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CHAPTER II

Binuclear Complexes Involving Symmetrical Tetradentate Schiff Bases

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The binuclear complexes prepared can be subgrouped into two general categories viz. $[Cu(TSB)Cu(ClO_4)_2]$ and $[Cu(TSB)Cu(A\text{-}A)](ClO_4)_2$, where TSB corresponds to tetradentate schiff bases of the type,

TSB^1 = N,N'-ethylene-bis(salicylaldiminate)

TSB^2 = N,N'-ethylene-bis(2-hydroxyacetophenoniminate)

TSB^3 = N,N'-propylene-bis(salicylaldiminate)

TSB^4 = N,N'-propylene-bis(2-hydroxyacetophenoniminate)

TSB^5 = N,N'-o-phenylene-bis(salicylaldiminate)

TSB^6 = N,N'-o-phenylene-bis(2-hydroxyacetophenoniminate)

TSB^7 = N,N'-butylene-bis(salicylaldiminate)

TSB^8 = N,N'-butylene-bis(2-hydroxyacetophenoniminate)

TSB^9 = N,N'-hexylene-bis(salicylaldiminate)

TSB^{10} = N,N'-hexylene-bis(2-hydroxyacetophenoniminate)

A-A corresponds to,

A^1 = 2,2'-bipyridyl

A^2 = 1,10-phenanthroline

A^3 = 2-(2'-pyridyl)benzimidazole.

The details of preparation of individual complexes and their characterization are given in the following sections.

EXPERIMENTAL

Material

Analytical Reagent grade chemicals (> 99.9% purity) were used for all the preparations. $Cu(ClO_4)_2.6H_2O$ was prepared by dissolving Cupric carbonate monohydrate (1.5 mol) in perchloric acid (2 mol). Cupric carbonate was taken in excess in order to avoid the perchloric acid remaining in solution. The mixture was boiled for 30 minutes. The excess Cupric carbonate was later removed by filtering. $Cu(ClO_4)_2.6H_2O$ was obtained by evaporating the above filtrate. The solid was recrystallised from ethanol and dried in vacuum to constant weight. The percentage of Copper(II) was estimated iodometrically and was found to correspond to the formula $Cu(ClO_4)_2.6H_2O$. Imine schiff base complexes were prepared by treating salicylaldehyde or 2-hydroxyacetophenone with Copper ammonia complex. This was further reacted with diamines to give rise to tetradentate schiff base complex.[124] 2-(2'-pyridyl)benzimidazole was prepared by the method suggested in literature.[125]

Preparation Of Binuclear Complexes $[Cu(TSB)Cu(ClO_4)_2]$

To a solution of $[Cu(TSB)]$ (0.003 mol in 50 ml chloroform) was added a solution of $Cu(ClO_4)_2.6H_2O$ (0.003 mol in 20 ml ethanol) and the mixture was refluxed for 1 hour with constant stirring. Resulting solid was filtered, washed thoroughly with 1 : 1 chloroform ethanol mixture and dried in vacuum to constant weight.

Preparation Of Binuclear Complexes [Cu(TSB)Cu(A-A)] $(ClO_4)_2$

A suspension of $[Cu(A\text{-}A)(ClO_4)_2]$ was prepared by adding A-A (0.003 mol) in 10 ml absolute ethanol to a solution of $Cu(ClO_4)_2.6H_2O$ (0.003 mol) in 10 ml absolute ethanol. This suspension was then added to [Cu(TSB)] (0.0035 mol) dissolved in 50 ml chloroform. The mixture was refluxed for about 2 hours with constant stirring. The resulting solid was filtered off, washed thoroughly with chloroform to remove excess of [Cu(TSB)] and dried under vacuum to constant weight.

Copper(II) was estimated iodometrically. N, C and H were estimated on Coleman Analyzer Models 29 and 33, respectively (Table II 1).

T.L.C. analyses were carried out on silica gel G (Sichem) plates using alcohol as developer. After the T.L.C. run the plates were exposed to iodine vapour till the spot developed.

Spectral Measurements

Infrared spectra were recorded using KBr discs on Perkin Elmer Infrared Spectrometer (Model No. 567). The band positions of all the complexes are given in Tables II 2 and II 3.

Reflectance spectra of representative complexes were obtained on a Reflectance spectrophotometer VS U2-P of CZ Jena. Magnesium carbonate (heavy) was used as a standard for light reflectance and as the base material to dilute the complexes, in order to obtain appropriate intensities in the reflected light. The preparation of the samples for the spectral measurements involves the following steps.

The compound was first ground in a small agate mortar and mixed with previously ground Magnesium carbonate. Grinding of the mixture was further continued till homogenity was achieved. The spectrophotometer was checked for wavelength calibration at 546.1 mμ by using a mercury lamp before and after each measurement. The measurements were made at constant temperature to obtain reproducibility (Table II 4).

UV spectra were recorded on a CZ SPECORD UV/VIS spectrophotometer with 1 cm matched quartz cells using ethanol as solvent (Tables II 5 and II 6).

Magnetic Susceptibility Measurements

Magnetic susceptibility measurements were carried out using the Guoy method.[126] The measurements were carried out at room temperature ($\sim 300^{o}K$). The compound was first dried thoroughly and was finely powdered. This dry and finely powdered compound was filled up in the calibrated tube (whose tube constant (β) was previously determined) up to the calibration mark. The tube was then suspended with its bottom at the centre of the gap between the pole faces of the electromagnet. The tube was weighed with and without the magnetic field and difference in weight of the tube (ΔW) containing 'w' gram of the sample was determined. The deflection in the weight of the empty tube (δ) was also determined at the same field strength.

The volume of the sample in the tube was determined in order to apply correction due to air displaced by the sample. The tube was calibrated using conductivity water ($\chi = -0.72 \times 10^{-6}$ c.g.s.u.) and $Hg\left[Co(CNS)_4\right]$ ($\chi = 16.44 \times 10^{-6}$ c.g.s.u.) as the standard. The specific susceptibility was calculated using the following expression,

$$\chi_g = \frac{\alpha + \beta \ dw}{W}, \quad \text{where}$$

$$\alpha = \chi_2 \rho_2 V = 0.029 \ V \times 10^{-6}$$

β = tube constant

dw = $\Delta W - \delta$ in milligrams

ΔW = apparent change in weight of the tube containing 'w' gram of the sample on application of field

δ = deflection in the weight of the empty tube

W = weight of the complex taken in grams

In order to minimize error due to packing of the solid into the tube, determination with each sample was repeated three or four times with fresh packing.

The molar susceptibility, χ_m, was obtained by multiplying the gram susceptibility (specific) by the molecular weight. Diamagnetic correction was applied using Pascal's constants[127] to get the corrected molar susceptibility, $\chi_{m\ (corr.)}$. Using values of $\chi_{m\ (corr.)}$, magnetic moments were calculated from the expression,

$$\mu_{eff} = 2.828 \sqrt{(\chi_{m\ (corr.)} - N\alpha)\, T}, \quad \text{where}$$

$N\alpha$ = temperature independent paramagnetic moment
$= 60 \times 10^{-6}$ c.g.s.u.

The μ_{eff} value of all binuclear complexes are given in Table II 1.

It has been observed earlier that $[Cu(TSB)CuX_2]$ type of complexes obey Bleaney and Bower's equation[100] for the calculation of J, at different temperatures.

$$\chi_m = \frac{2g^2\beta^2N}{3\ kT}\left[\frac{1}{1 + \frac{1}{3}\ e^{(-2J/kT)}}\right] + N\alpha$$

In the case of $[Cu(TSB)Cu(A\text{-}A)]\ (ClO_4)_2$ complexes, it was assumed that they obey Bleaney and Bower's equation, though this could not be verified by variable temperature susceptibility measurements due to the lack of facilities. The value of spin spin exchange interaction constant, J, was calculated by substituting χ_m and g values at room temperature ($\sim 300^{o}K$) in the above equation. The values thus calculated for some representative complexes are given in Table II 7.

The ESR spectra of some binuclear complexes (Table II 7) in powder form were recorded on a Varian E 112 X band Superheterodyne spectrometer at room temperature. In case of $[Cu(TSB^1)Cu(A^1)](ClO_4)_2$ ESR spectrum was also obtained at liquid N_2 temperature. The value of g for the complexes was calculated using the following equation,

$$g_1 = \frac{g_2 H_2}{H_1}, \quad \text{where}$$

g_1 = spectroscopic splitting factor for the complex

g_2 = spectroscopic splitting factor for free electron i.e. 2.0023

H_2 = field strength of marker

H_1 = field strength of the sample.

Diphenyl picryl hydrozide (DPPH) was used as the g marker. In the case of $[Cu(TSB^1)Cu(A^1)](ClO_4)_2$ complex for which g values were calculated at room temperature and at liquid nitrogen temperature, it was observed that the g values are same at two temperatures. Therefore, the room temperature g values have been used for the calculation of spin spin exchange interaction constant, J.

Table II 1 : Analytical and Magnetic Data of Binuclear Complexes

Compound	Colour	Analyses % *				μ_{eff}/ Cu(II) ion in B.M.
		Cu	N	C	H	
$[Cu(TSB^1)Cu(ClO_4)_2]$	Brown	21.15 (21.46)	5.13 (4.52)	- -	- -	1.02
$[Cu(TSB^1)Cu(A^1)](ClO_4)_2$	Brown	16.78 (16.99)	6.80 (7.49)	41.06 (41.71)	3.35 (2.94)	1.19
$[Cu(TSB^1)Cu(A^2)](ClO_4)_2$	Brown	16.63 (16.46)	6.88 (7.25)	42.89 (43.52)	3.08 (2.87)	1.17
$[Cu(TSB^1)Cu(A^3)](ClO_4)_2$	Brown	15.98 (16.15)	9.09 (8.89)	41.88 (42.69)	3.24 (2.98)	1.20
$[Cu(TSB^2)Cu(ClO_4)_2]$	Brown	20.35 (20.49)	5.13 (4.52)	36.70 (34.83)	4.05 (2.90)	1.02
$[Cu(TSB^2)Cu(A^1)](ClO_4)_2$	Brown	16.21 (16.37)	6.88 (7.22)	43.40 (43.29)	3.23 (3.35)	1.17
$[Cu(TSB^2)Cu(A^2)](ClO_4)_2$	Brown	15.66 (15.88)	7.27 (7.00)	45.40 (45.00)	3.46 (3.12)	1.12

cont...

$[Cu(TSB^2)Cu(A^3)](ClO_4)_2$	Brown	15.19 (15.59)	8.94 (8.59)	44.52 (44.17)	3.39 (3.31)	1.16
$[Cu(TSB^3)Cu(ClO_4)_2]$	Olive green	20.57 (20.97)	4.71 (4.62)	- -	- -	0.95
$[Cu(TSB^3)Cu(A^1)](ClO_4)_2$	Olive green	16.27 (16.68)	7.59 (7.35)	42.26 (42.52)	3.05 (3.15)	0.92
$[Cu(TSB^3)Cu(A^2)](ClO_4)_2$	Olive green	15.85 (16.17)	6.48 (7.12)	44.22 (44.27)	3.18 (3.05)	0.95
$[Cu(TSB^3)Cu(A^3)](ClO_4)_2$	Olive green	15.76 (15.86)	8.65 (8.74)	43.00 (43.44)	3.54 (3.12)	1.02
$[Cu(TSB^4)Cu(ClO_4)_2]$	Brown	19.53 (20.04)	5.32 (4.42)	- -	- -	0.82
$[Cu(TSB^4)Cu(A^1)](ClO_4)_2$	Bluish black	15.66 (16.08)	7.28 (7.09)	44.54 (44.05)	3.90 (3.54)	0.83
$[Cu(TSB^4)Cu(A^2)](ClO_4)_2$	Grey	15.90 (15.61)	6.68 (6.88)	46.00 (45.70)	3.63 (3.44)	0.92
$[Cu(TSB^4)Cu(A^3)](ClO_4)_2$	Olive green	15.36 (15.33)	8.65 (8.44)	45.34 (44.87)	3.91 (3.50)	0.99
$[Cu(TSB^5)Cu(ClO_4)_2]$	Brown	19.42 (19.85)	4.06 (4.37)	- -	- -	1.06

cont...

$[Cu(TSB^5)Cu(A^1)](ClO_4)_2$	Brown	15.60 (15.96)	7.06 (7.03)	45.20 (45.22)	2.72 (2.76)	1.06
$[Cu(TSB^5)Cu(A^2)](ClO_4)_2$	Brown	15.07 (15.50)	7.01 (6.83)	46.69 (46.82)	2.68 (2.68)	1.06
$[Cu(TSB^5)Cu(A^3)](ClO_4)_2$	Brown	15.10 (15.22)	8.32 (8.38)	45.76 (45.98)	2.73 (2.75)	1.00
$[Cu(TSB^6)Cu(ClO_4)_2]$	Brown	19.61 (19.02)	4.15 (4.19)	39.36 (39.52)	2.59 (2.69)	0.99
$[Cu(TSB^6)Cu(A^1)](ClO_4)_2$	Olive green	15.04 (15.42)	6.67 (6.80)	46.45 (46.60)	3.20 (3.16)	1.05
$[Cu(TSB^6)Cu(A^2)](ClO_4)_2$	Olive green	14.95 (14.98)	6.46 (6.60)	47.87 (48.11)	2.93 (3.07)	1.06
$[Cu(TSB^6)Cu(A^3)](ClO_4)_2$	Olive green	14.66 (14.72)	8.02 (8.11)	46.98 (47.27)	3.02 (3.13)	0.99
$[Cu(TSB^7)Cu(A^1)](ClO_4)_2$	Green	16.63 (16.37)	7.17 (7.21)	43.39 (43.29)	3.52 (3.35)	1.17
$[Cu(TSB^7)Cu(A^2)](ClO_4)_2$	Green	15.98 (15.88)	7.19 (7.00)	45.35 (45.00)	3.15 (3.25)	1.12
$[Cu(TSB^7)Cu(A^3)](ClO_4)_2$	Green	15.61 (15.59)	8.49 (8.59)	44.75 (44.17)	3.54 (3.31)	1.12

cont...

$[Cu(TSB^{8})Cu(A^{1})](ClO_4)_2$	Green	16.12 (15.80)	6.38 (6.96)	44.43 (44.77)	3.52 (3.73)	1.19
$[Cu(TSB^{8})Cu(A^{2})](ClO_4)_2$	Green	15.82 (15.35)	6.32 (6.76)	- -	- -	1.15
$[Cu(TSB^{8})Cu(A^{3})](ClO_4)_2$	Green	15.45 (15.07)	8.41 (8.30)	44.26 (45.55)	4.07 (3.68)	1.12
$[Cu(TSB^{9})Cu(A^{1})](ClO_4)_2$	Green	15.62 (15.80)	7.11 (6.96)	45.34 (44.77)	3.64 (3.73)	1.26
$[Cu(TSB^{9})Cu(A^{2})](ClO_4)_2$	Green	15.21 (15.35)	6.33 (6.76)	46.43 (46.37)	3.71 (3.62)	1.14
$[Cu(TSB^{9})Cu(A^{3})](ClO_4)_2$	Green	15.37 (15.07)	8.19 (8.30)	45.67 (45.55)	3.90 (3.68)	1.13
$[Cu(TSB^{10})Cu(A^{1})](ClO_4)_2$	Green	15.49 (15.27)	6.42 (6.73)	46.34 (46.15)	4.24 (4.09)	1.23
$[Cu(TSB^{10})Cu(A^{2})](ClO_4)_2$	Green	15.29 (14.84)	6.26 (6.54)	48.03 (47.66)	4.11 (3.97)	1.08
$[Cu(TSB^{10})Cu(A^{3})](ClO_4)_2$	Green	15.88 (15.59)	8.52 (8.04)	46.69 (46.84)	4.72 (4.02)	1.14

*Calculated values are given in parentheses

Table II 2 : Infrared Spectra (cm^{-1}) of $[Cu(TSB)]$ Complexes

Compound					
$[Cu(TSB^1)]$	3 040 (w),	2 900 (m),	1 620 (m),	1 600 (m),	1 575 (m),
	1 530 (w),	1 480 (w),	1 460 (m),	1 450 (s),	1 425 (s),
	1 380 (w),	1 325 (m),	1 300 (w),	1 240 (m),	1 190 (s),
	1 140 (m),	1 050 (w),	1 020 (w),	980 (w),	955 (w),
	920 (w),	850 (w),	800 (w),	770 (m),	760 (w),
	730 (m),	670 (w),	640 (w)		
$[Cu(TSB^2)]$	3 040 (w),	2 905 (m),	1 620 (m),	1 600 (m),	1 590 (s),
	1 560 (m),	1 530 (m),	1 480 (m),	1 465 (w),	1 440 (s),
	1 370 (m),	1 350 (m),	1 330 (s),	1 260 (m),	1 230 (s),
	1 190 (s),	1 160 (w),	1 140 (m),	1 090 (w),	1 040 (w),
	1 030 (w),	970 (w),	940 (w),	910 (w),	850 (w),
	815 (w),	770 (w),	730 (m),	690 (w)	

cont...

[Cu(TSB^3)]	3 040 (w),	2 900 (m),	1 620 (m),	1 600 (s),	1 570 (s),
	1 535 (m),	1 480 (m),	1 450 (s),	1 380 (s),	1 350 (s),
	1 320 (s),	1 250 (m),	1 200 (m),	1 150 (m),	1 070 (w),
	1 020 (m),	950 (w),	900 (w),	840 (w),	770 (w),
	730 (m),	680 (w).			
[Cu(TSB^4)]	3 040 (w),	2 900 (w),	1 620 (m),	1 600 (s),	1 580 (s),
	1 535 (m),	1 480 (w),	1 450 (w),	1 430 (s),	1 370 (w),
	1 340 (m),	1 300 (w),	1 235 (s),	1 190 (w),	1 150 (w),
	1 060 (w),	980 (w),	955 (w),	910 (w),	840 (b,w),
	800 (w),	760 (w),	720 (w),	640 (w)	
[Cu(TSB^5)]	3 030 (w),	3 000 (w),	2 940 (m),	1 620 (m),	1 600 (s),
	1 570 (m),	1 525 (m),	1 480 (w),	1 450 (s),	1 440 (s),
	1 370 (s),	1 330 (s),	1 250 (m),	1 205 (m),	1 185 (s),
	1 150 (s),	1 140 (s),	1 050 (w),	1 030 (m),	980 (m),
	950 (m),	920 (m),	890 (w),	860 (s),	850 (m),
	800 (s),	760 (s),	730 (m),	615 (w)	

cont...

$[Cu(TSB^7)]$	3 030 (w),	3 000 (w),	2 950 (w),	2 900 (w),	1 625 (m),
	1 600 (s),	1 580 (s),	1 525 (m),	1 480 (m),	1 450 (m),
	1 375 (s),	1 335 (w),	1 250 (m),	1 180 (m),	1 145 (m),
	1 090 (s),	1 060 (s),	1 035 (s),	980 (m),	940 (w),
	910 (w),	880 (w),	760 (m),	730 (m),	690 (w),
	650 (w)				
$[Cu(TSB^8)]$	3 025 (w),	3 000 (w),	2 900 (w),	1 625 (m),	1 600 (s),
	1 580 (s),	1 535 (m),	1 480 (m),	1 460 (m),	1 440 (s),
	1 370 (m),	1 335 (m),	1 320 (m),	1 250 (m),	1 225 (s),
	1 200 (w),	1 190 (m),	1 140 (w),	1 050 (s),	980 (m),
	950 (w),	860 (w),	825 (w),	755 (m),	725 (m),
	680 (w),	650 (w)			
$[Cu(TSB^9)]$	3 040 (w),	2 900 (w),	1 620 (m),	1 600 (s),	1 580 (s),
	1 535 (m),	1 480 (s),	1 440 (s),	1 380 (w),	1 350 (m),
	1 300 (w),	1 260 (m),	1 230 (w),	1 190 (m),	1 070 (s),
	1 050 (s),	980 (m),	950 (w),	890 (w),	840 (w),
	760 (m),	730 (m),	620 (w)		

cont...

$[Cu(TSB^{10})]$	3 040 (w),	2 905 (w),	1 620 (m),	1 600 (s),	1 580 (s),
	1 535 (m),	1 470 (s),	1 435 (s),	1 380 (s),	1 340 (m),
	1 330 (w),	1 290 (w),	1 260 (w),	1 230 (w),	1 190 (m),
	1 140 (m),	1 050 (m),	970 (w),	950 (m),	880 (w),
	850 (w),	760 (m),	730 (m),	660 (w),	625 (w)

Table II 3 : Infrared Spectra (cm^{-1}) of Binuclear Complexes

Compound				
$[Cu(TSB^1)Cu(A^1)](ClO_4)_2$	3 100 (w),	3 045 (w),	2 900 (m),	1 630 (m),
	1 595 (s),	1 580 (m),	1 555 (m),	1 490 (w),
	1 460 (m),	1 440 (s),	1 420 (m),	1 410 (m),
	1 375 (m),	1 330 (w),	1 320 (w),	1 295 (m),
	1 270 (s),	1 210 (m),	1 150 (w),	1 100 (s),
	1 070 (s),	990 (w),	970 (w),	920 (w),
	890 (w),	790 (m),	770 (m),	730 (s)
$[Cu(TSB^1)Cu(A^2)](ClO_4)_2$	3 050 (w),	2 860 (w),	1 635 (s),	1 600 (s),
	1 550 (m),	1 485 (m),	1 460 (w),	1 450 (s),
	1 440 (m),	1 380 (m),	1 340 (w),	1 320 (w),
	1 280 (s),	1 265 (m),	1 240 (w),	1 205 (w),
	1 155 (m),	1 100 (s),	1 080 (s),	980 (w),
	920 (w),	900 (w),	850 (w),	795 (m),
	765 (w),	720 (w)		

cont...

$[Cu(TSB^1)Cu(A^3)](ClO_4)_2$	3 100 (w),	2 910 (w),	1 625 (s),	1 595 (s),
	1 580 (m),	1 550 (m),	1 485 (m),	1 465 (w),
	1 440 (s),	1 420 (w),	1 390 (w),	1 375 (w),
	1 300 (w),	1 280 (m),	1 240 (m),	1 200 (w),
	1 150 (w),	1 130 (w),	1 100 (s),	1 060 (s),
	1 020 (w),	1 005 (w),	980 (w),	920 (w),
	900 (m),	890 (w),	780 (w),	750 (m),
	650 (w)			
$[Cu(TSB^2)Cu(A^1)](ClO_4)_2$	3 050 (w),	2 890 (w),	1 625 (m),	1 600 (m),
	1 580 (s),	1 565 (w),	1 555 (m),	1 485 (m),
	1 460 (m),	1 435 (s),	1 380 (m),	1 355 (m),
	1 300 (s),	1 270 (m),	1 220 (s),	1 170 (m),
	1 150 (m),	1 095 (s),	1 070 (s),	1 050 (s),
	980 (w),	920 (w),	860 (m),	820 (w),
	775 (w),	740 (s),	620 (w)	

cont...

$[Cu(TSB^2)Cu(A^2)](ClO_4)_2$	3 050 (w),	2 885 (w),	1 630 (m),	1 600 (s),
	1 560 (m),	1 545 (m),	1 520 (w),	1 485 (m),
	1 450 (s),	1 380 (m),	1 350 (m),	1 330 (m),
	1 300 (m),	1 280 (w),	1 230 (s),	1 150 (w),
	1 100 (s),	1 050 (s),	950 (w),	920 (w),
	850 (w),	830 (w),	800 (m),	765 (m),
	660 (w)			
$[Cu(TSB^2)Cu(A^3)](ClO_4)_2$	3 140 (w),	2 900 (w),	1 625 (m),	1 600 (s),
	1 590 (s),	1 550 (m),	1 520 (w),	1 490 (m),
	1 445 (s),	1 375 (s),	1 330 (w),	1 300 (m),
	1 270 (w),	1 230 (m),	1 160 (w),	1 150 (m),
	1 100 (s),	1 060 (s),	1 020 (w),	980 (w),
	900 (w),	855 (w),	770 (w),	750 (w),
	630 (m)			

cont...

$[Cu(TSB^3)Cu(A^1)](ClO_4)_2$	3 100 (w),	2 900 (w),	1 625 (s),	1 600 (s),
	1 580 (s),	1 565 (w),	1 555 (m),	1 480 (w),
	1 460 (m),	1 445 (s),	1 420 (w),	1 405 (w),
	1 380 (m),	1 370 (m),	1 350 (w),	1 320 (w),
	1 300 (w),	1 285 (s),	1 245 (w),	1 210 (m),
	1 155 (m),	1 100 (s),	1 080 (m),	1 065 (s),
	1 040 (w),	1 000 (w),	970 (w),	920 (w),
	865 (w),	850 (w),	765 (m),	730 (m),
	700 (w)			
$[Cu(TSB^3)Cu(A^2)](ClO_4)_2$	3 090 (w),	2 895 (w),	1 625 (s),	1 595 (s),
	1 550 (m),	1 510 (w),	1 480 (w),	1 450 (m),
	1 435 (s),	1 370 (m),	1 350 (m),	1 330 (w),
	1 300 (w),	1 285 (s),	1 250 (w),	1 215 (w),
	1 200 (w),	1 155 (m),	1 100 (s),	1 060 (s),
	1 040 (w),	980 (w),	920 (w),	875 (w),
	865 (w),	850 (m),	800 (w),	765 (m),
	740 (m),	660 (w)		

cont...

$[Cu(TSB^3)Cu(A^3)](ClO_4)_2$	3 060 (w), 2 880 (w), 1 630 (m), 1 605 (m), 1 590 (s), 1 550 (m), 1 510 (w), 1 484 (m), 1 465 (w), 1 450 (w), 1 440 (s), 1 410 (w), 1 360 (m), 1 340 (m), 1 290 (w), 1 275 (s), 1 235 (w), 1 155 (m), 1 130 (w), 1 100 (s), 1 080 (s), 1 050 (s), 980 (w), 890 (w), 820 (w), 785 (w), 750 (w), 700 (w), 660 (w)
$[Cu(TSB^4)Cu(A^1)](ClO_4)_2$	3 040 (w), 2 900 (w), 1 625 (m), 1 600 (s), 1 590 (s), 1 545 (s), 1 480 (m), 1 440 (s), 1 380 (m), 1 340 (m), 1 300 (m), 1 270 (m), 1 250 (m), 1 210 (w), 1 160 (w), 1 100 (s), 1 080 (m), 1 050 (s), 1 020 (w), 920 (w), 900 (w), 880 (w), 850 (w), 765 (m), 700 (w), 625 (w)

cont...

$[\dot{C}u(TSB^4)Cu(A^2)](ClO_4)_2$	3 050 (w),	2 900 (w),	1 630 (m),	1 600 (s),
	1 590 (s),	1 555 (s),	1 490 (m),	1 450 (s),
	1 390 (s),	1 370 (s),	1 350 (m),	1 310 (s),
	1 270 (m),	1 250 (s),	1 210 (w),	1 150 (m),
	1 100 (s),	1 050 (s),	970 (m),	940 (w),
	920 (w),	890 (w),	850 (m),	770 (w),
	630 (w)			
$[Cu(TSB^4)Cu(A^3)](ClO_4)_2$	3 050 (w),	2 890 (w),	1 635 (m),	1 600 (s),
	1 590 (s),	1 580 (s),	1 555 (s),	1 515 (m),
	1 490 (m),	1 440 (s),	1 380 (m),	1 360 (m),
	1 340 (w),	1 300 (s),	1 270 (m),	1 250 (w),
	1 235 (s),	1 210 (w),	1 150 (m),	1 100 (s),
	1 045 (s),	970 (w),	920 (w),	850 (w),
	810 (w),	770 (m),	750 (m),	710 (w),
	670 (w),	610 (w)		

cont...

$[Cu(TSB^5)Cu(A^1)](ClO_4)_2$	3 040 (w),	2 900 (m),	1 625 (m),	1 600 (s),
	1 590 (s),	1 540 (m),	1 490 (m),	1 450 (s),
	1 445 (s),	1 380 (m),	1 340 (m),	1 275 (m),
	1 210 (m),	1 160 (s),	1 150 (m),	1 100 (s),
	985 (m),	920 (w),	880 (w),	855 (m),
	810 (m),	770 (s),	700 (w),	615 (w)
$[Cu(TSB^7)Cu(A^1)](ClO_4)_2$	3 030 (w),	3 000 (w),	2 950 (m),	1 630 (s),
	1 600 (s),	1 580 (m),	1 545 (m),	1 515 (w),
	1 485 (m),	1 460 (m),	1 440 (s),	1 410 (w),
	1 375 (m),	1 340 (w),	1 310 (m),	1 280 (m),
	1 250 (w),	1 210 (w),	1 180 (m),	1 145 (m),
	1 100 (s),	1 055 (s),	1 040 (s),	950 (m),
	920 (w),	900 (w),	880 (m),	770 (m),
	710 (w),	690 (w),	650 (w)	

cont...

$[Cu(TSB^7)Cu(A^2)](ClO_4)_2$	3 020 (w),	2 900 (w),	1 630 (m),	1 590 (s),
	1 545 (m),	1 510 (w),	1 480 (m),	1 460 (m),
	1 450 (s),	1 425 (s),	1 375 (m),	1 360 (m),
	1 310 (m),	1 280 (m),	1 210 (w),	1 185 (m),
	1 150 (m),	1 100 (s),	1 060 (s),	1 030 (w),
	980 (w),	920 (w),	900 (w),	870 (w),
	770 (m),	720 (m),	660 (w)	
$[Cu(TSB^7)Cu(A^3)](ClO_4)_2$	3 060 (w),	2 900 (w),	1 625 (m),	1 600 (s),
	1 550 (m),	1 510 (w),	1 480 (s),	1 460 (m),
	1 440 (s),	1 420 (m),	1 380 (s),	1 370 (m),
	1 310 (w),	1 280 (w),	1 240 (w),	1 190 (w),
	1 100 (s),	1 080 (s),	1 030 (s),	960 (w),
	920 (w),	900 (m),	810 (w),	770 (m),
	740 (m),	710 (m),	660 (w)	

cont...

$[Cu(TSB^8)Cu(A^1)](ClO_4)_2$	3 060 (w), 3 000 (w), 2 900 (w), 1 630 (m), 1 600 (s), 1 580 (s), 1 555 (s), 1 480 (m), 1 460 (m), 1 440 (s), 1 370 (m), 1 340 (m), 1 275 (m), 1 250 (m), 1 210 (w), 1 160 (w), 1 150 (m), 1 100 (s), 1 050 (s), 980 (m), 920 (w), 900 (w), 860 (w), 830 (w), 800 (w), 765 (m), 720 (m), 680 (w), 650 (w)
$[Cu(TSB^8)Cu(A^2)](ClO_4)_2$	3 040 (w), 2 900 (w), 1 630 (m), 1 600 (s), 1 570 (s), 1 555 (m), 1 510 (w), 1 485 (m), 1 450 (s), 1 430 (s), 1 375 (m), 1 325 (m), 1 280 (w), 1 250 (w), 1 220 (m), 1 170 (w), 1 150 (m), 1 100 (s), 1 070 (s), 1 020 (w), 990 (w), 920 (w), 880 (w), 845 (m), 770 (m), 750 (w), 720 (w), 700 (w), 650 (m)

cont...

$\left[Cu(TSB^8)Cu(A^3)\right](ClO_4)_2$	3 040 (w), 2 900 (w), 1 640 (m), 1 600 (s), 1 590 (s), 1 550 (m), 1 470 (s), 1 450 (s), 1 385 (s), 1 340 (m), 1 315 (w), 1 270 (m), 1 240 (s), 1 210 (w), 1 150 (m), 1 100 (s), 1 090 (s), 1 050 (s), 980 (w), 920 (w), 900 (w), 865 (m), 840 (m), 780 (m), 750 (w), 710 (w), 690 (w), 660 (w)
$\left[Cu(TSB^9)Cu(A^1)\right](ClO_4)_2$	3 030 (w), 2 900 (w), 1 630 (m), 1 600 (s), 1 580 (s), 1 550 (s), 1 515 (w), 1 485 (m), 1 460 (w), 1 435 (s), 1 420 (s), 1 400 (m), 1 370 (s), 1 350 (m), 1 310 (s), 1 275 (s), 1 240 (w), 1 205 (m), 1 160 (w), 1 145 (w), 1 100 (s), 1 070 (s), 1 050 (s), 1 020 (s), 980 (w), 920 (w), 900 (w), 890 (w), 850 (w), 820 (w), 770 (w), 720 (w), 650 (w)

cont...

$[Cu(TSB^9)Cu(A^2)](ClO_4)_2$	3 040 (w),	2 905 (w),	1 640 (w),	1 600 (s),
	1 580 (s),	1 550 (s),	1 515 (w),	1 485 (m),
	1 450 (s),	1 420 (s),	1 370 (s),	1 330 (m),
	1 300 (w),	1 280 (m),	1 250 (m),	1 200 (m),
	1 170 (m),	1 140 (w),	1 100 (s),	1 080 (m),
	1 050 (s),	1 010 (w),	970 (m),	920 (w),
	905 (m),	870 (w),	850 (w),	775 (w),
	715 (w),	680 (w)		
$[Cu(TSB^9)Cu(A^3)](ClO_4)_2$	3 040 (w),	2 900 (w),	1 640 (w),	1 600 (s),
	1 585 (s),	1 555 (s),	1 485 (s),	1 445 (s),
	1 380 (w),	1 365 (m),	1 320 (w),	1 300 (s),
	1 275 (s),	1 240 (w),	1 210 (w),	1 150 (m),
	1 100 (s),	1 075 (s),	1 050 (s),	1 030 (s),
	980 (w),	920 (w),	900 (w),	890 (w),
	840 (w),	780 (w),	750 (m),	620 (w)

cont...

$[Cu(TSB^{10})Cu(A^{1})](ClO_4)_2$	3 020 (w),	2 900 (w),	1 640 (w),	1 600 (s),
	1 570 (s),	1 560 (m),	1 485 (m),	1 440 (s),
	1 380 (s),	1 340 (s),	1 270 (s),	1 250 (m),
	1 205 (w),	1 150 (m),	1 100 (s),	1 055 (s),
	980 (w),	920 (w),	900 (w),	850 (m),
	780 (m),	755 (m),	620 (w)	
$[Cu(TSB^{10})Cu(A^{2})](ClO_4)_2$	3 020 (w),	2 905 (w),	1 635 (w),	1 600 (s),
	1 570 (s),	1 555 (m),	1 510 (w),	1 470 (m),
	1 430 (s),	1 380 (s),	1 335 (m),	1 290 (w),
	1 260 (w),	1 210 (m),	1 170 (w),	1 150 (m),
	1 100 (s),	1 070 (s),	1 055 (m),	980 (m),
	920 (w),	905 (w),	880 (w),	840 (w),
	770 (m),	660 (w)		

cont...

$\left[Cu(TSB^{10})Cu(A^3)\right](ClO_4)_2$	3 060 (m), 2 900 (w), 1 640 (m), 1 600 (s), 1 590 (s), 1 545 (s), 1 510 (m), 1 485 (m), 1 450 (m), 1 440 (m), 1 385 (m), 1 345 (m), 1 275 (s), 1 240 (s), 1 210 (w), 1 100 (s), 1 070 (m), 1 055 (m), 1 000 (w), 960 (w), 920 (w), 900 (w), 870 (w), 760 (m), 720 (w), 650 (w)

Table II 4 : Reflectance Spectra (cm^{-1})

Compound	
$[Cu(TSB^2)]$	28 570, 18 180
$[Cu(TSB^2)CuCl_2]$	26 665, 17 390, 10 640
$[Cu(TSB^2)Cu(ClO_4)_2]$	27 780, 17 390, 10 360
$[Cu(TSB^2)Cu(A^1)](ClO_4)_2$	27 780, 17 860, 12 500 (sh)
$[Cu(TSB^2)Cu(A^2)](ClO_4)_2$	27 780, 16 660 - 12 500 (broad band)
$[Cu(TSB^2)Cu(A^3)](ClO_4)_2$	27 780, 19 610, 12 500

Table II 5 : Electronic Spectra (cm^{-1}) of $[Cu(A\text{-}A)]^{2+}$ and $[Cu(TSB)]$ Complexes in Ethanol

Compound	
$[Cu(A^1)]^{2+}$	49 000, 41 000, 33 200, 32 000
$[Cu(A^2)]^{2+}$	48 000, 44 200, 36 400, 34 000 (sh)
$[Cu(A^3)]^{2+}$	48 500, 41 300, 40 400, 31 000
$[Cu(TSB^1)]$	43 250, 41 250, 36 500, 28 900
$[Cu(TSB^2)]$	47 250, 42 250, 36 230, 28 000
$[Cu(TSB^3)]$	43 500, 41 500, 36 300, 27 500
$[Cu(TSB^4)]$	48 000, 43 000, 36 750, 28 500

cont...

$[Cu(TSB^5)]$	47 000, 41 300, 38 000 (sh), 32 500, 31 750 (sh), 29 000, 26 000 (sh), 24 000
$[Cu(TSB^6)]$	43 500, 38 000, 34 250 (sh), 28 500 (sh)
$[Cu(TSB^7)]$	44 440, 41 670, 36 630, 32 790 (sh), 27 140
$[Cu(TSB^8)]$	45 450, 39 220, 32 790 (sh), 27 030
$[Cu(TSB^9)]$	44 450, 39 500, 32 500 (sh), 27 500
$[Cu(TSB^{10})]$	45 470, 41 250, 32 540 (sh), 27 050

Table II 6 : Electronic Spectra (cm^{-1}) of Binuclear Complexes in Ethanol

Compound	
$[Cu(TSB^1)Cu(ClO_4)_2]$	43 800, 41 000, 36 400, 28 000
$[Cu(TSB^2)Cu(ClO_4)_2]$	42 800, 36 400, 28 300
$[Cu(TSB^3)Cu(ClO_4)_2]$	44 000, 41 200, 36 200, 27 800
$[Cu(TSB^4)Cu(ClO_4)_2]$	48 000, 44 000, 37 000 (sh), 28 500
$[Cu(TSB^5)Cu(ClO_4)_2]$	47 000, 41 250, 33 500 (sh), 32 250 30 800 (sh), 29 000, 26 000 (sh), 24 000
$[Cu(TSB^6)Cu(ClO_4)_2]$	43 500, 38 400, 34 500 (sh), 28 250
$[Cu(TSB^1)Cu(A^1)](ClO_4)_2$	48 000, 43 800, 41 000, 36 000, 33 200, 32 000, 28 000

cont...

$[Cu(TSB^1)Cu(A^2)](ClO_4)_2$	48 000, 43 800, 41 000, 36 600, 33 800 (sh), 28 000
$[Cu(TSB^1)Cu(A^3)](ClO_4)_2$	48 000, 43 800, 41 000, 36 400, 29 200
$[Cu(TSB^2)Cu(A^1)](ClO_4)_2$	48 500, 42 800, 36 400, 33 200, 32 000, 28 200
$[Cu(TSB^2)Cu(A^2)](ClO_4)_2$	48 000, 42 800, 36 600, 33 800 (sh), 28 200
$[Cu(TSB^2)Cu(A^3)](ClO_4)_2$	47 780, 42 800, 36 500, 28 800
$[Cu(TSB^3)Cu(A^1)](ClO_4)_2$	48 000, 44 000, 41 200, 36 000, 33 200, 32 000, 28 800
$[Cu(TSB^3)Cu(A^2)](ClO_4)_2$	48 000, 44 000, 41 000 (sh), 36 400, 33 800 (sh), 27 800
$[Cu(TSB^3)Cu(A^3)](ClO_4)_2$	48 100, 44 000, 41 900, 36 000, 29 200

cont...

$[Cu(TSB^4)Cu(A^1)](ClO_4)_2$	48 000 (sh), 43 000, 37 000 (sh), 33 200, 32 000, 28 500
$[Cu(TSB^4)Cu(A^2)](ClO_4)_2$	48 000 (sh), 44 000, 36 400, 33 800 (sh), 28 750
$[Cu(TSB^4)Cu(A^3)](ClO_4)_2$	48 000 (sh), 43 000, 36 500, 30 000
$[Cu(TSB^5)Cu(A^1)](ClO_4)_2$	47 000, 41 350, 38 500 (sh), 33 200, 32 000, 30 500 (sh), 29 000, 26 000 (sh), 24 000
$[Cu(TSB^5)Cu(A^2)](ClO_4)_2$	47 000, 43 300, 36 500, 34 000 (sh), 30 750, 29 000, 26 000 (sh), 24 000
$[Cu(TSB^5)Cu(A^3)](ClO_4)_2$	47 000, 41 250, 38 000 (sh), 32 000 (sh), 31 000, 29 000, 26 000 (sh), 24 000
$[Cu(TSB^6)Cu(A^1)](ClO_4)_2$	43 750, 38 500, 33 250, 32 250, 27 500
$[Cu(TSB^6)Cu(A^2)](ClO_4)_2$	44 000, 36 600, 34 000 (sh), 28 000

cont...

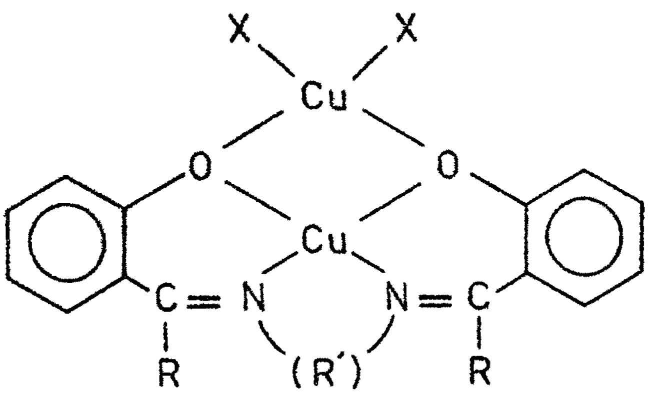
$[Cu(TSB^6)Cu(A^3)](ClO_4)_2$	42 000, 38 000 (sh), 30 500
$[Cu(TSB^7)Cu(A^1)](ClO_4)_2$	46 000, 40 000, 33 250, 32 200, 30 000 (sh), 25 500
$[Cu(TSB^7)Cu(A^2)](ClO_4)_2$	46 000, 43 200 (sh), 38 750 (sh), 37 000, 34 000 (sh), 29 000 (sh), 25 500
$[Cu(TSB^7)Cu(A^3)](ClO_4)_2$	46 250, 41 000, 39 000 (sh), 36 500, 31 000, 25 200 (sh)
$[Cu(TSB^8)Cu(A^1)](ClO_4)_2$	45 600, 40 100, 33 000, 32 000, 26 000
$[Cu(TSB^8)Cu(A^2)](ClO_4)_2$	45 500, 42 700 (sh), 38 700 (sh), 36 500, 33 900 (sh), 29 000 (sh), 26 000
$[Cu(TSB^8)Cu(A^3)](ClO_4)_2$	46 000, 41 000, 40 250, 39 000 (sh), 35 750, 30 500, 24 200 (sh)
$[Cu(TSB^9)Cu(A^1)](ClO_4)_2$	46 000, 39 750, 33 200, 32 000, 25 500

cont...

$[Cu(TSB^9)Cu(A^2)](ClO_4)_2$	46 000, 43 000 (sh), 38 700 (sh), 36 600, 34 000 (sh), 29 000 (sh), 25 500
$[Cu(TSB^9)Cu(A^3)](ClO_4)_2$	46 000, 41 000, 40 200, 38 500 (sh), 36 000, 30 500, 25 500 (sh)
$[Cu(TSB^{10})Cu(A^1)](ClO_4)_2$	45 750, 40 000, 33 000, 32 000, 30 000 (sh), 26 000
$[Cu(TSB^{10})Cu(A^2)](ClO_4)_2$	45 500, 43 000 (sh), 38 500 (sh), 36 500, 33 900 (sh), 30 000 (sh), 25 880
$[Cu(TSB^{10})Cu(A^3)](ClO_4)_2$	46 000, 41 000, 40 200, 35 750 (sh), 30 200, 24 250 (sh)

Table II 7 : The Exchange Integral J (cm^{-1}) and the Average g- Factor of Binuclear Complexes at Room Temperature (300^oK)

Compound	J	g
$[Cu(TSB^1)Cu(A^1)](ClO_4)_2$	- 43	2.064
$[Cu(TSB^1)Cu(A^2)](ClO_4)_2$	- 55	2.070
$[Cu(TSB^2)Cu(ClO_4)_2]$	- 151	2.195
$[Cu(TSB^2)Cu(A^1)](ClO_4)_2$	- 54	2.067
$[Cu(TSB^2)Cu(A^2)](ClO_4)_2$	- 79	2.070
$[Cu(TSB^2)Cu(A^3)](ClO_4)_2$	- 89	2.191
$[Cu(TSB^3)Cu(A^1)](ClO_4)_2$	- 160	2.067
$[Cu(TSB^3)Cu(A^2)](ClO_4)_2$	- 152	2.089
$[Cu(TSB^3)Cu(A^3)](ClO_4)_2$	- 130	2.119



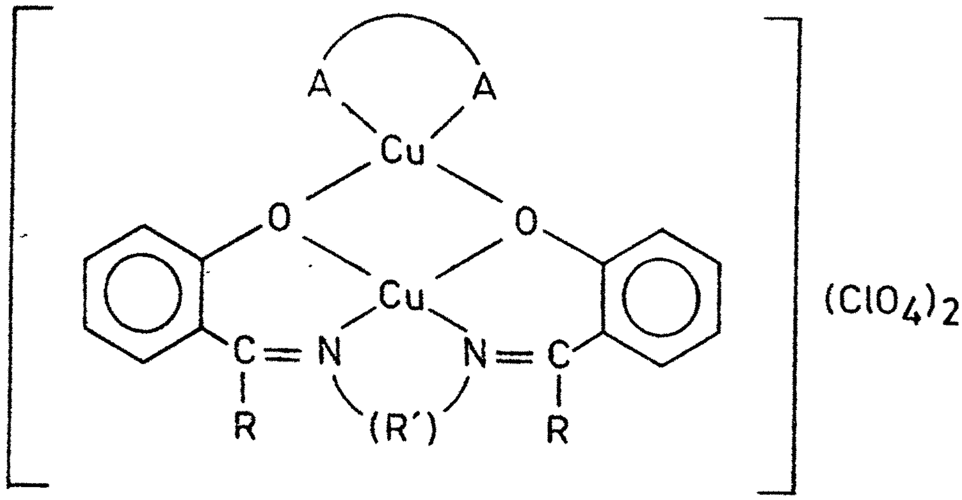
$R = H$ or CH_3

$R' = -(CH_2)_2-$; $-(CH_2)_3-$ or

$-O-$phenylene$-$

$X = ClO_4^-$

Figure II 1

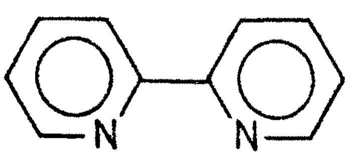


R = H or CH_3

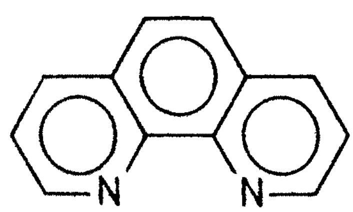
R' = $-(CH_2)_2-$; $-(CH_2)_3-$; $-(CH_2)_4-$;

$-(CH_2)_6-$; - O - phenylene -

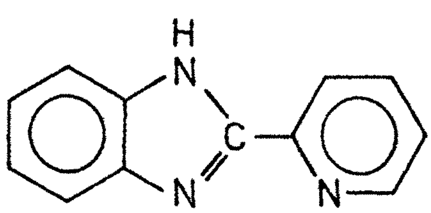
A - A = A^1, A^2 or A^3



2, 2'- bipyridyl (A^1)



1, 10 - phenanthroline (A^2)



2 - (2'- pyridyl)benzimidazole (A^3)

Figure II 2

RESULTS AND DISCUSSION

T.L.C. of all compounds showed single dots on the T.L.C. plates, confirming their purity. The elemental analyses of the complexes corresponded to the expected formulae (Table II 1). The structures can be represented in general as shown in Figures II 1 and II 2.

It is observed that, addition of water breaks the binuclear complex into two phases, viz a green solid and a blue aqueous solution. This is because, the bridging O^- bond is very weak in the binuclear complexes. The addition of water breaks the bridge resulting in the separation of the $[Cu(TSB)]$ complex and the formation of water soluble $[Cu(H_2O)_6](ClO_4)_2$ or $[Cu(A\text{-}A)(H_2O)_2](ClO_4)_2$.

The complexes are only sparingly soluble in most solvents and hence their molar conductance could not be determined.

Infrared Spectra

IR spectral bands corresponding to ClO_4^- have been used to establish the ionic nature or otherwise of the complexes of Type I and Type II.[128] In Type I complexes, non-electrolytic nature of complexes is confirmed by the presence of ν_{sy} (Cl—O) band at ca. 900 cm^{-1} and ν_{asy} (Cl—O) band at ca. 1 100 cm^{-1} (split into two), indicating presence of coordinated perchlorates with C_{3v} symmetry. In Type II complexes, there is one band obtained at ca. 1 100 cm^{-1} corresponding to ν_{asy} (Cl—O). The absence of ν_{sym} (Cl—O) at ca. 900 cm^{-1} indicates Td symmetry and hence the presence of ionic ClO_4^-.

The formation of binuclear complexes from the appropriate parent compounds leads to significant and consistent changes in the IR spectrum of the TSB part of mononuclear TSB complex. Bands due to schiff base segment of [Cu(TSB)] complex, show small shifts of the order of 5 to 10 cm^{-1} in their binuclear complexes. These changes are sufficiently specific to be considered[111] as diagnostic for the binuclear complex formation. The effect of coordination is expected to be maximum for bands associated with the bridging O^- ions and progressively lower for linkages farther from the coordination sites.

It is observed that the ν_{C-O} band occurs at 1530 cm^{-1} in [Cu(TSB)]. It, therefore, appears that the phenolic C—O link attains a considerable amount of partial double bond character in [Cu(TSB)] complexes. This ν_{C-O} band is consistently shifted by 15 to 20 cm^{-1} in the binuclear complexes indicating bridging through the phenolate O^-.

It is seen that the shifts in the band positions in the different binuclear complexes are of the same order. This shows that the coordination of [Cu(TSB)] with either CuX_2 or $[Cu(A-A)]^{2+}$ produces similar effect on the IR spectral bands.

Ligand Field Spectra

The electronic spectra of the binuclear complexes, containing [Cu(TSB)] as complex ligand, clearly support the assignment of the general structure (Type I and Type II) for these compounds. The electronic spectra of tetradentate schiff base complexes of Copper(II) are typified well by [Cu(salen)] . It shows three intense charge transfer bands at 41 000, 35 000 and 27 000 cm^{-1} and a weaker ligand field d-d transition band at 17 500 cm^{-1}. A ligand field band is often asymmetric, or has a small shoulder in few cases, suggesting, further, lower energy ligand field transitions of lower intensity.

Sinn and Harris[27] have reported earlier that in binuclear complexes, $[Cu(BSB)CuX_2]$, derived from bidentate schiff base complexes, [Cu(BSB)] , only one band is observed in the ligand field region, owing to the presence of two equivalent Copper(II) ions. However, in binuclear complexes $[Cu(TSB)CuX_2]$, derived from tetradentate schiff base complexes, [Cu(TSB)] , two separate bands arise in the ligand field region due to two non-equivalent Copper(II) centres.

In $[Cu(TSB)CuX_2]$ complexes, band in the region 8 000 to 12 000 cm^{-1} is due to the Copper atom, bonded to two halogens and placed in an enviornment approximately pseudotetrahedral, similar to $CuCl_4^{2-}$.[27,111] The band due to $[Cu(TSB)]$ part comes in the region 16 000 to 18 000 cm^{-1}.

It has also been observed by Sinn et al[111] that when the geometry around the first Copper ion in the complex becomes planar, the enviornment of the adjacent Copper ion is distorted away from planarity and vice versa. According to them, the main ligand field transition of the complex ligand $[Cu(TSB)]$, shifts to higher energies during complexing indicating that the complex ligand becomes more planar when it coordinates to metal halide or perchlorate.

In binuclear complexes, $[Cu(TSB)Cu(A\text{-}A)]\ (ClO_4)_2$, studied in the present work, second Copper is coordinated with the bidentate ligands like 2,2'-bipyridyl. This produces a stronger field than halides, and hence the band due to this part of the binuclear complex appears at higher energy ($\sim$12 500 cm^{-1}). The main ligand field band of $[Cu(TSB)]$ part of the binuclear complex also shows a shift from the value in free $[Cu(TSB)]$. This is because of the change in the planarity of $[Cu(TSB)]$ on coordination with $[Cu(A\text{-}A)]^{2+}$, as suggested in the case of $[Cu(TSB)CuCl_2]$ complexes.[111] Further, coordination with $CuCl_2$ or

$[Cu(A-A)]^{2+}$ also lowers the strength of Cu(II) — O bond in the $[Cu(TSB)]$ part and hence there should be lowering in the ligand field band energy. The change in the position of $[Cu(TSB)]$ band supports the formation of binuclear complexes.

Ultraviolet Spectra

It is interesting to see if there is any exchange interaction between the π-electron clouds over the ligands on the two Copper centres through the p_z orbital of the O^- bridge. This can be realised by comparing the UV spectra of TSB^1, $[Cu(TSB^1)]$, A^1, $[Cu(A^1)]^{2+}$ and $[Cu(TSB^1)Cu(A^1)]^{2+}$.

The schiff base TSB^1 shows bands at 44 330, 41 170, 36 170 and 24 800 cm^{-1}. The first three are known to be $\pi \rightarrow \pi^*$ transitions in the aromatic ring and the $>C{=}N$ chromophore. This assignment is on the basis of the high intensity of the bands and the solvent dependence of the band position.[129] The band at 24 800 cm^{-1} is due to $n \rightarrow \pi^*$ transition.

$[Cu(TSB^1)]$ shows bands at 43 250, 41 250, 36 500 and 28 900 cm^{-1}. The high intensity bands at 41 250, 36 500 and 28 900 cm^{-1} have been assigned to charge transfer transitions. There may be intra-ligand bands also in this region.[111] The shift in the position of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands of TSB^1 in $[Cu(TSB^1)]$ shows that there is π-interaction between the Copper and TSB^1 π orbitals.

2,2'-bipyridyl (A^1) shows bands at 49 500, 42 200 and 35 200 cm^{-1}. The later two high intensity bands correspond to $\pi \rightarrow \pi^*$ transitions. In $[Cu(A^1)]^{2+}$, the bands are observed at 49 000, 41 000, 33 200 and 32 000 cm^{-1}. Similar spectra have been reported earlier for 2,2'-bipyridyl Copper(II) complexes.[130] The appearence of a new band (with high intensity) and the shift in the $\pi \rightarrow \pi^*$ transition shows that there is an interaction between π orbitals of Copper(II) and those of the 2,2'-bipyridyl molecule.

The spectrum of binuclear complex $[Cu(TSB^1)Cu(A^1)](ClO_4)_2$ has bands at 48 000, 43 500, 41 000, 36 000, 33 200, 32 000 and 28 000 cm^{-1}, showing all the electronic transitions possible in $[Cu(TSB^1)]$ and $[Cu(A^1)]^{2+}$ without any significant change. It can thus be concluded that, albeit there is a superexchange interaction in the binuclear complex, there is no π interaction between the ligands over the two Copper ions. Any interaction between the π orbitals of TSB^1 and A^1, through the metal ions, would have changed the positions of the near UV bands in the binuclear complex.

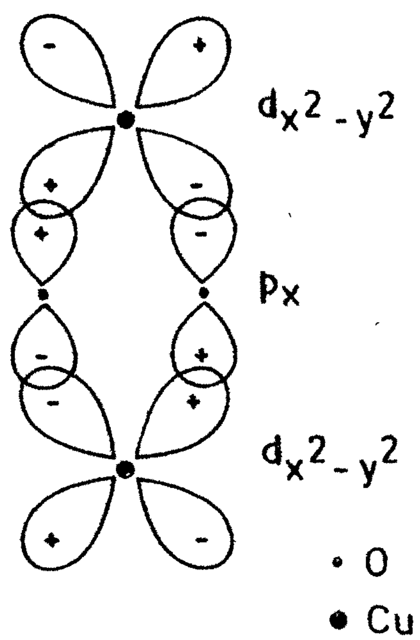


Figure II 3

Magnetic Properties

In the binuclear complexes, it has been observed that the magnetic moments are subnormal (Table II 1). The extent of lowering in the magnetic moment varies in the different complexes with different TSB and A-A. Correspondingly spin-spin exchange interaction constant also varies in different complexes as shown in Table II 7. This has been explained to be arising due to the antiferromagnetic interaction between the two Copper(II) ions.

In the present type of complexes, as in case of $[Cu(TSB)CuX_2]$, Copper - Copper distance is comparatively larger and hence it seems unlikely that a direct exchange due to overlap of Copper(II) d orbitals is possible. The probable path of spin-spin exchange, between the unpaired electrons in $d_{x^2-y^2}$ orbitals of the two Copper(II) centres, is the superexchange by either σ - or π - type interaction through the bridging O^-.

UV spectral studies show that there is no significant interaction between ligand π orbitals through metal d orbitals. Hence, π orbitals may not be significantly involved in the superexchange interaction.

The unpaired electron present in each of the $d_{x^2-y^2}$ orbitals of the two Copper(II) ions undergo σ overlap with the filled s and p orbitals of the bridging phenolate O^- [111] as shown in Figure II 3 leading to a superexchange.

Superexchange interaction gives rise to a diamagnetic spin singlet ground state and an excited paramagnetic triplet state. At room temperature, the singlet ground state is more populated and hence there is a lowering of magnetic moment.

Sinn et al [111,114] observed that in the case of [Cu(TSB)$CuCl_2$] , with a long $-(CH_2)_n-$ chain, the molecular geometry deviates away from planarity with increasing chain length. This type of distortion also brings about a shift of d-d bands of both Cu^1 and Cu^2 of binuclear complexes to lower energies. A shift of the d-d band in Copper(II) complexes to lower energies is specifically correlated with the deviation of stereochemistry of the Copper ion from planar to tetrahedral symmetry. Further, it can be seen that the stereochemistry of the two Copper ions is mutually dependent on each other, so that the overall effect could be considered as arising from the Copper ion itself.

The net result of the distortion, away from planarity, is that the decrease in effective magnetic moment is lower, due to the reduced superexchange interaction. However, in the complexes studied here, we did not observe any systematic variation in the magnetic moment with differing chain lengths.

It may be because in the binuclear complexes of the type discussed here viz. [Cu(TSB)Cu(A-A)] $(ClO_4)_2$, there are two factors affecting the planarity of the molecule. Increase in chain length $-(CH_2)_n-$, as already mentioned, gradually distorts the planarity, whereas the presence of 2,2'-bipyridyl like ligands tends to stabilize a planar structure of the second Copper(II). The net effect on structure would, therefore, depend on the magnitude of each of these influence.