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Studies on Ruthenium(II) Complexes with Ligands Containing the Amide Group

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Reactions of $RuCl_2(DMSO)_4$ with some of the biologically active polydentate ligands containing an amide group yielded a number of stable complexes, effecting partial or complete displacement of DMSO groups from the complex, depending on the type of ligand. The interaction of anionic bidentate ligands with $RuCl_2(DMSO)_4$ yielded neutral complexes of the type $Ru(DMSO)_2(L-L)_2$ (L–L = AAB, BAB, MA, ACB, PACB and NACB) displacing only two DMSO groups and the two chlorides. With uninegative terdentate ligands, all the DMSO groups were displaced and complexes of the formula $Ru(L)_2$ (L = ABAB, APACB and ABB) were obtained. A complex $RuCl_2(DMSO)_2(ABA)_2$ was also obtained by a similar method. The infrared and proton NMR spectra of these complexes have been found to be useful in identifying and characterising them.

Introduction

There are numerous examples of the *in vivo* interactions of transition metal ions with ligands containing amide groups, and these interactions can be of biological importance [1–3]. Therapeutical ligands such as aminopterin and phenylalanine mustard (which contain amide groups) show an increased anticancer activity when administered as metal complexes [4]. Bleomycins are a family of glycopeptide antibiotics clinically prescribed for the treatment of selected neoplastic diseases [5], which chelate with metal ions and bind to deoxyribonucleic acid (DNA), induce a degradation of DNA in a reaction that depends on the presence of ferrous ion and molecular oxygen [6].

The compounds of Group VIII elements in the d-block have been reported as being particularly successful as anticancer metallotherapeuticals. A series of nickel, palladium and platinum complexes have been reported in this regard [7, 8]. Some of the rhodium and iridium complexes were also reported to exhibit such characteristics [9]. An amide group offers two potential binding sites, the oxygen and nitrogen, for complexation with metal ions [3]. In view of potential biological significance it is considered important to study the interaction of some ligands containing this group with ruthenium(II), a group VIII metal ion. In the present investigation, we now report the synthesis and characterisation of some ruthenium(II) complexes obtained by the interaction of $RuCl_2(DMSO)_4$ and a series of ligands represented by the general formula, X-NH-CO-Y, where X = *o*-$C_6H_4(COOH)$ and Y = CH_3(AABH), C_6H_5(BABH), *o*-$C_6H_4(NH_2)$(ABABH); X = C_6H_5 and Y = CH=CH-(COOH)(MAH); X = H(ACBH), C_6H_5(PACBH), $C_{10}H_7$(NACBH), *o*-$C_6H_4(NH_2)$(APACBH) and Y = *o*-C_6H_4(COOH); X = H and Y = *o*-$C_6H_4(NH_2)$(ABA). The compound 2-(2-aminobenzoyl)benzoic acid (ABB) was also used as a ligand in this work.

Experimental

Literature methods were used to prepare the ligands used in this work: 2-(acetylamino)benzoic acid (AABH) [10], 2-(benzoylamino)benzoic acid (BABH) [11], 2-(2-aminobenzoylamino)benzoic acid (ABABH) [12], maleanilic acid (MAH) [13], 2-(aminocarbonyl)benzoic acid (ACBH) [14], 2-[(phenylamino)carbonyl]benzoic acid (PACBH) [15], 2-[(1-naphthalenylamino)carbonyl]benzoic acid (NACBH) [15], 2-[(2-aminophenylamino)carbonyl]-benzoic acid (APACBH) [16] and 2-aminobenzamide (ABA) [12]. The compound 2-(2-aminobenzoyl)-benzoic acid (ABBH) was obtained from Aldrich Chemical Company (U.S.A.). $RuCl_3 \cdot 3H_2O$ used was from Johnson Matthey (England). An analytically pure sample of $RuCl_2(DMSO)_4$ was prepared by the published method [17].

Microanalyses of the complexes were done by the Micro-analytical Laboratory, Calcutta University, Calcutta, India. Magnetic susceptibility measurements and melting point determinations were performed as reported earlier [18]. Conductivity measurements

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TABLE I. Analytical and Other Physical Data of Ruthenium(II) Complexes.

No.	Complex	Colour	M.Pt.[a] (°C)	Analyses (%)[b]				Molar conductance (Mho $cm^2 M^{-1}$)[c]
				C	H	N	S	
1	$Ru(DMSO)_2(AAB)_2$	Greenish yellow	226	42.9 (43.0)	4.4 (4.5)	4.6 (4.6)	10.5 (10.4)	23
2	$Ru(DMSO)_2(BAB)_2$	Dark green	232	52.2 (52.0)	4.3 (4.3)	3.9 (3.8)	8.7 (8.6)	20
3	$Ru(DMSO)_2(MA)_2$	Dirty yellow	220	47.6 (47.4)	4.6 (4.6)	4.5 (4.6)	10.7 (10.5)	24
4	$Ru(DMSO)_2(ACB)_2$	Brown	225	41.1 (40.9)	4.0 (4.1)	4.7 (4.8)	11.0 (10.9)	21
5	$Ru(DMSO)_2(PACB)_2$	Snuff brown	228	52.2 (52.0)	4.2 (4.3)	3.8 (3.8)	8.8 (8.6)	18
6	$Ru(DMSO)_2(NACB)_2$	Reddish brown	235	57.1 (57.3)	4.3 (4.3)	3.4 (3.3)	7.7 (7.6)	16
7	$Ru(ABAB)_2$	Orange yellow	265	55.0 (54.9)	3.7 (3.6)	9.2 (9.1)	–	16
8	$Ru(APACB)_2$	Pink	257	55.1 (54.9)	3.7 (3.6)	9.1 (9.2)	–	14
9	$Ru(ABB)_2$	Orange yellow	250	57.9 (57.7)	3.4 (3.4)	4.8 (4.8)	–	19
10	$RuCl_2(ABA)_2(DMSO)_2$[d]	Orange yellow	215	35.7 (36.0)	4.6 (4.7)	9.4 (9.3)	10.7 (10.6)	22

[a] All complexes decompose above the temperature cited. [b] Calculated values are given in parentheses. [c] Conductivity measurements were done in 10^{-3} *M* solutions in methanol at room temperature. [d] Cl analysis: Found, 12.0%; Calcd., 11.8%.

were done on 10^{-3} *M* solutions of complexes in methanol at room temperature using a Digisun Digital Conductivity Meter (DL-909). IR spectra of the ligands and complexes were recorded in the 200–4000 cm^{-1} range with a Perkin Elmer-283 spectrophotometer. The compounds were prepared as Nujol mulls or KBr pellets and the far-IR spectra were recorded using CsI plates. ^1H NMR spectra were recorded on a Jeol 100 MHz FT NMR instrument in both $CDCl_3$ and D_2O. Electronic spectra were recorded on a Shimadzu MPS 5000 spectrophotometer.

Microanalytical and other physical characteristics of complexes are presented in Table I. The infrared, ^1H NMR and electronic spectral data are presented in Tables II, III and IV respectively.

All complexes prepared by the procedures described below were dried under vacuum.

Preparation of Complexes

The yellow complex $RuCl_2(DMSO)_4$ was suspended in toluene (30 ml) and the appropriate ligand in methanol added in a 1:4 molar ratio. The suspension mixture was refluxed for one hour, when the whole suspension dissolved giving a homogeneous solution. The solution was evaporated to a small volume under vacuum and the products precipitated with diethyl-ether. The products were washed repeatedly with ether and filtered. Pure complexes were obtained by recrystallising them from a methanol–ether mixture. Yields: ~70%. The complexes are soluble in methanol, ethanol, chloroform, dichloromethane, dimethyl formamide, dimethylsulphoxide, and appreciably so in water.

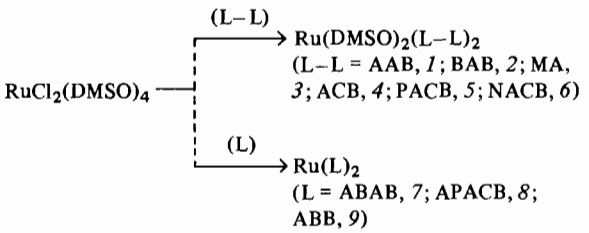
Results and Discussion

The general synthetic approach that was employed for the preparation of the complexes reported in this work has involved the reaction of $RuCl_2(DMSO)_4$ with various bidentate and terdentate ligands containing mixed donor atoms. The synthesis of these complexes provides evidence for the variety of substitution reactions that the complex $RuCl_2(DMSO)_4$ can undergo; thus, bidentate ligands displacing only two of the four DMSO groups, and the terdentate ligands displacing all the four from the coordination sphere of the metal ion. The displacement reactions can be summarized by the following equation:

TABLE II. Some Stretching Frequencies Occurring in the Infrared Spectra of Ruthenium(II) Complexes.

No.	Complex	Stretching frequencies, cm^{-1} [a]				
		ν(N–H)		ν(C=O)	ν(S=O)	ν(Ru–X)[b] X = N, O, S
		-NH_2	-NH-			
1	$Ru(DMSO)_2(AAB)_2$		3260m (3380m)	1640s (1640s)	1090s	460m, 425m, 270w
2	$Ru(DMSO)_2(BAB)_2$		3350m (3460m)	1635s (1640s)	1100s	470m, 430m, 275w
3	$Ru(DMSO)_2(MA)_2$		3360m (3340m)	1610s (1630s)	1080s	485s, 425m, 280m
4	$Ru(DMSO)_2(ACB)_2$		3380s (3060m, b)	1620s (1660s)	1070s	490s, 420m, 275m
5	$Ru(DMSO)_2(PACB)_2$		3310m (3300m)	1615s (1640s)	1090	460m, 430m, 300w
6	$Ru(DMSO)_2(NACB)_2$		3300m (3280m)	1620s (1660s)	1080s	470s, 430m, 290w
7	$Ru(ABAB)_2$	3420s 3300m (3500s) (3400s)	3120m (3210m)	1650s (1650s)	–	540m, 460m, 265w
8	$Ru(APACB)_2$	3340m 3300sh (3400s) (3340m)	3220m (3200m)	1620s (1640s)	–	540m, 480m, 290m
9	$Ru(ABB)_2$	3350s 3200m (3460s) (3340s)		1650s (1710–1670s, b)	–	460m, 270m
10	$RuCl_2(DMSO)_2(ABA)_2$	3400s 3330s (3400s) (3340s)	3140s (3200s)	1660s (1660s)	1100s	450m, 420m, 340s[c]

[a] Some of the absorptions in free ligands are given in parentheses. [b] The metal–ligand vibrational bands corresponding to Ru–N, Ru–O and Ru–S could not be assigned with certainty since they contain a great deal of ligand character. [c] The band at 340 cm^{-1} can be assigned to ν(Ru–Cl) for trans-$RuCl_2$ unit in this complex after ν(Ru–Cl) at 345 cm^{-1} in $RuCl_2(DMSO)_4$ (ref. 17).



The single concentration molar conductivities (10^{-3} *M*) of all the complexes are similar and low for any electrolyte behaviour in methanol [19], suggesting their formulation as neutral complexes (Table I). The complexes are diamagnetic ruthenium(II) species with spin-paired t_{2g}^6 ground configuration.

The ligands, AABH, BABH, MAH, ACBH, PACBH and NACBH which contain an amide group in addition to a carboxylic group behave in an identical manner in their reactions with $RuCl_2(DMSO)_4$ affording the stable crystalline complexes of the type $Ru(DMSO)_2(L–L)_2$. It has been reported that $RuCl_2(DMSO)_4$ is a neutral monomeric complex in chloroform and has a trans-chloride configuration, with three of the four DMSO groups S-bonded and one O-bonded [17]. The ligands appear to be acting as anionic bidentate chelates, thus displacing at least two of the four DMSO groups along with the chlorides from the complex $RuCl_2(DMSO)_4$. The substitution of the first bidentate ligand may presumably occur by the displacement of the weakly held O-bonded DMSO group and one of the chlorides. Similarly the substitution by the second chelate takes place cis- or trans- to the first with the displacement of one of the S-bonded DMSO groups and the other

TABLE III. ^{1}H NMR Spectral Data of Ligands and Their Complexes of Ruthenium(II).[a]

No.	Complex	Chemical shifts δ/ppm[b]				
		-CH_3 (br)	-NH_2 (br)	-NH- (br)	Aromatic protons (m)	-COOH (s)
1	$Ru(DMSO)_2(AAB)_2$	2.26(2.20)[c] 3.00–3.20	– –	– (6.80)	7.10–8.70 (7.05–8.66)	– (11.20)
2	$Ru(DMSO)_2(BAB)_2$	3.00–3.20	–	– (6.70)	6.86–8.76 (7.20–8.76)	– (12.18)
3	$Ru(DMSO)_2(MA)_2$	3.00–3.20 6.00–6.60(m)[d] (6.00–6.54)(m)[d]	– – –	3.40 (3.30)	7.00–7.80 (7.00–7.67)	– (10.35)
4	$Ru(DMSO)_2(ACB)_2$	3.00–3.20 –	–	3.50 (3.50)	7.00–8.24 (7.00–8.10)	– –
5	$Ru(DMSO)_2(PACB)_2$	3.00–3.20	–	[e] (3.20)	7.10–7.80 (7.00–8.00)	– (10.32)
6	$Ru(DMSO)_2(NACB)_2$	3.00–3.20 –	– –	3.80 (3.80)	7.20–8.40 (7.30–8.40)	– (10.30)
7	$Ru(ABAB)_2$	–	4.00 (3.50)	– (4.70)	6.70–8.36 (6.72–8.34)	– (11.88)
8	$Ru(APACB)_2$	–	[f] (3.80)	5.20 (5.20)	6.60–8.20 (6.54–7.86)	– (10.64)
9	$Ru(ABB)_2$	–	4.30 (3.30)	– –	6.24–8.10 (6.24–8.04)	– –
10	$RuCl_2(DMSO)_2(ABA)_2$	3.00–3.20 –	3.50 (3.40)	4.0 (3.10)	6.40–7.80 (6.36–7.62)	– –

[a] Free ligand values are given in parentheses. All chemical shifts are measured relative to tetramethylsilane, δ = 0. [b] s, singlet; m, multiplet; br, broad. [c] Methyl protons of -CO–CH_3 of the ligand (AAB). [d] Proton absorptions corresponding to -CH=CH- group in the ligand, MA. [e] The signal due to these protons merges with that of DMSO group methyl protons. [f] The signal merges with that of -NH–CO- group.

TABLE IV. Ultraviolet–Visible Spectra of Ruthenium(II) Complexes in Methanol.

No.	Complex	λ_{max} (nm)
1	$Ru(DMSO)_2(AAB)_2$	550, 452, 350, 234
2	$Ru(DMSO)_2(BAB)_2$	553, 440, 352, 316
3	$Ru(DMSO)_2(MA)_2$	560, 465, 330, 270
4	$Ru(DMSO)_2(ACB)_2$	570, 470, 342, 261
5	$Ru(DMSO)_2(PACB)_2$	580, 460, 359, 282
6	$Ru(DMSO)_2(NACB)_2$	523, 450, 355, 280
7	$Ru(ABAB)_2$	545, 436, 326, 279
8	$Ru(APACB)_2$	542, 440, 286, 234
9	$Ru(ABB)_2$	546, 456, 266, 230
10	$RuCl_2(DMSO)_2(ABA)_2$	530, 442, 350, 260

chloride. Our attempts to prepare tris-chelate complexes of the type $[Ru(L–L)_3]^-$ using the large excess (10 mol) of these uni-negative bidentate ligands in a reaction with $RuCl_2(DMSO)_4$ met with no success, and a bis-complex was always obtained. This may be because of the much greater steric requirements of the chelating ligands.

The infrared spectra of the complexes *1–6* show evidence for the presence of the respective ligands in them. Dimethyl sulphoxide was characterised by its ν(S=O), which decreases by bonding to the metal through oxygen and increases upon coordination through the sulphur atom [20]. In free DMSO, the ν(S=O) mode occurs at 1055 cm^{-1} as a very strong and broad band [17]. The infrared spectra of complexes *1–6* show ν(S=O) at 1070–1100 cm^{-1} as strong bands corresponding to the S-bonded DMSO ligands [17] (Table II).

The infrared C=O and C–O stretching frequencies at 1700 and 1330 cm^{-1} in uncomplexed ligands containing carboxylic groups [16, 21] are shifted to 1550 and 1380 cm^{-1} in complexes *1–6* and are assigned to ν(COO) (asymmetric) and ν(COO) (symmetric) modes respectively [22]. The ν(O–H) of the carboxylic group appearing at 2600 cm^{-1} in free ligands disappears in the infrared spectra of their complexes. The ν(N–H) frequencies of complexes *1* and *2* appear at 3260 and 3350 cm^{-1} respectively, with a lower shift of about 100–120 cm^{-1} compared to those in free ligands AABH and BABH. Shifts of

such type and magnitude suggest that the -NH group is involved in coordination to ruthenium. On the other hand, the ν(C=O) of the amide group at 1640 cm^{-1} in the uncomplexed ligands AABH and BABH remains unaffected after complexation by the ligands, indicating that the amide group is held to the metal ion through the N-end and not through the O-end [23]. This kind of a coordination results in the formation of a six-membered chelate ring, the minimum possible ring size in complexes *1* and *2*.

Complexes *3–6* show similar infrared characteristics, except for the fact that the amide oxygen of the ligands MAH, ACBH, PACBH and NACBH participates in coordination with the metal ion, as revealed by ν(C=O) and ν(N–H) absorption modes. The ν(N–H) in the complexes shifts towards slightly higher regions when compared to that in uncomplexed ligands. This might indicate the possibility of the nitrogen end of the amide group being uninvolved in coordination with the metal [24]. However, negative shifts of about 20–40 cm^{-1} are observed in the ν(C=O) modes of the amide group in the infrared spectra of complexes *3–6*, suggesting the possible coordination of this group through oxygen [24]. Some of the stretching frequencies relevant to the characterisation of the complexes are listed in Table II.

The proton NMR spectra of complexes *1–6* are well-resolved and provide information to support the configurations assigned to these complexes (Table III). In the free DMSO molecule, the methyl resonance signal appears at 2.60 δ [17]. The methyl resonance of O-bonded DMSO group is close to that of free DMSO and appears around 2.72 δ, whereas the signal corresponding to S-bonded DMSO groups appears about 1 ppm downfield from the free DMSO resonance [17]. Complexes *1–6* exhibit only one resonance at 3.0–3.2 δ in their ^{1}H NMR spectra for the methyl protons of the coordinated DMSO groups. The positions of these resonance signals are about 0.60 ppm downfield from free DMSO, indicating the presence of S-bonded DMSO ligands in the complexes. The appearance of only one strong resonance signal in this region implies that the DMSO groups are probably trans to each other in complexes *1–6*. Besides, the NMR spectra of complexes also contain peaks corresponding to the other ligands. The integrated intensity of all the protons is in agreement with the number and different types of protons present in them. The absorption values of different protons for uncomplexed ligands are also given in Table III for comparison. The ligands containing carboxylic groups show resonance absorptions between 10.30–12.20 δ, except for the ligand ACBH where such an absorption is not observed, probably due to a rapid exchange taking place between carboxylic and amine protons. The signals due to carboxylic group proton absorptions disappear in the NMR spectra of their complexes, confirming the involvement of carboxylate oxygen in bonding to the metal ion (Table III).

The NMR spectra of complexes *1* and *2* show multiplets due to phenyl protons at 7.10–8.70 δ and 6.86–8.76 δ respectively. The signals at 6.70 and 6.80 δ for -NH protons in ligands AABH and BABH respectively were found to disappear upon metal coordination in complexes *1* and *2*. This would indicate that the signals had either merged with those due to phenyl protons, or shifted largely downfield, and this is in accord with the coordination of amide nitrogen atoms to ruthenium.

Based on this information the structure proposed tentatively for the complexes *1* and *2* would be octahedral with a chelated six-membered ring formed with each of the bidentate ligands in the equatorial base and two DMSO groups in the axially transposition. The structure containing eight-membered chelate rings when both the ligands coordinate through the oxygen of the amide group in complexes *1* and *2* is untenable, due to the large size of the ring as compared to the stable six-membered ring formed when amide nitrogen is involved in bonding to the metal ion.

In contrast to complexes *1* and *2*, the shift observed for -NH protons in the ^{1}H NMR spectra of complexes *3–6* is insignificant, indicating the non-participation of this group in coordination with the metal ion (Table III). Instead, it is the carbonyl oxygen of the amide group which binds to ruthenium in these complexes. A multiplet ranging from 6.00–6.54 δ observed due to methine protons (-CH=CH-) in the ligand MAH remains unshifted upon complexation (Complex *3*). The signal at 3.20 δ due to -NH protons in free PACBH merges with that of S-bonded DMSO, which absorbs in the same region in complex *5*. These facts indicate that complexes *3–6* are octahedral with two DMSO groups being trans to each other and the bidentate ligands forming the minimum possible seven-membered chelate rings.

The uni-negative terdentate ligands, ABABH, APACBH and ABBH react with $RuCl_2(DMSO)_4$ to give neutral monomeric complexes of the type $Ru(L)_2$ (*7–9*).

The fact that no DMSO group is present in complexes *7–9* is confirmed by the absence of the bands characteristic of this ligand from the infrared spectra. The ν(N–H) frequencies in the free ligands, ABABH, APACBH and ABBH occurring as sharp bands around 3400 cm^{-1} were reduced by about 100 cm^{-1} upon coordination (Table II). The infrared spectra show evidence for the participation of at least one of the two nitrogens coordinating with the metal ion. There is a difference in the coordinating behaviour of ABABH and APACBH ligands in that the former utilizes amide nitrogen while the latter uses carbonyl oxygen of the amide groups along with anilinic nitro-

gen and carboxylate oxygen atoms for binding with the metal. The ^{1}H NMR spectra of complexes *7* and *8* support this proposition.

There is a large downfield shift observed for -NH proton absorption in ABABH and the signal merges with those of phenyl protons in the downfield at 6.70–8.36 δ in complex *7*. The anilinic proton (-NH_2) signal also undergoes a downfield shift from 3.50 δ to 4.0 δ, clearly suggesting the coordination of anilinic nitrogen to the metal ion. An octahedral structure is proposed for complexes *7–9*, with each terdentate ligand probably occupying meridonial positions on the metal ion. Thus in complex *7*, each chelate forms two non-planar six-membered rings with carboxylate oxygen, amide group nitrogen and anilinic nitrogen atoms as donor sites. Complex *8* contains two non-planar seven-membered rings formed by each of the two chelates APACBH, whereas complex *9* contains two non-planar rings, one six-membered and the other seven-membered, formed with each terdentate ligand.

When the displacement reaction was conducted between $RuCl_2(DMSO)_4$ and a neutral ligand, 2-aminobenzamide (ABA), the product obtained was $RuCl_2(DMSO)_2(ABA)_2$ (*10*). The complex behaves as a non-electrolyte in methanol, confirming the presence of both chlorides inside the coordination sphere of the metal ion (Table I). The chlorides while readily displaced from the complex $RuCl_2(DMSO)_4$ by the negative ligands as in complexes *1–9*, were not displaced even when a large excess of the neutral ligand ABA was employed in the reaction. Complex *10* is characterised by its infrared bands corresponding to S-bonded DMSO at 1100 cm^{-1} due to ν(S=O) and the ligand ABA at 3200 cm^{-1} due to ν(N–H). A single strong band at 340 cm^{-1} in the far infrared spectrum of the complex suggests the presence of trans-disposed chlorides. Although the ligand ABA has two donor sites, it appears to coordinate in a monodentate fashion through amide nitrogen. The proton NMR spectrum is also consistent with this assignment. The resonance signal corresponding to anilinic protons (-NH_2) of the ligand ABA at 3.50 δ is not shifted much upon complexation, whereas the signal for amide protons (-NH) at 3.10 δ is shifted to downfield at 4.0 δ (Table III). An all-trans structure can be tentatively proposed for complex *10*, since the NMR spectrum of the complex displays a strong resonance signal at 3.0–3.2 δ corresponding to two trans-disposed DMSO groups.

The electronic spectral data for complexes *1–10* are presented in Table IV. The molar extinction coefficients are all much higher than conventional values for d–d transitions. All complexes are diamagnetic ruthenium(II) species with spin-paired t_{2g}^6 ground configuration. Generally, two spin-allowed d–d transitions are expected in the electronic spectra of strong-field octahedral Ru(II) complexes: $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ with increasing order of energy. Sometimes the higher energy transition is totally obscured by intense charge transfer bands. However, these two bands can be tentatively assigned for all the complexes reported in this work as occurring in the regions around 530–570 and 430–470 nm (Table IV). It is possible for complexes *1–6* and *10* to have tetragonal distortion, and if such a distortion of octahedral symmetry occurs the lower energy band at 530–570 nm should be split into two components [25]. However, there is no splitting of this band in the complexes to indicate any significant tetragonal distortion. The other higher energy bands occurring in complexes can be assigned as ligand $\pi \rightarrow \pi^*$ and other LMCT transitions.

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