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Short Communication

SYNTHESIS AND CHARACTERIZATION OF MONO AND BIS HEXAMETHYLENETETRAMINE IRON(III) CHLORIDE IN NONAQUEOUS SOLVENT ($CHCl_3$)

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Abstract

Mono and bis hexamethylenetetramine iron(III) chloride, $Fe(N_4C_6H_{12})\ Cl_3$ (I) and $Fe(N_4C_6H_{12})_2Cl_3$(II) were synthesized by the reaction of iron(III) chloride and hexamethylenetetramine (HMTA) in chloroform. Chemical analysis and spectral results show the coordination of HMTA to the iron(III). Electronic transition spectra of compound I and II were also studied in coordinating and noncoordinating solvents.

Introduction

Considerable work has been done to investigate the complex compounds which are formed by the reaction of $CoCl_2$, $ZnCl_2$, $AgNO_3$ and HMTA [1-3], but there is no report about iron(III) salts and other ions with this ligand. The majority of iron complexes are octahedral, but tetrahedral and square pyramidal ones are also important [4].

In this paper, we report the synthesis and characterization of complex compound I and II with formula $Fe(N_4C_6H_{12})Cl_3$ and $Fe(N_4C_6H_{12})_2Cl_3$, respectively in nonaqueous solvents.

Results and Discussion

A solution of 0.67 mmol HMTA in 12 ml chloroform was added dropwise to 20 ml chloroform containing 1.73 g (10.67 mmol) of anhydrous ferric chloride. The resulting reddish-brown solution was stirred at room temperature for one hour. The solution was then cooled in an ice bath for 30 minutes. The precipitate was collected by filtration, washed with chloroform and air-dried. 0.2025 g of compound I was obtained (yield, 99.5%). Anal. Calcd. for $Fe(HMTA)Cl_3$: C; 23.8; N, 18.5; H, 3.9; Fe 18.48; Cl, 35.32, Found C, 23.58; N, 17.6; H, 4.03; Fe, 18.46; Cl, 35.5. Decomp P. was 128°C.

The procedure was repeated, but this time 1.8 m mole of anhydrous ferric chloride in 40 ml chloroform and 17 m mole HMTA in 20 ml chloroform were used, by similar workup, compound II with 100% yield was obtained. Decomp. P. was 160°C. Anal. Calcd. for $Fe(HMTA)_2Cl_3$, C, 32.52; N, 25.30; H, 5.46; Fe, 12.66; Cl, 24.06, Found; C, 32.2; N, 25.35; H, 5.9; Fe, 12.65; Cl, 24.0. On the basis of chemical analysis, the formula of I and II should be $Fe(N_4C_6H_{12})Cl_3$ and $Fe(N_4C_6H_{12})_2Cl_3$, respectively.

Studies on complexes which are formed with HMTA and different salts such as $CoCl_2$, $ZnCl_2$ and so on, reveal that they are formed as $MX_2(HMTA)_2$ and $MX_2(HMTA)$ (3) but octachedral-complexes such as $MX_2(HMTA)_4$ are not obtained because of steric hinderance. Therefore, in the reaction of HMTA with iron(III) chloride only two HMTA can coordinate to the central ion even though the ratio of L/M increased to 10 and a complex with C.N equal to 5 is formed. But in aqueous solutions, these two com-

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pounds are not formed because of the precipitation of iron(III) ions as $Fe_2O_3 . XH_2O$. As mentioned before, the affinity of iron(III) for amine ligands is very low and no simple amine complex exists in solution (4). The observed frequencies of the infrared spectra of HMTA, Fe (HMTA) Cl_3 and Fe(HMTA)$_2$Cl$_3$ are listed in Table I. The vibration in the region 2900 cm^{-1} as multiplet is due to C-H stretching. C-H bending vibration appears in the region 1480 to 1300 cm^{-1}, CN vibration comes at 1230 to ~ 1000 cm^{-1} and the region ~900 to 500 cm^{-1} is due to rocking vibration of C-N and C-H [5,6]. The appearance of CN vibration as multiplets instead of a broad singlet reveals that the HMTA is coordinated to the iron(III). This situation might have arisen because one nitrogen atom in HMTA is coordinated and the other three are free, and this leads to two different C-N vibrations.

Table I. Vibrational spectra of HMTA, Fe(HMTA)Cl_3 and Fe(HMTA)$_2$$Cl_3$

obsd freq, Cm^{-1} and rel intense

	HMTA Cm^{-1}	Fe(HMTA)Cl_3 Cm^{-1}	Fe(HMTA)$_2$$Cl_3$ Cm^{-1}
V_1	2952 (b.m)	2952 (b.m)	2526 (b.m)
V_2	1458 (s)	1462 (s)	1466 (s)
V_3	1372	1397-1356 (m)	1413-1380 (m)
V_4	1237	1258	1312-1207 (m)
V_5	1049-965	1070-965 (m)	1055-965 (m)
V_6	808(s)	876-655 (m)	876-796 (m)
V_7	~ 669 (s)	742-655	691-662
V_8	508	497 (s)	498 (s)
V_9	—	374 (m)	365 (m)

Electronic absorption results suggest that the compound I dissociates in CH_2Cl_2 as indicated in equation(1), since the position and type of two absorptions is exactly similar to the absorption of $FeCl_3$ solution (λ_{max1} = 360.7 nm, λ_{max2} = 312.4nm, ε_1 and ε_2, are 6 x 10^3 and 8x10^3 lit mol^{-1} cm^{-1}, respectively). Our calculation shows 25% of complex I dissociates in this solution, but the addition of HMTA forces the equilibrium to the left and therefore forms complex I.

$$Fe(N_4C_6H_{12})Cl_3\,(soln) \Leftrightarrow FeCl_3\,(soln) + N_4C_6H_{12}\,(soln) \quad (eq.1)$$

This complex does not show special electronic transition in the region 250-800 nm because of laporte and spin forbidden transitions from the sixtet ground state of spin free d^5 configuration to the excited states. * [7].

When the solvent is DMF (Table II), around 60% of complex I and 18.5% of complex II are dissociated in solution. The UV spectra of solution b also shows two absorptions which represent the dissociation of complex II as equations 2 and 3, but the addition of HMTA forces the reaction to the left and forms complex compound species (in this case no free Fe^{3+} was detected).

Table II. UV results of a) $FeCl_3$, b) Fe(HMTA)Cl_3, and c) Fe(HMTA)$_2$$Cl_3$ in DMF, the concentration of these three compounds are the same (2x10^{-4} M).

Type of solution	λ_{max1} (nm)	λ_{max1} (nm)	% of dissociation
Solution a	360.7	312.4	100
Solution b	360.7	312.4	60
Solution c	360.7	312.4	18.5

* Molar absorptivity coefficient ε_1 and ε_2 are 6x10^3 and 8x10^3 lit Mol^{-1} cm^{-1}, respectively.

$$Fe(N_4C_6H_{12})_2Cl_3\,(soln) \Leftrightarrow Fe(N_4C_6H_{12})Cl_3 + N_4C_6H_{12} \quad (eq.2)$$
$$Fe(N_4C_6H_{12})_2Cl_3\,(soln) \Leftrightarrow FeCl_3\,(soln) + N_4C_6H_{12} \quad (eq.3)$$

In summary, the complex compounds of Fe(HMTA)Cl_3 and Fe(HMTA)$_2$$Cl_3$ are formed in nonaqueous solution. The chemical analysis supports the suggested formulas. The IR data shows the coordination of HMTA to the metal ions. UV spectra also indicate the dissociation of these two in solution, and by increasing the ligand to metal ions ratio, complexes are formed.

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* For example, for high spin complexes with d^5 configuration and good solubility like Mn^{2+} nonaqueous solution, six forbidden transitions with very low intensities are observed [8] but in this case, because of the very low solubility of this complex, when it is formed by addition of HMTA, no forbidden transition will be observed.

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