

SHORT COMMUNICATIONS

INFRARED AND PLASMA EMISSION SPECTROSCOPIC METHOD OF ANALYSIS OF HUMAN URINARY BLADDER STONES

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THE precipitation of certain chemicals in the urinary bladder leads to the formation of insoluble solid deposits called urinary calculi or stones. The determination of the composition of the stones is important for the following reasons: (i) The composition will reveal the conditions existing at the time of precipitation. (ii) As the dietary habit is one of the predisposing factors for the formation of stones, a knowledge of the composition of the stones may help in preventing the recurrence of the stones by restricting or regulating the food rich in the components of the stones. Several methods are available for the analysis of the composition of stones¹⁻⁴. The infrared spectroscopic method may not reveal the full composition of the stones and it is also difficult to identify the trace elements in the samples. The metallic bonds will not occur in the usual range of measurement. The metals having relatively the same mass will vibrate at the same frequency. The chemical method is tedious to identify the trace elements. The plasma emission spectroscopic

method is fast, precise and highly sensitive when compared to other emission methods. Hence in the present investigation, plasma emission spectroscopic method of elemental analysis was undertaken.

Samples of urinary bladder stones were obtained from the Jawaharlal Institute Hospital. The stones were cleaned carefully and dried and finely powdered. The infrared spectra of the samples in the KBr pellet were recorded at 25°C in the wave number range 4000–650 cm⁻¹ using Perkin Elmer model 257 spectrophotometer. Comparing the recorded spectra with the spectra of pure compounds and identifying the characteristic frequencies, the chemical nature of the samples was determined^{5,6}. For the elemental analysis, 40 mg of the sample was taken and 2 ml of concentrated nitric acid was added and the mixture heated to boiling. After cooling, the solution was diluted. Standard solutions prepared by the dilution of the appropriate stock solutions had the same amount of nitric acid. The elemental analysis was carried out using Beckman Spectraspan V plasma emission spectrometer. Seven samples were analysed.

The results of the analysis are given in table 1. All the samples (A to G) contain P, Mg and Ca as the major components and Fe and Mn in trace quantities. Only the sample A was analysed for rare elements and found to contain Cr (0.01%), Sr (0.5%), Cu (0.01%), Na (1%), Al (0.1%), Ba (0.0005%). The samples (A & D) identified as magnesium ammonium phosphate by

Table 1 Infrared and Elemental analysis of the human bladder stone samples

Sample code	Identification by IR spectra	Elements present (% in original sample)				
		P	Mg	Ca	Mn	Fe
A	Magnesium ammonium phosphate	13.2 ± 0.20	4.15 ± 0.03	19.2 ± 0.20	≤ 0.002	0.013 ± 0.001
B	Calcium oxalate + calcium hydrogen phosphate	5.03 ± 0.06	4.20 ± 0.03	5.18 ± 0.06	≤ 0.002	0.038 ± 0.001
C	Calcium phosphate	12.4 ± 0.20	7.63 ± 0.06	8.25 ± 0.09	≤ 0.002	0.012 ± 0.001
D	Magnesium ammonium phosphate	15.0 ± 0.20	4.38 ± 0.03	22.1 ± 0.20	≤ 0.002	0.010 ± 0.001
E	Calcium dihydrogen phosphate	14.6 ± 0.20	7.00 ± 0.06	15.4 ± 0.20	≤ 0.002	0.015 ± 0.001
F	Calcium dihydrogen phosphate	9.65 ± 0.15	6.90 ± 0.06	9.18 ± 0.10	≤ 0.002	0.009 ± 0.001
G	Magnesium ammonium phosphate + some carapatite	12.5 ± 0.20	9.55 ± 0.08	2.73 ± 0.03	≤ 0.002	0.007 ± 0.001

infrared have calcium in large quantities. Similarly sample C identified as calcium phosphate by infrared contains significant amount of magnesium. The present investigation indicates that plasma emission spectroscopic method will completely identify all the elements present in the sample.

The difference in the contents of the various elements in the stones may be due to the defect in the mineral metabolism or due to difference in the dietary habits of the individual. The human body is known to contain several elements⁷. As the elements are extracted from the blood and precipitated in the urinary bladder, the comparison of the elemental analysis of the blood with that of stones will throw more light on the mechanism of formation of stones.

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PREPARATION AND CHARACTERIZATION OF SOME DIALKOXYTUNGSTEN(VI) OXYPSEUDOHALIDES

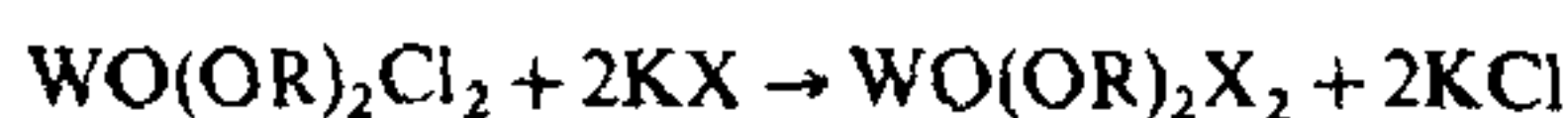
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PSEUDOHALIDE complexes of dicyclopentadienyltungsten(VI) oxydichloride and those of WOCl_4 and WO_2Cl_2 have been prepared¹⁻². Complexes of the type $(\pi\text{-C}_5\text{H}_5)\text{MX}_2$ and $(\pi\text{-C}_5\text{H}_5)\text{WXY}$ (where $\text{M} = \text{W}$ or Mo ; $\text{X} = \text{N}_3$, NCS ; $\text{XY} =$ mixed ligands Cl/NCS , NCS/SCN , MeO/CN , EtO/CN) have also been reported³. However, there is no mention in the literature about the pseudohalide derivatives of dialkoxytungsten(VI) oxydichlorides. We have already prepared and characterized the derivatives of dialkoxytungsten(VI) oxydichloride, $\text{WO}(\text{OR})_2\text{Cl}_2$ (I) by the interaction of WOCl_4 with corresponding alcohols in dry benzene in the absence of ammonia gas. Thus we thought it worthwhile to study the displacement reactions of (I) with pseudohalogens.

In the present communication, we report the pseudohalide derivatives of the general formula $\text{WO}(\text{OR})_2\text{X}_2$ (where $\text{R} = \text{CH}_3$, C_2H_5 , $\text{iso-C}_3\text{H}_7$, $n\text{-C}_4\text{H}_9$, $\text{tert-C}_4\text{H}_9$; $\text{X} = \text{SCN}$, NCO , N_3) prepared by the interaction of potassium (or sodium) pseudohalide with $\text{WO}(\text{OR})_2\text{Cl}_2$ in $\text{THF/C}_6\text{H}_6$.



The complexes are characterized by elemental analysis and infrared studies (tables 1, 2).

All operations were carried out under strictly anhydrous conditions using liquid nitrogen trap since the compounds involved are sensitive to moisture. The solvents were dried and purified before use. Tungsten was precipitated as oxinate and then ignited to WO_3 . The carbon and hydrogen were determined by semi-micro analytical methods. The presence of various pseudohalogen ligands and alkoxy groups was inferred from the IR spectra recorded on a Pye Unicam (SP 1200) spectrophotometer in KBr pellets.

Preparation of thiocyanato, cyanato and azido complexes of $\text{WO}(\text{OR})_2\text{Cl}_2$

Dimethoxytungsten(VI) oxydichloride (0.5 g, 0.0018 mole) was dissolved in 80 ml of dry $\text{THF/C}_6\text{H}_6$. Pseudohalide (KCNS , KCNO or NaN_3), in twice the