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A Study of the Electronic Properties of M(CO)$_4$DAB (M = Cr, Mo, W; DAB = Diazabutadiene).

II*. Conformational Change below 200 K as evidenced from Absorption and Resonance Raman Spectra

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The resonance Raman and electronic absorption spectra of M(CO)$_4$DAB (M = Cr, Mo, W; DAB = 1,4-Diazabutadiene) in alkane solutions or glasses at temperatures below 200 K indicate the existence of a second isomer in which the M(CO)$_4$ moiety has a pseudo C_{4v} symmetry. In polar solvents a continuous shift of the CT band is found when the temperature is lowered. This thermochromism is caused by an increase of the solvatochromism at low temperature.

Introduction

In the course of our study on the coordinating properties of nitrogen donor ligands with conjugated double bonds we investigated the electronic properties of M(CO)$_4$DAB (M = Cr, Mo, W). In a previous article on this subject we assigned the absorption band between 450 and 600 nm to various CT transitions from the metal to the DAB ligand. This assignment was based on Resonance Raman (RR) data [1, 2]. Furthermore, the remarkable solvatochromism of these compounds reported by tom Dieck *et al.* [3–6] appeared to be accompanied by an electron shift from the DAB ligand along the dipole moment vector (see Figure 1) as a result of solvent interaction. This causes a weakening of the π-bonding between the metal and DAB ligand and a strengthening of the π-back-bonding from the metal to the *trans* CO groups [1].

We now report the temperature dependence of the metal to DAB CT band and of the ν_s (C=N) Raman band of the coordinated diazabutadiene.

Experimental

The syntheses of the Mo(CO)$_4$DAB complexes were carried out according to the literature while for the Cr and W complexes a new method was developed which is more convenient than the literature methods [1, 3, 7]. 3 mmol of M(CO)$_6$ (M = Cr, W) and 3 mmol DAB were stirred for 8 hours in 50 ml xylene at 130 °C while light was excluded. The hot solution was filtered, 50 ml pentane was added and the mixture was allowed to stand overnight at –60 °C. The crude product precipitated and was filtered and washed twice with 50 ml pentane. The excess M(CO)$_6$ was removed by vacuum sublimation at 50 °C and finally the product was recrystallized from 1:1 toluene–pentane at –20 °C, giving dark purple crystals in 70% yield. The products were identified by their IR and NMR spectra and the results were in agreement with literature values [1, 3, 7]. All electronic absorption spectra were recorded on a Cary 14 spectrophotometer and the Raman spectra on a Coderg pH 1 Raman spectrophotometer using the red line (λ = 6471 Å) of a Krypton CR model 500 K laser as excitation source. The organic glass rigisolve, an 8:3 mixture of 2,2-dimethylbutane and n-pentane was obtained from Merck in Uvasol grade.

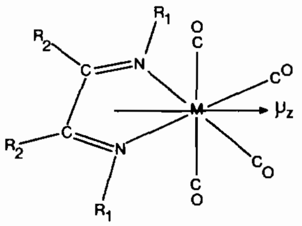

Fig. 1. Structure of M(CO)$_4$DAB complexes. The dipole vector is represented by an arrow.

Results

Electronic Absorption Spectra

According to the diagram shown in Fig. 2 five metal to DAB CT transitions are allowed. In fact, already at room temperature the broad CT band is

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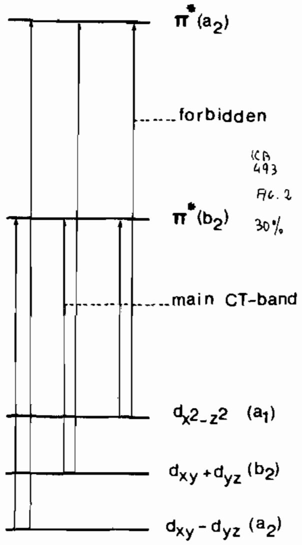

Fig. 2. Electronic transitions from the d-orbital combinations to the DAB ligand π* orbitals. Order of d-orbitals is arbitrary.

structured and it is obvious that it consists of at least three electronic transitions (see Figure 3). Furthermore, it has been shown that the excitation profiles of the Resonance Raman bands for these and related complexes possess three to four maxima which indicate the presence of four different electronic transitions [1, 2]. At temperatures below 200 K in alkanes and mixtures of alkanes as solvents or low temperature glasses drastic changes are observed in the absorption spectra of those $M(CO)_4DAB$ complexes (M = Cr, Mo, W) which possess bulky substituents at the nitrogen atoms of the DAB ligand. The main absorption band at 565 nm assigned to the $b_2 \rightarrow b_2^*$ transition (see Figure 2) gradually disappears and at the same time a new band is found at 520 nm. The intensity of the band at 270 nm belonging to a CT transition from the metal to the CO ligands strongly decreases while the $\pi \rightarrow \pi^*$ transition of the DAB ligand is unaffected. In Figure 3 this low temperature effect is shown for $Mo(CO)_4$(tbu–N=CH–CH=N–tbu) in rigisolve.

In Table I the maxima of the CT bands are listed at room temperature and at 120 K for $Mo(CO)_4DAB$ complexes showing this effect.

The phenomena mentioned above only occur in non polar and non polarizable solvents and low temperature glasses of alkanes and mixtures of alkanes. In polar solvents another effect is observed. When the temperature of a solution of $M(CO)_4DAB$ in such a solvent is lowered a continuous shift to higher energy is observed for the CT band without any important increase or decrease of the intensity of the band. This thermochromism shown in Figure 4 is quite similar to the already described solvatochromism of these compounds [1–6].

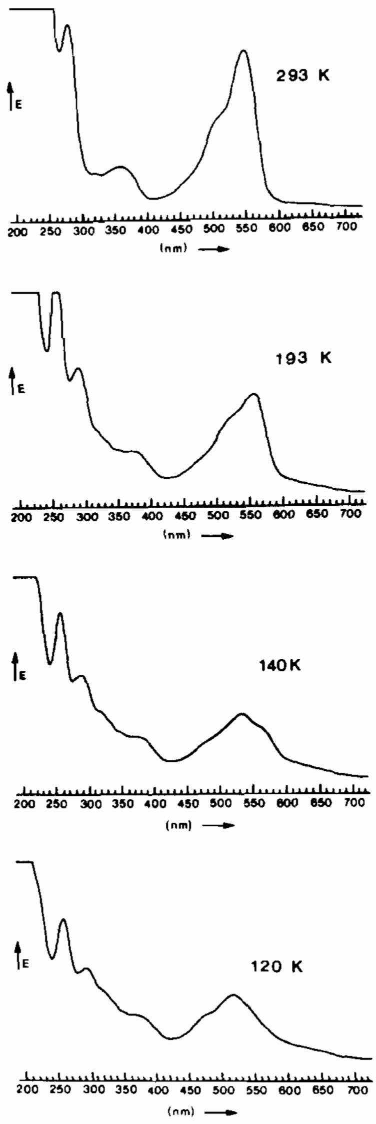

Fig. 3. Electronic absorption spectra between 200 and 650 nm of $Mo(CO)_4$(tbu–N=CH–CH=N–tbu) in rigisolve at various temperatures.

TABLE I. Maxima of the CT Bands at Room Temperature and 120 K in Rigisolve.

M	R_1	R_2	λ_{nm} (290 K)	λ_{nm} (120 K)
Mo	tbu	H	565	517
Mo	chex	H	563	503
Mo	neop	H	558	532
Mo	ipr	H/CH_3	554	509
Mo	n-bu	CH_3	535	493

The thermochromic shifts of $Mo(CO)_4$(tbu–N=CH–CH=N–tbu) in various solvents are listed in Table II.

TABLE II. Thermochromism of Mo(CO)$_4$(tbu–N=CH–CH=N–tbu) in Polar Solvents: A = diethylether/2,2-dimethylpropane 1:1, B = EPA (Ethanol/2,2-dimethylpropane/diethylether, 2:5:5), C = toluene/ethanol 9:1, D = 2-methyl-THF.

T(K)	A (λ_{nm})	B (λ_{nm})	C (λ_{nm})	D (λ_{nm})
293	550	530	525	520
180	525	509	509	501
110	490	490	502	490

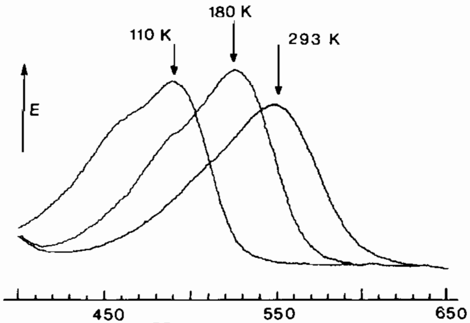

Fig. 4. Electronic absorption spectra between 400 and 650 nm of Mo(CO)$_4$(tbu–N=CH–CH=N–tbu) in a 1:1 mixture of diethylether and 2,2-dimethylpropane.

Although this continuous shift in polar solvents is in contrast with the effects observed in non polar ones, the final position and structure of the CT band at about 100 K appears to be nearly the same in both types of solvents.

Resonance Raman (RR) Spectra

The Raman spectrum of Mo(CO)$_4$(tbu–N=CH–CH=N–tbu) shows a preresonance effect even when the 6471 Å line is used as excitation source. As a result the Raman bands are much more intense than in a normal Raman spectrum, which enabled us to measure the Raman spectra of the same dilute solutions of the complex in rigisolve as were used for the electronic absorption measurements. On the other hand, only a few Raman bands are enhanced in intensity by the resonance effect. For example, only one CO stretching mode is observed at 2020 cm^{-1} which has been assigned to the symmetrical stretching mode of the *cis* carbonyl groups [1, 8]. The symmetrical CN stretching mode of the coordinated DAB ligand is found at 1511 cm^{-1} in rigisolve at room temperature. When the temperature is lowered to about 200 K the band at 1511 cm^{-1} gradually disappears and a new one comes up at 1541 cm^{-1}. This effect is observed at about the same temperature as the shift of the CT band discussed in the previous section and is quite similar in behaviour, as shown in Figure 5.

The $\nu_s(CO)_{cis}$ only shows a very small frequency shift on cooling and decreases in intensity.

In order to get more information about structural changes of the complexes that might cause these effects, we tried to investigate the infrared spectra of the alkane solutions at low temperature. This attempt failed due to the low solubility of the complexes.

Discussion

Low temperature shifts as we observed for the M(CO)$_4$DAB complexes (M = Cr, Mo, W) have been reported by Wrighton and Morse for W(CO)$_4$(1,10-phenanthroline [9] and for related manganese(I) and binuclear manganese and rhenium complexes [10, 11]. Unfortunately only the spectra at room temperature and 100 K have been reported while no explanation of the effect was given by the authors.

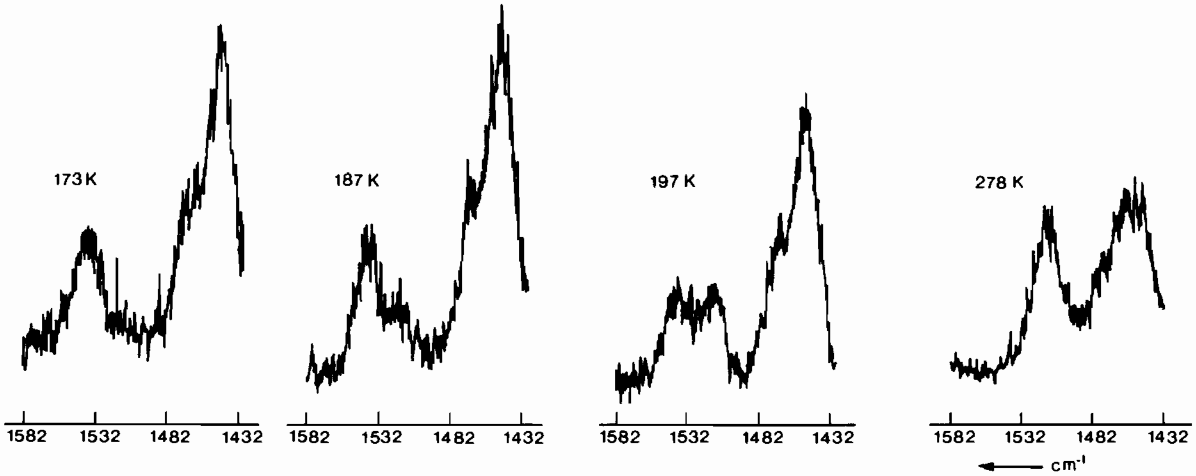

Fig. 5. The ν_s(C=N) Raman band of Mo(CO)$_4$(tbu–N=CH–CH=N–tbu) in rigisolve at various temperatures. The band at 1448 cm^{-1} is a solvent band.

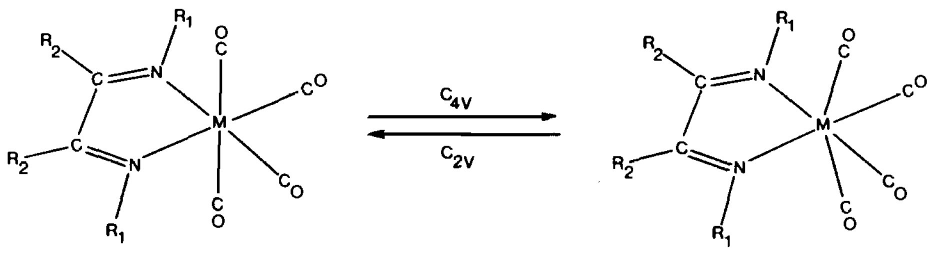

Fig. 6. The conformational change of the M(CO)$_4$-moiety from C_{2v} to C_{4v} symmetry.

Kisch *et al.* [12] observed a blue shift at low temperature of the CT band of (azoalkane)Fe(CO)$_4$ which they explained by hindered rotation around the metal–ligand bond. The same effect has been observed recently by Daamen *et al.* [13] for M(CO)$_5$L complexes (M = Cr, Mo, W; L = 4R-pyridine, pyrazine, pyridazine).

Low temperature shifts have been observed in the absorption, fluorescence and phosphorescence spectra of zinc and magnesium porphine in n-octane Spholskii matrices after addition of a coordinating solvent [14]. The same effect has been observed in the electronic absorption spectra of (bipyridine)NiL complexes (L = heterodiene ligand) by Walter [15].

In our discussion of the low temperature effects in the spectra of M(CO)$_4$DAB (M = Cr, Mo, W) we shall distinguish between the results for non polar, non polarizable solvents and those for polar ones.

Apolar Solvents and Glasses

The shifts observed in the RR and absorption spectra in rigisolve clearly show the presence of two conformations of M(CO)$_4$DAB at low temperatures. Between these conformations an equilibrium exists because all spectral changes were reversible.

Moreover, these shifts and in particular the frequency increase of ν_s(C=N) show that on going from the high temperature to the low temperature conformation, an electron shift takes place from the DAB ligand along the dipole moment vector, which results in an increase of the dipole moment. On the basis of these results and in accordance with the findings of tom Dieck [16] we assume that below 200 K a conformational change of the M(CO)$_4$ moiety takes place to a structure with pseudo C_{4v} symmetry as shown in Figure 6.

Tom Dieck *et al.* prepared some Mo(CO)$_4$DAB complexes with substituted phenyl groups on the imine nitrogen atoms in which the M(CO)$_4$ moieties have a pseudo C_{4v} symmetry.

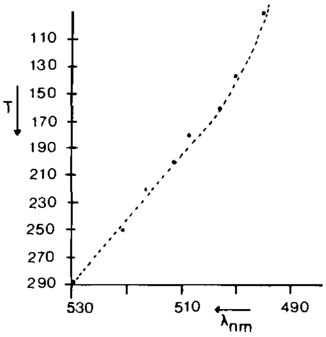

Fig. 7. Diagram of T against λ_{max} of Mo(CO)$_4$(tbu–N=CH–CH=N–tbu) in EPA. (EPA = ethanol/2,2-dimethylpropane/diethylether 2:5:5).

The two *cis* carbonyls are bent out of their axial positions as a result of which they will contribute to the dipole moment. This will cause the electron shift which is responsible for the changes in the RR and absorption spectra below 200 K. The very small frequency shift which we observed for $\nu_s(CO)_{cis}$ also agrees with the observations of tom Dieck that such a structural change is accompanied by only minor changes of the CO stretching frequency at 2020 cm^{-1}.

It has been shown for Mo(CO)$_4$DAB complexes that ^{13}C labeled *cis* carbonyl groups can exchange with the carbonyl groups in *trans* position and it has been assumed that this exchange takes place via an intermediate with pseudo C_{4v} symmetry [16]. Such an exchange, however, is not a general property of Mo(CO)$_4$L complexes (L = bidentate ligand) since it does not occur for Mo(CO)$_4$(ethylenediamine) [17].

The low temperature effect and accordingly the conformational change occurs for complexes of Cr^0, Mo^0 and W^0, but only for those which possess bulky substituents on the nitrogen atoms of the DAB ligand (Table I). Apparently, the steric interaction of these substituents with the carbonyl groups stimulates the formation of the isomer with pseudo C_{4v} symmetry. It has already been shown that DAB ligands with bulky aliphatic substituents behave differently in other cases. In Fe(CO)$_3$DAB complexes σ,π-coordination can only occur for DAB ligands with bulky aliphatic groups [20, 21], while such groups also influence the behaviour of [Mo(CO)$_4$DAB]$^-$ with respect to oxidizing agents [22].

As seen from Figure 5 the intensity of the ν_s (C=N) Raman band is only slightly lowered when the temperature is changed from 278 K to 173 K. On the other hand, the intensity of $\nu_s(CO)_{cis}$ is lowered drastically, which means that the relative intensities of these two modes are strongly affected. Part of this effect may certainly be caused by the shift to higher energy of the CT band which will influence the intensities of these Raman bands. It is however also expected that the conformational change of the complex will influence the relative Raman intensities. The RR spectra of these complexes at room temperature have shown that interaction between π^*-orbitals of the *cis* carbonyl groups and of the DAB ligand causes a RR effect for $\nu_s(CO)_{cis}$ [1, 2]. This interaction and as a result the RR effect of $\nu_s(CO)_{cis}$ is expected to decrease when the two *cis* carbonyls are bent out of their axial position in the low temperature modification. However, only complete excitation profiles of both conformations can demonstrate which effect dominates here.

Polar Solvents

The continuous shift of the CT band observed for all $M(CO)_4DAB$ complexes (M = Cr, Mo, W), in polar solvents when the temperature is lowered (Figure 4) closely resembles the solvatochromism of these complexes. This solvatochromism is a result of the orientation of polar or polarizable (*e.g.* benzene) molecules in the dipole field of the complexes which possess a high dipole moment (μ = 8–10 D) [2, 18, 19]. At lower temperatures this orientation will increase until complete orientation is achieved, giving rise to the observed thermochromism.

In Figure 7 the maximum of the CT band of $Mo(CO)_4$(tbu–N=CH–CH=N–tbu) in EPA is shown as function of temperature. The asymptotic behaviour at low temperature shows the complete orientation of the solvent molecules.

Contrary to the results for apolar solvents, no conformational change of the complexes could be deduced from the continuous shifts in the absorption spectra although such an effect cannot be excluded.

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