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Coordination Compounds of Heterocyclic Azo Derivatives. III. Co(II), Ni(II) and Cu(II) Complexes of Some Arylazo-4,5-diphenylimidazole Derivatives

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The 3 d transition metal ion [Co(II), Ni(II) and Cu(II)] complexes of some 4,5-diphenylimidazole azo derivatives have been isolated and characterized by chemical analysis, conductance, electronic and IR spectra. These dyes are characterized by a high tendency towards complex formation with the neutral molecules coordinated to the metal ion as bidentate ligands. The molecular formula of the 1 : 1 and 1 : 2 complexes are suggested to be $[MLX_2(H_2O)_2]$ and $[ML_2X_2]$ or $[ML_2X_2] \cdot 2\,H_2O$ respectively, where $X = Cl^-$ or NO_3. The different bands observed in the visible spectra of methanolic solutions of the complexes have been assigned to the possible electronic transition type ($L \rightarrow M$CT and d-d). It is suggested that the complexes studied have a distorted octahedral geometry.

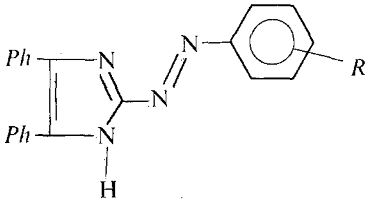
(Keywords: Coordination compounds; Azoimidazole; Transition metals)

Koordinatsverbindungen von heterocyclischen Azo-Derivaten, 3. Mitt.: Co(II)-, Ni(II)- *und* Cu(II)-*Komplexe einiger Arylazo-4,5-diphenylimidazol-Derivate*

Es wurden einige Komplexe von 4,5-Diphenylimidazol-azo-Derivaten mit den 3 d-Übergangsmetallen Co(II), Ni(II) und Cu(II) isoliert und mittels chemischer Analyse, Leitfähigkeitsmessungen und den Elektronen- bzw. IR-Spektren charakterisiert. Diese Farbstoffe zeigen eine sehr starke Tendenz zur Komplexbildung, wobei die neutralen Moleküle als zweizähnige Liganden an das Metallion koordinieren. Die Formeln für die 1 : 1- und 1 : 2-Komplexe werden mit $[MLX_2(H_2O)_2]$ und $[ML_2X_2]$ bzw. $[ML_2X_2] \cdot 2\,H_2O$ vorgeschlagen ($X = Cl^-$ oder NO_3^-). Die verschiedenen Absorptionsbanden in den VIS-Spektren in methanolischer Lösung werden den möglichen e-Übergängen ($L \rightarrow M$CT und d-d) zugeordnet. Für die Komplexe werden verzerrte oktaedrische Geometrien vorgeschlagen.

Introduction

Azoimidazole compounds were found to be valuable dyes[1], as well as they were applied for analytical separation and microdetermination of some metal cations[2–4]. It was proved that the heterocyclic nitrogen atom is a vital part of the structure of such compounds, since it greatly improves their chelating properties[3]. However, metal complexes of this class of compounds have received not much attention[1, 5–7]. Thus, in continuation of our work on the metal complexes of heterocyclic azo derivatives[7, 8], we report in this paper an investigation of Co(II), Ni(II) and Cu(II) complexes of some azoimidazole derivatives. The study involves synthesis and characterization of such complexes. The dyes used are:



R = 4-CH_3 (L_1), 4-OCH_3 (L_2), 2-OCH_3 (L_3), 4-NO_2 (L_4) and 2-NO_2 (L_5).

Experimental

All the chemicals used in this study were of reagent grade (A. R. Merck or BDH).

Preparation of the Ligands

The ligands were prepared by coupling 4,5-diphenylimidazole with the appropriate diazotate in alkaline pyridine or alcoholic solutions[2]. The diazotate was prepared by the appropriate method for each amine. The crude products were recrystallized from (1 : 1) aqueous-ethanol and dried *in vacuo* over silica gel. The purity of the crystalline compounds were checked by elemental analysis:

R = 4-CH_3 (L_1) $C_{22}H_{18}N_4$ requires C 78.08, H 5.36, N 16.55. Found C 77.89, H 5.25, N 15.82. M. p. 231°.

R = 4-OCH_3 (L_2) $C_{22}H_{18}N_4O$ requires C 76.5, H 5.25, N 15.80. Found C 76.40, H 5.21, N 15.60. M. p. 185°.

R = 2-OCH_3 (L_3) $C_{22}H_{18}N_4O$; found C 76.44, H 5.11, N 14.86. M. p. 202°.

R = 4-NO_2 (L_4) $C_{21}H_{15}N_5O_2$ requires C 68.28, H 4.10, N 18.95. Found C 68.30, H 4.0, N 17.71. M. p. 215°.

R = 2-NO_2 (L_5) $C_{21}H_{15}N_5O_2$: found C 68.21, H 3.98, N 18.21. M. p. 192–193°.

Preparation of the Solid Complexes

A hot solution of the required amount of the ligand in the least amount of absolute methanol was added to the appropriate amount of the methanolic salt solution in 1 : 1 and 2 : 1 molar ratios. The salts used are $Co(NO_3)_2 \cdot 6\,H_2O$, $NiCl_2 \cdot 6\,H_2O$, and $Cu(NO_3)_2 \cdot 3\,H_2O$. The mixture is then refluxed for ca. 3 h and cooled whereby fine crystals were separated. These were filtered, washed with cold

Table 1. *Analytical data, colour, decomposition temperature and molar conductance values of the azo imidazole complexes*

Complex	Colour	Decomp. Temp. °C	% Calculated (Found)			Molar Conductance*
			C	H	Cl	
Complexes of L_1						
$[Co(L_1)_2(NO_3)_2](H_2O)_2$	deep red	300	59.00	4.30	–	30.04
			(58.70)	(4.30)		
$[Ni(L_1)Cl_2(H_2O)_2]$	brownish-red	287	52.52	4.40	13.91	19.50
			(53.00)	(4.50)	(14.05)	
$[Cu(L_1)_2(NO_3)_2]$	reddish-violet	294	61.14	4.16	–	43.20
			(61.50)	(4.20)		
Complexes of L_2						
$[Co(L_2)(NO_3)_2(H_2O)_2]$	yellowish-red	271	46.09	3.86	–	24.23
			(46.60)	(4.10)		
$[Ni(L_2)Cl_2(H_2O)_2]$	orange red	300	50.90	4.27	13.48	18.60
			(49.80)	(4.40)	(13.52)	
$[Cu(L_2)(NO_3)_2(H_2O)_2]$	red	283	45.71	3.11	–	24.30
			(45.90)	(3.10)		
Complexes of L_3						
$[Co(L_3)(NO_3)_2(H_2O)_2]$	red	300	46.09	3.86	–	21.03
			(46.30)	(4.00)		
$[Ni(L_3)Cl_2(H_2O)_2]$	dark red	300	50.90	4.27	13.48	22.00
			(50.90)	(4.30)	(13.51)	
$[Cu(L_3)(NO_3)_2(H_2O)_2]$	deep violet	300	45.71	3.11	–	33.20
			(45.80)	(3.20)		
Complexes of L_4						
$[Co(L_4)(NO_3)_2(H_2O)_2]$	reddish-violet	278	42.87	3.25	–	27.70
			(42.60)	(3.19)		
$[Co(L_4)_2(NO_3)_2](H_2O)_2$	violet	300	52.67	3.57	–	25.90
			(52.38)	(3.60)	–	
$[Ni(L_4)Cl_2(H_2O)_2]$	deep violet	300	47.22	3.58	13.10	26.80
			(46.98)	(3.70)	(13.31)	
$[Cu(L_4)(NO_3)_2(H_2O_2)]$	deep violet	291	45.53	2.53	–	20.74
			(45.60)	(2.60)		
Complexes of L_5						
$[Co(L_5)(NO_3)_2(H_2O)_2]$	red	278	42.87	3.25	–	15.00
			(42.70)	(3.30)		
$[Co(L_5)_2(NO_3)_2](H_2O)_2$	deep red	300	52.67	3.59	–	17.30
			(52.80)	(3.60)		
$[Ni(L_5)_2Cl_2](H_2O)_2$	deep red	283	55.84	3.74	7.74	20.90
			(55.00)	(3.80)	(7.81)	
$[Cu(L_5)(NO_3)_2(H_2O)_2]$	reddish-violet	228	45.29	2.70	–	47.00
			(45.40)	(2.81)		
$[Cu(L_5)_2(NO_3)_2]$	violet	262	56.66	3.37	–	67.00
			(57.10)	(3.40)		

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* $cm^2 ohm^{-1} mol^{-1}$ at 25 °C.

alcohol and dried *in vacuo* over silica gel. The carbon, nitrogen and chlorine content of the solid complexes were determined and the analytical data are given in Table 1.

Preparation of Solutions of the Complexes

Standard metal solutions: High purity metal salts were dissolved in the appropriate volume of methanol to obtain $10^{-2} M$ stock solutions. The solutions were standardized using the recommended procedure[9].

Ligand solutions: methanolic stock solutions ($10^{-2} M$) were prepared by dissolving the accurately weighed amounts in the required volume of absolute methanol.

Physical Methods

Electronic spectra were recorded in the region 250–800 nm on a UNICAM SP 8000 spectrophotometer using 1 cm matched silica cells.

The infrared spectra of ligands and their metal complexes in the region 400–4000 cm^{-1} have been recorded on a Perkin-Elmer 599 B infrared spectrophotometer using KBr discs.

Electric conductance measurements were carried out using an YSI conductance bridge model 31, using an immersion cell. All experiments were carried out at room temperature (~ 25 °C).

Results and Discussion

The molar conductance values of $10^{-3} M$ methanolic solutions of the different complexes synthesized are found to be in the range 15–67 $Ohm^{-1} mol^{-1} cm^2$ which indicates a non-electrolytic nature of these complexes[10]. It should be noted that the relatively high molar conductance values of the complexes in methanol is due to the probable solvolysis and dissociation of the complexes by methanol[10].

The chemical analysis data clearly indicate that the neutral molecules and not their monovalent anions are coordinated to the metal ion. The proposed formulae are $[MLX_2 \cdot 2\,H_2O]$ and $[ML_2X_2]$ or $[ML_2X_2] \cdot 2\,H_2O$ for the 1 : 1 and 1 : 2 complexes, respectively (where M = Co(II), Ni(II) or Cu(II), $L = L_1$–L_5 and $X = Cl^-$ or NO_3^-). This behaviour indicates that the N–H group of the imidazole ring does *not* participate in complex formation, a fact which is further substantiated by the results of conductometric titrations and IR spectra as shown below.

The stoichiometry of the different complexes formed in solution was detected from conductometric titration in methanol. Representative results are shown in Fig. 1. It is evident that 1 : 1 complexes are formed in solution. The observed small change in conductance during the titration indicates that the neutral ligands are coordinated to the metal ion.

Spectrophotometric investigation (in the visible region) of the different complexes was performed to inspect the formation and composition of the most stable complexes possibly formed in solution. The absorption spectra of the ligands (L_1–L_5) were characterized by a main visible band in the range 414–460 nm. This band was assigned to an intramolecular CT transition taking place within the ligand molecule[11]. Generally, in all cases this band shows a red shift in presence of metal ion. This behaviour reveals an instantaneous complex formation between the imidazole azo derivative

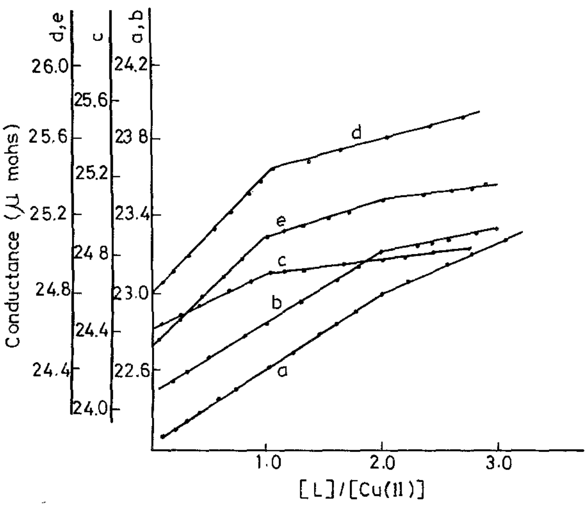
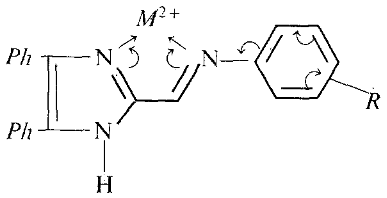


Fig. 1. Conductometric titration of 50 ml of $1 \cdot 10^{-3} M$ Cu(II) solution with $5.0 \cdot 10^{-3} M$ ligand solution. *a* L_1, *b* L_2, *c* L_3, *d* L_4, *e* L_5

and the metal ions studied, i.e. such dyes are characterized by a high tendency towards complex formation. The observed low excitation energy of the CT band in the complexed ligand relative to that in the free one can be ascribed to the expected easier intramolecular CT interaction in the former case. This is due to the high positive charge of the coordinated metal ion. The intramolecular CT interaction within the complexed ligand can be represented schematically as below:



The stoichiometric ratio of the different complexes studied was examined by two different spectrophotometric procedures: the molar ratio method[12] and *Job*'s continuous variation method[13]. In all cases, a solution of the azodye of the same concentration as in the complex solution was used as a blank. The corresponding results are represented graphically in Figs. 2 and 3. The results are in agreement with those obtained from the conductometric titrations.

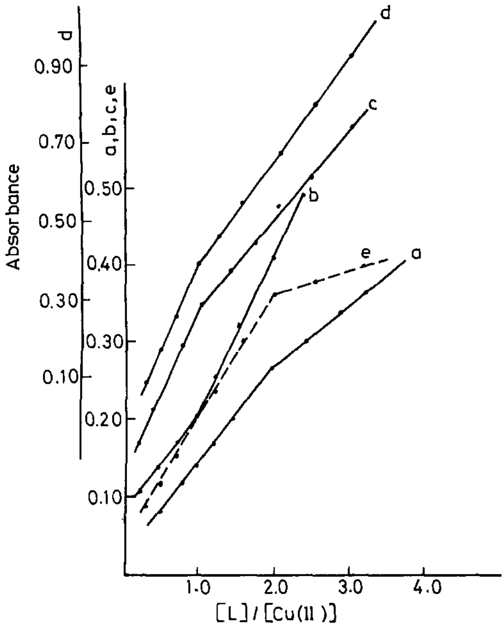


Fig. 2. Molar ratio method for Cu(II)—ligand complexes. *a* L_1, $\lambda = 500$ nm, *b* L_2, $\lambda = 503$ nm, *c* L_3, $\lambda = 530$ nm, *d* L_4, $\lambda = 530$ nm, *e* L_5, $\lambda = 520$ nm

The data from the continuous variation method were applied for the determination of the apparent formation constant values (K_f) of the different complexes formed in solution[14]. The K_f values obtained are listed in Table 2. Examination of these results reveals that the stability of 1 : 1 and 1 : 2 [*M*(II) : ligand] complexes increases in the order: Co(II) < Ni(II) < Cu(II). This is in agreement with the general order of stability of complexes of these metal ions which was established by *Grinberg* and *Yatsimirski*[15] and by *Irving* and *Williams*[16].

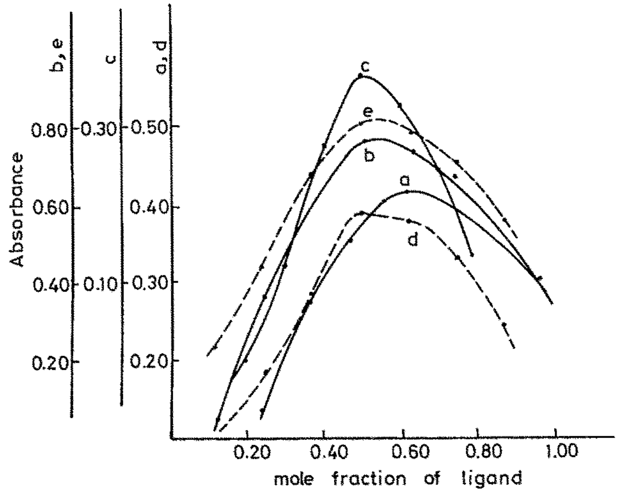


Fig. 3. *Job*'s continuous variation method for Cu(II)—ligand complexes. *a* L_1, $\lambda = 500\,\text{nm}$, *b* L_2, $\lambda = 503\,\text{nm}$, *c* L_3, $\lambda = 530\,\text{nm}$, *d* L_4, $\lambda = 530\,\text{nm}$, *e* L_5, $\lambda = 520\,\text{nm}$

Table 2. *Apparent formation constant* (K_f) *values of the different azoinidazole complexes*

Ligand	K_f values of the complexes					
	Co(II)		Ni(II)		Cu(II)	
	1:1	1:2	1:1	1:2	1:1	1:2
L_1	—	$1.95 \cdot 10^{10}$	$2.07 \cdot 10^5$	—	—	$1.60 \cdot 10^{12}$
L_2	$1.07 \cdot 10^6$	—	$1.50 \cdot 10^6$	—	$4.20 \cdot 10^6$	—
L_3	$2.10 \cdot 10^6$	—	$2.46 \cdot 10^6$	—	$5.30 \cdot 10^6$	—
L_4	$9.2 \cdot 10^6$	—	$1.02 \cdot 10^6$	—	$3.23 \cdot 10^6$	—
L_5	$9.00 \cdot 10^5$	—	—	$6.0 \cdot 10^{10}$	$2.10 \cdot 10^6$	—

In general, the IR spectra of the different complexes show a marked shift in the frequencies of both the phenyl-N and $C=N$ stretching bands relative to that observed in the IR spectra of the free ligands (Table 3). These observations can be explained by assuming the participation of both the arylazo group and the N-3 of the imidazole ring in complex formation. Moreover, the $N=N$-*Ar* stretching appearing in the region 1 440–1 410 cm^{-1} in the IR spectra of the free ligands, is shifted towards

Table 3. *Some infrared frequencies (in cm^{-1}) of the azo imidazoles and their metal complexes*

Ligand	Complex			Assignment (stretching)
	Co(II)	Ni(II)	Cu(II)	
Complexes of L_1				
1 228	1 210 sh	1 220	1 180	N-phenyl
1 438	1 435	1 438	1 438	N=N-Ar
1 595	1 596	1 595	1 592	C=N
3 420 b, w				N—H
	3 220 b	3 360	3 420 b	
				O—H
Complexes of L_2				
1 240	1 250	1 255	1 255	N-phenyl
1 435	1 440	1 450	1 450	N=N-Ar
1 594	1 592	1 592	1 592	C=N
3 350 b, w		3 150 w		N—H
	3 400 b		3 400 b	
—		3 400 b		O—H
Complexes of L_3				
1 243	1 240	1 248	1 242	N-phenyl
1 440	1 438	1 440	1 438	N=N-Ar
1 596	1 586	1 598	1 584	C=N
3 300 b, w				N—H
—	3 400 b	3 400 b	3 300 b	O—H
Complexes of L_4				
1 220	1 215	1 215	1 215	N-phenyl
1 430	1 442	1 445	1 445	N=N-Ar
1 600	1 585	1 596	1 582	C=N
3 400 b		3 150 w		N—H
	3 300 b		3 300 b	
—		3 400 w		O—H
Complexes of L_5				
1 220	1 220	1 220	1 218	N-phenyl
1 438	1 435	1 438	1 440	N=N-Ar
1 595	1 592	1 593	1 594	C=N
3 400 b, w			3 400 w	N—H
—	3 300 b	3 360 b	—	O—H

higher frequencies on complexation. This can be considered as a further evidence for the participation of the azo group in complex formation. The observed shift in the position of the N=N-*Ar* stretching band towards higher frequencies on complexation can be ascribed to the formation of π-orbitals in the chelated ring involving the d-orbitals of the metal ion which

Table 4. *Electronic spectral bands of the different complexes of ligands L_1–L_5*

Complex	λ_{max} ($\varepsilon_{max} \cdot 10^{-3}$)	Assignment
Co-L_1 (1 : 1)	420 (2.30) 466 (2.27)	$L \to M$ CT $L \to M$ CT
Ni-L_1 (1 : 1)	425 (2.31) 452 (2.05)	$L \to M$ CT $L \to M$ CT
Cu-L_1 (1 : 2)	405 (1.17) 454 (1.12) 500 sh (0.93)	$L \to M$ CT $L \to M$ CT $^2E_{2g} \to {}^2T_{2g}$
Co-L_2 (1 : 1)	415 (3.20) 465 (1.21)	$L \to M$ CT $L \to M$ CT
Ni-L_2 (1 : 1)	416 (3.12) 474 (1.30)	$L \to M$ CT $L \to M$ CT
Cu-L_2 (1 : 1)	420 (1.60) 476 (1.81)	$L \to M$ CT $L \to M$ CT
Co-L_3 (1 : 1)	445 (0.70) 465 (0.68) 545 (0.39)	$L \to M$ CT $L \to M$ CT $^4T_{1g}(F) \to {}^4T_{1g}(P)$
Ni-L_3 (1 : 1)	430 sh (1.73) 475 (2.24) 540 (2.00)	$L \to M$ CT $L \to M$ CT $L \to M$ CT
Cu-L_3 (1 : 1)	525 (2.10) 550 sh (0.70)	$L \to M$ CT $L \to M$ CT
Co-L_4 (1 : 1)	486 (1.64)	$L \to M$ CT
Co-L_4 (1 : 2)	486 (2.78)	$L \to M$ CT
Ni-L_4 (1 : 1)	492 (2.47)	$L \to M$ CT
Cu-L_4 (1 : 1)	518 (1.11) 558 (0.82)	$L \to M$ CT $L \to M$ CT
Co-L_5 (1 : 1)	438 (1.33) 575 (0.19)	$L \to M$ CT $^4T_{1g}(F) \to {}^4T_{1g}(P)$
Co-L_5 (1 : 2)	438 (2.00) 570 (0.38)	$L \to M$ CT $^4T_{1g}(F) \to {}^4T_{1g}(P)$
Ni-L_5 (1 : 1)	452 (3.78) 580 (0.29)	$L \to M$ CT $^3A_2(F) \to {}^3T_1(F)$
Ni-L_5 (1 : 2)	446 (1.17) 580 (0.76)	$L \to M$ CT $^3A_2(F) \to {}^3T_1(F)$
Cu-L_5 (1 : 1)	504 (2.38)	$L \to M$ CT
Cu-L_5 (1 : 2)	510 (1.05)	$L \to M$ CT

reflects itself in a high mesomeric interaction in this ring[17]. This observation is confirmed by studying the electronic spectra of the different synthesized complexes where the intensity of the d-d transition is enhanced due to such an intraction (see below).

The weak broad band found at 3420–3300 cm^{-1} in the IR spectra of the free ligands can be assigned to the N—H stretching vibration. The shape of this band as well as its tapering off in the direction of lower frequencies can be attributed to the association of azoimidazole molecules through an intermolecular hydrogen bonding[18]. Except in case of the IR spectra of the 1 : 2 Cu(II) complexes of L_2 and L_5, the N—H stretching band is obscured by the strong band due to the stretching of the OH group of the water molecules existing in the complexes. The presence of water molecules in the complexes prepared is confirmed by the results of chemical analysis of these complexes (Table 1).

Electronic Spectra of the Complexes

The (visible) electronic spectra of the complexes in methanol were recorded (Figs. 4 and 5). The λ_{max} and ε_{max} values of the absorption bands observed are listed in Table 2. Generally, the spectra of all the complexes are characterized by one or more broad bands in the region 405–540 nm (the molar extinction coefficients are 680–3780 $mol^{-1} cm^{2}$). These bands can be ascribed to an intermolecular CT transition from the ligand molecule to the vacant orbital localized on the metal ion ($L \rightarrow M$ CT).

The $L \rightarrow M$ CT character of such bands can be substantiated by considering the following two facts.

(i) For different metal complexes of the same ligand the $L \rightarrow M$ CT band acquires a red shift in its λ_{max} on changing the coordinated metal ion from Co(II) → Ni(II) → Cu(II) (Fig. 4). This behaviour is in accordance with the fact that the third ionisation potentials of these metal ions increase in the same direction[19], therefore the electron accepting character of the metal ions is expected to increase in the same order i.e. easier $L \rightarrow M$ CT transition.

(ii) In general, for the same metal complex with different ligands studied, the $L \rightarrow M$ CT band becomes well shaped and characterized by low excitation energy in case of L_4 and L_5 (R = 4-NO_2 and 2-NO_2, respectively) relative to L_1–L_3 (R = 4-CH_3, 4-OCH_3 and 2-OCH_3, respectively) (Fig. 5). This agrees with the expected high delocalization energy of electrons in case of the former ligands relative to the latter ones[11]. Thus, one should expect an easier electron transfer from L_4 and L_5 molecules to the coordinated metal ion compared to the other ligands.

The long wavelength visible band observed in the spectra of

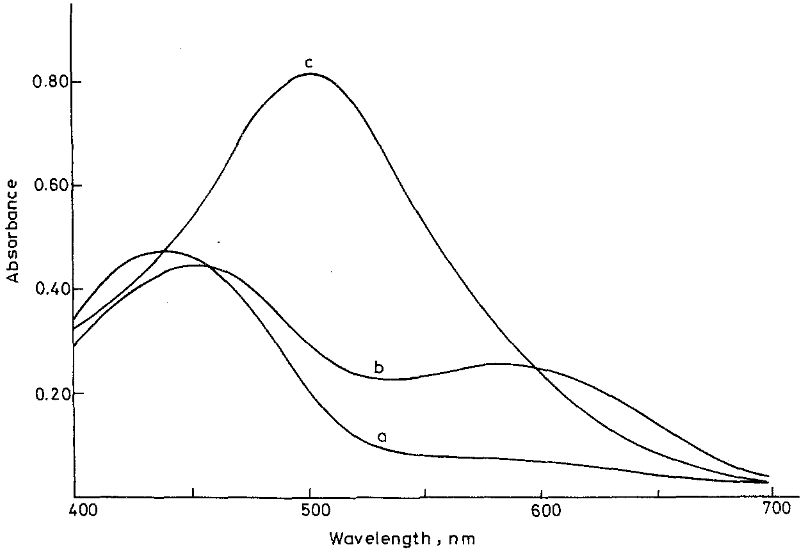


Fig. 4. Electronic spectra of methanolic solutions of L_5 complexes with M(II) ions. *a* Co(II) (1 : 1), *b* Ni(II) (1 : 1), *c* Cu(II) (1 : 2)

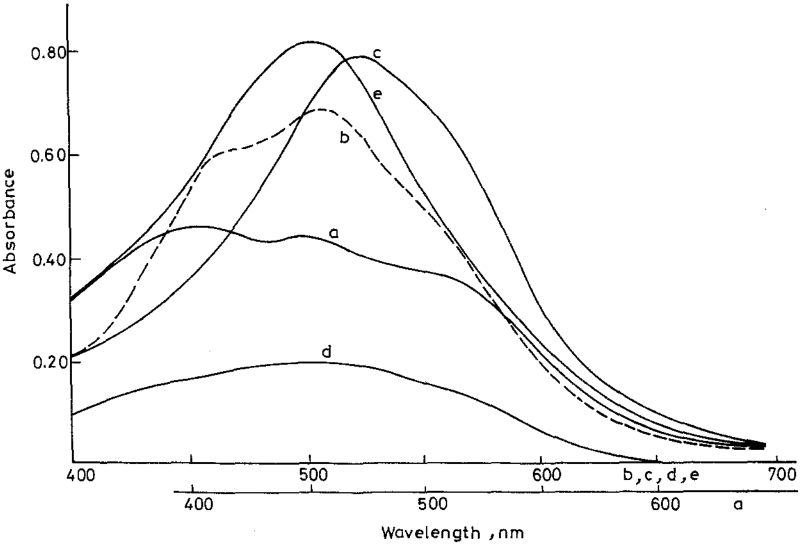


Fig. 5. Electronic spectra of a methanolic solution of (1 : 1) Cu(II) complexes. *a* L_1 (1 : 2), *b* L_2, *c* L_3, *d* L_4, *e* L_5

Cu(II)$-L_1$(1 : 2), Co(II)$-L_3$(1 : 1), Co(II)$-L_5$(II), Co(II)$-L_5$(1 : 2), Ni(II)$-L_5$(1 : 1), and Ni(II)$-L_5$(1 : 2) can be attributed to a d-d electronic transition. The unexpected relatively high molar extinction coefficient of this band (190–1 290 g mol^{-1} cm^2) suggests a distorted octahedral geometry of such complexes[20]. Furthermore, since the visible electronic spectra of the studied complexes are characterized by $L \rightarrow M$CT bands one may suggest that in such complexes there is a possibility for the metal d-orbitals to overlap and mix with the various ligand atomic orbitals. Accordingly, the d-orbitals wave functions are no longer being pure d-orbitals. Thus the intensity of the d-d band is expected to be enhanced to a significant degree[19].

Based on the suggested distorted octahedral geometry of the studied complexes the d-d band observed in the electronic spectra of Co(II), Ni(II) and Cu(II) complexes can be assigned to the transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, ${}^3A_2(F) \rightarrow {}^3T_2(F)$, and ${}^2E_{2g} \rightarrow {}^2T_{2g}$, respectively.

It should be noted that the d-d transition bands in the electronic spectra of some of the complexes are completely obscured by the broad and intense $L \rightarrow M$CT bands of such complexes[21].

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