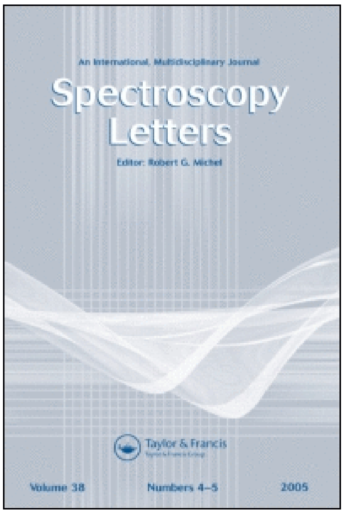

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Solvent Effects on the Electronic Absorption Spectrum of $CrC(NO_3)_36H_2O$

Józef Myrczek[a]; Adam Bartecki[a]
[a] Institute or Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wrocław, Wrocław, POLAND

To cite this Article Myrczek, Józef and Bartecki, Adam(1987) 'Solvent Effects on the Electronic Absorption Spectrum of $CrC(NO_3)_36H_2O$', Spectroscopy Letters, 20: 5, 431 — 438
To link to this Article: DOI: 10.1080/00387018708081563
URL: http://dx.doi.org/10.1080/00387018708081563

SPECTROSCOPY LETTERS, 20(5), 431-438 (1987)

SOLVENT EFFECTS
ON THE ELECTRONIC ABSORPTION SPECTRUM OF $Cr(NO_3)_3 6H_2O$

Józef Myrczek and Adam Bartecki
Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, POLAND.

key words: electronic absorption spectra, solvent effects, transition metal complexes, chromium (III) compounds, computer resolution of spectra

ABSTRACT

Non-specific solvent effects on the electronic absorption spectra of $Cr(NO_3)_3 6H_2O$ in water, methanol, ethanol, t-butanol and in their binary mixtures were investigated. The spectra were carefully treated using a computer resolution technique. The high correlation between dielectric constant of solvents and the crystal field parameter Dq as well as between refractivity index and oscillator strength of the d-d bands were observed. A concept of a new spectrochemical series has been formulated.

As well known, the d-d bands in electronic absorption spectra of transition metal complexes are succesfully interpreted with the ligand field theory. The fundamental parameter of this theory (the so called Dq quantity or splitting parameter) is derived formally without taking into account other surroundings than the electrostatic field of the ligands only. However, studying these spectra in solutions one should consider in addition an influence created by solvent molecules. Experimentally one states that solvent effects on the electronic absorption spectra of transition metal complexes result in both the shifting of absorption bands and changes of oscillator strengths. The shifting of the d-d bands is strictly connected with changes of crystal field parameters.

Some years ago the simple formulae were derived which expressed the relationships between crystal field parameters of complex compounds and dielectric constant of solvent, using the reaction field model (1). The proposed model treated the solute molecule as a multipole series enclosed in a spherical cavity, surrounded by a polarisable solvent medium. For an octahedral complex the proper formula is described by Eq.1

$$Dq^{eff} = Dq^{o} + const*[5(\varepsilon-1)/(5\varepsilon+4)] \qquad 1$$

where Dq^{eff} is the effective value of crystal field strength parameter Dq which includes the non-specific interaction between solute complex molecules and solvent, Dq^{o} is the approximated value of Dq for the complex molecule in vacuum ($Dq^{o}=\lim Dq^{eff}$ when $\varepsilon \longrightarrow 1$) and const means the constant parameter equal to $Dq^{o}(a/a_{o})$. a_{o} is the distance between the central ion and ligand in O_{h} complexes, a is the radius of cavity.

In the meantime Tai-ichi-Shibuya presented the theory for the solvent effect on the absorption band intensity (2,3). The ratio of the observed oscillator strength (f'') of the solute molecule to the 'true', respective oscillator strength (f^{o}) of the molecule is given by the Eq.2. equivalent to the Eq.3..

$$f''/f^{o}=[s(n^{2}-1)+1]^{2}/n \qquad 2$$

$$(n\, f'')^{1/2}= (\, f^{o}\,)^{1/2}\, s\, (n^{2}-1)+(\, f^{o}\,)^{1/2} \qquad 3$$

In these expressions, n is the refractive index of the solvent medium and s is a shape parameter which can be identified with the depolarization factor of a dielectric in the same shape as the cavity (in which the solute molecule is supposed to lie), for the direction of the transition moment. The Eq.2. was derived on two assumptions : 1) both solute and solvent molecules are nonpolar and mutually inert, 2) the absorption band is strong enough (the imaginary part of the polarizability should be well approximated by the absorption band). However, reasonable results were obtained even if these conditions were not strictly satisfied (3).

The connection of these two mentioned approaches gave an opportunity to analyse the whole changes of the spectral contour due to non-specific solute-solvent interaction. Such an analysis was applied for $Cr(NO_3)_3$ $6H_2O$ spectra using a computer resolution technique.

EXPERIMENTAL

Electronic absorption spectra of 0.025M solutions of $Cr(NO_3)_36H_2O$ in water, methanol (Met), ethanol (Et) t-butanol (t-but) and their binary mixtures, were recorded in the range of 14000-29000 cm^{-1} with a Hitachi 356 UV/VIS spectrophotometer connected with a system CAMAC. The spectra were thermostatted at 25^oC. The investigated range included two spin-allowed ($^4T_{2g} \leftarrow {}^4A_{2g}$, $^4T_{1g} \leftarrow {}^4A_{2g}$) and four spin-forbidden bands. The spectra were smoothed and resolved into Gaussian components using a non-linear least-squares method, then the crystal field parameters B, Dq and C were calculated (4). The regression analysis of the data according to the Eq.1. and Eq.3. were performed. The following values of dielectric constants and refractive index were taken (5,6):

ε: H_2O - 78.54 , Met - 32.63 , Et - 24.3 , t-but - 12.5
n: H_2O - 1.33 , Met - 1.25 , Et - 1.36 , t-but - 1.39

For the binary mixtures of solvents the extrapolated values of ε and n were used.

All the calculations were performed on an IBM PC and MERA-60D microcomputers.

RESULTS AND DISCUSSION

An example of the resolved spectrum is displayed in Fig.1. Transition energies and oscillator strengths of the spin-allowed bands as well as values of Dq

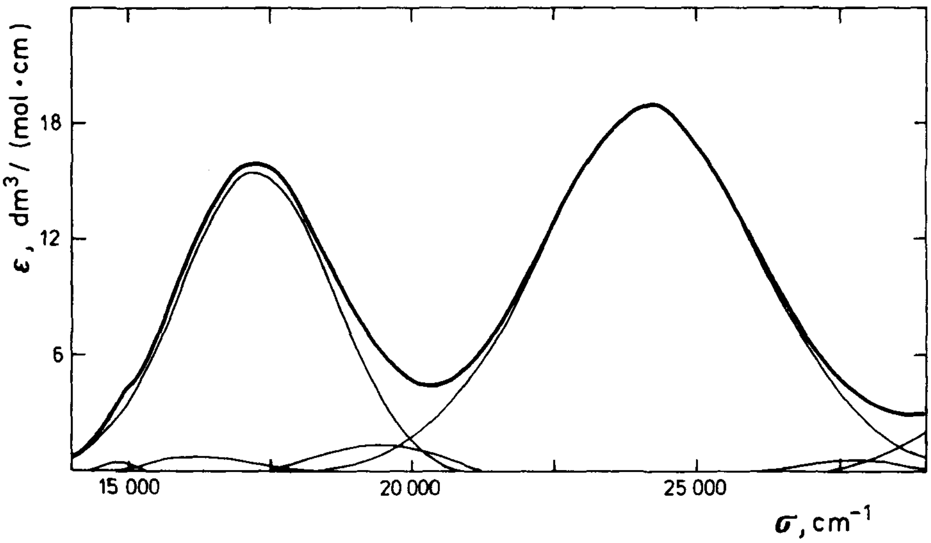

FIG.1. The resolved electronic absorption spectrum of $Cr(NO_3)_3 6H_2O$ in water.

parameters are listed in Tab.1, for all twelve measured spectra. Values of Dq were reproducible typically to 1 cm^{-1}.

The regression analysis according to the Eq.1. showed the high correlation between Dq and $5(\varepsilon-1)/(5\varepsilon+4)$ with a correlation coefficient equal to 0.986. It enabled us to calculate values of $Dq^{o} = 1416(\pm 19)\ cm^{-1}$ and $Dq^{\infty} = \lim Dq^{eff}$ when $\varepsilon \longrightarrow \infty = 1747(\pm 2)\ cm^{-1}$, $a/a_o = 0.85(\pm 0.02)$.

Dq^{o} and Dq parameters are very important as they create limits of the range of the possible values of Dq for a given complex. Furthermore, parameter Dq^{o} appears to be a general measure of the real strength of the field in the complex which is due to the ligand field

TABLE 1

Some calculated spectroscopic data of the electronic absorption spectra of $Cr(NO_3)_3\ 6H_2O$ in solutions.

No	Solvent^a	${}^4T_{2g}$<- ${}^4A_{2g}$		${}^4T_{1g}$<- ${}^4A_{2g}$		Dq^d
		X^b	f''^{c}	X^b	f''^{c}	
1.	H_2O	17392	1.79	24426	3.19	1739
2.	H_2O+Met (1:1)	17353	1.72	24450	3.20	1735
3.	H_2O+Et (1:1)	17342	1.77	24409	3.32	1734
4.	H_2O+t-but(1:1)	17336	1.72	24419	3.10	1734
5.	Met	17306	1.59	24379	2.89	1731
6.	Et+Met (1:1)	17268	1.93	24287	3.31	1727
7.	Et+Met (4:1)	17259	2.09	24133	3.54	1726
8.	Et	17243	2.22	24132	3.88	1724
9.	t-but+Met(1:1)	17223	2.06	24233	3.51	1722
10.	t-but+Et (1:1)	17165	2.40	24089	4.22	1717
11.	t-but+Et (4:1)	17122	2.59	23941	4.67	1712
12.	t-but	16984	2.69	23803	4.86	1698

^{a} in brackets the volume proportion of components is given,

^{b} position of the maximum of the resolved band in cm^{-1}

^{c} oscillator strength of the resolved band * 10^{-4}

^{d} data in cm^{-1}

only and independent of solvent surroundings. It seems that the parameter Dq^o could be a good basis for a new spectrochemical series.

The analysis of the intensities according to the Eq.3. was performed only for non-aqueous solutions. The estimated values of f^o and s parameters are equal to 0.81(±0.06) 10^{-4} and 2.0(±0.3) for the first band and to 0.91(±0.10) 10^{-4} and 2.2(±0.5) for the second band, respectively. A good correlation of empirical intensity data has been noted, so the prediction of the band intensities in other solvents is possible. The correlation coefficients are 0.985 (first band) and 0.965 (second band). However, the obtained values of s parameter are too high as theoretically they should be between 0 and 1. This fact may be due to a presence of ligand fields in the systems molecule-cavity-solvent. The influence of such extra fields was not taken into consideration by Tai-ichi-Shibuya.

The parameter B does not change essentially in all recorded spectra (changes are below 5%) but it slightly decreases in the order: Met - H_2O - Et - t-but On the contrary, the band halfwidths increase slightly in the same order. Parameter C is almost constant (mean value = 3190 cm^{-1}, mean square deviation = 34 cm^{-1}).

Generally, the last mentioned changes are small and we do not regard them as significant for spectral contours. Future studies will provide an answer to whether these changes are systematic or casual. Such studies are continued in our laboratory with the purpose of:

(i) checking the formulated concept of a new spectrochemical series connected with the parameter Dq^{o}

(ii) simulation of the absorption spectral contour of transition metal complexes in different surroundings.

ACKNOWLEDGMENTS

We are indebted to Mrs Maria Raczko for carefully recording the spectra and to Mr Leszek Stelmaszek for helpful discussion.

REFERENCES

1. Bartecki A., Stelmaszek L. Solvent Effect on Electronic Spectra of Transition Metal Complexes. Bull. Ac. Pol. : Chim. 1981; 29:297.
2. Shibuya T. A Dielectric Model for the Solvent Effect on the Intensity of Light Absorption. J. Chem. Phys. 1983; 78: 5175.
3. Shibuya T. Solvent Effects on the $n - \pi^*$ Absorption Intensities of Acetone and Cyclopentanone. Bull. Chem. Soc. Jpn. 1984; 57: 2991.
4. Bartecki A., Sołtowski J., Kurzak K. Curve Resolution of Electronic Absorption Spectra by Least-squares Methods as Applied to Transition Metal Complexes. Comp. Enh. Spectr. 1983; 1: 31.
5. Griffiths T.R., Pugh D.C. Correlations among Solvent Polarity Scales, Dielectric Constants and Dipole Moment, and a Means to Reliable Predictions of Polarity Scale Values from Current Data. Coord. Chem. Rev. 1979; 29: 129.
6. CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, Florida: 1984.

Date Received: 03/11/87
Date Accepted: 04/21/87