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On the Solvent Dependence of the Spectra of Complex Ions

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In recent studies of the absorption spectra of dissolved complexes of transition group elements the so-called crystal field bands are treated as due to electronic transitions between levels caused by the perturbation of the electric fields of the ligands in the first co-ordination sphere. In order to examine the correctness of the assumption of the non-influence of the second sphere we have measured the spectra of some robust complexes of iron(II), chromium(III) and cobalt(III) in other solvents than water. Acetone, nitromethane, chloroform, ethanol, and especially methanol were used as solvents, and in the cases where the complexes were sufficiently soluble the spectra of the solutions were measured at a Cary recording spectrophotometer.

Of the complexes examined dicyano-bis(*o*-phenanthroline)iron(II) was prepared according to Barbieri¹ and recrystallized from chloroform until the spectrum was unchanged by further recrystallization. (Found: Fe 10.81; N 16.32; C 60.90. Calc. for $[\text{Fe}(\text{o-phen})_2(\text{CN})_2] \cdot 3\text{H}_2\text{O}$: Fe 10.70; N 16.22; C 60.25). Tris(*o*-phenanthroline)iron(II) bromide was prepared according to Blau² and recrystallized once. The Reinecke's salt $\text{K}[\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]$ was prepared after Nordenskjöld³. An analyzed preparation of $(\text{NH}_4)_3[\text{Cr}(\text{SCN})_6] \cdot 4\text{H}_2\text{O}$ was kindly made to us and measured in

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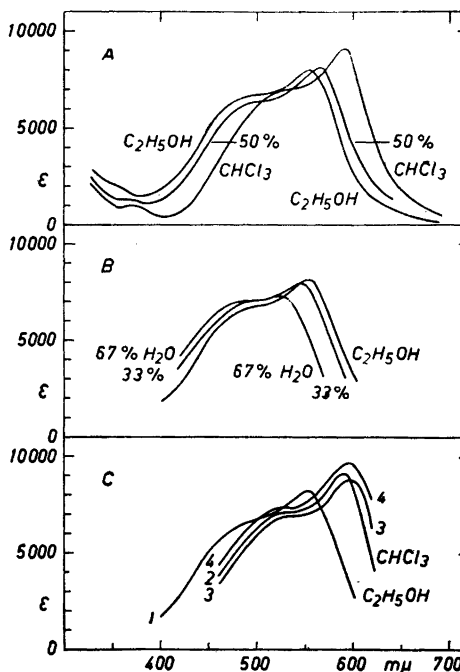


Fig. 1. Extinction curves for $[\text{Fe}(\text{o-phen})_2(\text{CN})_2]$ in different solvents.

- A. In CHCl_3 , 50% $\text{CHCl}_3 + 50\%$ $\text{C}_2\text{H}_5\text{OH}$ and $\text{C}_2\text{H}_5\text{OH}$
 B. In $\text{C}_2\text{H}_5\text{OH}$, 67% $\text{C}_2\text{H}_5\text{OH} + 33\%$ H_2O , 33% $\text{C}_2\text{H}_5\text{OH} + 67\%$ H_2O
 C. In $\text{C}_2\text{H}_5\text{OH}$ (curve 1), CHCl_3 (curve 2), 50% $\text{CHCl}_3 + 50\%$ petrolether (curve 3), 50% $\text{CHCl}_3 + 50\%$ CCl_4 (curve 4).

water, methanol and acetone by C. E. Schäffer. Pure samples of Nos. 4–10 in Table 1 were kindly put at our disposal by Professor Fred Basolo, who prepared⁴ the compounds during his stay at this laboratory.

The data for 10 complex salts are summarized in Table 1. For each absorption band are given the value of λ_{max} (wavelengths of maximum in $\text{m}\mu$) and ϵ_{max} (molar extinction coefficient) in water, and for the organic solvents the changes in λ_{max} and ϵ_{max} as % of values in water. The examples given in the table show that λ_{max} usually is practically independent of the solvent. A significant change of λ_{max} is only found in one case, viz. $[\text{Co}(\text{en})_2(\text{SCN})_2](\text{SCN})$. This compound has a crystal field band ($\epsilon_{\text{max}} =$

Table 1. Data for absorption maxima, and changes in λ_{\max} and ϵ_{\max} as per cent of value in water

No.	Compound	Water		Methanol		Nitromethane		Acetone	
		λ_{\max}	ϵ_{\max}	$\Delta\lambda\%$	$\Delta\epsilon\%$	$\Delta\lambda\%$	$\Delta\epsilon\%$	$\Delta\lambda\%$	$\Delta\epsilon\%$
1	[Fe(o-phen) ₂]Br ₂	510	11 200	0	+ 5.3				
		266	67 200	0	+ 2				
2	K[Cr(NH ₃) ₂ (SCN) ₄]	515	107	+1.7	- 5.5	+2	+ 2.8		
		390	96	+1	-15.7	+1	- 8.3		
		303	14 800	+2	+17				
3	(NH ₄) ₂ [Cr(SCN) ₆]	564	159	-1.7	-28	-0.7	-16.2	-1.4	-35
		420	129	-1.5	-29	-0.5	-17	-1.4	-36
		309	25 000	0	+12				
		234	19 200	(0)	(+33)				
4	<i>cis</i> -[Coen ₂ (Cl) ₂]Cl	525	72.5	+2	+ 7.2				
5	<i>trans</i> -[Coen ₂ (Cl) ₂]Cl	617	36	-1.1	~ 2				
		455**	27	(0)	- 7				
		387**	36	(0)	+25				
6	<i>trans</i> -[Coen ₂ (Br) ₂]Br	648	45	0	+ 9				
7	<i>cis</i> -[Coen ₂ (SCN) ₂]SCN	487	340	+1	+20			+1	+29 *
		308	2 900	+6	- 4			+7.8	+14 *
8	<i>cis</i> -[Coen ₂ (NO ₂) ₂]NO ₂	430	129	+1.8	+13.5				
		323	2 830	+1.3	+21				
9	<i>trans</i> -[Coen ₂ (NO ₂) ₂]NO ₂	430	133	+1	+13.2				
		340	2 470	+1	+21				
10	[Co(NH ₃) ₂ (NO ₂) ₂]	435	235	0	+11.3				
		345	4 900	+1.5	+ 7.2				
		258	16 500	+1	- 6				

* Acetone with 10 % CH₃OH.

** A shoulder in H₂O and a peak in CH₃OH. This difference in shape is independent of concentration.

340) as well as an electron transfer band ($\epsilon_{\max} = 2\,900$), and it is noteworthy that it is only the last mentioned band which is displaced considerably (6–8 %) by going from water to organic solvent. The influence of the solvent on the intensities of the bands is more varied, and ϵ_{\max} shows some changes in most cases. The data seem to show that compared with water ϵ_{\max} is generally higher for cations and lower for anions in methanol. For one and the same solvent Beer's law was found to be sufficiently obeyed in all cases in which measurements were performed at different concentrations.

[Fe(o-phen)₂(CN)₂] represents a case even more anomalous than *cis*[Co(en)₂(SCN)₂](SCN). The dicyano complex is so insoluble in water, carbon-tetrachloride and ether that measurements cannot be performed in the pure solvents, but it is sufficiently soluble in methanol, ethanol and chloroform. In Fig. 1 extinction curves for this non-electrolyte in different solvents are shown. It is seen that three electron transfer bands are found in visible and near ultraviolet, e. g. in chloroform at the wavelengths 591 m μ , 525 m μ (shoulder) and 367 m μ , respectively. The whole appearance of the curves, and the absence

of any isobestic points rule out the possibility of a chemical equilibrium between two forms which shift with solvent composition. *cis*[Coen₂(SCN)₂](SCN) behaves similarly in water-methanol mixtures. Evidence for a true solvent effect is also found in the fact that light absorption in the various solvents does not show any time effect.

That a crystal field band of a saturated complex ion only to a slight degree is dependent on the solvent can be predicted from the theoretical expression for λ_{\max}

$$1/\lambda_{\max} = \text{const. } \mu/r^6$$

(see *e. g.* Ballhausen⁵) where μ is the point dipole moment and r the distance of the ligand from the central atom. Denoting the quantities in the first and second spheres by μ' , μ'' , and r' , r'' , respectively, the relative contribution of the second sphere to the wavelength is given by

$$\frac{\Delta\lambda_{\max}}{\lambda_{\max}} = \frac{\mu''}{\mu'} \cdot \left(\frac{r'}{r''}\right)^6$$

Now introducing $\mu' \gtrsim \mu''$ and $r'' = 2r'$, we get

$$\frac{\Delta\lambda_{\max}}{\lambda_{\max}} \lesssim \frac{1}{64}$$

According to this estimation the displacement of a crystal field band of a saturated complex should always be smaller than 2% in agreement with what is found experimentally. The greater variability of the electron transfer band found in some cases is quite natural considering that the orbitals of the solvent molecules are closer to the orbitals of the ligands than to the electron systems of the central atom.

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On the Proton Conductivity in Water

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It is commonly agreed that the large mobilities of the H_3O^+ and OH^- ions in water must be explained by a proton transfer over hydrogen bridges. By assuming this proton transfer mechanism, Gierer and Wirtz^{1,2} derived the following equation to explain the mobility as a function of temperature:

$$u = \frac{C}{T} f(T) \exp\left(-\frac{q}{RT}\right) \quad (1)$$

Here u is the mobility of the H_3O^+ or OH^- ion in excess of the value expected for ions of that size. C is a factor which incorporates some constants of the system, T is the absolute temperature and q is the activation energy of the rate determining process. $f(T)$ is a function of temperature (and also pressure), which describes the influence of the liquid structure upon the mobility.

If this equation is to be useful, the structural influence $f(T)$ should be known. Gierer and Wirtz used Eucken's structure model of water³ for their treatment. Eucken assumed that the water structure consisted of a few definite types of molecular species. There is very little evidence to support this assumption, however. An alternative derivation of $f(T)$ from the model of water proposed by Grjotheim and Krogh-Moe⁴ shall therefore be suggested.

If the proton transfer across a hydrogen bridge is the rate determining process, one might expect $f(T)$ to be proportional to the total number of hydrogen bonds present in water. Contrary to this assumption the extra mobility increases with temperature in a certain temperature interval, though the number of hydrogen bonds decreases monotonously. By assuming that $f(T)$ is proportional to the number of water molecules with only one hydrogen bond established, consistent results may be derived. This is reasonable if the breaking of the hydrogen bond is the rate determining process. When a proton transfer over a hydrogen bridge has occurred, a reorientation of the water molecule is necessary if the molecule is to participate in further proton transfers. A water molecule