Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

SOLVENT EFFECTS ON THE VISIBLE ABSORPTION SPECTRA OF $Mo(CO)_4(Bipy)$ AND $W(CO)_4(Bipy)$

J. BURGESS

Chemistry Department, University of Leicester, Leicester LE1 7RH (England)

(Received May 26th, 1969)

Usually visible absorption spectra of inorganic compounds are fairly insensitive to solvent effects[1], though a few compounds are known, for example $Fe(Bipy)_2(CN)_2$ and $Fe(Bipy)(CN)_4^{2-}$, whose wavelengths of maximum absorption change greatly with solvent[1,2,3]. In the course of recent studies of reactions of 2,2′-bipyridinemolybdenum tetracarbonyl, $Mo(CO)_4(Bipy)$, and its tungsten analogue we have observed that the spectra of these compounds, which are formally related to $Fe(Bipy)(CN)_4^{2-}$, are also solvent sensitive, and that the frequencies of maximum absorption can be correlated with the solvent parameters E_T[4,5] and Z[4,6].

EXPERIMENTAL

The compounds $Mo(CO)_4(Bipy)$ and $W(CO)_4(Bipy)$ were prepared by Stiddard's method[7], and purified by recrystallisation from toluene. They were dissolved in the solvents listed in Table 1 and solution spectra obtained, at 20°, on a Unicam SP 800A recording spectrophotometer. The wavelength calibration of this machine was checked using standard didymium and holmium glass filters.

RESULTS AND DISCUSSION

The spectra in the visible region generally consist of a pair of peaks of high molar extinction coefficient, which may be assigned to molybdenum or tungsten to bipyridine charge-transfer, as in the analogous $Fe(CN)_4(Bipy)^{2-}$ case[2,3]. The lower wavelength band sometimes appears only as a shoulder, so results are reported only for the higher wavelength charge-transfer peak. Wavelengths of maximum absorption for this band are reported in the Table, which also includes values of E_T, which are a measure of "solvating power", for each solvent. A graph of wavelengths of maximum absorption for the molybdenum compound plotted against those for the tungsten compound is a good straight line of slope approximately one; solvent interactions with the two compounds are thus very similar, as might be expected.

The correlation between frequencies of maximum absorption and E_T values is shown, for the tungsten compound, in Fig. 1. As E_T and Z values correlate closely, a frequencies *vs.* Z graph would look very similar. The points fall on two correlation

TABLE 1

WAVELENGTHS OF MAXIMUM ABSORPTION (λ_{max}) FOR $Mo(CO)_4(Bipy)$ AND $W(CO)_4(Bipy)$ IN VARIOUS SOLVENTS, WITH THE RESPECTIVE SOLVENT E_T VALUES (kcal·mole^{-1})

No.	Solvent	E_T	λ_{max}	
			$Mo(CO)_4(Bipy)$	$W(CO)_4(Bipy)$
1	MeOH	55.5	459	473
2	EtOH	51.9	467	480
3	n-PrOH	50.7	475	488
4	n-BuOH	50.2	478	492
5	iso-PrOH	48.6	475	495
6	tert-BuOH	43.9	479	498
7	$MeNO_2$	46.3	441	452
8	MeCN	46.0	441	452
9	Me_2CO	42.2	453	463
10	CH_2Cl_2	41.1	469	485
11	PhCl	37.5	484	500
12	Et_2O	34.6	495	510
13	C_6H_6	34.5	493	509
14	CCl_4	32.5	504	520

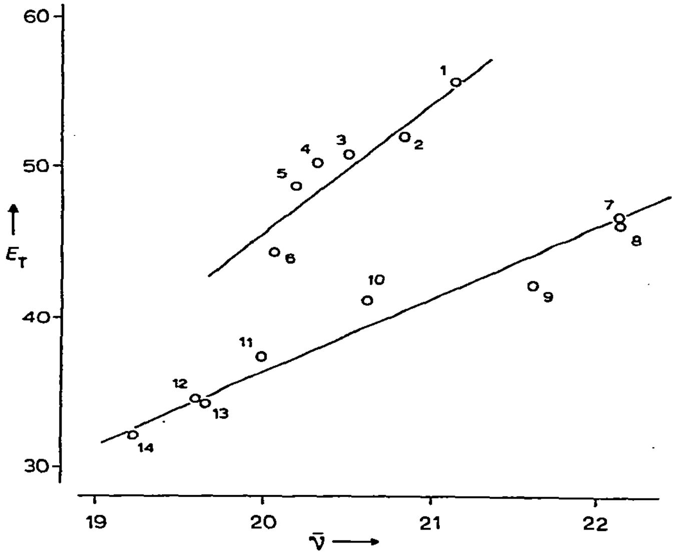

Fig. 1. Graph of frequencies of maximum absorption ($\bar{\nu}$, kc·cm^{-1}) against solvent E_T values (kcal·mole^{-1}) for $W(CO)_4(Bipy)$. The numbers of the points correspond to the solvent numbers in Table 1.

lines, one for hydrogen-bonding solvents, the other for non-hydrogen-bonding solvents. For each set of solvents there is good correlation between frequency and E_T. That hydrogen-bonding and non-hydrogen-bonding solvents have separate correlation lines is not surprising in view of the differences between the present system and the organic systems which provide the E_T and Z reference scales. Indeed it is difficult to see how one solvent parameter applicable to all situations could be derived[8]. Separate correlation lines in frequencies *vs.* E_T plots have also been obtained in other systems, for instance for $Fe(Bipy)_2(CN)_2$ and related compounds[3], for trinitrobenzene iodide[9], and for a series of charge transfer complexes of *N,N*-dimethylaniline, chloranil, and similar organic donors and acceptors[10]. The last case is the most extreme in that the frequencies *vs.* E_T plots for hydrogen- and non-hydrogen-bonding solvents have slopes of opposite sign; the plots for $Mo(CO)_4(Bipy)$ merely differ in the magnitudes of their slopes.

Presumably the solvent effect arises from solvent interaction with the carbonyl groups affecting the metal to bipyridine charge transfer energy. Solvent interaction with the carbonyl groups of $Mo(CO)_4(Bipy)$ has been established by infra-red methods[11]. Direct solvent interaction with the bipyridine ligand is unlikely to be the cause of solvent effects on frequencies of maximum absorption*.

ACKNOWLEDGEMENT

Thanks are due to the Royal Society for a Grant-in-aid for the purchase of the spectrophotometer.

REFERENCES

1 J. Bjerrum, A. W. Adamson and O. Bostrup, *Acta Chem. Scand.*, 10 (1956) 329.
2 A. A. Schilt, *J. Amer. Chem. Soc.*, 82 (1960) 3000.
3 J. Burgess, *Spectrochim. Acta*, submitted.
4 C. Reichardt, *Angew. Chem. Int. Ed. Engl.*, 4 (1965) 29.
5 K. Dimroth, C. Reichardt, T. Siepmann and F. Bohlmann, *Justus Liebigs Ann. Chem.*, 661 (1963) 1.
6 E. M. Kosower, *J. Amer. Chem. Soc.*, 80 (1958) 3253.
7 M. H. B. Stiddard, *J. Chem. Soc.*, (1962) 4712.
8 W. Liptay, *Angew. Chem. Int. Ed. Engl.*, 8 (1969) 177.
9 K. M. C. Davis, *J. Chem. Soc., B*, (1967) 1128.
10 P. H. Emslie and R. Foster, *Rec. Trav. Chim. Pays-Bas*, 84 (1965) 255.
11 D. M. Adams, *J. Chem. Soc., A*, (1969) 87.

---

* In the iron(II)/2,2'-bipyridine/cyanide systems solvent effects on spectra of $Fe(Bipy)_2(CN)_2$ and $Fe(Bipy)(CN)_4^{2-}$ are large, of $Fe(Bipy)_3^{2+}$ negligibly small[3].