Research Journal of Applied Sciences 2 (5): 587-589, 2007

Syntheses and Physicochemical Studies of Manganese (II) Aminobenzoates and Their Adducts

I.O. Adeoye
Department of Pure and Applied Chemistry, Ladoke Akintola,
University of Technology, Ogbomoso, Nigeria

Abstract: The complexes of Mn (II) aminobenzoates of the form $[Mn(ABzt)_2X_2]$, {Abzt = o-$NH_2C_6H_4COO^-$ X = $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5N(CH_3)_2$ C_6H_5N and p-$NH_2C_5H_4N$} have been synthesized and characterized by microanalysis room temperature magnetic susceptibility measurements infrared and electronic reflectance spectral studies. In the complexes studied, some weak bands were observed in the region 26,000-29,000 and 18,000-19,000 cm^{-1}. These have been assigned to the $^6A_{1g}(G) \rightarrow {}^4T_{2g}(G)$ and $^6A_{1g}(G) \rightarrow {}^4T_{1g}(G)$ transitions, respectively. This pair is highly indicative of an octahedral geometry.

Key words: Manganese (II), aminobenzoates, adducts, syntheses, physicochemical

INTRODUCTION

There has been a spate of renewed interest in transition metal carboxylates (Eugenio *et al*., 2004; Odunola *et al*., 1992; Patel and Odunola, 1990a, b; Sorensen, 1988; Arindam *et al*., 2004) because of their application in pharmaceuticals (Bojan *et al*., 2000) catalysts (Pennigton, 1974), oxidation systems water repellents polymer dispersants (Patel *et al*., 1980) fertilizer pigments (Sunderberg *et al*., 1996) packing materials (Mehrotra and Bohra, 1983) in wood protection by retarding fungal growth (Richardson, 1993; Kozlevcar and Petric, 1993) Metal carboxylates are among the classes of compounds being explored for their capability to form multidimensional frameworks through the metal ion centerd via organic carboxylate bridges to create a hybrid inorganic compound with interesting chemical properties.

Apart from these, Mn (II) carboxylates have been proposed as veritable models for the little understood catalytic function of polynuclear manganese complexes in mechanistically challenging oxidation of water to dioxygen O_2 In earlier studies we have employed the use of benzoates and hydroxybenzoates as types of these models (Adeoye *et al*., 2004a, b).

In this study, we report the synthesis, magnetic, infrared and diffuse electronic reflectance spectra of manganese (II) aminobenzoate and their adducts using substituted amines like Aniline (An), N-Methylaniline (NMA), N,N-Dimethylaniline (DMA), p-Aminopyridine (Apy) and Pyridine (Py) and deduce structures on the basis of spectroscopic and magnetic properties.

MATERIALS AND METHODS

Reagents and solvents: Aminobenzoic acid, manganese acetate, aniline, N-methylaniline, N,N-dimethylaniline, p-aminopyridine and pyridine were purchased from Aldrich Chemical Company. All the chemicals and solvents were of reagent grade or purer and were used without further purification. The sodium salts were prepared by reacting stoichiometric amounts of the aminobenzoic acid with sodium hydroxide in aqueous medium.

Syntheses of the complexes

Preparation of [Mn (Abzt)$_2$]: 2-Amino benzoic acid (2.76 g, 20 mL) was dissolved in 10 mL of 1 M NaOH and stirred at room temperature. 2.45 g (10 mL) of Mn (CH_3COO). $4H_2O$ dissolved in 10 mL of water was added dropwise to the solution while stirring. The filtrate produced was filtered and dried over silica gel. (Yield 1.44 g, 44%).

Preparation of [Mn (Abzt)$_2$(An)$_2$]: Aniline (0.91 mL, 10 mmol) in 25 mL of mixed ethanol and water (3:1) was added to a ethanolic solution of [Mn (Abzt)$_2$] (1.65 g, 5 mmol) while stirring at 60°C followed by refluxing for 20 min. A light pink precipitate was observed, the reaction mixture was cooled to room temperature and the precipitates filtered and dried over anhydrous calcium chloride (Yield 1.39 g, 62%).

The other adducts of manganese (II) complexes of 2-aminobenzoates were similarly prepared.

Physical measurements: The elemental analyses for carbon, hydrogen and nitrogen were determined using

Perkin-Elmer series II 2400 CHNS/O analyzer while Mn was estimated by complexometric method (Vogel 1969). The infrared spectra were recorded on a Perkin-Elmer Spectrum 1000 spectrometer between 350-4000 cm^{-1} using KBr discs. Electronic reflectance spectra of the complexes were recorded on a Varian Cary 1E spectrometer between 190-900 nm. Melting points of the compounds were determined using a Buchi (B-540) melting point apparatus. The room temperature magnetic susceptibility measurements were carried out by the Gouy method using $HgCo(CNS)_4$ as a calibrant and diamagnetic corrections were calculated using Pascal constants (Mabbs and Machin, 1971).

RESULTS AND DISCUSSION

The colour, analytical data, melting point, percentage yield and room temperature effective magnetic moments (μ_{eff}) are presented in Table 1. The manganese (II) aminobenzoate was obtained in reasonable yield from aminobenzoic acid and manganese acetates according to the following equation:

$$Mn(CH_3COO)_2.\ 4H_2O + 2\ (o\text{-}NH_2C_6H_4COOH) \rightarrow [Mn\ (o\text{-}NH_2C_6H_4COO)_2] + 2CH_3COOH + 4H_2O \quad (1)$$

The equation of the reaction for the formation of the adduct is given below:

$$Mn\ (o\text{-}NH_2C_6H_4COO)_2] + 2Y \rightarrow [Mn\ (o\text{-}NH_2C_6H_4COO)_2\ (Y)_2] \quad (2)$$

$$Y = C_6H_5NH_2,\ C_6H_5NHCH_3,\ C_6H_5N\ (CH_3)_2,\ p\text{-}NH_2C_5H_4N \text{ and } C_5H_5N$$

The manganese (II) aminobenzoate and the adducts formed exhibited different shades of brown to pink. They decompose at temperatures above 250°C. They show poor solubility in polar and non polar solvents.

Infrared spectra: The relevant infrared spectra data of the complexes are presented in Table 2. The N-H stretching frequency of the amines in the complexes were observed as broad and weak bands in the region between 3354-3400 cm^{-1}. The direction of the shifts relative to the free carboxylate ion value of the asymmetric stretching frequency $v_a(COO^-)$ and symmetric stretching frequency $v_s(COO^-)$ and frequency difference between them Δv have been used in predicting the mode of bonding of the carboxylate to the metal. The bands in the region 1588-1591 and 1452-1455 cm^{-1} have been assigned to the asymmetric stretching frequency $v_a(COO^-)$ and symmetric stretching frequency $v_s(COO^-)$ of the carboxylate group. In each of the complexes, the frequencies indicate a reduction in the $v_a(COO^-)$ and either a slight increase or decrease in the $v_s(COO^-)$ leading to a consequent reduction in Δv ($\Delta_v = v_a\ COO^- - v_sCOO^-$). This clearly suggests bidentate attachment of the benzoate ion to manganese (Nakamoto, 1969). Other metal ligand vibrations were observed below 500 cm^{-1}.

Electronic spectra: The electronic spectra of the complexes are presented in Table 2. The configuration d^5 is so exceptional in that no spin-allowed transitions are to be expected since the ^6S ground state is not split significantly by the field and all excited states are of lower multiplicity (Lever, 1986). It follows that only weak absorption corresponding to sextet-quartet transitions is to be expected. The sextet-doublet transitions are almost

Table 1: Analytical data of the complexes

					Observed (calculated)				
Compound	F.W	Colour	Yield	M.pt	C	H	N	Mn	μ_{eff}(BM)
Mn $(ABzt)_2$ $(C_{14}H_{14}O_2N_2Mn)$	327.19	Reddish brown	49	260[d]	51.42 (51.39)	4.40 (4.31)	8.46 8.56	11.45 (11.32)	
Mn $(Abzt)_2$ An $(C_{26}H_{28}O_4N_4Mn)$	516.44	Reddish brown	62	252[d]	61.00 (60.82)	5.44 (5.50)	10.65 (10.91)	16.61 (16.69)	
Mn $(ABzt)_2$ $(DMA)_2$ $(C_{30}H_{32}O_4N_4Mn)$	569.55	Pink brown	77	360[d]	63.22 (63.26)	5.56 (5.66)	9.77 (9.83)	10.87 (10.66)	
Mn $(ABzt)_2$ $(NMA)_2$ $(C_{28}H_{32}O_4N_4Mn)$	541.51	Brown	54	320[d]	62.15 (62.11)	5.88 (5.96)	10.33 (10.34)	10.07 (10.11)	
Mn $(ABzt)_2$ $(APy)_2$ $(C_{24}H_{22}O_6N_4Mn)$	515.42	Brown	73	280[d]	55.88 (55.93)	5.30 (5.08)	16.22 (16.30)	10.23 (10.62)	
Mn $(ABzt)_2$ $(Py)_2$ $(C_{24}H_{18}O_6N_2Mn)$	483.37	Brown	27	276[d]	59.77 (59.63)	4.63 (4.59)	11.44 (11.59)	11.45 (11.32)	

Lt = Light, d = decomposition

Table 2:Relevant infrared bands positions and electronic transitions for the complexes

Compounds	Infrared Bands (cm^{-1})			Electronic uv	Bands visible	($\times 10^3$cm)
	$V_a(COO^-)$	$v_s(COO^-)$	Δv			
[Mn $(Abzt)_2$]	1591	1455	136	20.40	18	14
Mn $(Abzt)_2$ $(An)_2$]	1588	1456	132	48.54	39.39	14
Mn $(Abzt)_2$ $(DMA)_2$]	1589	1454	135	41	40	26..31
Mn $(Abzt)_2$ $(NMA)_2$]	1590	1452	138	45	40	26
Mn $(Abzt)_2$ $(Apy)_2$]	1588	1453	135	26.11	18.76	13.96
Mn $(Abzt)_2$ $(Py)_2$]	1589	1452	136	26		

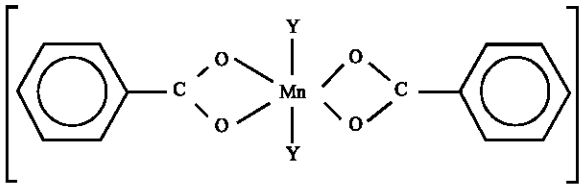

Fig. 1: Suggested structure for the complexes

too weak to be observed. Normally, high spin d^5 Mn (II) complexes are weakly coloured, the intense colour associated with some of the complexes could be due to charge transfer from the ligand orbitals to the metal orbitals. The electronic spectra display three electronic transition except Mn (Abzt) $_2$(py) where a single band was observed. The other bands may have been obscured by charge transfer to higher energy. In the complexes studied, some weak bands were observed in the region 21,000-28,000 and 17,000-19,000 cm^{-1}. These have been assigned to the $^6A_{1g}(G) \rightarrow {}^4T_{2g}(G)$ and $^6A_{1g}(G) \rightarrow {}^4T_{1g}(G)$ transitions, respectively. This pair is highly indicative of an octahedral geometry.

Magnetic moment:

Y = $C_6H_5NH_2$; $C_6H_5NHCH_3$; $C_6H_5N(CH_3)_2$; $NH_2C_5H_4N$ and C_5H_5N

CONCLUSION

The infrared spectra of the compounds show that the carboxylates are coordinated to the central metal ion in a bridging bidentate fashion. The electronic spectra and magnetic susceptibility measurement suggests some measure of metal-metal interactions. In the absence of X-ray crystallographic studies, the proposed structure in Fig. 1 is only tentative.

REFERENCES

A.B.P. Lever 1986 . Inorganic Electronic Spectroscopy, (4th Edn.), Elsevier, London, F.A. Cotton (Ed). Prog. Inorg. Chem., pp: 481-579.

Adeoye, I.O., J.A.O. Woods, O.O.P. Faboya and O.A. Odunola, 2004a. Symthesis and Physicochemical studies of manganese (II) hydroxybenzoates and their adducts. Sci. Focus, 6: 104-106.

Adeoye, I.O., O.O.P. Faboya, O.A. Odunola and J.A.O. Woods, 2004b. Symthesis and Physicochemical studies of manganese (II) benzoates and their adducts with nitrogenous bases. Int. J. Chem., 14: 53-58.

Arindam Mukherjee Manas, K., Saha Munirathinam Nethaji, R. Akhil Chakravarty, 2004. Dicopper (II) Sciff base aminobenzoates with discrete molecular ID-chain polymeric structures Polyhedron, 23: 2177-2182.

Bojan Kozlevcar, Nina Lah, Simon Makuc and Primoz Segedin, 2000. Acta. Chim. Slov., 47: 421-434.

Garriba, E., G. Micera and M. Zana, 2004. Monomeric versus dimeric structures in ternary complexes of manganese (II) with derivatives of benzoic acid and nitrogenous bases: Structural details and spectra properties Inorgnica. Chemca. Acta, 357: 2038-2048.

Kozlevcar, B. and M. Petric, 1993. Internat. Res. Group Wood Preser. Document No. IRG/WP., pp: 96-3010.

Mabbs, E. and D.J. Machin, 1971. Magnetism and Transition Metal Complexes. Chapman Hall London, pp: 85.

Mehrotra, R.C. and R. Bohra, 1983. Metal Carboxylates Academic Press, London.

Nakamoto, K., 1969. Infrared Spectra of Inorganic and Coordination Compounds. John Wiley and Sons, New York.

Odunola, O.A., J.A.O. Woods and K.S. Patel, 1992. Synthesis and Physicochemical studies of some Mn, Co and Ni (II) substituted benzoates Synth. React. Inorg. Met-Org. Chem., 22: 941-953.

Patel, K.S. and O.A. Odunola, 1990a. Synthesis and Physicochemical studies of some Oxovanadium (IV) Complexes of hydroxy and aminobenzoates Synth. React. Inorg. Met-Org. Chem., 20: 773-781.

Patel, K.S., R.S. Kharsan and R.K. Mishra, 1980. Proc Indian Acad. Sci. 88A, 297 Chem. Abstr., 92: 51338y.

Pennigton, B.T., 1974. Univ South Missipipi Avail Xerox Univ Microfilms. Ann. Arbor. Mich Order No 75-9600 from Diss Abstr. Int. B 1975, 35: 4825-6 Abs 83, 66042, 19.

Richardson, B.A., 1993. Wood Preservation (2nd Edn.), E and FN Spon, an Imprint of Chapman and Hall, London.

Sorensen, J.R.J., 1988. In Metal Ions in Biological Systems (Eds. H. Sigel) Marcel Dekker New York, 14: 77-124.

Sunderberg, M.R., R. Uggla and M. Melnik, 1996. Polyhedron, 15: 1157-1163.