

Preparation, Spectroscopic Properties and Resonance Raman Excitation Profiles of the Binuclear Complex $[\{W(CO)_5\}_2\mu\text{-pyrazine}]$ and the Preresonance Raman Spectra of $[W(CO)_5\text{pyridazine}]$

H. DAAMEN, D. J. STUFKENS* and A. OSKAM

Anorganisch Chemisch Laboratorium, University of Amsterdam, J. H. van't Hoff Instituut, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

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The binuclear complexes $[\{M(CO)_5\}_2\mu\text{-pyrazine}]$ ($M = Cr, W$) were readily prepared by heating the mononuclear compounds in an inert atmosphere. The spectroscopic data demonstrate that the $M(CO)_5$ moieties in these complexes have retained C_{4v} symmetry. The two allowed metal to pyrazine CT transitions could be detected and assigned with the use of the Resonance Raman effect.

The preresonance Raman spectra of $[W(CO)_5\text{-pyridazine}]$ are reported and related to the properties of the W to pyridazine CT transition.

Introduction

In the last few years much attention has been paid in our laboratory, to the coordination of nitrogen donor ligands in the complexes $M(CO)_5L$ [1–3] and $M(CO)_4L$ [4–6] ($M = Cr, Mo, W$; $L =$ nitrogen donor ligand). The bonding properties of the $M(CO)_5L$ complexes have been investigated with the use of PES, electronic absorption, vibrational and ^{13}C NMR spectroscopy and with differential scanning calorimetry [7]. The effect that the variation of the ligand L has on the bonding and electron distribution in these complexes has been discussed. There are, however, two aspects of this work which need further attention.

During the investigation of the formation enthalpy of $[M(CO)_5\text{pyrazine}]$ ($M = Cr, W$) we observed a transformation of these complexes into $[\{M(CO)_5\}_2\mu\text{-pyrazine}]$ when they were heated at $95^\circ C$ in an inert atmosphere [7]. Up to now the existence only

of these binuclear compounds has been noted by Herberhold *et al.* [8] without further characterization of the structure and bonding. These properties will be reported in this article.

Furthermore, we were especially interested in the characterization of the MLCT transitions of those complexes in which the nitrogen donor ligand L possesses a low-lying π^* orbital (e.g. pyrazine, pyridazine). Although several articles have appeared about the properties of these MLCT transitions [1, 9], we were especially interested in obtaining further information which could be derived from the Resonance Raman (RR) spectra. Quite recently, this RR effect has been used successfully by us for the detection, characterization and assignment of MLCT transitions in a series of $M(CO)_4(\alpha\text{-diimine})$ ($M = Cr, Mo, W$) complexes [4–5]. The RR spectra of both $[W(CO)_5\text{pyridazine}]$ and $[\{W(CO)_5\}_2\mu\text{-pyrazine}]$ will be reported and discussed.

Experimental

Preparations

The preparation of the mononuclear complexes from $M(CO)_5\text{THF}$ has been described elsewhere [2].

The red solid $[\{M(CO)_5\}_2\mu\text{-pyrazine}]$ complexes ($M = Cr, W$) were prepared by heating solid $[M(CO)_5\text{-pyrazine}]$ at $95^\circ C$ in an inert atmosphere. Based on a loss of weight of 40 a.u. per $[M(CO)_5\text{pyrazine}]$ molecule the following reaction is proposed. $2[M(CO)_5\text{pyrazine}] (s) \rightarrow [\{M(CO)_5\}_2\mu\text{-pyrazine}] (s) + \text{pyrazine} (g)$ [7]. Elemental analysis of the solids before and after the reaction gave the following results for the unpurified reaction products:

Author to whom correspondence should be addressed.

	%C		%H		%N	
	calc.	exp.	calc.	exp.	calc.	exp.
$Cr(CO)_5\text{pyrazine}$ (1a)	39.73	39.54	1.48	1.62	10.29	9.82
$\{Cr(CO)_5\}_2\mu\text{-pyrazine}$ (2a)	36.23	36.01	0.87	1.22	6.03	6.21
$W(CO)_5\text{pyrazine}$ (1b)	26.76	26.91	1.00	1.01	6.93	6.98
$\{W(CO)_5\}_2\mu\text{-pyrazine}$ (2b)	23.10	23.56	0.55	0.66	3.85	4.14

TABLE I. Vibrational Frequencies of the $M(\text{CO})_5$ Moiety in $[\{M(\text{CO})_5\}_2\mu\text{-pyrazine}]$ in the Infrared Spectrum.

Compound	$\nu(\text{CO})^a$		$\nu(\text{MC})^b$		
	A_1^2	$E + A_1^1$	A_1^1	A_1^2	E
Cr	2071	1940	481	398	442, 430
W	2072	1942	475	—	377, 356

^a CHCl_3 solution. ^bNujol mull.

The binuclear complexes are only sparingly soluble in most solvents. The chromium complex readily decomposes in solution in contrast to the tungsten one.

Spectroscopic Measurements

Electronic absorption spectra were recorded on a Cary model 14 spectrophotometer. A diffuse reflection accessory with integrating sphere was used for the diffuse reflectance spectra of the powdered samples with magnesium carbonate as a standard.

The Raman spectra of the solid mononuclear complexes were obtained from a Coderg PH-1 at -160°C . Raman spectra of the binuclear complex were recorded on a Jobin-Yvon HG-2S spectrophotometer for 10^{-4} M solutions in CH_2Cl_2 and C_6H_6 . A spinning cell was used to suppress decomposition in the laser beam and a solvent band was used as internal standard. Band areas were measured with a Hewlett Packard digitizer model 64 controlled by a calculator model 10 and corrections were made for absorption of the scattered light and for the sensitivity of the spectrophotometer. A Krypton CR model 500 K, a SP model 171 argon ion laser and a CR490 tunable dye laser with sodium fluoresceine in ethyleneglycol as a dye were used as excitation sources.

Infrared spectra were recorded on a Beckman 4250 instrument.

Results and Discussion

$[\{W(\text{CO})_5\}_2\mu\text{-pyrazine}]$

Both the Cr- and W-complexes could be prepared by heating solid $[\text{M}(\text{CO})_5\text{pyrazine}]$ at 95°C in an inert atmosphere. The red solid products appeared to be stable up to about 170°C . The same type of reaction has been observed at ambient temperature by Beck and Danzer for solid $[\text{W}(\text{CO})_5\text{diazirine}]$ [10]. In accordance with the measured loss of weight of 40 a.u. the following reaction was proposed [7]:

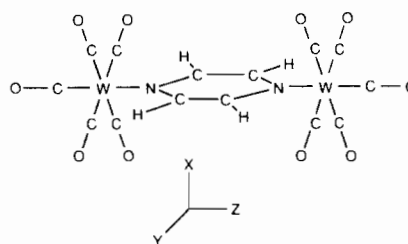
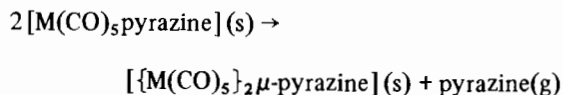


Fig. 1. The structure of $[\{W(\text{CO})_5\}_2\mu\text{-pyrazine}]$ with x, y and z axes.

Although accurate molecular weights could not be obtained due to the low solubility of the complexes formed the measurements clearly showed that the molecular weight was far too high for a mononuclear complex. The correctness of the molecular formula of the binuclear complex was confirmed by elemental analysis. Only $[\{W(\text{CO})_5\}_2\mu\text{-pyrazine}]$ (2b) has been investigated in more detail because it is much more stable in solution than the corresponding Cr-complex (2a). The presence of the $W(\text{CO})_5$ moieties in 2b was deduced from the vibrational spectra (Table I) which show band patterns in the CO and WC stretching region which clearly resemble those of the corresponding mononuclear complex. The IR spectrum of a CHCl_3 solution shows only two bands instead of three ($2A_1 + E$) in the CO stretching region, A_1^1 and E coincide. No extra vibrations were observed in the Resonance Raman spectrum. This means that the local C_{4v} symmetry of the $W(\text{CO})_5$ moieties is retained in 2b.

The coordination of pyrazine in 2b cannot deviate much from that in 1b because the pyrazine modes are nearly the same in both complexes and hardly differ from those of the free ligand [11]. These results are confirmed by the absorption spectra of 1b and 2b. Both complexes (Figs. 2 and 5) show the characteristic LF band at about the same position (400 nm). The assignment of this LF band for $M(\text{CO})_5\text{L}$ complexes to the ${}^1E_g \leftarrow {}^1A_1$ transition [12] assuming local C_{4v} symmetry of the $M(\text{CO})_5$ moiety, has recently been confirmed by m.c.d. measurements [13]. These m.c.d. spectra showed a single A-term coinciding with the LF band as was expected for an ${}^1E \leftarrow {}^1A_1$ transition. A similar A-term is observed for the LF band of 2b which confirms the local C_{4v} symmetry of the $W(\text{CO})_5$ moieties in 2b. According to the above results the structure shown in Fig. 1 is proposed for 2b.

Electronic absorption spectra

The absorption spectra of 2b in CH_2Cl_2 and C_6H_6 are shown in Figs. 2 and 3, respectively. Apart from LF transitions between 300–400 nm a broad structureless metal to pyrazine CT (MLCT) band is observed between 450 and 600 nm. The $d(M) \rightarrow \pi^*(\text{CO})$ transitions occur below 300 nm.

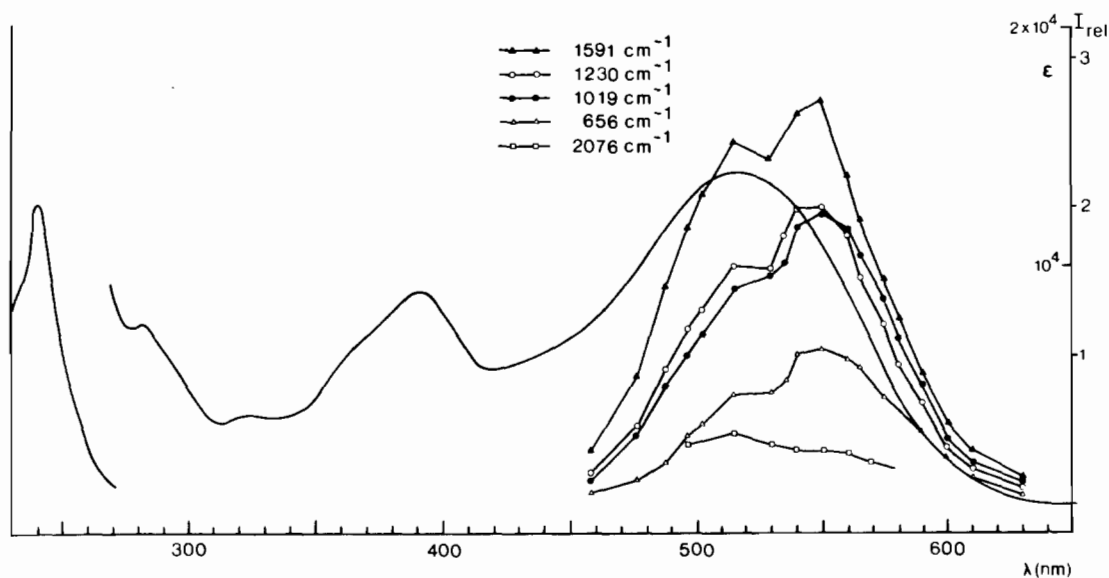


Fig. 2. Excitation profile of $[\{W(CO)_5\}_2\mu\text{-pyrazine}]$ in CH_2Cl_2 relative to the 1423 cm^{-1} band of CH_2Cl_2 .

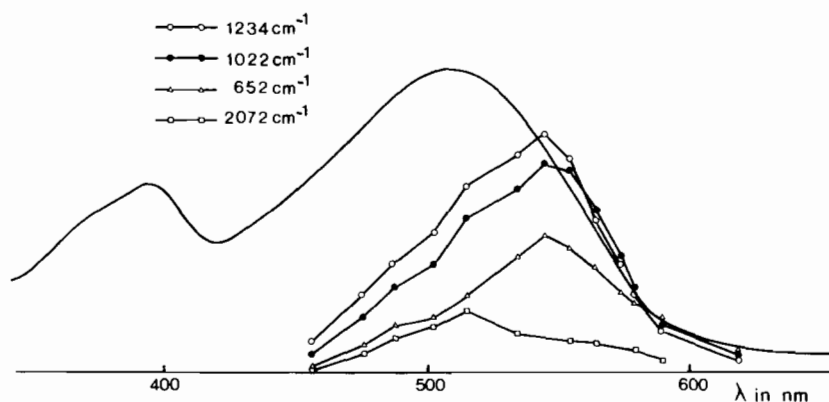


Fig. 3. Excitation profile of $[\{W(CO)_5\}_2\mu\text{-pyrazine}]$ in C_6H_6 relative to the 606 cm^{-1} band of C_6H_6 .

The position of the LF band (about 400 nm) hardly deviates from that of 1b, but the molar extinction ϵ_{\max} is approximately twice as large. This is in accordance with the presence of two $M(CO)_5$ groups in the binuclear complex.

The structure shown in Fig. 1 is assumed with the pyrazine ring in the yz -plane and the tungsten equatorial carbonyl bonds at angles of 45° with respect to the pyrazine plane. The allowed MLCT transitions can be derived from the diagram shown in Fig. 4. In this diagram the appropriate metal d and pyrazine π and π^* orbitals together with their interactions are indicated for symmetry D_{2h} . Two MLCT transitions are allowed which are z and y polarized, respectively. The z -polarized transition will be more intense than the overlap forbidden y -polarized transition and will be located close to the maximum of the absorption band. The y -polarized transition is then

responsible for the asymmetric shape of the absorption band at the high energy side.

The MLCT band shifts to higher energy when a more polar solvent is used. This shift is caused by the two opposing partial dipole moments along the z -axis of the complex. The z -polarized MLCT transition is accompanied by a decrease in these dipole moments in the excited state and will therefore shift to higher energy in more polar solvents.

Furthermore a significant red shift of this band is observed (5.6 kK) with respect to the same band for the mononuclear compound 1b (compare Figs. 2 and 5). Creutz and Taube [14] observed a similar but less pronounced shift for $[\{(NH_3)_5Ru\}_2\mu\text{-pyrazine}]^{4+}$ with respect to $[(NH_3)_5Ru\text{-pyrazine}]^{2+}$. Two effects can cause this shift. Firstly, coordination of a second $M(CO)_5$ group to pyrazine will create a more positive charge on this ligand which causes a stabilization

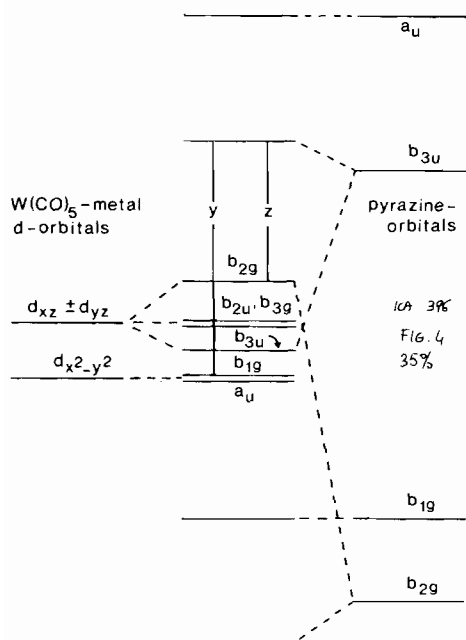


Fig. 4. Simplified molecular orbital diagram of $[\{W(CO)_5\}_2\mu\text{-pyrazine}]$ with polarization characteristics of the two allowed MLCT transitions.

of orbitals. Such a stabilization effect has been observed by us in the photoelectron spectra of free pyrazine and compound 1b [2]. Going from free to coordinated pyrazine a stabilization of 4.4 kK was found for the b_{1g} π -orbital of pyrazine as a result of the charge effect. A second effect, which might have influenced the position of the MLCT band is the different type of metal d-orbitals involved in the transitions for both types of complexes.

Resonance Raman spectra

In order to get more information about the MLCT transitions we investigated the Resonance Raman (RR) spectra of the binuclear complex 2b in CH_2Cl_2 and C_6H_6 .

Enhancement of Raman intensity was observed for the symmetric pyrazine modes ν_1 (ring stretch), ν_{6a} (in plane ring bend), ν_{8a} (ring stretch) and ν_{9a} (in plane hydrogen bend) for which vibrations the numbering of Lord [15] has been used. The RR effect for these pyrazine modes confirms the MLCT character of the absorption band.

Furthermore, a RR effect was observed for $\nu(\text{CO})-(A_1^2)$, the symmetrical stretching mode of the equatorial carbonyls. Much weaker effects were found for the two symmetric WC stretching modes. No Raman band could be assigned to $\nu_s(\text{WN})$ although spectra were recorded as low as 120 cm^{-1} .

For $\nu(\text{CO})(A_1^2)$ and the pyrazine modes excitation profiles were derived, which represent the changes of Raman intensity with variation of the exciting laser

frequency (see Figs. 2 and 3). These curves possess two maxima which coincide for all vibrations. This indicates that these maxima belong to different electronic transitions in accordance with the diagram in Fig. 4. The excitation profiles are red shifted with respect to the absorption band. Such a red shift has been observed previously and has been discussed in more detail by Friedman, Rousseau and Bondybey [16] for matrix isolated Br_2 . It is therefore assumed that the strongest maximum of the excitation profiles corresponds to the z-polarized transition, which has its maximum close to the maximum of the absorption band. The second maximum then corresponds to the y-polarized MLCT transition at the short wavelength side of the absorption band. Although the resonance effects differ for both transitions, no appreciable change of relative intensities is observed for the pyrazine modes. This means that both MLCT transitions are directed to the same excited orbital of pyrazine.

There is, however, a remarkable difference between the two maxima of the excitation profiles which is most evident in the spectrum of the benzene solution. Going from the first, low energy, maximum to the second one, all pyrazine modes decrease in intensity. On the other hand, the intensity of $\nu(\text{CO})-(A_1^2)$ increases. This difference in the behaviour of the pyrazine and CO stretching modes is most likely due to the different characters of the d-orbitals involved in the electronic transitions. The z-polarized transition arises from the metal $d(b_{2g})$ orbital which is anti-bonding with respect to a pyrazine π -orbital. The y-polarized transition on the other hand arises from the b_{1g} orbital which is bonding with respect to the equatorial carbonyls. The enhancement of $\nu(\text{CO})-(A_1^2)$ will be discussed in more detail for the mononuclear complex 1b.

No resonance effect has been observed for the asymmetric mode ν_{10a} of pyrazine, which shows a large enhancement of Raman intensity for free pyrazine as a result of vibronic coupling between the excited B_{3u} and B_{2u} states [17].

$[W(\text{CO})_5\text{pyridazine}]$

For the Cr- and W pentacarbonyl compounds of pyrazine and pyridazine, the lowest excited state has CT character. The electronic absorption spectra of three of the complexes, which have already been assigned [2, 18] are shown in diffuse reflectance in Fig. 5. These spectra, closely resembling the spectra in apolar solvents, show the ${}^1E_a \leftarrow {}^1A_1$ LF transition at 400 nm and the $d(\text{M}) \rightarrow \pi^*(\text{L})$ CT transition at about 450 nm. The $d(\text{M}) \rightarrow \pi^*(\text{CO})$ transition is observed at 250 nm.

Preresonance Raman spectra

Because solutions of these complexes easily decompose in the laser beam, resonance Raman

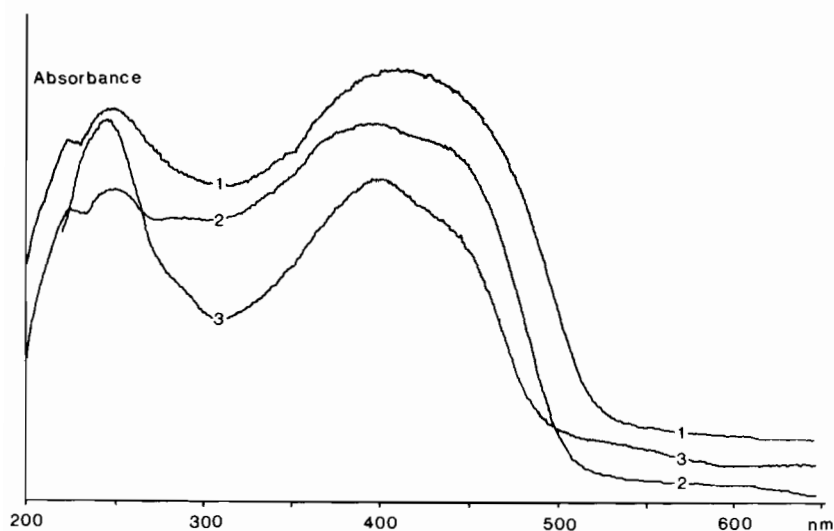


Fig. 5. Diffuse reflectance spectra of 1) $[\text{Cr}(\text{CO})_5\text{pyridazine}]$, 2) $[\text{W}(\text{CO})_5\text{pyridazine}]$ and 3) $[\text{W}(\text{CO})_5\text{pyridazine}]$.

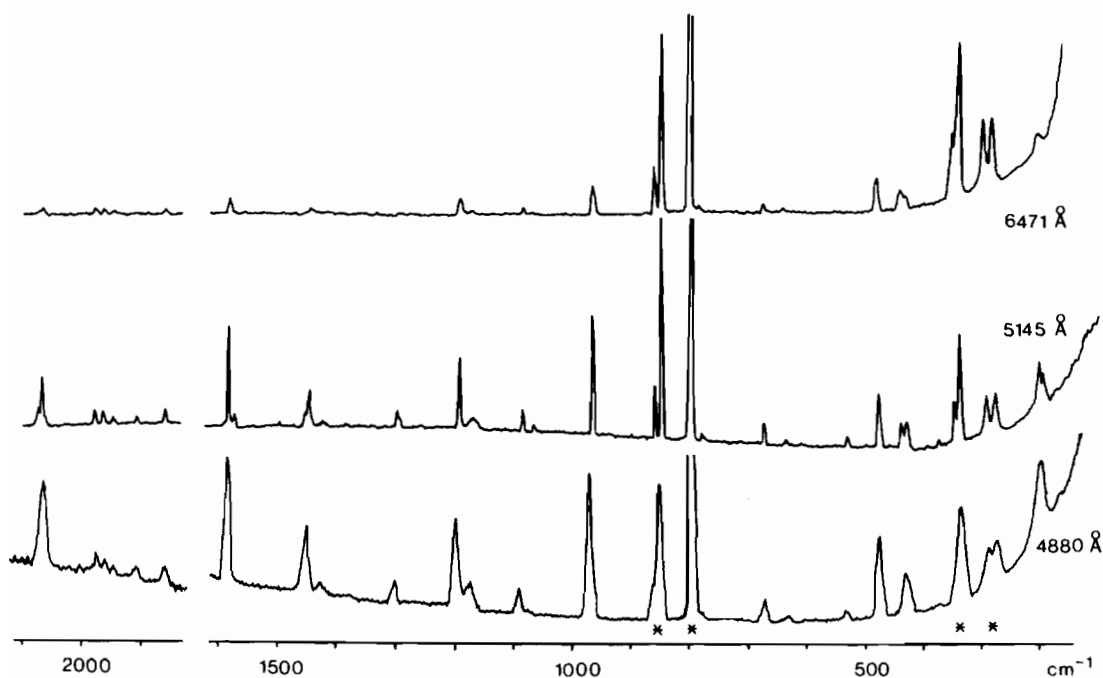


Fig. 6. Solid state preresonance Raman spectra of $[\text{W}(\text{CO})_5\text{pyridazine}]$ mixed with KIO_4 as internal reference excited at 6471, 5145 and 4880 Å. The reference bands are indicated with an asterisk. If the intensities are corrected for the sensitivity of the spectrophotometer, those of *e.g.* the CO stretching modes have to be multiplied by 1.7 (6471 Å), 0.6 (5145 Å) and 0.7 (4880 Å) with respect to the intensity of the KIO_4 band at 846 cm^{-1} .

spectra had to be obtained from solid samples at low temperatures (-160°). Raman spectra were taken in preresonance instead of in resonance in order to avoid fluorescence. Because the complexes of both pyridazine and pyridazine gave similar resonance effects we shall only discuss the results for $[\text{W}(\text{CO})_5\text{pyridazine}]$ which gave the best Raman spectra. The spectra recorded with three different laser lines are shown in

Fig. 6. The vibrations of the internal standard KIO_4 are indicated with an asterisk.

The spectrum excited with the $\lambda = 6471\text{ Å}$ line shows a very weak non-resonance Raman spectrum of the pyridazine complex of W which becomes more intense when the exciting laser line approaches the MLCT band. All ligand vibrations which are enhanced in intensity, are collected in Table II together with

TABLE II. Assignment^a of the Ligand Vibrations with Relative Intensities in Parenthesis of the Solid State Raman Spectrum ($\lambda_{\text{exc}} = 6471 \text{ \AA}$).

Cr(CO)₅pyridazine: ν_1 966(10); ν_{6a} 637(1); ν_{6b} 676(3); ν_{8a} 1580(6); ν_{9a} 1186(5); ν_{14} 1294(1); ν_{15} 1081(1); ν_{18a} 1065(1); ν_{19a} 1445(3); ν_{19b} 1419(-);

W(CO)₅pyridazine: ν_1 963(10); ν_{6a} 639(1); ν_{6b} 684(3); ν_{8a} 1580(6); ν_{9a} 1192(3); ν_{14} 1295(1); ν_{15} 1082(2); ν_{18a} 1067(1); ν_{19a} 1446(2);

Cr(CO)₅pyrazine: ν_1 1019(7); ν_{6a} 632(8); ν_{8a} 1592(10); ν_{9a} 1234(6); ν_{12} 1054(6); ν_{18a} 1129(2); ν_{19a} 1485(-).

^aNumbering according to Lord's convention [15], the assignment is based on reference 11.

their assignments. The metal–ligand vibrations, which all have a frequency lower than 800 cm^{-1} show a weak or moderate resonance Raman effect. This indicates changes in the metal–ligand bond strength in the CT excited state with respect to the ground state. These changes are caused by depopulation of the metal $\pi(d)$ orbitals and by oxidation of the central metal atom as a result of the MLCT transition.

A similar weak resonance effect is observed for the A_1^1 CO stretching mode. Much stronger resonance effects are observed for the pyridazine modes between $950\text{--}1600 \text{ cm}^{-1}$ and for $\nu(\text{CO})(A_1^2)$ at 2072 cm^{-1} . The enhancement of intensity of the pyridazine modes reflects the change in bonding in pyridazine when the lowest π^* -orbital is occupied. The resonance Raman effect for $\nu(\text{CO})(A_1^2)$, which is much stronger than for the metal–ligand modes and for $\nu(\text{CO})(A_1^1)$ makes an explanation in terms of depopulation of the metal $\pi(d)$ orbitals improbable. There is no reason why solely $\nu(\text{CO})(A_1^2)$ would be strongly affected by this process. We ascribe this resonance effect of $\nu(\text{CO})(A_1^2)$ to a through space interaction of π^* -orbitals of pyridazine and the equatorial carbonyls in the lowest excited CT state of the complex. This explanation is confirmed by the fact that the relative intensity of this mode increases when W is replaced by the much smaller Cr-atom. The same effect has been observed for a large number of $\text{M}(\text{CO})_4(\alpha\text{-diimine})$ compounds [6]. For these latter complexes a large enhancement of Raman intensity has been observed for $\nu_s(\text{CO})_{\text{cis}}$, the symmetrical stretching mode of the carbonyls *cis* with respect to the α -diimine. On the other hand, $\nu_s(\text{CO})_{\text{trans}}$ could not be observed for these complexes. For the binuclear complex a much weaker resonance Raman effect was observed for $\nu(\text{CO})(A_1^2)$ than for the mononuclear one. We therefore gave a different explanation for the enhancement of this mode for both complexes. An explanation in terms of depopulation of metal $d(\pi)$ orbitals is more likely in the case of the binuclear complex.

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