Ambidenticity of a tridentate oxygen–nitrogen donor towards bivalent and trivalent transition metal ions

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Summary

N-salicylidene anthranilamide (H_2SAA) and its Cr^{III}, Mn^{II}, Fe^{III}, Co^{II}, Ni^{II} and Cu^{II} complexes were prepared and characterized by physicochemical and spectroscopic data. H_2SAA enolizes to give a dibasic ONO donor set in the divalent metal complexes. It also binds to the trivalent metal ions in a nonenolized form using a monobasic ONN donor set. Co^{II} is oxidized to Co^{III} during complexation. Octahedral geometries are proposed for Cr^{III}, Mn^{II}, Fe^{III} and Co^{III} complexes, while square planar geometries are suggested for the Ni^{II} and Cu^{II} complexes. Phenoxide bridging in the Cr^{III} and Fe^{III} complexes and enoxide bridging in the Ni^{II} and Cu^{II} complexes is proposed.

Introduction

Tridentate oxygen and nitrogen containing donor ligands have been studied recently in view of their tendency to form dinuclear metal complexes with substantial metal–metal interactions[1]. These Schiff base complexes are known to have significant applications as biologically active analytical reagents[2]. Amide and azomethine groups are of considerable interest in biocoordination processes[3]. Tridentate ligands containing such centres can be more flexible and be of considerable potential in metal binding processes, owing to amide–iminol tautomerism[4]. In this paper we present one such system: *N*-salicylidene anthranilamide (H_2SAA) and the synthesis and characterization of its transition metal complexes.

Experimental

Materials

Metal chlorides were of AR Grade. Salicylaldehyde was obtained from E. Merck and anthranilamide from the Aldrich. Solvents were purified by established procedures.

Physical measurements and analysis

I.r. spectra were recorded in nujol and KBr in the $4000–200\,cm^{-1}$ region on a Perkin-Elmer 283-B spectrophotometer. Reflectance spectra of solids were recorded on a Cary-17D instrument. ^1H n.m.r. spectra were recorded on a Jeol Fx-90 spectrometer. Magnetic susceptibility measurements were made on a Faraday balance CAHN-7550-03 at room temperature using $HgCo(NCS)_4$ as calibrant. Diamagnetic corrections using Pascal's constants and temperature-independent paramagnetic corrections were computed[5]. The electrical conductance measurements were done in $10^{-3}\,mol\,dm^{-3}$ solutions in

DMSO using Elico conductivity bridge (Model CM-180) and a dip-type cell calibrated with KCl solutions.

C, H and N were estimated at the microanalysis unit at Calcutta University, India. The chloride contents were estimated argentometrically after igniting a definite weight of the complex in an oxygen flask in the presence of KOH and H_2O_2[6]. The complexes were decomposed by slow evaporation of $HClO_4$ and HNO_3 solutions and the resulting metal salts were dissolved in H_2O to give aqueous solutions of known dilutions. The metal contents were estimated by emission spectrophotometry technique using a Lab tam plasma Scan-8410.

Synthesis of H_2SAA

Anthranilamide (16.8 g) and salicylaldehyde ($12\,cm^3$) were added to MeOH ($150\,cm^3$) and the reaction mixture was stirred thoroughly for 30 min. The orange-yellow compound which then separated was removed by filtration, washed successively with Et_2O and MeOH and dried *in vacuo*. H_2SAA can tautomerize in solution owing to mobility of amide protons. Yield: 20.2 g (68%); M.p. 158° C (Found: C, 70.8; H, 4.8; N, 11.2%. $C_{14}H_{12}N_2O_2$ calcd: C, 70.8; H, 5.0; N, 11.7%). ^1H n.m.r. (DMSO-d_6) δ: 13(s, phenolic OH), 10.77(s, CH=N), 7.91–9.3(m, aromatic), 7.46(m, —CO—NH$_2$): $m/z = 240$. U.v.–vis. (ν_{max}, cm^{-1}); 45 450, 43 480, 36 364, 31 250–27 027 (CO—NH$_2$), 23 256–19 500 (CH=N).

The characterization data for H_2SAA are consistent with the expected structure as shown in Figure 1.

Synthesis of the complexes

The following general procedure was adopted. An MeOH solution of the metal chloride was mixed with H_2SAA in 1:2 mole ratio. To this a 5% MeOH solution of NH_3 was added so as to maintain the pH of the reaction at 5, and the mixture was boiled under reflux on steam bath for 2 h, except for the Co complex where the mixture was boiled
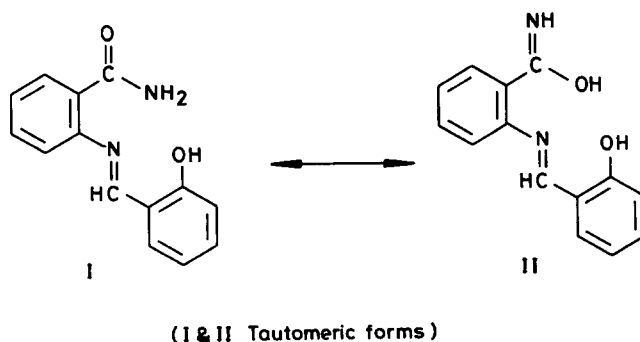

(I & II Tautomeric forms)

Figure 1. Structure of Ligand H_2SAA. I and II are tautomeric forms.

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Table 1. Analytical and i.r. data (cm⁻¹) of metal complexes of $H_2SAA^{a,b}$.

Complex/ stoichiometry	Colour	Decomp. temp. (°C)	Found (Calcd.)% M	N	$\nu(NH_2)$ amide	$\nu(=NH)$ imide	$\nu(C=O)$ carbonyl	$\nu(C=N)$	$\nu(C—O)$	New bands
$[Cr^{III}LCl_2]\cdot H_2O$	Light green	230	13.5 (13.7)	7.0 (7.4)	3200–3100	–	1660	1560	1400ᵉ	660–240
$[Mn^{II}L'(H_2O)_3]$	Silver white	230	15.7 (15.8)	7.9 (8.1)	–	3380	–	1570 / 1620ᶜ	1370ᵉ / 1300ᵈ	670–540 / 460–440
$[Fe^{III}LCl_2]\cdot H_2O$	Light green	240	14.5 (14.6)	7.0 (7.3)	3200–3100	–	1660	1550	1390ᵉ	670–240
$[Co^{III}L(NH_3)Cl_2]$	Brown red	235	15.3 (15.3)	11.0 (10.9)	3240–3120	–	1660	1520	1360ᵉ	820, 560–240
$[Ni^{II}L']$	Orange	230	19.6 (19.8)	9.2 (9.4)	–	3300	–	1570 / 1620ᶜ	1360ᵉ / 1330ᵈ	670–600 / 550–460
$[Cu^{II}L']$	Olive green	245	20.5 (21.1)	9.1 (9.3)	–	3310	–	1570 / 1620ᶜ	1360ᵉ / 1330ᵈ	660–500 / 480–450

ᵃAll i.r. bands in cm⁻¹; ᵇabbreviations—H_2SAA = N-salicylidene anthranilamide ($C_{14}H_{12}N_2O_2$), L = $C_{14}H_{11}N_2O_2$, L' = $C_{14}H_{10}N_2O_2$; ᶜ,ᵈenolic; ᵉphenolic.

under reflux for 12 h. The complex which precipitated was removed by filtration, washed with MeOH and dried *in vacuo* at 25° C. The purities of H_2SAA and metal complexes were checked by t.l.c. The analytical data and proposed formulae for the complexes are given in Table 1.

Results and discussion

The H_2SAA complexes are coloured and stable in the atmosphere. They are insoluble in common organic solvents but soluble in dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF). These solutions are stable for ca. 2 h. The complexes do not melt but decompose above 230° C. Analytical data indicate that the metal-to-ligand stoichiometry is 1:1 in all the complexes. They have low molar conductance values ($\Omega_M = 1.0$–7.5 ohm⁻¹ mol⁻¹ cm²) in 1×10^{-3} mol dm⁻³ DMSO solutions at room temperature, indicating nonelectrolyte nature and the chlorides present in chromium(III), iron(III) and cobalt(III) (oxidation of cobalt(II) to cobalt(III), supported by magnetic data) complexes are present within the coordination sphere.

T.g.a. shows the presence of water in chromium(III), manganese(II) and iron(III) complexes as indicated by endotherms in the 220–300° C range. The weight-loss measurements suggest three molecules of water in manganese(II) and one molecule in chromium(III) and iron(III) complexes per metal ion.

¹H n.m.r. studies

¹H n.m.r. data (δ) of the complexes provide evidence for two modes of binding to metal ions. In the trivalent metal ion complexes, the absence of a phenolic proton[7] (suggesting deprotonation and subsequent coordination), the downfield shift of amide protons (7.53–7.6) and small upfield change of azomethine proton (10.5) are indicative of a monobasic ONN donor sequence in the nonenolized form.

The divalent metal ion complexes also exhibit no signal due to (phenolic) —$OH^{[7]}$. Other significant features are the absence of a multiplet due to amide protons (7.46 in free ligand) and the appearance of a signal at higher field (6.48–6.5) which is consistent with =NH proton of

enolized form. Furthermore, the absence of signal due to —OH (enolic) suggests deprotonation and subsequent coordination[8] The appearance of an azomethine proton at slightly higher field (10.34–10.5) in comparision with that in free ligand may be attributed to chelation and consequent changes in conjugation. ¹H n.m.r. data also provides evidence for water molecules in manganese(II) [6H], chromium(III) and iron(III) [2H] and ammonia molecules in cobalt(III) [3H] complexes.

I.r. studies

Free H_2SAA exhibits i.r. bands (cm⁻¹) at 3400–3100br, 1650s, 1610s and 1350s due to $\nu(NH_2) + \nu(OH)$, $\nu(C=O)$, $\nu(C=N)$ and $\nu(C—O)$(phenolic), respectively. The spectra of metal complexes elucidate two modes of bonding, differentiating trivalent and divalent metal complexes.

The spectra of chromium(III), iron(III) and cobalt(III) complexes show the absence of $\nu(OH)$(phenolic)[9], a positive shift of $\nu(C—O)$(phenolic) and a negative $\nu(C=N)$ shift[10], and a negative $\nu(NH_2)$ shift with upward shift in $\nu(C=O)(+20 cm^{-1})^{[11]}$. These changes suggest an ONN donor sequence and coordination through deprotonated phenolic oxygen, amide nitrogen and azomethine nitrogen. In the chromium(III) and iron(III) complexes the high positive shift of $\nu(C—O)$(phenolic) by 40–50 cm⁻¹ unambiguously establishes phenoxide bridging[12].

In manganese(II), nickel(II) and copper(II) complexes the disappearance of $\nu(OH)^{[9]}$, the upward shift in $\nu(C—O)$-(phenolic) and the downward shift in $\nu(C=N)^{[10]}$ suggest coordination similar to that of trivalent metal ions. However, the shift in $\nu(C—O)$(phenolic) is not as high as in trivalent metal complexes, thus ruling out the possibility of phenoxide bridging. Notable features in the complexes are the disappearence of $\nu(C=O)^{[13]}$ and the appearence of a new sharp band in the 3380–3310 cm⁻¹ region assignable to $\nu(NH)$(imide), a strong band at 1330(C—O)-(enolic) and another characteristic band at 1620 cm⁻¹ due to new $\nu(C=N)^{[14]}$, suggesting enolization of the ligand during complex formation. The absence of $\nu(OH)$(enolic) suggests deprotonation and coordination through enolic oxygen[15]. In the absence of phenolic oxygen bridging, the position of $\nu(C—O)$(enolic) at relatively high frequency

(free v(C—O)(enolic) is expected at 1300–1280 cm^{-1}) is taken as evidence for enolic oxygen bridging[16].

The presence of a broad nonligand band at 3300 cm^{-1} in the spectra of the chromium(III), iron(III) and manganese(II) complexes is assigned to water molecules. In the manganese(II) complex, the medium-intensity band observed at 970 cm^{-1} is assignable to the rocking mode of coordinated water molecules[17]. However, this is absent in the iron(III) and chromium(III) complexes. In the cobalt(III) complex the bands observed at 3240–3120 and 820 cm^{-1} are due to stretching and rocking modes of coordinated ammonia molecule[18]. The new bands observed in the far-i.r. region are presented in Table 1 and are attributed to v(M—O), v(M—N) and v(M—Cl)[18].

Magnetic moments and electronic spectra

Magnetic moment and electronic spectral data, together with tentative assignments, are presented in Table 2. These data suggest square planar geometry for nickel(II) and copper(II) complexes and octahedral geometry for the remainder.

Iron(III)(d^5), cobalt(III)(d^6) and nickel(II)(d^8) complexes are diamagnetic. The nickel(II) complex in square planar stereochemistry and cobalt(III) in low-spin octahedral geometry are expected to be diamagnetic. Iron(III) in low-spin octahedral configuration $(t_{2g})^5$ is likely to have a magnetic moment equivalent to one unpaired electron, but owing to the dinuclear structure the unpaired electron on each iron(III) ion can undergo pairing and thus the complex becomes diamagnetic. Chromium(III)(d^3), manganese(II)(d^5) and copper(II)(d^9) complexes are paramagnetic. In the manganese(II) complex, which is not dimeric, the magnetic moment is indicative of low-spin configuration in octahedral geometry. The copper(II) complex in spite of dinuclear structure, exhibits no spin–spin interactions at room temperature, while the chromium(III) complex, which is also dinuclear, exhibits a subnormal magnetic moment. In the light of the magnetic data in paramagnetic dinuclear complexes, metal–metal interactions are manifested only in the iron(III) and
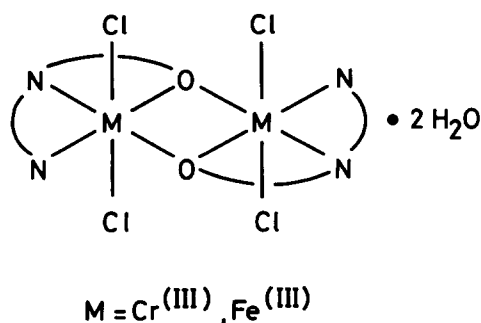

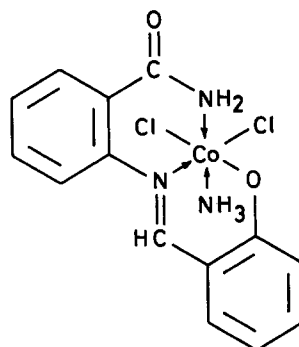Figure 2. H$_2$SAA complexes of chromium(III) and iron(III).

M = Cr$^{(III)}$, Fe$^{(III)}$

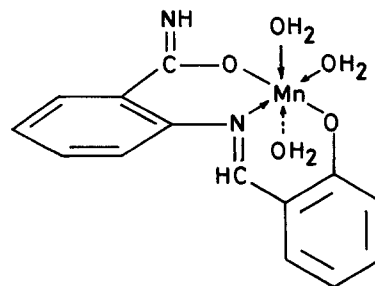Figure 3. Cobalt(III) complex.

Figure 4. Manganese(II) complex.

Table 2. Magnetic moment and electronic spectral data of metal–H$_2$SAA complexes[a].

Complex	μ_{eff} (BM) (temp. K)	v_{max} (cm^{-1})	Assignment
[Cr^{III}LCl$_2$]·H$_2$O	2.05 (298)	31 750	$^4A_{2g} \rightarrow {}^4T_{1g}$(P)
		24 290	$^4A_{2g} \rightarrow {}^4T_{1g}$(F)
		19 608[b]	$^4A_{2g} \rightarrow {}^4T_{2g}$
[Mn^{II}L'(H$_2$O)$_3$]	2.30 (298)	32 500–15 000	$^2T_{2g} \rightarrow {}^4T_{1g}$(P), $^4T_{1g}$(F)
			$^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$, ^2E_g
[Fe^{III}LCl$_2$]·H$_2$O	Dia.	32 500–15 000	$^2T_{2g} \rightarrow {}^4T_{1g}$(P), $^4T_{1g}$(F)
			$^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$, ^2E_g
[Co^{III}L(NH$_3$)Cl$_2$]	Dia.	33 330	$^1A_{1g} \rightarrow {}^1T_{2g}$
		25 640	$^1A_{1g} \rightarrow {}^1T_{1g}$
		20 000	$^1A_{1g} \rightarrow {}^3T_{2g}$
		17 000	$^1A_{1g} \rightarrow {}^3T_{1g}$
[Ni^{II}L']	Dia.	25 974	$^1A_{1g} \rightarrow {}^1B_{1g}$
		18 182	$^1A_{1g} \rightarrow {}^1A_{2g}$
[Cu^{II}L']	1.85 (298)	25 000–16 673	$^2B_{1g} \rightarrow {}^2B_{2g}$, $^2A_{1g}$, ^2E_g

[a]Abbreviations: H$_2$SAA = N-salicylidene anthranilamide (C$_{14}$H$_{12}$N$_2$O$_2$), L = C$_{14}$H$_{11}$N$_2$O$_2$, L' = C$_{14}$H$_{10}$N$_2$O$_2$; [b]10D_q = 19 608, B = 433.45, β = 0.4208.
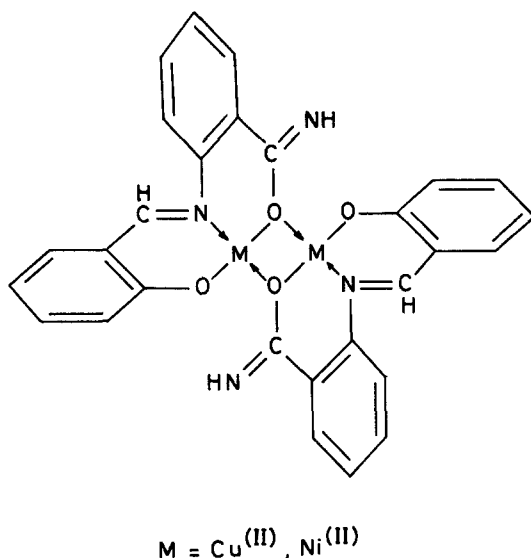
M = Cu$^{(II)}$, Ni$^{(II)}$

Figure 5. Nickel(II) and copper(II) complexes.

chromium(III) species but not in the copper(II) complex. Iron(III) and chromium(III) complexes have $(t_{2g})^5$ and $(t_{2g})^3$ configurations, respectively, while copper(II) has an $(e_g)^4(a_{1g})^2(b_{2g})^2(b_{1g})^1$ configuration. The typical difference in the magnetic behaviour can be rationalized by assuming that the metal–metal interaction is operating only through t_{2g} orbitals, preferably through the d_{xz}, d_{yz} orbitals, which are in the vertical plane, and not through the $b_{1g}(d_{x^2-y^2})$ orbital in the horizontal (xy) plane. Electronic spectral data are consistent with the proposed geometries[19]. The suggested structures for the complexes are shown in Figures 2–5.

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