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NOTE

Reactions of Di(Alkoxy) Dichlorooxotungsten(VI) with 2,2′-Bipyridyl

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All the di(alkoxy)dichlorooxotungsten(VI) complexes give bipyridyldichlorooxotungsten(IV) on treatment with 2,2′-bipyridyl in alcohol/benzene medium. The two alkoxy groups are knocked off and the oxidation state of tungsten is reduced from (VI) to (IV). The resulting compound is one and the same is confirmed by IR and UV spectra, and other physical data.

It has been observed that alkoxy chlorides of some metals form addition complexes with certain neutral donor ligands. $MO(OR)_2Cl_3$ forms coordination complexes with bipyridyl of the type $MO(OR)_2Cl_3\cdot$ bipy and even with excess of bipyridyl only one molecule of it is attached to the compounds $MO(OR)_2Cl_3$.[1] $Nb(OR)_3Cl_2$ gave the complex $Nb(OR)_3Cl_2\cdot$bipy.[2] Preparation of $MoO(OR)_2Cl_2\cdot$ bipy from $MoO(OR)_2Cl_2$ has been reported.[3] In all these reactions the oxidation state of the metal remained unchanged. When WOX_4 reacts with 2,2′-bipyridyl (bipy) the six coordinate compounds of the type $WOX_3\cdot$bipy are obtained; the oxidation state of metal tungsten is reduced to (V).[4] We have recently reported the preparation of $WO(OR)_2Cl_2$ from $WOCl_4$.[5] Hence curiosity was aroused to work on the reactions of 2,2′-bipyridyl on these di(alkoxy)-dichlorooxotungsten(VI) complexes and to see whether or not the oxidation state of tungsten changes from (VI).

The di(alkoxy)dichlorooxotungsten(VI) compounds were prepared by adding dry alcohol to $WOCl_4$ in benzene and refluxing for 4–5 h. and evaporating the resulting solution to dryness. The di(alkoxy)dichlorooxotungsten(VI) compounds were dissolved in benzene/alcohol mixture. To this solution solid 2,2′-bipyridyl was slowly added in 1 : 1 molar ratio with constant stirring. The reaction mixtures were refluxed for 3–4 h. The solvent from the reaction mixture was evaporated under reduced pressure. The residue was thoroughly washed with methanol and then with petroleum ether. In each reaction a creamish pink solid was obtained which showed a negative test for the alkoxy groups. The elemental analysis corresponded to the formula $WOCl_2\cdot$bipy.

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The compound is essentially non-electrolyte as it has a very low conductivity in acetonitrile. Magnetic susceptibility measurements of the compound showed that it is paramagnetic with two unpaired electrons (μ = 2.74 BM). The electronic spectra of the compound showed intense sharp band at 325 nm (ε_{max} = 11325) which could be assigned to charge-transfer N → W and charge-transfer Cl → W[6]

The IR spectra of all the products are identical indicating them to be the same compound. No bands are obtained for the alkoxy groups ν(CO) pointing the absence of alkoxy groups in them. The high frequency region bands in the compound are identical with the ligand bands. The ν(C—H) appeared at 3350 cm^{-1}. The bands at 1220, 1160 and in the range 1100–1060 cm^{-1} may be assigned to δ(CH) while the π(CH) bands appeared at 770 and 725 cm^{-1}. The ring stretchings appear at 1590, 1490 and 1440 cm^{-1} and the bands at 1030 and 910 cm^{-1} may be assigned to the ring skeletal vibrations.[7–9] The ν(W—N) may be assigned[10] at 540 cm^{-1} while ν(W—Cl) bands appeared[11] in the range 450–430 cm^{-1}. A medium sharp band at 950 cm^{-1} may be assigned to ν(W=O) and is an indication that no W—O—W bridging occurs in the compound.[6]

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