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Complexes of Cu(II), Ni(II) and Co(II) with the Schiff Base: 1H-Indole-3-ethylensalicylaldimine as Ligand

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Abstract

Complexes of Cu(II), Ni(II) and Co(II) with the Schiff base 1H-indole-3-ethylensalicylaldimine as ligand are studied. The isolated complexes correspond to the general formulae ML_2 (where L = ligand).

The complexes were characterized by mass spectra, IR, ^1H NMR, UV–Vis spectra and magnetic measurements.

The results indicated that the ligands coordinate through N and O with the metal ions in different stereochemistries.

Introduction

The study of complexes of Schiff bases with transition metals is of interest, since they frequently exhibit unusual structural properties [1]. Until now metal complexes with the Schiff base 1H indole 3 ethylensalicylaldimine (abbreviated Sal-Tpa) have not been described, so it seemed desirable to study the transition metal complexes systematically with this ligand.

This paper describes, for the first time, the complexes of Cu(II), Ni(II) and Co(II) with the Schiff base as ligand. This study forms part of a line of work on biochemical applications of coordination compounds.

Experimental

Schiff Base Preparation

The Sal-Tpa was obtained in accordance with ref. 2 but using ethanol instead of benzene as solvent. In both solvents the reaction between tryptamine (1H indole-3-ethylenamine) and salicylaldehyde provided good yields of Schiff base without Pictet–Spengler cyclization of the tryptamine. The compound was recrystallized from hot ethanol. Yield, 73%.

$Cu(Sal\text{-}Tpa)_2$ Preparation

A solution of copper(II) acetate monohydrate (0.945×10^{-3} mol) in ethanol (40 ml) was added slowly to a solution of Schiff base (1.89×10^{-3} mol) in the same solvent (40 ml). The resulting mixture was refluxed for 20 min until a brown solid was obtained. The mixture was left for 24 h at a temperature of 283 K, filtered and then the solid was washed with cold EtOH and dried in a dry air current. The product was soluble in the usual organic solvents and was poorly soluble in water. Yield, 72%.

$Co(Sal\text{-}Tpa)_2$ Preparation

A solution of sodium acetate (0.384 mol) and Sal-Tpa (0.378 mol) in methanol (20 ml) was added slowly and with stirring to a solution of cobalt(II) acetate tetrahydrate (0.189 mol) in methanol (20 ml). The reaction mixture was refluxed for 2 h at which time an orange solid is obtained. All operations were carried out under nitrogen. Yield, 88%.

The complex was stable at room temperature in the solid phase. It was insoluble in methanol, ethanol, water and chloroform; poorly soluble in diethylether, n-hexane, dioxane and very soluble in acetone, DMSO and pyridine.

$Ni(Sal\text{-}Tpa)_2$ Preparation

The complex was obtained by a procedure analogous to $Cu(Sal\text{-}Tpa)_2$, using nickel(II) acetate tetrahydrate and methanol as solvent. The reaction mixture was refluxed for 45 min until a green solid was formed. The product was soluble in hot benzene, chloroform, acetone, DMSO and pyridine; poorly soluble in diethylether and insoluble in ethanol, water and carbontetrachloride. It was recrystallized from benzene. Yield, 84%.

Analysis

The metals were determined by atomic absorption with a Unicam SP 1900, and C, H and N with a Carlo Erba Mod. 1102 automatic analyser. The results are given in Table I.

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TABLE I. Analytical Data and some Physical Properties of the Compounds Prepared

Compound	Color	Melting point[a] (K)	Found (%)				Calculated (%)			
			M	C	N	H	M	C	N	H
Sal-TPA	Yellow	373		77.20	10.58	6.18		77.25	10.60	6.10
Cu(Sal-TPA)$_2$	Brown	483d	10.75	69.10	9.60	5.22	10.77	69.20	9.49	5.12
Ni(Sal-TPA)$_2$	Green	499d	10.22	69.31	9.26	5.11	10.03	69.76	9.57	5.17
Co(Sal-TPA)$_2$	Orange	463d	9.72	69.12	9.72	5.20	10.06	69.67	9.57	5.16

[a] d = decomposition.

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 453 K. Samples were placed directly into the ionization chamber.

^{1}H NMR spectra were taken on a Brucker WP 200 SI apparatus. The spectrum was obtained at 200 MHz using TMS as an internal standard. Deuterated chloroform was used as a solvent. UV–Vis spectra were recorded on a Perkin-Elmer 550 S apparatus, equipped with a 561 integrator; DMSO, chloroform and pyridine were used as solvents for spectroscopy.

The samples were also dispersed in $BaSO_4$ (diffuse reflectance).

The magnetic susceptibilities of the complexes were measured at room temperature using the Gouy method, with $Hg[Co(SCN)_4]$ as calibrant. Determinations were made at two different field strengths to establish independence of field. Diamagnetic corrections were taken from ref. 3.

Finally, infrared spectra were recorded with a Perkin-Elmer 457 apparatus in the range 4000–250 cm^{-1}. Samples were dispersed in KBr.

Results and Discussion

The mass spectrum of the Schiff base presents the peak corresponding to the molecular ion M^+ at *m/e* 264 (5.3 relative intensity (r.i.)) and its elementary composition, determined by high resolution, agrees with the proposed formula: $C_{17}H_{16}N_2O$ (*m/e* measured 264.1243; *m/e* theoretical 264.1259). The spectrum also shows peaks corresponding to tryptamine.

Cu(Sal-Tpa)$_2$ complex mass spectrum does not exhibit the molecular ion, indicating a greater weakness of the metal–ligand bonding. The ion already found in the free Schiff base spectrum can be observed in the mass spectrum of this complex.

Mass spectra of the complexes Ni(Sal-Tpa)$_2$ and Co(Sal-Tpa)$_2$ show the peaks corresponding to molecular ions at *m/e* 584 (5.1 r.i.) (*m/e* measured 584.1603; *m/e* theoretical for $[C_{34}H_{30}N_4O_2{}^{58}Ni]$ 584.1722) and *m/e* 585 (4.6 r.i.) (*m/e* measured 585.1760; *m/e* theoretical for $[C_{34}H_{30}N_4O_2Co]$ 585.1701), respectively. For both complexes peaks are observed corresponding to fragments whose elementary compositions determined by high resolution are: *m/e* 322 (13.4 r.i.) (*m/e* measured 322.0676; *m/e* theoretical 322.0538) for ^{58}Ni(Sal-Tpa)$_2$ and *m/e* 324 (4.6 r.i.) (*m/e* measured 324.0432; *m/e* theoretical 324.0492) for ^{60}Ni(Sal-Tpa)$_2$ and for the Cobalt complex: *m/e* 322 (4.3 r.i.) (*m/e* measured 322.0575; *m/e* theoretical 322.0516). In accordance with the above, a splitting pattern is proposed in Fig. 1.

The resonances of ^{1}H spectra of ligand and Ni(Sal-Tpa)$_2$ are given in Table II. The ^{1}H NMR spectrum of the Schiff base agrees with the structure proposed in Fig. 2.

It is important to emphasize the ^{1}H resonance of the O–H group at 10.85 ppm, due to the presence of an intramolecular hydrogen bonding. In other Schiff bases with an intramolecular hydrogen bonding, this resonance appears at slightly lower fields [4]. In the complexes this signal disappears as a result of proton

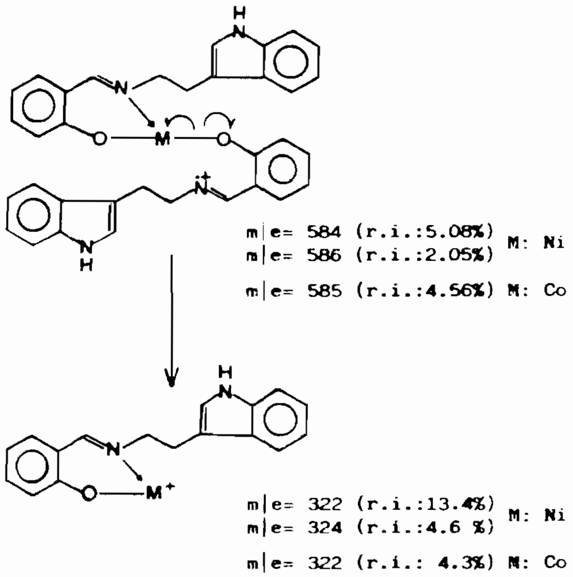

Fig. 1. Splitting pattern of the complexes Ni(Sal-Tpa)$_2$ and Co(Sal-Tpa)$_2$.

TABLE II. ^1H NMR Chemical Shifts of Schiff Base and its Nickel Complex in ppm (δ)^a

Compound	H_a	H_b	H_c	H_d	$H_{aromatics}$	H_e
Sal-TPA	10.85s	3.80t	3.09t	8.05s	6.5–7.6m	7.99
Ni(Sal-TPA)$_2$		4.13t	3.40t	8.70s	6–7.4m	

^{a}s = singlet, t = triplet, m = multiplet.

TABLE III. Infrared Spectra of the Compounds^a

Sal-TPA	Cu(Sal-TPA)$_2$	Ni(Sal-TPA)$_2$	Co(Sal-TPA)$_2$	Assignments
3400vs	3400vs	3400vs 3420vs	3400vs	ν(N–H) indole
2700–2500m				ν(O–H)
1625s	1590s	1610vs	1610vs	ν(C=N–)
1570m	1530m	1530s	1530s	ν(–C=O) phenolic
	575s	460s	455s	ν(Cu–N) } coupled
	420s		435s	ν(Cu–O) } coupled

^{a}vs = very strong; s = strong; m = medium.

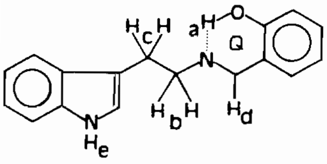

Fig. 2. Schiff base: Sal-Tpa.

substitution by a cation. The largest shifts in δ of the complexes with respect to the ligand are presented by the hydrogens nearest the metal, especially of the –CH=N– group, due to the effect of coordination.

Table III presents the most important band of the infrared spectra of the compounds with their assignments. The broad band at 2700–2500 cm^{-1} is assigned to stretching vibration of the O–H group associated intramolecularly with the nitrogen of the –CH=N– group, a fact previously described in the NMR study. This band disappears in the complex as a result of proton substitution by cation coordination to oxygen. The 1625 cm^{-1} band of the base is assigned to the stretching vibration of the azomethine group [5, 6]. This band is shifted in the complexes towards lower values as a result of the coordination of the nitrogen to metal. A similar effect is observed in the stretching vibration of the Schiff base phenolic C–O group with respect to the same group of the complex, indicating oxygen coordination to the metal [5, 6]. The value of 1530 cm^{-1} for the stretching vibration of the phenolic group suggests an appreciable proportion of double bonding –C=O in the metal complex. The bands between 575–435 cm^{-1} are assigned to vibrations that are probably coupled Cu–N and Cu–O, in accordance with bibliographical data [6].

It is important to indicate the splitting of the band of the N–H group of indole of the Ni(Sal-Tpa)$_2$ with respect to ligand, a fact not described in the consulted bibliography. This splitting is not observed in the spectrum of the deuterated complex of nickel. Such behaviour is attributed to the existence of a weak interaction between the hydrogen of the N–H group of the indole and the oxygen of chelate ring Q of another molecule, forming a hydrogen intermolecular bonding. In the complexes of copper and cobalt, a shift or splitting of the band of the N–H group of indole, with respect to the ligand, is not observed.

The electronic spectra of the compounds with their assignments are given in Table IV. The energy of the $\pi \rightarrow \pi^*$ transition of the chelate ring of the ligand is characteristic of Schiff bases which exhibit delocalized systems with an intramolecular hydrogen bonding [7]. The existence of $\eta \rightarrow \pi^*$ transition of the Schiff base seems to indicate that the molecule has a planar conformation in solution [8], with no rotation of the chelate ring Q around the bonding =N–CH$_2$. In the complex of copper, the band at 362 nm is due, in part, to an internal transition of the ligand and also to a charge transference, probably from the metal to the ligand [5]. The band at 620–580 nm of the same complex is typical of a ligand field transition. The position of this band seems to indicate the presence of a square planar environment around the copper ion in solution [5, 9]. However, in the solid phase the band at 700 nm indicates a distortion towards a pseudotetrahedra symmetry around the copper ion [10, 11].

TABLE IV. Electronic Spectra of the Compounds (λ (nm), ϵ (l mol^{-1} cm^{-1}))^a

Compound	DR	Chloroform	DMSO	Pyridine	Assignments
Sal-Tpa		260 (1.5×10^4)	255 (1.2×10^4)		
		284 (8.4×10^3)	274 (1.1×10^4)		$\pi \rightarrow \pi^*$ indole group
		294 (7.3×10^3)			
		319 (4.6×10^3)	310 (3.74×10^3)		$\pi \rightarrow \pi^*$ chelate ring
		410(269)	398 (2.26×10^3)		$\eta \rightarrow \pi^*$ chelate ring
$Cu(Sal\text{-}Tpa)_2$	700		362 (1.16×10^3)		
			620–580sh(134)		
$Ni(Sal\text{-}Tpa)_2$	615	608	606(78)		$^1A_{1g} \rightarrow {}^1B_{1g}$
				580(16)	$^3A_{2g} \rightarrow {}^3T_{1g}$
				~1000	$^3A_{2g} \rightarrow {}^3T_{2g}$
$Co(Sal\text{-}Tpa)_2$	550–500		560(56)	560(19)	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$
	~1000		~1000	~1000	$^4T_{1g} \rightarrow {}^4T_{2g}$

^{a}DR = Diffuse Reflectance.

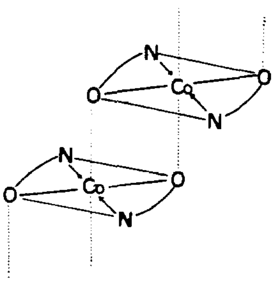

Fig. 3. The most probable arrangements for complex $Co(Sal\text{-}Tpa)_2$.

The value of the magnetic moment for the copper complex at 299 K is 1.95 M_B. The complex gives a slightly anisotropic axial ESR spectrum with $g_\perp = 2.040$ ($g_\parallel$ is more difficult to measure accurately). The value recorded for the magnetic moment is greater than those exhibited by Cu(II) complexes with planar symmetry Schiff bases (1.85–1.86 M_B) and suggests a pseudo-tetrahedral configuration in the solid phase [5] in accordance also with the electronic spectrum.

The nickel complex is diamagnetic and the electronic spectra both in diffuse reflectance and in solution of chloroform and the DMSO (Table IV) are consistent with a square planar arrangement around the Ni(II). The electronic spectrum of the same complex in pyridine suggests an octahedral stereochemistry around the nickel ion [11] by coordination of two molecules of solvent in an axial position on the planar NiO_2N_2.

For the cobalt complex the value of the magnetic moment at 294 K is 4.31 M_B. This value together with the electronic spectra is consistent with an octahedral stereochemistry around the cobalt ion. This configuration implies the existence of polymerizations of the type described in Fig. 3.

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