Complexes of Iron(II), Cobalt(II), Nickel(II), Palladium(II), and Copper(II) with 4-(3,5-Diphenyl-2-pyrazolin-1-yl)benzenesulfonic Acid

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Complexes of Fe(II), Co(II), Ni(II), Pd(II), and Cu(II) with 4-(3,5-diphenyl-2-pyrazolin-1-yl)-benzenesulfonic acid have been prepared and characterized by conductivity and magnetic moments measurements, solubility, thermal analysis, IR, electronic, and EPR spectra. The data show that the ligand coordinates with metal ions Fe(II), Co(II), Ni(II), and Pd(II) in the bidentate form, with the Cu(II) ion in the unidentate form and the structure was proposed. The complexes are nonelectrolytes in dimethylformamide and methanol.

A series of studies on 2-pyrazoline compounds have been carried out for the purpose of using them as optical brighteners [1, 2], scintillators [3, 4], and photoconductive materials [5]. In view of this, NaDPBS · $2H_2O$ has been prepared [6], however, complexes of HDPBS (4-(3,5-diphenyl-2-pyrazolin-1-yl)benzenesulfonic acid) have not been reported so far. As a part of our systematic investigation on the coordination chemistry of 2-pyrazoline ligands, the present study describes the synthesis and characterization of Fe(II), Co(II), Ni(II), Pd(II), and Cu(II) complexes with HDPBS.

EXPERIMENTAL

HDPBS was prepared according to the literature method [6]. The metal salts of anal. grade were used.

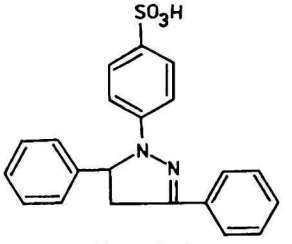
The IR spectra of the prepared complexes (KBr pellets) were recorded using a NIC-5DX spectrophotometer, electronic spectra (solid state) in the region of $\tilde{\nu}$ = 11 200—29 400 cm^{-1} with a DJ-240 spectrophotometer, EPR spectra on an X-band E-112 spectrometer (Varian) (powder state, at room temperature and 77 K using DPPH (g = 2.0036) as the standard). Molar conductivities were examined with a DDS-IIA conductometer using dimethylformamide and methanol as solvents separately at 25 °C. Magnetic moments were measured with a Guoy balance using $Hg[Co(SCN)_4]$ as the calibrant and diamagnetic corrections were applied [7]. TG and DTA measurements were made in a nitrogen atmosphere at 20—800 °C using a TG—DTA meter (Thermoflex, Japan). Elemental analysis was carried out by elemental analyzer 1106 (Erba).

Metal(II) Complexes

A hot solution of HDPBS (2 mmol) in water (30 cm^3) was added dropwise with stirring to a solution of metal(II) chloride or sulfate (1 mmol) in warm water (20 cm^3) and immediately a precipitate was produced. The reaction mixture was heated at 80 °C for 30 min. The solid that separated out was collected on a filter, washed several times with warm water and dried at 105 °C. The complexes were obtained as hydrates and the yields were nearly quantitative. Iron(II) complex was prepared under nitrogen atmosphere from anal. grade ferrous ammonium sulfate. Characterization of products obtained is given in Table 1.

RESULTS AND DISCUSSION

Complexes of HDPBS (Formula 1) with transition element are insoluble in nonpolar solvents such as pentane and acetonitrile. These complexes are air-



Formula 1

stable and their elemental analyses conform to the formula $M(DPBS)_2 \cdot (2—4)H_2O$. The measurements of molar conductivity, magnetic moments, TG and DTA, IR, EPR, and electronic spectra suggest the structure shown in Fig. 1.

Table 1. Characterization of the Prepared Complexes $M(DPBS)_2 \cdot nH_2O$

Complex	Formula	Colour	M_r	w_i(found)/% w_i(calc.)/%				Decomposition temperature
				M	C	H	N	°C
I	$Fe(DPBS)_2 \cdot 2H_2O$	dark-red	846.72	6.59	59.58	4.50	6.64	232
				6.60	59.57	4.52	6.62	
II	$Co(DPBS)_2 \cdot 2H_2O$	brown-red	849.80	6.93	59.34	4.50	6.61	224
				6.94	59.36	4.51	6.60	
III	$Ni(DPBS)_2 \cdot 2H_2O$	green	849.59	6.91	59.35	4.49	6.68	216
				6.91	59.37	4.51	6.60	
IV	$Pd(DPBS)_2 \cdot 2H_2O$	yellow	890.45	11.9	56.16	4.24	6.22	203
				11.9	56.22	4.27	6.24	
V	$Cu(DPBS)_2 \cdot 4H_2O$	light-green	897.29	7.14	56.59	4.72	6.29	289
				7.14	56.65	4.75	6.22	

The IR wavenumbers along with their relative assignments are given in Table 2. The data of the IR spectra of the complexes show some changes as compared with those of the ligand. The bands due to ν(C=N) and ν(N—N) remain almost unshifted indicating that nitrogen atom has not coordinated to the metal ion [8—14]. The vibrations $\nu_{as}(SO_3)$ and $\nu_s(SO_3)$ observed at $\tilde{\nu}$ = 1178 and 1036 cm^{-1}, respectively in $NaDPBS \cdot 2H_2O$ are shifted to $\tilde{\nu}$ = 1194—1216 and 1032 cm^{-1} in case of the complexes Fe(II), Co(II), Ni(II), and Pd(II). The wavenumbers difference $\Delta\tilde{\nu}$ of 162—184 cm^{-1} indicates that HDPBS is a bidentate ligand in these complexes but a unidentate one in the Cu(II) complex [15]. All these complexes manifest vibrations ν(OH) around $\tilde{\nu}$ = 3300 cm^{-1}

The FIR spectra of complexes Fe(II), Co(II), Ni(II), and Pd(II) indicate the presence of the M—O band (Eu) of the ligand at $\tilde{\nu}$ = 280—290 cm^{-1}. The bands around $\tilde{\nu}$ = 600, 460, and 390 cm^{-1} can be assigned to the wagging, rocking, and stretching vibration (A_2u) of coordinated water M—OH_2 [16, 17]. In the FIR region of the Cu(II) complex, two new bands which are observed at $\tilde{\nu} \approx 279$ and 398 cm^{-1} may be attributed to ν(Cu—O)(A_2u) and ν(Cu—OH_2)(Eu), respectively.

The effective magnetic moments μ_{eff} measured at room temperature and the details of the

Table 2. IR Spectral Data ($\tilde{\nu}/cm^{-1}$) of $NaDPBS \cdot 2H_2O$ and the Complexes

Compound	$\nu_{as}(SO_3)$	$\nu_s(SO_3)$	$\Delta\nu(SO_3)$	ν(C=N)	ν(M—O)	ν(M—OH_2)	ν(OH)
$NaDPBS \cdot 2H_2O$	1178	1036	142	1128			3472
I	1194	1032	162	1125	290	416	3332
II	1208	1032	176	1124	286	410	3333
III	1215	1032	183	1124	284	408	3335
IV	1216	1032	184	1124	280	402	3342
V	1143	1034	109	1124	279	398	3347

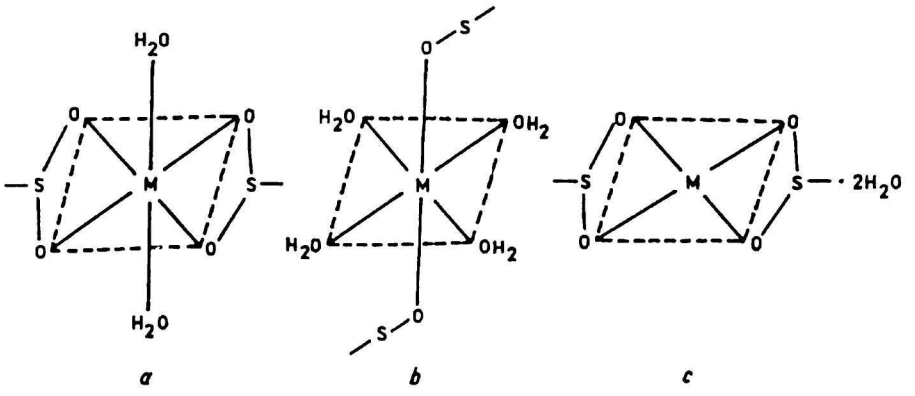


Fig. 1. Proposed structure for the complexes *a* (M = Fe(II), Co(II), and Ni(II)), *b* (M = Cu(II)), *c* (M = Pd(II)).

Table 3. Magnetic Moments and Electronic Spectral Data for the Complexes in the Solid State

Complex	μ_{eff}/μ_B[a]	$\tilde{\nu}$/cm^{-1}	Possible assignments	10*Dq* / cm^{-1}
I	5.03	19 608	CT	3226
		13 330	$^5T_{2g}\rightarrow{}^5E_g$	
II	4.30	24 690	CT	8130
		20 530, 18 890	$^4T_{1g}\rightarrow{}^4E_{1g}$(P), $^4A_{2g}$	
III	3.06	22 580, 22 990	$^3B_{1g}\rightarrow{}^3A_{2g}$(P), ^3E_g(P)	9680
		18 660	$^3B_{1g}\rightarrow{}^3E_g$(F)	
		16 970	$^3B_{1g}\rightarrow{}^3A_{2g}$	
		13 250	$^3B_{1g}\rightarrow{}^3A_{2g}$	
IV	dia-	19 240	$^1A_{1g}\rightarrow{}^3A_{2g}$	
	magnetic	23 360	$^1A_{1g}\rightarrow{}^1A_{2g}$	
		28 980 sh	$^1A_{1g}\rightarrow{}^1E_{1g}$	
V	1.82	26 180	LMCT	9810
		14 390	*d*—*d*	

a) Per metal ion. CT — charge transfer, LMCT — ligand-to-metal charge transfer.

electronic spectra of the complexes in solid state are given in Table 3. The iron(II) complex, $Fe(DPBS)_2\ 2H_2O$, exhibits two main bands, the first at $\tilde{\nu}$ = 13 850 cm^{-1} which is due to the spin-allowed transition $^5T_{2g}\rightarrow{}^5E_g$ suggesting an octahedral structure [18]. The second band at $\tilde{\nu}$ = 19 610 cm^{-1} may be due to a charge transfer [19]. The μ_{eff} value (5.4 μ_B) is in the range of the spin the only value reported for d^6 system (5.1—5.4 μ_B) in an octahedral structure. The high-spin character of the iron(II) complex suggests that the ligand field effect exerted by DPBS ion is weak. The characteristic transitions and magnetic moment value (4.3 μ_B) indicate a high-spin octahedral configuration for the cobalt(II) complex [20, 21]. The μ_{eff} value of the nickel(II) complex shows a small orbital contribution, in accord with the octahedral structure [19, 20]. The *d*—*d* transition spectra of the solid nickel(II) complex contain bands of higher wavenumbers. From the presence of splitting in the 14 400—20 400 cm^{-1} spectral region it is concluded that tetragonal distortion arising from the nature of ligand and water is significant [22]. The magnetic moment (1.82 μ_B) for the copper(II) complex falls in the range reported for an octahedral structure. The presence of the characteristic bands further supports the distorted octahedral configuration [19, 23]. Square-planar structure is assigned to the diamagnetic complex, $Pd(DPBS)_2 \cdot 2H_2O$, on the basis of its electronic spectra [24].

Dissolving the complexes in methanol and dimethylformamide afforded 10^{-3} M solutions, separately. The molar conductivities (Table 4) of these solutions approach those reported for nonelectrolytes [25]. It is fairly evident that there

Table 4. Molar Conductivities of the Complexes at 25 °C

Complex	Methanol		Dimethylformamide	
	$c \cdot 10^3$ / mol dm^{-3}	λ / S cm^2 mol^{-1}	$c \cdot 10^3$ / mol dm^{-3}	λ / S cm^2 mol^{-1}
I	1.04	35.9	1.28	12.5
II	1.12	42.7	1.07	11.9
III	1.11	50.2	1.01	12.8
IV	1.08	46.3	1.05	13.2
V	0.98	38.6	1.14	12.1

Table 5. EPR Spectral Data for the Complexes Prepared

Complex	*T*/K	$g_\parallel$ or g_1	g_2	$g_\perp$ or g_3	g_{av}[a]
I	295	2.020		1.936	1.964
	77	2.018		1.934	1.962
II	295	2.088		4.764	3.875
	77	2.090	3.725	5.860	3.982
III	295	2.041		2.236	2.171
	77	2.039		2.238	2.172
IV	295	2.101		1.965	1.995
	77	2.011		1.965	1.995
V	295	2.228		2.045	2.106
	77	2.226		2.049	2.108

a) $g_{av} = 1/3(g_\parallel + 2g_\perp)$.

are two ligands which participate in coordination.

To get further insight into the nature of bonding, EPR spectra of the complexes prepared in the powder form were recorded at room and liquid N_2 temperature (Table 5). The copper(II) complex exhibits an axial spectrum with four copper hyperfine lines (I = 3/2). The ordering of g values $g_\parallel > g_\perp > g_e$ in the copper(II) complex indicates that the unpaired electron remains in the $d_{x^2-y^2}$ ground state and that the complex is tetragonally distorted. A considerable difference between $g_\parallel$ and $g_\perp$ values suggests a marked Jahn—Teller distortion of the octahedral structure [26—28].

The g values observed for the complexes of Fe(II), Co(II), and Ni(II) correspond to the reported ranges for the corresponding distorted octahedral structure and those for the Pd(II) complex are in agreement with its square-planar structure [29—33]. Since in the spectrum of the complexes any further hyperfine lines arising from ^{14}N (I = 3/2) have not been observed, it can be assumed that the nitrogen atom is not coordinated to the metal ions.

The thermogravimetrical studies not only confirmed that the water molecules in the complexes of Fe(II), Co(II), Ni(II), and Cu(II) participate in coordination, and the complex of Pd(II) is in the crystal form, but also revealed that these complexes are more thermostable than the ligand, HDPBS (decomposition temperature 195 °C), and the thermal

stability decreases in the series Cu, Fe, Co, Ni, and Pd. The unusual properties may be due to the differential coordination chromosphere [34].

The authors are quite confident from the above discussion that the nitrogen of the pyrazoline ring under investigation does not participate in coordination in any of the complexes prepared. However, it is interesting that the ligand coordinates with Fe(II), Co(II), Ni(II), and Pd(II) in the bidentate form but with the Cu(II) ion in the unidentate form.

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