

EPR Spectra and Covalency of Bis(amidinourea/*O*-alkyl-1-amidinourea)copper(II) Complexes

Part II. Properties of the CuN_4^{2-} Chromophore*

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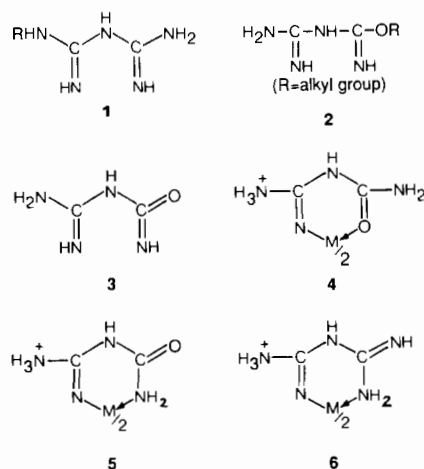
(Received October 2, 1989; revised January 29, 1990)

Abstract

EPR and optical absorption studies have been made on some square planar pink CuN_4^{2-} chromophore complexes, viz. bis(amidinourea/*O*-isopropyl-1-amidinourea/*O*-ethoxyethyl-1-amidinourea/*O*-methoxyethyl-1-amidinourea)copper(II) complexes, in the solid state and in different solvents (water, DMF and DMSO) to investigate solute–solvent interaction, if any; spin-Hamiltonian constants of the copper(II) ion; metal–ligand bond parameters; and the environment around the copper(II) ion. In an aqueous medium nine nitrogen superfine lines on the high field $3/2 \leftrightarrow 3/2$ copper hyperfine splitting component is indicative of four equivalent or nearly equivalent nitrogen atoms surrounding the copper(II) ion. The spectra obtained from different media permitted calculation of the degree of covalency of σ - and π -bonds of the copper(II) ion with the four nitrogen atoms of the ligands. The metal–ligand covalency in these compounds is comparable to that found in copper(II) phthalocyanine and porphine complexes. The covalency of the bis(ligand)copper(II) complexes is attributed to the strong σ -interaction of the copper(II) ion with a deprotonated imino ligand bonding site, and electron delocalization occurs throughout the entire chelate ring.

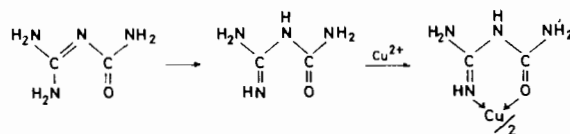
Introduction

Biguanides (1), *O*-alkyl-1-amidinourea (2) and amidinourea (3) are closely related ligands [1–6]. Chugaev [7] and Weinland [8] suggested structures 4 and 5, respectively, for metal(II)–amidinourea complexes. From the rose-red color of the copper(II) complexes, their chemical properties, and their



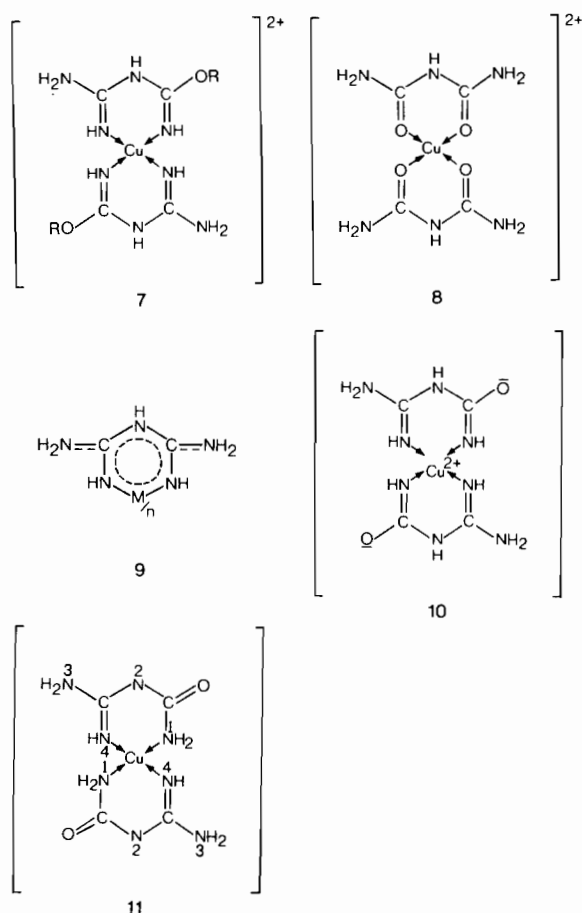
electronic and infrared spectra, Rây and Bando-padhyay [9] and later Syamal [6, 10, 11] concluded that the donor strength of amidinourea is comparable to that of other strong field ligands such as biguanides [1–3] (6) and *O*-alkyl-1-amidinourea [4, 5, 12] (7). This supported the formation of four copper–nitrogen bonds [2, 6, 7] as shown in structure 5 instead of copper–nitrogen and copper–oxygen bonds as suggested by Chugaev [7] (4).

In a study of the crystal and molecular structure of the bis(amidinourea)copper(II) complex, Begley *et al.* [13] noted that the ligand undergoes proton transfer from a terminal amine group to the central nitrogen atom, and then the transformed ligand coordinates to the metal ion by one imine and one carbonyl group:



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The coordination of amidinourea (4) is thus intermediate between that of biguanide (6) and biuret (8). In metal–biguanide, metal–biuret, metal–amidinourea and metal–1-amidino-*O*-alkylurea complexes none of the ligands coordinate to the transition metal through the amine ($-\text{NH}_2$) group – a coordination mode generally accepted by Ráy and his followers [1]. From $\text{N}(1s)$ photoelectron spectra Swartz and Alfonso [14] ruled out the presence of a quaternary nitrogen atom in the complex. The photoelectron studies indicate the presence of two types of nitrogen atoms in a 2:3 abundance ratio and show that π -electron delocalization extends to all the nitrogen atoms including those outside the chelate ring. The NMR data for bis(biguanide)nickel(II) chloride also support the absence of a quaternary nitrogen atom [15]. Therefore the metal biguanide salt may be formulated as 9.

Because the ligand is planar, extensive delocalized π -system must extend over the entire C–N–O skeleton, resulting in sp^2 hybridization of the amine groups [14–16]. As a result, these groups do not have lone pairs of electrons which can be directed towards a transition metal, and hence coordination through amine residues is unlikely. Therefore the only functional groups linked to the metal are the

imine and carbonyl groups. From X-ray, ultraviolet, visible and other spectroscopic data and by comparing studies of biguanide/biuret metal complexes Begley *et al.* later proposed another structure (10) for the bis(amidinourea)copper(II) complex [13, 17].

From infrared studies Babykutty and others [18] concluded that the carbonyl group of amidinourea is coordinated to the metal ion. Their conclusions were based on the fact that the $\nu(\text{C}=\text{O})$ mode of the ligand occurring at 1700 cm^{-1} underwent a negative shift by 20 cm^{-1} in $[\text{Cu}(\text{amidinourea})_2] \cdot 2\text{H}_2\text{O}$ (11). The carbonyl stretch is subjected to strong vibrational coupling involving the C–N₍₁₎ and C–N₍₂₎ groups in the chelate ring system (11). This would cause a lowering of the energy of the carbonyl stretch in the two-in-bonded complex $[\text{Cu}(\text{amidinourea})_2] \cdot 2\text{H}_2\text{O}$ in comparison with that in the ligand [6]. This lowering of the energy of the carbonyl stretch in the CuN_4 system may also arise partially because of the strong hydrogen bonding between the water of crystallization and the carbonyl group of the chelated ligand. The negative shift of the $\nu(\text{NH})$ and $\delta(\text{NH}_2)$ modes indicate nitrogen coordination of the amidinourea. While working on copper(II) biuret complexes, Kedzia and others observed a greater decrease in the $\nu(\text{C}=\text{O})$ mode in the N-bonded complex, potassium bis(biuret)copper(II), in comparison with that in the O-bonded chelate, bis(biuret)copper(II) chloride [19]. Moreover, electronic spectra reveal that compounds having a CuN_2O_2 chromophore show $\nu_{\text{max}} \sim 15760\text{ cm}^{-1}$, whereas compounds containing a CuN_4 chromophore exhibit $\nu_{\text{max}} \sim 19600\text{ cm}^{-1}$ [12, 20].

EPR has proven useful for investigating the bonding in copper(II) complexes. Information on the covalency of the bonding can be deduced from g values and the copper nuclear hyperfine interaction. Inasmuch as the bonding natures of amidinourea and *O*-alkyl-1-amidinoureas are not entirely unambiguous and inasmuch as the effect of replacing the amino group by various alkoxy groups has not been previously studied, we have therefore studied the bonding nature (degree of covalence of σ - and π -bonds) of the bis(amidinourea/*O*-alkyl-1-amidinourea)copper(II) complexes in order to ascertain whether structure 5 is correct or not. Furthermore, the solute–solvent interactions, if any, of copper(II)–amidinourea/1-amidino-*O*-alkylurea complexes are investigated for the first time.

Experimental

Materials

All bis(ligand)copper(II) hydroxides and their corresponding chloride salts (Table 1) were prepared according to standard methods [4, 6–9]. The corre-

TABLE 1. Electronic absorption spectra of some copper(II) complexes

Compound ^a	Positions of band maxima		
	State	Color	Absorption band (cm ⁻¹)
[Cu(AMH) ₂](OH) ₂	mull	purple	19600
	DMF	purple	19750
	DMSO	purple	19780
[Cu(AMH) ₂]Cl ₂ ·H ₂ O	mull	purple	19230
	water	purple	18520
	CH ₃ OH	purple	18850
	DMSO	purple	19410
	mull	rose-red	21200
[Cu(AP ⁱ UH) ₂](OH) ₂ ·2H ₂ O	DMF	rose-red	20500
	DMSO	rose-red	20500
	mull	rose-red	19540
[Cu(AP ⁱ UH) ₂]Cl ₂ ·H ₂ O	water	rose-red	19640
	DMF	rose-red	20400
	DMSO	rose-red	20450
	mull	rose-red	19650
	DMF	rose-red	19830
[Cu(AMEUH) ₂](OH) ₂ ·3H ₂ O	DMSO	rose-red	19850
	mull	rose-red	19550
	DMF	rose-red	20850
[Cu(AMEUH) ₂]Cl ₂ ·1.5H ₂ O	DMSO	rose-red	20210
	mull	rose-red	19560
	DMF	rose-red	19850
[Cu(AEEUH) ₂](OH) ₂ ·3H ₂ O	DMSO	rose-red	20010
	mull	rose-red	19600
	DMF	rose-red	20500
[Cu(AEEUH) ₂]Cl ₂ ·2H ₂ O	DMSO	rose-red	20530
	mull	rose-red	19600

^aAMH = amidinorea; APⁱUH = *O*-isopropyl-1-amidinorea; AMEUH = *O*-methoxyethyl-1-amidinorea; AEEUH = *O*-ethoxyethyl-1-amidinorea; DMF = *N,N*-dimethylformamide; DMSO = dimethyl sulfoxide.

sponding orange–yellow diamagnetic nickel(II) complexes were prepared by the methods described earlier [4, 6–9]. CuL₂·*n*H₂O (L = AMH, amidinorea; APⁱUH, *O*-isopropyl-1-amidinorea; AMEUH, *O*-methoxyethyl-1-amidinorea; AEEUH, *O*-ethoxyethyl-1-amidinorea) and NiL₂·*n*H₂O were dehydrated by heating *in vacuo* at about 70 °C for 3 days. The stoichiometry of the complexes was confirmed by carbon, hydrogen, nitrogen and metal analyses.

Copper(II)-doped Ni(L)₂ was prepared by adding about 4% of CuL₂·*n*H₂O to NiL₂·*n*H₂O dispersed in 8 M aqueous NaOH. The resulting mixture was stirred well, filtered under suction, washed with water and ethanol, air-dried and finally dehydrated.

Spectral Measurements

Electronic spectra were recorded on a Cary 14 spectrophotometer using 1-cm cells. EPR spectra were obtained on a Varian V4502-12 X band spectrometer with 100 kHz modulation. A cylindrical quartz sample tube was used for the spectra of powdered and frozen solution samples. A minute, powdered sample of diphenylpicrylhydrazil (DPPH) 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

The electronic spectra of bis(ligand)copper(II) salts show a typical absorption band at about 19 600 cm⁻¹ in both solid and aqueous media, an indication of the presence of a square planar [CuN₄] chromophore [1–5]. Other square planar [CuN₄] chromophores appear in tetrakis(benzimidazole)copper(II) (19 000 cm⁻¹ in the solid), bis(biguanide)copper(II) (19 230 cm⁻¹ in water and 20 410 cm⁻¹ in solid and 19 840 cm⁻¹ in water), bis(guanylurea)copper(II) (20 202 cm⁻¹ in the solid), bis(1-amidino-*O*-ethylurea)copper(II) (19 417 cm⁻¹ in the solid) and bis(1-amidino-*O*-propylurea)copper(II) (19 417 cm⁻¹ in the solid) [12, 21–28]. The IR spectra of amidinorea show δ(N₍₁₎H₂) at 1700 cm⁻¹ and δ(N₍₃₎H₂) at 1630 cm⁻¹. The greater negative shift of δ(N₍₁₎H₂) (20–30 cm⁻¹) in the metal complexes in comparison

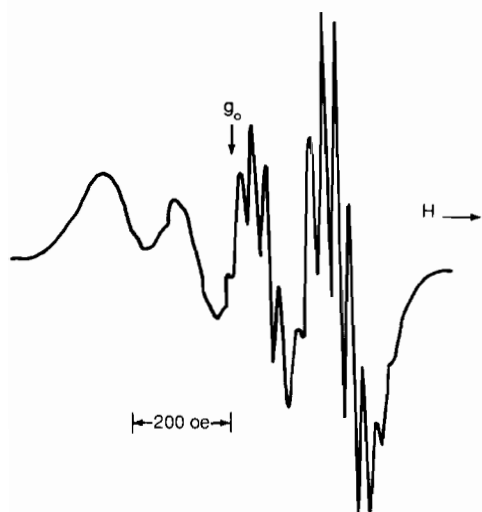


Fig. 1. Solution EPR spectrum of $[\text{Cu}(\text{AMH})_2](\text{OH})_2$ in *N,N*-dimethylformamide at room temperature: frequency 9.423 kMc; $g_0 = 2.092$.

with a smaller shift (10 cm^{-1}) of $\delta(\text{N}_{(3)}\text{H}_2)$ supports the N_1 -coordination and non-participation of the $\text{N}_{(3)}$ atom in coordination.

Solution spectra (Fig. 1) provided a measure of the isotropic or average g value (g_0), isotropic hyperfine structure constant (A_0^{Cu}), and isotropic ligand superfine structure constant (A_0^{N}). All the complexes in solution show nine nitrogen superfine components, caused by the interaction of the odd electron of copper with the nuclear spins of the atoms by which the ligand molecules are bound. The spectra further reveal that all four nitrogen atoms surrounding the copper(II) ion are almost equivalent with the $[\text{CuN}_4]$ chromophore.

From room temperature EPR spectra of powdered samples (Fig. 2) approximate g values were determined [29]. The parameters g_{\parallel} , g_{\perp} , $A_{\parallel}^{\text{Cu}}$ and A_{\perp}^{Cu} were obtained from anisotropic spectra of the powdered, magnetically dilute solid (Fig. 3) and the frozen solution (Fig. 4) (Table 2). g_{av} and A_{av} values were obtained from the standard relations [30, 31]

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

The average g value in powder ($g_{\text{av}} = 2.09$) agrees well with the corresponding values in DMF ($g_{\text{av}} = 2.029$ – 2.110) and in DMSO ($g_{\text{av}} = 2.094$ – 2.110), indicating negligible interaction between solute and solvent molecules. The anisotropic spectra of the magnetically dilute powders gave no indication of more than two g values. All the compounds that were studied show $g_{\parallel} < 2.3$. It should be noted that for an ionic environment $g_{\parallel} \geq 2.3$, while for a covalent environment $g_{\parallel} < 2.3$, indicating that these complexes possess considerable covalent character

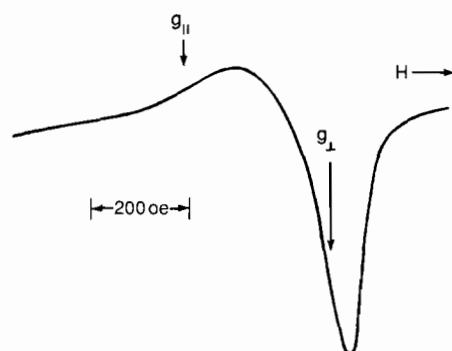


Fig. 2. Room temperature EPR spectrum of powdered $[\text{Cu}(\text{AMH})_2]\text{Cl}_2$: frequency 9.474 kMc; $g_{\parallel} = 2.22$, $g_{\perp} = 2.056$.

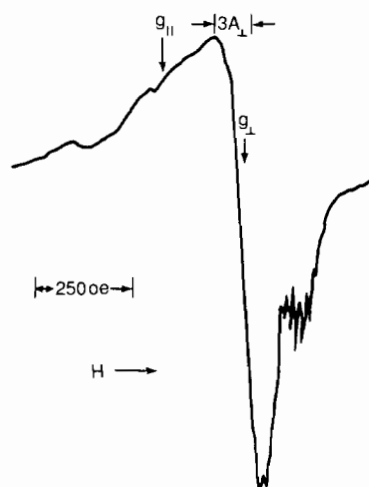


Fig. 3. Room temperature EPR spectrum of $[\text{Cu}(\text{AMH})_2]\text{Cl}_2$ diluted into the corresponding nickel(II) complex (about 4% copper): frequency 9.476 kMc; $g_{\parallel} = 2.177$, $g_{\perp} = 2.062$.

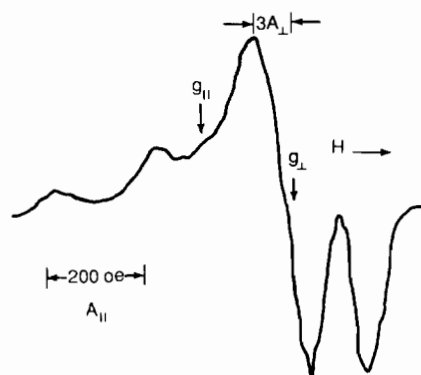


Fig. 4. Frozen solution EPR spectrum of $[\text{Cu}(\text{AMH})_2](\text{OH})_2$ in dimethyl sulfoxide: liquid nitrogen temperature; frequency 9.133 kMc; $g_{\parallel} = 2.177$, $g_{\perp} = 2.058$.

and that the $d_{x^2-y^2}$ orbital will be the ground state [32]. The low g_{\parallel} and high A_{\parallel} values found appear to be characteristic of complexes containing the equiv-

TABLE 2. g Values and hyperfine structure constants for copper(II) complexes

Complex	Medium ^a	g_0	g_{av}	$g_{ }$	g_{\perp}	Hyperfine constants $\times 10^4$ (cm ⁻¹)			
						$A_{ }^{\text{Cu}}$	A_{\perp}^{Cu}	A_0^{Cu}	A_0^{N}
[Cu(AMH) ₂](OH) ₂	Ni(II) complex		2.094	2.171	2.056	210	21		15.7
	DMF	2.092						92.1	15.8
	DMSO (frozen)	2.093	2.097	2.177	2.058	218	24	89.6	15.8
[Cu(AMH) ₂]Cl ₂	Ni(II) complex		2.10	2.177	2.062	205	25		15.0
	water	2.102						90.1	14.8
	DMF	2.106						89.4	14.9
	DMSO	2.107						88.9	15.0
[Cu(AP ⁱ UH) ₂](OH) ₂	Ni(II) complex		2.097	2.175	2.058	202	24		15.8
	DMF	2.098	2.10	2.175	2.064	202	25	93.2	15.9
	DMSO (frozen)	2.100	2.06	2.174	2.057	204	17	98.8	15.8
[Cu(AP ⁱ UH) ₂]Cl ₂	Ni(II) complex		2.09	2.179	2.054	202	17		14.7
	water	2.105						85.9	14.9
	DMF	2.110						97.7	15.9
[Cu(AMEUH) ₂]Cl ₂	Ni(II) complex		2.09	2.173	2.058	203	24		14.9
	DMF	2.110						97.7	15.9
[Cu(AEEUH) ₂]Cl ₂	Ni(II) complex		2.10	2.181	2.065	205	25		14.7
	DMF	2.112						87.9	15.2

^aDMF = *N,N*-dimethylformamide; DMSO = dimethyl sulfoxide.

alent [CuN₄]²⁻ chromophore and are a result of the strong covalency in the complexes.

Considering the EPR spectra and square planar geometry as evidenced by the electronic spectra, we conclude that the copper(II) ion in these complexes is in a tetragonal field (D_{4h} symmetry). The odd electron is placed in the antibonding B_{1g} orbital in the ground state.

The approximate antibonding wave functions [33–36] are

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

$$\psi_{B_{2g}} = \beta_1 d_{xy} - \beta'_1(p_y^{(1)} + p_x^{(2)} - p_y^{(3)} - p_x^{(4)})/2$$

$$\psi_{A_{1g}} = \alpha_1 d_{z^2} - \alpha'_1(\sigma_x^{(1)} + \sigma_y^{(2)} - \sigma_x^{(3)} - \sigma_y^{(4)})/2$$

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

The B_{1g} , B_{2g} and E_g states represent σ -bonding, in-plane π -bonding and out-of-plane π -bonding, respectively. The ligand orbitals involved in the in-plane σ -bonding are considered to be sp^2 hybrid orbitals [37, 38]. Overlap is included for the function describing in-plane σ -bonding. α , α_1 , α' and α'_1 are the σ -bonding 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 is the bonding. The larger the square of α' , β'_1 , α'_1 and β' , the more covalent is the bonding of the type associated with each parameter [31]. These coefficients are related to the spin-Hamiltonian for copper(II) ion in a tetragonal crystal field given by

$$\mathcal{H} = \beta_0 [g_{||} H_z S_z + g_{\perp} (H_x S_x + H_y S_y)] + A_{||}^{\text{Cu}} S_z I_z + A_{\perp}^{\text{Cu}} (S_x I_x + S_y I_y)$$

where

$$g_{||} - 2.0023 = \frac{-8\lambda_0\alpha\beta_1}{\Delta E_{xy}}$$

$$\times \{\alpha\beta_1 - \alpha'\beta_1 S - \alpha'(1 - \beta_1^2)^{1/2} T(n)/2\}$$

$$g_{\perp} - 2.0023 = \frac{-2\lambda_0\alpha\beta}{\Delta E_{xz}}$$

$$\times \{\alpha\beta - \alpha'\beta S - \alpha'(1 - \beta^2)^{1/2} T(n)/2^{1/2}\}$$

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

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

H is the applied field; β_0 is the Bohr magneton; $T(n) = 0.333$ [34]; $P = -0.036$ cm⁻¹; λ_0 ($= -828$ cm⁻¹) is the spin-orbit coupling constant for the copper(II) ion; k_0 ($= 0.43 \pm 0.02$) is the Fermi contact term [39, 40] for Cu²⁺. ΔE_{xy} and ΔE_{xz} are the electronic transition energies of ${}^2B_{2g} \leftarrow {}^2B_{1g}$ and ${}^2E_g \leftarrow {}^2B_{1g}$, respectively.

TABLE 3. Orbital reduction factors and covalency parameters^a

Complex	Medium	G	k_{\parallel}^2	k_{\perp}^2	K	$\alpha_{N^2}^2$	$\alpha_{Cu^2}^2$	β^2	β_1^2	$\Delta E_{xy} \times 10^3$ (cm ⁻¹)	$\Delta E_{xz}^b \times 10^3$ (cm ⁻¹)
[Cu(AMH) ₂](OH) ₂	Ni(II) complex	3.13	0.50	0.69	0.79	0.34	0.73	0.93	0.68	19.60	21.06
	DMF					0.33	0.76			19.75	21.06
[Cu(AMH) ₂]Cl ₂	DMSO (frozen)	3.12	0.52	0.71	0.80	0.35	0.69	0.95	0.72	19.78	21.06
	Ni(II) complex	2.92	0.51	0.76	0.82	0.35	0.69	1.02	0.67	19.23	21.05
	water					0.35	0.69			18.70	
[Cu(AP ² UH) ₂](OH) ₂	DMF					0.36	0.69			19.40	21.05
	DMSO (frozen)					0.36	0.68			19.41	21.05
	Ni(II) complex	3.08	0.55	0.80	0.84	0.35	0.69	1.09	0.75	21.20	23.54
	DMF	2.80	0.53	0.88	0.87	0.35	0.69	1.27	0.77	20.50	23.53
[Cu(AP ¹ UH) ₂]Cl ₂	DMSO (frozen)	3.12	0.53	0.78	0.83	0.35	0.69	1.13	0.77	20.50	23.53
	Ni(II) complex	3.40	0.52	0.66	0.78	0.36	0.69	0.96	0.75	19.54	21.04
	[Cu(AMEUH) ₂]Cl ₂	3.05	0.50	0.71	0.80	0.37	0.72	0.80	0.97	19.55	21.03
	[Cu(AEUEH) ₂]Cl ₂	2.84	0.53	0.80	0.84	0.37	0.72	0.81	1.11	19.60	21.05
	[Cu(big) ₂]	2.78				0.36	0.68			20.41	23.40
[Cu(β -phthalocyanine)] free ligand		3.69				0.35	0.69	0.99	0.79	20.40	23.40
	chloroform, free ligand	2.77	0.59	0.98		0.36	0.69	1.39	0.85	20.41	23.53
	[Cu(tetraphenylporphine)]	4.88	0.66	0.54		0.27	0.77	0.88	0.76	18.70	18.70
	[Cu(pyridine) ₄](NO ₃) ₂	3.26	0.50	0.71		0.35	0.69	1.05	0.70	20.41	23.53

^aDMF = *N,N*-dimethylformamide; DMSO = dimethyl sulfoxide; bigH = biguanide. ^b ΔE_{xz} has been assumed to correspond to the wavelength at the half intensity of the maxima of the band, on the lower wavelength side. bigH = biguanide; AMUH = *O*-methyl-1-amininourea.

The orbital reduction factors k and G values were measured following the standard expressions [41–44] where k_{\parallel} and k_{\perp} are the parallel and perpendicular components of the orbital reduction factor:

$$k^2 = \frac{k_{\parallel}^2 + 2k_{\perp}^2}{3}$$

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

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

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

The low values of k (0.78–0.84) of the copper(II) complexes studied (Table 3) are indicative of the covalent nature of the complexes. The σ -bonding parameter α'_{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 ($= 0.093$) is the overlap between the copper $d_{x^2-y^2}$ orbital and the ligand orbitals [32].

As the G values of the complexes studied are less than 4 (Table 3), all the title ligands are strong field in character. Some reported G values are also given in Table 3 for comparative purposes; almost all the ligands are strong field in nature [2–6, 12, 45]. The in-plane α -covalency parameter α_{Cu^2} was calculated using Kivelson and Neiman's simplified expression [32]

$$\alpha_{\text{Cu}^2} = -\left(\frac{A_{\parallel}}{0.036}\right) + (g_{\parallel} - 2.002) + \frac{3}{7}(g_{\perp} - 2.002) + 0.04 \quad (1)$$

The α_{Cu^2} ($= 0.79$ – 0.83) value accounts for the fraction of the unpaired electron density located on the copper(II) ion. A comparison of these α_{Cu^2} values with those of [Cu(tetraphenylporphine)] ($\alpha_{\text{Cu}^2} = 0.82$), [Cu(phthalocyanine)] ($\alpha_{\text{Cu}^2} = 0.80$), [Cu(biguanides)₂] ($\alpha_{\text{Cu}^2} = 0.71$ – 0.84) indicates the similarity of the complexes studied with the copper(II) complexes of other strong field ligands such as phthalocyanine, tetraphenylporphine and biguanides, all having the [CuN₄] chromophore. The α_{N^2} values, calculated from the nitrogen super-fine structure, are slightly smaller than those of the 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. (1) [46].

The in-plane and out-of-plane metal π -bonding coefficients β_1^2 and β^2 , respectively are obtained from the following equations [43, 47]:

$$\alpha^2\beta^2 \approx (g_{\perp} - 2.002)\Delta E_{xz}/1656 \text{ cm}^{-1}$$

$$\alpha^2\beta_1^2 \approx (g_{\parallel} - 2.002)\Delta E_{xy}/6624 \text{ cm}^{-1}$$

The uncertainty involved in the assignment of ΔE_{xz} and g_{\perp} as obtained from polycrystalline samples [12, 47] usually precludes a reliable estimate of the out-of-plane π -bonding parameter β^2 . However, in cases where ΔE_{xz} is not known accurately, a 20% error in ΔE_{xz} values results in only about a 5% error in β . Likewise, $\beta^2 = 1$ indicates 100% ionic character, and $\beta^2 = 0.5$ indicates a total covalent character of the in-plane π -bonding [32]. The complexes studied show $\beta^2 = 0.67$ – 0.73 , indicating a pronounced covalent in-plane π -bonding.

Thus on the basis of the unusual pink color (which may be attributed to the presence of a planar, equivalent CuN₄²⁻ chromophore), IR spectra, optical absorption spectra and EPR studies, the possibility of O-coordination of the ligand to the copper(II) ion is totally eliminated. Therefore the structures of bis(amidino-urea)copper(II) base and bis(1-amino-*O*-alkylurea)copper(II) salt may be depicted as 11 and 7, respectively.

Acknowledgements

The senior author (R.K.R.) wishes to thank Professor N. Saha, Department of Chemistry, University College of Science, Calcutta, and Professor P. Hubberstey, Department of Chemistry, Nottingham University, U.K., for constant encouragement and for laboratory and other facilities. He also thanks Mr Sukul Banerjee, Professor Nemai Basu Majumder and Mr Dulal Roy of the Rama Krishna Mission P.G.B.T. College, Rahara for technical assistance.

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