

Complexes of Biguanidoethyl Acetate & Biguanidoacetic Acid with Copper(II) & Nickel(II)

S R SAHA* & AMITAVA BAGCHI

Department of Chemistry, Jadavpur University, Calcutta 700 032

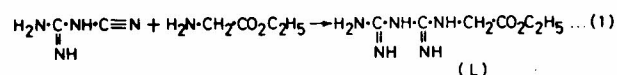
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Biguanide derivatives containing ethyl acetate and acetic acid fragments form 1:1 and 1:2 complexes with copper(II), and 1:2 complexes with nickel(II). The complexes have been characterised on the basis of analytical, spectral and magnetic data. A square planar geometry is assigned to 1:1 complexes and tetragonally distorted octahedral geometry is assigned to 1:2 complexes. The biguanide derivatives behave as uninegative tridentate ligands coordinating through two N atoms and an O atom of the carbonyl group.

Although some biguanide derivatives containing an additional potential donor site have been studied, participation of that site in coordination is, however, not well established¹⁻³. It was, therefore, thought worthwhile to synthesise and characterise the metal complexes of such ligands in order to elucidate the ligational behaviour of the biguanide fragment⁴⁻⁶. The present paper deals with the study on the coordination compounds of copper(II) and nickel(II) with biguanidoethyl acetate and biguanidoacetic acid.

Materials and Methods

Dicyandiamide (1 mol), glycine ester hydrochloride (1 mol) [glycin (1 mol), hydrochloric acid (1 mol)] and copper chloride (1 mol) were mixed together in aqueous solution, which on standing for a few days gave a deep blue crystalline copper complex. The yield was generally poor. Nickel and cobalt chloride, under identical conditions, did not form any compound. The reaction which gives rise to biguanidoethyl acetate is represented by Eq. 1,



The free ligand (L) was isolated from the copper complex by removing copper as CuS and evaporating the filtrate on a water bath. It formed a very light yellow sticky solid. In a similar way, the free acid ligand (L') was isolated from its copper complex and was found to be physically similar to its ester.

The blue copper complex is a 1:1 chloroderivative of the ligand L or L'. The corresponding bromo, iodo and thiocyanato derivatives were prepared from it by double decomposition with ammonium salts of the anions. 1:2 complexes of copper and nickel were

obtained as precipitates by adding metal chloride solution to excess ligand solution and then making it ammoniacal.

Elemental analyses of the complexes and their different physicochemical properties are listed in Table 1. The ligands were characterised by IR and NMR spectra. The ester ligand (L) gave a positive test with hydroxyl amine and ferric chloride. Philips conductivity Bridge Model PR 9500 with a dip type cell was used for conductivity measurements in water. Magnetic moments were measured using PAR Vibrating Sample Magnetometer (VSM) Model 155. NMR spectra were recorded on a JEOL 269.65 MHz instrument using CDCl₃-DMSO solvent and TMS as internal standard at 24°C. IR spectra were recorded in KBr/CsBr on a Beckman IR 20A instrument while PYECO 150 UV-Visible spectrophotometer was used to record electronic spectra in nujol.

Results and Discussion

Except the chloroderivatives, all other complexes are insoluble in water. 1:1 complexes are blue with varying shades and 1:2 complexes are red. 1:1 copper complex, unlike other biguanide complexes, is formed in acid medium (pH 1-2) and is not protonated.

Molar conductance of CuLCl in aqueous solution is 93.4 ohm⁻¹ cm² mol⁻¹ suggesting it to be 1:1 electrolyte. Since the compound does not readily dissolve in water without heating and also the corresponding bromo, iodo and thiocyanato derivatives are insoluble in water, the halogen is probably covalently bonded. Due to dipole-dipole interaction, it goes into solution and exists as CuL(H₂O)⁺ and Cl⁻.

The ester ligand, in conformity with its structure, shows the characteristic NMR signals at δ 1.280 ppm

(3H, *t*, $J=6.92$ Hz, $-\text{CH}_2-\text{CH}_3$); δ 3.748 ppm (2H, *s*, $-\text{NH}-\text{CH}_2-\text{C}(=\text{O})-$; and δ 4.228 ppm (2H, *q*, $J=7.25$ Hz, $-\text{C}(=\text{O})-\text{O}-\text{CH}_2-$).

An additional singlet which integrates for four protons also appears at δ 6.645 ppm and this may be due to any of the four NH protons; but in absence of D_2O spectrum, this proposition cannot be fully established.

$\nu(\text{C}=\text{O})$ in ethyl glycinate hydrochloride appears at 1725 cm^{-1} but in the ester ligand (L) the same band appears at 1705 cm^{-1} , which may be due partly to some intermolecular hydrogen bonding and partly to the presence of bulky biguanide residue. Both the ligands show different IR bands, characteristic of NH, $=\text{NH}$ and $\text{C}=\text{O}$ groups and the bands shift towards lower frequencies due to complexation; the bands of the complexes from the ester ligand usually appear at

slightly higher frequencies. The bands at 3410 , 3370 and 3210 cm^{-1} assigned to $\nu(\text{N}-\text{H})$ and $\nu(=\text{NH})$ for the ester ligand shift to 3380 , 3330 and $3180\text{--}3130\text{ cm}^{-1}$ on complexation indicating deprotonation of one of the N-H groups of the terminal guanyl unit ($-\text{C}(=\text{NH})-\text{NH}_2$)⁷. The band at 1705 cm^{-1} attributed to $\nu(\text{C}=\text{O})$ shifts to $1680\text{--}1670\text{ cm}^{-1}$ in the complexes and this gives a clear indication of the participation of the carbonyl group in coordination. The bands at 1600 cm^{-1} for $\nu(\text{NH})$ and at $1260\text{--}1240\text{ cm}^{-1}$ for $\nu(\text{CO}_2\text{C}_2\text{H}_5)$ also shift to 1585 and $1250\text{--}1215\text{ cm}^{-1}$ respectively. The thiocyanate derivative shows a very sharp additional band⁸ at 2100 cm^{-1} which is characteristic of $\nu(\text{CN})$, but the structural diagnosis on the basis of $\nu(\text{C}=\text{S})$, which appears at $860\text{--}780\text{ cm}^{-1}$ for N-bonded and at $720\text{--}690\text{ cm}^{-1}$ for S-bonded complexes, is not possible in the present case as these

Table 1—Characterisation Data of Copper(II) and Nickel(II) Complexes with Biguanidoethyl Acetate (L) and Biguanidoacetic Acid (L')

Compound	Found (Calc.), %						$\mu_{\text{eff.}}$ (B.M.)	λ_{max} (nm)
	M	C	N	X	H	H ₂ O		
CuLCl	22.31	25.05	24.79	12.50	4.30	—	1.89	600
	(22.20)	(25.17)	(24.47)	(12.41)	(4.19)	—	—	—
CuLBr	19.25	—	21.19	24.20	—	—	1.86	575
	(19.21)	—	(21.18)	(24.12)	—	—	—	—
CuLI	16.85	—	18.59	33.50	—	—	1.86	555
	(16.82)	—	(18.54)	(33.62)	—	—	—	—
CuLNCS*	20.74	—	26.97	—	—	—	1.88	570
	(20.58)	—	(27.22)	—	—	—	—	—
CuL'Cl	24.62	18.50	26.92	13.81	3.18	—	1.90	605
	(24.61)	(18.60)	(27.13)	(13.75)	(3.10)	—	—	—
CuL'Br	21.10	—	22.94	26.60	—	—	1.88	585
	(20.99)	—	(23.14)	(26.42)	—	—	—	—
CuL'I	18.22	—	19.91	36.05	—	—	1.86	565
	(18.17)	—	(20.03)	(36.31)	—	—	—	—
CuL'NCS*	22.70	—	29.59	—	—	—	1.85	570
	(22.63)	—	(29.94)	—	—	—	—	—
CuL ₂ ·2H ₂ O	13.37	—	28.80	—	—	7.46	1.95	550,480
	(13.41)	—	(29.56)	—	—	(7.60)	—	—
CjL ₂ ·2H ₂ O	15.30	—	33.40	—	—	8.40	1.96	520
	(15.20)	—	(33.53)	—	—	(8.62)	—	—
NiL ₂ ·2H ₂ O	12.33	—	29.48	—	—	7.31	2.76	490,420
	(12.52)	—	(29.86)	—	—	(7.68)	—	—
NiL ₂ '·2H ₂ O	14.42	—	34.00	—	—	8.50	2.72	570,470
	(14.22)	—	(33.92)	—	—	(8.72)	—	420

*Satisfactory S analyses were also obtained.

M = Cu/Ni, X = Cl⁻, Br⁻, I⁻, L = biguanidoethyl acetate and

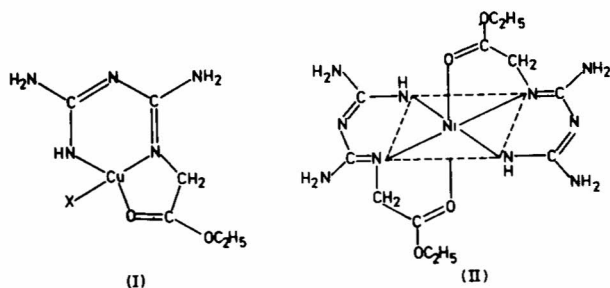
L' = biguanidoacetic acid

spectral regions contain ligand bands. The IR spectra for 1:2 complexes of both ligands, unlike those of 1:1 complexes, show a broad band around 3300 cm^{-1} which is attributed to lattice held water molecules⁸ present in the complex. The shift of the band to such a lower frequency might have occurred due to extensive hydrogen bonding. The remaining parts of the spectra are nearly matching with those of 1:1 complexes.

Room temperature magnetic moments of 1:1 Cu(II) complexes are around 1.9 B.M. which, in conjunction with the coordination sites of the ligands, suggest a square planar geometry. In confirmation of this view, the electronic spectra show only a single, somewhat asymmetric broad band around 600-560 nm covering approximately the transitions⁹ ${}^2B_{1g} \rightarrow {}^2A_{1g}(\nu_1)$ and ${}^2B_{1g} \rightarrow {}^2B_{2g}(\nu_2)$; the transition ${}^2B_{1g} \rightarrow {}^2E_g(\nu_3)$ being in the higher energy region probably escapes detection. An important feature of these spectra is that $\lambda_{\max}$ values show a notable correlation with the positions of anions present in the complexes in the nephelauxetic series. The observed order of $\lambda_{\max}$ values, viz. $\text{Cl}^- > \text{Br}^- > \text{NCS}^- > \text{I}^-$, is in accord with the nephelauxetic series except the position of NCS^- which may suggest its bonding through S- end.

$\mu_{\text{eff.}}$ values of 1:2 Cu(II) complexes at room temperature are around 1.95 B.M., which together with analytical data indicate a distorted octahedral geometry. The electronic spectra show a broad asymmetric band around 550-520 nm with an additional band at 480 nm for the complex from the ester ligand. These bands, as in 1:1 complexes, correspond to ν_1 and ν_2 transitions and are in agreement with a distorted octahedral geometry (D_{4h} local symmetry).

$\mu_{\text{eff.}}$ values of 1:2 Ni(II) complexes at room temperature are around 2.75 B.M. which are somewhat less than that expected for O_h symmetry suggesting tetragonal distortion (D_{4h}). The electronic spectra show two bands at 570-490 nm and 420 nm which correspond respectively to transitions¹⁰ ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_2)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)(\nu_3)$ as in O_h symmetry. The transition ${}^3A_{2g} \rightarrow {}^3T_{2g}(\nu_1)$ which also occurs in O_h symmetry splits into two components in D_{4h} symmetry; however, these may have escaped detection being in the range beyond 800 nm. The band at 470 nm, which occurs for the complex of the acid ligand (L), is probably due to the transition¹¹ ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ on tetragonal distortion.



1:2 complexes of both copper and nickel show a reddish colour and this may be due to strong charge transfer¹² bands tailing off into the blue end of the visible region. For 1:2 complexes, it is not certain whether the ligand occupies 1,2,3 or 1,2,6 positions in the coordination zone. For D_{4h} local symmetry, 1,2,3 arrangement is more probable.

Following the structural pattern suggested⁵ for simple biguanide complexes, the structures of 1:1 and 1:2 complexes under study may be represented by (I) and (II).

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