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Photoreactivity of the Lowest MLCT Excited State of $Cr(CO)_5$pyridazine in an Ar Matrix at 10 K

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Although the MLCT photochemistry of several $M(CO)_5L$ and $M(CO)_4L$ complexes has been studied in solution [1–3], no results have been reported so far for any of these complexes in a rare gas matrix. Here we report for the first time the photochemistry in an Ar matrix of the lowest MLCT excited state of such a pentacarbonyl compound, *viz.* $Cr(CO)_5$pyridazine. The absorption spectrum of $Cr(CO)_5$pyridazine in an Ar matrix at 10 K shows three main bands, a $M \rightarrow \pi^*(CO)$ band at about 240 nm, a LF band at 395 nm and a $M \rightarrow \pi$(pyridazine)(MLCT) band at 450 nm. Short wavelength irradiation (λ = 254 nm) results in the formation of free CO (2140 cm^{-1}) and of *cis*-$Cr(CO)_4$pyridazine (2022.8 (A'), 1923.4 (A') and 1886.2 cm^{-1} (A'')†).These frequencies correspond with those of other *cis*-$Cr(CO)_4L$ fragments [4]. Photolysis with longer wavelengths (λ = 366 and 436 nm) yields $Cr(CO)_5$ and *cis*-$Cr(CO)_4$pyridazine, whereas irradiation into the MLCT band with λ = 520 nm gives only free CO and *cis*-$Cr(CO)_4$pyridazine (see Fig. 1). At this wavelength the lowest LF transition does not absorb.

Non-radiative decay constants rapidly decrease for this type of complexes upon cooling [5, 6] and photochemical reactions in matrices at 10 K are therefore expected to take place in the excited state. This means that the lowest MLCT excited state of $Cr(CO)_5$pyridazine is photoreactive with respect to CO rupture. This result is in accordance with the resonance Raman spectrum of this complex which shows a strong activation of the equatorial CO bonds upon excitation within the MLCT band [7, 8]. On the other hand, this photochemical behaviour differs from the observation of Wrighton *et al.* for the corresponding $W(CO)_5L$ (L = 4-substituted pyridine) complexes that the lowest MLCT excited is virtually unreactive in solution [1].

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†The fourth ν(CO) (A') is obscured by parent bands.

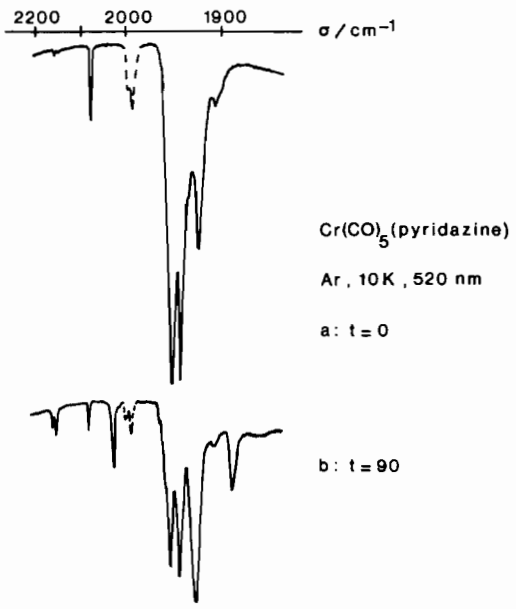

Fig. 1. Infrared spectrum of $Cr(CO)_5$pyridazine in an Ar matrix at 10 K (- - - = $Cr(CO)_6$); (a) after deposition, (b) after 90 hours photolysis with λ = 520 nm.

In a forthcoming article we will discuss the MLCT photochemistry of this type of complexes in solution and matrix in more detail [8].

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