Asian Journal of Chemistry Vol. 4, No. 4 (1992), 675–679

Characterisation and Electron Paramagnetic Resonance Spectra of Some Copper(II) Complexes Derived from Heterocyclic Ligand 5,5′-diethyl-2,4,6(1H)-Pyrimidinetrione and Amines

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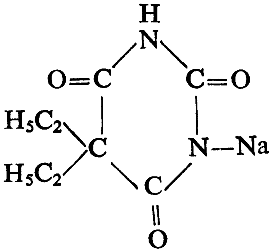
Some tetracoordinated complexes of 5,5′-diethyl-2,4,6-(1H) pyrimidinetrione (barb) of copper(II) with amines have been prepared and characterised. The general molecular formula on the basis of analytical data is [Cu(barb)$_2$(amine)]. The EPR data suggest monomeric nature of the complexes and very low exchange coupling. The infrared, magnetic and electronic data of the complexes are discussed in the light of the structures assigned.

INTRODUCTION

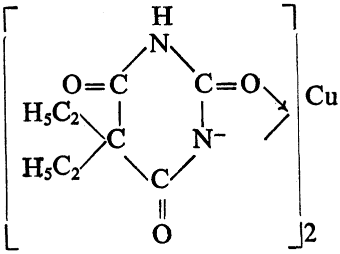
The chemistry of pyrimidinetrione and their derivatives has attracted attention of chemists by virtue of their applicability as potential ligands and biological activity.[1-3] It is also found that two adjacent positions having C=O and –NH– groups are active for coordinate bond formation. We have attempted a systematic study of the complexes derived from 5,5′-diethyl-2,4,6 (1H)-pyrimidinetrione (3Na) and amines. The structures of the complexes have been established using analytical, conductance, infrared, magnetic, EPR and electron spectral data.

EXPERIMENTAL

The pyrimidinetrione used in the study has the following formula.



Treatment of this compound with copper(II) sulphate gives blue precipitate, which does not give the test of sulphate ion. In that case the compound behaves as a mononegative ion, two of which are added to copper(II) as shown below:



The complexes have been prepared by the following method.

2 gm of di-5,5′-diethyl-2,4,6(1H)-pyrimidinetrione copper(II) was suspended in 100 ml of ethanol. The calculated quantity of amine was added to the suspended ethanol solution. The reaction mixture was shaken (or refluxed) for about 10 days. At the end of reaction the reactants were completely dissolved in the solvent and intense coloured solution is obtained. Half the amount of the solvent was distilled and the complex crystallised at low temperature after several days. The complexes were dried in a vacuum oven (30–70°C).

Molar conductance was measured in nitrobenzene at a concentration of 10^{-3} M using Elico type CM 82T magic eye instrument. The infrared spectra were recorded on Perkin Elmer Model 577 and 1310 Spectrophotometers in KBr. The magnetic measurements were done at room temperature using Gouy's method. The EPR spectra were recorded on a Varian V_3 spectrometer at room temperature on polycrystalline samples. The settings used were RF power, 2 mV; frequency, 9.47 CHz; scan range 1000 gauss; DPPH standard at 3401 gauss.

RESULTS AND DISCUSSION

The molecular formulae of the complexes have been obtained from the analytical data given in Table 1. The molar conductance values indicate that the complexes are non-electrolytes. Evidence for the coordination of ligands is obtained from the infrared spectra as discussed below.

(i) The particular amines which have actually been used in the investigations are: 1,2-diaminethane, 1,2-diaminepropane, diethylenetriamine, triethylenetetramine and tetraethylenepentamine. The coordination of these amines takes place through the primary and secondary amine groups and the infrared spectral bands are found to undergo a negative shift as a consequence of coordination.

The NH vibration is usually observed in the spectra in the form of a doublet in the region 3400–3300 cm^{-1} corresponding to asymmetric and symmetric NH stretching. These bands usually merge together and are observed in the complexes as a single peak near 3200 ± 50 cm^{-1} due to

TABLE 1

ANALYTICAL DATA OF Cu(II) COMPLEXES; FOUND (CALC)

Complex	% M	% C	% H	% N	Molar conductance mhos (nitrobenzene)	Colour
$[Cu(C_8H_{11}O_3N_2)_2]$	14.56	44.14	5.89	12.86	Insoluble	Blue
	(14.77)	(44.70)	(5.15)	(13.03)		
$[Cu(C_8H_{11}O_3N_2)_2(C_2H_8N_2)]$	12.77	43.76	6.34	17.46	0.86	Oxford blue
	(12.96)	(44.12)	(6.17)	(17.15)		
$[Cu(C_8H_{11}O_3N_2)_2(C_3H_{10}N_2)]$	12.24	44.87	5.98	16.46	1.02	Chocolate
	(12.60)	(45.27)	(6.39)	(15.67)		
$[Cu(C_8H_{11}O_3N_2)_2(C_4H_{13}N_3)]$	12.43	44.88	6.38	18.42	0.98	Chocolate
	(11.91)	(45.06)	(6.61)	(18.39)		
$[Cu(C_8H_{11}O_3N_2)_2(C_6H_{18}N_4)]$	10.78	45.51	6.44	19.31	0.64	Azure blue
	(11.02)	(45.86)	(6.99)	(19.44)		
$[Cu(C_8H_{11}O_3N_2)_2(C_8H_{23}N_5)]$	9.98	46.06	6.88	20.01	0.77	Olive green
	(10.26)	(46.55)	(7.32)	(20.35)		
$[Cu(C_8H_{11}O_3N_2)_2(C_{10}H_8N_2)]$	10.46	52.88	4.76	14.11	0.97	Blue
	(10.84)	(53.28)	(5.15)	(14.33)		
$[Cu(C_8H_{11}O_3N_2)_2(C_{12}H_8N_2)]$	10.22	54.72	4.63	13.55	0.55	Aquamarine
	(10.41)	(55.12)	(4.95)	(13.77)		

TABLE 2

EPR DATA

Complex No.	g_1	g_{11}	g_{ave}	G	μ_{eff} B.M.	μ_{eff} Gouy's method
1	2.21	2.12	2.18	0.57	1.87	1.92
2	2.20	2.10	2.16	0.50	1.85	2.00
3	2.22	2.07	2.17	0.31	1.86	1.93
4	2.21	2.12	2.18	0.57	1.87	1.98
5	2.21	2.11	2.17	0.52	1.86	1.93
6	2.21	2.11	2.17	0.52	1.86	2.18
7	2.22	2.09	2.17	0.40	1.86	2.14
8	2.22	2.08	2.17	0.36	1.86	1.94

the coordinations[4, 5]. The CH stretching vibrations are weak in nature occurring near 2950 cm^{-1}, 2930 cm^{-1} and 2880 cm^{-1}. In the complexes, these bands are seen near 2950 ± 30 cm^{-1}, 2900 ± 30 cm^{-1} and 2860 ± 30 cm^{-1} indicating coordination[6, 7]. The NH bending vibration occurs around 1630 cm^{-1} in free ligands. The band near 1600 ± 20 cm^{-1} is assigned to be due to this mode in complexes and its negative shift is an indication of coordination. In the complexes a strong band appears at 1010 ± 10 cm^{-1} which is assigned to CN stretching mode. The large negative shift of this band, when compared to free ligands (1250 cm^{-1}) suggest coordination.

The infrared spectra of 2,2′-dipyridyl and 1,10-phenanthroline complexes are very complicated and most of the bands show shifts on coordination, while some are split and often new bands appear as well[8, 9]. The $>\!C=C\!<$, $>\!C=N-$, ring stretching vibrations and CH in-plane deformation and ring breathing vibrations show positive shifts indicating coordination. A strong to medium band appears near 730±10 cm^{-1} which is due to out-of-plane ring deformation vibration. This band in free ligands is observed at 765 cm^{-1} and its negative shift is due to coordination.

(ii) The 5,5′-diethyl-2,4,6(1H) pyrimidinetrione has two bands which occur near 3200 cm^{-1} and 3100 cm^{-1} due to NH stretching vibration. In complexes its position is not altered. A series of four medium to intense bands occurs in the region 3000–2800 cm^{-1} and is due to alkyl CH stretching of the substituent at position five. These bands are not much altered in the complexes as these are not directly involved in coordination. The ligand has three strongly absorbing bands in the region 1765–1670 cm^{-1}. These bands are due to C=O stretching vibrations[10]. The band occurring at the highest frequency about 1760 cm^{-1} to 1740 cm^{-1} is due to C=O vibrations at position 4 to 6 which are perpendicular to the axis of symmetry of molecule. The next band occurring at 1720 cm^{-1} to 1700 cm^{-1} is also due to C=O at position 4 and 6 but is affected by the C=O vibration at position 2. The band at lowest frequency 1700 cm^{-1} to 1670 cm^{-1} is due to C=O vibration at position 2. In the complexes the band at highest frequency is less intense than the other two because of the symmetry of the molecule. These are also shifted slightly to lower frequency because of the change in the environment at position 3 which is the coordination site[11–13].

All the complexes are paramagnetic to the extent of one unpaired electron and the μ_{eff} values are around 2.00 B.M. The ligands used are sufficiently strong to form planar complexes[14–16]. It can be generalised that the planar complexes possess lower orbital contribution and this gives low μ_{eff} values, while tetrahedral complexes possess higher magnetic moments due to higher orbital contribution[17–22]. The μ_{eff} values agree well with the values obtained from EPR data. The two g values are obtained from EPR spectra. The g_{ave} μ_{eff} and G are calculated from the $g_{\perp}$ and $g_{\parallel}$ values. These data suggest monomeric nature of the complexes. Low values of G indicate very little exchange coupling.

All the complexes contain only one main broad band between 12.00–18.00 kK with one or two shoulders on either side around 11.00 kK and 20.00 kK. All the complexes are Jahn Teller susceptible. The ^2E_g state does not remain degenerate but splits into three sublevels and thus three transitions as indicated are seen in distorted complexes[23]. The transitions are $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$.

REFERENCES

1. W. Parri, *Bull. Chim. Farm.*, **63**, 4011 (1924).
2. J. T. L. Zwikker, *Phar. Weekblad.*, **68**, 975 (1931).
3. ———, *Phar. Weekblad.*, **69**, 1178 (1932).
4. L. Levi and C. E. Hubley, *Anal. Chem.*, **28**, 1591 (1956).
5. D. W. Powell and N. Sheppard, *J. Chem. Soc.*, **79** (1959).
6. P. C. H. Mitchell, *J. Inorg. Nucl. Chem.*, **25**, 966 (1969).
7. D. A. Baldwin and C. J. Leigh, *J. Chem. Soc.*, **A**, 1437 (1968).
8. A. Cristini, G. Ponticelli and A. Bıaz, *J. Chem. Soc.*, **A**, 1861 (1972).
9. P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 4547 (1962).
10. F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 1780 (1967).
11. W. C. Price, J. E. S. Bradley, R. D. B. Fraser and J. P. William, *J. Pharm. Pharmac*, **6**, 552 (1954).
12. B. C. Wang, *J. Coord. Chem.*, **3**, 179 (1973).
13. B. C. Wang and B. M. Craven, *Chem. Commun.*, 290 (1971).
14. D. P. Graddon, K. B. Heng and E. C. Walton, *Aust. J. Chem.*, **21**, 121 (1968).
15. Sacconi, A. Sabatini and P. Gans, *Inorg. Chem.*, **3**, 1772 (1964).
16. A. K. Mazumdar and M. M. Chakrawarty, *Z. Anal. Chem.*, **162**, 96 (1958).
17. W. Bayers, A. B. P. Lever and R. V. Parish, *Inorg. Chem.*, **7**, 1835 (1968).
18. S. P. Ghosh, *J. Indian Chem. Soc.*, **28**, 710 (1951).
19. P. Roy and D. N. Sen, *J. Indian Chem. Soc.*, **25**, 473 (1948).
20. K. Ito and T. Ito, *Aust. J. Chem.*, **11**, 406 (1958).
21. R. J. H. Clark and C. S. Williams, *J. Chem. Soc.*, **A**, 1425 (1966).
22. A. B. P. Lever and J. Lewis, *J. Chem. Soc.*, 1235 (1962).
23. H. A. Goodwin and R. N. Sylv , *Aust. J. Chem.*, **20**, 217 (1967).
24. L. E. Orgel, *J. Chem. Phys.*, **23**, 1824 (1955).

[*Received*: 31 January 1990; *Accepted*: 15 June 1991] AJC-333