Visible and Near IR Spectra of Some Divalent Transition Metal Cupferron Complexes

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The visible and near IR spectra of the ammonium salt of cupferron and manganese, cobalt, nickel and copper divalent cupferrate complexes are investigated. New absorption bands observed are given and assigned using the Tanabe-Sugano diagrams. In the absorption spectra of the divalent transition metal cupferrates a characteristic shift in the maxima and minima appears. Solvent effects on this shift were investigated.

Cupferron is a well known chelating agent. The IR spectrum of cupferron was first reported by PISKORZ *et al.*¹ and recently YOSHIMURA *et al.*² studied the UV and IR spectra of cupferron and neo-cupferron and assigned the different absorption bands detected. Very recently, the IR spectra of the ammonium salt of cupferron and some divalent transition cupferron complexes were reported³ and the different absorption bands observed were assigned. A tetrahedral crystal field structure for the divalent transition metal cupferrates was suggested, therefore, the UV absorption bands observed⁴ were satisfactorily assigned and the excited electronic states corresponding to these bands were identified.

In the present work the visible and near IR spectra of cupferron and some divalent transition metal cupferron complexes are presented and discussed. The absorption bands observed in the region 400 nm-2000 nm are given and assigned and the electronic states are identified.

Experimental

All chemicals used were A. R. grade, B. D. H. Label. The ammonium salt of cupferrone was obtained from Hungary "Reanal" Finomvegyszer-gyar, Budapest. The different cupferrate complexes were prepared by the method described earlier³. Elemental chemical analysis³ for the metal complexes prepared gave a chemical composition of

ML_2 , where M stands for the metal (Mn, Co, Ni and Cu) and L for the ligand ($C_6H_5O_2N_2$).

The visible and near IR measurements were carried out using a spectrophotometer Beckmann model 15800 DR monochromator.

Results and Discussion

The visible and near IR spectra of the ammonium salt of cupferron and its metal complexes with divalent manganese, cobalt, nickel and copper in various solvents: Methyl, ethyl, isopropyl alcohols and dioxane measured for small concentrations for which Lambert's law is obeyed are given in Figs. 1-4. In Table I the wavelength and molar extinction coefficients of the absorption maxima and minima observed for the different complexes are tabulated. The obtained spectra of ammonium cupferron are characterized by three absorption bands. Two intense absorption bands were observed for different solvents near 733 ± 32 nm and 1900 ± 100 nm. The 733 ± 32 nm band shows a solvent effect, the absorption band maximum shifts to longer wavelengths and its intensity decreases as the solvent changes from methyl alcohol to dioxane, while the 1900 nm band maximum shifts to shorter wavelengths. The $n \rightarrow \pi^*$ transition bands of the nitroso group, which are observed in the nitroso-amine derivatives around 350 nm and in the monomer of C-nitroso compounds around 700 nm⁵ are responsible for the color of these compounds. According to the assumption of HASZELDINE *et al.*⁶ the $n \rightarrow \pi^*$ transition band, which originates from the excitation of a non-bonding electron of the nitrogen atom

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to the antibonding π^* -orbital could appear in the spectrum of N-nitroso compounds near 700 nm. However, YOSHIMURA² reported that no absorption bands were observed near 700 nm in the spectrum of cupferron. The absorption band observed near 733 nm in the present work could be assigned to

$n \rightarrow \pi^*$ transition, while the shift resulting from solvent effect could be attributed to the effect of the polarity of the solvent on the transition. Further, the weak band appearing near 1000 nm could be ascribed to the effect of the interaction of cupferron and solvent on charge transfer bands.

Fig. 1. Spectral dependence of the molar extinction coefficient of cupferron and Mn, Co, Ni and Cu cupferrates, in methyl alcohol (conc. 10^{-2} mole/lit, $T = 300^\circ\text{K}$, cell thickness 1 cm).

Fig. 2. Spectral dependence of the molar extinction coefficient of cupferron and Mn, Co, Ni and Cu cupferrates, in ethyl alcohol.

Fig. 3. Spectral dependence of the molar extinction coefficient of cupferron and Mn, Co, Ni and Cu cupferrates, in isopropyl alcohol.

Fig. 4. Spectral dependence of the molar extinction coefficient of cupferron and Mn, Co, Ni and Cu cupferrates, in dioxane.

Table I. The molar extinction coefficient and the wavelengths of the absorption maxima for some divalent transition cupferron complexes in the visible and near IR region.

	Methyl alcohol		Ethyl alcohol		Iso-propyl alcohol		Dioxane	
	$\lambda_{\max}$ [nm]	ϵ	$\lambda_{\max}$ [nm]	ϵ	$\lambda_{\max}$ [nm]	ϵ	$\lambda_{\max}$ [nm]	ϵ
Cupferrone	760	74	765	26.5	765	29.2	700	0.5
	990	1						
	1100	1						
	2150	230						
Mn(Cup) ₂			755	83	750	12	580	2
	755	80.5					770	7.6
	990	1					1050	0.7
	1150	2					1150	0.5
	1600 sh	11.2						
	1900	105					1700	55
Co(Cup) ₂	460 sh	89	740	6.4	725-800 b	1	520	31
	755	27						
							1150	0.1
	2090	180					1680	43
Ni(Cup) ₂	675	18	675	14	625-725 b	2.6	580	1.5
			1050 b	12.5	1050	2	750	8
	1125	16.2			1150	2.5		
	1900	99	1900	92.5	1650	45	1700	44
Cu(Cup) ₂			670	29	580	5		
	625 sh	18						
	750	35			700	3	750	5.2
					820 sh	2.1		
	980	10			1000	2.4	1050	2
	1600	24			1500	13	1800	82

sh = shoulder; b = broad.

The other intense band observed near 1900 nm shows a strong solvent effect, the absorption band maximum shifts towards shorter wavelengths on decreasing solvent polarity. This band may be assigned as an overtone of the N-H stretching vibrations of the ammonium ion which has a strong band near 3170 cm⁻¹ in the solid state IR spectrum³.

Electronic spectra of divalent transition cupferrates

The visible and near IR absorption spectra of Mn, Co, Ni, and Cu cupferrates are given in Figs. 1-4. Some of the absorption bands observed are similar to that of the ammonium cupferron. However, a slight shift of the observed bands is found for metal complexes. Such behaviour could be explained on the premises that by replacing the ammonium group by relatively stronger electron acceptor metal cations, electrons will be shifted from benzene ring through the oxygen ligand. Thus, with a removal of electrons from the benzene ring, the energy required to remove an electron to higher

orbitals will increase with a subsequent decrease in position of the band wavelength.

Manganese cupferrate; IR measurements reported³ suggest a tetrahedral structure for the cupferrate complexes investigated. High spin 3d⁵ complexes have only one spin sextet, the ground state; all excited d-manifold states are either quartets or doublets. All transitions between states are thus formally spin forbidden and are only observed as the result of spin-orbit coupling between the excited quartets and either higher lying sextet states (non-d-manifold: *e.g.* charge transfer) and/or the ground sextet state⁷. The manganous ion has four excited terms within the 3d⁵ configuration: ⁴G, ⁴P, ⁴D and ⁴F. Following TANABE and SUGANO⁸ the crystal field strength in tetrahedral manganese complexes does not enough to force the change of the ground state from ⁶A₁(S) to ²T₂(³T), therefore, the absorption band observed in dioxane at 580 nm, which fades in polar solvents, could be assigned to the transition ⁶A₁(S) → ⁴T₁(¹G). The 755 nm band

shows a shift of ≈ 5 nm in methyl alcohol and 70 nm in dioxane with respect to that of cupferron. Moreover, two weak bands were observed near 1000 nm and 1150 nm in methyl alcohol and dioxane solutions. The strong band appeared at 1800 ± 200 nm shows strong solvent effect, a band shift ≈ 200 nm was observed when solvent changes from methyl alcohol to dioxane.

Cobalt cupferrate: High spin $3d^7$ complexes have a spin quartet ground state $^4A_2(F)$; all excited d-manifold states are either quartets or doublets. In the absorption spectrum of cobalt cupferrate two strong bands were observed near 460 nm, 1800 nm and two weak bands near 740 nm and 1000 nm. The TANABE-SUGANO diagram⁸ predicts the following spin-allowed transitions $^4A_2(F) \rightarrow ^4T_1(P)$ near 740 nm and $^4A_2(F) \rightarrow ^4T_1(F)$ at 1800 nm. However, a 755 band appears also in the spectrum of cupferron and therefore, the 740 nm band of nickel cupferrate is mainly attributed to the $n \rightarrow \pi^*$ transition. The broad band around 740 nm in polar solvents and 520 nm in dioxane could be assigned to the transition $^4A_2(F) \rightarrow ^2T_2(G)$ expected at 440 nm and $^4A_2(F) \rightarrow ^2T_1(G)$ expected at 490 nm influenced by the solvent polarity and hydrogen bonding.

Nickel cupferrate: $3d^8$ complexes have a spin triplet state $^3T_1(F)$; all excited d-manifold states are triplets or singlets. Four absorption bands were observed in the spectrum of nickel cupferrate at 580 nm, 700 nm, 1100 nm and 1775 ± 125 nm. The 1775 nm absorption band shows a strong solvent effect, the band maximum moves to shorter wavelengths on decreasing solvent polarity. There-

fore, polar solvents give rise to a decrease in the excitation energy of the 1775 nm band. The TANABE-SUGANO diagram⁸ for tetrahedral nickel complexes shows that there are three spin allowed transitions from $^3T_1(F)$ ground state. The bands observed near 528 nm and 625 nm could be ascribed to the single transition $^3T_1(F) \rightarrow ^3T_1(P)$ and the band observed at 1775 nm could be assigned to the $^3T_1(F) \rightarrow ^3A_2(F)$ transition.

Copper cupferrate: One intense band at 1675 ± 125 nm and four weak bands at 580 nm, 647 nm, 720 nm and 820 nm were observed in the absorption spectrum of copper cupferrate. Copper complexes have a spin doublet ground state 2E . Ligand field theory⁹ predicts only one transition between the doublet states of Cu^{2+} ion in tetrahedral field $^2T_2(D) \rightarrow ^2E$ at about 6000 cm^{-1} in the near IR region. Therefore, the absorption band observed at 1675 ± 125 nm could be ascribed to this transition. This band shows a shift to lower wavelengths on increasing solvent polarity, in opposite to other cupferrates. A band shift of 200 nm was observed when the solvent changes from methyl alcohol to dioxane. This shift shows that polar solvents increase the excitation energy of the $^2T_2(D) \rightarrow ^2E$ transition in copper cupferrate.

Since copper is a very strong electron acceptor, other bands observed at 580 nm, 645 nm, 720 nm and 820 nm could be considered as charge transfer bands¹⁰ related to the electron donating and accepting properties of the ligand and the metal ion and could be assigned as transitions between the molecular orbitals of the complex ion.

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