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SHORT COMMUNICATIONS

SYNTHESIS AND INFRARED STUDY OF SOME NEW BINUCLEAR MOLYBDATO AND TUNGSTATO MX_2 AND $BiCl_3$ ADDUCTS

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INTRODUCTION

The main reactions of oxyanions acting as Lewis bases have been summarized recently by Hathaway [1]. This paper, dealing with the synthesis and the infrared study of some new tetrahedral oxyanions containing MX_2 and MX_3 adducts, is a continuation of the research work carried in our laboratory on the coordination ability of the oxyanions [2-9].

RESULTS AND DISCUSSION

The infrared bands of the adducts are presented in Table 1 together with the assignments based on literature [10] data.

Table 1. Infrared spectral data of the binuclear molybdato and tungstato complexes*

Adducts	ν_3	ν_1	ν_4	ν_2	νMO	νMX_n
$2MnCl_2.MoO_42NMe_4$ (1)	860 *brvs* 760 *sh*	--	400 *m*	--	250 *w*	285 *vs*
$2CoCl_2.MoO_42NMe_4$ (2)	850 *brvs*	--	420 *m*	--	250 *w*	298 *vs*
$2HgCl_2.WO_42NMe_4$ (3)	820 *vs* 780 *vs*	935 *m*	400 *m* 365 *m*	--	--	260 *s*
$2HgCl_2.WO_42NEt_4$ (4)	817 *vs* 745 *s*	930 *vs*	415 *s* 360 *m*	530 *m*	--	230 *s*
$2BiCl_3.WO_42NMe_4$ $1/6BiCl_6.3NMe_4$ (5)	890 *m* 818 *vs*	970 *s*	440 *s* 360 *m*	585 *m*	295 *m*	245 *vs*
$2CdBr_2.WO_42NMe_4$ (6)	807 *vs* 740 *vs* 646 *vs*	918 *s* --	402 *m* 311 *vs* 250 *vs*	502 *m* 430 *m*	--	181 *vs*

**brvs*: broad and very strong; *vs*: very strong; *s*: strong; *m*: medium; *sh*: shoulder; *w*: weak.

The absence of ν_1 and ν_2 suggests T_d symmetry of the oxyanion in adducts (**1**) and (**2**); the splitting of ν_3 into two bands indicates C_{3v} symmetry for the oxyanion in adducts (**3**), (**4**) and (**5**) while the splitting of ν_3 into three bands and of ν_2 into two bands reveal C_1 or C_s symmetry for the tungstate in (**6**). From these data we can reasonably suggest the following: 1) A discrete bichelating molybdate containing structure (Fig. 1a) or a tri-dimensional tetra-unidentate molybdate containing structure (Fig. 1b) when the oxyanion has T_d symmetry.

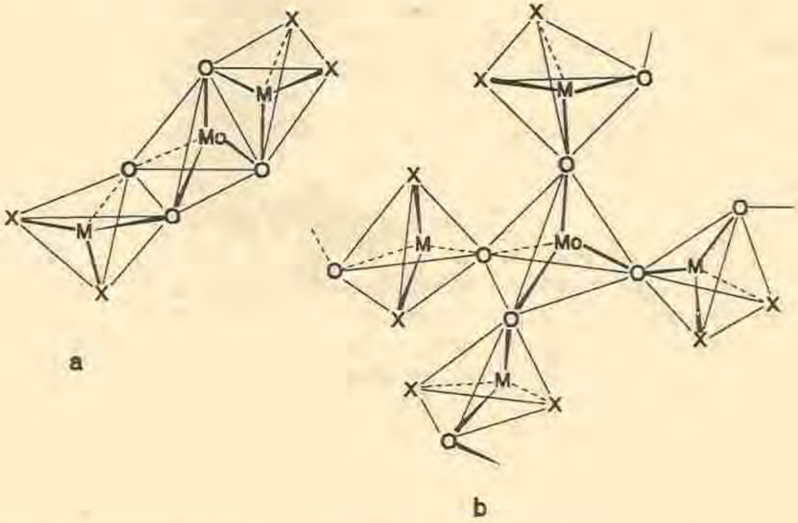

Fig. 1. Suggested structures for oxyanion containing adducts with T_d symmetry.

The presence of R_4NX (R = Alkyl, X = halide) *in situ* in a mixture of ethanolic oxyacid salts and metal halide solutions reported in [11] explains the formation of $(Me_4N)_3.BiCl_6$ beside the main adduct $2BiCl_3.WO_42NMe_4$. 2) A discrete tetra-dentate (tri-O-chelating and unidentate) tungstate containing structure for all the tungstato adducts; when the anion is of C_{3v} symmetry the tri-O-chelation is symmetrical (three equivalent oxygens) while being unsymmetrical (only two equivalent oxygens) when the symmetry of the oxyanion is C_s and all different when the symmetry is C_1. The difference of symmetry of the anion in the mercury and the cadmium adducts may be related to the size of the cadmium bromide.

Figure 2 shows the suggested structure of the mercury adducts. In the bismuth adduct, $BiCl_3$ replaces $HgCl_2$. The adducts were obtained as precipitates on mixing ethanolic solutions of tetra-alkylammonium oxyacid salts and MX_2 or $BiCl_3$ in defined metal-to-ligand ratio: 2:1 for $2MnCl_2.MoO_42NMe_4$ (**1**), 2:1 for $2CoCl_2.MoO_42NMe_4$ (**2**), 5:1 for $2HgCl_2.WO_42NMe_4$ (**3**), 1:1 for $2HgCl_2.WO_42NEt_4$ (**4**), 3:1 for $2BiCl_3.WO_42NMe_4.1/6BiCl_63NMe_4$ (**5**), 2:1 for $2CdBr_2.WO_42NMe_4$ (**6**). The solid was then filtered off, washed with ethanol and dried *in vacuo*.

Elemental analyses were performed by the "Service Central d'Analyses", Vernaison, France. In all cases satisfactory data were obtained. The infrared equipment is described in [2].

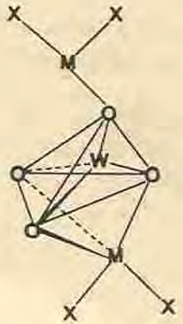

Fig. 2. Suggested structures for oxyanion containing adducts with C_{3v}, C_s, or C_1 symmetry.

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