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The geometric features and spectral characteristics of some pentaamineruthenium(II) complexes

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Abstract

The geometric and bonding parameters of Ru(II) pentaaminepyridine and cyanopyridine complexes are examined via ab initio molecular orbital calculations. The results show that the nitrile bonded complexes are more stable than the pyridine bonded ones by 71–625 kJ mol^{-1} depending on the position of the nitrile group. Solvent dependence of MLCT bands are interpreted and discussed. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The discoveries of pentamine and tetramine ruthenium (II) complexes of molecular nitrogen [1,2] stimulated the interest in corresponding organo-nitrile compounds. A very interesting ligand, in this respect, is cyanopyridine. The properties of 2-,3- and 4-cyanopyridines have been the subject of several investigations [3–5]. This interest stems primarily from the existence of two potential coordination sites, the nitrile nitrogen and the pyridine nitrogen, on each ligand. The presence of two sites raises the possibility of linkage isomerism and provide the opportunity of comparison of coordination bond strengths with a particular metal ion. This comparison is only valid when the complexes are sufficiently labile to establish thermodynamic equilibria.

Complexes between organic nitriles and metal moieties in both zero [6] and positive [7] oxidation states are well known. With very few exceptions the coordinate bond consists of the linear array of metal, nitrogen and carbon atoms. Infrared spectra of complexes of this type always show an increase in the C≡N stretching frequency. Surprisingly, pentaamineruthenium (II) complexes show the opposite trend [1]. In fact, a substantial decrease in the v(CN) of coordinated benzonitriles is observed. This behaviour was qualitatively interpreted in terms of the unusually strong π-back donation of the Ru(NH$_3$)$_5^{2+}$ moiety. Unfortunately, the literature does not seem to contain any systematic study of bonding characteristics of this interesting class of ruthenium (II) complexes [8].

The present work presents a detailed quantitative investigation of the geometric features and

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Table 1
Bond lengths (Å) for $[Ru(NH_3)_5X]^{2+}$ complexes[a]

X	Ru-N$_2$	Ru-N$_3$	Ru-N$_4$	Ru-N$_5$	Ru-N$_6$	Ru-N$_7$
NH$_3$	1.959	1.958	1.959	1.948	1.961	1.959
Py	2.023	1.969	1.970	1.921	1.970	1.962
3-CN	1.961	1.960	1.960	1.879	1.959	1.959
4-CN	1.960	1.961	1.960	1.878	1.959	1.959
2-CP	1.972	1.967	1.960	1.913	1.952	1.959
4-CP	1.962	1.970	1.962	1.921	1.970	1.962

[a] For numbering system see Fig. 2.

bonding characteristics of pentaamine ruthenium (II) complexes with pyridine and cyanopyridines. Molecular orbital computations at the ab initio level provides a much better understanding of different modes of bonding and charge density distributions. The electronic absorption spectra of some of the studied complexes in a number of solvents will be presented and quantitatively analyzed and discussed.

2. Method of calculations

All computations reported in the present work were carried out using the Gaussian 94 w program package [9]. Molecular orbital calculations were carried out at the HF-SCF level using LanL2DZ frozen-core basis set [10]. This basis set has proved to give reliable geometries and ground state properties for molecular complex compounds. The procedure adopted in the present work to arrive at the equilibrium geometries is to optimize the initial structure at the molecular mechanics level using the MM+ parameters. The

resultant geometry would then be used as initial geometry input for the HF-SCF /LanL2DZ run.

3. Experimental

Doubly distilled water was used in all preparations. The solvents acetone, methanol, acetonitrile, pyridine, dimethylformamide (DMF), dimethylsulfoxide (DMSO) and pyridine (Py) were all obtained from BDH and/or Fluka in the highest possible purity grade available and used without further purification. All other chemicals were reagent grade. The complexes $[Ru(NH_3)_5Py]$ $(ClO_4)_2$ and $[Ru(NH_3)_5$ (2-cyanopy)] $(ClO_4)_2$ were prepared by the method developed by Clarke and Ford [2] and characterized by spectral and elemental analysis.

The spectra were recored on Shimadzo UV 260 spectrophotometer using a 1 cm fused silica cell.

4. Results and discussion

4.1. Geometric computations

Tables 1 and 2 present the geometric structural parameters of the studied ruthenium(II) complexes. The hexaamineruthenuim(II) complex ion was taken as the reference structure; a prospective drawing of its equilibrium structure is given in Fig. 1. The structure of this complex ion is a typical regular octahedron, with Ru-N bond of 1.96 Å and an interplane angle of $\sim 90°$. Group arrangements and net charges for the studied Ru(II) complexes are shown in Fig. 2. The ruthe-

Table 2
Bond angles (degrees) for $[Ru(NH_3)_5X]^{2+}$ complexes[a]

X	<213	<315	<415	<615	<715	<314	<416	<617	<713
NH3	173.70	83.49	89.39	95.65	89.45	89.99	90.00	90.00	90.00
PY	175.77	96.10	91.41	95.30	89.77	86.23	87.26	93.06	93.21
3-CN	176.97	91.98	91.29	92.21	95.31	89.38	89.09	96.21	88.96
4-CN	177.22	90.68	91.89	93.18	93.18	89.50	89.19	91.61	89.09
2-CP	175.08	100.42	89.76	105.47	89.17	86.95	85.64	95.53	92.34
4-CP	175.77	96.10	91.41	95.30	89.77	86.23	87.26	93.06	93.21

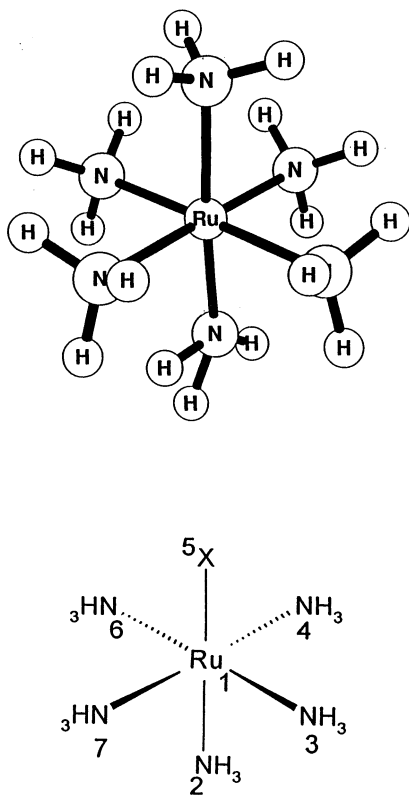[a] For numbering system see Fig. 2.

Fig. 1. A prospective drawing of the equilibrium structure of the hexamine, ruthenium(II) complex and the numbering system for the complexes studied.

nium atom acts as an electron donor where 0.9 e has been donated to the amine ligands. The electronic configuration of Ru(II) in this octahedral complex ion is $p^{5.93}d^{6.85}s^{0.32}$.

The HOMO of the pentaamineruthenium (II)

complex ion is a σ-bonding MO with 76% d character. The LUMO, on the other hand, seems to be localized to a large extent on the ruthenium s and p orbitals, with a relatively large HOMO-LUMO energy gap of ~ 11 eV. Replacement of one of the axial amine groups with pyridine, destroys the octahedral symmetry and produces some geometrical disturbances. Thus, a slight shortening of the Rti-N (pyridine) bond length is observed with a subsequent elongation of the *trans* Ru-N (amine) bond length. Thus, there is a much tighter binding in the Ru-pyridine bond region on the expense of the other Ru-amine bonds. It is interesting to notice that the equatorial four amine nitrogen: atoms each carry a pronounced negative charge of ~ 1 e whereas the axial amine nitrogen carries a positive charge of ~ 0.5 e. Thus, while the equatorial amine groups act as electron- acceptors and show a high Ru-N ionic character, yet the axial amine group acts as electron donor with a much less ionic nature. The pyridine nitrogen atom on the other hand, shows a net charge of -0.24 e. It should be noted that the polarization of the sigma framework of the complex ion is opposite to that of the π-framework. Analysis of the σ- and π-migration of charge shows that the pyridine ligand acts as σ-acceptor and π-donor.
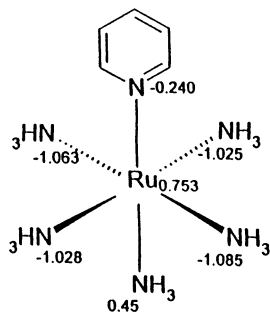
The HOMO of the Ru(II) pentaamine pyridine complex ion still shows the same character as previously outlined for the hexamine complex ion. The LUMO on the other hand, shows in addition to the Ru(II) s and p orbital contributions, more than 24% contribution from the pyridine orbitals. This would certainly indicate a marked difference

Table 3
HOMO, LUMO energies and dipole moment of $[Ru(NH_3)_5X]^{2+}$ complexes

X	Energy (a.u.)			Dipole moment (D)			Total
	HOMO	LUMO	Gap	X	Y	Z	
NH_3	−0.5980	−0.1938	0.4041	−0.1303	−0.3473	−1.2446	1.2987
PY	−0.5951	−0.1845	0.4106	2.8277	1.5202	−1.7900	3.6757
3-CN	−0.5870	−0.1963	0.3907	9.5860	2.3765	3.6880	10.5424
4-CN	−0.5969	−0.2032	0.3938	−11.7188	−0.6318	2.6333	12.0276
2-CP	−0.5854	−0.1840	0.4013	−6.4930	−3.6051	0.4534	7.4405
4-CP	−0.5793	−0.2127	0.3666	10.1644	1.5146	−1.7737	10.4286
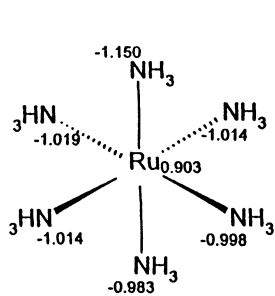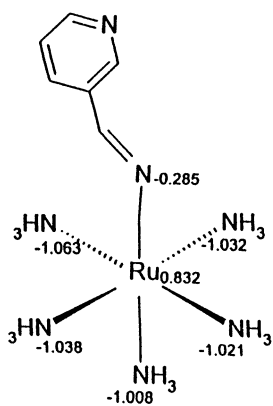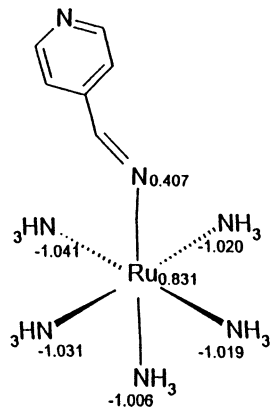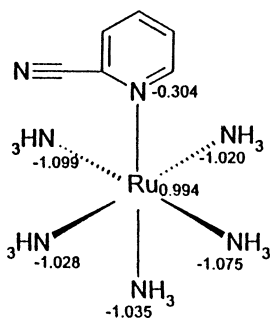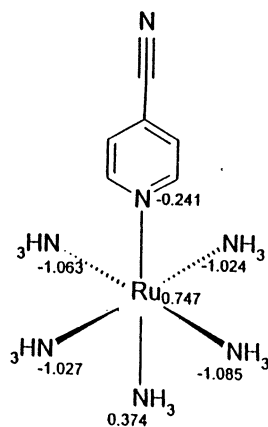
Fig. 2. Group arrangments and net charges for $[Ru(NH_3)_5X]^{2+}$ complexes.

Table 4
The relative stabilities of the studied Ru(II) pentaarnine cyanopyridine complexes

| R(II) complex | Total energy (a.u.) | | Energy difference (ΔE) | |
| | Pyridine nitrogen | Nitrile nitrogen | Between nitrile and pyridine sites | |
			a.u	KJ/mol
2-CP	−711.71447	−711.6874	0.027	70.85
3-CP	−711.71235	−711.68353	0.029	76.10
4-CP	−711.70504	−711.46606	0.238	624.55

in the electronic behaviour of the hexaamine and the pentaaminepyridine complexes (Table 3).

The electronic configuration of Ru(II) in the pentaaminepyridine complex is $p^{6.16}d^{6.97}s^{0.29}$. Comparison with the electronic configuration of the hexaamine complex reveals that a slight increase of electron population of the p and d orbitals has occurred. This increase (mainly in the $p\pi$ and $d\pi$ type orbitals) is most probably due to the back π donation from the pyridine moiety.

Cyanopyridine ligands have two comparable coordination sites; the pyridine nitrogen and the nitrile nitrogen. Table 4 compares the relative stabilities of the studied Ru(II) amine complexes as a function of the coordination site of the cyanopyridine. It is evident that, in all cases studied, coordination through the nitrile nitrogen atom is energetically more favorable than coordination through the corresponding pyridine nitrogen. The difference is small in case of the 2-cyanopyridine ligand (~ 71 kJ/mol) and become appreciably large for the 4-cyano derivative (~ 625 kJ/mol).

The presence of the CN group does not introduce any appreciable geometric changes around the Ru(II), yet one can trace a slight relaxation of the bond angle when the coordination site is the nitrile nitrogen atom (Table 2).

It is interesting to note that the HOMO-LUMO energy gap for all studied complexes is almost constant (~ 0.4 au) and does not show any dependence on the position of the cyano-group or the type of coordination site (Table 3). This is due to the nature of the frontier orbitals involved, which are localized to an appreciable extent on the Ru(II) and perturbed by all other coordinated nitrogen orbitals. The HOMO in all studied complex ions is not affected by the ligands and may safely be assigned as Ru(II) d-orbital. The LUMO, on the other hand, has a much higher contribution from the ligand orbitals, especially when an amine group is replaced by a pyridine or a cyanopyridine ligand.
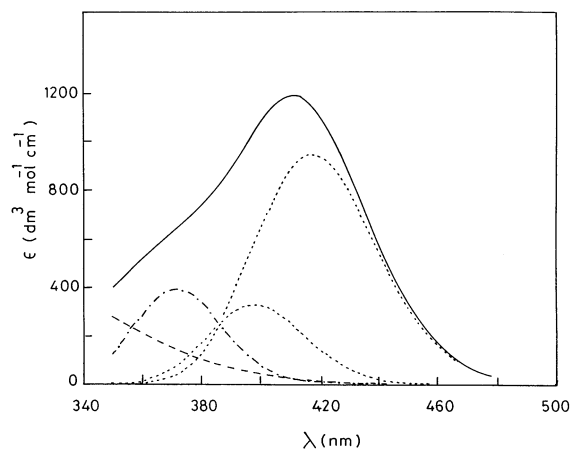

Fig. 3. Electronic absorption spectrum of 10^{-3} M solution of [Ru(NH$_3$)$_5$Py] (ClO$_4$)$_2$ in methanol and its Gaussian analysis.

Table 5
Electronic absorption characteristics of the Ru(II) pentaamine pyridine and 2-cyano pyridine complexes

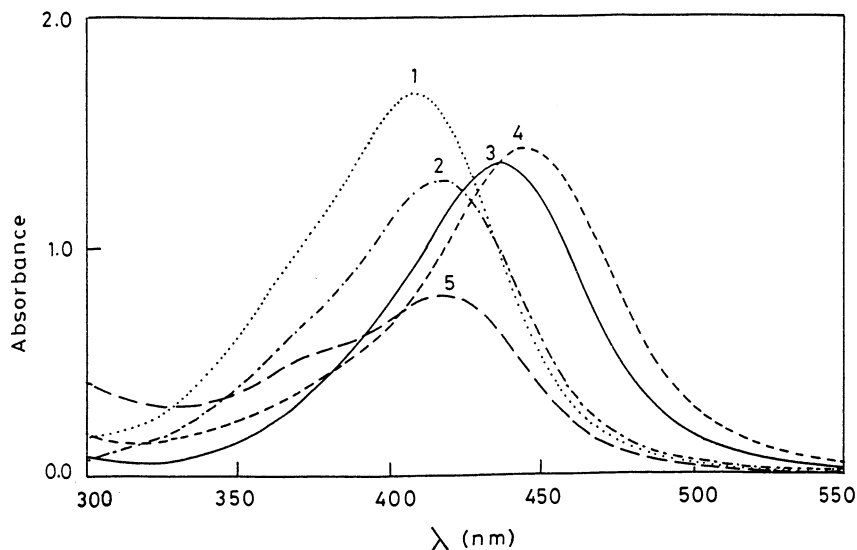| Ru(II) complex	λ_{max} (mn)	f
Py	417	0.011
	398	0.005
	371	0.001
2-CP	416	0.004
	387	0.011
	351	0.025

Fig. 4. Electronic absorption spectra of 10^{-3} M of [Ru(NH$_3$)$_5$Py] (ClO$_4$)$_2$ in: (1) acetonitrile; (2) methanol; (3) DMSO; (4) DMF; (5) acetone.

Table 6
Effect of solvent on MLCT spectra of Ru(II) pentaamine pyridine and 2-cyano pyridine complexes

	Dielectric constant	Acceptor number	Donor number	$\lambda_{\max}$ (nm)	
Solvent	ε	AN	DN	PY	2-CP
Water	78.5	54.8	18.0	407	383
Acetonitrile	38.0	18.9	14.1	408	375
Methanol	32.6	37.0	19.0	417	385
Acetone	20.7	12.5	17.0	418	387
DMSO	48.9	19.3	29.8	446	410
DMF	36.7	16.0	26.6	435	405
Piperidine	15.8	14.2	51.0	445	425
Pyridine	12.3	14.2	33.1	430	405

4.2. Electronic absorption spectra

Ruthenium(II), a low spin d^6 system can have [11] the d–d transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ apart from MLCT (metal to ligand charge transfer) and LMCT (ligand to metal charge transfer) spectra. The charge transfer bands generally [12,13] obscure the d–d bands. Low energy charge transfer bands are assigned to MLCT class and the high energy ones to LMCT. The position of the bands [14,15] are sensitive to solvent polarity. The solvatochromism (band sensitivity to solvent) of the MLCT bands of poly-pyridine carbonyl complexes [16,17] has been explained in terms of differences in the ground and excited states in both electric dipole moment and solvent polarizability. For the dicyano [17] as well as 2-N-methylformamidoyl [18] analogues, however, the solvatochromism correlates with the solvent acceptor number (AN). This was attributed to the specific acid base interactions between the ligand and solvent molecules. In general, however, several solvent parameters [19,20] can be used to correlate solvatochromic effects of transition metal complexes.
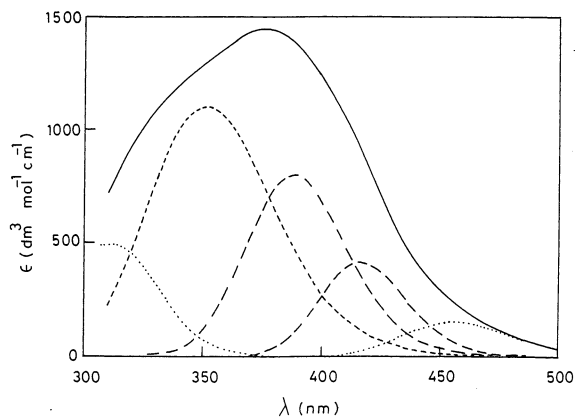
Fig. 5. Electronic absorption spectrum of 10^{-3} M of $[Ru(NH_3)_5(2\text{-}CNPy)](ClO_4)_2$ in methanol and its Gaussian analysis.

The electronic absorption spectra of Ru(II) pentaaminepyridine complex ion in methanol and its Gaussian analysis is presented in Fig. 3. The spectrum shows one main band centered at ~ 415 nm. Computer deconvolution of this envelope, with the criteria of minimum number of Gaussians reveals the presence of two further absorption bands. The low intensity band ($\lambda = 398$) may be assigned as a d–d transition localized on the Ru(II). The forbidden transitions are obscured by the more intense and broad band at ~ 417 nm. This intense band ($\varepsilon \sim 943$) can be safely assigned as a MLCT transition. The other bands appear at the short wavelength side of the spectrum and are the reason for the asymmetry of the observed envelope. The electronic characteristics of these bands are given in Table 5.

The main absorption band (~ 417 nm) which dominates the absorption profile of the Ru(II) pentaaminepyridine complex is highly solvent dependent (Fig. 4). This complex ion is polar. The present MO computations predict a dipole moment of 3.67 D (Table 3). The dipole moment is predicted to point away from the pyridine ligand. Therefore, a metal-to-ligand transition would transfer charge density from the metal to the pyridine orbitals i.e. opposite to the dipole moment vector. Hence, the excited

state would be less polar than the ground state. Increasing solvent polarity would therefore, cause a blue shift of the observed transition. This is not strictly true for the case at hand. Table 6 presents the solvent dependence of λ_{max} for the MLCT absorption band. It is clear that the aforementioned trend is followed nicely for some solvents namely, H_2O, acetonitrile, methanol and acetone. Whereas, the absorption profile of the complex in DMF, piperidine and DMSO show red shift upon increasing solvent polarity. This would suggest that there is no one solvent parameter that solely govern the behaviour of the absorption profile. Other factors such as Gutman's acceptor number (AN) and donor number (DN) seem to play important roles in determining the relative stabilities of the ground and excited states of the complex.

Fig. 5 gives the electronic absorption spectrum of Ru(II) pentaamine-2-cyanopyridine complex in methanol and its Gaussian analysis. The similarity of the spectra of the pyridine and the 2-cyano pyridine complexes is striking. This is supported by the results of the MO computations which show that introduction of the nitrile group does not introduce dramatic changes in geometry or in charge density distributions. The MLCT band in the 2-cyanopyridine complex shows exactly the same solvent dependence as that discussed before for the pyridine complex. Results of the present work rule out the possibility of solvent–ligand exchange previously suggested [2].

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