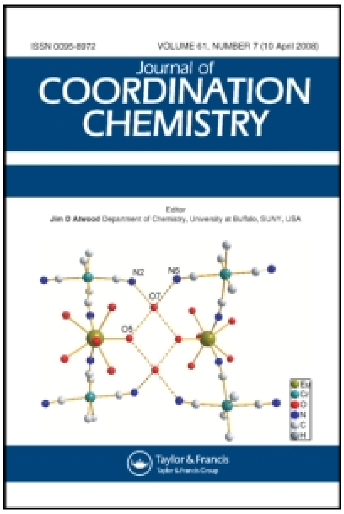

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Synthesis, Spectroscopic and Magnetic Studies of Cobalt(II), Nickel(II) and Copper(II) Complexes with 3'- and 5'-Methoxysalicylaldimine-3-Ethylene-1H-Indole. X-Ray Structure of BIS(1H-Indole-3-Ethylene-5'-Methoxysalicylaldimine)Copper(II)

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SYNTHESIS, SPECTROSCOPIC AND MAGNETIC STUDIES OF COBALT(II), NICKEL(II) AND COPPER(II) COMPLEXES WITH 3′- AND 5′-METHOXYSALICYLALDIMINE-3-ETHYLENE-1H-INDOLE. X-RAY STRUCTURE OF BIS(1H-INDOLE-3-ETHYLENE-5′-METHOXYSALICYLALDIMINE)COPPER(II)

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Two bidentate ligands and their cobalt(II), nickel(II) and copper(II) complexes are reported; these ligands were prepared by 1 : 1 Schiff base condensation of 3-(2-aminoethyl)indole (tryptamine, TPA) with salicylaldehyde derivatives. The structures of the compounds were assigned on the basis of IR, electronic, mass and ^{1}H NMR data. Bis(1H-indole-3-ethylene-5′-methoxysalicylaldimine)copper(II), ($C_{36}H_{34}N_4O_4Cu$), crystallized in monoclinic space group $P2_1/c$ and was subjected to a single-crystal X-ray structure analysis. The structure was solved by direct and Fourier methods, refined by full-matrix least-squares, and converged to a R value of 0.038 for 1358 observed reflections. The coordination of the copper(II) complex is *trans*-planar (CuO_2N_2) with Cu–O and Cu–N bond lengths of 1.88(1) Å and 2.01(1) Å, respectively. The magnetic susceptibilities of the two copper complexes show normal magnetic behaviour in the range 79–279 K. The coordination of the two nickel complexes is *trans*-planar (NiO_2N_2) and both complexes are diamagnetic at room temperature (297 K). The spectroscopic and magnetic data for bis(1H-indole-3-ethylene-5′-methoxy-salicylaldimine)cobalt(II) is consistent with an octahedral environment around the metal.

Keywords: Schiff base, indole, complexes, X-ray structure, first row

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INTRODUCTION

Few references to metal complexes with Schiff bases and an indole group are encountered in the literature.[1,2] The presence of bulky groups such as indole in metal complexes may produce distortions in the stereochemistry around the metal with consequent uncommon physical properties, the structural interpretation of which has aroused controversy.[3-10] To complement known information we have prepared ligands of the type shown in Figure 1 by carrying out the condensation of 3-[2-aminoethyl]indole (tryptamine) with salicylaldehyde derivatives.

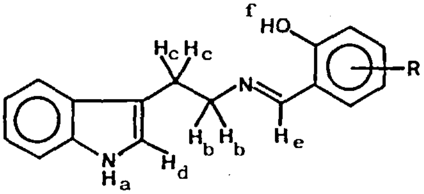


FIGURE 1 The Schiff base, with proton numbering scheme.

The Schiff bases 1H-indole-3-ethylene-3′-methoxysalicylaldimine (3MeOsalTPA), 1H-indole-3-ethylene-5′-methoxysalicylaldimine (5MeOsalTPA) and their cobalt(II), nickel(II) and copper(II) complexes were prepared and studied as described below.

EXPERIMENTAL

Chemicals

The starting materials were obtained commercially and used without further purification. All solvents were of reagent grade.

Analysis

Microanalyses were performed with a Carlo Erba 1106 automatic analyzer. The metals were determined by atomic absorption with a Perkin-Elmer 3030 spectrophotometer.

Physical Measurements

High resolution mass spectra of the compounds were obtained using a ZAB-2F Micromass VG spectrometer. Ionization voltage was 70 eV and the temperature 473 K. Samples were introduced directly into the ionization-chamber.

^1H nmr spectra were recorded on a Bruker WP 200 SI instrument at 200 MHz using TMS as an internal standard. Electronic spectra were obtained using a Perkin-Elmer 550S spectrophotometer equipped with a 561 integrator. Diffuse reflectance was also studied with the samples dispersed in $BaSO_4$. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer in the range 4000–250 cm^{-1}, in KBr. Magnetic susceptibility data were collected using the Faraday technique from liquid nitrogen to room temperatures with $Hg[Co(SCN)_4]$ as calibrant and by the Gouy method at room temperature. The data were corrected to compensate for the diamagnetism of the constituent atoms.[11] E.p.r. spectra were recorded at X band frequencies on a Bruker ER-200tt spectrometer. The magnetic field was calibrated with DPPH (g = 2.0036) and measured on a Bruker BNM 20 Gaussmeter.

X-Ray Data Collection and Structure Determination

Single prismatic crystals of Ni(3MeOsalTPA)$_2$ and Cu(5MeOsalTPA)$_2$ were mounted at the end of a glass fibre attached to a goniometer head. The unit cell constants and crystal orientation matrix for both complexes were refined by a least-squares fit to the angular positions of 25 accurately located reflections in the range $21 < 2\theta < 35°$. The systematic absences indicated space group $P2_1/c$ for both compounds. Crystallographic data are given in Table I.

TABLE I
Crystallographic data for the complexes.

	Ni(3MeOsalTPA)$_2$	Cu(5MeOsalTPA)$_2$
Crystal size, mm	0.20 × 0.40 × 0.30	0.19 × 0.08 × 0.46
Crystal symm.	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Absorption Coefficient	6.9 cm^{-1}	7.7 cm^{-1}
F(000)	676	678
Max. and min. electron densities in final difference map	2.34, −4.33 eÅ^{-3}	0.19, −0.025 eÅ^{-3}
Max. and min. transmission factors		0.7986, 0.6783
a, Å	18.285(4)	19.639(5)
b, Å	5.426(2)	5.445(1)
c, Å	17.134(3)	21.567(4)
β°	116.92(2)	137.02(8)
V, Å^3	1515.7(7)	1572.0(2)
Z	2	2
d_{calc}, g cm^{-3}	1.41	1.37
d_{obs}, g cm^{-3} (pycnometry)	1.40	1.39
range, *h*	−20, 19	−23, 15
range, *k*	0, 6	0, 6
range, *l*	0, 10	0, 25
R	0.1651	0.0377
R_w	0.1651	0.0470

Intensity data for both complexes were collected at room temperature by the ω-2θ scan technique up to $2\theta = 50°$ and measured on a Phillips PW1100 four-circle automatic diffractometer with graphite monochromatized MoK_α radiation ($\lambda = 0.71069$ Å). A total of 2670 independent reflections for Ni(3MeOsalTPA)$_2$ and 2775 for Cu(5MeOsalTPA)$_2$ were collected. As a check on crystals and electronic stability, one standard reflection was measured every 50 reflections and no significant changes were noted for both compounds. Lorentz and polarization corrections were applied to the data. Absorption corrections[12] were made only for Cu(5MeOsalTPA)$_2$. Only 1651 reflections for Ni(3MeOsalTPA)$_2$ having $I > 2.5\sigma(I)$ and 1358 observed reflections for Cu(5MeOsalTPA)$_2$ having $I > 2.5\sigma(I)$ were used in the refinement.

The structures were solved by direct methods.[13] The non-hydrogen atoms were located in successive difference Fourier syntheses and refined by full-matrix least-squares[14] minimizing the function $\Sigma w(\Delta F)^2$. Scattering factors were taken from the International Tables.[15] For the nickel(II) compound the structural refinement converged to a final residual $R = 0.1651$ due to the poor quality of the crystal. Attempts to lower the R value for the nickel(II) complex were unsuccessful and therefore fractional atomic coordinates, bond lengths and angles are not given for this compound. For the copper compound, anisotropic thermal motion was assumed for all non-hydrogen atoms. Hydrogen atoms for the copper compound were located after anisotropic refinement. In the last cycle of least-squares R and R_w were 0.0377 and 0.0470, respectively; $w = [\sigma^2(F) + 0.00189F^2]^{-1}$. Final atomic coordinates are given for the copper complex in Table II. Bond distances, bond angles, torsion angles, planes and dihedral angles were calculated by the Parst program.[16] Selected bond distances, bond angles and planes for the structure are listed in Table III. The anisotropic thermal parameters for the atoms and lists of observed and calculated structure factors are available as supplementary material from the Editor-in-Chief upon request.

TABLE II

Fractional atomic coordinates with e.s.d's in parentheses and B_{eq} (Å)^2 for the complex Cu(5MeOsalTPA)$_2$ ($B_{eq} = \Sigma_i \Sigma_j \beta_{ij} a_i a_j$).

Atom	x/a	y/b	z/c	B_{eq}.
Cu	0.5000	0.0000	0.0000	3.47
O2	0.5834(3)	−0.2720(7)	0.0707(3)	4.94
N3	0.4376(3)	−0.0242(8)	0.0432(3)	3.29
C4	0.4662(3)	−0.1786(10)	0.1041(3)	3.22
C5	0.5409(3)	−0.3657(9)	0.1481(3)	3.23
C6	0.5595(3)	−0.5141(11)	0.2125(3)	3.72
C7	0.6292(4)	−0.6974(11)	0.2572(3)	3.88
C8	0.6805(4)	−0.7418(11)	0.2374(4)	4.90
C9	0.6630(4)	−0.6001(12)	0.1730(4)	4.85
C10	0.5945(4)	−0.4067(10)	0.1285(3)	3.83
O11	0.6424(3)	−0.8291(9)	0.3205(3)	6.06
C12	0.7180(5)	−1.0096(13)	0.3722(4)	5.77
C13	0.3566(3)	0.1474(10)	0.0079(3)	3.18
C14	0.2569(3)	0.0651(9)	−0.0857(3)	3.84
C15	0.1744(3)	0.2343(10)	−0.1186(3)	3.24
C16	0.1355(4)	0.4324(10)	−0.1740(4)	4.09
N17	0.0639(3)	0.5394(10)	−0.1849(3)	4.47
C18	0.0553(4)	0.4104(11)	−0.1367(4)	3.81
C19	−0.0093(5)	0.4460(12)	−0.1299(5)	5.49
C20	−0.0001(6)	0.2850(15)	−0.0759(6)	6.77
C21	0.0659(7)	0.0878(14)	−0.0330(6)	7.23
C22	0.1284(4)	0.0506(11)	−0.0415(4)	4.95
C23	0.1237(3)	0.2160(9)	−0.0939(3)	3.29

TABLE III

Selected bond lengths, bond angles and planes for the Cu(5MeOsalTPA)$_2$ complex.

Bond Lengths (Å)	
Cu–O2	1.88(0)
Cu–N3	2.01(1)
O2–C10	1.32(1)
N3–C4	1.29(1)
C16–N17	1.37(1)
N17–C18	1.36(1)
O11–C12	1.41(1)
C7–O11	1.38(1)
N3–C13	1.48(1)

Bond Angles (deg)	
O2–Cu–N3	92.1(3)
Cu–O2–C10	130.3(5)
Cu–N3–C13	120.5(4)
Cu–N3–C4	123.6(5)

Planes

Plane 1:	Deviation (Å)	Plane 2:	Deviation (Å)
Cu	−0.0097	C5	0.0028
N3	0.0387	C6	0.0073
C4	−0.0091	C7	−0.0099
C5	−0.0298	C8	0.0008
C10	0.0115	C9	0.0138
102	0.0247	C10	−0.0116

Angle (deg) between planes 1 and 2: 2.56(17)

Preparation of the Ligands and Complexes

3MeOsalTPA and 5MeOsalTPA

A solution containing 0.013 mol of 3-methoxy- or 5-methoxy-salicylaldehyde in 20 cm^3 ethanol was added slowly to another containing 0.013 mol of 3-(2-aminoethyl)indole in 20 cm^3 ethanol. The mixture was refluxed while being stirred magnetically for half an hour. When it was left to cool, a yellowish-orange precipitate appeared which was filtered off and recrystallized twice from ethanol. 3MeOsalTPA: Yield 74%; mp 112–114°C; calcd. for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52%. Found: C, 73.19; H, 6.25; N, 9.64%. 5MeOsalTPA: Yield 59%; mp 110°C; calcd. for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52%. Found: C, 73.37; H, 6.17; N, 9.60%.

Cu(3MeOsalTPA)$_2$.H$_2$O

The method described in ref. 2 was applied and a brown solid obtained. Yield: 45%. Calcd. for $CuC_{36}H_{36}N_4O_5$: Cu, 9.51; C, 64.71; H, 5.43; N, 8.38%. Found: Cu, 9.57; C, 64.77; H, 5.41; N, 8.30%.

Cu(5MeOsalTPA)₂

A solution of sodium acetate (10^{-3} mol) and 3MeOsalTPA (10^{-3} mol) in 30 cm³ of methanol was added slowly to another solution of copper(II) acetate monohydrate (0.5×10^{-3} mol) in ethanol (30 cm³) and stirred at room temperature. Almost immediately a greenish precipitate was observed and after half an hour this was filtered off and recrystallized from hot ethanol to yield a greenish-yellow powder. Yield: 70%; mp 210°C with decomposition. Single crystals suitable for X-ray diffraction analysis were obtained by liquid diffusion[17] using acetone as solvent and *n*-hexane as precipitating agent. Calcd. for $CuC_{36}H_{34}N_4O_4$: Cu, 9.77; C, 66.50; N, 8.62; H, 5.27%. Found: Cu, 9.78; C, 66.36; N, 8.49; H, 5.32%.

Ni(3MeOsalTPA)₂

0.27 g of sodium acetate was added to a solution containing 3.4×10^{-3} mol of 3MeOsalTPA in 20 cm³ of methanol in order to maintain pH *ca* 5 throughout the reaction. The solution was heated and while it was stirred another solution containing 1.7×10^{-3} mol of nickel acetate tetrahydrate in 20 cm³ methanol was added drop by drop. As this metal salt was being added, the solution turned dark green. It was refluxed for 1 hour, but no precipitate was observed. It was then concentrated in a rotavapor, reduced to about 1/3 of its original volume and left to cool. When the solution was cold, distilled water was added and a copious precipitate, light green in colour, appeared immediately. This was filtered off and recrystallized from chloroform/*n*-hexane. Yield: 40%; mp 226°C with decomposition. Green single crystals were obtained as described above. Calcd. for $NiC_{36}H_{34}N_4O_4$: Ni, 9.09; C, 66.96; H, 5.31; N, 8.68%. Found: Ni, 9.02; C, 66.74; H, 5.35; N, 8.36%.

Ni(5MeOsalTPA)₂

This was obtained in the same way as the previous product except that it was not necessary to add water. Yield: 66%; mp 220°C with decomposition. Calcd. for $NiC_{36}H_{34}N_4O_4$: Ni, 9.09; C, 66.96; H, 5.31; N, 8.68%. Found: Ni, 9.10; C, 66.95; H, 5.33; N, 8.47%.

Co(5MeOsalTPA)₂

Nitrogen was bubbled into a solution containing 10^{-3} mol of 5MeOsalTPA and 10^{-3} of sodium acetate in 30 cm³ methanol and then another solution (10 cm³ water and 15 cm³ ethanol) containing 0.5×10^{-3} mol of cobalt(II) acetate tetrahydrate, which had also been previously treated with nitrogen, was added drop by drop. The mixture was stirred for 2 hours under nitrogen and the reaction temperature was kept at *ca* 30°C. A precipitate was obtained from the resulting mixture and this was filtered off under nitrogen. It was difficult to recrystallize this reddish orange precipiate so it was washed thoroughly with cold methanol. Yield 58%; mp 226°C with decomposition; Calcd. for $CoC_{36}H_{34}N_4O_4$: Co, 9.13; C, 66.97; N, 8.68; H, 5.31%. Found: Co, 9.20; C, 67.02; N, 8.61; H, 5.53%.

Various attempts to obtain Co(3MeOsalTPA)₂ were unsuccessful.

TABLE IV

200 MHz ^{1}H NMR spectral assignments for the ligands and their nickel(II) complexes.[a]

Compound	H_a	H_d	J_{ad}	H_c	H_b	H_e	Aromatics	H_f
3MeOsalTPA	8.04s	7.02t	2.3	3.15t	3.89t	8.12s	7.03–7.9m	14.16*s
5MeOsalTPA	8.00s			3.13t	3.88t	8.10s	6.64–7.64m	13.18*s
Ni(3MeOsalTPA)$_2$	7.09s*			3.47t	5.42t	11.60s	6–7.5m	
Ni(5MeOsalTPA)$_2$	7.97s*			3.48t	4.30t	8.98s	6–7.5m	

[a] In ppm relative to Me_4Si as internal standard; the relative intensities of all peaks are in accord with the assignments given; key: s, singlet; m, multiplet; d, doublet; t, triplet. * This peak disappears on addition of D_2O.

TABLE V
Infrared spectral data for the compounds (cm^{-1}).[a]

3MeosalTPA	5MeOsalTPA	Cu(3MeOsalTPA)$_2$H$_2$O	Ni(3MeOsalTPA)$_2$	Co(5MeOsalTPA)$_2$	Cu(5MeOsalTPA)$_2$	Ni(5MeOsalTPA)$_2$	Assignments
3300–2700bvs	3380vs	3470, 3400s	3460, 3405s	3400s, 3250s	3400s	3450, 3370s	v(N–H)indole
		3300					v(O–H)H$_2$O
	2940–2830m						v(O–H . . N)
1650vs	1630s	1610vs	1600vs	1600vs	1605vs	1595vs	v(C=N)
1350m	1255m	1329m	1329vs	1335m	1328s	1310s	v(C–O)Phenolic
1240, 1220vs	1220vs	1240, 1200vs	1240, 1200vs	1215m	1225m	1220–1210m	O–CH$_3$

[a] Intensities: b = broad; vs = very strong; s = strong; m = medium.

RESULTS AND DISCUSSION

Characterization of the Ligands

The reaction between 3-(2-aminoethyl)indole and aldehyde-type salicylaldehydes leads to a Schiff base without Pictet-Spengler cyclization at position 2 of the indole, as is shown in the single crystal structural study of the ligand 3MeOsalTPA.[18] An analogous result was observed for 1H-indole-3-ethylenesalicylaldimine (salTPA).[19] The ^1H nmr spectral assignments (in $CDCl_3$) for the ligands are listed in Table IV. They are in agreement with the structure of 3MeOsalTPA[18] and with data for salTPA[2] published earlier. Significant proton H_f signals are to be observed, due to the presence, in solution, of an intramolecular hydrogen bond between the phenolic oxygen and the iminic nitrogen atoms (see Fig. 1).

The mass spectra of the ligands show a peak corresponding to the molecular ion in both cases at *m/e* 294 (77.1%) for 3MeOsalTPA and (33.8%) for 5MeOsalTPA. The elemental composition of both fragments, $C_{18}H_{18}N_2O_2$, was determined by high resolution. As was to be expected, in view of the greater relative intensity of the molecular ion, the order of stability is salTPA < 5MeOsalTPA < 3MeOsalTPA. Other important peaks observed in the spectra of 3MeOsalTPA and 5MeOsalTPA, respectively, were *m/e* 265 (8.7%), 164 (64.9%, 19.7%), 137 (50.8%, 7.8%) and 130 (100% for both compounds).

Table V shows the most important infrared signals for the ligands, together with their assignments. When the ligand 3MeOsalTPA is in the solid, the characteristic band of the indole N–H group is not observed: in related compounds,[20,21] this usually appears at around 3400 cm^{-1}. The band at 3120 cm^{-1} loses intensity in the spectrum of the deuterated ligand while two intense bands are found at 2270 and 2360 cm^{-1}. The ir spectrum run in deuterated chloroform showed a very intense band at 3400 cm^{-1}. These results would seem to indicate that for 3MeOsalTPA in the solid, there is a hydrogen bond between the indole N–H group and other donor groups of neighbouring molecules. The other bands observed in this region (3100 cm^{-1}) have been attributed to the N–H groups in this type of system.[20]

In support of this assignment, the band corresponding to the stretching vibration of the carbon–nitrogen bond for an imonium-type group ($-C{=}N^+{-}H$) was observed at 1650 cm^{-1}. These bands generally appear at 1680 cm^{-1} but are shifted towards lower wave numbers due to conjugation of the enoliminic group, as shown in Figure 1, favoured by the formation of a hydrogen bond.

From the foregoing, it can be deduced that the 3MeOsalTPA ligand exhibits an imonium-type structure as indicated by X-ray structural analysis.[18] Thus, the distance found for the intramolecular hydrogen (N–H ··· O) bond is 2.61(8) Å, and the C–O distance of 1.29(1) Å indicates a bond intermediate between a single and a double bond. Furthermore, the distance between an indolic hydrogen and a phenolic oxygen in a neighbouring molecule proved to be 2.77(1) Å. For 5MeOsalTPA, the band characteristic of indolic N–H vibration was observed, as well as bands at 2940 and 2830 cm^{-1}, these being assigned to an intramolecular hydrogen bond between the iminic nitrogen and phenolic oxygen atoms[20] as had been observed for salTPA.[2] Accordingly, 5MeOsalTPA should exhibit a structure similar to that already shown for salTPA. The carbon–nitrogen vibration for the iminic group appears at 1630 cm^{-1} for 5MeOsalTPA.

The electronic spectra data for the ligands are given in Table VI together with their assignments. For salTPA, the band corresponding to the $n \rightarrow \pi^*$ transition in the solid state (diffuse reflectance) is centred at 389 nm and for 5MeOsalTPA at 420 nm, while for 3MeOsalTPA it is shifted to greater wave lengths (450–460 nm). This bathochromic shift is due to the greater C–O double bond in 3MeOsalTPA [C–O bond length, 1.29(1) Å][18] as compared to salTPA [1.34(1) Å],[19] producing a conjugative effect on the chelate ring.[22] The former bands undergo shifts in chloroform solution, the greatest being that of 3MeOsalTPA. According to Kazitsyna[23] and Davis *et al*,[24] these shifts can be explained by the existence of an equilibrium between enoliminic and ketoiminic tautomeric forms.

The two ligands exhibit a band 300–400 nm which corresponds to $\pi \rightarrow \pi^*$ transitions of the chelate ring.[25] The position of this signal is affected by the strength of the hydrogen bond in the system and by the existence of the ketoenolic balance. A bathochromic shift of this band in those cases where the C–O bond has a markedly ketonic nature is therefore to be expected. Thus, in salTPA,[2] it is found at 319 nm, and in 5MeOsalTPA, at 345 nm. In 3MeOsalTPA and 5MeOsalTPA, the O–CH_3 groups deactivate the *ortho*- and *para* positions, respectively, increasing the ketonic character of the C–O bond.

TABLE VI
Electronic spectral data for the compounds: λ(nm) (ε(M^{-1} cm^{-1})).

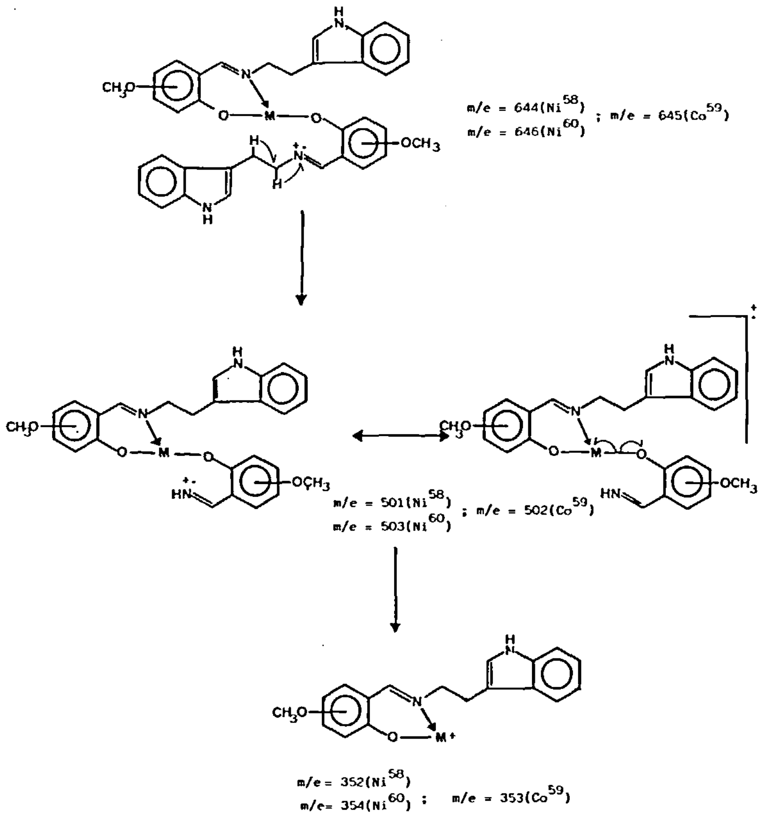
Compound	DR*	Chloroform	Pyridine	Assignments
3MeOsalTPA	450–460	424(6.31×10^2)		
		325(2.89×10^3)		
		290(8.39×10^3)		
		263(1.69×10^4)		
5MeOsalTPA	420	440(1.40×10^2)		
		345(4.92×10^3)		
		280(1.10×10^4)		
		260(1.56×10^4)		
Cu(3MeOsalTPA)$_2$.H_2O	740	620(1.75×10^2)	610–580(1.31×10^2)	
		370(9.68×10^3)	370(8.54×10^3)	
Ni(3MeOsalTPA)$_2$	620	620(0.80×10^2)		$^1A_{1g} \rightarrow {}^1B_{1g}$
			580(1.38×10^1)	$^3A_{2g} \rightarrow {}^3T_{1g}$
			1000(1.81×10^1)	$^3A_{2g} \rightarrow {}^3T_{2g}$
Cu(5MeOsalTPA)$_2$	700	630(1.53×10^2)	625sh.(1.40×10^2)	
Ni(5MeOsalTPA)$_2$	650	630(1.26×10^2)		$^1A_{1g} \rightarrow {}^1B_{1g}$
			580(1.53×10^1)	$^3A_{2g} \rightarrow {}^3T_{1g}$
Co(5MeOsalTPA)$_2$	560	590sh(1.00×10^2)	580sh(6.5×10^1)	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$

* DR = Diffuse Reflectance.

Characterization of the Metal Complexes

Complexes of the type ML_2 were obtained by reaction of the ligands with the appropriate metal acetate in a solvent such as a methanol or ethanol. All the complexes obtained were soluble in acetone, chloroform, dichloromethane, DMSO and dimethyformamide. They do not dissolve in methanol, ethanol, isopropanol or water, but are partially soluble in hot benzene.

In the ^1H spectra of the nickel complexes (see Table IV), when compared with those of the ligands, shifts in the resonance frequencies were observed. The most pronounced shifts were for the protons nearest to the metal, such as H_b and H_e. Mass spectra of the nickel and cobalt complexes show peaks corresponding to molecular ions as follows. Ni(3MeOsalTPA)$_2$: *m/e* 644 (1.52%; $C_{36}H_{34}N_4O_4{}^{58}Ni$) and *m/e* 646 (0.62%, $C_{36}H_{34}N_4O_4{}^{60}Ni$); Ni(5MeOsalTPA)$_2$: *m/e* 644 (1.49%; $C_{36}H_{34}N_4O_4{}^{58}Ni$) high resolution: *m/e* experimental, 644.3485; *m/e* theoretical, 644.692) and *m/e* 646 (0.66%, $C_{36}H_{34}N_4O_4{}^{60}Ni$); high resolution: *m/e* experimental, 646.1762; *m/e* theoretical, 646.692); Co(5MeOsalTPA)$_2$: *m/e* 645 (12.1%, $C_{36}H_{34}N_4O_4{}^{59}Co$; high resolution: *m/e* experimental, 645.3675; *m/e* theoretical, 645.622. The assignments and intensities of the major mass spectral peaks for both complexes are in accordance with the proposed pathways in Scheme I and also with those for similar complexes.[2] Mass spectra of the copper complexes do not show peaks corresponding to molecular ions, even when a chemical ionization (methane) method was employed, due to greater weakness of metal–ligand bonding. The ions found are the same as in the ligand spectra.



SCHEME I Proposed fragmentation pathways for the complexes.

The molecular structure of Cu(5MeOsalTPA)$_2$ (Fig. 2) is consistent with discrete monomer units and the molecule is centrosymmetric (D_{2h} symmetry) with six-membered chelate rings on both sides of the central ion. Thus, deviations in the planarity of the *trans*-MN_2O_2 group can occur (Table III). The Cu–O distance is 1.88(1) Å and the Cu–N distance is 2.01(1) Å, and hence the planar coordination around the metal is rhombically distorted with the longer axis along N–M–N, with N–M–O angles in the complex similar to those found in other planar complexes.[26–28] This distortion is similar to that observed in bis (*N*-methylsalicylaldimine)nickel(II) with Ni–O (1.80 Å) and Ni–N (1.90 Å) also in a *trans*-planar arrangement.[26] In the $Cu(5MeOsalTPA)_2$ complex the C–N bond distance of the imine group, 1.29(1) Å, is indicative of electronic delocalization in this group. The X-ray structural analysis of $Ni(3MeOsalTPA)_2$ shows a planar coordination around the Ni(II) with *trans* disposition of the N_2O_2 group. This result helps to explain magnetic measurements and electronic spectra as described below.

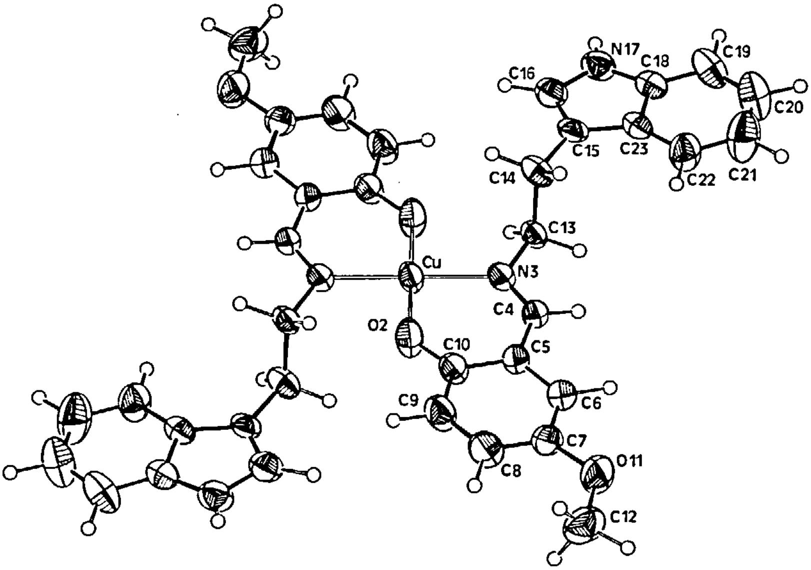


FIGURE 2 Molecular structure of $Cu(5MeOsalTPA)_2$.

The infrared spectra of the complexes (Table V) give an indole NH signal (*ca* 3400 cm^{-1}) divided in two, except in the $Cu(5MeOsalTPA)_2$ and $Cu(salTPA)_2$[2] complexes. This splitting indicates intermolecular hydrogen bond associations between the indole NH group and others[1,29,30] with scant likelihood of this indole NH group taking part in the coordination, as has been demonstrated in the structure of $Cu(5MeOsalTPA)_2$. The band at 1650 cm^{-1} for the ligand 3MeOsalTPA assigned to the imonium group and that at 1630 cm^{-1} assigned to the imine group in 5MeOsalTPA shift to lower wave numbers in the complexes, due to the coordination of the nitrogen atom with the metal.[2,31,32] In the case of the 3MeOsalTPA complexes, the band is sharpened due to the loss of the imonium group proton. The bands for the ligands at 1350 and 1325 cm^{-1} assigned to the stretching vibration of the phenolic C–O bond,[33] undergo shifts in the complexes due, probably, to slight changes in C–O bond lengths.

The bands between 575–350 cm^{-1} are characteristic of coupled M–N and M–O vibrations in accordance with reported data.[2,34,35] In the $Cu(3MeOsalTPA)_2.H_2O$ complex the band at 3300 cm^{-1} corresponds to symmetric and antisymmetric vibrations of the OH group of the water molecule. The complex loses water between

303 and 345 K (found: 2.69%; calcd.: 2.70%). This result indicates that the water molecule is weakly bonded in the complex, probably by means of hydrogen bonds. Differential thermal analysis shows an endothermic effect at 337° K, confirming the water molecule loss.

The compounds Ni(5MeOsalTPA)$_2$ and Ni(3MeOsalTPA)$_2$ are diamagnetic, corresponding to planar complexes. The electronic spectral bands at 630 and 620 nm in chloroform solution (650 and 620 nm in the solid state) correspond to the transition $^1A_{1g} \rightarrow {}^1B_{1g}$ in the same way as in the Ni(salTPA)$_2$ complex.[2] For both nickel complexes the electronic spectrum in pyridine suggests an octahedral stereochemistry around the nickel(II)[2,36] caused by coordination of the solvent molecules in axial positions (Table VI).

The electronic spectrum of Cu(5MeOsalTPA)$_2$ is similar to that of Cu(3MeOsalTPA)$_2$.H$_2$O, with a band at *ca* 700 nm suggesting a *trans*-planar arrangement for the CuN$_2$O$_2$ chromophore, rhombically distorted in the case of the latter. Both complexes show a band in chloroform solution shifted to 620 nm which may indicate a change in the stereochemistry of the complex compared with that of the solid form, and passing to a less distorted planar arrangement.[37]

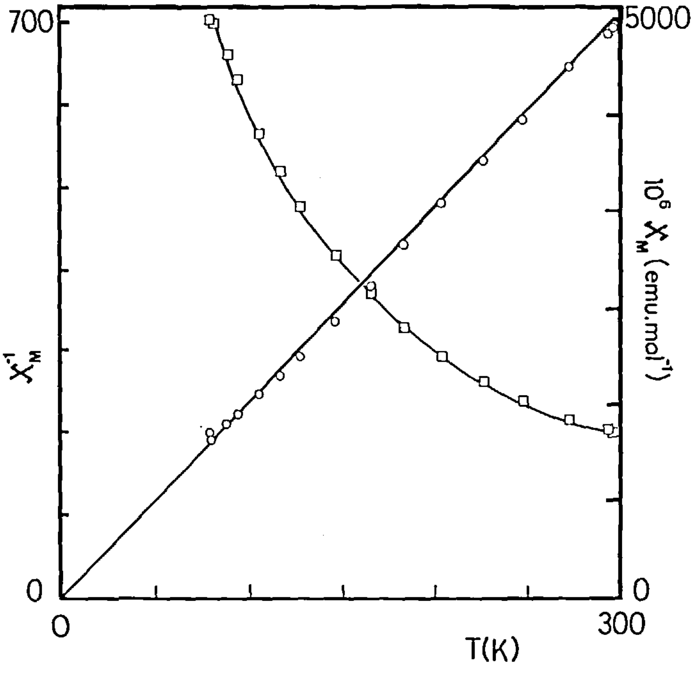


FIGURE 3 Molar magnetic susceptibilities (□) and inverse molar magnetic susceptibilities (O) *vs* T(K) plots for Cu(3MeOsalTPA)$_2$.H$_2$O.

Figure 3 shows magnetic susceptibilities and their inverses *vs* temperature for Cu(3MeOsalTPA)$_2$.H$_2$O. A similar behaviour is shown by the Cu(5MeOsalTPA)$_2$ complex. In the range of temperatures studied (79–297 K), both complexes obey the Curie Law (C *ca* 0.42 for both). The magnetic moment of Cu(3MeOsalTPA)$_2$.H$_2$O is 1.86 BM at 297 K and for Cu(5MeOsalTPA)$_2$ complex it is 1.85 BM at 296.8 K. This magnetic behaviour is consistent with the presence of isolated paramagnetic species.

For both copper complexes a normal axial e.p.r. spectrum was recorded in a powder at room temperature with $g_{\parallel} > g_{\perp}$. For Cu(3MeOsalTPA)$_2$.H$_2$O, $g_{\parallel} = 2.21$ and $g_{\perp} = 2.05$ while for Cu(5MeOsalTPA)$_2$, $g_{\parallel} = 2.27$ and $g_{\perp} = 2.05$. These values are in accord with a rhombic symmetry with slight misalignment of the "tetragonal" axes.[38]

For Co(5MeOsalTPA)$_2$ the magnetic moment at 297 K is 4.33 BM. This value taken together with the electronic spectra is consistent with an octahedral stereochemistry around the cobalt ion. This configuration implies the existence of oligomerization of the type described for the Co(salTPA)$_2$ complex.[2] For the cobalt complex with 3MeOsalTPA, this oligomerization is probably hindered by the steric effects of the methoxy group in an *ortho* position in relation to the OH group and all attempts to obtain it were unsuccessful.

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