

ionized donor density and hence an increase in the field for the same voltage is achieved. The increase in the field will further enhance impact ionization and donor density further increases and the entire process becomes cumulative and instantaneous till all the traps are ionized and switching takes place. The transition from high to low conductivity state can be explained on similar lines. In this case negative bias is applied to the upper electrode (i.e., the direction of the bias is reversed). The reverse bias increases the width of the depletion region near cadmium sulphide aluminium interface and for large applied voltage, impact ionization supercedes field ionization. Thus warm electrons are generated near cadmium sulphide aluminium interface which are trapped by barrier surrounded trapping centres near oxide semiconductor interface. This reduces the effective ionized donor density thereby resulting in a decrease of conductivity.

CONCLUSION

It is thus concluded that the memory switching in the system considered is due to filling and emptying of barrier-surrounded traps, which change its occupancy and hence the conductivity at threshold voltage when switching takes place.

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1. Chopra, K. L., *Proc. IEEE*, 1963, 51, 1242.
2. Braunstien, M., Braunstien, A. I. and Juleeg, R., *Appl. Phys. Letters*, 1967, 10, 313.
3. Hiatt, W. R. and Hickmott, T. W., *Ibid.*, 1965, 6, 106.
4. Argall, F., *Solid State Electronics*, 1968, 11, 535.
5. Hovel, H. J., *Appl. Phys. Letters*, 1970, 17, 141.
6. Ota, T., Morizumi, T. and Takahashi, K., *Jap. J. Appl. Phys.*, 1971, 10, 1652.
7. Duncan, W., *Electronics Letters*, 1972, Vol. 8, 26, 636.
8. Antic B. M. and Sinha, A. P. B., *Proc. IEEE*, 1968, 56 (7), 1259.
9. Klein, K., *Thin Solid Film*, 1971, 7, 149.
10. Ovshinsky, *Phys. Rev. Letters*, 1968, 21, 1450.
11. Gibbons, J. F. and Beadle, *Solid State Electronics*, 1964, 7, 785.
12. Sze, S. M., *Physics of Semiconductor Devices*, John Wiley and Sons, 1969, p. 400.
13. Srivastava, S. K., *Journal of Inst: of Tele comm. Engrs.*, 1969, 15 (11), 715.

MAGNETIC PROPERTIES OF COPPER (II) COMPLEXES OF SCHIFF BASES DERIVED FROM PYRROLE-2-ALDEHYDE AND ISOPROPANOLAMINE/2-AMINO-2-METHYLPROPANOL

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ABSTRACT

The synthesis of new copper(II) complexes of Schiff bases derived from pyrrole-2-aldehyde and isopropanolamine or 2-amino-2-methylpropanol is described. The Schiff bases coordinate through O, N and N as tridentate dibasic ligands. The complexes are characterised by magnetic susceptibility (84–294° K), infrared and electronic spectral studies. The magnetic moment of the copper (II) complex of pyrrole-isopropanolamine increases as the temperature is lowered indicating ferromagnetic nature of the complex while that of the copper(II) complex of pyrrole-2-amino-2-methylpropanol decreases with lowering of temperature indicating antiferromagnetic nature of the complex. The difference in magnetic properties has been attributed to the presence of steric hindrance arising out of two methyl groups in the latter complex.

INTRODUCTION

TRIDENTATE dibasic ligands yield metal complexes which frequently exhibit novel structural and magnetic properties¹⁻³. The dibasic character of these ligands force the metal (II) ions to dimerise or polymerise leading to metal complexes with unusual magnetic properties. The size of the chelate rings influence the magnetic properties of the copper(II) complexes⁴. We now report the effect of steric hindrance on the magnetic behaviour

of the copper(II) complexes of Schiff bases. We have prepared new copper(II) complexes with the tridentate dibasic ONN donor ligands I and II and studied the magnetic properties of the complexes from 84 to 294° K.

EXPERIMENTAL

Pyrrole-2-aldehyde (0.02 M) was dissolved in 40 ml ethanol and isopropanolamine (0.02 M) was mixed with 10 ml ethanol. These solutions were

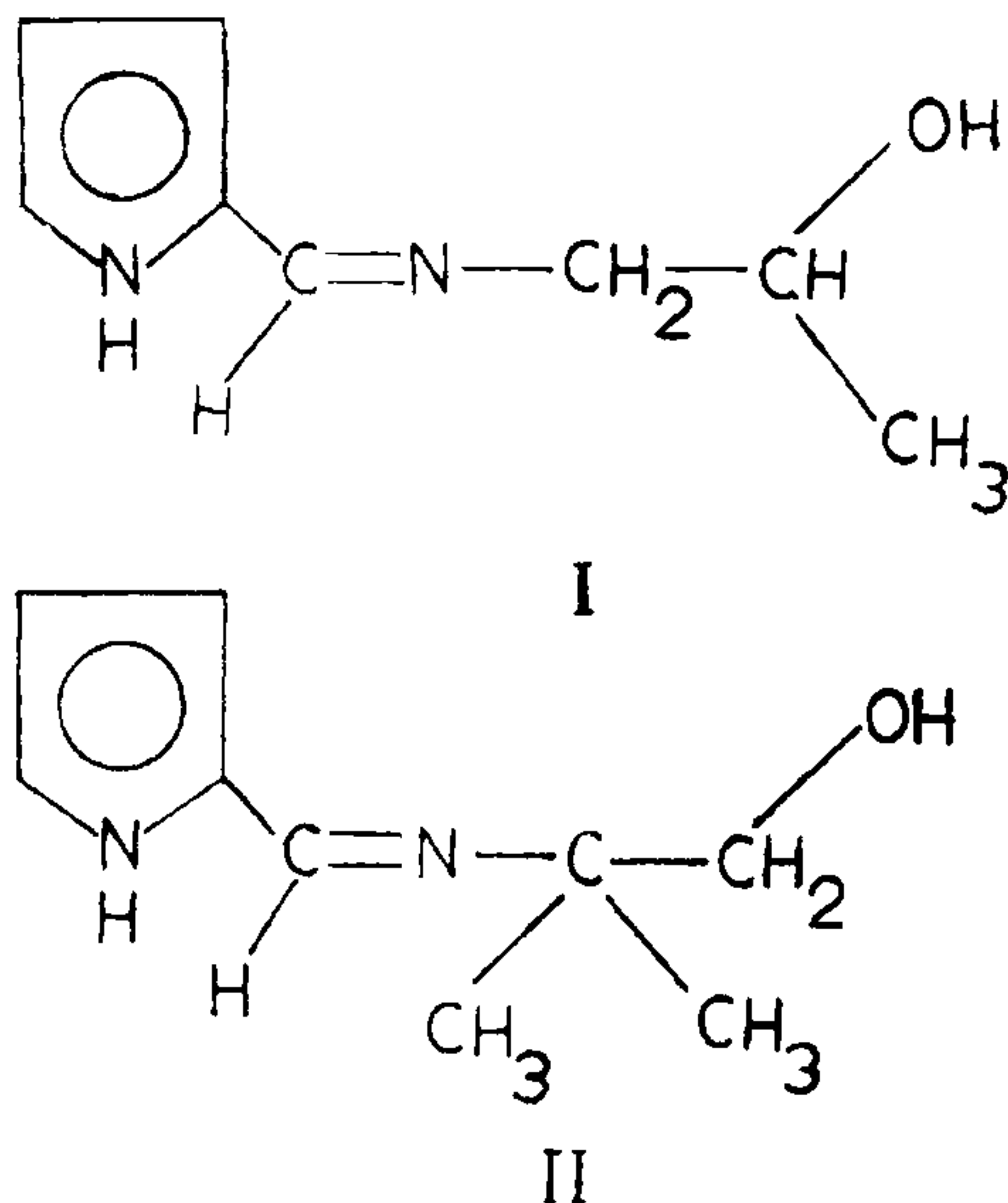
mixed and the mixture was refluxed on a water bath for 20 min. to give a yellow solution of the Schiff base. An aqueous solution of copper (II) nitrate trihydrate (0.01 M in 20 ml) was added slowly to the Schiff base solution with stirring followed by an aqueous solution of sodium carbonate (0.01 M in 20 ml). The mixture was stirred magnetically at 60°C for one hr and then cooled to room temperature. The separated green precipitates were suction filtered washed with ethanol and dried under vacuum. It was recrystallised from benzene and dried under vacuum (Yield 50%).

were done by the Gouy method. Diamagnetic corrections of the metal and ligand atoms were calculated using a standard source⁵. Electronic spectra were recorded in chloroform with a Beckman DK2 recording spectrophotometer using 10 mm matched quartz cells. IR spectra were recorded in KBr pellets on a Perkin Elmer Model 21 instrument. The molecular weights were determined in chloroform at 37°C using a Hewlett-Packard Mechrolab Model 301A vapour pressure osmometer calibrated with benzil.

RESULTS AND DISCUSSION

The infrared spectra of the complexes do not exhibit the $\nu(\text{OH})$ stretching vibration indicating the ligand coordination, dibasic character of the ligands and the absence of coordinated water in the complexes. The osmometric molecular weight measurements in chloroform indicate that the copper (II) complex of I is tetrameric (Found: 840, Calcd. 854), and of II is dimeric (Found: 410, Calcd. 455). Apparently the steric factor associated with the presence of two methyl groups in the ligand II is preventing the formation of tetrameric copper (II) complex. The electronic spectra in chloroform of copper (II) complexes of I and II exhibit a broad absorption band at 15950 and 17030 cm^{-1} respectively. This difference in band position may be attributed to the presence of different structures in these complexes^{6,7}.

The magnetic susceptibilities and magnetic moments of the complexes at several temperatures are presented in Table II. The magnetic moments of the copper (II) complex of I increase as the temperature is lowered. On the other hand, the magnetic moments of the copper (II) complex of II decrease with lowering of temperature. Approximating the magnetic properties using the Bleaney and Bowers equation⁸ gave positive J value ($J = +35 \text{ cm}^{-1}$) for the copper (II) complex of I and negative J value ($J = -133 \text{ cm}^{-1}$) for the copper (II) complex of II. Thus the magnetic data indicate that the copper (II) complexes of I and II are ferromagnetic and antiferromagnetic,



Cu(pyrrole-2-amino-2-methylpropanol) was prepared by following a similar procedure as described above. The complex was recrystallised from chloroform. (Yield 50%).

The microanalyses were done at the University of Bombay. The analytical data are given in Table I. The magnetic susceptibility measurements

TABLE I
Analytical and electronic spectral data of copper (II) complexes^a

Complex	Stoichiometry	%C	%H	%N	$\lambda_{\text{max}} (\epsilon)$
Cu (pyrrole-isopropanol-amine)	$\text{CuC}_8\text{H}_{10}\text{N}_2\text{O}$	Calcd. : 44.95 Found : 44.60	4.68 4.70	13.1 13.0	16950 (140*)
Cu (pyrrole-2-amino-2-methylpropanol)	$\text{CuC}_9\text{H}_{12}\text{N}_2\text{O}$	Calcd. : 47.47 Found : 47.60	5.3 6.0	12.3 12.1	17030 (115*)

^a Abbreviation : pyrrole = pyrrole-2-aldehyde. * litre mole⁻¹ cm⁻¹

TABLE II

Magnetic susceptibilities and magnetic moments of copper (II) Schiff base complexes^{a, b}

Cu (pyrrole-isopropanolamine)				Cu (pyrrole-2-amino-2-methyl-propanol)			
Temp. (°K)	$\chi_{\text{corr}}^{\text{M}}$ (10^{-6} cgs unit)	μ_{eff} (BM)	J° cm^{-1}	Temp. (°K)	$\chi_{\text{corr}}^{\text{M}}$ (10^{-6} cgs unit)	μ_{eff} (BM)	J° cm^{-1}
293	1371	1.80		294	1059	1.58	
215	1946	1.83		215	1295	1.50	
161	2646	1.85	+35	159	1553	1.41	-133
128	3388	1.87		126	1694	1.31	
101	4310	1.87		105	1764	1.22	
84	5283	1.89		84	1812	1.11	

^a Magnetic moment was calculated using the Curie equation:

$$\mu_{\text{eff}} = 2.84 (\chi_{\text{corr}}^{\text{M}} T)^{\frac{1}{2}} \text{ BM.}$$

^b T.I.P. = 50×10^{-6} cgs units.^c $g = 2.05$ was used.

respectively^{1,4,9,10}. This difference in magnetic behaviour in these two complexes may be related to the presence of different structures in these complexes—One a tetramer and the other, a dimer. As the ligands I and II both form five membered chelate rings around copper (II) in aminoalcohol part of the molecules, we believe this significant difference in magnetic behaviour is due to the steric hindrance of the two methyl groups which prevent the formation of tetramer in copper (II) complex of II. On the basis of X-ray structure determination of known copper (II) complexes of tridentate dibasic Schiff bases with comparable magnetic properties, we propose a square planar structure for the dimeric, antiferromagnetic copper (II) complex of II and a distorted trigonal bipyramidal arrangement for the tetrameric, ferromagnetic copper (II) complex of I^{1,6,7}.

It is interesting to note that the copper (II) complex of pyrrole-2-aldehyde-propanolamine is dimeric with square planar arrangement around each copper (II) and the complex is involved in the antiferromagnetic spin-spin coupling⁶. This ligand forms a six membered chelate ring around copper (II) in aminoalcohol part of the molecule. When the size of the chelate ring is five membered in the copper (II) complex of the ligand I one gets a ferromagnetic copper (II) compound. We do not

see this chelate ring effect in the copper (II) complex of the ligand II due to the steric hindrance as described earlier.

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1. Hatfield, W. E. and Whyman, R., *Transition Metal Chemistry*, 1969, 5, 47.
2. Bertrand, J. A., Breece, J. L., Kalyanaraman, A. R., Long, G. J. and Baker, Jr., W. A., *J. Amer. Chem. Soc.*, 1970, 92, 5233.
3. — and Eller, P. G., *Inorg. Chem.*, 1974, 13, 928.
4. Syamal, A. and Theriot, L. J., *J. Coord. Chem.*, 1973, 2, 241.
5. Figgis, B. N. and Lewis, J., cited in *Modern Coordination Chemistry*, Edited by Lewis, J. and Wilkins, R. G. (Interscience Publishers, Inc., New York), 1960, p. 403.
6. Bertrand, J. A. and Kirkwood, C. E., *Inorg. Chim. Acta*, 1972, 6, 248.
7. — and Kelley, J. A., *Ibid.*, 1970, 4, 203.
8. Bleaney, B. and Bowers, K. D., *Proc. Roy. Soc.*, 1952, 214 A, 451.
9. Casey, A. T., Hoskins, B. F. and Williams, F. D., *Chem. Comm.*, 1970, p. 904.
10. Barnes, J. A., Hodgson, D. J. and Hatfield, W. E., *Inorg. Chem.*, 1972, 11, 144.