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Effect of temperature on *N*-ethylcarbazole chromium tricarbonyl complex studied by two-dimensional infrared correlation spectroscopy

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Abstract

Temperature-dependent variation of *N*-ethylcarbazole chromium tricarbonyl complex by itself without the solid support has been studied by carefully examining their IR spectra with the aid of two-dimensional correlation analysis. Two obvious stages have been observed during the heating process. In the first stage, the crystalline ECzC undergoes a slow process to change into the amorphous form due to the strong interactions of the hydrogen bonding. In the second stage, ECzC gradually decomposes, which results in the formation of $Cr(CO)_6$. The results suggest that the interaction between the organometallics and its solid support may not have direct influence to the final product generated under the thermal treatment.

Keywords: Infrared spectroscopy; Two-dimensional correlation analysis; *N*-ethylcarbazole chromium tricarbonyl complex

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1. Introduction

The thermal behavior of the adsorbed organometallic complex, especially (η^6-benzene) tricarbonylchromium(0) [(η^6-C_6H_6)$Cr(CO)_3$] has attracted major attention since several researchers reported that the thermal treatment can affect the catalytic capability of the solid-supported (η^6-C_6H_6)$Cr(CO)_3$ [1–4]. For example, Hunter et al. observed the formation of sub-carbonyl species and incompletely coordinated Cr on the surface after heating the alumina- and silica–alumina-supported (η^6-C_6H_6)$Cr(CO)_3$ [1,2]. Shirley and Scoville suggested that the interactions between the (η^6-C_6H_6)$Cr(CO)_3$ and zeolite NaX may induce the formation of $Cr(CO)_3$/NaX surface species under the thermal treatment [4]. On the other hand, in the work of Huang and Poissant, the thermal behavior of (η^6-C_6H_6)$Cr(CO)_3$/zeolite Y was investigated and they reported two different decomposition processes [3]. Interestingly, according to the work they carried out, it was suggested that the interactions between the (η^6-C_6H_6)$Cr(CO)_3$ and zeolite did not play a major role in the formation of final product.

It is noted that there exist surprisingly different conclusions in the two very similar systems. In our opinion, this divergence originates from the lack of the systematic information about the thermal behavior of a pure organometallic complex. For this reason, we have investigated the thermal behavior of a pure organometallic complex: *N*-ethylcarbazole chromium tricarbonyl complex (ECzC). The benzene ring in *N*-ethylcarbazole is π-coordinated to Cr as a η^6-ligand, so that ECzC has some common properties related with (η^6-C_6H_6)$Cr(CO)_3$. The structure of the single crystal of ECzC identified by SHELXS 97 is shown in Scheme 1A [5]. ECzC is studied for its potential capability

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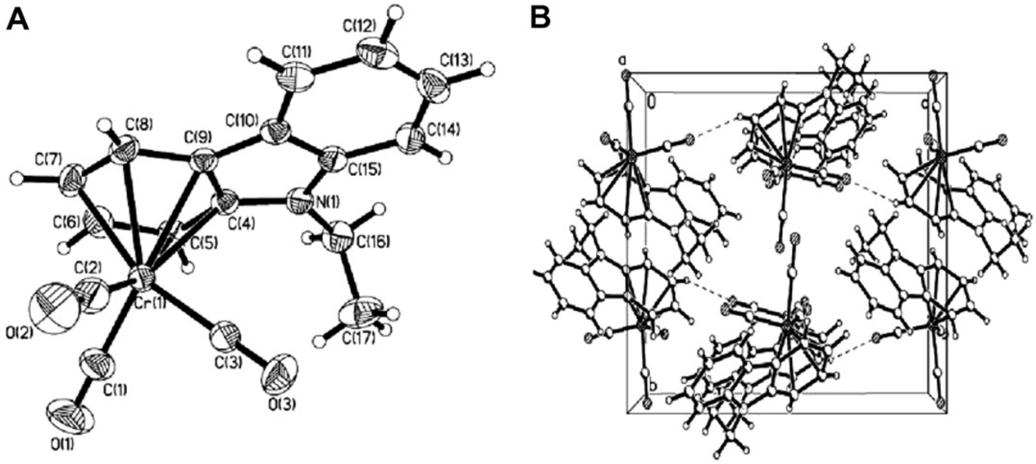


Scheme 1. (A) The single crystal structure of ECzC. (B) The cell-packing graph of ECzC.

of photoconductivity [6–10], so the thermal stability is a very significant parameter in the evaluation of this material in the applications for optical devices.

It is well known that, by monitoring the intensity and shape change of the bands in the FTIR spectra, we can trace the corresponding structural change of the studied material. In this work, we used *in situ*-FTIR spectroscopy to investigate the effect of temperature on ECzC by monitoring the change of the spectral signals appearing in the ν(CO) stretching region. Furthermore, in order to improve the spectral resolution and discern the sequential order of the spectral signal changes, we employed the two-dimensional (2D) correlation analysis in our study. 2D IR correlation is a spectral analysis method originally proposed by Noda [11–15]. Due to its capability to identify the number and peak position of underlying bands, sometimes not so apparent in conventional one-dimensional (1D) spectra, 2D spectroscopy is often looked upon as a useful initial probing tool to aid in the analysis of complex IR spectra [15]. 2D IR correlation analysis has received great attention for its another ability: it can discern the specific order of events taking place under the influence of a controlling physical variable, such as temperature, concentration, time and so on. 2D analysis can often simplify spectral features corresponding to various inter- and intramolecular interactions and elucidate the relationships between spectral elements.

With the application of 2D IR correlation spectroscopy, it appears that pure ECzC by itself without a solid support can undergo a slow process to generate $Cr(CO)_6$ after the thermal treatment.

2. Experimental section

Chromium tricarbonyl complex of *N*-ethylcarbazole (ECzC) was supplied by East China University of Science and Technology and was used without further purification [5].

2.1. Recording of spectra

All FTIR spectra were recorded with a Nicolet Nexsus 470 FTIR spectrometer equipped with a DTGS detector in NaCl pellets. The resolution was 4 cm^{-1}, and 32 scans were accumulated. During the experiment, the temperature was gradually increased from 50 up to 200 °C at an interval of 5 °C.

2.2. 2D FTIR

All the FTIR spectra in the temperature range 50–200 °C were collected sequentially to perform the 2D IR correlation analysis. The 2D contour maps were generated by the software POCHA (Kwansei-Gakluin University). The 1D spectra shown at the side and top of the 2D correlation maps are the average spectrum calculated over the entire temperature range, and they used as the reference. In the 2D contour maps, unshaded regions correspond to the positive correlation intensities, while shaded regions are the negative ones.

3. Results and discussion

Fig. 1A shows the IR spectrum of the sample ECzC recorded at 50 °C. The spectral range 2050–1800 cm^{-1} attracts our main focus of attention (Fig. 1B), because most spectral intensities in this region are assignable to the stretching modes of the different $Cr(CO)_3$moieties. The IR spectrum in the C=O stretching region displaying three principal ν(CO) bands at 1938, 1880, and 1851 cm^{-1} indeed provides some useful insight. Most of the spectral bands can be assigned easily according to the previous research work about $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ in the literatures [3,16–18]. However, we do observe some differences of the ν(CO) stretching frequencies in this work. For example, the ν(CO) band occurred at 1938 cm^{-1} for ECzC is obviously lower wavenumber shifted by 30 cm^{-1} from that of pure solid $(\eta^6\text{-}C_6H_6)Cr(CO)_3$at 1968 cm^{-1}.

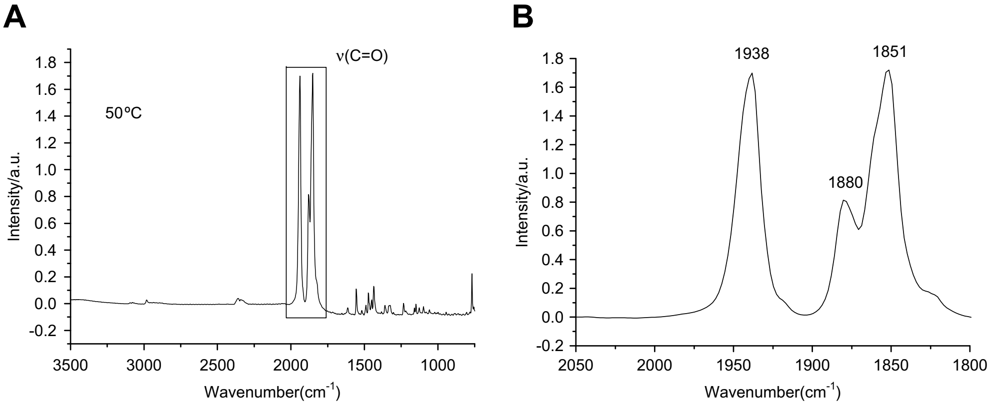


Fig. 1. (A) IR spectrum of ECzC at 50 °C. (B) A close-up view of the ν(CO) stretching region.

Thus, it is not suitable to assign the band at 1938 cm^{-1} as the a_1 mode of the crystalline form (the common assignment of the band 1968 cm^{-1}) [3].

In the literatures of zeolite-supported (η^6-C_6H_6)Cr(CO)$_3$, numerous studies have shown that the metal carbonyl complexes can strongly interact with the extraframework cations [19,20]. The interactions weaken the C=O bands, resulting in the decrease in ν(CO) stretching frequencies. In this work, hydrogen bonds exist between the Cr(CO)$_3$ moieties and benzene rings according to the cell-packing graph (Scheme 1B). The hydrogen bonding interactions also weaken the C=O band. Thus, it is our contention that the band at 1938 cm^{-1} should be assigned to the carbonyl moieties under the hydrogen bonding interactions. In a similar manner, other main bands are reasonably assigned and listed in Table 1 [18].

A series of IR spectra of ECzC in the spectral range 2050–1800 cm^{-1} recorded at different temperatures are shown in Fig. 2A. For the sake of clarity, only 25 °C intervals are shown. With the increase of the temperature, the shape and intensity of all the spectral signals exhibit significant changes. It is worth noting that two distinct stages occur in the observed interval. In the first stage (in the temperature range 50–125 °C), the ν(CO) bands at 1938, 1880, and 1851 cm^{-1} still exist as the dominating bands in the ν(CO) stretching range though a gradual loss of these spectral intensities has been observed. The result indicates that the hydrogen bonding interactions still exist in the ECzC crystallites in this temperature range. On the other hand, up to 150 °C, only two rather broad ν(CO) bands centering around 1951 and 1870 cm^{-1} are present in the ν(CO) stretching range. The higher-wavenumber shift of the band at 1938 cm^{-1} (1938 cm^{-1} → 1951 cm^{-1}) and the disappearance of the splitting of the ν(CO) $2a_g$ mode indicate that the crystalline form of the ECzC gradually changes to the amorphous form, accompanied by the gradual dissociation of the hydrogen bonds. More interestingly, with the further increase in the temperature, a new weak shoulder at 1980 cm^{-1} appears. By the time the temperature reaches 200 °C, all the other bands disappear, and this band eventually becomes the principal band. In the literature, the band at 1980 cm^{-1} is assigned to the t_{1u} mode of the hexacarbonyl species Cr(CO)$_6$ [3]. Thus, spectral features shown in Fig. 2A indicate that the thermal treatment of ECzC may lead to the decarbonylation and the eventual loss of the *N*-ethylcarbazole ligand.

Table 1
Tentative assignment of the main bands in ν(CO) stretching region [3,16–18]

Peak position)	Assignment (tentative)
1980	t_{1u} mode of Cr(CO)$_6$
1951	a_1 mode of amorphous ECzC
1938	b_g mode of crystalline ECzC, with strong hydrogen bonds
1880	a_g mode of crystalline ECzC, with strong hydrogen bonds
1870	e mode of amorphous ECzC
1851	a_g mode of crystalline ECzC, with strong hydrogen bonds

This notion is partly substantiated by examining the ν(CH) stretching range shown in Fig. 2B. At a lower temperature, ECzC exists in the crystalline form, leading to the appearance of two relatively sharp ν(C–H) bands due to the correlation splitting at 3096 and 3078 cm^{-1} in the ν(CH) range. Upon thermal treatment, these bands gradually lose their intensities, indicating the loss of the crystalline form. Above 150 °C, only one rather broad peak is present around 3060 cm^{-1} in the ν(CH) range. Compared with the positions of the aforementioned three bands, the position of this band has a significant lower wavenumber shift. The bands at 3078 and 3060 cm^{-1} are usually assigned to the complexed and uncomplexed benzene rings in the literatures of (η^6-C_6H_6)Cr(CO)$_3$ [3,18]. Similarly, it seems that in our system the vast majority of ECzC decomposes upon the thermal treatment, and (*N*-ethylcarbazole) ligand is eventually released.

From the above results, we can briefly summarize that under the experimental conditions, most of the ECzC has changed from the crystalline form into the amorphous form with the disruption of hydrogen bonds. In the last stage of the observed period, the continuous heating process results in the decomposition of ECzC and the formation of Cr(CO)$_6$:

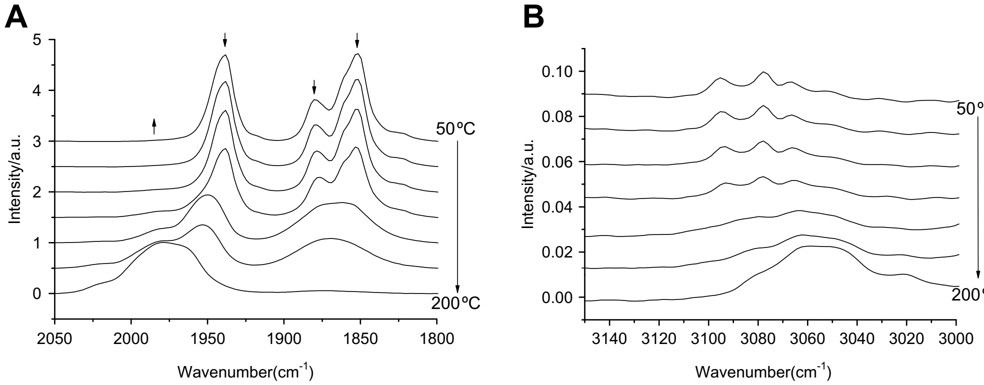
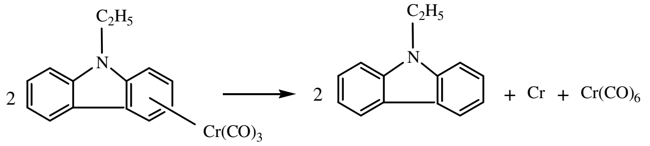


Fig. 2. IR spectra of ECzC collected under different temperatures: (A) in ν(CO) stretching region; (B) in ν(CH) stretching region.



Several research workers have reported that (η^6-C_6H_6)$Cr(CO)_3$ can undergo a decomposition process and form $Cr(CO)_6$ under some special perturbations [21]. Thus, the conversion described here is not entirely unreasonable.

The above-mentioned conversion infers the sequential creation of different functionalities of ECzC. We therefore employed 2D IR correlation spectroscopy to investigate the detailed information about the conversion process. Fig. 3A and B, respectively, shows the 2D synchronous and asynchronous correlation spectrum of ECzC over the temperature range 50–200 °C. Three autopeaks at 1980, 1938, and 1851 cm^{-1} appearing in the synchronous contour map indicate that these bands change intensities to a great extent under the thermal perturbation. Three negative cross-peaks at (1980/1851 cm^{-1}), (1980/1880 cm^{-1}), (1980/1938 cm^{-1}) and three positive cross-peaks at (1938/1851 cm^{-1}), (1938/1880 cm^{-1}), and (1880/1851 cm^{-1}) reveal that while the intensities of the bands assigned to the $Cr(CO)_3$ moieties involved in the hydrogen bonding interactions decrease, the band due to $Cr(CO)_6$ is increasing.

Compared with Fig. 3A, the apparent features of the asynchronous spectrum in Fig. 3B seem to be much more complex. It is of particular note that the band at 1951 cm^{-1} shares three negative cross-peaks with the bands at 1851, 1938, and 1980 cm^{-1}. According to the so-called Noda's rules [11,15], the appearance of a cross-peak $\Psi(\nu_1/\nu_2)$ in an asynchronous 2D correlation spectra indicates that the intensities of bands ν_1 and ν_2 vary out of phase with each other. The sign of an asynchronous cross-peak becomes positive if the intensity change at ν_1 occurs predominantly before ν_2 in the sequential order of the external variable. It becomes negative, on the other hand, if the change occurs after ν_2. This rule, however, is reversed if the intensity of the corresponding synchronous peak is negative, i.e., $\Phi(\nu_1/\nu_2) < 0$. On the basis of the above set of rules, the above-mentioned three negative asynchronous cross-peaks indicate

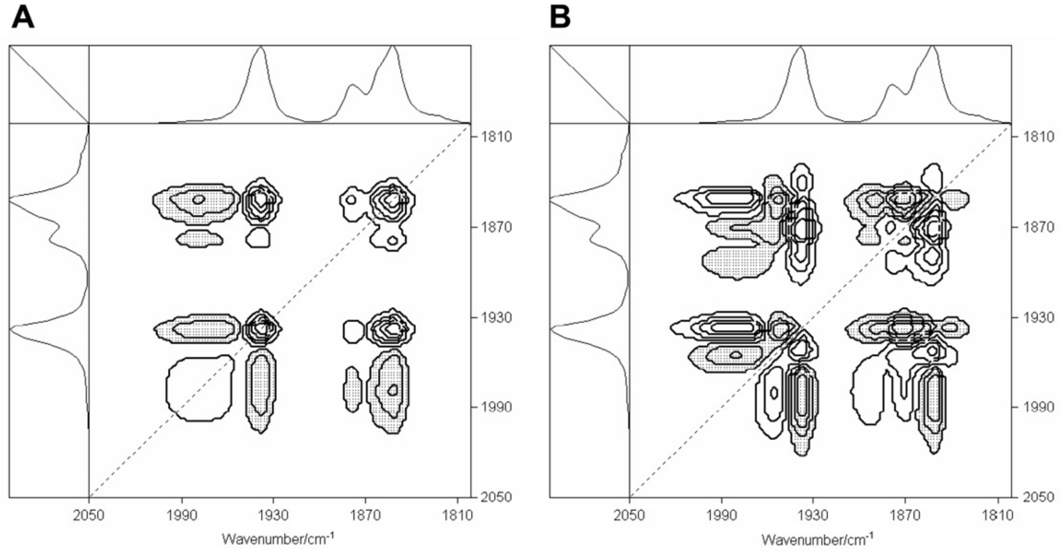


Fig. 3. (A) Synchronous and (B) asynchronous 2D IR correlation spectra of ECzC in the temperature range from 50 to 200 °C.

that the intensity change of the bands at 1851 and 1938 cm^{-1} occurs prior to that of the band at 1951 cm^{-1}, and the band at 1980 cm^{-1} changes intensity at the last stage. The negative asynchronous cross-peak Ψ(1870/1851 cm^{-1}) also indicates that the intensity change at 1851 cm^{-1} occurs before that at 1870 cm^{-1}. And three positive asynchronous cross-peaks located at 1938/1870, 1980/1851, 1980/1938 cm^{-1} just confirm the similar sequential order. By sorting out the sequential relations mentioned above, the order of the spectral intensity change is:

$$1938,\ 1851\ \text{cm}^{-1} \rightarrow 1951, 1870\ \text{cm}^{-1} \rightarrow 1980\ \text{cm}^{-1}.$$

Here, it should be pointed out that the circular feature centering around (1890/1851 cm^{-1}) probably delivers the false information, because we cannot follow any trace of the "band" at 1890 cm^{-1}. It is our contention that the fluctuation of the intensity at 1890 cm^{-1} is caused by the shape change of the neighboring bands.

In summary, the results of the 2D correlation analysis strongly support the conclusion that during the heating process, the crystalline form of ECzC gradually changes into the amorphous form. Upon reaching a higher temperature, ECzC decomposes and finally generates the $Cr(CO)_6$ species.

Some very interesting information is indeed implied in this conclusion which seems very convincing. Although the conversion of $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ to $Cr(CO)_6$ has been previously reported [3], the $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ studied were usually adsorbed on various solid supports. It has been believed that the interactions between $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ and the solid support probably induce the conversion and control the product. While some results suggested that the solid support such as zeolite may not play a major role in the formation of $Cr(CO)_6$ [3], to our knowledge, little further work addressing this point has been reported. Our current work clearly reveals that only pure crystalline ECzC can convert to $Cr(CO)_6$ after the heat treatment. Taking account for the importance of the thermal behavior of supported $(\eta^6\text{-}C_6H_6)Cr(CO)_3$, most of the literatures focus on the study of the result of the interactions between $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ and the solid support, while ignoring the behavior of $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ by itself. In fact, in the present system, hydrogen bonding is found to play an important role in influencing the thermal stability of ECzC. In the literature, $Cr(CO)_6$ was observed after heating as low as 120 °C. In our work, hydrogen bonds strengthen the interactions between the different molecules, leading to the high critical temperature between the crystallite and the amorphous state.

4. Conclusion

Generalized 2D IR correlation spectroscopy has been employed to study the thermal behavior of pure crystalline *N*-ethylcarbazole chromium tricarbazole complex (ECzC). The results indicate that after the heat treatment, the crystalline ECzC undergoes a slow process to change into the amorphous form due to the strong interactions of the hydrogen bonding. At a relatively higher temperature, the thermal decomposition of the sample occurs yielding $Cr(CO)_6$, *N*-ethylcarbazole and Cr. The result strongly suggest that the solid support plays a relatively minor role in the formation of $Cr(CO)_6$. This conclusion provides valuable information in the study of the thermal behavior of the supported organometallic complex.

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