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Preparation and Properties of Dimeric Dialkoxo-bridged Chromium(III) Complexes with 3-Bromo-2,4-pentanedione

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Synopsis. μ,μ'-Dialkoxotetraquis(3-bromo-3,4-pentanedionato)dichromium(III), where alkoxo is methoxo, ethoxo, *n*-propoxo or *n*-butoxo, has been prepared. These complexes have been identified by means of the elementary analysis, determination of molecular weight and the spectrometry.

The dimeric dimethoxo bridged copper(II) complex with 2,4-pentanedione has been reported by Bertrand and Kaplan,[1)] and dimeric dialkoxo bridged iron(III) complexes with 2,4-pentanedione and 2,2,4,6-tetramethylheptane have been synthesized by Wu, Rossman, Gray, Hammond, and Schugar.[2)] In the course of our studies of the substitution reaction of 3-bromo-2,4-pentanedione complexes, we have found the formation of such dimeric dialkoxo bridged chromium(III) complexes as the methoxo, exthoxo, *n*-propoxo and *n*-butoxo dimers.

Experimental

Materials. Tris(3-bromo-2,4-pentanedionato)chromium(III) was refluxed in methyl alcohol for a few days. The dark green precipitates thus formed were recrystallized from benzene. The product(1) consisted of yellowish-green needles. By the same procedure, ethyl, *n*-propyl and *n*-butyl alcohol give similar precipitates. The precipitates in ethyl alcohol were recrystallized from ethanol-dichloromethane, thus giving green crystals(2). Both (3) (the product with *n*-propyl alcohol) and (4) (that with *n*-butyl alcohol) were recrystallized from heptane. These four products show a similar green colour, but of a little different shade. These products are soluble in dichloromethane and chloroform, and a little soluble in alcohol, but insoluble in water. The molecular weights and analytical data of the products are summarized in Table 1.

Measurements. The infrared spectra were measured on a Hitachi 215-type spectrophotometer using KBr pellets. The electronic spectra were measured on a Hitachi 124-type spectrophotometer. The data of the molecular weights were obtained with a Hitachi 115 vapour-pressure osmometer, using chloroform as the solvent. The molecular weight of the methoxo dimer was also measured on a Hitachi Perkin-Elmer RMS-4 single focussing mass spectrometer.

Results and Discussion

In addition to these molecular weights and analytical results, the dimeric forms were identified on the basis of the following facts.

Infrared Spectra. The bands which are not observed for the starting material are shown in Table 2. The bridging alkoxo group is said to have a band at 1040—1070 cm^{-1} which can be assigned to its C–O stretching vibration.[3)] The band at 1064 cm^{-1} of (1) should be that of the methoxo group, in view of the IR results on dimeric dimethoxo 2,4-pentanedionato complexes of copper(II)[1)] and iron(III).[2)] The copper(II) complex shows a band at 1018 cm^{-1} and the iron(III) complex at 1050 cm^{-1}, both of which have been assigned to the C–O stretching of the bridging methoxo group. The similar ethoxo-bridged complex of iron(III) has also been reported to have bands at 1091, 1048 and 885 cm^{-1}, one of which, 1048 cm^{-1}, is assigned to C–O stretching of the ethoxo group.[2)] The bands of (2), as shown in Table 2, correspond to these data. By a similar inference, it might be said that the bands at 1095, 1070 and 975 cm^{-1} of (3) as well as 1070 and 970 cm^{-1} of (4) may be attributed to the existence of the bridging propoxo and

TABLE 1. MOLECULAR WEIGHT AND ANALYTICAL DATA

	Compound	Mol. wt.		Analysis (%)			
				Found		Calcd	
		Found	Calcd	C	H	C	H
(1)	$[(BrP)_2CrOCH_3]_2$	913, 876*	878.2	30.20	3.60	30.10	3.40
(2)	$[(BrP)_2CrOC_2H_5]_2$	925	906.3	32.10	3.90	31.80	3.80
(3)	$[(BrP)_2CrOC_3H_7]_2$	919	934.3	33.65	4.19	33.42	4.07
(4)	$[(BrP)_2CrOC_4H_9]_2$	974	962.4	35.40	4.65	34.94	4.41

* Datum of mass spectrometry. BrP = 3-bromo-2,4-pentanedione

TABLE 2. INFRARED SPECTRA (cm^{-1})

(1)	$[(BrP)_2CrOCH_3]_2$		1064	
(2)	$[(BrP)_2CrOC_2H_5]_2$	1095	1064	895
(3)	$[(BrP)_2CrOC_3H_7]_2$	1095^{sh}	1070	975^{sh}
(4)	$[(BrP)_2CrOC_4H_9]_2$		1070	970^{sh}

sh = shoulder

Table 3. Electronic spectra λ_{max} (nm) ($\log \varepsilon$)

	$(BrP)_3Cr$	560(1.95)	410^{sh} (2.80)	358(4.10)	275(4.27)	
(1)	$[(BrP)_2CrOCH_3]_2$	580(2.14)	405^{sh} (2.77)	352(4.24)	290^{sh} (4.05)	267(4.14)
(2)	$[(BrP)_2CrOC_2H_5]_2$	580(2.13)	410^{sh} (2.78)	352(4.33)	290^{sh} (4.19)	267(4.21)
(3)	$[(BrP)_2CrOC_3H_7]_2$	577(2.18)	410^{sh} (2.91)	352(4.33)	290^{sh} (4.19)	267(4.21)
(4)	$[(BrP)_2CrOC_4H_9]_2$	577(2.10)	410^{sh} (2.81)	351(4.26)	290^{sh} (4.11)	267(4.20)

butoxo groups respectively.

Electronic Spectra. As is shown in Table 3, the somewhat lower energies of the d-d bands($^4A_{2g}$—$^4T_{2g}$) of the products as compared to those of the starting material are probably due to the decreased ligand-field splitting by the replaced group. In the case of iron(III) with the same environment, the energies of the dimer d-d bands are higher than those of the monomer.[2] Therefore, the inter-electronic repulsion terms should also be considered in these cases.

While the dialkoxo bridged complex was obtained by the reaction of the 3-bromo-2,4-pentanedionato chromium(III) complex with alcohol, the reflux of the 2,4-pentanedionato chromium(III) complex in ethyl alcohol did not show any change even after a month. The bond between the central metal and carbonyl oxygen might be weaker for the 3-bromo-2,4-pentanedionato complex than for the 2,4-pentanedionato complex. Thus, the bond formation between central metal of the bromo compound and the oxygen atoms of alcohol may be promoted as compared with the case of the nonbrominated compound. Therefore, alcohol molecules react more easily with the central metal of the bromo compound.

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References

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