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SYNTHESIS OF trans-(DICHLOROMETHYL)BIS(2,4-PENTANEDIONATO)(AQUA, PYRIDINE, OR METHANOL)CHROMIUM(III) AND CRYSTAL STRUCTURE OF trans-(DICHLOROMETHYL)BIS(2,4-PENTANEDIONATO)PYRIDINECHROMIUM(III)

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The complexes, $[Cr(CHCl_2)(acac)_2L]$ (L = H_2O, CH_3OH, and pyridine), were prepared, where $acac^-$ denotes 2,4-pentanedionate ion. $[Cr(CHCl_2)(acac)_2(CH_3OH)]$ reacts with pyridine(py) rapidly to give $[Cr(CHCl_2)(acac)_2(py)]$. The structure of $[Cr(CHCl_2)(acac)_2(py)]$ has been determined to be trans by single crystal X-ray diffraction. The Cr-N(py) bond lengthens to 2.16(1) Å. This may be associated with that rapid substitution reaction.

It has been found that one of the coordinated water molecules in alkylpentaaquachromium(III) complexes, $[CrR(H_2O)_5]^{2+}$, undergoes much faster ligand substitution reactions than ordinary chromium(III) complexes.1) Although the labilization of the coordinated water molecule trans to the alkyl group has been proposed, lack of information on the structure of the alkylchromium(III) species hampered definitive discussion concerning the "trans-labilization". This situation prompted us to isolate alkylchromium species from the solution of $[CrR(H_2O)_5]^{2+}$ by replacing part of its coordinated water molecules with ligands other than H_2O, and determine the molecular structure. Herein, we report the products obtained from the reaction of $[Cr(CHCl_2)(H_2O)_5]^{2+}$ with 2,4-pentanedionate ions ($acac^-$), and the X-ray structure of $[Cr(CHCl_2)(acac)_2(pyridine)]$.

A solution containing 27 g of $CrCl_3\cdot6H_2O$, 60 g of $CHCl_3$, 8.3 ml of concd HCl, 10 ml of water, and 40 ml of ethanol was stirred with 50-100 g of amalgamated zinc under nitrogen. After two hours, the dark reddish brown solution was filtered. To this solution, was added 20 g of 2,4-pentanedione. Then, 2 M triethylamine-2 M triethylammonium chloride buffer solution was added dropwise to adjust the pH between 5 and 6.2) When the reaction mixture was concentrated under reduced pressure, orange-red crystals appeared.3) The crystals were dissolved into 200 ml of 1:1 ethanol-water containing 0.5 M $ZnCl_2$. When the solution was concentrated to a small volume, air stable red compound, $[Cr(CHCl_2)(acac)_2(H_2O)]$(1), crystallized.4) Yield: 7.7 g. Complex 1 reacts very rapidly with pyridine(py) or methanol to replace the water ligand in 1. Upon cooling a methanol solution saturated with 1, red crystals of $[Cr(CHCl_2)(acac)_2(CH_3OH)]$ (2) appeared.4) When a methanol solution containing 1 and 1 M pyridine was concentrated, [Cr(CHCl$_2$)(acac)$_2$(py)] (3) was obtained.$^{4)}$ The X-ray crystal structure of 3 is given in Fig. 1 along with atom numbering scheme.$^{5)}$ The relevant bond lengths and bond angles are listed in Table 1. The geometry around the chromium atom is octahedral. The CHCl$_2$ and pyridine ligands occupy trans positions. Although X-ray data for Cr(III)-C bond lengths of alkyl or arylchromium(III) complexes are reported to be 2.01-2.11 Å,$^{7,8)}$ the Cr-C bond length (2.13 Å) found for 3 appears to be a little longer than those data. This may be due to the bulkiness of CHCl$_2$ group. The coordination of the bulky CHCl$_2$ group also affects the bond angle: The Cr-C-Cl angle (115.2°) is larger than that of sp^3 carbon (109.5°).

The average Cr-O bond length of 3 is comparable to that of [Cr(acac)$_3$] (1.95 Å).$^{9)}$ Thus, there is no special influence caused by the alkyl group to the Cr-ligand bond at cis positions. The Cr-N bond of 3 is noticeably longer than the average Cr-N bond (2.10 Å) of [Cr(CF$_3$CO$_2$)$_3$(py)$_3$] (4).$^{10)}$ Since the Cr-O bond length (1.95 Å) of 4 is almost the same as those of 3 (1.96 Å), the longer Cr-N bond in 3 is likely due to the trans effect of the alkyl group. A similar trend is also found for cis-[(aryl)$_2$Cr(bpy)$_2$]$^+$.$^{8,11)}$ The lengthened Cr-N bond trans to the alkyl group in 3 suggests weakening of the Cr-ligand bond trans to the alkyl group.

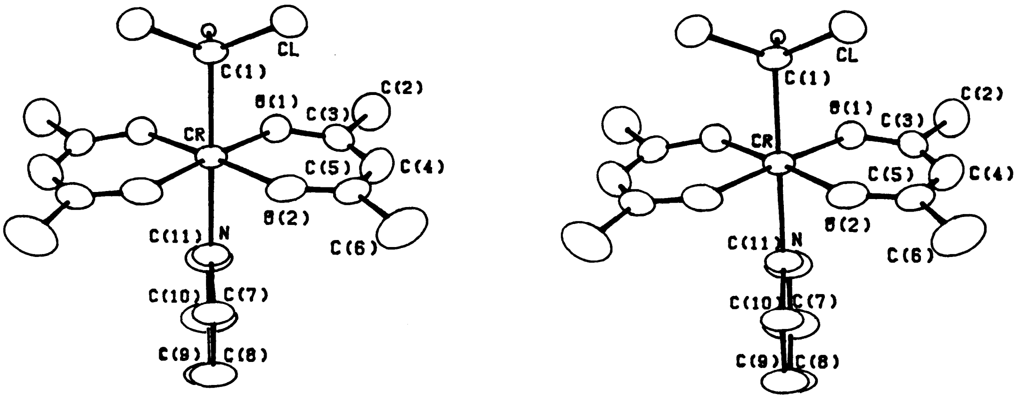

Fig. 1. Stereoscopic view of trans-[Cr(CHCl$_2$)(acac)$_2$(py)].

Table 1. Bond lengths and bond angles for trans-[Cr(CHCl$_2$)(acac)$_2$(py)] a)

Bond length / Å

Cr-C(1)	2.13(1)	C(2)-C(3)	1.53(2)	N-C(11)	1.34(2)
Cr-O(1)	1.953(6)	C(5)-C(6)	1.55(2)	C(7)-C(8)	1.36(2)
Cr-O(2)	1.957(7)	C(3)-C(4)	1.36(2)	C(10)-C(11)	1.41(2)
Cr-N	2.16(1)	C(4)-C(5)	1.39(2)	C(8)-C(9)	1.38(2)
C(1)-Cl	1.777(8)	N-C(7)	1.35(2)	C(9)-C(10)	1.34(2)
C(1)-H	1.07(1)				

Bond angle / degree

C(1)-Cr-N	173.2(5)	C(4)-C(5)-C(6)	123(1)	Cr-N-C(7)	120.8(8)
C(1)-Cr-O(2)	96.5(3)	C(3)-C(4)-C(5)	125(1)	C(7)-N-C(11)	119(1)
O(1)-Cr-O(1)' b)	88.6(3)	C(7)-C(8)-C(9)	118(1)	Cr-O(2)-C(5)	125.6(6)
O(1)-Cr-N	89.1(3)	C(9)-C(10)-C(11)	121(1)	C(2)-C(3)-C(4)	119(1)
Cr-C(1)-Cl	115.2(5)	C(1)-Cr-O(1)	86.3(3)	O(2)-C(5)-C(6)	112(1)
Cl-C(1)-Cl' b)	108.1(7)	O(1)-Cr-O(2)	91.1(3)	O(2)-C(5)-C(4)	126(1)
Cr-N-C(11)	120.2(9)	O(1)-Cr-O(2)' b)	177.2(3)	N-C(7)-C(8)	123(1)
Cr-O(1)-C(3)	127.0(6)	O(2)-Cr-N	88.1(4)	C(8)-C(9)-C(10)	120(1)
O(1)-C(3)-C(2)	115(1)	Cr-C(1)-H	98.7(8)	C(10)-C(11)-N	119(1)
O(1)-C(3)-C(4)	126(1)				

a) Numbers in parentheses are the estimated standard deviations in the least significant digits. b) Apostrophe denotes symmetry operation x, -y, z.

In fact, reversible reaction,

$$[\mathrm{Cr(CHCl_2)(acac)_2(CH_3OH)}] + \mathrm{py} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Cr(CHCl_2)(acac)_2(py)}] + \mathrm{CH_3OH}$$

occurs very rapidly in methanol. Kinetic experiments gave rate constants for the forward and backward reactions, $k_1 = 85\ \mathrm{M^{-1}\ s^{-1}}$, $k_{-1} = 15\ \mathrm{s^{-1}}$ at 25.0 °C. These values are much greater than the rate constants for the ligand substitution of ordinary chromium(III) complexes.12) Thus, the present work has shown that the coordination position trans to the Cr-C bond is the site where labilized ligand substitution takes place. The kinetic features indicate that the complexes, [Cr(CHCl$_2$)(acac)$_2$(H$_2$O)] and [Cr(CHCl$_2$)(acac)$_2$(CH$_3$OH)] also take trans configuration.

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2) 1 M = 1 mol dm^{-3}.

3) The crystals decompose slowly on standing to give green solid, but their identity is not yet certain.

4) All the complexes gave satisfactory elemental analyses.

5) The analysis of 3 was made using a Rigaku AFC-5 four-circle diffractometer by using Mo-K_α (0.71073 Å) radiation. All calculations were carried out on a HITAC M-200H computer at the Computer Center of the Institute for Molecular Science using the Universal Crystallographic Computation Program System UNICS III.[6)] Crystals belong to the orthorhombic system, space group $A2_1ma$, a = 14.527(2) Å, b = 17.198(4) Å, c = 8.097(1) Å, V = 2023.1(6) $Å^3$ Z = 4, D_c = 1.357 g cm^{-3}, and D_m = 1.351 g cm^{-3}. Refinement of the positional parameters gave R = 0.0611 (R_w = 0.0688).

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11) bpy = 2,2'-bipyridine.

12) For example, aquation of $[Cr(H_2O)_5(py)]^{3+}$ proceeds with the rate constants of 1.2×10^{-8} s^{-1} at 25 °C: A. Bakač and M. Orhanović, Inorg. Chem., 10, 2443 (1971).

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