On the Formation of Mn(II) Anthranilic Acid Anilide Complexes. Structural Elucidation by TGA, IR, Electronic, EPR Spectra and Potentiometric Studies

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Summary: A new series of Mn(II)-anilide complexes have been prepared and characterized by elemental analysis, TGA and IR spectra. Electronic and EPR spectra indicate octahedral geometry around the MN(II) ion, where the solvent molecules (H_2O or EtOH) occupy axial positions leading to the trans structure. The stability constants of the complexes in 50% dioxane are determined by potentionetric techniques. The values of the conditional stability constants depend on molecular structure. Deviation of the σ^*-log K plots slopes from unity is attributed mainly to steric effect, π-electron back donation from the metal on or structural changes in the ligand.

Introduction

It is generally accepted that the specific and selective reaction of organic reagents towards metal ions depends upon the presence and position of certain functional groups [1-3]. These groups should be capable of forming coordination bonds. In view of this fact it seemed of interest to test the behaviour of anthranilic acid anilides towards Mn(II) ion, where each anilide ligand contains different characteristic functional groups liable to form coordination bonds with transition metal ions [4,5].

As a matter of fact, the transition metal complexes of anilide ligands has applications as catalysts in various chemical and photo-chemical reactions [6-8] as well as in biological systems [9]. The applications of such metal chelates to any one system depends to a large extent on its molecular structure [10].

The aim of the present work is to prepare Mn(II) complexes with some anthanilic acid anilides. The prepared complexes are subjected to elemental analysis, TGA and some spectroscopic techniques Viz IR, electronic and EPR spectra. The composition, nature and stability of the complexes formed in 50% aqueous dioxane are also investigated.

Experimental

ii Preparation of Complexes

The complexes were prepared by dissolving (0.025 M) KOH in 10 ml of distilled water and mixing with (0.03 mole) of the ligand in 100 ml ethanol. The mixture was stirred causing the ligand to dissolve then (0.015 mole) of Mn(II) chloride (dissolved in the least amount of distilled water) was added dropwise and the reaction mix-

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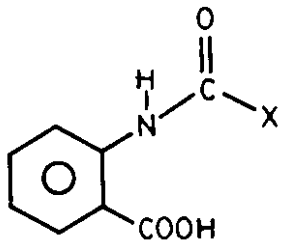
ture was stirred for about two hours. The yellow solid precipitate was filtered off, washed several times with bidistilled water to remove any traces of metal ions, finally washed by ether and then dried in vacuo.

All the prepared complexes were then subjected to elemental microanalysis, the results are listed in Table-1. The ligands used in the present investigation gave the following formula:



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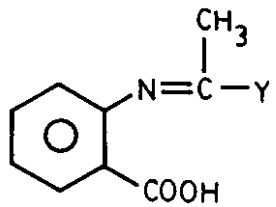


II

in which X and Y are as follows:

Series I	X	Series II	Y
anben	$-C_6H_5$		CH_3
annit	$-CH_2CN$	anox	$-C=N-OH$
anacet	CH_2CONH_2	anbis	H
aneth	$-CH=CH_2$		N
anacac	$-CH_2COCH_3$		HOOC
anbenac	$-CH_2COC_6H_5$		
anethacet	$-CH_2COOEt$		
anethprop	$-CH_2CH_2COOEt$		

ii) Physical Measurements

The apparatus and working procedures are the same as described previously [11-13].

Results and Discussion

A) Complexes in the solid state

The results of elemental analysis (Table 1) show that all the prepared complexes have one or more H_2O or EtOH molecules coordinated to the central Mn(II) ion which are not removed by static vacuum for three hours at room temperature. This conclusion is also supported by the results of the thermogravimetric analysis (TGA) of Mn(II) complexes which show the removal of the lattice and coordinated solvent molecules (H_2O or EtOH) from the complexes under investigation at 65-90°C and 120-130°C respectively.

On examining the ir spectra of the complexes, Table (II), in comparison to those of the free ligands the following can be pointed out:

The bands located at 3380-3250, 1680-1665 and 1625-1590 cm^{-1} due to ν_{NH} and ν_{CC} respectively in the spectra of the free ligands, display obvious shifts to lower frequency on complex formation by 85-100 and 30-65 cm^{-1} respectively. Thus, the bonding between the metal ion and ligands under investigation would take place through the interaction of the carboxy and NH groups with the MN(II) ion. The disapperance of the bands at 1390-1370 cm^{-1} and 1140-1120 cm^{-1} due to the ν_{OH} and ν_{C-OH} of the COOH groups in the spectra of the chelates is an indication for the displacement of a proton from the COOH group through the Mn(II) ions on chelation.

The existence of lattice or coordinated water or ethanol molecules in all complexes renders it difficult to investigate the behaviour of the ν_{OH} band of the carboxy group which is covered by those of H_2O or EtOH molecules. Actually, the spectra of most complexes exhibit a broad band around 3600-3340 cm^{-1}. This band is assigned to ν_{OH} of H_2O or EtOH molecules associated with complex formation, the existence of which is

Table-1: Analytical and Conditional Stability Constants Data for Mn(II)-Anthranilic Acid Anilides Complexes

Complex	% C	% H	% N	% Mn	2:1	1:1	1:2
$[Mn(annit)_2(EtOH)_2]$	51.80 (52.08)	5.05 (4.70)	10.40 (10.12)	10.56 (9.92)	9.75	9.40	9.10
$[Mn(anacet)_2(EtOH)_2]EtOH$	49.50 (49.14)	5.30 (5.67)	10.37 (10.08)	8.80 (8.64)	10.15	9.60	9.20
$[Mn(aneth)_2(H_2O)_2].2H_2O$	47.65 (47.34)	3.55 (3.15)	5.24 (5.52)	11.00 (10.83)	9.70	9.35	9.10
$[Mn(anacac)_2EtOH]_2$	53.26 (53.24)	5.12 (4.80)	5.00 (5.17)	10.08 (10.14)	9.85	9.35	9.10
$[Mn(anbenac)_2(EtOH)_2].H_2O$	59.15 (59.26)	5.44 (5.21)	3.58 (3.84)	7.70 (7.53)	9.05	8.85	8.70
$[Mn(anethacet)_2EtOH]_2$	51.81 (51.90)	5.00 (4.32)	4.60 (5.04)	9.90 (9.89)	10.00	9.88	9.70
$[Mn(anethprop)_2(H_2O)_2]$	50.96 (50.41)	4.88 (5.17)	4.68 (4.52)	8.80 (8.87)	10.14	9.70	9.32
$[Mn(anben)_2(H_2O)_2].7H_2O$	48.70 (48.21)	4.67 (5.16)	3.41 (4.01)	8.25 (7.87)	3.05	3.09	3.11
$[Mn(anox)_2(EtOH)]_2$	53.07 (53.56)	4.86 (4.46)	11.00 (11.36)	11.22 (11.14)	3.05	3.07	3.10
$[Mn(anbis)EtOH]_2$	54.20 (54.71)	3.48 (3.42)	8.00 (7.97)	16.06 (15.65)	9.08	9.06	9.07

* % Found (% Calculated).

supported from TGA measurements. The participation of carboxy OH in chelate formation through proton displacement findes support from potentiometric titration studies, discussed below.

The two new bands observed at 400-480 and 350-380 cm^{-1}, which do not exist in the spectra of the free ligands, can be assigned to ν_{M-O} and ν_{M-N} respectively [14].

The electronic reflectance spectra of the Mn(II) complexes under investigation exhibit four absorption bands with λ_{max} situated at 320-345, 359-375, 410-460 and 500-530 nm, Table (II). The first two bands can be assinged to π-π^* transitions within the aromatic ring and- CONH part respectively, whereas the last two bands can be assigned to $^6A_{1g} - {}^4T_{2g}$ (G) and $^6T_{1g} - {}^4T_{1g}$ (G) Mn(II) transitions respec-

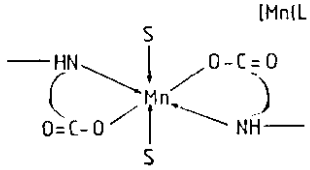
Table-II: Spectral Data Mn(II)-Anthranilic Acid Anilides Complexes

Complexes	ν_{NH}	$^{d}_{free}$	ν_{N-H}	ν_{COOH}	$^{d}_{free}$	ν_{COO}	ν_{M-O}	ν_{M-N}	Reflectance λ(nm)	EPR g_{eff}
$[Mn(annit)_2(EtOH)_2]$	3290		(3190)	1665		(1605)	440	360	350-375,420-460,500-530	1.9846
$[Mn(anacet)_2(EtOH)_2]EtOH$[a]	3385		(3110)	1665		(1600)	470	350	350-370,420-455,500-530	1.9846
$[Mn(aneth)_2(H_2O)_2.2H_2O$	3300		(3200)	1665		(1600)	480	380	310-330,320-375,420-455, 510-530.	1.9817
$[Mn(anacac)_2EtOH]_2$[a]	3285		(3200)	1675		(1610)	450	360	350-375,420-455,500-530	1.9787
$[Mn(anabenac)_2(EtOH)_2].2H_2O$	3380		(3310)	1665		(1600)	470	360	310-330,350-375,400, 500-530.	1.9758
$[Mn(anethacet)_2EtOH]_2$[a,b]	3380		(3110)	1665		(1600)	480	350	355-375,420-455,510-530	1.9846
$[Mn(anethprop)_2(H_2O)_2]$[a,b]	3380		(3110)	1680		(1630)	475	350	350-524,425-455,510-530	1.9846
$[Mn(anben)_2(H_2O)_2].7H_2O$	3285		(3200)	1665		(1600)	470	380	350-375,400-455,500-530	1.9787
$[Mn(anox)_2EtOH]_2$[a,c]	-		-	1665		(1635)	440	360	310-345,350-375,420-460 510-530	1.9846
$[Mn(anbis)EtOH]_2$[a,c]	3375		3290	1680		(1635)	480	360	350-370,420-455,510-530	1.9551

a] OH bending at 965-996 cm^{-1} b] ν_{COO} free ester at 1700-1720 cm^{-1} c] $\nu_{C=N}$ at 1600 cm^{-1}, d_{free} ligand, (corrdinated).

tively. The spectral patterns are relevant to an octahedral arrangement of the ligands around the central Mn(II) ion. The data of elemental analysis for all complexes, except those of ligands anacac, anethacet, anox and anbis, are in accordance with six coordinated ligand groups.

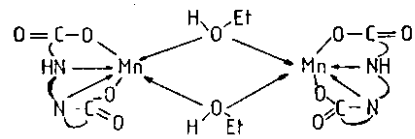
$[Mn(L)_2S_2]$



S=H_2O or EtOH , L=annit, anacet, aneth, anbenac, anethprop or anben

For the latter four ligands, only five ligated groups are present. The fulfillment of the sixth coordination site can only take place if the solvent molecules can interact in bridging manner. The bridging of the solvent molecules is further supported from the appearance of the OH bending mode at 965-955 cm^{-1} in the spectra of anacac, anethacet, anox or anibis-Mn (II) complexes which is not present in the spectra of other Mn(II) anilides complexes under investigation [14].

$[Mn(anbis)EtOH]_2$



X-band EPR spectra of the Mn(II) complexes under investigation at room temperature (Fig. 1) exhibit anisotropic signal consisting of a pattern of six doublets. The amplification and expansion show that the hyperfine splitting is probably due to dissimilar bonds coordinated to the Mn(II) ion. It is possible that the solvent molecules (H_2O or EtOH) occupy axial positions leading to the trans structure. Molecular models indicate that the trans

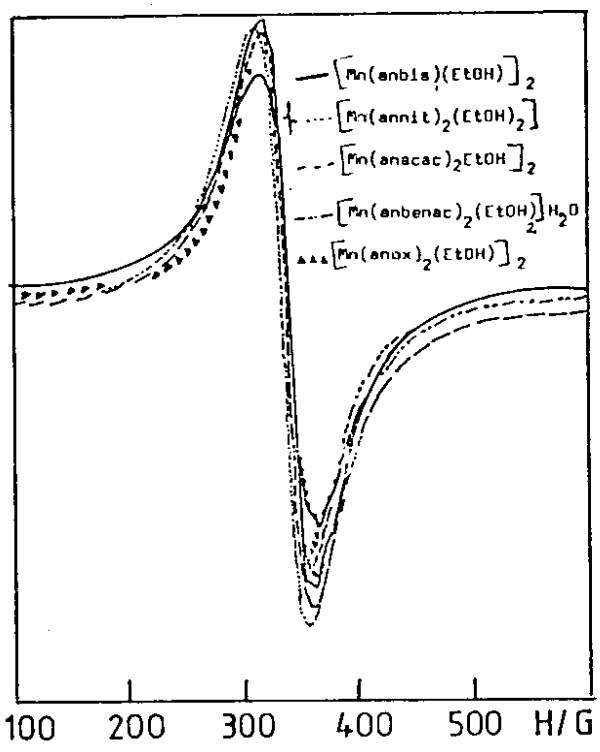


Fig.1: X-band EPR spectra of Mn(II) complexes at room temperature.

structure is more favourable. The g_{eff} values have a negative contribution from the value of the free electron (g = 2.0023) which may be due to a decrease in covalent bonding between ligand and Mn(II) ion [15].

B) Complexes in solution

The formation of the Mn(II) complexes with the anilides is associated with the liberation of H^+ ions from the ligands, hence it is possible to apply the pH- metric method for the determination of the composition and conditional stability constants of the chelates formed in solution [16].

The pH titration curves of the Mn(II) chelates under investigation are S-shaped, the volume of alkali consumed in the titration corresponds to the liberation of one or two H^+ ions per metal ion on complex formation. The titration curves exhibit one inflection within the pH range 8.0-9.0, which can be ascribed to the formation of some different types of complexes, probably of the hydroxo type [17]. The formation curves obtained, for the different complexes investigation indicated the formation of three types of chelates having the stiochiometric ratios 2:1,1:1,1:2 (Mn^{+2} :L).

The conditional stability constants of the three types of chelates log K_1, log K_2 and log K_3 were determined by the method of Bjerrum [18] and Albert [19] applying the least square method and the graphical representation method (n. vs. pL).

The data obtained, table (I) indicate that the values of the conditional stability constants depend on the nature of the ligand where a linear relation is obtained for the σ^* vs log K_1 or log K_2 plots, Fig. (2). The negative

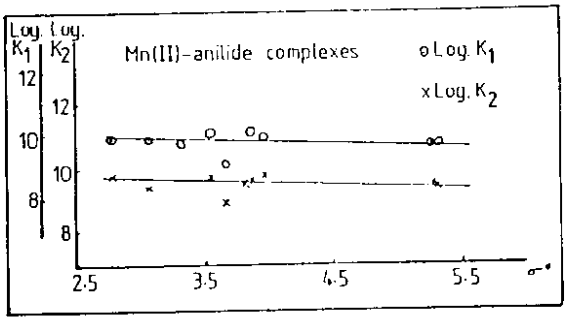


Fig.2: Effect of Stability Constants of Mn(II) Anilide Complexes on Molecular Structure.

slopes indicate that complex formation is favoured by increased electron densities at the coordination sites, a factor which favours increased covalent character of the metal-ligand bond. Deviation from a slope of unity is attributed mainly to steric effect, πelectron back donation from the metal

ion, or structural changes in the ligand which alter the strength of the donor atom within the ligand [20].

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