

Resonance Raman study of $(\eta^2\text{-TCNE})\text{M}(\text{CO})_5$ (M = Cr, W; TCNE = tetracyanoethene). Evidence for an olefin-complex \rightarrow metallacyclopropane transition upon low-energy metal-to-ligand charge-transfer excitation

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Abstract

A solid state resonance Raman investigation of the non-hydrogen-containing title complexes was performed with long-wavelength laser excitation (514.5–611 nm). The spectra confirmed the η^2 -coordination of the π -acceptor olefin tetracyanoethene (TCNE) and showed that the absorption bands near 700 nm arise from transitions between the metal and TCNE. The metal-to-ligand charge-transfer (MLCT) character of these transitions is much more pronounced for the tungsten complex. These observations confirm the higher degree of metal (d)/ligand(π^*) orbital mixing in the chromium complex and also provide evidence for a structural change from that of an alkene π -complex towards a metallacyclopropane arrangement upon MLCT excitation

Introduction

In contrast to n -donor-bonded metal carbonyl compounds the simple olefin complexes of metal carbonyl fragments have received relatively little attention in respect of their charge-transfer (CT) spectroscopy and photochemistry [1]. The main reasons for this is that most such complexes have CT absorption bands at higher energies in the UV region and that photodissociative ligand-field ($d-d$) excited states lie below the charge transfer excited states [1].

The bonding in such complexes is usually described in terms of the Dewar–Chatt–Duncanson model (Fig. 1) [2,3] which, in particular, takes account of the back-donation into the π^* orbital of the olefin.

However, use of the tetracyanoethene (TCNE) ligand with its extremely low-lying π^* orbital often results in virtually complete electron transfer in the ground state, after which complexes such as $(\text{Ph}_3\text{P})_2\text{Pt}(\text{TCNE})$ [4] may better be formulated as

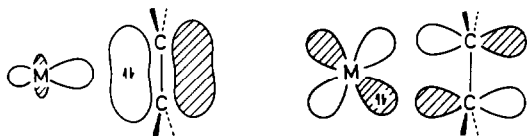
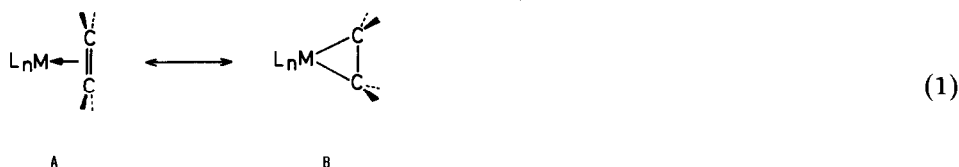


Fig. 1. Depiction of the Dewar-Chatt-Duncanson model.

metallacyclopropanes (eq. 1, **B**) containing a doubly reduced olefin—a textbook example [3]. Again, such complexes display little absorption in the visible and the charge transfer bands must lie in the UV region of the spectrum.



We recently characterized the two highly coloured complexes $(\eta^2\text{-TCNE})\text{M}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{W}$) as $\pi(\text{C}=\text{C})$ coordinated species with extensive but not complete electron transfer in the ground state from the metal carbonyl fragments to the TCNE ligand [5]. Along with IR vibrational, UV-Vis and ESR spectroscopic evidence, the electrochemical behaviour was quite revealing; the chromium complex is reduced at the same potential as free TCNE, indicating a virtual match of olefin(π)-to-metal electron donation and metal(d)-to-olefin(π^*) back donation (Fig. 1). Back donation was found to be a little weaker in the case of the tungsten analogue [5].

We now report and discuss the resonance Raman (rR) spectra of both complexes, obtained by excitation into the 700 nm band. Such spectra should show improved resolution and give information about IR silent vibrations (such as $\nu_{\text{C}=\text{C}}$) and about the geometrical parameters most affected by the long-wavelength MLCT transition. Previous observations on a series of α -diimine complexes have shown that such MLCT transitions can be very satisfactorily characterized by rR spectroscopy [6].

Results

Laser irradiation of the two complexes in THF solution gave rise to partial decomposition and formation of strongly luminescing photoproducts. The rR spectra were therefore recorded with the complexes in KNO_3 pellets. The spectra of the

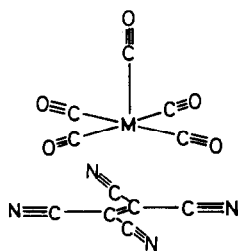


Fig. 2. The structure of $(\eta^2\text{-TCNE})\text{M}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{W}$).

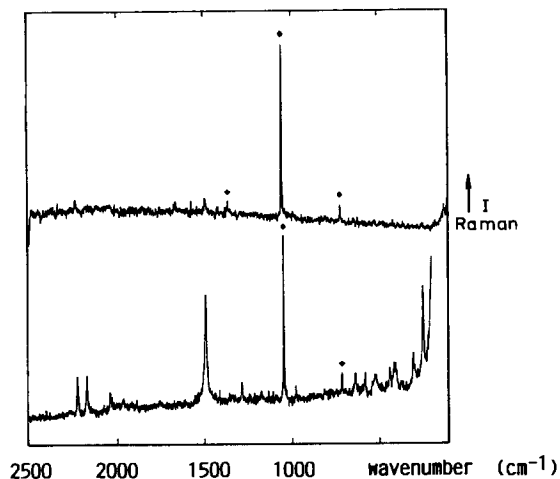


Fig. 3. (Resonance) Raman spectra of $(\eta^2\text{-TCNE})\text{W}(\text{CO})_5$ in a KNO_3 disk (top, $\lambda_{\text{exc}} = 514.5$ nm; bottom, $\lambda_{\text{exc}} = 600.0$ nm) $\blacklozenge = \text{NO}_3^-$.

pure solids and those in KNO_3 discs showed bands at identical wavenumbers, but the spectra in KNO_3 were of much better quality. Figures 3 and 4 show the non-resonance (top) and resonance Raman spectra (bottom) of the complexes at about 600 nm excitation wavelength; in both cases the excitation occurs at the high-energy side of the MLCT band. Table 1 lists the wavenumbers of peak maxima, together with data for free TCNE and TCNE anion radical salts.

Broad absorption and diffuse reflectance bands with maxima around 700 nm were found for both solid complexes in KBr pellets or on filter paper, so that the rR excitation at 600 nm still falls within the high-energy flanks of the broad absorption

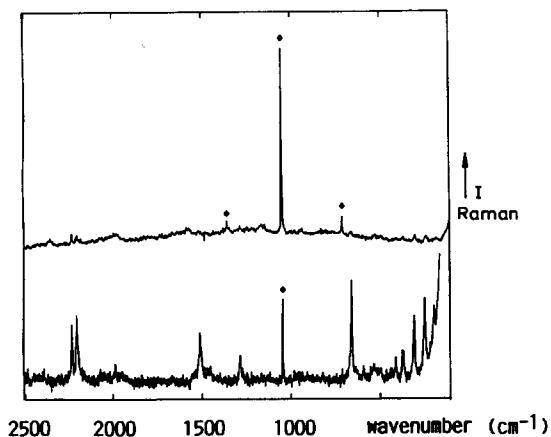


Fig. 4. (Resonance) Raman spectra of $(\eta^2\text{-TCNE})\text{Cr}(\text{CO})_5$ in a KNO_3 disk (top, $\lambda_{\text{exc}} = 514.5$ nm; bottom, $\lambda_{\text{exc}} = 601.4$ nm) $\blacklozenge = \text{NO}_3^-$.

Table 1

Vibrational frequencies (cm^{-1}) of TCNE and its complexes from (resonance) Raman spectra

TCNE ^a	TCNE ^b	$(\eta^2\text{-TCNE})\text{M}(\text{CO})_5$ ^c		Na-TCNE ^a	Assignment
		M = Cr	M = W		
2247	2245	2224	2223	2225	$\nu(\text{C}\equiv\text{N})$
2235	2234	2196	2171	2188	$\nu(\text{C}\equiv\text{N})$
			2040		$\nu(\text{C}\equiv\text{O})$ (“ a_1^2 ”)
		1981	1963		$\nu(\text{C}=\text{O})$ (“ a_1^1 ”)
1569	1567	1507	1491	1430	$\nu(\text{C}=\text{C})$
1282		1285	1286		$\nu(\text{C}-\text{C})$
	670	661	636	(630) ^d	$\nu(\text{M}-\text{C}=\text{C})$
		586	579		$\delta(\text{MCO})$
535	530	530	530		$\delta(\text{CCC})$
		501	501		$\delta(\text{MCO})$
490			439		$\nu(\text{M}-\text{C}(\equiv\text{O}))$
		410	411		$\nu(\text{M}-\text{C}(\equiv\text{O}))$
		371			$\nu(\text{M}-\text{C}(\equiv\text{O}))$
		309	307	(320) ^d	$\delta(\text{CMC})$
254	252	249	253		$\delta((\text{NC})-\text{C}-(\text{CN}))$
					rocking
130	133	198 ^e	169 ^e		$\delta((\text{NC})-\text{C}-(\text{CN}))$
					scissoring

^a Ref. 7. ^b This work, excitation wavelength 514.5 nm. ^c From resonance Raman experiments at about 600 nm excitation wavelength. ^d n.p.L. ^e Tentative assignment.

bands. In keeping with this, the spectrum of the W complex showed an increasing rR effect upon going from 514.5 to 611 nm excitation wavelength.

Discussion

The increase in the intensity of the rR effect on approaching the maximum of the long-wavelength band indicates that this low-energy band, attributed previously to a metal-to-TCNE ligand charge-transfer transition [5], is involved in the observed enhancement of Raman bands. Several bands from vibrations of the TCNE ligand and of the metal carbonyl fragment are unambiguously identifiable (Table 1) on the basis of previous studies involving $\text{TCNE}^{0/-/2-}$ or complexes $(\text{L})\text{M}(\text{CO})_5$ [7,8]. The assignment of the new intense band at 661 cm^{-1} (Cr complex) or 636 cm^{-1} (W complex) is not obvious solely from consideration of the metal carbonyl fragment or TCNE; it will be shown later that this band probably belongs to the stretching of new bonds $\text{M}\cdots\text{C}(\text{TCNE})$ formed in the complex.

The changes occurring upon complexation are discussed below in relation to the effects of the reduction of TCNE and with respect to rR enhancement.

There are two well resolved bands of approximately equal intensity for the CN stretching modes, as expected for a C_{2v} symmetric system (Fig. 2) with two symmetric (A_1) stretching modes for resonance Raman enhancement. In contrast, the IR spectra of $\eta^2(\text{C}=\text{C})$ -coordinated TCNE complexes often show only one strong band, with just a weak shoulder at the high-energy side [4,5]. The bands are shifted to lower frequencies upon complexation (Table 1) and their positions are

comparable with those reported for anion radical salts $(M)^+(\text{TCNE})^-$ [7]. It is noteworthy that the splitting of these two bands is almost twice as large for the tungsten complex as for the chromium analogue.

Very weak carbonyl bands are visible (Fig. 3), especially for the tungsten complex, at frequencies which are not too different from those in the IR solution spectra [5]. Since excitation into an allowed electronic transition will give rise to resonance enhancement of Raman intensity only for symmetrical stretching modes, the two $\nu(\text{CO})$ bands are assigned to the symmetrical stretching modes of the equatorial (a_1^2) and axial (a_1^1) carbonyl(s), respectively.

There was no $\text{C}=\text{C}$ stretching band visible in the IR spectra of the two complexes [5], immediately indicating $\pi(\text{C}=\text{C})$ coordination. In the rR spectra this band is very prominent, especially for the tungsten complex, confirming the qualitative structural assignment (Fig. 2) and implying considerable changes of this bond upon excitation. This result supports the assignment [5] of the pertinent transition as of the MLCT type which should transfer an electron to the ligand and in particular reduce the bond order of the central "double" bond of TCNE [9]. The position of this band is very relevant to the formulation of the electronic structure in these complexes; for both complexes the frequency lies halfway in between the values for non-reduced and singly reduced TCNE [7]. This result is compatible with an almost even balance between olefin-to-metal bonding and back-donation from the metal into the low-lying π^* orbital of olefin antibonding character; both components help to lower the $\text{C}=\text{C}$ stretching frequency. At the same time these intermediate values support the previous conclusion [5] that transfer of one electron from the metal fragment to the ligand is not complete. Other complexes such as $(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Mn}(\eta^1\text{-TCNE})$ [5] or $(\eta^5\text{-C}_5\text{H}_5)_2\text{BrV}(\eta^1\text{-TCNE})$ [10] containing nitrile N-bonded carbonyl-metal moieties and clearly more reduced TCNE ligand [5] show $\text{C}=\text{C}$ stretching vibrations at 1410 cm^{-1} or below [5,10].

Bands around 1285 and 530 cm^{-1} have been attributed to $\text{C}-\text{C}$ stretching and deformation modes of TCNE [7] respectively; these frequencies are little changed upon complexation.

Except for the 530 cm^{-1} band, all the rR bands between 370 and 600 cm^{-1} belong to metal-carbon stretching and metal-carbonyl deformation modes of the $\text{M}(\text{CO})_5$ moiety [8]. They show only weak rR effects, as expected for excitation into a metal to TCNE transition.

The assignment of the remaining low-frequency bands is mainly based on a comparison of the rR data of the two complexes. For the W-complex the strongest rR effects are observed for $\nu(\text{C}=\text{C})$ at 1491 cm^{-1} and for a band at 250 cm^{-1} belonging to the $(\text{NC})-\text{C}-(\text{CN})$ rocking mode of TCNE. This means that the electronic transition involved definitely has metal to TCNE character and that the reduction of the $\text{C}-\text{C}$ double bond to a partially single bond in the excited state of TCNE involves a distortion along this $(\text{NC})-\text{C}-(\text{CN})$ rocking mode. This will lead to an arrangement with sp^3 -“olefin” centers ($4\text{A} \rightarrow \text{B}$), as described structurally for ground state metallacyclopropanes [2-4].



The rR spectra of the Cr-complex show a different intensity pattern although the vibrational frequencies are very similar. The band belonging to $\nu(\text{C}=\text{C})$ is now much weaker and the strongest rR effects occur for bands at 661, 309 and 249 cm^{-1} . Evidently the electronic transition has lost much of its MLCT character, and become in part metal to TCNE bonding to antibonding. Such a transition will, however, primarily affect the metal–ligand bond strength and induce a strong rR effect for the symmetrical metal–olefin stretching mode. The 661 cm^{-1} band is therefore assigned to this vibration. The corresponding vibration of the W-complex appears as a much weaker band at 636 cm^{-1} . The higher frequency for the Cr-complex is in accordance with the smaller mass of the metal and with the larger metal(*d*)/ligand(π^*) delocalization, as observed before [5].

The stronger rR effect of the metal–olefin stretching mode for the Cr-complex is accompanied by an increase in intensity for a Raman band at 309 cm^{-1} (307 cm^{-1} for the W-complex). This band is therefore assigned to the deformation mode of the metallacyclopropane ring ($=\delta(\text{C}-\text{M}-\text{C})$) which is also symmetric. The distortion of the ring is apparently induced by the antibonding character of the excited state. Finally, a similar strong rR effect is observed for the (CN)–C–(CN) rocking mode of both complexes.

These effects of the changing character of electronic transitions on the rR spectra have been observed before for many other complexes. They have recently been described in detail for a series of low valent transition metal α -diimine compounds [6].

The rather strong enhancement of the 661 and 309 cm^{-1} band in case of the chromium complex suggests that this system contains carbonylmetal–TCNE bonds that are more affected by MLCT excitation than the bonds in the tungsten analogue for both steric and electronic reasons, an effect which would also be consistent with the less pronounced photodecomposition of the latter complex.

Experimental Section

The complexes $(\eta^2\text{-TCNE})\text{M}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{W}$) were prepared as described previously [5]. rR spectra were recorded with complexes incorporated into KNO_3 pellets; laser light of wavelength 514.5, 569, 600 and 611 nm (W complex) or 573 and 601.4 nm (Cr complex) was used. The spectrum of TCNE was recorded for the pure solid with excitation at 514.5 nm.

rR spectra were recorded on a Dilor XY Raman spectrophotometer. They were excited by the lines of a Spectra Physics Stabilite 2016 argon ion laser and a Model CR 490 tunable dye-laser with Rhodamine 6G as a dye.

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