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A study of the Electronic Properties of $M(CO)_4DAB$ ($M = Cr, Mo, W$; DAB = Diazabutadiene). I. Electronic Absorption, Resonance Raman, Infrared, ^{13}C- and ^{15}N-NMR Spectra

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During the reaction of $M(CO)_5THF$ with DAB an intermediate $M(CO)_5DAB$ was formed, in which DAB is coordinated as a monodentate ligand. The complexes $M(CO)_4DAB$ possess structured absorption bands in the visible which were assigned, mainly on the basis of resonance Raman results, to different CT transitions from the metal to DAB. The resonance Raman spectra showed that orbitals of both DAB and the cis carbonyls are involved in the first excited states. A very pronounced enhancement of Raman intensity was found in polar solvents for a polarized band at about 215 cm^{-1}, which could therefore be assigned to the $\nu_8(M–N)$. The character of this mode was investigated by ^{15}N enrichment of DAB. ^1H, ^{13}C and ^{15}NMR spectra show a large electron shift from DAB to the metal in polar solvents.

Introduction

Part of the work at our laboratory is concerned with the coordinating properties of nitrogen bases with cumulated or conjugated double bonds, which may show ambident bonding behaviour. In this respect the diazabutadienemetaltetracarbonyls (M = Cr, Mo, W) recently prepared by tom Dieck and coworkers [2–4] attracted our attention because of their analogy with the sulfurdiiminemetaltetracarbonyls (M = Cr, Mo, W) studied by Meij [1]. Both type of complexes obey the symmetry rules of the pointgroup C_{2v}, they are both strongly coloured and both bidentate nitrogen donor ligands show a strong π-bonding interaction with the VI B metals. Although tom Dieck paid much attention to the bonding properties of $M(CO)_4DAB$ [2–10] information about the complicated absorption spectra is scarce. These spectra have therefore been investigated in more detail and an assignment of the band is given. The resonance Raman spectra are reported and some important infrared and ^{15}N-NMR results for ^{15}N-enriched compounds are also given.

Experimental

All infrared spectra were recorded using a Beckman IR 4250 spectrophotometer. The absorption spectra were recorded on a Cary model 14 spectrophotometer and the Raman spectra on a Coderg PH 1 Raman spectrophotometer, using a krypton CR model 500 K and argon CR model 53 ion laser and a CR 490 tunable dye laser with sodiumfluoresceine in ethyleneglycol as a dye and cyclooctatetraene as photosensitizer. A spinning cell according to Kiefer [11] was used to suppress decomposition of the complex in solution in the laser beam.

The resonance Raman spectra were recorded for 10^{-4}–10^{-3} M solutions in CH_2Cl_2 and C_6H_6 using a solvent band as an internal standard. Band intensities were measured with a Hewlett Packard model 10 calculator with a 9864 A Digitizer and corrected for variation of absorption of the scattered light and for the sensitivity of the spectrophotometer.

^{13}C-NMR spectra were recorded with a Varian CFT 20 instrument, ^1H NMR spectra on a Varian AT 60 and ^{15}N-NMR on a Bruker WH 270 NMR apparatus.

The preparation of the $M(CO)_4DAB$ complexes (M = Cr, Mo, W) has been described by tom Dieck [2, 8]. For the preparation of the chromium and tungsten complexes the following method was applied.

A solution of 10 mmol chromium- or tungsten hexacarbonyl in 200 ml THF was irradiated for 24 hours with a Hanovia medium pressure mercury lamp under a slow stream of nitrogen. The product obtained, $M(CO)_5THF$ (M = Cr, Mo, W) is very unstable with respect to substitution reactions. When the diazabutadiene was allowed to react with $M(CO)_5$-THF the DAB complex was formed at once at room temperature.

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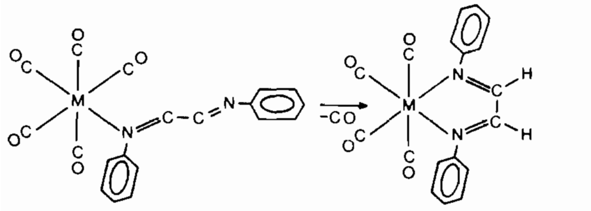

Figure 1. The intramolecular conversion of $M(CO)_5$ DAB to $M(CO)_4DAB$. The structure given on the right is the general structure for the compounds $M(CO)_4DAB$. In this case: R_1 = phenyl and R_2 = H.

After evaporation of most of the THF, the complex was precipitated with hexane and filtered off. The crude product contained some hexacarbonyl which was removed by sublimation under reduced pressure at 60 °C. The complexes were recrystallized from a THF/hexane mixture. The reaction of $Cr(CO)_6$ with THF can be accelerated by adding benzophenone to the solution before the irradiation is started. Benzophenone acts as a photosensitizer for the photosubstitution reactions of $Cr(CO)_6$ [12].

Extensive analytical data have been given by tom Dieck [28]. For ^{15}N-NMR and infrared studies glyoxalbismethylimine$Mo(CO)_4$ ($R_1{=}CH_3$; $R_2{=}H$) and diacetylbismethylimine$Mo(CO)_4$ ($R_1{=}CH_3$; $R_2{=}CH_3$) were prepared with 98,6% ^{15}N-enriched methylamine, obtained from Merck, Sharp and Dohme.

Results and Discussion

When the substitution reaction of $M(CO)_5THF$ (M=Cr, Mo) was carried out with glyoxalbisphenylimine (R_1=phenyl, R_2=H) at −60 °C, a green product was formed. This product could not be isolated because it was slowly converted at about −20 °C and rather rapidly at room temperature to a blue stable compound (see Fig. 1). The IR and NMR spectra clearly showed that this green product must be $M(CO)_5DAB$ (M=Cr, Mo) in which DAB acts as a monodentate ligand. Quite recently a stable Pd^{2+} compound has been isolated in our laboratory in which the DAB is also bonded as a monodentate ligand to the metal [13]. At room temperature $M(CO)_5DAB$ was converted to $M(CO)_4DAB$ in which DAB acts as a bidentate ligand.

IR Data

The complexes have the structure shown in Figure 1 and they obey the symmetry rules of the point group C_{2v}. In the infrared spectra four intense bands are found in the CO-stretching region ($2A_1 + B_1 + B_2$) which are characteristic for disubstituted octahedral metal carbonyls [14, 15]. A remarkable property of the complexes is the dependency of some vibrational frequencies on the polarity of the solvent, an effect which has been described by tom Dieck for the CO-stretching frequencies [2, 3] and which has been used by Walter to determine the polarity of organic solvents and polymers [16].

The δ(MCO) and ν(MC) vibrations are in the same frequency region as found for other disubstituted hexacarbonyls [14, 17].

Two weak bands were observed in the IR spectra at about 250 and 220 cm^{-1} respectively and are assigned to the antisymmetric (B_1) and symmetric (A_1) metal–nitrogen stretching vibrations. The latter vibration is also found in the resonance Raman spectra as a polarized band and appears to be vibronically coupled to the CT transition. This result which will be discussed later in more detail, justifies these assignments.

An assignment of a cobalt–nitrogen stretching vibration for cobaloximes has been made by Yamazaki and Hohokabe who found this mode at about 515 cm^{-1}. This greatly differs from our results although in cobaloximes two diazabutadienes are coordinated to the central metal [18].

There appears to be no measurable difference between the ν(M–N) frequencies of the ^{15}N-enriched complexes and the non-enriched compounds. This effect, which has also been observed for Pt–pyridine complexes, is due to a strong coupling of this mode with vibrations of the DAB ligand.

On the other hand the ν(C=N) frequencies of the enriched complexes are shifted to lower frequency by about 35 cm^{-1} and the ν(C–C) by about 10 cm^{-1}. There is a remarkable difference between the ν(C=N) frequencies of the alkyl and aryl substituted DAB compounds. This must be caused by conjugation between the aryl and diimine groups, which means that the aryl groups are in one plane with the diimine groups in the complex, this being in contradiction to what is found for cyclohexyl groups.

Electronic Absorption Spectra

The free DAB ligands are four centre π-electron systems with two bonding π-orbitals and two antibonding π*-orbitals. There are two linear combinations of nonbonding orbitals which are located on the nitrogen atoms and occupied by the two lone pairs. An orbital transformation is necessary in order to obtain C_{2v} symmetry adapted orbitals on the metal.

d-orbital transformation

$d_{(z')^2}$ — d_{y^2} (a_1)
$d_{(x')^2-(y')^2}$ — d_{x^2} (b_1)
$d_{x'y'}$ — $d_{x^2-z^2}$ (a_1)
$d_{x'z'}$ — $d_{xy} + d_{yz}$ (b_2)
$d_{y'z'}$ — $d_{xy} - d_{yz}$ (a_2)

TABLE I. Some Relevant Vibrational Frequencies (cm^{-1}).[a],[b]

M	R_1	R_2	νCO^{cis} A_1	νCO^{cis} B_2	νCO^{trans} A_1	νCO^{trans} B_1	νCN B_1	νCN A_1	δMCO A_1	δMCO	δMCO A_1	δMCO	νMC	νMC A_1	νMC	νMC	νMN B_1	νMN A_1
Cr	phenyl	H	2010	1930	1893	1851	1605	1590	650	625	555	525	465	455(sh)[c]	410	398	236	218
Cr	t-bu	H	2015	1905	1888	1836	1526	1510	650	624	550	525	460	425	385	365	277	262
Mo	phenyl	H	2023	1939	1885	1814	1601	1590	645	601	579	555	468	456(sh)	400	376	245	210
Mo	t-bu	H	2024	1910	1870	1805	1556	1540	650	616	582	548	470	450(sh)	398	365	248	209
Mo	CH_3	H	2029	1910	1885	1820	1525	1515	640	594	573	537	457	435(sh)	403	371	238	218
Mo	CH_3	CH_3	2014	1915	1881	1823	1540	sh	638	598	569	540	463	445(sh)	405	368	237	220
W	t-bu	H	2015	1905	1870	1805	1537	1525	635	606	579	557	481	448	405	373	259	226
^{15}N-enriched compounds																		
Mo	CH_3	H	2029	1910	1885	1820	1490	sh	640	594	573	537	457	435(sh)	403	367	238	218
Mo	CH_3	CH_3	2015	1915	1887	1823	1533	sh	638	598	569	540	463	445(sh)	405	368	237	220

[a] The infrared frequencies are given; the symmetry assignments are in accordance with polarization results of the Raman spectra. [b] The infrared measurements were carried out in nujol mulls. [c] Shoulder.

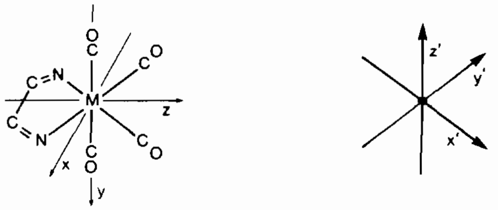

Figure 2. Coordinate transformation for obtaining symmetry adapted orbitals.

DAB-ligand orbitals

π	: $\frac{1}{2}(py^a + py^b + py^c + py^d)$	(b_2)
π	: $\frac{1}{2}(py^a + py^b - py^c - py^d)$	(a_2)
π^*	: $\frac{1}{2}(py^a - py^b - py^c + py^d)$	(b_2)
π^*	: $\frac{1}{2}(py^a - py^b + py^c - py^d$	(a_2)
n_1	: $\frac{1}{2}\sqrt{2}\ ((sp^2)^a + (sp^2)^d)$	(a_1)
n_2	: $\frac{1}{2}\sqrt{2}\ ((sp^2)^a - (sp^2)^d)$	(b_1)

Bonding between the DAB ligand and metal atom occurs when the lone pairs on the nitrogen atoms are donated to the empty d-orbitals of the metal. The strong π-backbonding which is evident from the ν(CO) frequencies in the infrared spectra, takes place between the metal d-orbitals of b_2 and a_2 symmetry and corresponding π^*-orbitals of the DAB ligand.

Electronic transitions from the metal to the CO π^*-orbitals are found in the U.V., L.F. transitions and metal to DAB CT transitions occur between 350–600 nm.

In this article only the CT transitions to the DAB ligand will be discussed and the relevant part of a tentative M.O. scheme is shown in figure 3a. The five allowed CT transitions are shown in figure 3b, together with their polarization characteristics.

Apart from the five symmetry allowed transitions there is one symmetry forbidden transition ($a_2 \leftarrow a_1$). The symmetry allowed transition $b_2 \leftarrow a_1$ is overlap forbidden.

Figure 4 shows the spectrum of $Mo(CO)_4$(glyoxal-bist.-butylimine at room temperature and at about 180 K. At room temperature a structured band is found at about 560 nm. Structured CT bands of DAB complexes have been reported before. Wrighton and Morse described a shoulder of the CT band of 1,10-phenanthroline$W(CO)_4$ which they assigned to a singlet–triplet LF transition [19]. Clark and coworkers described a shoulder of the CT band (Fe(diacetylbismethylimine))$^{2+}$ and analogous complexes, which they assigned to a vibrational progression on the basis of resonance Raman results [20]. As will be shown, the structured CT bands of the complexes described in this article belong to different electronic transitions.

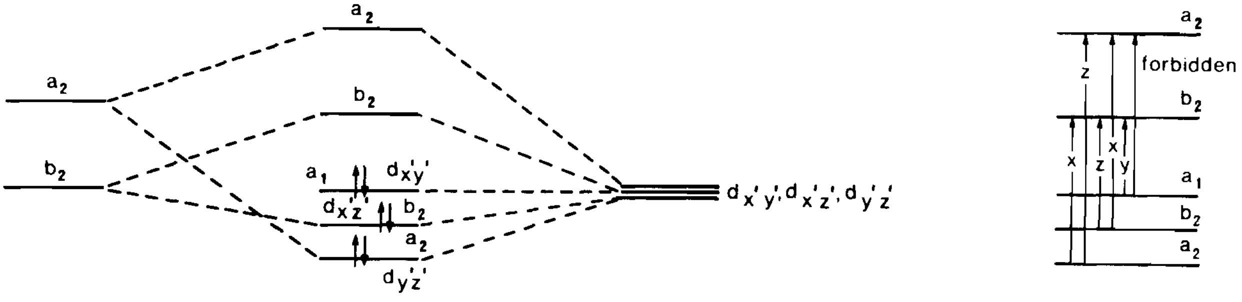

Figure 3. a)Part of a tentative M.O. scheme relevant to the CT transitions between the metal and the DAB ligand. b) Metal to DAB ligand CT transitions with their polarization directions.

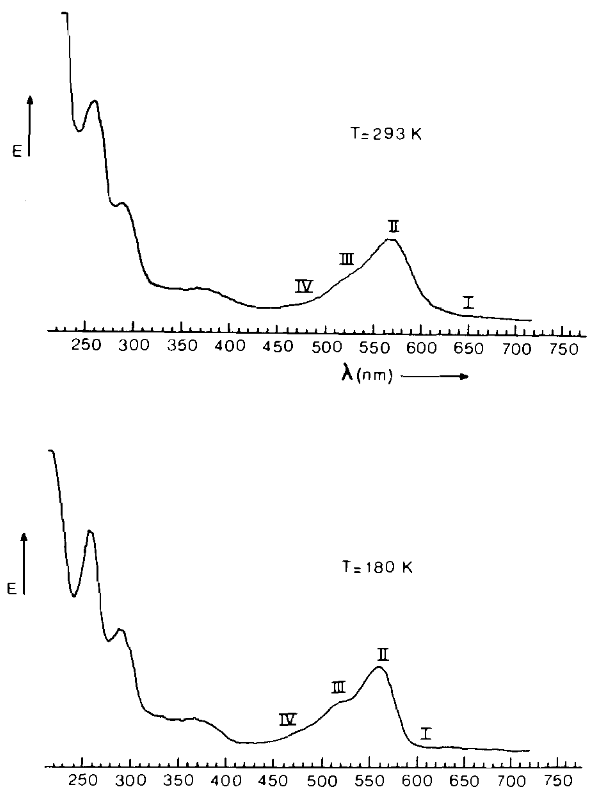

Figure 4. The spectrum of glyoxalbist.-butylimineMo(CO)$_4$ in an 8:3 mixture of 2,2-dimethylbutane and n-pentane at room temperature and 180 °K.

The CT bands were shown to be solvatochromic, *i.e.* that the absorption maximum shifts with changing polarity of the solvent. Strong solvatochromism only occurs for electronic transitions in which the electron transfer takes place along the dipole moment vector. Accordingly, the solvatochromic band II must be the z-polarized $b_2 \leftarrow b_2$ transition [2, 3, 4, 21, 22].

Apart from the shift of the absorption maximum of the z-polarized band II the maximum molar extinction coefficient changes with increasing polarity of the solvent. When the intensity of the band is taken as the area underneath the absorption band divided by the wavelength of the absorption maximum, according to Strickler and Berg [23], a significant variation of the intensity of the structured CT band is found when the polarity of the solvent changes. Only for glyoxalbist.-butylimineW(CO)$_4$ is an increase of intensity found with decreasing polarity of the solvent. For the analogous chromium and molybdenum compounds no simple dependence on the polarity of the solvent is found as is shown in Table II.

At the long wavelength side of band II a weak shoulder is observed, which is assigned to the overlap forbidden transition $b_2 \leftarrow a_1$. Bands III and IV which become more distinct at lower temperature are assigned to the x-polarized transitions $b_2 \leftarrow a_2$ and $a_2 \leftarrow b_2$ on the basis of resonance Raman results, which are discussed in the next section. The $a_2 \leftarrow a_2$ transition is not observed for these complexes, but is found in the spectra of M(CO)$_3$DAB(PR$_3$)*.

Resonance Raman Spectra

In order to get more information about the character of the CT transitions and properties of the excited states discussed in the previous chapter, we investigated the resonance Raman spectra of glyoxalbist.-butylimineMo(CO)$_4$. This compound was chosen because it is photochemically more stable in the laser beam than the other DAB complexes. The photosensitivity of these complexes illustrates the difference in electronic structure between these DAB compounds and the corresponding phenanthroline complexes. Wrighton and Morse have shown that 1,10-phenanthrolineW(CO)$_4$ and related compounds do not react in their CT excited state [19].

Strong resonance enhancement of Raman intensity has been found for $\nu_s(\text{Mo–N})(A_1)$, $\nu_s(\text{C=N})(A_1)$ and $\nu_s(\text{C≡O})$ (A_1) and weaker effects were observed for $\nu_s(\text{Mo–C})$, $\delta(\text{Mo–C≡O})$ and $\nu_s(\text{C–C})$. An important result of this resonance Raman study is the

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*Private communication. R. W. Balk.

TABLE II. Absorption Maxima of the CT Band II of Glyoxalbist.-ButyliminеM(CO)$_4$ (M=Cr, Mo, W; R_1=t-butyl, R_2=H); Molar Coefficients and Relative Intensities in Arbitrary Units of the Complete CT Band.

Solv.	λ_{max} (nm) (ϵ_{max} (lmol^{-1} cm^{-1})) Cr	Mo	W	$I_{rel.}$ Cr	Mo	W
CH_3OH	536 (3570 ± 50)	503 (4900 ± 60)	517 (4830 ± 60)	2.3	3.6	2.8
$CHCl_3$	517 (5100 ± 100)	531 (7200 ± 200)	539 (6600 ± 100)	3.4	4.1	3.0
CH_2Cl_2	548 (4670 ± 15)	517 (4500 ± 500)	531 (6000 ± 100)	2.9	4.1	2.9
CS_2	592 (6200 ± 200)	558 (9800 ± 300)	560 (8830 ± 70)	3.3	5.0	3.4
C_6H_6	565 (5200 ± 100)	532 (6200 ± 100)	532 (9100 ± 200)	3.2	3.8	4.3
n-C_5H_{12}	–	567 (8400 ± 100)	–	–	4.1	–

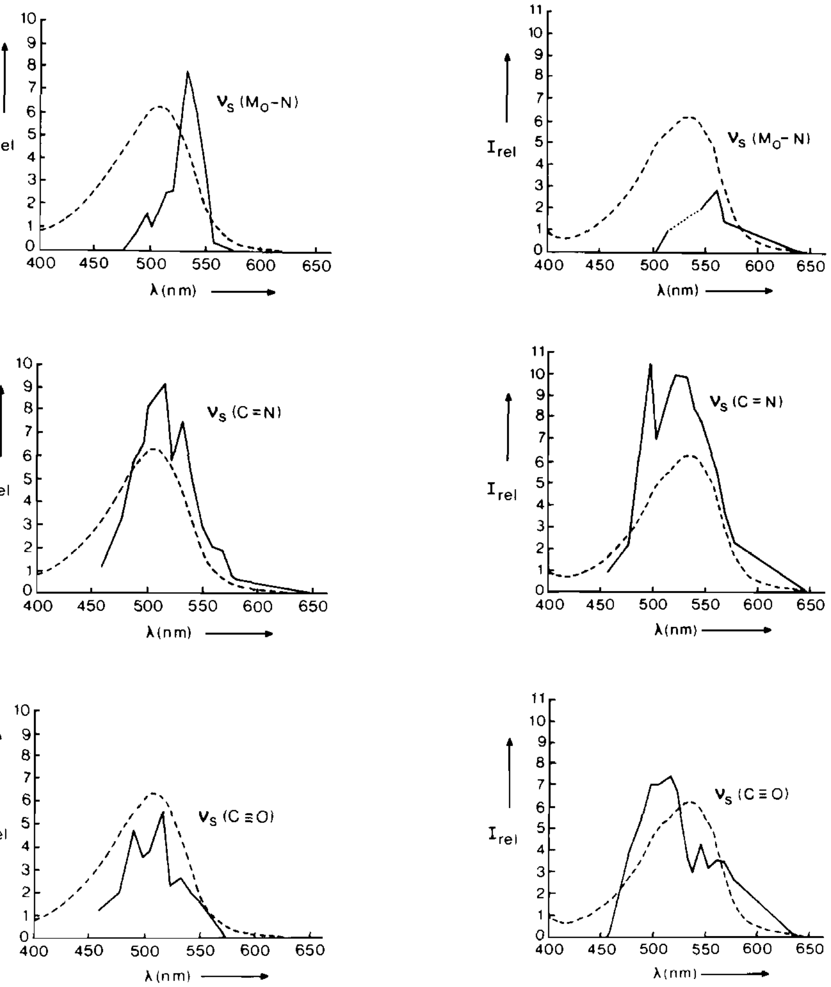

Figure 5. a) The excitation profiles of ν_s(Mo–N), ν_s(C=N) and $\nu_s(C\equiv O)_{cis}$ for the complex in CH_2Cl_2 solution. b) The excitation profiles of ν_s(Mo–N), ν_s(C=N) and $\nu_s(C\equiv O)_{cis}$ for the complex in C_6H_6 solution.

assignment beyond any doubt of the metal–nitrogen vibrational mode.

The resonance enhancement of ν_s(C–C) is partly due to mixing of this mode with ν_s(C=N). This mixing of ν_s(C–C) is shown to be present because of the frequency lowering of the latter mode when ^{15}N is substituted in the DAB ligand.

Although B-terms [24] might contribute to the intensity enhancement of modes with symmetry B_1 as a result of vibronic coupling between the close-lying excited states of the DAB ligand with symmetry b_2 and a_2, no such effects have been observed. Intensity enhancement has only been observed for symmetric modes (A_1).

The excitation profiles for ν_s(Mo–N), ν_s(C=N) and $\nu_s(C\equiv O)_{cis}$ for both benzene and dichloromethane solutions are shown in Figure 5. The intensity enhancement for ν_s(Mo–N) and ν_s(C=N) clearly

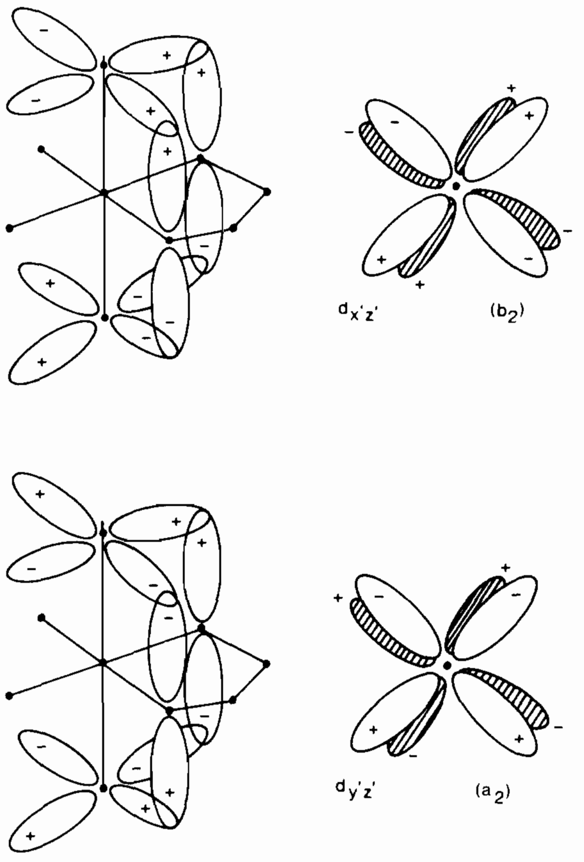

Figure 6. The overlap of π^*-orbitals of the *cis* CO-groups and the π^*-orbitals of the DAB ligand with the same symmetry. The metal d-orbital combinations which give π-backbonding with these π^*-orbitals are shown on the right.

shows that the absorption bands belong to transitions from the metal to the DAB ligand. On the other hand, the resonance effect of $\nu_s(C{\equiv}O)_{cis}$ shows that these CT transitions are not purely metal to DAB ligand in character as has previously been assumed [2, 3]. Just as for $M(CO)_4DBSD$ (M=Cr, Mo) [1, 25], orbitals of the *cis* carbonyl groups appear to be mixed in the first excited states of this complex. Such an overlap can exist between the orbitals shown in Figure 6.

The excitation profiles do not completely coincide with the absorption bands of the complex. This effect which is most pronounced for ν_s(Mo–N) is normally only found for compounds with closely spaced electronic transitions. It has been explained by Friedman and Hochstrasser [26] as due to interference between amplitudes of preresonant and more nearly resonant states.

The excitation profiles show four or less maxima in agreement with the presence of four electronic transitions in the absorption band.

Both $\nu_s(C{\equiv}O)_{cis}$ and ν_s(Mo–N) show a remarkable difference in resonance behaviour when excitation occurs at different parts of the absorption band. The metal–nitrogen vibrational mode is only strongly enhanced in intensity at the long wavelength side of the band and $\nu_S(C{\equiv}O)_{cis}$ is much more stronger enhanced at shorter wavelengths. This is in agreement with the assignment of band II to the z-polarized $b_2 \leftarrow b_2$ transition. The excitation profiles for band III and IV are much alike and these bands are therefore assigned to the x-polarized $b_2 \leftarrow a_2$ and $a_2 \leftarrow b_2$ transitions. The excitation profiles of band I are not strongly solvatochromic and they do not show a large resonance enhancement for the ν_s(Mo–N). This is in agreement with the given assignment of this band to the y-polarized $b_2 \leftarrow a_1$ transition. Comparing the results for C_6H_6 and CH_2Cl_2 solutions, a large difference between the excitation profiles of ν_s(Mo–N) for the complex in both solvents can be observed. The resonance effect is more pronounced in the z-polarized transition $b_2 \leftarrow b_2$ for the more polar solvent CH_2Cl_2. This means that the electronic transition belonging to band II has more CT character in CH_2Cl_2 than in C_6H_6. The electrons are more localized on the metal in CH_2Cl_2 solution. Evidently, the polar solvent induces a shift of negative charge along the dipole moment vector. This is in agreement with NMR results.

NMR-data

^{1}H-NMR data and the solvent dependence of the resonance signals of glyoxalbist.-butylimineMo(CO)$_4$ have been published by tom Dieck and coworkers [27]. In this section we report the solvent dependence of the ^{1}H NMR data for the free ligand and the three glyoxalbist.-butylimineM(CO)$_4$ complexes (M=Cr, Mo, W) and also the solvent dependence of the resonance signals of ^{13}C and ^{15}N nuclei in the ligand skeleton of some complexes.

In Figure 7 the hydrogen and carbon atoms are characterized.

The ^{13}C-NMR spectra of the ^{15}N enriched complexes show a coupling of the nuclear spins ^{15}N and $^{13}C_{II}$ (see figure 7). In glyoxalbismethylimine-

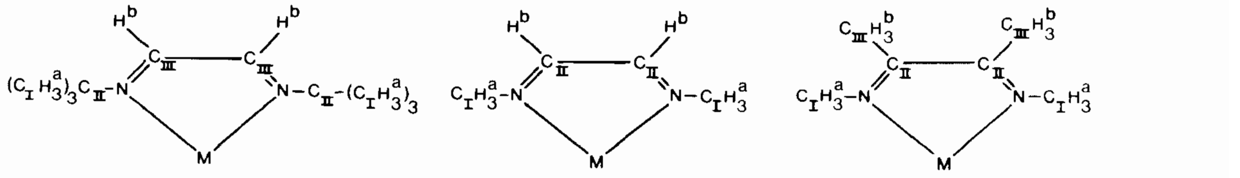

Figure 7. Characterisation of carbon atoms for ^{13}C-NMR and hydrogen atoms for ^{1}H-NMR.

TABLE III. ^{1}H-NMR Data of Glyoxalbist.-butylimineM(CO)$_4$ (M=Cr, Mo, W) (Relative to TMS).

Solv.	M	H^a (δ ppm)	H^b (δ ppm)
$CDCl_3$	Free Ligand	1.21	7.84
	Cr	1.63	8.22
	Mo	1.59	8.25
	W	1.66	8.62
CD_3OD	Free Ligand	1.25	7.91
	Cr	1.59	8.23
	Mo	1.56	8.30
	W	1.62	8.74
CS_2	Free Ligand	1.17	7.76
	Cr	1.61	8.20
	Mo	1.69	8.24
	W	1.68	8.60
C_6D_6	Free Ligand	1.14	7.89
	Cr	1.57	7.18
	Mo	1.29	7.11
	W	1.36	7.11

TABLE IV. ^{15}N-NMR Data of ^{15}N-enriched GlyoxalbismethylimineMo(CO)$_4$ (Relative to Dimethylformamide).

Solv.	M	R_1	R_2	δ^{15}N (ppm)
$CDCl_3$	Mo	CH_3	H	200.52
C_6D_6	Mo	CH_3	H	198.47

Mo(CO)$_4$ (R_1=CH_3; R_2=H) no coupling is found between H^b and ^{15}N. The couplings between ^{15}N and ^{13}C are: $J(^{15}N–^{13}C_I)$ = 6.4 Hz and $J(^{15}N–^{13}C_{II})$ = 10.9 Hz. The couplings between ^{15}N and ^{13}C in the ^{15}N-enriched diacetylbismethylimineMo(CO)$_4$ (R_1=CH_3; R_2=CH_3) are: $J(^{15}N–^{13}C_I)$ = 5.5 Hz and $J(^{15}N–^{13}C_{II})$ = 3.9 Hz.

For glyoxalbist.-butylimineCr(CO)$_4$ a downfield shift is found for the resonance signal of C_{III}, with increasing polarity of the solvent. There is also a downfield shift of the resonance signal of ^{15}N in the enriched complex glyoxalbismethylimineMo(CO)$_4$ with increasing polarity of the solvent. From this we may conclude that there is a shift of negative charge along the dipole moment vector from the DAB ligand to the metal, when the polarity of the solvent increases. This electron transfer also causes the differences in the excitation profiles of glyoxalbist.-butylimineMo(CO)$_4$ in C_6H_6 and CH_2Cl_2, the strong solvatochromism in the absorption spectra, and the large shift of the ν(CO) and ν(C=N) frequencies in the infrared and Raman spectra.

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TABLE V. ^{13}CNMR Data of Glyoxalbist.-butylimineM(CO)$_4$ (M=Cr, Mo, W) (Relative to TMS).

Solv.	M	δC^I	δC^{II}	δC^{III}	δC(CO-*trans*)	δC(CO-*cis*)
CD_3CN	Cr	30.70	65.81	158.64	–	–
C_7D_8	Cr	30.67	–	157.86	–	–
$CDCl_3$	Cr	30.73	65.48	155.11	211.90	230.37
	Mo	30.49	64.86	155.73	202.40	233.42
	W	31.19	66.29	157.91	–	–

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