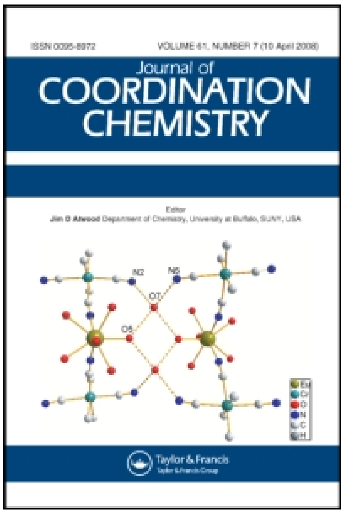

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SYNTHESES OF TWO NEW OXOMOLYBDENUM(IV) COMPOUNDS BY A NOVEL METHOD AND THEIR CHARACTERIZATION

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INTRODUCTION

Syntheses of stable oxomolybdenum(IV) species in aqueous solution have been rather recent,[1–4] excepting a long known compound[5,6] [$MoO(C_2O_4)\cdot 3H_2O$], which is stable in solid state and in aqueous solution as a trimeric species. Following the method of Ardon and Pernick,[3] Cotton *et al.*[7] isolated and determined the structure of the cesium salt of the oxobridged anion $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$, the isolation being done from aqueous solution. Ammonium and pyridinium salts of this type were reported by Wardlaw,[6] and a trimeric structure was proposed by him in aqueous solution on the basis of data available to him at that time.

The study of Mo(IV) compounds have been a subject of keen interest over the last few years because of the fact that it is supposed to be one of the species actively participating in enzymatic catalysis in several biological processes and otherwise.[8–12] We have synthesised the compounds following a completely different chemical method and not the electrolytic method usually followed for this purpose,[5] or the method of Ardon and Pernick[3] which uses Mo(III) and Mo(V) prepared by Wardlaw's method.[5] The compounds have been characterized by analytical and physico-chemical methods. They exhibit remarkable stability in solid state as well as in aqueous solutions.

EXPERIMENTAL SECTION

About 4 g of $(NH_4)_2MoOCl_5$ prepared by the method of Saha and Banerjee,[13] was taken in a round bottomed flask, treated slowly with hydrazine hydrate and was stirred continuously. First a vigorous reaction sets in and when it subsided, 15 ml of excess hydrazine was added and the mixture was refluxed for 10 hours. During refluxing, 3–4 ml of hydrazine hydrate was added four times at equal intervals. After the reflux, the resulting solid was filtered, washed 3–4 times with liquor ammonia and then twice with acetone and dried in a vacuum desiccator over solid KOH. By repeated evacuation, drying was completed in 2–3 hours and the brownish black solid (*) was used for preparation of the compounds by taking utmost care to give minimum exposure to air.

[$MoO(C_2H_3O_2)_2\cdot H_2O$] was prepared by quickly pouring 2 g of the reduced material (*) mentioned above (with least possible exposure to air) in a bottle (fitted with a standard joint inlet dipping into the liquid and containing an outlet for the gas to be passed) containing 40 ml of glacial acetic acid, CO_2 gas was passed for four hours and the bottle was kept heated at 80°C in a water bath throughout. Part of the solid dissolved giving a deep reddish solution which was filtered through a G-4 crucible and the solution was poured in excess ether (500 ml) when a pink solid separated out which was filtered through G-4 crucible, dried in vacuum. Yield 1 g., color, shining pinkish black.

[$MoO(C_3O_4H_2)\cdot 3H_2O$] was prepared as follows. About 4 g of malonic acid was dissolved in 30 ml of air free water, about 2 g of reduced brownish black solid (*) was quickly taken out from vacuum desiccator and added to the solution and CO_2 gas was passed for 5 hours, the container being kept at 75°C in a water bath. The resulting deep red solution was filtered out and was poured in 500 ml acetone with stirring when a dirty pink solid separated out, which was allowed to settle, filtered through G-4 crucible, dried in a vacuum desiccator, yield, 0.4 g; Color, dirty pink.

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Analysis

Molybdenum in these compounds was estimated by direct oxidation to MoO_3 at 510°C. C, H were estimated by microanalytical methods. Oxidation state determination by ceric sulphate was possible only in case of acetate and not in the case of malonate due to obvious oxidation of malonic acid. IR spectra were recorded in Perkin Elmer 621 spectrophotometer, conductance was measured in Leeds and Northrup (U.S.A.) Electrolytic Conductivity Bridge, pH was measured in Radiometer pH meter, Denmark and P.M.R. was recorded in Perkin Elmer R-32 NMR spectrometer using a frequency of 90 MHz. Magnetic measurement was carried out in a Gouy balance.

RESULTS

Compound
1. $[MoO(C_2H_3O_2)_2(H_2O)]$

% Mo		% C		% H	
Found	Calc.	Found	Calc.	Found	Calc.
39.24	38.69	19.10	19.36	3.60	3.25

Compound
2. $[MoO(C_3H_2O_4)(H_2O)_3]$

% Mo		% C		% H	
Found	Calc.	Found	Calc.	Found	Calc.
35.66	35.81	13.75	13.44	3.25	3.01

Oxidation state of acetato-complex found was 4.04. The major infrared bands obtained for $[MoO(C_2H_3O_2)_2(H_2O)]$ along with possible assignments[14] are (in cm^{-1}) 465 s (ν M–O for coordinated water), 730 vs ($\rho_r H_2O$), 950 vs (M=O stretch), 1400 vs (νCOO stretch), 1600 s (H—O—H bending and νCOO stretch), 3200–3500 vs, b (antisymmetric and symmetric —OH stretch of water). The corresponding major bands obtained for $[MoO(C_3H_2O_4)(H_2O)_3]$ are 475 m, 745 vs, 950 vs, 1400 vs, 1620 vs, b; 3200–3500 vs, b. Molar conductance of the acetato-complex in aqueous solution (M/50) at 32.5°C is 13.21 ohm^{-1} cm^2 and the solution has a pH of 4.24 (which remains constant for 24 hours). The p.m.r. of the acetato complex shows a peak at 1.64 ppm (δ-scale) in D_2O. Molar magnetic susceptibilities (after diamagnetic correction) of the acetato- and malonato-complexes are 32.85×10^{-6} and 53.5×10^{-6} respectively in cgs units.

DISCUSSIONS

The analytical data along with oxidation state and the infrared bands with their probable assignments clearly indicate the formulation given by us for the compounds. The molar conductance value of the aqueous solution is quite low indicating a non-electrolytic complex, but is slightly higher than a pure non-electrolyte which may have been caused due to hydrolysis and oxo-bridge formation, a species envisaged by Ardon and Pernick[3] and recently confirmed by Cramer and Gray.[15] The pH-value which is slightly lower than neutral is also indicative of hydrolysis in aqueous solution. Cotton *et al.*[7] who isolated a trinuclear species from aqueous solution also inferred that the dinuclear species of Ardon and Pernick[3] changes over to the trinuclear species. Even though, Sykes[4] *et al.* preferred a monomeric formulation for the aqueous species of Mo(IV), it appears from the work of Cramer and Gray[15] that Ardon and Pernick's[3] formulation of a dinuclear species is correct. It looks rational to think that the predominant species in aqueous solution is dimeric along with negligible percentages of mono and trimeric species in equilibrium. The equilibrium shifts to a preferred direction depending on circumstances as from aqueous solution, Cotton[7] could isolate the trinuclear species $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$. In less polar non-aqueous solvents, it is more probable that the monomeric variety will predominate.

In our case, the compounds have been isolated in ether and acetone and the most expected species to come out of solution is the monomeric non-ionic species which is also corroborated by chemical analysis, the I.R. data which show very strong characteristic M=O stretching[16,17] at 950 cm^{-1} in both the cases not expected from a dimeric or trimeric species which contains only bridged oxygens.

The p.m.r. peak at 1.64 ppm is due to methyl hydrogen as compared to 1.52 ppm observed in the same instrument for glacial acetic acid. The molar susceptibility values clearly indicate a ground state configuration of $(b_2)^2$ resulting in a $^1A_1$ ground state caused by tetragonal distortion due to the strong M=O bond[17] mentioned, which is confirmed by I.R. data.

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