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An EPR Study of Copper(II)-substituted Biguanide Complexes. Part III*

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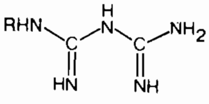
Abstract

The EPR and optical spectra of bis(diethylbiguanide)copper(II) base and its salts and mono(diethylbiguanide)copper(II) salts have been measured both in the solid state and in *N*,*N*-dimethylformamide (DMF) in order to elucidate the structure and nature of the bonding between the central metal atom and the ligand. From the spectral data the degree of covalency of σ- and π-bonds of the copper(II) ion with the nitrogen atoms of the ligands have been calculated. The σ-bonds present a moderate degree of covalence while the in-plane π-bonds possess a strong covalent character. The covalency of the biguanide complexes is attributed to the strong σ-interaction of the copper(II) ion with deprotonated imino ligand bonding sites and electron delocalization over the chelate ring. The superfine structure of some compounds may be ascribed to the interaction of the unpaired electron of the copper(II) ion with four equivalent or nearly equivalent nitrogen atoms of the ligands. The general properties of the complexes studied, which contain the equivalent CuN_4^{2-} chromophore, are summarized.

Introduction

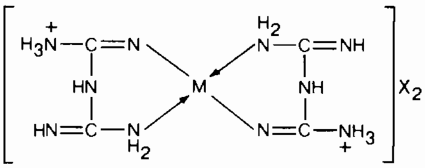
Coordinated biguanides (**1**) show a residual basicity which accounts for the large number of complex compounds of characteristic colors and specific geometry [1–3]. On treatment of the complex base with ammonium chloride evolution of ammonia takes place and cationic complex salts are formed, showing that at least one of the amino groups of the ligand remains free even after metal chelate formation [1].



1

Biguanide, R = H; substituted biguanide, R = alkyl or aryl group

The pink to reddish coloration of bis(biguanide)copper(II) complexes arises from the strong ligand field character of biguanide in the $[CuN_4]^{2-}$ chromophore [4–6] (2^- indicates the strong σ-bonding nitrogen atoms of the deprotonated ligands). Such a formidable character of the biguanides may also be manifested by their yellow, diamagnetic, square planar nickel(II) complexes and low-spin cobalt(II) complexes [1–3]. Although various metal(II) biguanide structures have been proposed. Râу and Saha's suggested structure 2 was considered reasonable [1]. They proposed that the metal replaces the hydrogen of the terminal imino group and that the nitrogen atom on the other terminal amino group donates a lone pair of electrons to the metal atom to form a coordinate bond. Structure 2 favors the presence of quaternary nitrogen atoms [1–3], yet it has several limitations [2, 3].



2

Bis(biguanide)metal(II) halides [M(II) = Cu(II), Ni(II); X = Cl, Br, or I]

From UV absorption studies Sen [7] suggested two structures: **3a** for the charged, metal(II) complex and **3b** for the uncharged metal(II) complex.

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*Dedicated to Professor R. L. Dutta, Department of Chemistry, Burdwan University, Burdwan, India, on the occasion of his 60th birthday.

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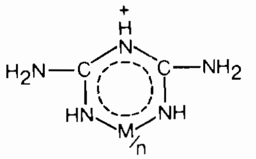
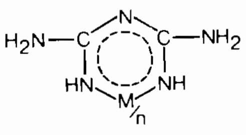


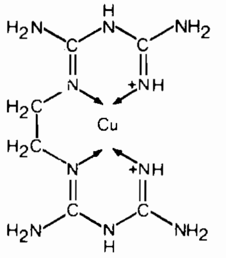
3a



3b

Charged metal complex (**3a**); uncharged metal complex (**3b**)

Kunchur and Mathew [8, 9], from a single-crystal X-ray study, confirmed Rây and Saha's structure 2 for a substituted biguanide complex, ethylenedibiguanide copper(II) chloride monohydrate, [CuEn(bigH)$_2$]Cl$_2$·H$_2$O (**4**). On the other hand, Creitz *et al.* [10], on the basis of ^{1}H NMR and X-ray diffraction studies, established structure **5** for anhydrous bis(biguanide)nickel(II) and bis(biguanide)nickel(II) chloride dihydrate. It is interesting to note that the X-ray studies of Creitz *et al.* [10] are quite different from those of Kunchur and Mathew (4) [8, 9]. Furthermore, the presence of a quaternary nitrogen atom in the complexes, as proposed by Rây and Saha, is questionable. We therefore became interested in the structure of copper(II)–biguanide complexes and hoped that some clues might emerge from EPR studies.



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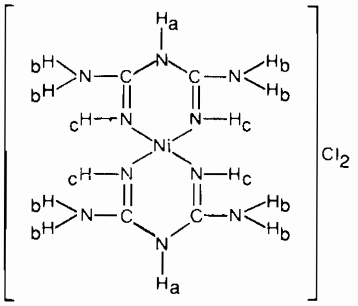

5

Bis(biguanide)nickel(II) chloride

The C–N bond distances of [Ni(bigH)$_2$]Cl$_2$ are the same length and do not differ much from those found in [CuEn(bigH)$_2$]Cl$_2$. Although structure 2 requires different bond orders for the various C–N bonds, their identical bond lengths indicate that all the nitrogen atoms have p_π-orbitals containing electrons that result in considerable delocalization of the π-system [10]. The crystal structure of [NiEn(bigH)$_2$]Cl$_2$·H$_2$O, isostructural with [CuEn(bigH)$_2$]Cl$_2$·H$_2$O, was determined by two different schools [11, 12]. Ethylenedibiguanide, En(bigH)$_2$, being a quadridentate ligand wrapping itself around the central nickel atom, forms a square planar array of Ni–N bonds. Through extensive hydrogen bonding involving the water of hydration and the two chloride ions, the molecules form infinite sheets parallel to the (100) planes. Additional hydrogen bonding between the sheets creates a rigidly bonded structure. Despite the double bond character in the C–N bonds, many of the hydrogen atoms are displaced appreciably from the plane of the cation toward the hydrogen bond acceptors, and the bonding about the nitrogen atoms thus becomes pyramidal.

Rây and Saha's [13] early structure for tris(biguanide)chromium(III) chloride has a total charge of +1. However, X-ray photoelectron spectroscopy indicates that it should be at least +2 [14]. With the lowest value of the chemical shift between $-NH_2$ and $-\overset{\oplus}{N}H_3$, i.e., 1.6 eV [14, 15], and with the separation of 1.5 eV as obtained from the spectrum of [Cr(bigH)$_3$]Cl$_3$, one would expect a spectrum with a full-width-half-maximum of 3.8 eV, which is broader by at least 0.9 eV than any spectra obtained for biguanide complexes. It thus excludes the possibility of the presence of a quaternary nitrogen atom in the complex molecule. Therefore the extensive π-electron delocalization in biguanide complexes by Sen [7] is consistent with this interpretation.

Recent crystallographic reports on metal(II)/metal(III)–biguanide complexes are very interesting [16–22]. Because the structure of metal–biguanide compounds is a subject of considerable speculation and an interesting, challenging, and controversial topic, we therefore became interested in the structure of copper(II)–biguanide complexes in the hope that some clues as to their structure might emerge from EPR studies. Moreover, the present study appears very interesting to us as it may serve as a good model for planar copper-containing molecules of biological interest.

Experimental

The red or red–violet crystals of bis(diethylbiguanide)copper(II) base and its corresponding salts such as the chloride, bromide and nitrate were prepared according to the procedure of Rây [1]. The corresponding mono(diethylbiguanide)copper(II) salts, [Cu(LH)X$_2$] (where LH = N',N'-diethylbiguanide and $X^- = Cl^-, Br^-, NO_3^-$, or N_3^-) were obtained in an alcoholic medium at pH ~5.0 as blue powders. The compounds are sparingly soluble in methanol, ethanol, acetone, but more soluble in DMF.

The electronic spectra were recorded with a Cary 14 spectrophotometer (Table 1). EPR spectra at room temperature and at liquid nitrogen temperature were obtained from the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras, the ESR Laboratory, I.I.T. Bombay, and the Calcutta Centre. A minute powder 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

All the compounds in magnetically nondiluted polycrystalline powder show asymmetrical EPR spectra from which the $g_\perp$ values were determined. These spectra reveal no hyperfine structure, which indicates the existence of some strong dipolar interaction between the central metal atom and the strong field molecules.

In solution at room temperature EPR spectra show a hyperfine structure with four components corresponding to the interaction of the unpaired copper electron with the nuclear spins of ^{63}Cu and ^{65}Cu, both of which have $I = 3/2$ (Fig. 1). No resolution of the splittings on ^{63}Cu and ^{65}Cu was noted, perhaps because of the line broadening, which may mask each line with respect to the others. From the solution spectra at room temperature the isotropic spectrochemical splitting factor (g_0), hyperfine structure constant ($A_0{}^{Cu}$), and isotropic ligand hyperfine structure constant ($A_0{}^{N}$) were determined. This ligand hyperfine structure is attributed to the interaction of the unpaired electron of the copper(II) atom with the nuclear spins of the nitrogen atoms from the ligand molecules. The analysis of this hyperfine structure results in nine components with a splitting of ~17 G and an intensity ratio very close to 1:4:10:16:19:16:10:4:1 (Fig. 2).

TABLE 1. Electronic absorption spectra[a]

Compound	State	ΔE_{xy} (cm^{-1})	ΔE_{xz} (cm^{-1})
$[CuL_2]$	Nujol mull	20410	23400
	DMF	20350	23400
	CH_3OH	19620	29750
$[Cu(LH)_2]Cl_2$	Nujol mull	20410	23400
	DMF	20000	23400
	CH_3OH	19620	29760
$[Cu(LH)_2]Br_2$	Nujol mull	20410	23400
	DMF	20450	23400
	CH_3OH	19900	29760
$[Cu(LH)_2](NO_3)_2$	Nujol mull	20410	23400
	DMF	20410	23400
	CH_3OH	19610	29760
$[Cu(LH)Cl_2]$	DMF	15380	23040
	CH_3OH	15620	23810
$[Cu(LH)Br_2]$	DMF	15630	27030
	CH_3OH	15150	23260
$[Cu(LH)(NO_3)_2]$	DMF	15630	23040
	CH_3OH	15150	23810
$[Cu(LH)(N_3)_2]$	DMF	16150	27030
	CH_3OH	16130	27170

[a] LH = N',N'-diethylbiguanide; DMF = N,N-dimethylformamide.

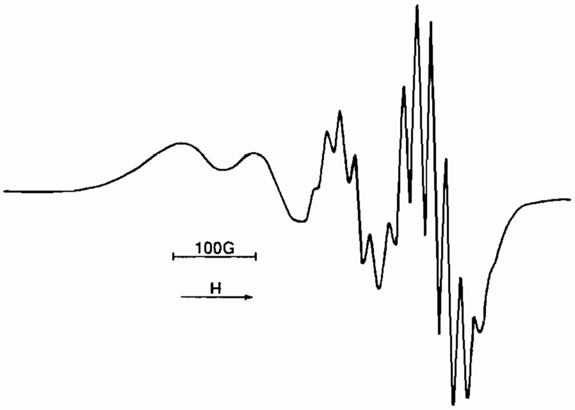

Fig. 1. Room temperature EPR spectrum of the $[CuL_2]$ complex in DMF.

The EPR spectra of frozen solution (77 K) provided two sets of superfine lines which correspond to $g_\parallel$ and $g_\perp$ tensors (Fig. 3). From these spectra the $g_\parallel$ and $A_\parallel$ values have been accurately deter-

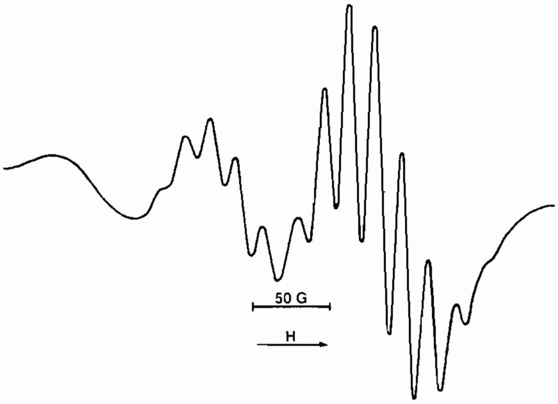

Fig. 2. Superfine structure from nitrogen atoms on the component of hyperfine structure located at high frequency field for the $[CuL_2]$ complex in DMF at room temperature.

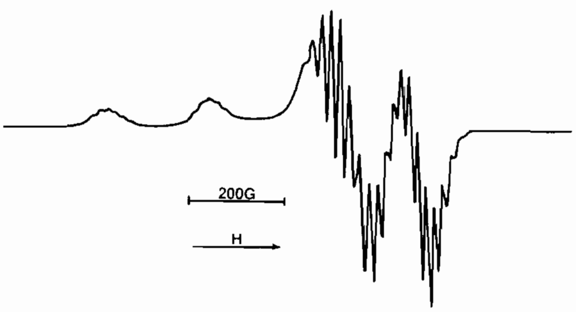

Fig. 3. EPR spectrum of the $[CuL_2]$ complex in DMF at 77 K.

mined. Inasmuch as the hyperfine structure corresponding to $g_\perp$ is not resolved, $A_\perp$ being much smaller than $A_\parallel$, the $g_\perp$ and $A_\perp$ values were obtained by using the standard relationships [23, 24]

$$g_0 = \frac{g_\parallel + 2g_\perp}{3} \quad \text{and} \quad A_0 = \frac{A_\parallel + 2A_\perp}{3}$$

These spectra also show a superhyperfine structure, generally observed on the hyperfine components situated at high fields corresponding to $g_\parallel$. The superfine structure of $[Cu(LH)_2]X_2$ (where LH = N',N'-diethylbiguanide; X = OH or Cl) is noted on the low-field components with $m = 3/2$ and $1/2$ corresponding to $g_\perp$ (Fig. 3), and on analysis of the superfine structure nine components were found, corresponding to the interaction of four equivalent nitrogen nuclei with a A_0^N splitting of about 17 G. The hyperfine structure corresponding to $g_\perp$ is difficult to analyze because of the overlap with the components of hyperfine and superfine structure situated at the high field of $g_\parallel$ (Fig. 3).

Frozen solutions of mono(biguanide)copper(II) compounds of the type $[Cu(LH)X_2]$ (X = Cl, NO_3, or N_3) show well resolved hyperfine structure, which corresponds to $g_\parallel$. The corresponding $g_\perp$ is not well resolved and overlaps the component situated at high field with $m = -3/2$ of $g_\parallel$.

The spin-Hamiltonian for copper(II) ion in a tetragonal crystal field [25] is given by

$$\mathcal{H} = g_\parallel \beta H_z S_z + g_\perp \beta (H_x S_x + H_y S_y) + A_\parallel^{Cu} I_z S_z + A_\perp^{Cu} (I_x S_x + I_y S_y)$$

where β is the Bohr magneton and H is the applied magnetic field. When the ligand superfine structure is present, an additional term of the general form $+ S\Sigma A_n I_n$ is necessary. Here S is the total spin operator, A_n is the superfine structure tensor for the n ligand atoms, and I_n is the ligand atom nuclear spin. The spin-Hamiltonian parameters of mono(diethylbiguanide)copper(II) and bis(diethylbiguanide)copper(II) complexes are presented in Table 2.

The EPR spectra of the base compound and its corresponding salts in solution (DMF) exhibit nine nitrogen superfine lines on the high field $3/2 \leftrightarrow 3/2$ copper hyperfine splitting component, indicating four equivalent or nearly equivalent nitrogen atoms surrounding the copper(II) ion. At liquid nitrogen temperature the anisotropic spectra provide two g values. In view of these reported results and planar geometry suggested by X-ray reports [8, 9] and electronic spectra (Table 1), an effective D_{4h} symmetry is assumed for the base compound and its salts. The ground-state wave function in the usual LCAO-MO model [26–32] is

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

Other appropriate antibonding wave functions are

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

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

TABLE 2. g Values and hyperfine structure constants for copper(II) complexes in DMF[a]

Complex	g_0	$g_\parallel$	$g_\perp$	A_0^{Cu} (G)	$A_\parallel^{Cu}$ (G)	$A_\perp^{Cu}$ (G)	A_0^N (G)
$[CuL_2]$	2.090	2.150	2.060	96	218	35	16.9
$[Cu(LH)_2]Cl_2$	2.109	2.175	2.076	89	211	28	16.0
$[Cu(LH)_2]Br_2$	2.098	2.185	2.05	91	213	30	15.7
$[Cu(LH)_2](NO_3)_2$	2.097	2.179	2.056	89	208	29.5	15.8
$[Cu(LH)Cl_2]$	2.119	2.253	2.052	76	174	27	17.6
$[Cu(LH)Br_2]$	2.118	2.269	2.042	75	173	26	17.5
$[Cu(LH)(NO_3)_2]$	2.121	2.259	2.052	76	181	23.5	15.9
$[Cu(LH)(N_3)_2]$	2.103	2.220	2.044	83	188	30.5	16.1
$[Cu(AMU)_2]$[b]	2.091			92.5			15.7
$[Cu(AEUH)_2](NO_3)_2$	2.108			86.2			14.9
$[Cu(AP^nU)_2]$	2.090			97.6			15.6

[a] The uncertainty in g_0 is ±0.0015 and in g is ±0.0020. AEUH = 1-amidino-*O*-ethylurea; AMUH = 1-amidino-*O*-methylurea; AP^nUH = 1-amidino-*O*-n-propylurea; LH = N',N'-diethylbiguanide; DMF = *N*,*N*-dimethylformamide. [b] g Values were calculated by measuring the EPR spectra both at room temperature and at liquid nitrogen temperature in two different laboratories.

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

Here B_{1g}, B_{2g} and E_g 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 parameters in the second order and so is not relevant to the present discussion. 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. α, β_1 and β are the coefficients which point to the ionic character of the orbitals B_{1g}, B_{2g} and E_g. Since the elctrons 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-, in-plane π- and out-of-plane π-bonding, respectively. The larger the square of α', β_1', α_1' and β', the more covalent the bonding of the type associated with each parameter [28]. The smaller the square of the coefficients α, α_1, β and β_1, the more covalent is the bonding. The ligand orbitals involved in the in-plane π-bonding are considered to be sp^2 hybrid orbitals. These coefficients are related to spin-Hamiltonian parameters for the axial symmetry by the relations [25, 29–31].

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

$$g_{\perp} - 2.0023 = \frac{-2\lambda_0\alpha\beta}{\Delta E_{xz}}\left\{\alpha\beta - \alpha'\beta S - \alpha' \frac{(1-\beta_1^2)^{1/2}T(n)}{2^{1/2}}\right\}$$

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

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

α and α' were obtained by using nitrogen superfine splittings; λ_0 is the spin–orbit coupling constant (-828 cm^{-1}) for the free copper(II) ion; $T(n) = 0.333$; $P = 2.0023\, g_N\beta_e\beta_N\langle r^{-3}\rangle = -0.036$ cm^{-1}; and k_0 ($= 0.43 \pm 0.02$) is the Fermi contact term for the copper(II) ion [25, 32, 33]. ΔE_{xy} and ΔE_{xz} are the electron transition energies of $^2B_{2g} \leftarrow {}^2B_{1g}$ and $^2E_g \leftarrow {}^2B_{1g}$, respectively.

In D_{4h} symmetry copper(II) complexes with a $^2B_{1g}$ ground state ($g_{\parallel} > g_{\perp}$), the g values may be expressed [33–36] by

$$g_{\parallel} = 2.002 - \left(\frac{8k_{\parallel}^2\lambda_0}{\Delta E_{xy}}\right)$$

and

$$g_{\perp} = 2.002 - \left(\frac{2k_{\perp}^2\lambda_0}{\Delta E_{xz}}\right)$$

where $k_{\parallel}$ and $k_{\perp}$ are the parallel and perpendicular components of the orbital reduction factor (k).

From the above relations, the orbital reduction factors (k_1, $k_{\parallel}$, $k_{\perp}$), which are a measure of covalency, and the G value may be calculated [36–39]. For an ionic environment $k = 1$ and for a covalent environment $k < 1$. The lower the value of k, the greater is the covalent character.

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

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

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

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

The low values of k (0.79–0.93) for copper(II)-substituted biguanide and other complexes (Table 3) are indicative of their covalent nature. It should be noted that for an ionic environment $g_{\parallel} > 2.3$ and for a covalent environment $g_{\parallel} < 2.3$. Theoretical work by Smith [39] seems to confirm this view. The complexes show $g_{\parallel}$ values less than 2.3, indicating that they have considerable covalent character. It may be mentioned here that $g_{\parallel}$ is a better measure of metal–ligand covalency than α^2 values [24].

For bis(ligand)copper(II) compounds, G values are less than four, indicating that the ligand is strong field in nature. This conclusion is also supported by electronic spectra which show that the positions of biguanide and dibiguanide in the spectrochemical series are slightly below that of the cyanide ion [2, 40]. The G values of the complexes may be compared to those reported for other square planar copper(II) complexes. All of them have the same [CuN$_4$] chromophore, and all the ligands are strong

TABLE 3. Orbital reduction factors and covalency parameters

Complex[a]	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} (cm^{-1})	ΔE_{xz} (cm^{-1})
[CuL_2]	DMF	2.55	0.46	0.82	0.84	0.34	0.74	0.82	0.61	1.11	20350	23400
[$Cu(LH)_2$]Cl_2	DMF	2.33	0.52	1.04	0.93	0.37	0.72	0.83	0.72	1.44	20000	23400
[$Cu(LH)_2$]Br_2	DMF	3.80	0.56	0.68	0.80	0.35	0.69	0.84	0.82	0.98	20410	23400
[$Cu(LH)_2$]$(NO_3)_2$	DMF	3.28	0.55	0.76	0.83	0.34	0.74	0.82	0.74	1.03	20410	23400
[$Cu(LH)Cl_2$]	DMF	5.00	0.58	0.69	0.81	0.41	0.69	0.79	0.84	1.00	15380	23040
[$Cu(LH)Br_2$]	DMF	6.67	0.63	0.65	0.80	0.40	0.69	0.80	0.91	0.94	15630	27030
[$Cu(LH)(NO_3)_2$]	DMF	5.14	0.60	0.69	0.81	0.40	0.69	0.82	0.87	1.00	15630	23040
[$Cu(LH)(N_3)_2$]	DMF	5.19	0.53	0.68	0.79	0.36	0.72	0.80	0.73	0.94	16150	27030
[Cu(glycinate)$_2$]	Cd complex	5.00				0.18	0.89	0.72				
[Cu(β-phthalocyanine)]	free ligand	3.69	0.55	0.68	0.80	0.38	0.72	0.80	0.80	0.99	20410	23530
[Cu(tetraphenylporphine)]	free ligand	2.77	0.59	0.98	0.92	0.36	0.69	0.82	1.39	0.85	20410	23530
[Cu(big)$_2$][b]	Ni(II) complex	2.78				0.36	0.68		0.76	1.25	20410	23400
[Cu(salicylaldoximate)$_2$]	glass	9.39	0.44	0.16		0.32	0.76	0.72			15040	18650
[Cu(AMU)$_2$][c]	Ni(II) complex	3.26	0.50	0.71	0.80	0.35	0.69	0.81	0.70	1.05	20410	23530
[Cu(pyridine)$_4$]$(NO_3)_2$[d]	Pt(II) complex	4.88	0.66	0.54	0.76	0.27	0.77	0.83	0.88	0.76	18700	18700

EPR spectra were measured both at room temperature and liquid nitrogen temperature in two different laboratories. [a] bigH = biguanide. [b] Ref. 4. [c] Ref. 5. [d] Ref. 50.

field in nature: tetraphenylporphine ($G = 2.77$) [41], phthalocyanine ($G = 3.69$) [42], and biguanide ($G = 2.78$) [6, 43–48]. The G values of all mono(biguanide)copper(II) complexes are greater than 4. For strong ligand field complexes G values are usually less than 4, but this does not provide conclusive evidence for strong out-of-plane π-bonding.

The in-plane σ-covalency parameter α_{Cu}^2 was calculated, following Kivelson and Neiman's simplified expression [25]

$$\alpha_{Cu}^2 = \frac{-A_{\parallel}}{0.0360} + (g_{\parallel} - 2.002) + \tfrac{3}{7}(g_{\perp} - 2.002) + 0.04 \qquad (1)$$

The smaller α_{Cu}^2 value (0.55) of copper(II)–dithiocarbamic acid compared to the α_{Cu}^2 values of copper(II)–biguanide complexes (Table 3) indicates the presence of a greater degree of covalence in the metal–ligand bonding in bis(dithocarbamic acidato)-copper(II) [49]. The σ-bonding parameter $\alpha_N'^2$ was calculated from the nitrogen hyperfine splitting constant A_0^N. The $\alpha_N'^2$ (0.33–0.41) values of the complexes approximately represent the percentage of electron delocalization of the unpaired electron of copper(II) to the nitrogen donor sites of the ligand, and thus the copper(II) unpaired electron ($3d^9$) spends about 33–41% of its time in the nitrogen donor sites of the substituted biguanide.

$\alpha_N'^2$ shows the unpaired electron to be more delocalized onto the substituted biguanides/1-amidino-*O*-alkylureas/tetraphenylporphine ligands than the pyridine ligand in $[Cu(py)_4]^{2+}$, another $[CuN_4]$ complex, i.e., the degree of covalence is much greater in the copper(II) complexes of biguanides, 1-amidino-*O*-alkylureas, phthalocyanine and tetraphenylporphine in comparison to that of bis(glycinato)copper(II) (Table 3). The larger σ-covalency of the complexes containing the equivalent $[CuN_4]^{2-}$ chromophore over that with the $[CuN_4]$ grouping is evidently due to the stronger σ-interaction with the deprotonated ligand nitrogen sites. The $\alpha_N'^2$ values of some genuine square planar complexes are given in Table 3 for purposes of comparison. The σ-bonding parameter $\alpha_N'^2$ values calculated from A_0^N helped us to evaluate α_N^2 values following the normalization conditions of the B_{1g} orbital,

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

where S is the overlap integral between the copper $d_{x^2-y^2}$ orbital and the nitrogen σ-orbital and is given by

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

Calculation shows that $S = 0.093$ [25].

The in-plane σ-covalency parameter, α^2_{Cu}, values account for the fraction of the unpaired electron density to be populated around the copper(II) ion. For the complexes studied these α^2_{Cu} values range from 0.79 to 0.84. The α^2_{Cu} values provide a reliable measure of the strong covalency of biguanide and are in general lower than the corresponding α^2_{Cu} values (Table 3). Such a discrepancy may be attributed to the variation of the 4s electron density of copper, which was assumed constant in eqn. (1) [41]. The $\alpha^{\prime 2}_{Cu}$ and α^2_N values of some authentic square planar compounds having a [CuN_4] chromophore are also shown in Table 3.

As expected, the strength of the σ-bonds (as manifested by the α^2 values) is very similar to that of the σ-bonds in copper(II)–β-phthalocyanine, copper(II)–tetraphenylporphine, copper(II)–biguanides and copper(II)–1-amidino-*O*-alkylureas. The parameter α'^2 is related to the interaction energy (W_L) by the expression [25]

$$W_L = \frac{4\pi}{9}\gamma_N\beta_0\alpha'^2|\rho_N(0)|^2S_zI_z^N$$

where the notation is that of Kivelson and Neiman [25].

$\alpha_N{}^2$ represents the degree of covalency of the bonding. While $\alpha_N{}^2 = 1$ indicates total ionic character and $\alpha_N{}^2 = 0.5$ implies total covalent character, the complexes in question show $\alpha_N{}^2$ values of 0.69–0.76. This indicates that the ligands studied have considerable covalent character. Although the values of α^2 and α'^2 can be measured very accurately, this is not true for β_1^2 (the in-plane π-bonding coefficient) and β^2 (the out-of-plane π-bonding coefficient), as both β_1^2 and β^2 are dependent upon the values of ΔE_{xy} and ΔE_{xz}, respectively

$$\alpha^2\beta^2 \cong \frac{(g_\perp - 2.002)\Delta E_{xz}}{2\lambda_0}$$

and

$$\alpha^2\beta_1^2 = \frac{(g_\parallel - 2.002)\Delta E_{xy}}{8\lambda_0}$$

Inasmuch as the electronic absorption spectrum consists of one very broad band, we 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. In cases in which ΔE_{xz} values are not known accurately, a 20% error in ΔE_{xz} values results in only about a 5% error in β. As in the α^2 case, $\beta_1^2 = 1$ indicates a total ionic character, while $\beta_1^2 = 0.5$ indicates 100% covalent character of the in-plane π-bonding. Table 3 shows that bis(ligand)copper(II) salts have very similar β_1^2 values (0.75–0.77), whereas the base compound has a considerably lower β_1^2 (0.65) value. This indicates that the base compound possesses much more covalent character. Complexes of the type [$Cu(LH)X_2$] (X = Cl, Br, NO_3, or N_3) show β_1^2 values of 0.73–0.91, indicating less covalent character than those of the corresponding bis(ligand)-copper(II) compounds. However, the prediction of metal–ligand covalence from β^2 and β_1^2 is less reliable in comparison to the evaluation of covalence from α^2_N and α'^2_N because of the uncertainty involved in the band positions of the ΔE_{xy} and ΔE_{xz} transitions.

A close inspection of Table 3 shows that replacement of one bidentate group by two monodentate groups such as Cl^-, Br^-, $NO_3{}^-$ or $N_3{}^-$ leads to a decrease in covalent character of the in-plane π-bonding. For an ionic compound $\beta^2 = 1$, and for a covalent compound $\beta^2 = 0.5$. The complexes studied show $\beta^2 \geqslant 1$ (except for [$Cu(LH)_2$](NO_3)$_2$), which indicates that these complexes have less covalent character of the out-of-plane π-bonding. The use of β^2 as a measure of out-of-plane metal-ligand π-bonding is not always reliable.

Table 3 further shows that replacement of the two hydrogen atoms linked to the N atom of biguanide by two alkyl groups definitely alters the spin-Hamiltonian and bonding parameters (α'^2_N, α^2_N, α^2_{Cu}) of the complexes studied. In another series of experiments Ray and Kauffman [6, 47, 48] obtained similar results. It is unfortunate that no major change was detected by Syamal [43, 46] while working on oxovanadium(IV) and copper(II) complexes of substituted biguanides.

The low $g_\parallel$ and large $A_\parallel$ values for the complexes studied suggest the characteristics of an equivalent $CuN_4{}^{2-}$ chromophore, and strong metal–ligand covalency is observed in these compounds. Moreover, the very close similarity in the bonding of biguanide with that of other strong field NN-type ligands such as 1-amidino-*O*-alkylureas and other highly conjugated ligands like phthalocyanine and tetraphenylporphine is probably due to the deprotonated nitrogen sites in the equivalent $CuN_4{}^{2-}$ chromophore.

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References

1 P. Rây, *Coord. Chem. Rev., 61* (1961) 313; P. Rây and H. Saha, *J. Indian Chem. Soc., 15* (1938) 353, 633.
2 A. Syamal, *J. Sci. Ind. Res., 37* (1978) 661.
3 R. K. Ray and G. B. Kauffman, *Coord. Chem. Rev.*, submitted for publication.
4 J. R. Wasson and P. Zacharopoulos, *J. Inorg. Nucl. Chem., 31* (1969) 3881.
5 J. R. Wasson and C. Trapp, *J. Phys. Chem., 73* (1969) 3763.
6 R. K. Ray, *Polyhedron, 8* (1989) 7.
7 D. Sen, *J. Chem. Soc. A*, (1969) 2900.
8 N. R. Kunchur and M. Mathew, *J. Chem. Soc., Chem. Commun.*, (1966) 86.
9 M. Mathew and N. R. Kunchur, *Acta Crystallogr., Sect. B, 26* (1970) 2054.
10 T. C. Creitz, R. Gsell and D. L. Wampler, *J. Chem. Soc., Chem. Commun.*, (1969) 1371.
11 B. L. Holian and R. E. Marsh, *Acta Crystallogr., Sect. B, 26* (1970) 1049.
12 D. L. Ward, C. N. Coughlan and G. D. Smith, *Acta Crystallogr., Sect. B, 27* (1971) 1541.
13 P. Rây and H. Saha, *J. Indian Chem. Soc., 14* (1937) 670.
14 W. E. Swartz, Jr. and R. A. Alfonso, *J. Electron Spectrosc. Relat. Phenom., 4* (1974) 351.
15 L. E. Cox, J. J. Jack and D. M. Hercules, *J. Am. Chem. Soc., 94* (1973) 6575.
16 C. H. L. Kennard, G. Smith and E. J. O'Reilly, *Inorg. Chim. Acta, 77* (1983) L113.
17 M. J. Begley, P. Hubberstey and C. H. M. Moore, *J. Chem. Res. S*, (1986) 121, 173.
18 M. J. Begley, P. Hubberstey, S. P. Martindale, C. H. M. Moore and N. S. Price, *J. Chem. Res. S*, (1988) 3.
19 T. Tada, Y. Kushi and H. Yoneda, *Bull. Chem. Soc. Jpn., 54* (1981) 1538; *55* (1982) 1063.
20 G. Schwarzenbach and D. Schwarzenbach, *J. Indian Chem. Soc., 54* (1977) 23.
21 A. A. Pinkerton and D. Schwarzenbach, *J. Chem. Soc., Dalton Trans.*, (1978) 989.
22 D. Schwarzenbach and R. Schmelczer, *Acta Crystallogr., Sect. B, 34* (1978) 1827.
23 D. Kivelson, *J. Chem. Phys., 33* (1960) 1094.
24 H. M. McConnell, *J. Chem. Phys., 25* (1956) 709.
25 D. Kivelson and R. Neiman, *J. Chem. Phys., 35* (1961) 149.
26 A. H. Maki and B. R. McGarvey, *J. Chem. Phys., 29* (1958) 31.
27 D. Kivelson and R. Neiman, *J. Chem. Phys., 35* (1961) 146.
28 A. K. Wiersma and J. J. Windle, *J. Phys. Chem., 68* (1964) 2316.
29 F. A. Cotton and J. J. Wise, *Inorg. Chem., 6* (1967) 915.
30 A. A. Abragam and M. H. L. Pryce, *Proc. R. Soc. London, Ser. A, 205* (1951) 135.
31 H. R. Gersman and J. D. Swallen, *J. Chem. Phys., 36* (1962) 3221.
32 A. A. Abragam and M. H. L. Pryce, *Proc. R. Soc. London, Ser. A, 230* (1951) 206.
33 A. A. Abragam, M. H. L. Pryce and J. Horowitz, *Proc. R. Soc. London, Ser. A, 230* (1955) 169.
34 C. J. Ballhausen, *Introduction to Ligand Field Theory*, McGraw-Hill, New York, 1962.
35 I. M. Procter, B. J. Hathaway and P. Nicholls, *J. Chem. Soc. A*, (1968) 1678.
36 A. A. G. Tomlinson and B. J. Hathaway, *J. Chem. Soc. A*, (1968) 1685, 1905.
37 M. Gerloch and J. R. Miller, *Prog. Inorg. Chem., 10* (1968) 1.
38 J. Owen and J. H. M. Thornley, *Rep. Prog. Phys., 29* (1966) 675.
39 D. W. Smith, *J. Chem. Soc. A*, (1970) 3108.
40 D. J. MacDonald, *Inorg. Chem., 6* (1967) 2269.
41 J. M. Assour, *J. Chem. Phys., 43* (1965) 2477.
42 S. E. Harrison and J. M. Assour, *J. Chem. Phys., 40* (1964) 365.
43 A. Syamal, *J. Indian Chem. Soc., 64* (1987) 719.
44 A. Syamal, *Indian J. Chem., 24A* (1985) 946.
45 A. Syamal, *Chem. Educ., 5* (1988) 26.
46 A. Syamal, *Indian J. Pure & Applied Phys., 21* (1983) 130.
47 R. K. Ray and G. B. Kauffman, *Inorg. Chim. Acta, 173* (1990) 207.
48 R. K. Ray and G. B. Kauffman, *Inorg. Chim. Acta, 174* (1990) 257.
49 K. Nakamoto and P. J. McCarthy, *Spectroscopy and Structures of Metal Chelate Compounds*, Wiley, New York, 1968.
50 W. Schneider and A. V. Zelewsky, *Helv. Chim. Acta, 48* (1965) 1529.