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Solvatochromic, Piezochromic and Thermochromic Behaviour of $Mo(CO)_4(\widehat{NN})$ Complexes

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Abstract

The solvent, pressure and temperature dependencies of the lowest energy metal to ligand charge transfer absorption bands were studied for a series of complexes of the type $Mo(CO)_4(\widehat{NN})$, where $\widehat{NN}$ = 2,2′-bipyridine, 1,10-phenanthroline and biacetylbis(phenylimine). Throughout the series of complexes the absorption bands shift to shorter wavelength in more polar solvents or on increasing the pressure in a particular solvent, but to longer wavelengths on increasing temperature. These main tendencies can be accounted for in terms of solvent polarity and its dependence on pressure and temperature.

Introduction

It is well known that a variety of diimine ($\widehat{NN}$) complexes of the type $M(CO)_4(\widehat{NN})$ and $Fe(\widehat{NN})_2(CN)_2$, where M = Cr, Mo and W, exhibit remarkable solvatochromic effects, which can be correlated with solvent parameters such as the E_T value [1]. Recently, the kinetics and high-pressure effects of the following reactions were investigated [2]:

$$cis\text{-}Mo(CO)_4(py)_2 + \widehat{NN} \xrightarrow{\text{toluene}} Mo(CO)_4(\widehat{NN}) + 2py \qquad (1)$$

where py = pyridine, $\widehat{NN}$ = bpy(2,2′-bipyridine), dab-(biacetylbis(phenylimine)):

$$Mo(CO)_5(4\text{-}Mepy) + \widehat{NN} \xrightarrow{\text{toluene}} Mo(CO)_4(\widehat{NN}) + CO + 4\text{-}Mepy \qquad (2)$$

where 4-Mepy = 4-methylpyridine and $\widehat{NN}$ = dab. The visible absorption spectra of the reaction mixtures at infinity, *i.e.* of the product solutions, exhibited meaningful piezochromic effects, which can be correlated with the solvatochromic behaviour of the product species. However, a contribution due to outer-sphere complexation with excess bpy or dab present in solution, as favoured by an increase in pressure, could not be ruled out. Furthermore, the known solvatochromic behaviour of these complexes [3–5] and its correlation with solvent polarity parameters [6, 7] have recently attracted attention [7, 8].

We have undertaken a detailed study of the solvatochromic piezochromic and thermochromic behaviour of solutions of the pure complexes $Mo(CO)_4(bpy)$, $Mo(CO)_4(phen)$ and $Mo(CO)_4(dab)$. The results clearly demonstrate that changes in solvent polarity are responsible for the observed spectral changes at elevated pressure and temperature.

Experimental

The complexes $Mo(CO)_4(bpy)$, $Mo(CO)_4(dab)$ and $Mo(CO)_4(phen)$ (phen = 1,10-phenanthroline) were prepared as described before [2], and were characterized by elemental analyses, IR- and UV-VIS-spectroscopy. Analytical reagent grade solvents were used throughout this study. Piezochromic measurements were performed on a Zeiss DMR 10 spectrophotometer equipped with a thermostatted (±0.1 °C) high-pressure cell [9]. Solvatochromic and thermochromic measurements were performed in the thermostatted cell compartment of a Shimadzu 240 spectrophotometer. In some cases the instrument was operated in the first derivative mode to enable an accurate determination of the peak position. A pressure range of 20 to 2000 bar and a temperature range of 10 to 70 °C was covered during these measurements. Enough time was allowed for pressure and temperature

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TABLE I. Solvent Parameters at Ambient and Elevated Temperatures and Pressures.

Solvent	E_T[a] (kJ mol^{-1})	π^*[a] (kJ mol^{-1})	E^*_{MLCT}[a]	ϵ	$(\delta\epsilon/\delta T)_P$[d] $(10\ °C)^{-1}$	$(\delta\epsilon/\delta P)_T$[e] ($kbar^{-1}$)
hexane	129.3	−0.08	0.00	1.889[b]	−0.0229[b]	+0.0885[f]
toluene	141.8	0.54	0.30	2.379[c]	−0.023[f] −0.018[f]	+0.098[f]
1,2-dichloroethane	175.3	0.81	0.64	10.36[c]	−0.568[f] −0.555[f]	+1.16[g]
1-butanol	210.0	0.46	0.55	17.1 [c]	−1.162[f] −1.205[f]	+1.674[f]

[a] Data quoted in ref. [7]. [b] From ref. [14]. [c] From ref. [15]. [d] The dependence of ϵ on T was assumed to be linear over the range 15 to 70 °C. [e] The dependence of ϵ on P was assumed to be linear over the range 1 to 2000 bar. [f] From ref. [16]. [g] From ref. [17].

TABLE II. Solvatochromic, Piezochromic and Thermochromic Effects.

Solvent	$Mo(CO)_4(bpy)$			$Mo(CO)_4(phen)$			$Mo(CO)_4(dab)$		
	λ_{max} (nm)	$(\delta\lambda/\delta T)_P$[a] $(nm(10\ °C)^{-1})$	$(\delta\lambda/\delta P)_T$[b] $(nm\ kbar^{-1})$	λ_{max} (nm)	$(\delta\lambda/\delta T)_P$[a] $(nm(10\ °C)^{-1})$	$(\delta\lambda/\delta P)_T$[b] $(nm\ kbar^{-1})$	λ_{max} (nm)	$(\delta\lambda/\delta T)_P$[a] $(nm(10\ °C)^{-1})$	$(\delta\lambda/\delta P)_T$[b] $(nm\ kbar^{-1})$
hexane	555	[c]	[c]	550	+0.3 ± 0.2	[c]	565	+0.0 ± 0.5	[c]
toluene	494	+2.0 ± 1.1	−3.6 ± 1.3	495	+1.4 ± 0.5	−3.9 ± 1.2	550	+0.9 ± 0.2	−2.3 ± 1.2
1,2-dichloroethane	467	+1.3 ± 0.2	~0[d]	467	+1.7 ± 0.6	−2.5 ± 0.9	533	+0.8 ± 0.6	−2.3 ± 1.3
1-butanol	477	+0.4 ± 0.2	−1.7 ± 0.9	480	+0.7 ± 0.3	−1.5 ± 0.5	544	+0.4 ± 0.1	−2.3 ± 2.1

[a] The dependence of λ_{max} on T at ambient pressure was assumed to be linear over the range 15 to 70 °C. [b] The dependence of λ_{max} on P at 25 °C was assumed to be linear over the range 1 to 2000 bar. [c] Could not be determined due to experimental difficulties – see Discussion. [d] No significant pressure effect due to interference of a decomposition reaction.

equilibration between each measurement. The observed spectral changes are reversible, and the results are reported as mean values for increasing and decreasing the temperature or pressure.

Results and Discussion

The electronic absorption spectra of $Mo(CO)_4$(diimine) complexes exhibit low lying metal to ligand charge transfer (MLCT) transitions that are markedly solvent-dependent. The solvatochromic properties of these MLCT states can be correlated on the basis of different solvent parameters, *viz.* Reichardt's E_T parameter [10], Kamlet and Kraft's π^* parameter [11, 12], Kosower's Z parameter [13], Lee's E^*_{MLCT} parameter [7], and ϵ, the dielectric constant of the solvent. These parameters represent different experimental approaches to describe the relative polarity of a solvent. As a consequence, the correlation between solvent-dependent experimental data and these parameters will vary, depending on the selected parameter.

Solubility and stability properties of the complexes studied restricted the series of solvents selected to those summarized in Table I. These solvents cover a wide range of polarities and exhibit characteristic temperature and pressure dependencies*. Throughout the series there is an increase in ϵ with increasing pressure but a decrease in ϵ with increasing temperature, which is in agreement with the general tendencies expected on the basis of the theory of liquids.

The results in Table II clearly demonstrate the significant solvent dependence of the MLCT band, especially in the case of the bpy and phen complexes. The nature of the solvent (polarity, H-bonding, etc.) can influence the ground state as well as the excited energy states of such conjugated π-electron systems.

Throughout the series of complexes, λ_{max} shifts to shorter wavelengths (*i.e.* blue shifted to higher energy) with increasing solvent polarity, as indicated by the solvent parameters in Table I. These results indicate that the solvent molecules can affect the delocalization of the ground state electrons in the

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*The data in Table I are those for between 20 and 30 °C and at ambient pressure.

metal–ligand bond, and as such the electronic energy levels also. Furthermore, the observed trends are in good agreement with observations for other systems [1, 6, 7].

λ_{max} for the bpy and phen complexes is very similar in all solvents studied. The effect, however, is much smaller in the case of the dab complex. The sequence in the shift of λ_{max} with solvent for all three complexes parallels the order expected on the basis of the E^*_{MLCT} values. A reversed sequence for λ_{max} in 1,2-dichloroethane and 1-butanol is expected on the basis of the E_T and ϵ values. It follows that the E^*_{MLCT} solvent polarity scale gives an excellent correlation for such low-lying MLCT states as observed for these complexes.

The MLCT bands also exhibit a meaningful temperature dependence for which a typical example is given in Fig. 1. For the series of complexes and solvents investigated, λ_{max} shifts throughout to longer wavelengths, *i.e.* to lower energy, with increasing temperature. These shifts are recorded in Table II as the average change in λ_{max} for a temperature increase of 10 °C. A linear correlation between λ_{max} and temperature was observed, within the experimental error limits of such measurements. An opposite effect *viz.* a decrease in λ_{max}, *i.e.* to higher energy, is observed with increasing pressure, and a typical example is given in Fig. 2. The shifts are recorded in Table II as the average change in λ_{max} for an increase in pressure of I kbar. A linear correlation between λ_{max} and pressure, within the experimental error limits, was also observed in this case. Such experiments could not be performed in hexane due to the low solubility and corresponding low absorbance of these complexes, requiring an optical path length of at least 5 cm (not possible with our present equipment).

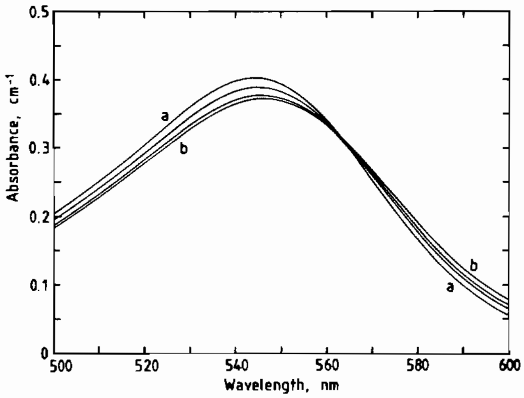

Fig. 1. Temperature dependence of the lowest MLCT band of $Mo(CO)_4(dab)$ in 1-butanol, a → b: 10 → 70 °C in 20° steps; [Mo] = 5 × 10^{-5} M.

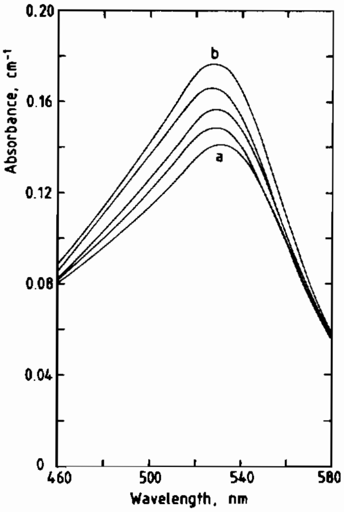

Fig. 2. Pressure dependence of the lowest MLCT band of $Mo(CO)_4(dab)$ in 1,2-dichloroethane, a → b: 20 → 2000 bar in 500 bar steps; [Mo] = 2 × 10^{-5} M.

The effects of temperature and pressure on λ_{max} are in opposite directions. However, these trends correspond exactly to those reported for the temperature and pressure dependencies of the dielectric constant of the solvent (see Table I). It follows that changes in the polarity of the solvent can account for the observed tendencies: a decrease in polarity with increasing temperature is accompanied by an increase in λ_{max}, whereas an increase in polarity with increasing pressure is accompanied by a decrease in λ_{max}. The absolute magnitudes of $(\delta\lambda/\delta T)_P$ and $(\delta\lambda/\delta P)_T$ seem to decrease along the series of solvents for the bpy and phen complexes, whereas the effects are almost constant for the dab complex. It follows that the MLCT absorption of the latter complex is not very sensitive to the polarity of the solvent, which is in agreement with the rather small solvatochromic effects. A comparison of the data in Tables I and II indicates that there is no direct correlation between the absolute magnitudes of the temperature and pressure dependencies of ϵ and λ_{max}.

We conclude that solvent polarity can account for most of the solvato-, piezo- and thermochromic effects observed in this investigation. The effects do depend on the nature of the diimine ligand as illustrated by the results for $Mo(CO)_4(dab)$, from which it follows that other effects such as electronic structure, π electron configuration and hydrogen bonding properties may partly account for the observations. This is clearly shown by the absence of significant temperature dependencies in the case of hexane as solvent. We are furthermore convinced that these results are of fundamental interest in the interpretation of solvent, temperature and pressure dependencies in kinetic studies on such systems.

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References

1 J. Burgess, J. G. Chambers and R. I. Haines, *Transition Met. Chem., 6,* 145 (1981), and references cited therein.
2 H.-T. Macholdt and H. Elias, *Inorg. Chem., 23,* 4315 (1984).
3 H. tom Dieck and I. W. Renk, *Chem. Ber., 104,* 110 (1971).
4 D. Walther, *J. Prakt. Chem., 316,* 604 (1974).
5 J. Burgess, *J. Organomet. Chem., 19,* 218 (1969).
6 K. Tamura and T. Imoto, *Bull. Chem. Soc. Jpn., 48,* 369 (1975).
7 D. M. Manuta and A. J. Lees, *Inorg. Chem., 22,* 3825 (1983).
8 (a) S. Sawamura, Y. Taniguchi and K. Suzuki, *Bull. Chem. Soc. Jpn., 52,* 3511 (1979).
(b) I. Jano, *Chem. Phys. Lett., 106,* 60 (1984).
9 F. K. Fleischmann, E. G. Conze, D. R. Stranks and H. Kelm, *Rev. Sci. Instrum., 45,* 1427 (1974).
10 C. Reichardt, *Angew. Chem., 91,* 119 (1979).
11 M. J. Kamlet, J. L. M. Abboud and R. W. Taft, *Prog. Phys. Org. Chem., 13,* 485 (1981).
12 R. W. Taft and M. J. Kamlet, *Inorg. Chem., 22,* 250 (1983).
13 E. M. Kosower, 'An Introduction to Physical Organic Chemistry', Wiley, New York, 1968, p. 293.
14 N. Isaacs, 'Liquid Phase High Pressure Chemistry', Wiley, Chichester, 1981.
15 'CRC Handbook of Chemistry and Physics', The Chemical Rubber Co., Cleveland, 1980/1981.
16 Landolt-Boernstein 'Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik, 6. Teil, Elektrische Eigenschaften I', Springer-Verlag, Berlin, 1959.
17 J. F. Skinner, E. L. Cussler and R. M. Fuoss, *J. Phys. Chem., 72,* 1057 (1968).