

Some benzimidazole amide complexes of ruthenium(II)

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Abstract. The synthesis and characterisation of ruthenium(II) complexes with 2-amidobenzimidazoles are reported. The complexes $\text{RuCl}_2(\text{DMSO})_4$ and $\text{RuCl}_2(\text{PPh}_3)_2$ react with 2-(acetamido)benzimidazole (AB) and 2-(benzamido)benzimidazole (BB) in acetone to give products of the type $[\text{Ru}(\text{L})_2(\text{N}-\text{O})_2]\text{Cl}_2$ [$\text{L} = \text{DMSO}, \text{PPh}_3, \text{N}-\text{O} = \text{AB}, \text{BB}$]. The displacement reactions are faster in the case of methyl (AB) than phenyl (BB) substituted ligands. The ligands are bifunctional chelating agents coordinating through the tertiary nitrogen of benzimidazole ring and amide oxygen. The complexes are characterised based on their elemental analysis, conductivity data, infrared, ^1H and ^{31}P nmr spectra. A *cis*-geometry is proposed for all the complexes reported.

Keywords. Ruthenium(II) complexes; benzimidazole amides; bifunctional ligands; ^{31}P and ^1H nmr; amide oxygen coordination.

1. Introduction

Metal amide complexes are an important class of coordination compounds and are currently drawing more attention since studies on these complexes help in understanding the mode of binding of the amide group in some of the closely related biological systems (Sigel and Martin 1982; Collins *et al* 1983; Che *et al* 1986). Also the coordination chemistry of chelate ligands having mixed functional groups has been extensively studied (Hedden and Roundhill 1985). An important outcome of this work is the development of hybrid ligands where one arm of the chelate will selectively bind to the metal ions and the hinging arm available for ready substitution (Hedden and Roundhill 1985, 1986; Rauchfuss and Roundhill 1973, 1974; Hedden *et al* 1984).

With the reports on the synthesis of platinum group metal complexes as anti-tumour agents containing various ligands have not been sufficient, the synthetic and structural aspects of some new and related complexes are of great interest. As part of a broad programme on the study of platinum group metal complexes with bifunctional ligands, we have undertaken the synthesis of some potential bidentate ligands, 2-(amido)benzimidazoles and their complexes with ruthenium(II). Recently we have reported the synthetic and structural aspects of some new carboxylate amide complexes with a low-valent platinum group metal ion, ruthenium(II) (Ravindar *et al* 1984). In continuation of our earlier work, we

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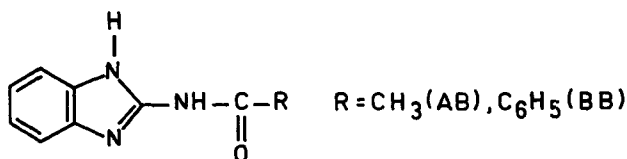


Figure 1. Structure of the ligand used in this work.

report in this paper the synthesis and characterisation of new chelate complexes of 2-(amido)benzimidazoles with both the tertiary nitrogen atom of the benzimidazole ring and the amidic oxygen complexed to ruthenium(II). The ligands used in this investigation are represented by the structure given in figure 1.

2. Experimental

Elemental analyses of C, H and N were done by microanalytical laboratory, CDRI, Lucknow, India. Magnetic measurements, conductivity and melting point determinations and infrared studies in KBr disc were carried out as reported earlier (Ravindar *et al* 1984). ¹H NMR spectra were recorded on saturated CDCl₃ solutions of complexes on Jeol FX 90. The ³¹P {¹H} nmr spectra in DMSO were recorded as reported earlier (Taqi Khan *et al* 1986).

The precursor materials, RuCl₂(DMSO)₄ (Evans *et al* 1973) and RuCl₂(PPh₃)₃ (Stephenson and Wilkinson 1966) were prepared by published methods. All analytical data are collected in table 1. Some important IR bands are compiled in table 2.

2.1 Synthesis of ligands

The ligands 2-(acetamido)benzimidazole (AB) and 2-(benzamido)benzimidazole (BB) were prepared by the reactions of the appropriate acid halides with 2-(amino)benzimidazole in pyridine (Bellasio *et al* 1973; Skaletsky 1971). The compound 2-(amino)benzimidazole was prepared by reacting cyanogen bromide with o-phenylenediamine (OPDA) by stirring for several hours (Pierron 1919; Wright 1951).

2.2 Preparation of complexes

- 1 Bis (dimethylsulphoxide)bis{2-(acetamido)benzimidazole} ruthenium(II) chloride;
2 Bis (dimethylsulphoxide)bis{2-(benzamido)benzimidazole} ruthenium(II) chloride

Complexes 1 and 2 were obtained by the addition of 3 mmol excess of AB (0.22 gm) and BB (0.32 gm), respectively, dissolved in acetone to a refluxing suspension of the yellow complex, RuCl₂(DMSO)₄ (0.2 gm; 0.4 mM). The colour of the solution changed from light to deep yellow (AB) and yellow orange (BB). The reaction mixtures were heated for 4–5 hours when the bulk of the complex had separated as yellow crystals. The crystals were washed with hot acetone and

Table 1. Physical data of ruthenium(II) complexes with bifunctional ligands.

Complex	Colour	M.P. (°C) ^a	μ_{eff}	Analysis (%) ^b			λ_{∞} (S cm ² mol ⁻¹)
				C	H	N	
[Ru(DMSO) ₂ (AB) ₂]Cl ₂	Yellow	187	Diamagnetic	32.8 (31.85)	2.70 (2.65)	12.54 (12.38)	90
[Ru(DMSO) ₂ (BB) ₂]Cl ₂	Pale yellow	193	"	48.60 (47.88)	3.96 (3.99)	10.20 (10.47)	94
[Ru(PPh ₃) ₂ (AB) ₂]Cl ₂	Yellow	200	"	62.10 (62.18)	4.66 (4.60)	8.00 (8.06)	85
[Ru(PPh ₃) ₂ (BB) ₂]Cl ₂	Red- brown	214	"	64.80 (65.64)	4.70 (4.78)	7.92 (7.17)	83

^a Decomposition temperatures; ^b Calculated values in parentheses.

methanol repeatedly and dried under vacuum Yields: 0.16 gm (57%) (1); 0.11 gm (33%) (2).

3 *Bis*(triphenylphosphine)*bis*{2-(acetamido)benzimidazole} ruthenium(II) chloride;

4 *Bis*(triphenylphosphine)*bis*{2-(benzamido)benzimidazole} ruthenium(II) chloride.

To refluxing acetone solutions of AB (0.11 gm; 6.3 mM) and BB (0.15 gm, 6.3 mM), solid RuCl₂(PPh₃)₃ (0.2 gm; 2.1 mM) was added and the resulting suspensions were refluxed to give clear light yellow (AB) and dark green (BB) solutions in about 20 minutes. When the solutions were refluxed for about 3 hours, complexes 3 and 4 were deposited as yellow (AB) and red brown (BB) crystals. The crystalline products were filtered and washed with hot acetone and methanol. Yields: 0.12 gm (55%) (3); 0.06 gm (25%) (4).

3. Results and discussion

The reactions of RuCl₂(DMSO)₄ and RuCl₂(PPh₃)₃ with both the ligands AB and BB were fast and gave cationic complexes of the type [Ru(L)₂(N-O)₂]Cl₂[L = DMSO, PPh₃; N-O = 2-(acetamido)benzimidazole (AB); 2-(benzamido)benzimidazole (BB)]. The yields are high when R is a methyl rather than a phenyl group. The cationic nature of the complexes was confirmed by the observed conductivity of the complexes in DMSO which is typical of a 1:2 electrolyte (Geary 1971) (table 1). Conductivity values of complexes when measured even 24 hours after their dissolution showed no changes, suggesting no rearrangement of the complexes in DSMO solution despite the strong donor capacity of the solvent.

The complexes are crystalline solids, stable in atmospheric conditions, soluble in DMSO, DMF and trifluoroacetic acid and to a large extent in chloroform.

Table 2. Some important IR spectral data for new benzimidazole amide complexes of ruthenium.

Complex	ν (N-H)	ν (C=O)	ν (C=N) ring	ν (S=O)	ν (Ru-P)
AB	3320(<i>m</i>)	1680(<i>s</i>)	1580(<i>s</i>)	-	-
BB	3310(<i>m</i>)	1658(<i>s</i>)	1560(<i>s</i>)	-	-
1.	3315(<i>m</i>)	1640(<i>s</i>)	1590(<i>m</i>)	1080(<i>s</i>) 1105(<i>sh</i>)	-
2.	3318(<i>m</i>)	1635(<i>s</i>)	1595(<i>m</i>)	1080(<i>s</i>) 1110(<i>sh</i>)	-
3.	3315(<i>m</i>)	1655(<i>s</i>)	1595(<i>s</i>)	-	515(<i>s</i>)
4.	3320(<i>m</i>)	1630(<i>s</i>)	1585(<i>m</i>)	-	520(<i>s</i>)

Key: *s* = strong; *m* = medium; *sh* = shoulder.

Considering the capacity of platinum group metals to form complexes with nitrogen containing ligands, it may be assumed that the tertiary nitrogen of the benzimidazole functionality of the ligand will be bound with the metal invariably in all the complexes. Studies on the complexation of imidazoles and benzimidazoles have also revealed that the tertiary nitrogen rather than the secondary nitrogen is the bonding site to the metal (Ghosh *et al* 1977). The characteristic absorptions in the IR which could be monitored for diagnostic assignments in the ligand before and after coordination to the metal have been compared in order to confirm the site of coordination in ligands. In the infrared spectra of ligands AB and BB, strong bands due to ν (C = N) of the benzimidazolyl ring are observed at 1580 and 1560 cm^{-1} respectively. It is found in the complexes 1–4 that the position of ν (C = N) is shifted to higher frequency by 15–35 cm^{-1} indicating that the bonding of benzimidazole takes place through the tertiary nitrogen atom only (Ghosh *et al* 1977) (table 2). The region 400–450 cm^{-1} assignable to ν (M–N) modes contains many ligational bands, therefore the bands due to ν (M–N) cannot be assigned with certainty.

In the ligands, the ring ν (N–H) and amido ν (N–H) together give rise to a sharp medium band in 3310–3320 cm^{-1} . The coincidence of these bands is typical for organic molecules containing both secondary amide and 2-imidazolyl or 2-benzimidazolyl groups. The position of the ν (N–H) bands in the complexes, however, are almost unchanged from those in the corresponding free ligands AB and BB, which confirms the inability of the amide nitrogen from coordination. In the infrared spectra of all the complexes, the amide I band, which is to a large extent ν (C–O), shifts to a lower frequency and this indicates amide oxygen coordination (Chapman and Vagg 1979; Chapman *et al* 1981; Mulqui *et al* 1982). The ligands form stable six-membered chelates through pyridine nitrogen and amidic oxygen in all the complexes.

The presence of DMSO in complexes 1 and 2 was characterized by its ν (S=O), which decreases when it is coordinated through oxygen and increases upon binding to the metal through sulphur (Gopalakrishnan and Patel 1967; Reynolds 1970). The infrared spectra of complexes 1 and 2 show strong bands due to ν (S=O) in the region 1050–1100 cm^{-1} and correspond to the S-bonded DMSO ligands (Evans *et al* 1973; Reynolds 1970) (table 2). The bands in this region appear to have

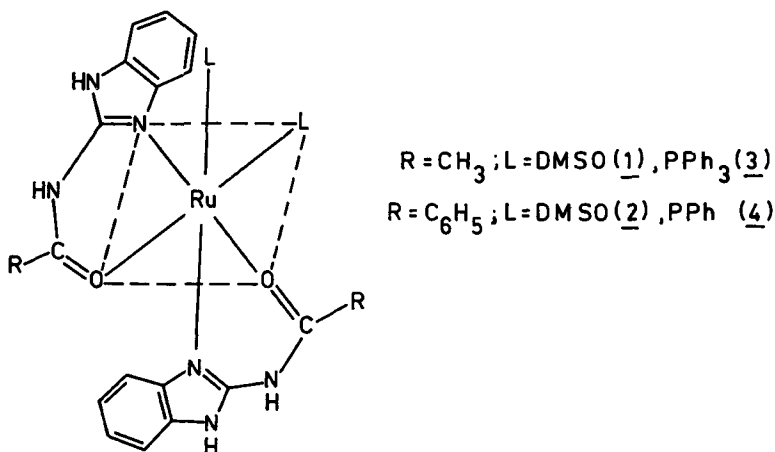


Figure 2. Structure with two non-equivalent ligands complexed in a *cis*-manner.

shoulders on the higher frequency side which may probably suggest that the two DMSO groups are coordinated in a *cis*-manner. Complexes 3 and 4 display strong bands in the far IR spectra at 520 and 515 cm^{-1} corresponding to $\nu(\text{Ru}-\text{p})$. The region 275–350 cm^{-1} is devoid of any bands confirming the total displacement of chlorides from the coordination sphere.

The ^1H nmr spectra of complexes show significant shifts due to coordination. The peaks observed in the range 3.0–3.5 δ are broad and correspond to CH_3 protons of S-bonded DMSO groups in complexes 1 and 2 (Evans *et al* 1973). Another singlet resonance at 2.33 δ due to CH_3 protons of AB ligand undergoes a downfield shift to 3.2 δ in complex 1. This observation can be interpreted on the basis of amidic oxygen coordination. Similarly, a large downfield shift of 1.37 ppm is observed for methyl protons in the ^1H nmr spectrum of complex 3. The aromatic proton resonances of benzimidazolyl ring of the ligands and PPh_3 groups absorb in the range 7.12–8.02 δ as complex multiplets and remain almost unchanged in the complexes. The resonances due to the solvent and concentration dependent amide protons of both the ligands and complexes in CDCl_3 were not observed in the range 0–10 ppm. However, addition of D_2O and recording the spectra after 24 hours caused the appearance of characteristic HOD signal at 5.0 δ (Kemp 1975). The ^{31}P nmr spectra recorded for complexes 3 and 4 in DMSO show the presence of two types of PPh_3 groups complexed to ruthenium(II). The resonances are shifted downfield by some 45–58 ppm from the free phosphine resonance at –5.2 ppm (Garrou 1981). The observation of two singlets at 51.89 and 40.63 ppm in ^{31}P nmr of complex 3 and 52.6 and 41.9 ppm in complex 4 requires a structure with two non-equivalent phosphorus ligands complexed in a *cis*-manner (figure 2).

It is well-established that amide groups must remain planar, as far as possible, even after binding to the metal (Freeman 1973). In fact the metal amide oxygen bond is weak in complexes since amide-oxygen is weakly basic, but the overall stability of complexes 1–4 is enhanced because of the closure of a six-membered chelate ring with the adjacent benzimidazolyl ring nitrogen. The amide nitrogen

binds to a metal ion only under the conditions of a deprotonation since the process of deprotonation makes nitrogen available for metal coordination without loss of the amide group resonance (Sigel and Martin 1982; Freeman 1973). However, deprotonation of ligands AB and BB and consequent complexation with ruthenium (II) have not yielded any stable chelates. This may be due to the formation of 4-membered rings which are untenable, particularly in the case of large metal ions like ruthenium(II).

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