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CHAPTER IV

Binuclear Complexes Involving Symmetrical Tetradentate Mannich Bases

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The binuclear complex can be considered as a macrocyclic ring complex with the second Copper(II) ion as a member of the heterocyclic ring. They are similar to O-O, N-N coordinating macrocyclic ring complexes reported by Lindoy.[152]

As discussed earlier, the extent of superexchange depends on the planarity of the binuclear complex. This gives rise to a situation where the magnetic properties of these binuclear complexes can be reviewed in relation to the macrocyclic ring complex. Keeping in mind this objective, synthesis and characterisation of complexes of the type $\left[Cu(TMB)CuX_2\right]$ (Type I) and $\left[Cu(TMB)Cu(A\text{-}A)\right](ClO_4)_2$ (Type II) have been carried out. TMB corresponds to tetradentate mannich bases obtained by the reduction of the corresponding tetradentate schiff bases.

TMB^1 = N,N'-ethylene-bis-(2-hydroxybenzylamine)

TMB^2 = N,N'-ethylene-bis-(2-hydroxy-α-methylbenzylamine)

TMB^3 = N,N'-propylene-bis-(2-hydroxybenzylamine)

TMB^4 = N,N'-propylene-bis-(2-hydroxy-α-methylbenzylamine).

A-A corresponds to,

A^1 = 2,2'-bipyridyl,

A^2 = 1,10-phenanthroline

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

and X is either Cl^- or ClO_4^-.

EXPERIMENTAL

Material

Analytical Reagent grade chemicals were used (>99.9 % purity) for all the preparations. $Cu(ClO_4)_2.6H_2O$ was prepared as described in Chapter II. Tetradentate schiff bases of salicylaldehyde and 2-hydroxyacetophenone were prepared by the direct reaction of the diamines with the aromatic aldehyde or ketone. 2-(2'-pyridyl)benzimidazole was prepared by the method suggested in literature.[125]

Preparation Of Mannich Bases (TMB)

Performed tetradentate schiff base was dissolved in minimum quantity of methanol. Solid sodium borohydride was added to the above solution with constant stirring. The addition was continued until the solution became colourless. The reaction mixture was then allowed to stand for 30 minutes and filtered. On addition of distilled water (50 ml) to this filtrate, a white solid separated out. This solid was filtered, washed first with water, then with ethanol and was recrystallised from absolute ethanol.

Preparation Of Mononuclear Complexes [Cu(TMB)]

To a warm solution of $CuCl_2.2H_2O$ in ethanol (1 mol), was added a solution of tetradentate mannich base (TMB) in ethanol (1 mol) with constant stirring. The pH of the solution

was raised to 5.5 by addition of a dilute solution of ammonia. The mixture was digested on a water bath for 2 to 3 hours. The solid which separated out was filtered, washed thoroughly with ethanol, recrystallised from absolute ethanol and finally dried under vacuum.

Preparation Of Binuclear Complexes $[Cu(TMB)CuX_2]$

To a solution of $[Cu(TMB)]$ in chloroform (3 mmol), a solution of $CuCl_2.2H_2O$ or $Cu(ClO_4)_2.6H_2O$ in absolute ethanol (3 mmol) was added. The reaction mixture was refluxed with constant stirring for about two hours. Resulting solid was filtered, washed thoroughly with a mixture of chloroform and ethanol (1 : 1), and dried under vacuum.

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

The suspension of $[Cu(A-A)(ClO_4)_2]$ was prepared by addition of a solution of (A-A) (2 mmol) in absolute ethanol to the solution of $Cu(ClO_4)_2.6H_2O$ (2 mmol) also in absolute ethanol. This suspension was then added to a solution of $[Cu(TMB)]$ in chloroform (2.2 mmol). The reaction mixture was refluxed with constant stirring for about 3 to 4 hours. The resulting solid was filtered, washed thoroughly with chloroform to remove excess of $[Cu(TMB)]$ and dried under vacuum.

Some binuclear complexes had to be isolated by ether

extraction because of their very high solubility in chloroform - ethanol mixture. They were further recrystallised from absolute ethanol.

The different compounds, thus prepared, were characterized by T.L.C., elemental analyses for carbon, hydrogen, nitrogen and metal (Tables IV 1 to IV 3), Infrared (Tables IV 4 to IV 6), Reflectance (Table IV 7) and UV Visible (Tables IV 8 and IV 9) spectral techniques and magnetic susceptibility measurements (Tables IV 2, IV 3 and IV 10). The details of the techniques employed are same as described in Chapter II. T.L.C. analyses were carried out on silica gel G (Sichem) plates using chloroform + methanol (1 : 1) mixture as developer. NMR spectra of N,N'-ethylene-bis-salicylaldimine (TSB^1) and N,N'-ethylene-bis-2-hydroxybenzylamine (TMB^1) were obtained in $CDCl_3$ using Perkin Elmer R-32 NMR Spectrometer. TMS was used as a standard.

Table IV 1 : Analytical Data of Tetradentate Mannich Bases

Compound	Colour	Analyses % *		
		N	C	H
TMB[1]	White	9.81 (10.29)	70.91 (70.59)	7.36 (7.35)
TMB[2] · 1/2 H_2O	White	8.71 (9.06)	69.44 (69.90)	7.02 (7.77)
TMB[3]	White	9.79 (9.79)	71.22 (71.33)	7.70 (7.69)
TMB[4] · 1/2 H_2O	White	8.93 (8.67)	71.11 (70.59)	8.12 (8.36)

* Calculated values are given in parentheses

Table IV 2 : Analytical and Magnetic Data of Mononuclear Complexes

Compound	Colour	Analyses % *				μ_{eff}/ Cu(II) ion in B.M.
		Cu	N	C	H	
$[Cu(TMB^1)]$	Green	19.35 (19.05)	8.03 (8.39)	57.10 (57.56)	5.49 (5.40)	1.91
$[Cu(TMB^2)]$	Violet	17.26 (17.57)	7.34 (7.74)	60.05 (59.74)	5.92 (6.09)	1.83
$[Cu(TMB^3)]$	Green	18.00 (18.28)	8.42 (8.06)	59.25 (58.70)	6.01 (5.75)	1.94
$[Cu(TMB^4)]$	Blue	16.67 (16.92)	7.19 (7.46)	61.19 (60.71)	6.65 (6.39)	1.79

* Calculated values are given in parentheses

Table IV 3 : Analytical and Magnetic Data of Binuclear Complexes

Compound	Colour	Analyses % *				μ_{eff}/ Cu(II) ion in B.M.
		Cu	N	C	H	
$[Cu(TMB^1)CuCl_2]$	Bluish black	26.85 (27.15)	5.43 (5.98)	40.92 (41.02)	3.91 (3.85)	0.78
$[Cu(TMB^1)Cu(ClO_4)_2]$	Brown	21.55 (21.32)	4.37 (4.70)	31.98 (32.21)	2.93 (3.02)	0.86
$[Cu(TMB^1)Cu(A^1)](ClO_4)_2$	Brown	16.61 (16.90)	7.52 (7.45)	41.37 (41.48)	3.27 (3.46)	0.86
$[Cu(TMB^1)Cu(A^2)](ClO_4)_2$	Brown	15.98 (16.37)	7.02 (7.22)	43.51 (43.29)	3.29 (3.35)	0.93
$[Cu(TMB^1)Cu(A^3)](ClO_4)_2$	Brown	15.86 (16.06)	8.87 (8.85)	42.13 (42.47)	3.21 (3.41)	0.97
$[Cu(TMB^2)CuCl_2]$	Bluish black	25.30 (25.62)	5.59 (5.64)	43.61 (43.51)	4.27 (4.43)	1.01
$[Cu(TMB^2)Cu(ClO_4)_2]$	Brown	19.97 (20.36)	4.53 (4.49)	33.48 (34.61)	3.61 (3.53)	0.84

cont...

$[Cu(TMB^2)Cu(A^1)](ClO_4)_2$	Brown	16.37 (16.29)	7.02 (7.18)	42.76 (43.07)	3.67 (3.85)	0.93
$[Cu(TMB^2)Cu(A^2)](ClO_4)_2$	Brown	15.42 (15.80)	6.51 (6.96)	45.13 (44.77)	3.97 (3.73)	1.08
$[Cu(TMB^2)Cu(A^3)](ClO_4)_2$	Brown	15.42 (15.51)	8.06 (8.55)	44.01 (43.95)	3.42 (3.78)	0.91
$[Cu(TMB^3)CuCl_2]$	Olive green	26.05 (26.36)	5.76 (5.81)	42.21 (42.32)	4.20 (4.15)	0.84
$[Cu(TMB^3)Cu(ClO_4)_2]$	Olive green	20.34 (20.83)	4.66 (4.59)	33.52 (33.44)	3.17 (3.28)	0.81
$[Cu(TMB^3)Cu(A^1)](ClO_4)_2$	Brown	16.43 (16.59)	7.21 (7.31)	42.03 (42.29)	3.57 (3.67)	0.86
$[Cu(TMB^3)Cu(A^2)](ClO_4)_2$	Olive green	15.62 (16.08)	6.78 (7.09)	44.50 (44.05)	3.39 (3.54)	0.88
$[Cu(TMB^3)Cu(A^3)](ClO_4)_2$	Olive green	15.85 (15.78)	8.49 (8.69)	43.61 (43.23)	3.36 (3.60)	0.90
$[Cu(TMB^4)CuCl_2]$	Olive green	24.66 (24.91)	5.52 (5.49)	44.37 (44.70)	4.82 (4.71)	1.20
$[Cu(TMB^4)Cu(ClO_4)_2]$	Brown	19.97 (19.92)	4.57 (4.39)	- -	- -	0.90

cont...

$\left[Cu(TMB^4)Cu(A^1)\right](ClO_4)_2$	Brown	15.89 (16.00)	7.36 (7.05)	43.90 (43.82)	3.97 (4.03)	0.97
$\left[Cu(TMB^4)Cu(A^2)\right](ClO_4)_2$	Grey	15.83 (15.53)	7.29 (6.85)	45.05 (45.47)	4.01 (3.91)	0.98
$\left[Cu(TMB^4)Cu(A^3)\right](ClO_4)_2$	Brown	15.22 (15.25)	8.17 (8.40)	44.71 (44.65)	4.07 (3.96)	0.89

* Calculated values are given in parentheses

Table IV 4 : Infrared Spectra (cm^{-1}) of TMB Compounds

Compound					
TMB^1	3 450 (m),	3 240 (m),	3 120 (m),	1 650 (w),	1 590 (m),
	1 565 (s),	1 510 (w),	1 480 (s),	1 445 (s),	1 410 (w),
	1 350 (m),	1 300 (s),	1 290 (s),	1 270 (s),	1 240 (m),
	1 200 (w),	1 145 (m),	1 120 (s),	1 090 (s),	1 060 (m),
	1 035 (s),	975 (m),	950 (m),	935 (m),	880 (s),
	750 (s),	730 (s),	610 (s),		
TMB^2	3 400 (m),	3 040 (w),	2 865 (m),	1 640 (m),	1 590 (s),
	1 510 (m),	1 475 (s),	1 430 (s),	1 370 (m),	1 335 (w),
	1 310 (m),	1 280 (s),	1 245 (m),	1 180 (w),	1 140 (m),
	1 110 (w),	1 050 (m),	980 (m),	870 (m),	850 (s),
	750 (m),	730 (s),	640 (w)		

cont...

TMB^3	3 410 (m),	3 180 (s),	3 040 (m),	3 010 (m),	1 640 (m),
	1 590 (s),	1 570 (m),	1 485 (s),	1 450 (s),	1 430 (m),
	1 350 (m),	1 310 (w),	1 280 (s),	1 245 (m),	1 150 (s),
	1 120 (s),	1 090 (s),	1 050 (m),	1 020 (s),	955 (s),
	930 (s),	890 (s),	850 (s),	755 (s),	730 (m),
	645 (m),	610 (m)			
TMB^4	3 400 (m),	3 040 (m),	2 960 (w),	1 630 (m),	1 580 (s),
	1 510 (s),	1 475 (s),	1 450 (s),	1 375 (m),	1 340 (m),
	1 290 (s),	1 240 (m),	1 190 (m),	1 150 (w),	1 110 (m),
	1 050 (m),	1 030 (w),	950 (w),	915 (w),	880 (s),
	840 (s),	750 (s),	720 (w),	650 (w),	600 (m)

Table IV 5 : Infrared Spectra (cm^{-1}) of [Cu(TMB)] Complexes

Compound	
[Cu(TMB^1)]	3 300 (b), 3 240 (m), 3 120 (m), 3 060 (w), 2 960 (w), 1 590 (s), 1 560 (s), 1 510 (w), 1 480 (s), 1 450 (s), 1 420 (w), 1 360 (m), 1 340 (w), 1 300 (s), 1 290 (s), 1 280 (s), 1 270 (s), 1 235 (m), 1 200 (w), 1 150 (m), 1 120 (s), 1 090 (s), 1 065 (m), 1 030 (s), 970 (m), 950 (m), 930 (m), 910 (w), 880 (s), 850 (s), 750 (s), 730 (s), 600 (s)
[Cu(TMB^2)]	3 300 (b), 3 040 (w), 2 860 (w), 1 590 (s), 1 510 (m), 1 470 (s), 1 435 (s), 1 365 (m), 1 335 (w), 1 310 (w), 1 285 (s), 1 260 (s), 1 235 (m), 1 180 (w), 1 140 (m), 1 110 (m), 1 055 (m), 1 030 (w), 980 (w), 920 (m), 880 (w), 850 (s), 750 (m), 740 (s), 730 (s), 650 (w), 610 (w)

cont...

$[Cu(TMB^3)]$	3 320 (b), 3 180 (s), 3 050 (s), 3 000 (m), 2 940 (m), 1 590 (s), 1 575 (m), 1 490 (s), 1 455 (s), 1 430 (m), 1 340 (m), 1 320 (m), 1 300 (s), 1 280 (s), 1 240 (m), 1 160 (s), 1 120 (s), 1 080 (s), 1 050 (s), 1 020 (s), 960 (s), 935 (s), 890 (s), 860 (s), 760 (s), 740 (s), 645 (m), 600 (s)
$[Cu(TMB^4)]$	3 320 (m), 3 050 (w), 2 960 (w), 1 580 (s), 1 510 (s), 1 470 (s), 1 440 (s), 1 370 (w), 1 345 (m), 1 290 (s), 1 235 (m), 1 180 (w), 1 145 (w), 1 110 (m), 1 055 (w), 1 030 (s), 950 (w), 915 (w), 880 (s), 845 (s), 750 (s), 740 (s), 730 (s), 630 (w)

Table IV 6 : Infrared Spectra (cm^{-1}) of Binuclear Complexes

Compound	
$\left[Cu(TMB^1)CuCl_2\right]$	3 310 (m), 3 160 (s), 3 060 (w), 2 850 (m), 1 590 (s), 1 560 (m), 1 470 (s), 1 440 (s), 1 425 (w), 1 385 (w), 1 325 (w), 1 310 (w), 1 300 (w), 1 260 (s), 1 250 (s), 1 180 (m), 1 150 (w), 1 110 (m), 1 080 (w), 1 060 (s), 1 035 (s), 1 000 (s), 950 (w), 880 (s), 850 (s), 765 (s), 750 (s), 720 (w), 600 (m)
$\left[Cu(TMB^1)Cu(ClO_4)_2\right]$	3 310 (m), 3 250 (m), 2 940 (w), 1 590 (m), 1 565 (w), 1 510 (w), 1 480 (s), 1 455 (s), 1 415 (w), 1 350 (w), 1 265 (s), 1 250 (s), 1 190 (w), 1 140 (m), 1 100 (doublet), 1 080 (s), 1 040 (w), 1 020 (w), 990 (w), 920 (s), 880 (m), 820 (w), 780 (m), 755 (s), 620 (m)

cont...

$\left[Cu(TMB^1)Cu(A^1)\right](ClO_4)_2$	3 310 (m), 3 240 (m), 3 030 (w), 1 590 (s), 1 570 (m), 1 485 (s), 1 455 (s), 1 340 (w), 1 315 (m), 1 270 (s), 1 250 (s), 1 200 (w), 1 150 (s), 1 120 (s), 1 100 (s), 1 080 (s), 1 050 (m), 930 (w), 885 (m), 860 (m), 765 (s), 640 (m), 625 (s)
$\left[Cu(TMB^1)Cu(A^2)\right](ClO_4)_2$	3 320 (v), 3 030 (w), 2 880 (w), 1 590 (s), 1 570 (m), 1 520 (s), 1 490 (s), 1 455 (s), 1 435 (s), 1 365 (w), 1 350 (w), 1 290 (s), 1 265 (s), 1 255 (m), 1 200 (w), 1 150 (s), 1 120 (s), 1 100 (s), 1 085 (s), 1 050 (s) 1 030 (m), 940 (s), 920 (w), 890 (s), 850 (s), 785 (s), 760 (s), 645 (m), 630 (m)

cont...

$\left[Cu(TMB^1)Cu(A^3)\right]\ (ClO_4)_2$	3 310 (b), 3 040 (w), 2 920 (w), 1 590 (s), 1 510 (w), 1 470 (s), 1 440 (s), 1 350 (w), 1 260 (s), 1 250 (s), 1 220 (w), 1 140 (s), 1 110 (s), 1 100 (s), 1 080 (s), 1 015 (w), 985 (w), 940 (w), 925 (m), 900 (w), 875 (m), 780 (m), 770 (m), 750 (s), 630 (m), 620 (s)
$\left[Cu(TMB^2)CuCl_2\right]$	3 305 (b), 3 040 (w), 2 920 (w), 1 585 (s), 1 515 (m), 1 480 (s), 1 445 (s), 1 350 (m), 1 310 (w), 1 280 (s), 1 255 (m), 1 210 (m), 1 190 (m), 1 150 (m), 1 115 (m), 1 050 (m), 1 035 (w), 970 (w), 955 (w), 920 (m), 870 (w), 840 (m), 770 (m), 745 (s), 655 (m), 620 (s)

cont...

$\left[Cu(TMB^2)Cu(ClO_4)_2\right]$	3 310 (m), 3 040 (w), 2 900 (w), 1 590 (s), 1 510 (m), 1 480 (s), 1 440 (s), 1 370 (m), 1 350 (w), 1 300 (m), 1 280 (s), 1 255 (s), 1 210 (w), 1 185 (w), 1 150 (m), 1 100 (doublet), 1 050 (m), 1 020 (w), 970 (m), 920 (s), 900 (w), 870 (s), 770 (m), 750 (m), 650 (w), 630 (s)
$\left[Cu(TMB^2)Cu(A^1)\right](ClO_4)_2$	3 310 (m), 3 030 (w), 2 900 (w), 1 585 (s), 1 510 (w), 1 480 (s), 1 450 (s), 1 380 (w), 1 340 (w), 1 295 (m), 1 270 (m), 1 250 (s), 1 190 (w), 1 150 (s), 1 120 (s), 1 100 (s), 1 050 (m), 1 020 (w), 980 (w), 930 (w), 860 (s), 770 (s), 740 (m), 630 (s)

cont...

$\left[Cu(TMB^2)Cu(A^2)\right](ClO_4)_2$	3 310 (m), 3 080 (w), 2 950 (w), 1 580 (s), 1 520 (w), 1 485 (s), 1 450 (s), 1 430 (s), 1 380 (m), 1 350 (w), 1 330 (w), 1 300 (m), 1 270 (s), 1 250 (s), 1 160 (s), 1 120 (s), 1 100 (s), 1 080 (s), 1 050 (s), 1 020 (m), 970 (w), 930 (m), 860 (s), 765 (s), 650 (m), 630 (s)
$\left[Cu(TMB^2)Cu(A^3)\right](ClO_4)_2$	3 310 (m), 3 040 (w), 2 920 (w), 1 580 (s), 1 520 (s), 1 470 (s), 1 450 (s), 1 430 (s), 1 370 (w), 1 340 (w), 1 310 (w), 1 275 (m), 1 255 (s), 1 210 (w), 1 180 (w), 1 150 (s), 1 100 (s), 1 070 (s), 1 030 (m), 975 (m), 910 (w), 890 (w), 845 (s), 780 (w), 745 (s), 620 (s)

cont...

$[Cu(TMB^3)CuCl_2]$	3 310 (m), 3 180 (m), 3 050 (w), 2 880 (m), 1 580 (m), 1 510 (w), 1 490 (s), 1 455 (s), 1 430 (m), 1 370 (w), 1 340 (w), 1 290 (s), 1 280 (s), 1 260 (s), 1 205 (m), 1 165 (m), 1 125 (s), 1 080 (s), 1 040 (m), 1 030 (s), 970 (m), 935 (m), 880 (s), 865 (m), 800 (s), 760 (s), 740 (m), 750 (m), 600 (s)
$[Cu(TMB^3)Cu(ClO_4)_2]$	3 330 (m), 3 040 (w), 2 890 (w), 1 590 (m), 1 570 (m), 1 480 (s), 1 450 (s), 1 420 (m), 1 330 (m), 1 310 (s), 1 275 (s), 1 255 (m), 1 150 (s), 1 100 (doublet), 1 080 (s), 1 050 (m), 970 (m), 920 (s), 900 (w), 870 (w), 780 (m), 750 (m), 650 (m), 620 (m)

cont...

$\left[Cu(TMB^3)Cu(A^1)\right](ClO_4)_2$	3 320 (m), 3 040 (w), 2 920 (w), 1 590 (s), 1 560 (w), 1 470 (s), 1 440 (s), 1 380 (w), 1 350 (w), 1 310 (m), 1 285 (s), 1 255 (s), 1 220 (w), 1 140 (m), 1 100 (s), 1 080 (s), 1 025 (m), 980 (w), 920 (w), 870 (m), 760 (s), 725 (m), 630 (m), 620 (s)
$\left[Cu(TMB^3)Cu(A^2)\right](ClO_4)_2$	3 320 (m), 3 060 (w), 2 880 (w), 1 590 (m), 1 520 (w), 1 485 (s), 1 450 (m), 1 430 (s), 1 340 (w), 1 290 (s), 1 260 (s), 1 250 (n), 1 210 (w), 1 150 (s), 1 120 (s), 1 100 (s), 1 080 (s), 1 030 (m), 970 (m), 935 (m), 880 (m), 855 (s), 790 (m), 755 (s), 730 (s), 630 (s),

cont...

$[Cu(TMB^3)Cu(A^3)]\ (ClO_4)_2$	3 325 (m), 3 060 (w), 2 920 (w), 1 590 (s), 1 570 (m), 1 480 (s), 1 450 (s), 1 410 (m), 1 330 (w), 1 285 (s), 1 270 (s), 1 255 (s), 1 200 (m), 1 140 (s), 1 100 (s), 1 070 (s), 1 025 (m), 1 010 (m), 930 (w), 890 (m), 870 (m), 790 (s), 760 (s), 750 (s), 630 (m), 620 (s)
$[Cu(TMB^4)CuCl_2]$	3 325 (m), 3 040 (w), 2 920 (w), 1 590 (s), 1 480 (s), 1 450 (s), 1 370 (w), 1 350 (w), 1 295 (s), 1 255 (s), 1 150 (w), 1 120 (w), 1 100 (w), 1 050 (w), 1 030 (m), 980 (m), 900 (w), 885 (s), 850 (m), 760 (s), 745 (s), 650 (w), 600 (s)

cont...

$\left[Cu(TMB^4)Cu(ClO_4)_2\right]$	3 315 (m), 3 030 (w), 2 920 (w), 1 590 (s), 1 485 (s), 1 450 (s), 1 380 (w), 1 340 (m), 1 300 (m), 1 280 (m), 1 250 (m), 1 185 (m), 1 150 (m), 1 100 (doublet), 1 080 (w), 1 050 (m), 1 020 (s), 970 (m), 920 (s), 870 (s), 850 (s), 770 (s), 730 (m), 620 (s)
$\left[Cu(TMB^4)Cu(A^1)\right](ClO_4)_2$	3 325 (m), 3 040 (w), 2 900 (w), 1 590 (s), 1 510 (m), 1 475 (s), 1 450 (m), 1 380 (m), 1 350 (m), 1 310 (w), 1 280 (m), 1 250 (m), 1 210 (w), 1 190 (w), 1 150 (m), 1 100 (s), 1 080 (w), 1 050 (m), 960 (w), 920 (w), 900 (w), 870 (w), 850 (s), 770 (s), 750 (m), 730 (s), 630 (s)

cont...

$\left[Cu(TMB^4)Cu(A^2)\right](ClO_4)_2$	3 320 (m), 3 050 (w), 2 920 (w), 1 580 (s), 1 500 (w), 1 480 (s), 1 435 (m), 1 420 (m), 1 350 (w), 1 280 (m), 1 255 (s), 1 220 (w), 1 150 (s), 1 100 (s), 1 075 (s), 1 050 (m), 960 (w), 920 (w), 900 (w), 885 (s), 840 (s), 770 (m), 710 (s), 620 (s)
$\left[Cu(TMB^4)Cu(A^3)\right](ClO_4)_2$	3 325 (b), 3 040 (w), 2 920 (w), 1 585 (s), 1 510 (w), 1 475 (s), 1 445 (s), 1 375 (w), 1 350 (w), 1 280 (s), 1 260 (s), 1 210 (w), 1 185 (w), 1 150 (w), 1 100 (s), 1 080 (s), 1 030 (m), 930 (w), 885 (s), 850 (m), 760 (s), 620 (s)

Table IV 7 : Reflectance Spectra (cm^{-1})

Compound			
$[Cu(TMB^1)]$	23 260,	14 290	
$[Cu(TMB^1)CuCl_2]$	24 100,	14 810,	10 420
$[Cu(TMB^1)Cu(ClO_4)_2]$	24 100,	16 390,	10 870
$[Cu(TMB^1)Cu(A^1)](ClO_4)_2$	24 390,	17 540,	12 500
$[Cu(TMB^1)Cu(A^2)](ClO_4)_2$	21 740,	17 540,	13 330
$[Cu(TMB^1)Cu(A^3)](ClO_4)_2$	21 050,	18 180,	12 350

Table IV 8 : Electronic Spectra (cm^{-1}) of Tetradentate Mannich Bases and their Complexes in Ethanol

Compound	
TMB^1	46 000 (sh), 36 000
TMB^2	46 000 (sh), 36 200
TMB^3	46 000 (sh), 36 000
TMB^4	46 000 (sh), 36 000
$[Cu(TMB^1)]$	42 000, 36 000, 26 000
$[Cu(TMB^2)]$	41 000, 35 200, 25 500
$[Cu(TMB^3)]$	42 000, 36 000, 25 000
$[Cu(TMB^4)]$	41 100, 34 500, 24 300

Table IV 9 : Electronic Spectra (cm^{-1}) of Binuclear Complexes in Ethanol

Compound	
$[Cu(TMB^1)CuCl_2]$	42 000, 36 000, 26 000
$[Cu(TMB^1)Cu(ClO_4)_2]$	42 000, 36 000, 26 000
$[Cu(TMB^1)Cu(A^1)](ClO_4)_2$	42 000, 35 800 (sh), 33 300, 32 000, 26 200
$[Cu(TMB^1)Cu(A^2)](ClO_4)_2$	43 000 (sh), 36 500, 34 000 (sh), 26 000
$[Cu(TMB^1)Cu(A^3)](ClO_4)_2$	42 000, 36 000, 30 300
$[Cu(TMB^2)CuCl_2]$	41 300, 35 700, 26 000
$[Cu(TMB^2)Cu(ClO_4)_2]$	41 700, 36 000, 26 000

cont...

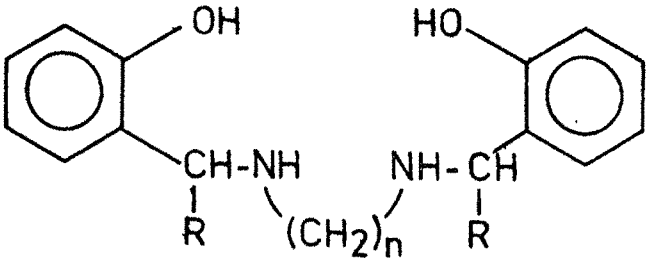
$[Cu(TMB^2)Cu(A^1)](ClO_4)_2$	41 500, 35 500, 33 200, 32 000, 26 000
$[Cu(TMB^2)Cu(A^2)](ClO_4)_2$	43 000, 36 500, 34 000 (sh), 26 000
$[Cu(TMB^2)Cu(A^3)](ClO_4)_2$	41 500, 35 200, 30 000
$[Cu(TMB^3)CuCl_2]$	41 800, 36 700, 26 000
$[Cu(TMB^3)Cu(ClO_4)_2]$	42 000, 36 200, 30 000, 25 800
$[Cu(TMB^3)Cu(A^1)](ClO_4)_2$	42 000, 38 500 (sh), 33 300, 32 200, 26 000
$[Cu(TMB^3)Cu(A^2)](ClO_4)_2$	43 200, 36 700, 34 000 (sh), 25 500 (sh),
$[Cu(TMB^3)Cu(A^3)](ClO_4)_2$	41 800, 36 000, 30 200, 25 000
$[Cu(TMB^4)CuCl_2]$	41 000, 35 000, 25 200

cont...

$\left[Cu(TMB^4)Cu(ClO_4)_2\right]$	42 000, 36 500, 25 200
$\left[Cu(TMB^4)Cu(A^1)\right]\ (ClO_4)_2$	41 700, 38 500 (sh), 34 800 (sh), 33 200, 32 200, 25 600
$\left[Cu(TMB^4)Cu(A^2)\right]\ (ClO_4)_2$	44 000, 36 700, 34 000 (sh), 25 600
$\left[Cu(TMB^4)Cu(A^3)\right]\ (ClO_4)_2$	41 500, 35 700, 30 000, 24 000

Table IV 10 : The Exchange Integral J (cm^{-1}) and the Average g- Factor of Binuclear Complexes at Room Temperature ($300^{o}K$)

Compound	J	g
$\left[Cu(TMB^{1})CuCl_{2} \right]$	- 214	2.083
$\left[Cu(TMB^{1})Cu(A^{1}) \right] (ClO_{4})_{2}$	- 182	2.066
$\left[Cu(TMB^{2})Cu(A^{1}) \right] (ClO_{4})_{2}$	- 156	2.066
$\left[Cu(TMB^{3})Cu(A^{1}) \right] (ClO_{4})_{2}$	- 183	2.070
$\left[Cu(TMB^{4})Cu(A^{1}) \right] (ClO_{4})_{2}$	- 146	2.096



TMB

R = H or CH_3

n = 2 or 3

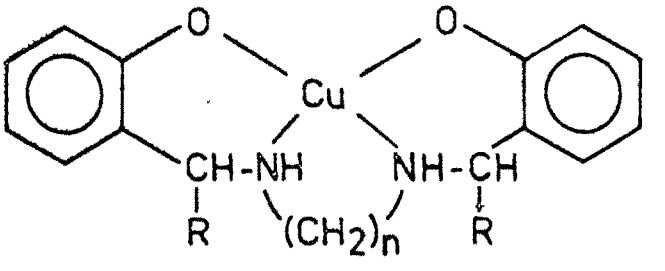
Figure IV 1

RESULTS AND DISCUSSION

T.L.C. of mannich bases show single dots confirming purity of the compounds. The elemental analyses of TMB corresponds to the expected formula (Table IV 1). Structure of TMB can be represented in general as shown in Figure IV 1.

In the IR spectra of TMB, (Table IV 4), there is no band at ca. 1 600 cm^{-1} corresponding to $>C=N-$ group, confirming the complete reduction of $>C=N-$ group. There is a band in the region 3 500 - 3 400 cm^{-1} in all TMB compounds indicating presence of phenolic -OH. A band due to ν_{N-H} appears at 3 310 cm^{-1} in TMB. ν_{C-O} band appears at 1 220 cm^{-1}.

In the NMR spectrum of TSB N,N'-ethylene-bis-(salicylaldimine) , a signal is observed at $\delta = 3.9$ corresponding to the integration of four equivalent protons. This is due to ethylene protons. The aldehydic $H-\underset{|}{C}=O$ proton is observed at low field $\delta = 8.3$ because of the deshielding due to the double bond. In the NMR spectrum of TMB[1], the signal due to $H-\underset{|}{C}=O$ proton disappears. Two signals of equal intensity corresponding to 4 protons each appeared at $\delta = 2.85$ and $\delta = 3.95$. These are due to ethyl protons and the two sets of CH_2 protons formed by the reduction of $\underset{H}{>}C=N-$ to $-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{|}{N}-$ group. NH proton was not



R = H or CH_3

n = 2 or 3

Figure IV 2

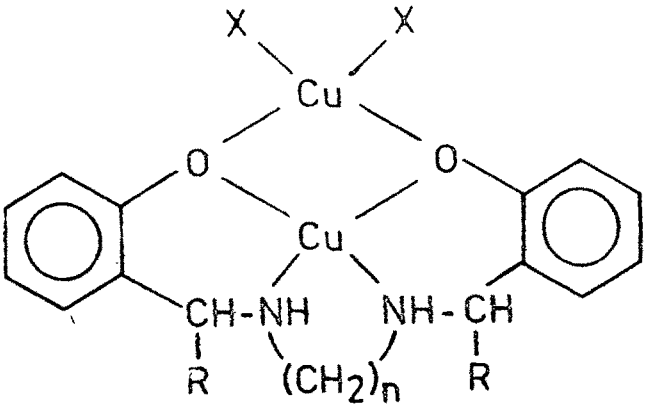
seen in the NMR spectrum of TMB due to fast exchange resulting in broadening of the signal. Signal due to -OH was observed at much lower field $\delta = 12.75$. Thus, the NMR spectrum confirms that the TSB is completely reduced to TMB.

Tetradentate mannich base complexes of Copper(II) showed single dot on TLC plates and their elemental analyses corresponds to the expected formula (Table IV 2). Their structures can be represented in general as shown in Figure IV 2.

In the IR spectra of [Cu(TMB)] complexes (Table IV 5) band at ca. 3 500 - 3 400 cm^{-1} disappears due to dissociation of phenolic proton after complexation. The band due to ν_{N-H} occurs at 3 300 cm^{-1}. Unlike in [Cu(TSB)] complexes, where $\nu_{C=O}$ band appears at ca. 1 530 cm^{-1}, in these [Cu(TMB)] complexes, ν_{C-O} band appears at ca. 1 235 cm^{-1}. This is because, on reduction of $>C=N-$ group, partial double bond character of phenolic C – O disappears.

Ligand field spectrum of mononuclear complex, [Cu(TMB^1)] shows a broad band at 14 290 cm^{-1}. It's unsaturated analogue i.e. [Cu(TSB^1)] complex shows a band at 17 700 cm^{-1}. This shows that on the saturation of $>C=N-$ group in the complex, ligand field is reduced.

All [Cu(TMB)] complexes are paramagnetic (Table IV 2) and have magnetic moments corresponding to one unpaired electron.

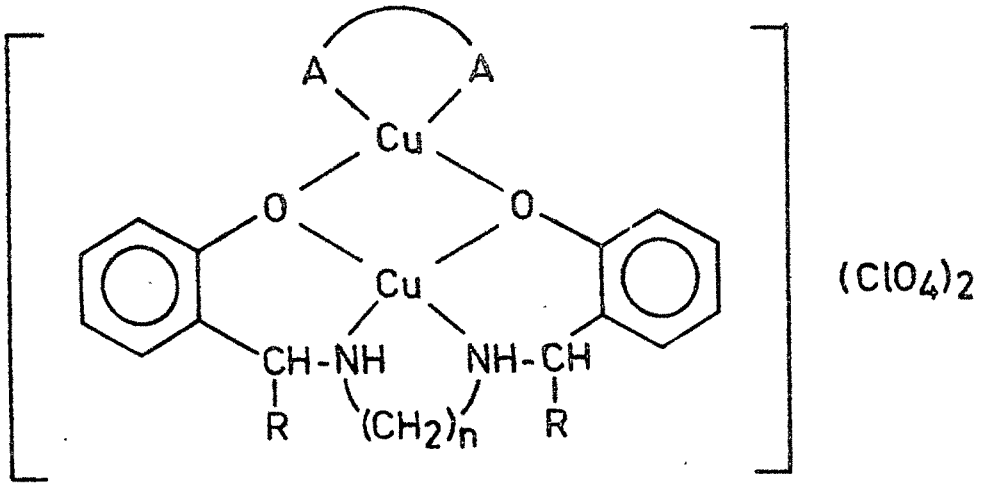


R = H or CH_3

n = 2 or 3

X = Cl^- or ClO_4^-

Figure IV 3



R = H or CH_3

n = 2 or 3

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

Figure IV 4

Binuclear Complexes

Elemental analyses of the binuclear complexes correspond to the expected formulae (Table IV 3). The structures can be represented in general as shown in Figures IV 3 and IV 4.

As the solubility of binuclear complexes is very low in almost all organic solvents, molar conductance could not be determined. The presence of coordinated or non-coordinated nature of perchlorate was confirmed[128] from their IR spectra (Table IV 6).

In binuclear complexes, $[Cu(TMB)CuX_2]$ and $[Cu(TMB)Cu(A\text{-}A)](ClO_4)_2$, all IR bands of $[Cu(TMB)]$ and $[Cu(A\text{-}A)]^{2+}$ occur but with slight change of 5 - 10 cm^{-1}. It is interesting to observe the ν_{C-O} band in binuclear complexes. This shows a shift of 15 - 20 cm^{-1} towards higher energy than in $[Cu(TMB)]$ indicating bridging through phenolic O^-.[111] Coordination of $[Cu(TMB)]$ with either $>CuX_2$ or $>[Cu(A\text{-}A)]^{2+}$ produces approximately similar effect on the IR spectral bands.

Ligand field spectra (Table IV 7) in solid state were taken for a few selected complexes. In the binuclear complex, $[Cu(TMB^1)CuCl_2]$, two separate bands arise at 14 810 cm^{-1} and 10 420 cm^{-1} for the two different Copper(II) centres. As in $[Cu(TSB)CuCl_2]$ complexes, Copper(II) of $>CuCl_2$ part in these

Pseudo
binuclear complexes also is in $_{\chi}$Td geometry and hence shows a band in the region 8 000 - 12 000 cm^{-1}, as expected for tetrahedral complexes.[111] Binuclear complex, $\left[Cu(TMB^1)Cu(A^1)\right]$ $(ClO_4)_2$, also shows two bands at 17 540 cm^{-1} and 12 500 cm^{-1} corresponding to its two non-equivalent Copper(II) centres. The $>\left[Cu(A^1)\right]^{2+}$ centre shows a d-d band at higher energy (12 500 cm^{-1}) than that observed for the $>CuCl_2$ (10 420 cm^{-1}) part in $\left[Cu(TMB)CuCl_2\right]$ complexes. This is because the diamine A-A creates a stronger field than two chlorides. In both types of complexes, band due to $\left[Cu(TMB)\right]$ part of the binuclear complex also shows a shift from the value in free $\left[Cu(TMB)\right]$ complex (14 290 cm^{-1}). This is due to the combined effects of the changes in the ligand field energy and the planarity of the $\left[Cu(TMB)\right]$ complex, because of its coordination with $\left[Cu(A^1)\right]^{2+}$.

Magnetic moment values of the binuclear complexes at room temperature are lower than expected for spin only value for one unpaired electron on each Copper ion (Table IV 3). This is due to the antiferromagnetic interaction between the two Copper(II) ions taking place via superexchange through the σ overlap of the metal $d_{x^2-y^2}$ orbital and the s and p orbitals of the bridging diamagnetic O^- of the Mannich base as in case of $\left[Cu(TSB)CuX_2\right]$ complexes.[111] The lowering in the magnetic moment in the binuclear complex should depend

upon the planarity of the molecule. In these complexes the extent of lowering in the magnetic moment is slightly larger than in case of binuclear complexes $[Cu(TSB)Cu(A\text{-}A)](ClO_4)_2$.

The extent of lowering in the magnetic moment shows that the superexchange in the $[Cu(TMB)Cu(A\text{-}A)](ClO_4)_2$ complexes is slightly more than in $[Cu(TSB)Cu(A\text{-}A)](ClO_4)_2$ complexes. This implies that the planarity of $[Cu(TMB)]$ part is more than in $[Cu(TSB)]$ part in the corresponding binuclear complexes. In the case of $[Cu(TMB)CuX_2]$ or $[Cu(TMB)Cu(A\text{-}A)](ClO_4)_2$ complexes, it appears that the coordination of the second Copper(II) makes $[Cu(TMB)]$ more planar. The second Copper(II) and the ligand over it controls the overall planarity of the molecule. Thus, these binuclear complexes $[Cu(TMB)CuX_2]$ and $[Cu(TMB)Cu(A\text{-}A)](ClO_4)_2$ differ in behaviour from the macrocyclic complexes of Lindoy,[153] where introduction of saturation into the macrocyclic ring does not significantly alter its ring size or the planarity in the complex.

In the present binuclear complexes, the π delocalization in mannich base part is comparatively less than in $[Cu(TSB)]$ part of the corresponding binuclear complex. However, the lowering of magnetic moment is more. This indicates that the role of π orbitals in the superexchange interaction in these binuclear complexes is less significant than of other structural features mainly planarity of the ring. This was

confirmed from the UV spectra of the [Cu(TMB)] and its binuclear complexes. No significant change was observed in the band position of the [Cu(TMB)] in its binuclear complexes (Tables IV 8 and IV 9) showing that there is no significant π interaction between the two ligands through the metal dπ orbitals.