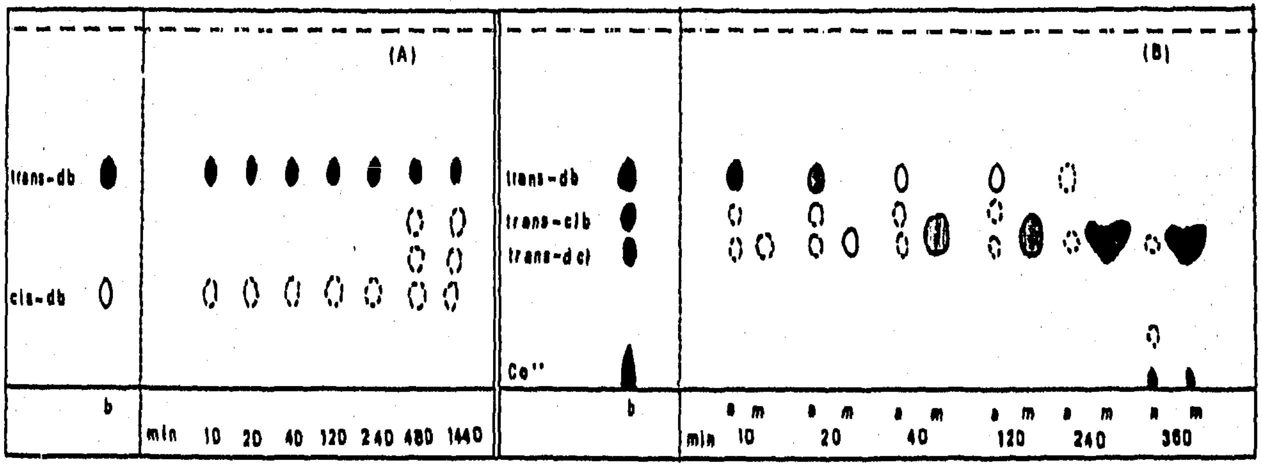

Fig. 3. TLC of the reaction products of *trans*-[Coen$_2$(OCOC$_6$H$_5$)$_2$]NO$_3$ (A) and of the same complex mixed with NH$_4$Cl (B). Otherwise heating, separations etc. as in Fig. 2.

Thus, chromatography has proved the formation of an intermediate species identified as *trans*-[Coen$_2$(OCOC$_6$H$_5$)Cl]Y.

The chromatograms of *trans*-dibenzoato or of a mixture of *trans*- and *cis*-dibenzoato heated at 135°C for several hours (Fig. 3a) show after 2 h, the presence of the *trans*- isomer only, contaminated with several minor products. In the presence of NH$_4$Cl (Fig. 3b), *trans*-[Coen$_2$Cl$_2$]Y is also produced as the final product, but chromatography has shown very little quantity only of the intermediate species, the compound characterized as *trans*-[Coen$_2$(OCOC$_6$H$_5$)Cl]Y.

Chromatograms and spectra show that the thermal behaviour of *cis*-[Coen$_2$(OCOC$_6$H$_5$)$_2$]NO$_3$ in the presence of NaCl, NaNO$_3$, Na$_2$SO$_4$ and (NH$_4$)$_2$SO$_4$ is almost the same as that of the pure compound: *cis* to *trans* isomerization is the prevalent reaction. In the presence of NH$_4$NO$_3$ a decomposition reaction prevails on the isomerization process.

cis- and trans-[*Coen*$_2$(*OCOC*$_6$*H*$_4$*X*)$_2$]*NO*$_3$ ($X = p\text{-}CH_3, p\text{-}OCH_3, p\text{-}Cl$)

In light of the above results, the ring substituted dibenzoato complexes were heated isothermally at 135°C, for 24 h, in both the presence and the absence of NH$_4$Cl. The conditions under which these reactions were examined are similar to those reported for the reactions of *cis*-dibenzoato. The results obtained are similar. Reflectance spectra have shown a *cis* to *trans* isomerization and, in the presence of NH$_4$Cl, the formation of *trans*-[Coen$_2$Cl$_2$]Y as final product. For the *cis*- isomers, chromatography put in evidence the formation of an intermediate species, probably the *trans*-[Coen$_2$(OCOC$_6$H$_4$X)Cl]Y, whereas the same product is not evident in the corresponding reaction of the *trans*-isomers.

A comparison of the rates of *cis*→*trans* isomerization of the [Coen$_2$(OCOC$_6$H$_4$X)$_2$]NO$_3$ complexes indicates a reactivity sequence for the stereochemical changes as X is p-OCH$_3$>p-CH$_3$>H>p-Cl, that is the inverse of their thermal stability[11].

In conclusion, in the solid–solid thermal reaction of *cis*-[Coen$_2$(OCOC$_6$H$_4$X)$_2$]NO$_3$ and inorganic salts, the most meaningful result is the chromatographic evidence of a stepwise reaction in the presence of NH$_4$Cl, resulting in the replacement of one carboxylato ligand and the formation of an intermediate species, characterized as *trans*-[Coen$_2$(OCOC$_6$H$_4$X)Cl]Y. Using the same chromatographic procedure, these intermediate species are scarcely detectable in the reaction products of the *trans*-dibenzoato complexes and NH$_4$Cl. These results may mean that in the *trans*-carboxylato compounds the reaction rate of the second step is higher than that of the first, while the reverse can be supposed in the corresponding reaction of the *cis*-isomers. Therefore, the above results indicate that in the thermal reaction of *cis*-dicarboxylato compounds and NH$_4$Cl two reactions occur: the *cis*-dibenzoato→*trans*-dibenzoato isomerization and the *cis*-dibenzoato→*trans*-dichloro substitution. The two reactions, the second of which is faster than the first, seem to be competitive and not consecutive. If indeed the second reaction proceeded via *trans*-dibenzoato (see the scheme), the same results should have been obtained as when the reaction was initiated with *trans*-dibenzoato, that is the intermediate *trans*-chlorobenzoato would not be detected.

$$\begin{tikzcd}
\textit{cis}\text{-Coen}_2(\text{OCOC}_6\text{H}_4\text{X})_2^+ \arrow[r] \arrow[d] \arrow[dr] & \textit{cis}\text{-Coen}_2(\text{OCOC}_6\text{H}_4\text{X})\text{Cl}^+ \arrow[d] & \\
\textit{trans}\text{-Coen}_2(\text{OCOC}_6\text{H}_4\text{X})_2^+ \arrow[r] & \textit{trans}\text{-Coen}_2(\text{OCOC}_6\text{H}_4\text{X})\text{Cl}^+ \arrow[r] & \textit{trans}\text{-Coen}_2\text{Cl}_2^+
\end{tikzcd}$$

The pathway via *cis*-chlorobenzoate would be excluded, since in the presence of both NH_4^+ and NO_3^- ions the reactions are *trans*-preferred[3,5]. An intramolecular rearrangement through a trigonal bipyramid intermediate, involving the opening of a chelate ring followed by the reattachment of the open end, can be postulated, when the *cis*-complexes are heated in absence of NH_4Cl and the *cis* to *trans* isomerization occurs. When a substitution reaction prevails because of the presence of NH_4Cl, a trigonal bipyramid intermediate should be formed in this case too, resulting from the displacement of a carboxylato group, which is more sensitive to acidic conditions due to the NH_4^+ ion.

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REFERENCES

1 W. W. Wendlandt, *Texas J. Sci.*, 10 (1958) 271.
2 N. Tanaka and K. Nagase, *Bull. Chem. Soc. Japan*, 42 (1969) 2854.
3 F. C. Chang and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, 32 (1970) 3535.
4 F. C. Chang and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, 32 (1970) 3775.
5 F. C. Chang and W. W. Wendlandt, *Thermochim. Acta*, 2 (1971) 293.
6 H. E. LeMay, Jr., *Inorg. Chem.*, 10 (1971) 1990.
7 F. C. Chang and W. W. Wendlandt, *Thermochim. Acta*, 3 (1971) 69.
8 L. W. Collins, W. W. Wendlandt and E. K. Gibson, *Thermochim. Acta*, 8 (1974) 205.
9 V. Carunchio, G. Grassini Strazza, G. Ortaggi and C. Padiglione, *J. Inorg. Nucl. Chem.*, 27 (1965) 841.
10 V. Carunchio, F. Giannetta and G. Grassini Strazza, *J. Inorg. Nucl. Chem.*, 33 (1971) 3025.
11 G. D'Ascenzo, V. Carunchio, A. Magri and A. Marino, *Atti Accad. Naz. Lincei, Rend. Classe Sci. Fis. Mat. Natur.*, 56 (1974) 355.
12 A. Cristalli and G. Grassini Strazza, *J. Chromatogr.*, 111 (1975) 452.
13 H. Seiler, C. Biebricher and H. Erlenmeyer, *Helv. Chim. Acta*, 46 (1963) 2636.
14 L. Ossicini and M. Sinibaldi, *J. Chromatogr.*, 42 (1969) 154.
15 J. C. Bailar, *Inorg. Syn.*, 2 (1946) 222.
16 F. Aprile, V. Caglioti and G. Illuminati, *J. Inorg. Nucl. Chem.*, 21 (1961) 300.
17 T. P. Dasgupta, W. Fitgerald and M. L. Tobe, *Inorg. Chem.*, 11 (1972) 2046.