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INFRARED EVIDENCE FOR THE NON-LINEARITY OF THE WO_2 GROUP IN SOME TUNGSTYL CHELATES

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The geometry of the dioxotungsten(VI) (tungstyl) group, WO_2^{2+} is not known with certainty. To the best of our knowledge, no detailed crystallographic study has been made on compounds containing this group and the spectroscopic data are also scarce.[1-3]

In a search for further data on the stretching frequencies and the geometry of the WO_2^{2+} group, we investigated several tungstyl chelates of the $WO_2(Chelate)_2$ type, with the chelating agents being : acetylacetone (HAA),[4] dibenzoylmethane (HDBM), 8-quinolinol (HQ) and α-benzoinoxime (HBOx).

EXPERIMENTAL

The chelates with 8-quinolinol and α-benzoinoxime were prepared by standard analytical procedures[5] and those with acetylacetone and dibenzoylmethane were first synthetized by one of us.[6]

RESULTS AND DISCUSSION

TABLE 1 lists the frequencies (in cm^{-1}) of the bands observed in the 1000 - 900 cm^{-1} region and attributable to

W=O stretching vibrations, as well as those reported by Kharitonov and Buslaev[1] and by Hull and Stiddard.[3] Where more bands were found in this region, the WO_2 stretching bands were easily identifiable owing to their sharpness. On similar grounds, the broad 880 cm^{-1} band reported by Kharitonov and Buslaev[1] is not considered to arise from W=O stetching of the WO_2 group.

TABLE 1

Observed W=O Stretching Frequencies (in cm^{-1}) and Calculated Approximate Force Constants (in md/A) for Some Compounds Containing WO_2^{2+} Group

	ν_1	ν_3	k	k_i
$WO_2(AA)_2$	954	908	7.52	0.42
$WO_2(DBM)_2$	951	905	7.47	0.42
WO_2Q_2	942	900	7.36	0.39
$WO_2(BOx)_2$	945	908	7.45	0.35
$WO_2BipyCl_2$ [a]	955 [b]	916 [b]	7.59	0.37
$WO_2BipyBr_2$ [a]	954 [b]	907 [b]	7.51	0.43
$K_2/WO_2F_4/$	954 [c]	910 [c]	7.54	0.41

[a] : Bipy = 2,2′ - bipyridyl ; [b] : Ref. 3 ; [c] : Ref. 1

The assignment of the higher-frequency band to the symmetric, ν_1 mode and that of the lower-frequency band to the asymmetric, ν_3 mode was made by analogy with the assignment of the corresponding modes in compounds containing the $/MoO_2F_4/^{2-}$ ion[2,7] and on the basis of the invariably lower intensity of the former band.

The fact that in all investigated chelates the two W=O stretching bands are of comparable intensity strongly indi-

cates a cis-configuration (skeletal symmetry C_{2v}) of the WO_2 group. The whole chelate molecules would then belong to the C_2 point group (or very nearly so) with a two-fold axis as the only element of symmetry, i.e. would have a geometry similar to that found for TiO_2Cl_2.[8]

The approximate force constants were calculated using the expressions given by Cotton and Wing[9] and assuming reasonable values for the OWO angle (95 - 105°). The constants listed in TABLE 1 were calculated assuming an OWO angle of 95°, similar to the value of the OMoO angle found in the $/MoO_2F_4/^{2-}$ ion.[7] Changing the OWO angle from 95° to 105° does not significantly alter the stretching force constants k ,whereas the stretch-stretch interaction constants k_i for 100° are for approximately 0.05 and those for 105° for approximately 0.1 md/A higher than those listed in TABLE 1.

The investigation of the corresponding molybdenum compounds is presently under way and the results will be reported shortly.

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