Asian Journal of Chemistry Vol. 6, No. 2 (1994), 393–404

Preparation and Characterization of Iron(II, III), Cobalt(II, III) and Nickel(II)-Complexes of 2,2-Dipyridyl

RAMADAN M. AWADALLAH
Chemistry Department, Faculty of Science
Aswan, Egypt

The Fe^{2+}, Fe^{3+}, Co^{2+}, Co^{3+} and Ni^{2+} dipyridyl complexes have been synthesised. The isolated complexes are soluble in H_2O, EtOH, MeOH, DMF and DMSO. The solid complexes are paramagnetic and have magnetic moment values near to the ground state values of the free ions. The magnetic measurements in connection with the electronic spectra were used to elucidate the different electronic geometrical structures of elements and hence the configuration of the coordination polyhedra around the central metal ions of the investigated complexes. The ligand behaves as a bidentate chelating agent in all the complexes and complexation takes place through two coordinate bonds between the two nitrogen atoms of the two pyridine rings and the central metal ion.

INTRODUCTION

On the basis of quantum mechanics, the μ_{eff} values in BM associated with the quantum, J, of a single electron is given by $g[J + 1]^{1/2}$, where the magnetogyric, g, (the g factor) is given by $g = [S(S + 1) - L(L + 1) + 3J(J + 1)]/2J(J + 1)$. It should be noted that magnetic behaviour depending on J values is qualitatively different from that depending on S values, *i.e.*, the spin only behaviour which gives a fair approximation for many of the d-block elements[1, 2] which is the subject of this paper. The d-d transition is thought to be a perturbation of the situation obtained after consideration of J and the effect of the ligand field, *i.e.*, the 3d electrons of the transition metal ions are more or less protected from the influence of the lattice by polarisation of $3s^2$ and $3p^6$ closed shells. However, the symmetry properties of the crystal field at the ion site will allow, forbid or quench transitions. 2,2ˉ-dipyridyl falls into the class of aromatic heterocyclic ring compounds and the unique structural feature involving pyridine nitrogen makes it an interesting ligand. Though the pyridine nitrogen of the ligand is normally considered to be the coordination site. The solid complexes of Fe^{2+}-, Fe^{3+}-, Co^{2+}-, Co^{3+}-, and Ni^{2+}- violurates[3], dinitrosoresorcinolates[4], murexide[5], eriochrome black-T[6], 2-thenoyl–2,6,6-trifluoroacetonates[7], dibenzoyl methanates[8] and Ni^{2+}- dipy complexes[9] were prepared and characterised by chemical and physical methods. V^{5+}-Nb^{5+}- and Ta^{5+}, Ce^{4+}-, Pr^{3+}- and Gd^{3+}-dipy complexes were also studied[10–12]. In the present investigation a trial was suggested to conclude different transitions of Fe^{2+}-, Fe^{3+}-, Co^{2+}-, Co^{3+}- and Ni^{2+}-2,2′-dipyridyl complexes, corresponding to maximum wavelength or shoulders in nm or wavenumber in cm^{-1}.

EXPERIMENTAL

The metal salts, ligand and organic solvents were of AnalaR grade (99.9%) and purchased from BDH, E. Merck, Aldrich and Riedel de Haën.

Synthesis of Complexes

The Fe^{2+}-, Fe^{3+}-, Co^{2+}-, Co^{3+}- and Ni^{2+}-2,2′-dipyridyl complexes were isolated in solid by the following method. An aqueous solution containing the respective metal salts [$(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $Na_3[Co(NO_2)_6$, $(NH_4)_2SO_4 \cdot NiSO_4 \cdot 6H_2O]$ and an alcoholic solution of the ligand were mixed well and placed on a water-bath (except Fe^{2+}-2, 2′-dipyridyl complexes). A small amount of absolute ethanol was added to dissolve any unreacted amount of ligand. A clear solution was thus obtained to which an amount of acetone was added, whereby the solid complexes started to separate. Butanol was added and the reaction mixtures of Fe^{3+}-dipy were stirred for 3 h. The isolated solid complexes were filtered off, washed several times with *n*-BuOH and then dried. Fe^{2+}-dipy mixtures were evaporated to near dryness by the aid of an electrical fan, then *n*-BuOH was added whereby the solid complexes were isolated. Ni^{2+}-dipy complexes were separated from ethyl alcohol and washed with an ethanol-water mixture.

RESULTS AND DISCUSSION

The results obtained are reported in Tables 1–4. The chelates are crystalline, coloured [Fe^{2+}-dipy (1 : 1, 1 : 2), red; Fe^{3+}- and Co^{3+}- (1 : 1, 1 : 2, 1 : 3), brown, Co^{2+} and Ni^{2+} (1 : 1, 1 : 2), blue] and soluble in H_2O, MeOH, EtOH and DMF. The results show that the complexes have high and sharp melting points. Melting points of the complexes are in the order 1 : 1 > 1 : 2 > 1 : 3. This is because the 1 : 2 complex contains higher concentration of 2,2ˉ-dipyridyl than the 1 : 1 species, whereas the 1 : 3 complex contains a much higher concentration of dipy than the 1 : 1 or 1 : 2 species. On the other hand, the 1 : 1 complex has two coordinate bonds, while in the 1 : 2 and 1 : 3 complexes, four and six coordinate bonds link between the central metal ion and the nitrogen atoms of the pyridine rings of the dipyridyl molecules.

Therefore, the structure of the bulky complexes plays an important role in melting behaviour. So, the complexes suffer from steric effect of ligand molecules. In addition to these, the number of ligand molecules has a profound effect on the molecular packing of the complexes. The decrease of the melting point may be due to the increase of energy separation and the decrease of

TABLE 1

ELEMENTAL ANALYSIS AND PHYSICAL CONSTANTS OF Fe^{2+}-, Fe^{3+}-, Co^{2+}-, Co^{3+}- and Ni^{2+}- Dipy Complexes.

Compound	M.pt., (°C)	Δm $\Omega^{-1}\,mol^{-1}\,cm^2$	Analysis % Found/(Calcd)						Mol. wt
			C	H	N	Cl	S	M	
$FeSO_4\cdot(H_2O)_4][dipy(H_2O)_2]$	310	37.0	28.40 (28.86)	5.27 (4.85)	6.92 (6.73)	—	7.45 (7.69)	13.95 (13.42)	416.13
$Fe(dipy)_2(H_2O)_4][SO_4\cdot(H_2O)_2]$	265	87.0	41.38 (41.97)	5.20 (4.93)	9.90 (9.97)	—	5.48 (5.59)	9.44 (9.76)	572.31
$Fe\cdot dipy\cdot Cl_2\cdot(H_2O)_2]Cl$	275	76.0	33.70 (33.88)	3.10 (3.40)	8.13 (7.09)	30.45 (30.01)	—	16.05 (15.75)	354.45
$Fe(dipy)_2\cdot Cl_2][Cl\cdot 4H_2O]$	248	84.5	43.19 (43.94)	3.96 (4.39)	9.89 (10.24)	19.55 (19.46)	—	10.74 (10.27)	546.65
$[FeCl_3\cdot(H_2O)_3][(dipy)_3\cdot(H_2O)_3]$	237	43.5	48.47 (48.76)	4.38 (4.91)	11.72 (11.37)	14.50 (14.40)	—	7.72 (7.56)	738.87
$[Co\ dipy\cdot Cl\cdot(H_2O)_3]Cl$	328	63.0	34.52 (35.31)	3.63 (4.10)	8.14 (8.24)	20.73 (20.85)	—	17.37 (17.33)	340.08
$[Co(dipy)_2\cdot Cl\cdot H_2O]Cl$	312	71.0	47.95 (48.40)	4.64 (4.47)	11.10 (11.29)	14.30 (14.26)	—	11.72 (11.87)	496.26
$[Co\ dipy\cdot(NO_2)_2(H_2O)_2]NO_2$	332	64.5	31.05 (30.87)	3.07 (3.10)	17.85 (18.00)	—	—	15.26 (15.14)	389.14
$[Co(dipy)_2(NO_2)_2][NO_2\cdot 2H_2O]$	322	89.5	43.35 (44.05)	3.63 (3.70)	17.62 (17.98)	—	—	11.02 (10.81)	545.32
$[Co(NO_2)_3][(dipy)_3(H_2O)_3]$	315	32.0	48.95 (48.86)	4.64 (4.37)	16.80 (17.09)	—	—	8.86 (8.99)	737.53
$[NiSO_4\cdot(H_2O)_4][dipy\cdot(H_2O)_2]$	372	19.0	29.22 (28.66)	4.38 (4.77)	6.59 (6.68)	—	7.50 (7.65)	14.15 (14.01)	419.05
$[Ni(dipy)_2(H_2O)_2][SO_4\cdot(H_2O)_4]$	363	61.0	41.52 (41.76)	4.56 (4.90)	9.62 (9.74)	—	5.61 (5.56)	10.25 (10.21)	479.17
$[Ni(dipy)_3][SO_4(H_2O)_8]$	358	72.0	46.87 (46.95)	3.30 (3.22)	10.78 (10.96)	—	4.22 (4.17)	7.82 (7.66)	766.7

TABLE 2

ELECTRONIC SPECTRAL AND MAGNETIC MOMENT DATA OF Fe^{2+}–, Fe^{3+}–, Co^{2+}–, Co^{3+}– AND Ni^{2+}–2,2′-DIPYRIDYL COMPLEXES

Complex	λ_{max}/nm		ν, cm^{-1}		ε × 10^2 as 1 × 10^{-3} M in DMF	Possible transitions	μ_{eff} B.M.
	N.M.	DMP	N.M.	DMP			
$[FeSO_4(H_2O)_4][dipy(H_2O)_2]$	290, 530	290, 530	34483, 18868	34483, 18868	142,62.5	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	5.30
$[Fe(dipy)_2(H_2O)_4][SO_4(H_2O)_2]$	360, 530	365, 540	27777, 18868	27397, 18518	70,24	$^2T_{2g}(F) \rightarrow {}^6A_{1g}$	5.0
$[Fe{\cdot}dipy{\cdot}Cl_2(H_2O)_2]{\cdot}Cl$	340, 385	335, 385	29411, 25974	29850, 25411	60,20	$^2T_{2g} \rightarrow {}^6A_{1g}$	5.40
$[Fe(dipy)_2{\cdot}Cl_2][Cl{\cdot}4H_2O]$	360, 530	370, 540	27777, 18868	27027, 18518	48,13	$^2T_{2g} \rightarrow {}^6A_{1g}$	5.70
$[FeCl_3(H_2O)_3][(dipy)_3(H_2O)_3]$	365, 545	360, 550	27397, 18348	27777, 18181	42,14	$^2T_{2g} \rightarrow {}^6A_{1g}$	5.03
$[Co(dipy){\cdot}Cl(H_2O)_3]Cl$	530, 630	350, 675	18868, 15873	28571, 14814	56,12	$d_{xy} \rightarrow d_{x^2-y^2}$ $^2Eg(G) \rightarrow {}^2T_{1g}(G)$	2.62
$[Co(dipy)_2{\cdot}Cl{\cdot}H_2O]Cl$	490, 642	350, 675	20408, 15576	28571, 14814	96, 8	$^2E_g(G) \rightarrow {}^2T_{1g}$	4.97
$[Co{\cdot}dipy{\cdot}(NO_2)_2(H_2O)_2]NO_2$	380, 500	315, 355	26315, 20000	31746, 28169	78,183	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	4.95
$[Co(dipy)_2(NO_2)_2NO_2{\cdot}2H_2O]$	365, 470	315, 355	27397, 21276	31746, 28169	68,153	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	4.34
$[Co(NO_2)_3][(dipy)_3(H_2O)_3]$	365, 470	315, 355	27397, 21276	31746, 28169	96,159	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	4.27
$[NiSO_4{\cdot}(H_2O)_4][dipy(H_2O)_2]$	305, 595	310, 600	32786, 16806	32258, 16667	89,11	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	3.30
$[Ni(dipy)_2(H_2O)_2][SO_4{\cdot}(H_2O)_4]$	300, 560	310, 570	33333, 17857	32258, 17543	105,13	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	3.50
$[Ni(dipy)_3][SO_4{\cdot}(H_2O)_8]$	310, 570	320, 575	32258, 17543	31250, 17391	116,15	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	3.70

binding energy force strength which results in the release of the binding energy linking between the metal and the ligand molecules. This leads to a decrease in the fusion temperature of the complexes. The elemental analysis data are consistent with the suggested chemical formulae of the complexes. Molar conductance values (Table 1) of the complexes in DMF are in an excellent accordance with the reference values[13], and show that (1 : 1) Fe^{2+}-, (1 : 3) Fe^{3+}-, (1 : 3)Co^{3+}- and (1 : 1) Ni^{2+}-dipy complexes are nonelectrolytes, while the other complexes are 1 : 1 electrolytes.

The UV spectra of the complexes in DMF exhibit two intense absorption maxima and can be assigned to pyridyl n–π and π–π* transitions[10, 14]. The absorption spectra of the complexes appear two or three bands (maxima) in the visible region and can be assigned as charge transfer (C.T.) and d–d transition bands. The magnetic moment values of the 1 : 1 and 1 : 2 Fe^{2}-dipy complexes lie in the range 5.0–5.3 B.M. which is characteristic of high spin octahedral complexes. The electronic spectra of (1 : 1) Fe^{2+}-dipy complex show two absorption bands at 18868 and 34483 cm^{-1} in nujol mull and in DMF ($v_1/v_2 = 1.83$, $\varepsilon = 1.2$ and 6.25×10^3). The first band may be identified with the $^4T_{1g}(F) \rightarrow T_{1g}(p)$ transition and the second band may be due to $^2T_{2g} \rightarrow {}^6A_{1g}$ transition. The electronic absorption spectral bands are similar to those reported for octahedral complexes. The observed magnetic moment values for the Fe^{3+}-dipy complexes are in the range 5.03–5.70 B.M. and support the octahedral stereochemistry of the Fe^{3+}-dipy complexes[15, 16]. The electronic spectra of Fe^{3+}-dipy complexes show two bands at 25971 cm^{-1} in nujol mull ($v_1/v_2 = 1.13$) and 25411 and 29850 cm^{-1} in DMF ($v_1/v_2 = 1.17$, $\varepsilon = 6$ and 2×10^3) for the (1 : 1) Fe^{3+}-dipy complex. In the case of the 1 : 2 Fe^{3+}-dipy complex, two bands at 18868 and 27777 cm^{-1} in nujol mull ($v_1/v_2 = 1.47$) and at 18518 and 27027 cm^{-1} ($v_1/v_2 = 1.46$, $\varepsilon = 4.8$ and 1.3×10^3) in DMF are shown. Whereas in the case of the (1 : 3) Fe^{3+}-dipy, two bands appear at 18348 and 27397 cm^{-1} ($v_1/v_2 = 1.49$) in nujol mull pattern and at 18181 and 27777 cm^{-1} in DMF ($v_1/v_2 = 1.53$, $\varepsilon = 4.2$ and 1.4×10^3). The electronic spectra values suggest octahedral geometrical structural configuration, and the bands may be assigned to $^2T_{2g} \rightarrow {}^6A_{1g}$ transition.[15]

Magnetic susceptibility measurements of the Co^{2+}–dipy compoexes suggest low (due to quenching by surrounding ligand molecules) and high spin octahedral geometry for the 1 : 1 and 1 : 2 complexes, respectively.[15] The electronic spectrograms show two bands at 15873 and 18868 cm^{-1} in nujol mull ($v_1/v_2 = 1.19$) and 14814 and 28571 cm^{-1} in DMF ($v_1/v_2 = 1.93$, $\varepsilon = 5.6$ and 1.2×10^3) for the (1 : 1) complex, and at 15576 and 20408 cm^{-1} in nujol

($\nu_1/\nu_2 = 1.31$) and 14814 and 28571 ($\nu_1/\nu_2 = 1.93$, $\varepsilon = 9.6$ and 8.0×10^3) cm^{-1} in DMF. The bands may be assigned to

$$d_{xy} \rightarrow d_{x^2-y^2},\ {}^2E_g(G) \rightarrow {}^2T_{1g}(G) \text{ and } {}^2E_g(G) \rightarrow {}^2T_{1g}$$

transition in octahedral field.

The μ_{eff} values (4.27–4.95 BM) of Co^{3+}-dipy complexes characterise high spin octahedral due to high orbital contribution. The electronic spectra of the 1 : 1 Co^{3+}-dipy complex exhibit two bands at 20000 and 26315 cm^{-1} in nujol mull ($\nu_1/\nu_2 = 1.32$) and 28169 and 31746 cm^{-1} in DMF ($\nu_1/\nu_2 = 1.14$, $\varepsilon = 7.8$ and 18.3×10^3). The electronic spectral data in nujol mull (1 : 2, $\nu_1/\nu_2 = 1.29$; 1 : 3, $\nu_1/\nu_2 = 1.29$) and in DMF (1 : 2, $\nu_1/\nu_2 = 1.13$, $\varepsilon = 6.8$ and 1.53×10^3; 1 : 3, $\nu_1/\nu_2 = 1.13$, $\varepsilon = 9.6$ and 1.59×10^3) show two bands. These complexes are 6-coordinate and, hence, the structural geometry of octahedron can be suggested. The bands can be assigend to ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(F)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and ${}^3A_{2g}(F) \rightarrow {}^1T_{1g}(P)$ transitions.

The magnetic moment values of Ni^{2+}-dipy complexes are in the region 3.3–3.7 B.M. which show the presence of two unpaired electrons. The values are typical of octahedral complexes indicating large orbital contribution. The octahedral stereochemistry of the complexes is also indicated by two electronic absorption bands at 16806 and 32786 cm^{-1} ($\nu_1/\nu_2 = 1.95$) in nujol mull and 16667 and 32258 ($\nu_1/\nu_2 = 1.94$, $\varepsilon = 8.9$ and 1.1×10^3) in DMF in the case of (1 : 1) Ni^{2+}-dipy complex, two bands at 17857 and 33333 cm^{-1} ($\nu_1/\nu_2 = 1.87$) in nujol mull and at 17543 and 32580 cm^{-1} ($\nu_1/\nu_2 = 1.84$, $\varepsilon = 10.5$ and 1.3×10^3) in DMF in the case of 1 : 2 while in the case of (1 : 3) Ni^{2+}-dipy complex, the bands appear at 17543 cm^{-1} ($\nu_1/\nu_2 = 1.27$) in nujol mull and at 17391 and 31250 cm^{-1} ($\nu_1/\nu_2 = 1.22$, $\varepsilon = 11.6$ and 1.5×10^3) in DMF. The bands can be assigned to ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions.

The Fe^{2+}-, Fe^{3+}-, Co^{2+}-, Co^{3+}- and Ni^{2+}-dipy complexes exhibit varied spectral patterns of splitting and sometimes of ligand bands. In the free dipy molecule, strong interactions between C=C and C=N vibrations give rise to two groups of doublets (1578, 1552) and (1750, 1415 cm^{-1}). These bands undergo remarkable changes due to coordination and new bands are found to appear in the complexes as 1600, 1595, 1790, 1585 and 1580 cm^{-1} confirming the coordinating nature of dipyridyl ligand[17, 18]. The infrared spectra of the complexes (4000–200 cm^{-1}) show that the bands due to $\nu(OH)H_2O$ appear at 4440, 4040, 3550, 3520, 3420, 3400, 3380, 3340, 3300, 3240, 3230, 3180, 3120 and 3100 cm^{-1}.

The bands appearing at 1620, 1605, 1600 and 1680 cm^{-1} may be assigned as $\delta(H_2O)$ while those appearing at 775, 770, 765 and 760 cm^{-1} can be assigned as $\gamma(H_2O)$ (coordination water) bands. 2,2′-Dipyridyl itself does not absorb in the region 300–200 cm^{-1} but six strong absorption bands in this region (210, 220, 225, 230, 235 and 250 cm^{-1}) in addition to strong and very strong bands (320, 330, 350, 370 and 385 cm^{-1}) are observed in the complexes.

These bands have been assigned to $\nu(M-Cl)$ and $\nu(M-N)$ bands. The stability of M–N band increases with the rise of atomic number of the metal. The presence of coordinated sulphate in the case of (1 : 1, 1 : 2) Fe^{2+}- and (1 : 1, 1 : 2, 1 : 3)

TABLE 3

X-RAY POWDER DIFFRACTION DATA OF THE Fe^{2+}-, Fe^{3+}-, Co^{2+}-, Co^{3+}-, AND Ni^{2+}-2,2′-DIPYRIDYL COMPLEXES

I		II		III		IV		V		VI		VII		VIII		IX		X		XI		XII		XIII	
d, Å	I/I0	d, Å	I/I0	d, Å	I/I0	d, Å	I/I0	d, Å	I/I0	d, Å	I/I0	d, Å	I/I0	d, Å	I/I0	d, Å	I/I0	d, Å	I/I0	d, Å	I/I0	d, Å	I/I0	d, Å	I/I0
12.92	34.96	21.92	19.50	21.25	60.65	24.51	54.22	24.21	39.78	23.82	40.20	24.31	44.21	20.95	59.95	21.24	23.75	24.51	65.63	12.91	18.40	21.53	24.83	20.67	25.56
12.00	42.82	18.82	20.25	18.95	38.75	20.34	54.48	16.74	45.22	17.10	46.75	19.42	47.37	16.91	63.55	18.78	54.25	15.40	75.63	11.79	16.40	18.86	26.02	18.45	28.32
11.42	50.80	17.58	25.65	17.20	65.82	19.42	54.22	14.38	48.50	14.35	50.60	17.21	53.16	15.37	67.15	17.25	48.95	14.86	96.23	8.57	18.20	17.99	26.53	17.84	26.72
11.21	52.92	12.42	27.96	15.72	68.95	17.89	57.25	11.59	53.31	11.21	54.50	15.59	53.16	14.73	68.11	16.78	51.28	10.44	100.00	8.48	18.60	16.40	28.91	16.50	31.75
10.62	54.25	9.90	37.85	14.72	75.25	15.97	59.64	10.55	51.77	10.56	52.72	12.71	55.79	14.01	69.54	14.38	52.76	9.72	93.75	8.10	17.8	13.11	36.22	13.20	36.50
9.75	50.62	8.75	57.30	13.65	70.82	14.42	60.84	9.72	49.86	9.75	48.95	12.48	56.84	13.62	71.94	11.10	56.57	8.31	92.50	7.84	15.7	12.91	38.69	12.85	47.95
9.10	45.84	8.10	100.00	12.80	78.82	13.85	60.76	9.09	47.68	8.98	56.75	11.02	67.63	12.74	74.34	10.70	48.25	7.92	90.63	7.50	100.00	12.48	36.22	12.50	58.87
7.50	100.00	6.75	42.76	11.89	82.20	12.11	67.17	6.99	100.00	6.99	100.00	9.48	57.89	11.89	75.30	9.75	62.78	6.92	90.63	9.73	24.0	9.93	98.98	9.95	97.87
6.87	79.25	6.40	37.25	11.56	76.78	11.82	67.77	6.85	74.39	6.87	73.72	8.63	68.42	11.54	78.42	9.10	78.75	6.60	91.25	6.38	31.2	8.75	71.43	8.82	75.56
6.78	82.75	6.15	42.75	11.38	72.80	10.85	66,27	6.81	75.20	6.78	76.75	8.26	100.00	11.41	79.14	6.99	100.00	6.08	93.75	6.11	24.2	8.09	100.00	8.10	100.00
6.61	64.32	5.40	48.75	11.10	76.25	9.74	66.57	6.64	69.48	6.61	65.50	7.78	80.26	11.07	77.70	6.90	82.79	5.46	96.25	5.47	28.6	7.28	38.27	70.30	56.85
5.88	50.65	4.90	34.20	10.6	85.90	8.61	100.00	5.87	49.59	5.82	47.90	7.37	61.32	10.57	80.58	6.82	85.90	5.38	34.38	5.42	28.2	7.12	46.82	6.57	46.75
5.60	55.75	4.78	30.90	9.35	100.00	7.82	79.82	5.58	50.68	5.52	57.86	6.97	63.16	9.35	100.00	5.90	92.75	5.15	90.63	4.85	30.4	6.68	40.14	5.98	56.26
5.15	50.85	4.67	56.10	8.72	87.90	7.55	86.72	5.15	62.67	5.00	65.70	6.30	57.89	8.69	80.34	5.72	91.25	5.07	90.63	4.80	29.2	6.46	61.56	5.47	47.53
4.72	71.25	4.42	42.50	7.69	85.75	6.98	65.06	4.72	64.03	4.83	69.62	5.45	58.42	7.67	84.65	5.25	78.72	4.90	84.38	4.68	51.6	5.82	51.36	4.98	60.62

I		II		III		IV		V		VI		VII		VIII		IX		X		XI		XII		XIII	
d, Å	I/Io	d, Å	I/Io	d, Å	I/Io	d, Å	I/Io	d, Å	I/Io	d, Å	I/Io	d, Å	I/Io	d, Å	I/Io	d, Å	I/Io	d, Å	I/Io	d, Å	I/Io	d, Å	I/Io	d, Å	I/Io
4.42	48.78	4.20	59.60	7.50	95.95	6.59	71.08	4.49	50.68	4.44	49.20	5.22	64.74	7.53	94.96	4.80	62.60	4.59	75.94	4.44	24.4	5.53	48.30	4.78	71.64
4.20	52.24	3.90	30.75	6.90	92.70	6.03	65.36	4.46	50.14	4.24	52.40	4.97	57.37	6.80	87.29	4.32	50.92	4.45	75.63	4.23	42.0	5.11	53.57	4.61	43.98
4.08	46.72	3.87	35.70	6.48	87.75	5.68	64.16	4.16	44.69	4.00	34.90	4.78	63.16	6.52	84.65	4.10	56.65	4.40	71.88	3.93	29.6	4.93	57.14	4.20	57.26
3.57	42.92	3.68	27.80	6.0	82.18	5.13	60.84	3.66	41.69	3.61	42.78	4.56	69.74	6.01	83.93	3.70	48.75	4.29	65.63	3.89	30.3	4.89	68.54	4.11	37.12
3.42	50.95	3.34	46.70	5.60	80.38	4.71	62.35	3.47	42.51	3.21	44.60	4.25	60.53	5.50	83.93	3.20	36.93	4.03	57.50	3.71	17.8	4.83	74.83	3.87	32.99
3.25	47.35	2.96	15.40	4.80	76.75	4.59	57.23	3.31	34.06	3.21	30.12	3.89	56.58	5.22	81.53	2.85	47.50	3.32	82.19	3.62	42.1	4.65	41.84	3.62	35.34
2.86	32.78	2.82	35.60	4.00	60.75	3.87	55.72	2.85	32.15	2.82	29.50	3.70	53.16	4.76	77.75	2.64	49.92	3.12	71.88	3.52	40.6	4.32	53.06	3.26	24.75
2.40	23.55	2.50	16.30	3.75	40.35	3.61	52.71	2.42	31.22	2.42	32.52	2.88	44.21	3.95	59.95	2.42	29.50	2.23	40.63	2.96	13.2	4.29	34.01	2.50	21.87
2.32	21.46	2.25	18.70	2.95	31.30	2.82	38.75	2.00	15.23	1.99	21.69	2.55	40.79	2.84	48.75	2.00	18.90	2.18	34.38	2.80	32.5	3.90	34.46	1.98	36.26
2.20	17.8	2.00		2.10	41.20							2.39	40.79	2.32	40.80			1.98	32.46	2.62	13.6	3.61	32.99	1.86	18.37
				1.99	21.25							2.09	39.47	1.98	36.67					2.33	15.7	2.32	36.39		
																				2.25	12.4	2.00	21.26		

I = Fe^{2+}-Dipy(1 : 1), II = Fe^{2+}-Dipy(1 : 2), III = Fe^{3+}-Dipy(1 : 1), IV = Fe^{3+}-Dipy(1 : 2), V = Fe^{3+}-Dipy(1 : 3), VI = Co^{2+}-Dipy(1 : 1), VII = Co^{2+}-Dipy(1 : 2); VIII = Co^{3+}-Dipy(1 : 1), IX = Co^{3+}-Dipy(1 : 2), X = Co^{3+}-Dipy(1 : 3), XI = Ni^{2+}-Dipy(1 : 1), XII = Ni^{2+}-Dipy(1 : 2), XIII = Ni-Dipy(1 : 3).

TABLE 4
INFRARED SPECTRA OF Fe^{2+}-, Fe^{3+}-, Co^{2+}-, Co^{3+}- AND Ni^{2+}-DIPY COMPLEXES

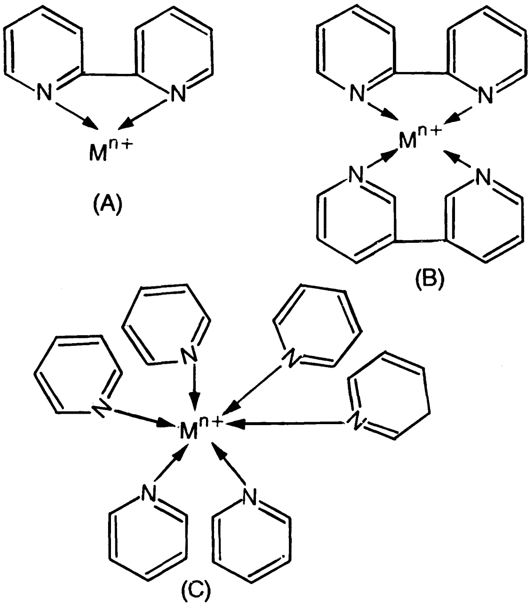
I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII
ν (cm^{-1})	ν (cm^{-1})	ν (cm^{-1})	ν (cm^{-1})	ν (cm^{-1})	ν (cm^{-1})	ν (cm^{-1})	ν (cm^{-1})	ν (cm^{-1})	ν (cm^{-1})	ν (cm^{-1})	ν (cm^{-1})	ν (cm^{-1})
230 vs	225 vw	230 vw	230 w	250 w	220 m	230 w	235 vw	250 vw	210 w	210 vw	330 vw	240 vw
250 s	250 v	320 s	250 vw	270 vw	250 m	265 vw	275 vw	360 m	230 m	230 w	260 w	255 vw
230 vs	320 m	370 vs	320 s	350 vw	350 vw	280 vw	330 w	385 vw	360 m	255 w	350 m	320 vw
370 vs	405 m	405 w	370 s	410 s	405 m	320 vw	360 m	425 vw	415 s	410 m	410 m	334 w
410 m	585 m	630 w	410 w	625 m	450 vw	360 w	410 vw	460 w	460 m	610 s	440 w	370 w
590 m	730 w	665 vw	625 w	645 s	465 vw	410 m	450 w	600 m	540 vw	640 w	610 s	420 w
630 m	770 s	325 s	645 m	730 vs	610 vw	440 w	540 w	640 m	560 vw	730 s	655 m	620 s
650 s	870 w	760 vs	730 s	760 vs	640 m	520 w	610 m	660 m	600 w	705 s	730 s	640 m
725 vs	975 w	800 w	760 vs	820 vs	660 vw	600 w	645 m	720 s	640 m	900 w	760 vs	735 s
770 vs	1140 vw	990 vw	1020 s	890 vw	710 m	630 m	710 s	765 vs	660 w	975 w	895 s	770 vs
800 vs	1180 vw	1020 m	1155 vw	1015 vs	720 s	650 vw	760 vs	810 vs	700 vw	1020 m	910 s	890 m
810 vs	1320 w	1060 w	1170 w	1045 vw	735 vw	725 s	820 vs	895 w	725 vs	1220 vw	980 m	920 m
820 vs	1395 w	1090 vw	1240 w	1055 m	760 vs	770 vs	905 vw	970 w	775 vs	1245 m	1025 s	970 m
900 vs	1430 w	1150 vw	1310 s	1155 m	800 vw	810 vw	965 w	1060 m	800 w	1310 vs	1150 w	1030 s
975 vw	1460 w	1170 m	1440 vs	1170 vw	830 w	840 w	1040 w	1120 vw	810 s	1440 vs	1220 vw	1160 w
1020 s	1590 vs	1210 w	1460 s	1240 m	890 m	900 m	1140 m	1150 vw	820 s	1460 vs	1245 vw	1230 vw

1060 w	2000 vs	1240 m	1460 m	1275 vw	910 vw	970 vw	1180 w	1165 vw	900 s	1485 m	1260 w	1320 vs
1090 vw	3100 w	1310 s	1595 vs	1310 vs	960 vw	1000 m	1215 w	1215 m	965 m	1565 w	1310 vs	1445 vs
1150 w	3400 w	1440 s	2000 vs	1440 vs	1005 s	1100 w	1320 vs	1310 vs	1010 m	1600 m	1440 vs	1480 s
1170 n		1465 s	2920 vw	1485 vs	1020 m	1150 m	1350 w	1330 vw	1030 w	2000 w	1475 s	1500 w
1210 vw		1490 m	3020 vw	1560 m	1040 m	1220 w	1420 vs	1410vs	1155 s	3100 w	1490 w	1540 vw
1240 m		1560 vw	3120 vw	1590 vs	1095 m	1240 s	1460 m	1435 s	1180 vw	3230 vw	1560 w	1580 w
1310 s		1570 vw		3080 vw	1140 s	1320 s	1480 s	1470 s	1240 vw		1570 vw	1600 s
1400 vw		1595 vs		3230 vw	1160 s	1440 s	1505 w	1495 s	1265 m		1600 s	1680 w
1440 vs		3050 vw			1210 vw	1480 m	1570 s	1565 m	1300 vs		1640 vw	3130 vw
1460 vw		3180 vw			1235 s	1570 m	1605 vs	1600 vs	1335 m		3120 vw	3380 vw
1490 s		3300 vw			1305 vs	1600 s	1620 m	1640 m	1380 w		3300 w	
1570 vw					1430 vs	1640 m	1720 w	1910 vw	1420 w			
1600 vs					1460 s	2000 w	2350 vw	2500 vw	1445 s			
3120 w					1480 m	3100 w	3020 vw	2600 vw	1470 s			
3340 vw					1550 m	3180 vw	3130 w	3060 vw	1500 vs			
4020 vw					1580 v	3300 w	3240 vw	3200 vw	1560 m			
4440 vw					1600 s		3420 vw	3550 vw	1600 s			
					3040 vw				1645 m			
					3520 w				3020 vw			
									3120 vw			
									3380 m			

Ni^{2+}-dipy SO_4 complexes is indicated by splitting the bands into triplets (1245, 1150 and 1020 cm^{-1}) and (650, 630 and 610 cm^{-1}). Furthermore, the appearance of the ν_2 band at 975 cm^{-1} and ν_1 at 1020 cm^{-1} supports the chelating nature of SO_4 in the complexes[19].

X-ray powder diffraction analysis (Table 4) indicates that the complexes are crystalline and they can be classified into six isomorphous groups, namely: $MSO_4(dipy)\cdot 6H_2O$ ($M = Fe^{2+}, Ni^{2+}$), $MSO_4(dipy)_2\cdot 6H_2O$ ($M = Fe^{2+}, Ni^{2+}$), MX_3 (dipy) · $2H_2O$ ($M = Fe^{3+}, Co^{3+}, X = Cl^-$ or NO_2^-), $MX_3(dipy)_2\cdot 4H_2O$ ($M = Fe^{3+}$, Co^{3+}, $X = Cl^-$ or NO_2^-), $MX_3(dipy)_3\cdot 3H_2O$ ($M = Fe^{3+}, Co^{3+}, Ni^{2+}, X = Cl^-, NO_2^-$ SO_4^{2-}) and $CoCl_2\cdot dipy\cdot 3H_2O$ and $CoCl_2(dipy)_2\cdot H_2O$. The X-ray patterns show very small deviation in the d-spacings and I/I_0. This may be attributed to different scattering power of the ions, strain in the crystal lattice, some preferential orientation of some (hkl) planes and the different crystalline size of the complexes. The changes in d and in I/I_0 values among the groups may be attributed to different structures arising from the involvement of a number of lattice or coordinated water molecules around the central metal ion in the composition, or from possible orientations of the ligands around it.

Based on the gained results, the chemical structural formulae of complexes can be typified as follows.



A. (1:1)M^{n+}-Dipy Complexes; B. (1:2)M^{n+}-Dipy Complexes; C. (1:3)M^{n+}-Dipy Complexes

REFERENCES

1. F.A. Hart and F.A. Cotton, The Heavy Transition Elements, **10**, 219 (1975).
2. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Wiley Eastern, New Delhi, p. 762 (1972).

3. R.M. Awadallah, A.E. Mohamed, M.A. El-Maghraby and A.M. Ramadan, *Transition Metal Chem.*, **13**, 250 (1988).
4. ________, *Transition Metal Chem.*, **15**, 273 (1990).
5. R.M. Awadallah, *Asw. Sci. Techn. Bull.*, **5**, 153 (1984).
6. ________, *Asw. Sci. Techn. Bull.*, **5**, 195 (1984).
7. ________, *Asw. Sci. Techn. Bull.*, **5**, 29 (1984).
8. ________, *Asw. Sci. Techn. Bull.*, **5**, 117 (1984).
9. I.S.A. Farag, A.A.M. Gad and R.M. Awadallah, *Cryst. Res. Technol.*, **27**, 83 (1992).
10. R.M. Awadallah, I.S.A. Frag and A.A.M. Gad, *Cryst. Res. Technol*, **27**, 2 (1992).
11. R.M. Awadallah, M.K. Sherif and F.S. Mohamed, *J Indian Chem. Soc.*, **61**, 459 (1984).
12. R.M. Awadallah, M.K. Sherif and T.I. EL Desouky, *J. Indian Chem.* Soc., **61**, 403 (1984).
13. K. Nakamoto, J. Fujita, S. Tanaka and J Kulayashi *J. Am. Chem. Soc;*, **79,** 4904 (1959).
14. R.M., Siliverstien , C.G. Bassler and T.C. Moril, Spectrophotometry or Organic Compounds, 3rd edn., John Wiley and Sons, New York (1967).
15. A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, New York, p. 333 (1963).
16. A. Earnshaw, Introduction to Magnetochemistry, Volumes **5** and **6,** London (1986).
17. H. Looker *J. Org. Chem.*, **27**, 361 (1962).
18. A.R. Kattritzky, J. Chem. Soc., 3674 (1962).
19. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Chemistry, John Wiley and Sons, Ltd., New York (1970).

(*Received*: 24 May 1993; *Accepted*: 26 June 1993) AJC–659