Inorganica Chimica Acta, 174 (1990) 257–262

An EPR Study of some Copper(II) Coordination Compounds of Substituted Biguanides. Part IV

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(Received October 2, 1989; revised March 12, 1990)

Abstract

EPR and optical absorption spectra of some bis(substituted biguanide)copper(II) bases and their corresponding chloride salts have been measured both in the solid state and in aqueous media in order to obtain information concerning the structure and nature of the bonding between the central metal atom and the ligands. Powder spectra of all copper(II) complexes provided approximate g values. In aqueous media and in nickel(II) complex matrix all the copper(II) complexes exhibited nine nitrogen superfine lines on the high field $\frac{3}{2} \leftrightarrow \frac{3}{2}$ copper hyperfine splitting components, indicating the presence of four equivalent or nearly equivalent nitrogen atoms surrounding the copper(II) ion. The evaluation of covalency parameters indicated that the unpaired electron of the copper(II) ion spends about 35–37% of its time in the nitrogen donor sites of the biguanides. The hyperfine structure of the compounds further revealed the interaction between the unpaired electron of the copper(II) ion with four equivalent nitrogen nuclei of the title ligands. The degree of covalence of the σ-bond calculated by the hyperfine splitting is consistent with that obtained by the hyperfine structure of the copper(II) ion. α'^2 values indicated that, like other strong field ligands (biguanides, β-phthalocyanine and tetraphenylporphine), substituted biguanides and their protonated forms are equally strong field in character and suggest the formation of an [CuN_4] chromophore.

Introduction

During the last quarter-century a considerable amount of work has been carried out on the chemistry of biguanides (I), which show the following properties.

1. They behave as bases, acids or zwitterions, which enhances their chelating ability as evidenced by the numerous colored chelate compounds formed with various transition metals [1–5].
2. These ligands have high crystal field strength and show a strong preference for square coordination, e.g. $[Ni(bigH)_2]^{2+}$ and $[Cu(bigH)_2]^{2+}$ exhibit square geometry and are more stable by about two orders of magnitude than the corresponding complexes with the reference ligand ethylenediamine [1, 6–10].
3. They stabilize a large number of unusual oxidation states of metal ions such as cobalt(I), nickel(III), nickel(IV), manganese(IV), silver(III), gold(III), molybdenum(III) etc. and yield metal complexes with very high formation constants [1, 4, 11–13].
4. Metal–biguanide complexes show aromaticity although the free ligands do not possess such properties [1, 9, 14].
5. Recent studies of the reaction kinetics and chromatography of these metal complexes are very interesting [1, 15–21].
6. The spectra of some of these metal complexes have already created a puzzling problem because while they closely parallel each other in the visible region of the circular dichroism spectrum, they display opposite signs in the UV spectral region [7, 22–24].
7. The role of biguanides as germicidal, bacteriostatic, hypoglycemic and anticarcinogenic agents is well documented. In living systems, biguanide is known to undergo cyclization to form triazine, which is an active antimalarial drug [25–31].
8. Thermodynamic aspects of the interaction of biguanide with aqueous protons reveal that the protonated base molecules are more rigid, resulting in unusually low and even negative entropy changes [3].
9. Recent EPR and X-ray studies of tetracoordinate square planar copper(II) complexes indicate imine coordination of the ligand to the copper(II) ion (**IIa**, **IIb**) rather than amine coordination (**III**) [32–37].

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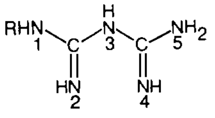
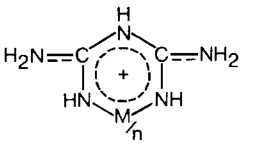
10. The structure of these compounds has been the subject of considerable speculation and debate. The older views favored the presence of a quaternary nitrogen atom in $[Cr(bigH)_3]Cl_3$ with a total cationic charge of +1 [38]. However, N(1s) photoelectron spectral data show the total cationic charge of the same complex to be at least +2 [39]. With the lowest value of the chemical shift between $-NH_2$ and $-NH_3$, i.e. 1.6 eV, and with the separation of 1.5 eV as obtained from the spectrum of $[Cr(bigH)_3]^{3+}$, one would expect a spectrum with a full-width-half maximum (FWHM) of 3.8 eV, which is broader by at least 0.9 eV than any spectra obtained for biguanide complexes. It therefore excludes the possibility of the presence of a quaternary nitrogen atom in the complex. The extensive π-electron delocalization in biguanide complexes postulated by Sen [14] is consistent with this interpretation. Because the charge is not localized on any particular nitrogen atoms, one can only conclude that it is delocalized over the entire ligand (**IIa, IIb**). In addition to the above studies, NMR data further indicated the absence of a quaternary nitrogen atom in $[Ni(bigH)_2]Cl_2$.

Considering all the above mentioned studies, it appears to us that the problem of the structures of metal–biguanide complexes is yet to be solved. In view of the significant importance of biguanides in many biological systems which may serve as good models for molecules of biological interest containing copper in which it achieves this planar coordination, we became very interested in this problem.



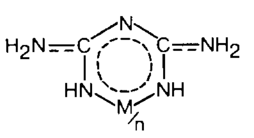
I

Biguanide, R = H; substituted biguanide, R = CH_3, C_2H_5, C_3H_7, C_6H_5, etc.



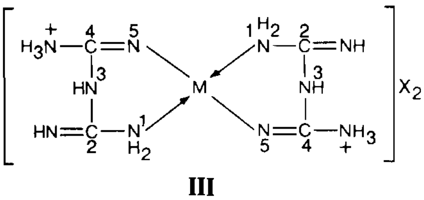
IIa

Charged metal biguanide complex



IIb

Neutral metal biguanide complex



III

Structure of bis(biguanide)metal(II) halides (M(II) = Cu(II) or Ni(II); X = Cl, Br, or I)

EPR studies provide useful information about metal–ligand interactions, and the spin-Hamiltonian parameters obtained from such studies provide an understanding of the nature of the bonding in coordination compounds. As the nature of the bonding in metal–biguanide complexes is not completely unambiguous and as the effect of replacing the H atom attached to the N^1 atom of the biguanide molecule (**I**) by different groups has not been previously studied, we have therefore undertaken an investigation of the EPR and optical spectra of some copper(II) substituted biguanide complexes in order to establish the extent of covalency in the metal–ligand interaction and the effect of protonation on the covalency as well as to confirm the bonding sites occupied by these ligands.

Experimental

Materials

N^1-(2-Hydroxyethyl)biguanide sulfate, N^1-(2-hydroxypropyl)biguanide sulfate, N^1-(3-hydroxypropyl)biguanide sulfate, N^1-(2-methoxyethyl)biguanide sulfate, N^1-(3-methoxypropyl)biguanide sulfate and their corresponding copper(II) and nickel(II) complexes were prepared according to the literature [1, 4, 9]. Dehydration of $[Cu(ligand)_2]\cdot nH_2O$ ($n = 0.5–2.5$) and $[Ni(ligand)_2]\cdot nH_2O$ ($n = 1–2.5$) complexes was accomplished by heating the complexes under vacuum at 70 °C for 4 days. The stoichiometry of the complexes was confirmed by metal, carbon, hydrogen and nitrogen analyses.

Copper(ligand)$_2$-doped-nickel(ligand)$_2$ was prepared by adding 4% of $[Cu(ligand)_2]\cdot nH_2O$ to $[Ni(ligand)_2]\cdot nH_2O$ dispersed in 8 M aqueous NaOH solution. The mixture was stirred well for several hours, and the doped complex was collected by filtration, washed thoroughly with water and then with ethanol and finally dried under reduced pressure at room temperature.

Physical Measurements

Solution and solid-state electronic spectra were recorded on a Cary 14 spectrophotometer, and EPR spectra were obtained on a Varian V4502-12X band spectrophotometer at the Regional Sophisticated Instrument Centre, Madras and Calcutta Centres and the ESR Laboratory, I.I.T. Bombay Centre. A cylindrical quartz sample tube was used for the spectra of powdered and solution samples. A minute, powdered sample of diphenylpicrylhydrazil free radical was used as a *g* marker in a dual channel cavity, and the frequency was monitored with a frequency meter.

Results and Discussion

From a room-temperature EPR spectrum of a powdered sample of $[Cu(L_1H)_2]Cl_2$ ($L_1H = N^1$-(2-

hydroxyethyl)biguanide) approximate g values were determined [40, 41] (Fig. 1). The spectra of all other biguanide complexes under the same conditions gave similar spectra with $g_{\parallel} = 2.194$ and $g_{\perp} = 2.09$. The parameters $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}^{\text{Cu}}$ and $A_{\perp}^{\text{Cu}}$ were also measured from anisotropic spectra of powdered, magnetically dilute solids [42] (Fig. 2) (Table 1). These were calculated following Vanngard and Aasa's [42] equations; g_{av} and A_{av} were measured from standard relations [43, 44]:

$$g_{\text{av}} = (g_{\parallel} + 2g_{\perp})/3; \qquad A_{\text{av}} = (A_{\parallel} + 2A_{\perp})/3$$

The anisotropic spectra of the magnetically dilute powders gave no indication of more than two g values. Kivelson and Neiman [45] have pointed out that compounds having $g_{\parallel} \geqslant 2.3$ are ionic compounds, whereas those with $g_{\parallel} < 2.3$ are covalent in character. The g values of the present complexes fulfill the latter criterion.

Average or isotropic g values (g_0), isotropic hyperfine structure constants (A_0^{Cu}) and isotropic ligand hyperfine structure constants (A_0^{N}) were computed from solution spectra (Fig. 3). All the complexes show nine nitrogen superfine components. This super hyperfine structure is attributed to the interaction of the copper unpaired electron with the nuclear spins of the atoms by which the ligand molecules are bonded. The spectra further reveal that low $g_{\parallel}$ and large $A_{\parallel}$ values for the complexes studied appear to be characteristic of all complexes containing the equivalent [CuN_4] chromophore. It may be mentioned here that bis(substituted biguanide)copper(II) salts show typical absorption bands at about 20 410 cm^{-1} in the solid and 19 230 cm^{-1} in aqueous media, which indicates the presence of a square planar [CuN_4] chromophore. Other square planar [CuN_4] chromophores appear in bis(1-amidino-*O*-alkylurea)-copper(II) (18 500–18 800 cm^{-1}), tetrakis(benzimidazole)copper(II) (19 000 cm^{-1} in the solid), bis(biguanide)copper(II) (19 230 cm^{-1} in water and

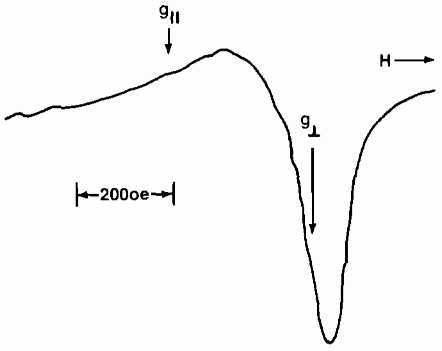


Fig. 1. Room temperature EPR spectrum of powdered [$Cu(2\text{-hydroxyethylbiguanide})_2$]. Frequency 9.474 kMc. $g_{\parallel} = 2.194$; $g_{\perp} = 2.09$.

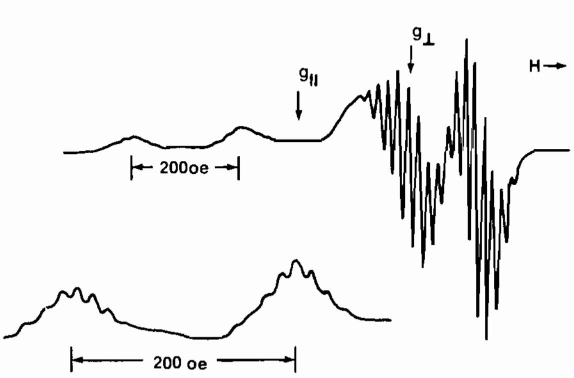


Fig. 2. EPR spectrum of [$Cu(2\text{-hydroxyethyl})\text{biguanide})_2$]$Cl_2$ in [$Ni(2\text{-hydroxyethylbiguanide})_2$]$Cl_2$ polycrystalline sample. In the lower left hand side of the figure the lowfield $A_{\parallel}^{\text{Cu}}$ hyperfine components are shown enlarged by a factor of 10. Frequency 9.518 kMc.

TABLE 1. g Values and hyperfine structure constants[a] for copper(II) complexes

Complex[b]	Medium	g_0	g_{av}	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}^{\text{Cu}}$	$A_{\perp}^{\text{Cu}}$	A_0^{Cu}	A_0^{N}
[$Cu(L_1)_2$]	Ni(II) complex		2.096	2.170	2.059	208	23		15.8
	water	2.099						85.9	15.7
[$Cu(L_1H)_2$]Cl_2	Ni(II) complex		2.099	2.176	2.061	207	22		15.7
	water	2.101						86.1	15.9
[$Cu(L_2)_2$]	Ni(II) complex		2.095	2.173	2.057	209	24		16.0
	water	2.101						86.2	15.9
[$Cu(L_3)_2$]	Ni(II) complex		2.098	2.174	2.061	204	20		15.4
	water	2.101						85.6	15.3
[$Cu(L_4)_2$]	Ni(II) complex		2.098	2.173	2.063	203	19		15.3
	water	2.099						85.6	15.2
[$Cu(L_5)_2$]	Ni(II) complex		2.098	2.173	2.061	203	19		15.3
	water	2.099						85.7	15.9
[$Cu(L_5H)_2$]Cl_2	Ni(II) complex		2.09	2.168	2.058	210	25		16.0
	water	2.098						86.1	15.9

[a] Values × 10^4 cm^{-1}. [b] L_1H = N^1-(2-hydroxyethyl)biguanide; L_2H = N^1-(2-hydroxypropyl)biguanide; L_3H = N^1-(3-hydroxypropyl)biguanide; L_4H = N^1-(2-methoxyethyl)biguanide; L_5H = N^1-(3-methoxypropyl)biguanide.

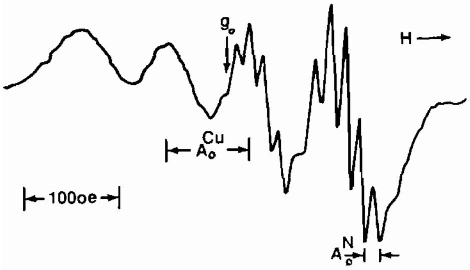


Fig. 3. Aqueous solution EPR spectrum of [Cu(2-hydroxyethylbiguanide)$_2$]Cl$_2$. Frequency 9.421 kMc.

20410 cm^{-1} in the solid) and bis(phenylbiguanide)-copper(II) (18 200 cm^{-1} in water) [46–51].

In view of the results and the square planar geometry suggested by the electronic spectra and X-ray studies [8, 9, 35, 37, 52], it may be assumed that the copper(II) ion in these complexes is in a tetragonal field (D_{4h} symmetry). With this in view, the following antibonding wave functions are used [45, 53–55]:

$$\psi B_{1g} = \alpha d_{x^2-y^2} - \alpha'(-\sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)})/2$$

$$\psi B_{2g} = \beta_1 d_{xy} - \beta_1'(p_y^{(1)} + p_x^{(2)} - p_y^{(3)} - p_x^{(4)})/2$$

$$\psi A_{1g} = \alpha_1 d_{z^2} - \alpha_1'(\sigma_x^{(1)} + \sigma_y^{(2)} - \sigma_x^{(3)} - \sigma_y^{(4)})/2$$

$$\psi E_{1g} = \begin{cases} \beta d_{xz} - \beta'(p_z^{(1)} - p_z^{(3)})/2^{1/2} \\ \beta d_{yz} - \beta'(p_z^{(2)} - p_z^{(4)})/2^{1/2} \end{cases}$$

where $\sigma^{(i)} = np^{(i)} \mp (1 - n^2)^{1/2} S^{(i)}$.

Here $0 \leqslant n \leqslant 1$, where the notation is that of Kivelson and Neiman [45]. The B_{1g}, B_{2g} and E_g states represent in-plane σ-bonding, in-plane π-bonding and out-of-plane π-bonding, respectively. The A_{1g} state does not affect the magnetic properties. α, α_1, α' and α_1' are the σ-bonding parameters, and β, β_1, β' and β_1' are the π-bonding parameters. The smaller the value of the coefficients α, α_1, β and β_1, the more covalent the bonding of the type associated with each parameter [44]. The ligand orbitals involved in the in-plane σ-bonding are considered to be sp^2 hybrid orbitals [56]. Overlap is included for the function describing in-plane σ-bonding, $\alpha^2 - 2\alpha\alpha' S + \alpha'^2 = 1$, where S (= −0.093) is the overlap integral between the copper $d_{x^2-y^2}$ orbital and the ligand orbital [45]. The coefficients α, β_1 and β, which express the covalent character of the σ-bonding and the in-plane and out-of-plane π-bonding, respectively, may be determined from the relations which connect them with spin-Hamiltonian parameters for axial symmetry [57–59], where

$$g_\parallel - 2.0023 = \frac{-8\lambda_0\alpha\beta_1}{\Delta E_{xy}} \times \{\alpha\beta_1 - \alpha'\beta_1 S - \alpha'(1 - \beta_1^2)^{1/2} T(n)/2\} \tag{1}$$

$$g_\perp - 2.0023 = -\frac{2\lambda_0\alpha\beta}{\Delta E_{xz}} \{\alpha\beta - \alpha'\beta S - \alpha'(1 - \beta^2)^{1/2} T(n)/2^{1/2}\} \tag{2}$$

$$A_\parallel = P\left[-\alpha^2\left(\frac{4}{7} + k_0\right) + (g_\parallel - 2) + \frac{3}{7}(g_\perp - 2) - \frac{8\lambda_0\alpha\beta_1}{\Delta E_{xy}}\{\alpha'\beta_1 S + \alpha'(1 - \beta_1^2)^{1/2} T(n)/2\} - \frac{6\lambda_0\alpha\beta}{7\Delta E_{xz}}\{\alpha'\beta S + \alpha'(1 - \beta^2)^{1/2} T(n)/2^{1/2}\}\right] \tag{3}$$

$$A_\perp = P\left[\alpha^2\left(\frac{2}{7} - k_0\right) + \frac{11}{14}(g_\perp - 2) - \frac{22\lambda_0\alpha\beta}{14\Delta E_{xz}}\{\alpha'\beta S + \alpha'(1 - \beta^2)^{1/2} T(n)/2^{1/2}\}\right] \tag{4}$$

H is the applied field; β_0 is the Bohr magneton; $T(n) = 0.333$ [45], $P = -0.036$ cm^{-1}; λ_0 (= −828 cm^{-1}) is the spin–orbit coupling constant for the copper(II) ion; and k_0 (= 0.43 ± 0.02) is the Fermi contact term for the copper(II) ion [58, 60]. ΔE_{xy} and ΔE_{xz} are the electronic transition energies of ${}^2B_{2g} \leftarrow {}^2B_{1g}$ and ${}^2E_g \leftarrow {}^2B_{1g}$, respectively. α and α' are obtained using the nitrogen superfine splitting. Because the electrons in the B_{1g} orbitals give rise to the σ-bonding of the central ion with the ligands, the electrons on the B_{2g} orbitals – the in-plane π-bonding – and those on the E_g orbital – the out-of-plane π-bonding, the coefficients α^2, β_1^2 and β^2 express the covalent character of the σ-bonding, the in-plane π-bonding and the out-of-plane π-bonding, respectively. The larger the square of α', β', α_1' and β', the more covalent the bonding of the type associated with each parameter [61]. The smaller the square of the coefficients α, α_1, β and β_1 the more covalent is the bonding.

Hathaway and others [62–65] determined the orbital reduction factors (k, $k_\parallel$, $k_\perp$), which are a measure of covalency, and the G value, following the expressions:

$$k_\perp^2 = (g_\perp - 2.002)\,\Delta E_{xz}/2\lambda_0$$

$$k_\parallel^2 = (g_\parallel - 2.002)\,\Delta E_{xy}/8\lambda_0$$

$$k^2 = \tfrac{1}{3}(k_\parallel^2 + 2k_\perp^2)$$

$$G = \frac{(g_\parallel - 2.002)}{(g_\perp - 2.002)} = \frac{4k_\parallel^2 \Delta E_{xz}}{k_\perp^2 \Delta E_{xy}}$$

TABLE 2. Orbital reduction factors and covalency parameters

Complex	Medium	G	$k_\parallel^2$	$k_\perp^2$	k	$\alpha_N'^2$	α_N^2	α_{Cu}^2	β_1^2	β^2	ΔE_{xy} [a]	ΔE_{xz} [a]
$[Cu(L_1)_2]$	Ni(II) complex	2.94	0.51	0.80	0.83	0.36	0.72	0.81	0.72	1.12	20.420	23.410
	water					0.36	0.72		0.68	1.05	19.235	22.010
$[Cu(L_1H)_2]Cl_2$	Ni(II) complex	2.94	0.53	0.83	0.85	0.37	0.72	0.81	0.74	1.15	20.410	23.400
	water					0.37	0.72		0.70	1.08	19.230	22.000
$[Cu(L_2)_2]$	Ni(II) complex	3.11	0.52	0.78	0.83	0.35	0.69	0.81	0.76	1.12	20.400	23.400
	water					0.35	0.71		0.71	1.06	19.240	22.020
$[Cu(L_3)_2]$	Ni(II) complex	2.91	0.53	0.83	0.85	0.35	0.69	0.80	0.76	1.20	20.410	23.440
	water					0.35	0.69		0.71	1.06	19.230	22.000
$[Cu(L_4)_2]$	Ni(II) complex	2.89	0.52	0.83	0.85	0.35	0.69	0.80	0.75	1.20	20.400	23.400
	water					0.35	0.69		0.71	1.06	19.230	22.000
$[Cu(L_5)_2]$	Ni(II) complex	2.89	0.52	0.83	0.85	0.35	0.69	0.80	0.75	1.20	20.415	20.450
$[Cu(L_5H)_2]Cl_2$	Ni(II) complex	2.96	0.51	0.77	0.82	0.35	0.69	0.81	0.73	1.14	20.400	23.400
	water					0.35	0.69		0.70	1.07	19.230	22.000

[a] Values × 10^3 cm^{-1}.

For an ionic environment $k = 1$, and for a covalent environment k is less than 1. The lower the value of k, the greater the covalent character. The low values of k (0.82–0.85) of the complexes studied are indicative of their covalent nature. Because the G values are less than 4 (Table 2), the ligands are strong field in character [1, 6, 8, 9, 32].

The σ-bonding parameter $\alpha_N'^2$ was calculated from A_0^N and used to calculate α_N^2 with the help of normalization conditions of the B_{1g} orbital,

$$\alpha^2 - 2\alpha\alpha' S + \alpha'^2 = 1$$

where S is the overlap integral,

$$S = \langle d_{x^2-y^2} | - \sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)} \rangle / 2$$
$$= 2\langle d_{x^2-y^2} | - \sigma_x^{(1)} \rangle$$

On calculation, $S = 0.093$ [45]. $\alpha_N'^2$ (= 0.35–37) indicates that the unpaired electron spends about 35–37% of its time in the nitrogen donor sites of the biguanide ligands. The $\alpha_N'^2$ values (roughly the measure of the extent of electron delocalization) show that both biguanide and substituted biguanide anions and their protonated forms are strong field ligands and lie slightly below the CN^- ion in the spectrochemical series (Table 2).

The in-plane σ-covalency parameter, α_{Cu}^2, was calculated using the expression given by Kivelson and Neiman [45]

$$\alpha_{Cu}^2 = -\left(\frac{A_\parallel}{0.036}\right) + (g_\parallel - 2.002) + \frac{3}{7}(g_\perp - 2.002) + 0.04 \qquad (5)$$

and compared (Table 2) with α^2 evaluated from the overlap expression given above and α'^2 obtained from the nitrogen superfine splitting.

The α_{Cu}^2 values (0.80–0.81) account for the fraction of the unpaired electron density on the copper(II) ion. The α_N^2 values calculated from the nitrogen superfine splittings are generally low in comparison to the analogous α_{Cu}^2 values. Such a discrepancy may be explained in terms of the variation of the copper 4s-electron density, which is considered to be constant in eqn. (5) [66]. The reported α_{Cu}^2 values of the copper(II) β-phthalocyanine and tetraphenylporphine complexes are 0.80 and 0.82 [66, 67].

The in-plane and out-of-plane π-bonding parameters β_1 and β are obtained from the expressions (1) and (2). In view of the fact that the electronic absorption spectra in aqueous media consist of one very broad band, we cannot unambiguously assign values to ΔE_{xy} and ΔE_{xz}. For the purpose of calculation we have assumed that the maximum in the band corresponds to ΔE_{xy} and that ΔE_{xz} can be taken from the wavelength of the band, at one half the intensity of the maximum, on the high energy side of the band. The uncertainty involved in the assignment of ΔE_{xz} and $g_\perp$ as obtained from polycrystalline samples usually precludes a reliable estimate of the out-of-plane π-bonding parameter β^2 [42]. However, in cases where values of ΔE_{xz} are not known accurately, a 20% error in ΔE_{xz} values results in only about a 5% error in β. Similarly, $\beta_1^2 = 1$ indicates total ionic character, and $\beta_1^2 = 0.5$ indicates a total covalent character of the in-plane π-bonding [45]. The complexes studied show $\beta_1^2 = 1.05$–1.20, indicating a pronounced covalent in-plane π-bonding.

Acknowledgements

The senior author (R.K.R.) wishes to thank Professor H. Yoneda, Department of Chemistry, Hiroshima University, Japan and Dr Peter Hubberstey, Department of Chemistry, University of Nottingham, U.K. for providing some research facilities. He is also indebted to Professor N. Basu Majumder, Rahara P.G.B.T. College, for technical assistance.

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