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Preliminary communication

$Cr(CO)_5(CNCN)$, a complex in which the coordinated CN group of isocyanogen binds and vibrates like a CO ligand

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Abstract

The IR and Raman spectra have been determined of the products formed by low-temperature (−20 °C) replacement of 2-MeTHF (2-methyltetrahydrofuran) in photochemically produced $Cr(CO)_5(2\text{-MeTHF})$ by isocyanogen, CNCN. The IR spectra are interpreted in terms of the formation of an isonitrile and a nitrile complex, $Cr(CO)_5(CNCN)$ and $Cr(CO)_5(NCNC)$. A detailed study of the IR and Raman spectra of $Cr(CO)_5(CNCN)$, which was formed in large excess, reveals that the coordinating CN group of CNCN has coordinating and vibrational properties almost identical to those of the CO ligands in this complex.

Although the structure, dipole moment and IR spectra of isocyanogen, CNCN, was predicted from ab initio calculations ten years ago [1,2], experimental evidence for its existence was first obtained by us only in 1988 [3]. It was prepared by flash vacuum thermolysis of norbornadienone azine as a volatile product that decomposed above −50 °C to give a brown polymer. The mass spectrum showed that a species C_2N_2 had been formed, and the ^{13}C and ^{14}N NMR spectra were initially assigned to the isomer diisocyanogen, CNNC. HFS calculations and He(I)-PE spectra seemed to confirm this interpretation [4]. However, recent calculations by Cederbaum et al. [5], and especially IR and microwave spectral data presented by Winnewisser et al. [6,7], favoured the other isomeric form, isocyanogen, CNCN. Finally, electron diffraction and low temperature X-ray data [8] recently established that the structure is $C{=}N{-}C{\equiv}N$.

An obvious method of distinguishing between the linear symmetric CNNC ($D_{\infty h}$) and linear asymmetric CNCN ($C_{\infty v}$) involves a comparison of the IR and Raman

Table 1

Observed fundamental vibrations of CNCN (cm^{-1})

	Raman (CS_2) [a]	IR (LXe) [a]	IR (gas) [b]	IR (Ar-matrix) [c]
ν_1	2290 vs	2292 vs	2302	2294.4
ν_2	2048 w	2045 s	2059.7	2053.7
ν_3	976 w	976 vw	975	979.2
ν_4	464 w		463.5	468.5/467.2
ν_5			194.7	198.9/200.8

[a] This work, LXe = liquid xenon ($T = 223$ K, $P = 150$ psi). [b] From [6]. [c] From [7].

spectra. The Raman spectra have not previously been reported, and we recorded them for solutions of CNCN in CS_2 (Table 1). The data clearly show that the molecule cannot have $D_{\infty h}$ symmetry since the vibrations in the IR are also present in the Raman spectra and vice versa. This further confirms the asymmetric CNCN structure.

In principle CNCN may coordinate to a metal via its terminal carbon atom as an isonitrile or via its terminal nitrogen as a nitrile. In order to study the preference for one of these bonding modes, we have prepared the $Cr(CO)_5$ (isocyanogen) complex of this ligand and studied its IR and Raman spectra. In addition, it was to be expected that complexation would lead to stabilisation of the ligand and allow additional confirmation of its structure.

Results and discussion

In order to avoid polymerisation of isocyanogen, the Cr complex had to be prepared at low temperature. This was achieved by irradiation (Osram HBO 200 W/2 Hg lamp) of $Cr(CO)_6$ (220 mg, 1 mmol) in 2-MeTHF (80 ml) at room temperature. The course of the reaction was monitored with samples by IR spectroscopy. When the conversion into $Cr(CO)_5$(2-MeTHF) was completed the solution was transferred to a Schlenk tube cooled to −196 °C containing one equivalent of isocyanogen (obtained from 330 mg of norbornadienone azine by pyrolysis, followed by distillation as previously described [3]; the yield of isocyanogen was ca 60% [3]). This mixture was slowly warmed up, and at −20 °C, isocyanogen started to replace the solvent molecule. When no isocyanogen was left in the mixture, the $Cr(CO)_5$(isocyanogen) complex was isolated at room temperature by evaporation of the solvent, extraction with n-pentane, and recrystallisation of the extract from n-pentane. The yield of the complex (yellowish powder) was low due to polymerisation of most of the isocyanogen. MS: *m/z* 243.9231, calc. for $C_7CrN_2O_5$ 243.9212, with a fragmentation pattern similar to that previously reported [9]. In 1982 Fehlhammer and coworkers [9] made $Cr(CO)_5(CNCN)$ by reaction of $NEt_4[Cr(CN)(CO)_5]$ with cyanogen chloride and carried out an X-ray structure determination. They observed five prominent bands for this complex in the CO- and CN-stretching region, and these closely correspond to those we observed for the $Cr(CO)_5$(isocyanogen) complex (see Table 2). This means that in our case also the complex $Cr(CO)_5(CNCN)$ was formed with the isocyanogen coordinated via its carbon atom to the metal. A closer look at the IR and the

Table 2

IR and Raman spectral data (cm^{-1}) of $Cr(CO)_5$(isocyanogen) and $Cr(CO)_6$ in the CO- and CN-stretching region

C_6H_{12}	$Cr(CO)_5$(isocyanogen)				$Cr(CO)_6$			
	IR		Raman		IR		Raman	
	C_6H_{12} [a]	CH_2Cl_2	C_6H_{12}	CH_2Cl_2	C_6H_{12}	CH_2Cl_2	C_6H_{12}	CH_2Cl_2
2251 m	2246 m	2250 m	2252 s	2252 s				
2103 w	2102 w	2104 w	2106 w				2114 w	2115 w
2020 m	2019 m	2024 m	2026 m	2030 m			2020 m	2022 m
1993 vs	1992 s	1991 vs		1995 w	1986 vs	1980 vs		
1962 sh		1953 sh						
1951 m,br	1952 s,br	1935 m,br						
1925 sh								

[a] From [9].

Raman spectra *, however, shows that this complex has remarkable bonding and vibrational properties which, to our knowledge, have never previously been observed for a $Cr(CO)_5$(isonitrile) complex.

The IR spectrum of the complex in cyclohexane (Fig. 1(a)) shows ν_1 of the CNCN ligand at 2251 cm^{-1}, 40 cm^{-1} lower in frequency than that for the free molecule. This frequency lowering must result from π-backbonding from Cr(0) to the ligand, since σ-donation normally gives rise to bond strengthening and a concomitant frequency increase in the CN-stretching modes in the case of isonitrile and nitrile complexes [10,11].

The three IR bands at 2103, 2020 and 1993 cm^{-1} have in common that their frequencies are hardly solvent dependent (Table 2, Fig. 1). Evidently, this complex has no dipole moment, and the charge shift caused by coordination of isocyanogen is similar to that induced by CO. As a result, the electron distribution around the central metal atom has octahedral symmetry. A similar situation appeared to exist for the complexes $Cr(CO)_5(PCl_3)$ [12–14] and *trans*-$Cr(CO)_4(C_2H_4)_2$ [15], which showed coincidence of their filled metal-*d* orbitals in the UV-PE spectra.

However, not only do isocyanogen and carbon monoxide have similar coordinating properties in the present case, their stretching vibrations are also so close in frequency in this complex that they almost obey the IR and Raman selection rules for an octahedron. This becomes evident when the spectra are compared with those of $Cr(CO)_6$ (Table 2). Because of the exclusion principle imposed by the centre of symmetry, the $\nu_3(t_{1u})$ stretching mode of $Cr(CO)_6$ is only observed as a very strong band in the IR (1986 cm^{-1}), whereas $\nu_1(a_{1g})$ (2114 cm^{-1}) and $\nu_2(e_g)$ (2020 cm^{-1}) only show up in the Raman spectrum. Of these latter bands, $\nu_2(e_g)$ is by far the stronger.

A similar pattern is observed for the complex under study, although the exclusion principle does not hold as strictly as for $Cr(CO)_6$. In addition to a very weak band at 1986 cm^{-1}, arising from $Cr(CO)_6$ which is present as an impurity, and the broad,

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* IR spectra were recorded on a Nicolet 7199B FTIR interferometer with a liquid-nitrogen-cooled MCT detector (32 scans, resolution 1.0 cm^{-1}). Raman spectra were measured on a Dilor XY spectrophotometer and excited by the 514.5 nm line of a Spectra Physics Stabilite 2016 argon ion laser.

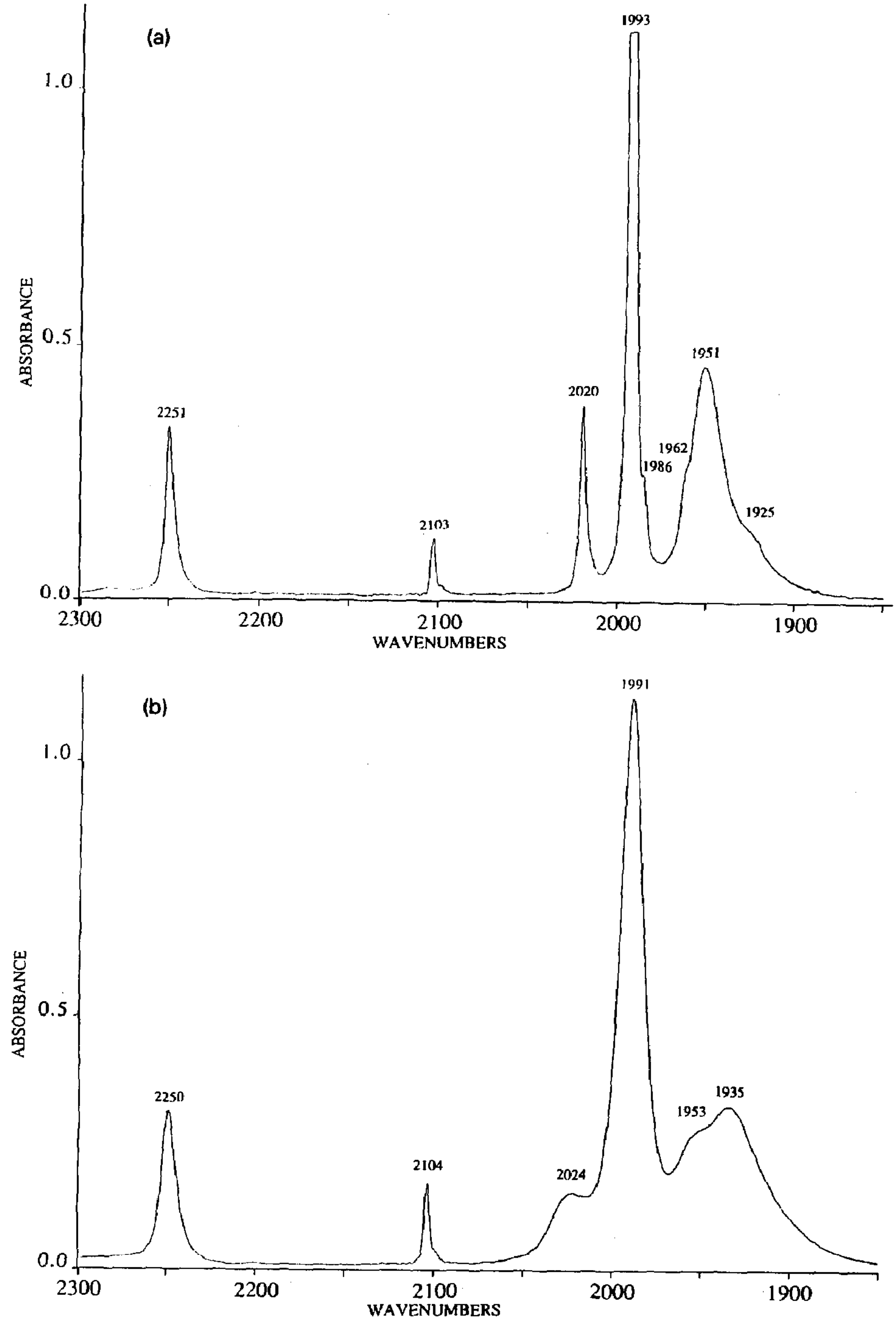

Fig. 1. IR spectra in the CO- and CN-stretching region of $Cr(CO)_5$(isocyanogen) in C_6H_{12} (a) and CH_2Cl_2 (b).

solvent-dependent band at lower frequency (vide infra), the IR spectrum of Fig. 1(a) shows a very intense band at 1993 cm^{-1} and two weaker ones at 2020 and 2103 cm^{-1}, respectively. In the Raman spectrum of this complex in cyclohexane only the latter two bands appear, of these the 2026 cm^{-1} band is most intense, just as for $Cr(CO)_6$. A solution of the complex in CH_2Cl_2 showed a weak Raman band at 1995 cm^{-1}.

Thus, apart from the fact that the exclusion principle does not hold as strictly for this complex as in the case of $Cr(CO)_6$, the frequency and intensity patterns for both these compounds are very similar. Replacement of CO by CNCN hardly changes the vibrational properties of the coordinating ligands!

The remaining composite IR band below 1970 cm^{-1} cannot be assigned to this $Cr(CO)_5(CNCN)$ complex. Its frequency and solvent dependent behaviour points to the presence of a second isomer, $Cr(CO)_5(NCNC)$, in which isocyanogen is coordinated to the metal via its nitrogen lone pair. For comparison, $Cr(CO)_5(NCMe)$ has its strongest IR bands in n-hexane at 1954 cm^{-1} (s, e-symmetry) and 1930 cm^{-1} (m, a_1-symmetry), very close in frequency to the 1951 and 1925 cm^{-1} IR bands of the complex under study in cyclohexane (Fig. 1a). The shoulder at 1962 cm^{-1} (C_6H_{12})/1953 cm^{-1} (CH_2Cl_2) may then arise from the b_2-vibration of the $Cr(CO)_5$ fragment in $Cr(CO)_5(NCNC)$. Thus, the IR spectra probably come from two isomeric forms of the $Cr(CO)_5$(isocyanogen) complex. If this interpretation is correct, it implies that there is an equilibrium between these two regioisomers, since in Fehlhammer's synthesis [9], only the carbon-to-metal isomer can be formed initially. Work is in progress to further establish the bonding properties of these isomers and the mechanism of their interconversion in solution.

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