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Determination of the structural formula of sodium tris-carbonatocobaltate(III), $Na_3[Co(CO_3)_3]\cdot 3H_2O$ by thermogravimetry

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Abstract The existence of an inner sphere water in sodium tris-carbonatocobaltate(III) prepared by the Bauer and Drinkard method was confirmed by thermogravimetry, which led to its formulation as sodium aquo-tris-carbonatocobaltate(III) dihydrate, $Na_3[Co(H_2O)(CO_3)_3]\cdot 2H_2O$. Hydrolytic study on 4-nitrophenylphosphate promoted by $[Co(tn)_3]^{3+}$ afforded corborating evidence for the existence of inner sphere water in the complex leading to its formulation as $[Co(tn)_3(H_2O)]^{3+}$. Another variety of the tris-carbonato anion, $[Co(NH_3)_6][Co(CO_3)_3]$, was prepared and subjected to thermogravimetric analysis, and the absence of inner sphere water in the compound was confirmed. The plausible existence of inner sphere water for the compounds that emanate from the synthetic routes utilizing the Bauer and Drinkard method in the crystalline phase is proposed.

Keywords Structural formula · Sodium tris-carbonatocobaltate(III) · Elemental analysis · Thermogravimetric analysis · Hydrolysis of 4-nitrophenylphosphate · Microemulsions

Introduction

In aqueous solutions containing no complexing agents, the oxidation of Co(II) to Co(III) is very unfavorable. Water rapidly reduces Co^{3+} at room temperature. Co^{3+} has an affinity for N donors and forms well-known Co(III) compounds.

Sodium tris-carbonatocobaltate(III) is a stable compound which provides a reactive source of Co(III) in the presence of a proton donor. Hence, it is an important intermediate in the synthesis of several cobalt(III) compounds [1]. Prior to the introduction of this procedure, symmetrical cobalt(III) complexes generally have been prepared by the oxidation of cobalt(II) ions in the presence of the desired ligand. Direct coordination of the ligand with freshly prepared hydrous cobalt(III) oxide or displacement of ammonia from hexamminecobalt(III) ion was used as alternative synthetic routes. Unfortunately, the latter methods suffer several drawbacks, such as competitive interaction of the solvent molecules for the metal center resulting in poor yield and low purity. The synthetic route using sodium tris-carbonatocobaltate(III) affords several advantages that circumvent the above drawbacks and hence makes it the preferred method of choice for the synthesis of several cobalt(III) complexes. The simplest formula was determined as $Na_3Co(CO_3)_3\cdot 3H_2O$, but the structural formula has not been verified to date. There has been some controversy as to whether all of the three carbonate species exist as four-membered bidentate rings or whether some of the water molecules occupy the inner coordination sphere of the cobalt thereby giving rise to aquocarbonato species in the crystalline state. Though the existence of stable four member carbonato species was reported in the literature for related compounds [2], the structure of sodium tris-carbonatocobaltate(III) remains unclear. In this study, we set out to investigate the structural formula of the compounds using a combination of thermogravimetry and hydrolysis data from cobalt(III) promoted hydrolysis reactions of 4-nitrophenylphosphate in aqueous and microemulsion media.

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Experimental

Materials and instruments

All reagents used were either analytical reagent grade or the purest available commercially and were used without further purification. Measurement of pH was made with Metrohm 632-pH meter with a combination electrode. A Thermo Spectronic Genesys 2 UV/Vis spectrometer was used to obtain spectra and a Genesys 10 UV/Vis spectrometer was used to collect rate data. The pH of the reaction mixture was maintained by adding drops of NaOH or $HClO_4$ from a glass rod. Thermal analysis was performed using a Varian TGA Q500 V6.2 thermogravimetric analyzer under nitrogen atmosphere.

Preparation of microemulsions

Microemulsions were prepared by mixing hexane, sodium dodecylsulfate (SDS), and butan-1-ol, titrating the slurry with water, and agitating mildly to give a clear solution [3]. The following compositions by mass were used for the cationic and anionic O/W microemulsions, respectively. Cetyltrimethylammoniumchloride (CTAC) 5%/hexane 3%/butan-1-ol 10%/water 82% and sodium dodecylsulfate (SDS)5%/hexane 3%/butan-1-ol 10%/water 82%.

Synthesis of the complexes

Sodium tris-carbonatocobaltate(III) trihydrate, $Na_3[Co(CO_3)_3]\cdot 3H_2O$, was synthesized using the method of Bauer and Drinkard [1]. Tris-trimethylene diaminecobalt(III) Perchlorate, $[Co(tn)_3](ClO_4)_3$, and carbonato-bis-trimethylenediaminecobalt(III) perchlorate, $[Co(tn)_2CO_3]ClO_4$, were then synthesized using $Na_3[Co(CO_3)_3]\cdot 3H_2O$ as the intermediate, by utilizing earlier methods [4]. The purity of the complexes was checked by comparing their electronic spectra with those reported in the literature [5]. Conversion of the carbonato to the diaquo species, $[Co(tn)_2(OH_2)_2]^{3+}$, was achieved by adding 2.5 mmol of $HClO_4$ to 1.0 mmol of the carbonato species and stirring in the dark under an aspirator vacuum.

Thermogravimetric (TG) analyses

The TG measurements of the compounds were carried out using a thermogravimetric analyzer (TA Instruments, TGA Q500) on samples of about 20–30 mg over the temperature range from 25 to 1000 °C at a heating rate of 10 °C per min. The percentage mass loss was obtained from the curves of mass loss (%) and derivative mass (% $°C^{-1}$) versus temperature (°C).

Monitoring the hydrolysis reaction

The protocol for the study consists of mixing 2 mL of an aqueous solution of 5×10^{-3} M 4-nitrophenyl phosphate (NPP) in a thermostated reaction vessel with 6 mL of solvent. The solvent was either water or one of the microemulsions. The pH of the solution was adjusted to 6.5. A 2-mL volume of temperature equilibrated working solution of the cobalt complex; pH 6.5, in which the hydroxoaqua form was predominant was then added, bringing the total volume to 10 mL. Aliquots (1 mL) were withdrawn from the reaction vessel at 1, 3, 5, 10, 15, 20, and 30 min, and mixed with 1 mL of phosphate buffer (pH 7.4) and 3 mL of water bringing the total volume to 5 mL. The buffer system was prepared by mixing 8.62 g sodium phosphate dibasic and 5.42 g of sodium phosphate monobasic salts and making up to 1000 mL with carbon dioxide-free distilled water. The absorbance of the reaction solution was then measured at 400 nm. The amount of 4-nitrophenolate produced was determined from the calibration curve and the percentage hydrolysis calculated, assuming 100% 4-nitrophenolate production for complete hydrolysis. The standard deviation for the triplicate analysis ranged from 0.1 to 0.2 in each case. The average value was used for analysis of the data. Calibration curve studies was done by preparing a series of 4-nitrophenol solutions ranging from a concentration of 10^{-3} to 10^{-6} M and the pH adjusted to 6.5. One milliliter of this solution was mixed with 1 mL of phosphate buffer and 3 mL of water, and its absorbance was measured at 400 nm. The absorbance values were plotted against concentration and the molar absorptivity determined as 4.925×10^3 L Mol^{-1} cm^{-1} at 400 nm with the protocol of the study. In unbuffered solution, the acid–base reaction of 4-nitrophenol changes in concentration resulting in a shift in the equilibrium position and a consequent deviation from Beer's law. In buffer solution, the pH would be fixed and the ratio of the concentration of 4-nitrophenolate to the 4-nitrophenol would be constant thereby obeying Beer's law. All absorbances were taken against water blank. Interference from other compounds in the analyte was not detected. Under slightly basic condition, the 4-nitrophenol is deprotonated to form the 4-nitrophenolate ion which is bright yellow and has an absorbance maximum at 400 nm, quite distinct from 4-nitrophenyl phosphate which has an absorbance maximum at 310 nm. The system conformed to Beer's law over the concentration range 0–20 mg L^{-1} of 4-nitrophenol when measured at 400 nm in a 1-cm cell. The UV/Vis profile is depicted in Fig. 1.

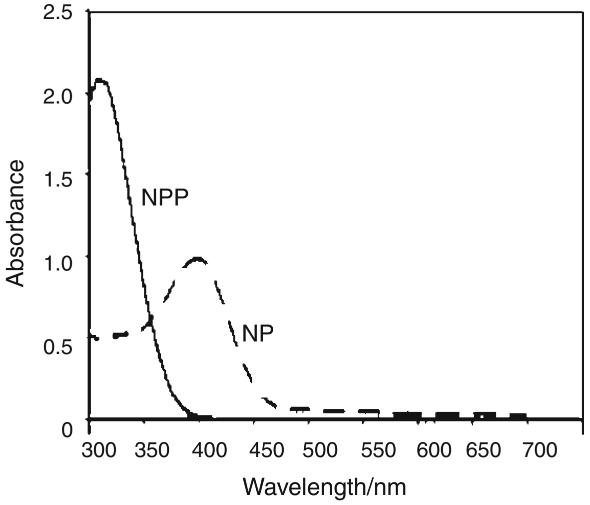


Fig. 1 Absorption spectra of NPP and NP at pH 6.5

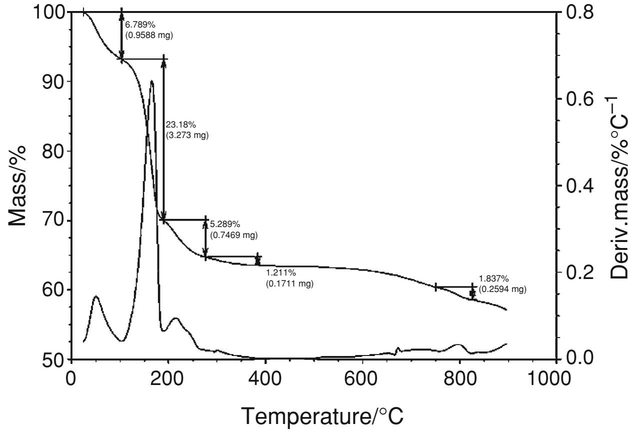


Fig. 3 Thermogravimetric curve of $Na_3[Co(CO_3)_3]\cdot 3H_2O$ after air drying for 1 day (sample size 14.1220 mg, ramp method)

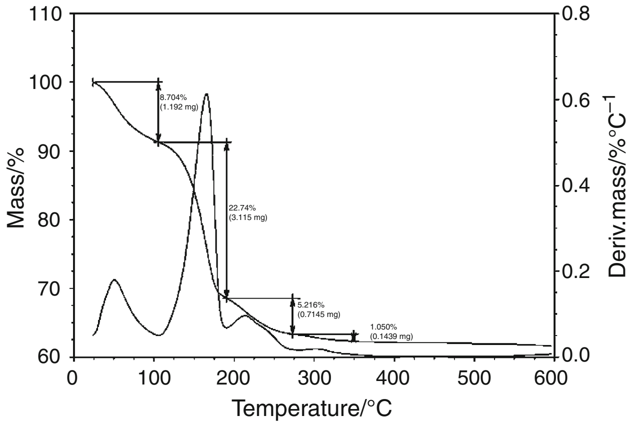


Fig. 2 Thermogravimetric curve of freshly prepared $Na_3[Co(CO_3)_3]\cdot 3H_2O$ after 4 h of air drying (sample size 13.6970 mg, ramp method)

Results and discussion

Typical thermogravimetric curves of $Na_3Co(CO_3)_3\cdot 3H_2O$ are depicted in Figs. 2 and 3. As is evident from the curves, the first peak showed maximum value for freshly prepared samples and the peak size decreased for samples that were exposed to ambient laboratory conditions in successive experiments. Further drying of the complex at 60 °C in a vacuum for about 4 h resulted in curves that showed the total disappearance of this peak. However, the features of the other peaks in the curves did not change much for all of the samples analysed. The first peak at 50 °C is attributed to surface water in the outer coordination sphere. The second peak that appears around 150 °C is due to the loss of CO_2 from decomposition of the carbonates. The third peak around 220 °C depicts the loss of coordinated H_2O from the compound. For a freshly prepared sample subjected to thermogravimetric analysis, the ensuing mass loss for the different peaks is summarized in Table 1. Analysis of Table 1 depicts that two moles of water are removed per mole of the compound as the temperature approaches 100 °C. The 2 mol of water is presumed to be outer sphere coordinated.

$$Na_3\left[Co(CO_3)_3\right]\cdot 3H_2O - 2H_2O \\ \rightarrow Na_3\left[Co(CO_3)_3\right]\cdot H_2O.$$

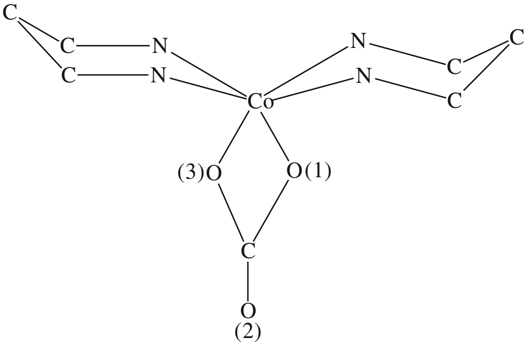
The mass loss around 150 °C is attributed to 2 mol of carbon dioxide. The mass loss at 220 °C is due to the removal of 1 mol of water which is presumed to be inner sphere coordinated. One molar ratio of carbonate ligand remains unaccounted for in the above analysis. Closer examination of the spectra reveals mass losses at temperatures of 300 and 800 °C. The conditions that prevail in the sample tube (i.e., high temperature coupled with the presence of cobalt, carbonate, and an atmosphere of carbon dioxide) presumably lead to the production of cobalt carbonate which is stable at high temperature. Literature evidences show that cobalt carbonate starts to decompose above 330 °C producing Co_3O_4 which remains stable up to 850 °C and then decomposes to give CoO above this temperature [6]. Since cobalt carbonate remains stable at high temperatures, the decomposition noted at 300 °C is presumed to be not 100% complete. We were not able to calculate exactly the mass loss from the curves at this temperature since the identity of the product that is lost is not ascertained and total decomposition was presumed not to be achieved. The possibilities of release of CO in addition to the anticipated CO_2 and other possible products did not allow us to calculate the actual mass loss to account for a total of 1 M ratio of carbonate. It is thus presumed that the unaccounted one molar ratio carbonate remains in the sample tube as some form of thermally stable cobalt–carbonate species.

Table 1 Mass loss analysis for the thermogravimetric curves of freshly prepared $Na_3[Co(CO_3)_3]\cdot 3H_2O$ (average results for triplicate analysis)

Peak number	Percentage mass loss				Calculated molar mass and molar ratio*
	Run 1	Run 2	Run 3	Average	
1	9.81	10.14	9.93	9.96	36 ($2H_2O$)
2	24.86	25.45	25.12	25.14	82 ($\sim 2CO_2$)
3	7.28	7.42	7.31	7.34	$\sim$18 ($1H_2O$)

* The molar mass loss was calculated from the percentage mass loss by using the formula weight of $Na_3[Co(CO_3)_3]\cdot 3H_2O$ as 362 g/mol. For peak 1, $(9.96/100) \times 362 = 36$. Similarly, for peak 2, $(25.14/100) \times (362 - 36) = 82$ and for peak 3, $(7.34/100) \times 238 = 17.5$ ($\sim$18)

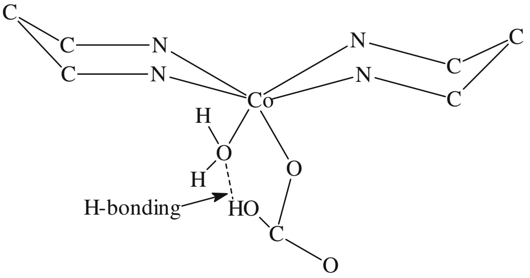
From elemental analysis conducted in previous work [1], it has been established that the empirical formula of the compound is $Na_3Co(CO_3)_3\cdot 3H_2O$. Our experiments clearly demonstrate that two of the water molecules are bound to the outer coordination sphere of cobalt as surface water and one of the water molecules is coordinated directly to the cobalt center. This points to the direction that the structural formula is $Na_3[Co(H_2O)(CO_3)_3]\cdot 2H_2O$, sodium aquo-tris-carbonatocobaltate(III) dihydrate, which has been incorrectly named as sodium tris-carbonatocobaltate(III) trihydrate. Further corborative support for our formulation is evident in the literature where the X-ray crystal structure of *cis*-[carbonatobis-(trimethylenediamine) cobalt(III)] was reported [7]. With the assumption that the starting material for the synthesis, sodium tris-carbonatocobaltate(III), has three bidentate carbonato ligands, it is logical to expect the product $Co(tn)_2(CO_3)(ClO_4)\cdot H_2O$ to have two bidentate (1,3-diaminopropane) ligands. The unsubstituted carbonato ligand should remain coordinated to the cobalt center in a bidentate fashion as depicted in the diagram below.



It was reported in the literature [7] that in the cobalt–carbonate ring, the Co–O(1) and Co–O(3) bond lengths were found to differ significantly. The authors were unable to provide a plausible explanation for this discrepancy. We now afford a plausible explanation for the above observation as resulting from a hydrogen bonding system between a coordinated inner sphere water molecule and a carbonato species coordinated to the cobalt center in a monodentate fashion. This explanation bodes well with our observation that the starting material is, $Na_3[Co(H_2O)(CO_3)_3]\cdot 2H_2O$, and hence its subsequent reaction with 2 mol of tn produces the desired product, $Co[(tn)_2(H_2O)(CO_3)](ClO_4)$, as depicted by the following equation.

$$Na_3\left[Co(H_2O)(CO_3)_3\right]\cdot 2H_2O + 2H_2N(CH_2)_3NH_2 + 2HClO_4 \rightarrow Co\left[(tn)_2(H_2O)(CO_3)\right](ClO_4).$$

It is to be noted that inner sphere coordinated water molecule is presumed to be preferred in the crystalline state in both of the above compounds. One of the driving forces for this thermodynamic stability might be favorable hydrogen bonding possibilities in the Co–water–carbonato six-membered ring as depicted below. The following structural geometry is proposed for $Co[(tn)_2(H_2O)(CO_3)](ClO_4)$. The proposed structure tries to address the discrepancy that was reported earlier regarding the different cobalt oxygen bond lengths.



Several experiments were conducted to test the effectiveness of $[Co(tn)_3]^{3+}$ in promoting hydrolysis of 4-nitrophenylphosphate. The result of the investigation is depicted in Table 2. Rates of the reaction of hydrolysis of 4-nitrophenyl phosphate in the pH range from about 4 to 9 are both essentially constant and very slow [8]. It has been observed in previous studies that the hydrolysis rate of phosphate esters mediated by divalent metal ions are higher in oil in water (O/W) microemulsion media compared to those in water in oil (O/W) systems [9, 10]. In microemulsion media, chemical reactions are considered to occur at the phase structure interface of the microemulsions [11]. Enhanced reactivity for hydroxoaqua ions in comparison to the dihydroxo or diaqua species is noted for all of the systems studied in line with literature reports [12]. The reactivity can be rationalized by assuming that the electron freed from the diaqua complex by the loss of a proton to form a hydroxoaqua moiety will labilize the

Table 2 Hydrolysis of 4-nitrophenylphosphate by $Co(tn)_2$ and $Co(tn)_3$ complexes for different metal to NPP ratio in aqueous and microemulsion media

System	% Hydrolysis							
	Media	1 min	3 min	5 min	10 min	15 min	20 min	30 min
NPP + $Co(tn)_2$	Water	10.85	10.81	10.77	10.75	10.73	10.72	10.70
	AME2	10.90	10.83	10.79	10.79	10.75	10.74	10.72
	CME2	19.46	19.38	19.37	19.37	19.34	19.32	19.30
NPP + $Co(tn)_3$	Water	0.55	0.58	0.53	0.53	0.50	0.47	0.46
	AME2	0.59	0.58	0.57	0.57	0.54	0.52	0.52
	CME2	0.97	0.94	0.91	0.91	0.90	0.90	0.90
NPP + $2Co(tn)_2$	Water	16.85	16.78	16.76	16.73	16.74	16.70	16.67
	AME2	17.29	17.23	17.20	17.17	17.20	17.14	17.12
	CME2	30.46	30.42	30.39	30.36	30.39	30.36	30.35
NPP + $2Co(tn)_3$	Water	0.63	0.59	0.57	0.57	0.56	0.54	0.50
	AME2	0.80	0.76	0.72	0.72	0.70	0.70	0.68
	CME2	1.18	1.14	1.14	1.13	1.09	1.07	1.07
NPP + $3Co(tn)_2$	Water	19.89	19.84	19.82	19.80	19.78	19.77	19.76
	AME2	20.58	20.54	20.49	20.48	20.46	20.46	20.44
	CME2	50.23	50.18	50.16	50.15	50.13	50.11	50.09
NPP + $3Co(tn)_3$	Water	0.94	0.89	0.89	0.90	0.87	0.84	0.83
	AME2	0.96	0.91	0.90	0.90	0.89	0.86	0.86
	CME2	1.79	1.71	1.71	1.70	1.67	1.63	1.61

Triplicate analyses were done for each system. The values given in the table are average values of those analyses. The standard deviation for the triplicate analyses ranged from 0.1 to 0.2 in each case

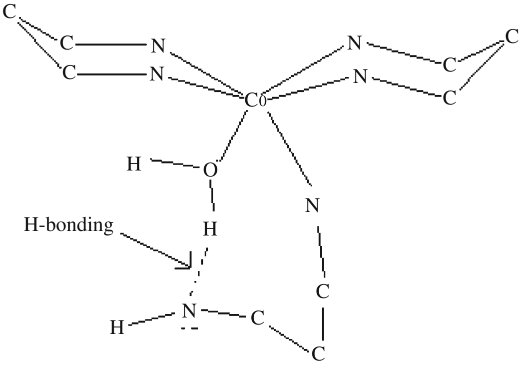
NPP, 4-nitrophenylphosphate; tn, trimethylenediamine; AME2, anionic microemulsion 2 (82% water, 3% hexane, 5% SDS, 10% butanol); CME2, cationic microemulsion 2 (82% water, 3% hexane, 5% cetyl-trimethyl ammonium chloride 10% butanol)

coordinated water molecule [13]. An enhancement of hydrolysis was noted in reaction solutions that contained 2:1 metal to NPP ratio. This can be explained by the fact that the second metal ion coordinates to one of the available oxygens on the NPP thereby creating a possibility of intramolecular attack on the phosphorous center by coordinated water or hydroxide of the metal ion. No significant additional hydrolysis was observed for reaction solutions that contained more than 3:1 metal to NPP ratio. Since the reaction is stoichiometric and not catalytic, it is anticipated that with an increase in the metal to phosphate ratio, the rate of hydrolysis should increase. However, above 3:1 metal to phosphate ratio, the concentration of the hydroxoaqua species in the system becomes large presumably triggering an olation reaction resulting in unreactive dimeric species in the solution as has been reported in similar studies [14–16]. The absence of reactive hydroxoaqua moieties explains the rate saturation in systems containing large metal to phosphate ratios.

An increase in hydrolysis was noted in microemulsion media compared to that in aqueous media. Microemulsions are thermodynamically stable transparent dispersions of two immiscible liquids, stabilized by an interfacial film of surfactants. They have the ability to solubilize and disperse the maximum amount of the substrate thereby enhancing the possibility of hydrolysis by the metal centers. The microemulsion droplets would act as molecular micro reactors. The cationic microemulsion systems consistently showed good rate accelerations in terms of their hydrolyzing abilities toward 4-nitrophenylphosphates. We presume that the cationic microemulsion system results in co-aggregates where the net cationic character is increased thereby increasing the positive character on the phosphate ester. The coordinated nucleophile (hydroxide or water) will then have better chance of attack on the phosphorous center compared to those in anionic microemulsion co aggregates.

Production of 4-nitrophenolate ion appears to be biphasic. There is an initial burst within 0.5 min which levels off dramatically after that. It is not possible to investigate the reaction profile between the time of addition (0 time) and 0.5 min under our experimental protocol. If one just looks at the 0.5 min data, it is clear that there is roughly a twofold increase in 4-nitrophenolate production with cationic micelle compared to what is seen in water. The anionic micelle data is more or less similar to that of water. Possible explanations to the above include enhanced substrate solubilization in the microemulsion systems thereby aiding hydrolysis by bringing the reacting species closer to each other. The rate differences between the cationic and anionic microemulsion systems may also be explained by the fact that negatively charged micelles/emulsions would repel negatively charged 4-nitrophenylphosphate but might attract the cations in the solutions. The net result is that in the anionic microemulsion systems, one might not expect much enhancement of hydrolysis. In contrast, the 4-nitrophenylphosphate might be associated with the surface of the cationic emulsions. This pre-organization might in turn attract the cations around the phosphate leading to an increase in hydrolysis.

Tris-trimethylenediaminecobalt(III) ion is envisioned to be fully chelated. Hence, no promotion of hydrolysis of 4-nitrophenylphosphate is anticipated. The observed low hydrolysis as shown in Table 2 for the various reactions of $[Co(tn)_3]^{3+}$ in the different media is presumably due to the existence of an inner sphere coordinated water as shown below. The possibility of weak hydrogen bonding between the coordinated water and the diamine ligand would seem to contribute to the stability of the proposed structure.



The reaction of 4-nitrophenylphosphate with $[Co(tn)_3]^{3+}$ will result in the loss of the coordinated water to form $Co(tn)_3$-NPP complex. An attack of the phosphorous center of this complex by solvent water or another coordinated H_2O/OH moiety accounts for the observed low hydrolysis. The effects of the microemulsion systems and the promotion of hydrolysis with high metal to NPP ratio are also evident for the system under study, even though the effects are not very much pronounced. An X-ray study on anhydrous $[Co(NH_3)_6][Co(CO_3)_3]$ revealed that the crystalline solid contains the $Co(CO_3)_3^{3-}$ ion, with three chelated carbonato ligands [17]. Thermogravimmetric study on the above compound showed the absence of coordinated water. It is impossible to get crystals of $Na_3Co(CO_3)_3{\cdot}3H_2O$ for X-ray study due to its insolubility and amorphous nature. The possibility of bridging carbonate or hydroxyl groups has been suspected by some investigators (Prof. R.B. Jordan, Personal Communication, University of Alberta). Hence, the evidence gathered from our thermochemical data, the kinetic results relating to hydrolysis reactions, and the corborating literature evidences make a case for the correct formulation of the anion having a coordinated water in synthetic procedures that utilize the Bauer and Drinkard protocol [1, 4].

Conclusions

The structural formula of tris-carbonatocobaltate(III) has been formulated based on the results from elemental analysis [1, 4] and thermogravimetry. It is formulated as $Na_3[Co(H_2O)(CO_3)_3]{\cdot}2H_2O$, sodium aquo-tris-carbonato-cobaltate(III) dihydrate. Similarly, the existence of inner sphere water in carbonatobis(trimethylenediamine) cobalt(III)] perchlorate was evident from the X-ray crystal structure studies that prevail in the literature [7]. The possible existence of inner sphere water in tris-trimethylenediaminecobalt(III) complex is also predicted from the hydrolytic studies of 4-nitrophenylphosphate with $[Co(tn)_3]^{3+}$. Plausible structures have been proposed for the compounds. The decomposition of the tris-carbonatocobaltate(III) at 93 °C [1] and the hazards associated with perchlorate compounds in the case of cis-[carbonatobis-(trimethylenediamine)cobalt(III)] perchlorate precluded further attempts to elucidate the structure by thermogravimetry. We have synthesized the nitrate analog of the above compounds and subjected them to thermogravimetric analysis. The results indicate the existence of inner sphere water in those compounds. Several compounds derived from the title compound have been utilized in model studies to elucidate the mechanisms of bioinorganic reactions. The positive features of Co(III) make it a very important reactant in model systems. Unfortunately, the detailed mechanistic studies of those reactions will be at jeopardy if the structural formula of the starting compound is unknown. This will lead to conclusions which do not reflect the real situation. Hence, our contribution should be viewed as important to the field that may overcome fundamental limitations associated with those types of studies utilizing cobalt(III) complexes derived from the tris-carbonatocobaltate(III) route. The implications of this studies are far reaching in mechanistic studies in bioinorganic chemistry where cobalt(III) compounds derived via the tris-carbonatocobaltate(III) synthetic route are widely used as model systems. The reason for the preference of inner sphere water in tris-carbonato species that emanate from the Bauer and Drinkard method and not from the other synthetic route remains to be unexplained. Thermogravimetry can provide sound data that may be utilized in the establishment of reaction mechanism [18]. In conjunction with thermogravimetry, other techniques such as spectroscopy, chromatography, and specific chemical reactions like hydrolysis may be utilized to fully characterize the structural and chemical changes which prevail in important model systems [19].

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