

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

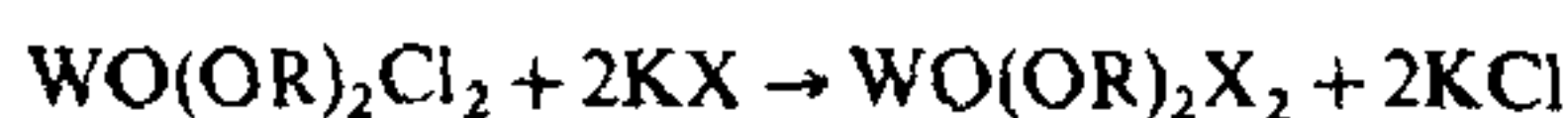
S. M. MUSLEH, P. DABAS, R. K. MULTANI and M. KATYAL*

Department of Chemistry, University of Delhi, Delhi 110007, India.

**St. Stephen's College, Delhi 110007, India.*

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

Table 1. Analytical data for dialkoxytungsten(VI) oxypseudohalides

Complex (solid)	% Analysis Found (Calcd.)		
	W	C	H
WO(OMe) ₂ (SCN) ₂	47.20 (48.65)	12.51 (12.70)	1.50 (1.59)
WO(OMe) ₂ (NCO) ₂	52.36 (53.16)	13.35 (13.88)	1.65 (1.73)
WO(OMe) ₂ (N ₃) ₂	52.50 (53.16)	6.88 (6.92)	1.70 (1.73)
WO(OEt) ₂ (SCN) ₂	44.30 (45.28)	17.60 (17.73)	2.10 (2.46)
WO(OEt) ₂ (NCO) ₂	48.86 (49.18)	18.80 (19.26)	2.55 (2.67)
WO(OEt) ₂ (N ₃) ₂	48.95 (49.18)	12.75 (12.84)	2.60 (2.61)
WO(OPr ⁱ) ₂ (SCN) ₂	42.10 (42.37)	22.00 (22.12)	3.15 (3.23)
WO(OPr ⁱ) ₂ (NCO) ₂	44.60 (45.75)	23.25 (23.89)	3.35 (3.48)
WO(OPr ⁱ) ₂ (N ₃) ₂	43.20 (45.75)	16.95 (17.92)	3.30 (3.48)
WO(OBu ⁿ) ₂ (SCN) ₂	38.60 (39.80)	25.10 (25.93)	3.20 (3.90)
WO(OBu ⁿ) ₂ (NCO) ₂	42.00 (42.77)	27.31 (27.92)	3.90 (4.19)
WO(OBu ⁿ) ₂ (N ₃) ₂	41.63 (42.77)	21.80 (22.33)	4.10 (4.19)
WO(OBu ^t) ₂ (SCN) ₂	38.85 (39.80)	25.16 (25.93)	3.80 (3.90)
WO(OBu ^t) ₂ (NCO) ₂	41.90 (42.77)	27.02 (27.92)	3.98 (4.19)
WO(OBu ^t) ₂ (N ₃) ₂	41.65 (42.77)	21.80 (22.33)	4.02 (4.19)

molar excess (0.0040 mole) was added to the solution. It was stirred and refluxed for about 8–10 hours at 70–80°C. The solution changed colour through various shades in the case of thiocyanates while in the case of cyanates and azides the colour change was much less even on prolonged refluxing and stirring. The reaction mixture was cooled and filtered through a G-4 sintered glass disc. The filtrate was evaporated to dryness under reduced pressure. The residue was washed with dry THF, dried and recrystallized from petroleum ether (60–80°C). The other compounds were prepared using a similar procedure.

The thiocyanato complexes are deep red in colour while the cyanato are yellow and the azido are brownish black. They are stable only in dry and inert atmosphere, and remain insoluble in common organic solvents. The complexes are non-volatile and decompose in the range 190–220°C.

The IR spectra of the complexes taken in KBr pellets

Table 2 Vibrational frequencies (cm⁻¹) of dialkoxytungsten(VI) oxypseudohalides

R	$\nu(\text{C-N})$ stretching	$\nu(\text{C-S})$ stretching	$\delta(\text{NCS})$ bending
<i>Thiocyanates</i>			
Me	2205(s), 2060(w)	750(m)	490(w), 440(m)
Et	2210(s), 2060(b)	740(m)	430(w), 410(m)
Pr ⁱ	2280(s), 2060(b)	745(m)	440(w), 410(m)
Bu ⁿ	2200(vs)	730(m)	480(w), 430(m)
Bu ^t	2295(s), 2090(b)	730(m)	470(w), 410(m)
R	$\nu_a(\text{NCO})$	$\nu_s(\text{NCO})$	$\delta(\text{NCO})$
<i>Cyanates</i>			
Me	2240(s), 2070(b)	1280(s)	620(m)
Et	2240(s), 2020(w)	1460(m), 1370(m)	605(m), 565(m)
Pr ⁱ	2110(s), 2030(b)	1330(m), 1290(m)	590(m)
Bu ⁿ	2230(s)	1460(m), 1270(b)	615(m), 590(w)
R	$\nu_a(\text{NNN})$	$\nu_s(\text{NNN})$	$\delta(\text{NNN})$
<i>Azides</i>			
Me	2200(vs), 2140(w), 2060(b)	1260(m), 1230(w), 1205(b)	630(m), 675(w)
Et	2240(s), 2140(m), 2040(w)	1270(m), 1230(m), 1205(w)	590(m)
Pr ⁱ	2200(s), 2140(m), 2130(m)	1300(m), 1265(m)	665(b), 615(m)
Bu ⁿ	2220(s), 2130(w), 2050(m)	1280(m), 1200(-)	620(m), 580(m)
Bu ^t	2210(s), 2130(w), 2040(b)	1270(m), 1210(m)	610(m), 600(w)

ν_a , ν_s and δ stand for asymmetric, symmetric and bending frequencies m (medium), w (weak), b (broad), s (strong), vs (very strong).

indicate the presence of both alkoxy and pseudohalogen groups.

The C–O stretching band for the alkoxy group normally appears in the region^{4,5} 1000–1200 cm⁻¹. The vibrational bands at about 1190 cm⁻¹ have been assigned according to the literature, to methoxy, at 1160 cm⁻¹ to ethoxy and at 1100 and 1150 cm⁻¹ to isopropoxy groups while the bands at 1100 and 1150–1170 cm⁻¹ are characteristics of butoxy groups^{6,8}. The sharp bands obtained in the region 1610–1700 cm⁻¹ are probably associated with the C–O linkage of the alkoxy groups.

Metal isothiocyanates (M–NCS) have C–S stretching frequency within the region 780–860 cm⁻¹ as compared to 690–720 cm⁻¹ for metal thiocyanates^{9,12} (M–SCN). A strong band at 720 cm⁻¹ may indicate M–SCN bonding¹³. Appearance of bands in the region 730–750 cm⁻¹ (due to C–S stretching, table 2) suggests that the bonding is probably through sulphur atom.

The NCS bending frequency in the range 400–440 cm⁻¹ of the prepared complexes (table 2)

accompanied by weaker bands at higher frequency side provide further evidence of their thiocyanate structure. The NCS bending frequency for isothiocyanates^{10,11} lies in the range 450–490 cm^{-1} .

Besides C–S stretching frequency and NCS bending frequency, confirmation regarding the bonding through sulphur atom can be obtained from the values of CN stretching frequency which are lower for M–NCS complexes as compared to M–SCN complexes^{14–16}. The presence of sharp bands at 2200 cm^{-1} (table 2) provides further indication of M–SCN bending in the prepared complexes.

Although both normal cyanates and isocyanates show asymmetric stretching band in the same region 2200–2300 cm^{-1} , the symmetric stretching band is quite different for them. The isocyanates have symmetric stretching frequency, $\nu_s(\text{NCO})$ in the region 1400–1320 cm^{-1} whereas this band appears below 1200 cm^{-1} in the normal cyanates^{17–20}. The appearance of medium intensity bands around 1300 cm^{-1} in the IR spectra of the prepared complexes clearly show that the bonding is through nitrogen i.e. M–NCO rather than M–CNO. Hence the cyanate complexes prepared are true isocyanates bonded through nitrogen.

The azide group in the complexes $\text{WO}(\text{OR})_2(\text{N}_3)_2$ is confirmed by the appearance of characteristic asymmetric N–N–N stretching frequency^{21,22} around 2100 cm^{-1} (table 2). The two bands in the spectral range 580–665 cm^{-1} are due to doubly degenerate azide bending motion.

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SOME TYPICAL PLATELET FORMS OF GEL GROWN BARIUM MOLYBDATE CRYSTALS

K. V. KURIEN and M. A. ITTYACHEN*

Mar Thoma College, Tiruvalla 695 004, India.

*Department of Materials Science, Gandhiji University, Kottayam 686 002, India.

BARIUM molybdate is an important crystal for laser studies¹. It has no natural occurrence, hence its growth and investigation on habit modification would be of great significance for better understanding of its physical properties. We have investigated the growth of this crystal in silica gel systems². The present paper gives a brief account of the typical platelet crystals grown in silica gel under some strictly controlled growth conditions.

Single and double diffusion techniques were attempted. Double diffusion technique could yield various habits in conglomeration, viz tetragonal bipyramids and its modified forms. Single diffusion tech-