X-Ray Crystal Structures of *trans*-(Chloromethyl)bis(2,4-pentanedionato)-(aqua and methanol)chromium(III) Complexes. Evidence for a Trans Influence Exerted in the Carbon-Bonded Chromium(III) Complexes

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The crystal and molecular structures of alkylchromium(III) complexes, *trans*-[$Cr(CH_2Cl)(acac)_2(H_2O)$]·EtOH and *trans*-[$Cr(CH_2Cl)(acac)_2(MeOH)$] ($acac^-$=2,4-pentanedionate anion, EtOH=ethanol, MeOH=methanol), have been determined by X-ray structure analyses. Both crystals are triclinic and the space group $P\bar{1}$; Z=2 with a=9.935(2), b=10.606(2), c=9.399(2) Å, α=90.39(2), β=92.44(2), γ=115.54(1)° for the aqua complex, and Z=4 with a=11.402(6), b=16.780(7), c=8.543(3) Å, α=98.83(3), β=102.00(4), γ=83.03(4)° for the methanol complex. Each complex has trans configuration. The carbon-bonded CH_2Cl group elongates specifically the Cr–O bond trans to the Cr–C bond in the aqua complex (Cr–O(H_2O)=2.134(6) Å) and methanol complex (Cr–O(MeOH)= 2.156(6), 2.136(6) Å).

Recently, we synthesized and isolated dichloromethyl- and chloromethyl-bonded chromium(III) complexes, *trans*-[CrR(acac)$_2$L] (R=$CHCl_2$, CH_2Cl; L=H_2O, MeOH, py).[1,2] Remarkably rapid substitution reactions

$$\textit{trans}\text{-}[CrR(acac)_2(MeOH)] + L \rightleftharpoons \textit{trans}\text{-}[CrR(acac)_2L] + MeOH$$

were observed for the complexes, where L denotes pyridine and its analogs. The X-ray crystal structure determinations of [$Cr(CHCl_2)(acac)_2$(py)] and [$Cr(CH_2Cl)$-$(acac)_2$(py)][2] revealed that the geometries of both complexes are trans and the carbon-bonded ligands lengthen specifically the Cr–N bonds trans to the Cr–C bonds in [CrR(acac)$_2$(py)]. Therefore, the labilized ligand substitution reactions are ascribed to a strong electronic effect of the alkyl group on the bond trans to the Cr–C bond. However, there has been no direct evidence that the geometries of [CrR(acac)$_2$(H_2O)] and [CrR(acac)$_2$(MeOH)] are trans. In this work the structural determinations for the [$Cr(CH_2Cl)(acac)_2$L] (L=H_2O, MeOH) are described. The structural features are compared with those of [CrR(acac)$_2$(py)] (R=$CHCl_2$, CH_2Cl).

Experimental

The syntheses of *trans*-[$Cr(CH_2Cl)(acac)_2(H_2O)$]·EtOH and [$Cr(CH_2Cl)(acac)_2$(MeOH)] were carried out by the methods reported previously.[2] The single crystals of the aqua and methanol complexes were obtained by the recrystallizations from H_2O–ethanol (1:5) and H_2O–methanol (1:3), respectively.

Intensity data were collected on a Rigaku AFC-6A four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å). Crystallographic and experimental parameters for both complexes are listed in Table 1. During data collection, three standard reflections showed decrease in intensities of approximately 10% for both complexes. The reflection data were corrected for the decays as well as Lorentz and polarization factors. The structures were solved by the heavy-atom method and refined by the block-diagonal least-squares method. Refinement was carried out with anisotropic temperature factors for all non-hydrogen atoms. The positions of the hydrogen atoms of the chloromethyl groups and those of the methine groups of $acac^-$ ligands for both aqua and methanol complexes were calculated and fixed. All other hydrogen atoms were not included in the calculation. The atomic-scattering factors including the anomalous scattering factors were taken from Ref. 3 for non-hydrogen atoms and from Ref. 4 for hydrogen atom.

All the calculations were performed on Nippon Electric Co. ACOS-1000 and -2020 computers at the computer center of Tohoku University, using the Universal Crystallographic Computation Program System (UNICS III) and its local version.[5]

Results and Discussion

Positional and isotropic thermal parameters of the *trans*-[$Cr(CH_2Cl)(acac)_2(H_2O)$]·EtOH and [$Cr(CH_2Cl)$-$(acac)_2$(MeOH)] are listed in Tables 2 and 3,[6] respectively. The structures of the aqua and methanol complexes are shown in Figs. 1 and 2 with atom numbering schemes.

The geometries of *trans*-[$Cr(CH_2Cl)(acac)_2(H_2O)$]·EtOH and [$Cr(CH_2Cl)(acac)_2$(MeOH)] have been proved unequivocally to be trans by the crystal structure determinations. The ethanol molecule in *trans*-[$Cr(CH_2Cl)(acac)_2(H_2O)$]·EtOH is hydrogen-bonded to the coordinated water molecule (O(5)···O(6) 2.656(9) Å). The structures of two crystallographically independent molecules in *trans*-[$Cr(CH_2Cl)(acac)_2$(MeOH)] are almost the same, but different slightly in the orientation of the coordinated methanol molecules and the chloromethyl groups (Fig. 2).

Selected interatomic distances and angles are summarized in Tables 4 and 5. The most striking feature observed in the interatomic distances is that Cr–O-(H_2O) bond (2.134(6) Å) in the aqua complex is

Table 1. Crystal Data for *trans*-[Cr(CH_2Cl)(acac)$_2$(H_2O)]·EtOH and *trans*-[Cr(CH_2Cl)(acac)$_2$(MeOH)]

	trans-[Cr(CH_2Cl)(acac)$_2$(H_2O)]·EtOH	*trans*-[Cr(CH_2Cl)(acac)$_2$(MeOH)]
Formula	$C_{13}H_{24}ClCrO_6$	$C_{12}H_{20}ClCrO_5$
Formula weight	363.78	331.74
Crystal color	Reddish orange	Reddish orange
Crystal shape	Plate	Plate
Crystal dimensions (l/mm)	0.5×0.2×0.1 0.5×0.3×0.1	0.3×0.2×0.1
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a(l/Å)	9.935(2)	11.402(6)
b(l/Å)	10.606(2)	16.780(7)
c(l/Å)	9.399(2)	8.543(3)
α(ϕ/°)	90.39(2)	98.83(3)
β(ϕ/°)	92.44(2)	102.00(4)
γ(ϕ/°)	115.54(1)	83.03(4)
U(v/Å^3)	892.4(3)	1573(1)
Z	2	4
D_c(d/g cm^{-3})	1.354	1.401
D_m(d/g cm^{-3})	1.34	—
μ(Mo $K\alpha$)(n/cm^{-1})	8.38	9.38
Temperature	Room temp	Room temp
Scan mode	ω-2θ	ω-2θ
Scan width (ω/°)	1.2+0.35 tanθ	1.2+0.5 tanθ
2θ range (ϕ/°)	3—55	3—55
Reflections measured	$\pm h$, $\pm k$, l	$\pm h$, $\pm k$, l
No. of reflections measured	4121	7273
No. of unique data used for calc. ($\|F_o\| > 3\sigma(\|F_o\|)$)	2493	3662
No. of parameters refined	191	360
R[a]	0.082	0.084
R_w[b]	0.107	0.114
Max. residual electron density (ρ/e Å^{-3})	0.86	0.83

a) $R=\sum||F_o|-|F_c||/\sum|F_o|$. b) $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w=[\sigma^2(|F_o|)+aF_o^2]^{-1}$, where $a=0.030$ for the aqua complex and $a=0.005$ for the methanol complex.

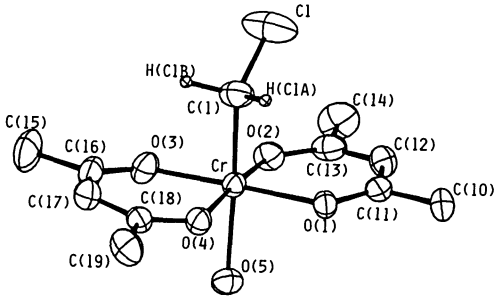

Fig. 1. ORTEP drawing of *trans*-[Cr(CH_2Cl)(acac)$_2$-(H_2O)] with the atom numbering schemes.

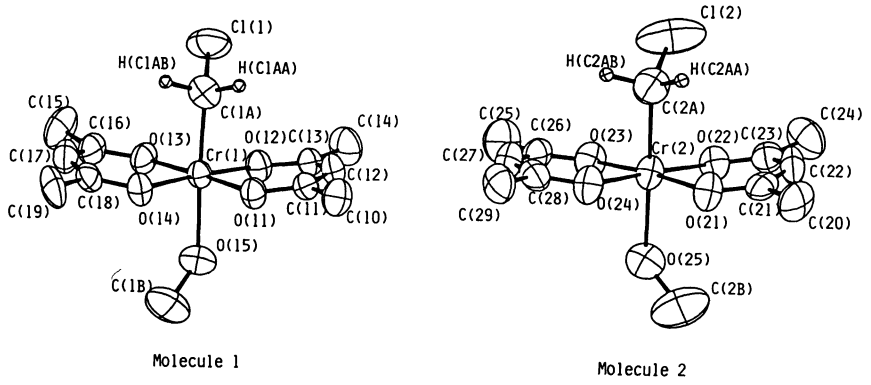

Fig. 2. ORTEP drawings of *trans*-[Cr(CH_2Cl)(acac)$_2$(MeOH)] with the atom numbering schemes.

considerably elongated, being compared to Cr–O(H_2O) bonds (1.975(4)—2.090(6) Å) in chromium(III) complexes which contain coordinated water molecules but have no Cr–C bonds.[7–12] This is also true for the methanol and pyridine complexes: The Cr–O(MeOH) bond (2.156(6) Å for molecule 1 and 2.138(6) Å for molecule 2) for the methanol complex and the Cr–N bond (2.201(4) Å) for the pyridine complex[2] are longer than those of *trans*-$[CrCl_2(MeOH)_4]^+$ (1.987 Å)[13] and *mer*-$[Cr(CF_3CO_2)_3(py)_3]$ (2.10 Å),[14] respectively. The trans influence exerted in the [CrR(acac)$_2$L] complexes is responsible for the labilized ligand substitution rates.[2] It should be noted that similar ground-state distortion and kinetic effect are also observed for coenzyme B_{12} and related model complexes.[15–20]

Table 2. Final Positional (×10^4) and Isotropic Thermal Parameters for *trans*-[Cr(CH_2Cl)(acac)$_2$(H_2O)]·EtOH

Atom	x	y	z	B_{eq}/Å^2[a]
Cr	434(1)	3519(1)	1956(1)	3.8
Cl	2820(3)	2289(3)	3003(3)	11.7
O(1)	1920(4)	4779(4)	680(4)	4.3
O(2)	1631(5)	4582(5)	3614(5)	5.0
O(3)	−1059(5)	2324(5)	3241(5)	5.4
O(4)	−857(4)	2562(4)	291(4)	4.4
O(5)	−647(5)	4875(4)	1937(4)	5.1
O(6)[b]	15(8)	7010(7)	3757(6)	9.7
C(1)	1349(9)	2108(8)	1837(9)	6.2
C(10)	4199(8)	6429(8)	−186(9)	6.1
C(11)	3220(7)	5706(6)	1059(8)	4.8
C(12)	3754(7)	6094(7)	2447(8)	5.3
C(13)	2943(8)	5550(7)	3647(8)	5.7
C(14)	3586(11)	6102(10)	5132(10)	8.3
C(15)	−3160(11)	429(10)	4116(11)	8.5
C(16)	−2258(8)	1218(7)	2864(9)	5.7
C(17)	−2729(8)	763(7)	1480(9)	5.5
C(18)	−2059(7)	1453(7)	271(8)	4.6
C(19)	−2773(9)	872(9)	−1189(9)	6.5
C(2)[b]	−673(17)	7985(14)	3569(14)	13.7
C(3)[b]	−1685(15)	7599(17)	2414(15)	15.2

a) The equivalent isotropic thermal parameters for non-hydrogen atoms were computed using the following expression: $B_{eq}=4/3(\beta_{11}a^2+\beta_{22}b^2+\beta_{33}c^2+\beta_{12}ab\cos\gamma+\beta_{13}ac\cos\beta+\beta_{23}bc\cos\alpha)$. The β_{ij}'s are defined by $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$. b) O(6), C(2), and C(3) denote the oxygen, methylene carbon, and methyl carbon atoms of EtOH solvate, respectively.

The Cr–C bond lengths of [Cr(CH_2Cl)(acac)$_2$L] (L=H_2O, MeOH, py) lie in the range of the values (2.01—2.11 Å) reported for those of other carbon-bonded chromium(III) complexes.[21–23] The Cr–C bond lengths of the present complexes show a slight but interesting dependence on the ligand L trans to the Cr–C bond; i.e. py (2.077(6) Å)>H_2O (2.06(1) Å)≥MeOH (2.049(9) Å for molecule 1 and 2.052(9) Å for molecule 2). This order appears to indicate that the electron donating trans ligand L affects the length of the Cr–C bond.

The existence of the Cr–C bond has no substantial influence on the equatorial ligands. Table 6 shows that Cr–O(acac) bond lengths in the [CrR(acac)$_2$L] complexes are essentially the same as those of [Cr(acac)$_3$][24,25] and related complexes.[26–28]

It has been reported that the pentane moieties of two acac$^-$ chelates in [Cr(CH_2Cl)(acac)$_2$(py)] are bent toward the CH_2Cl group.[2] This seems to be due to the intermolecular repulsion between a hydrogen atom of a chloromethyl group and a methyl group. Similar bending modes are observed for the aqua and methanol complexes. The degree of the bending can be expressed by the dihedral angles between the plane 1 (the least-squares plane which is defined by a chromium atom and the four oxygen atoms of two

Table 3. Final Positional (×10^4) and Isotropic Thermal Parameters for *trans*-[Cr(CH_2Cl)(acac)$_2$(MeOH)]

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
Cr(1)	1635(1)	4092.7(7)	3813(1)	3.2	C(15)	−237(11)	3136(6)	6813(14)	6.6
Cr(2)	−3103(1)	699.2(8)	1312(2)	3.8	C(16)	266(7)	3195(5)	5329(11)	4.5
Cl(1)	3474(3)	3657(2)	7055(3)	7.3	C(17)	241(8)	2564(5)	4093(12)	4.8
Cl(2)	−3792(4)	1629(3)	4680(4)	11.0	C(18)	612(6)	2559(5)	2663(11)	4.2
O(11)	2503(5)	4325(3)	2231(6)	3.9	C(19)	453(9)	1836(6)	1366(14)	6.2
O(12)	2041(5)	5100(3)	5175(6)	3.9	C(1A)	3159(8)	3456(6)	4893(11)	4.8
O(13)	696(5)	3866(3)	5366(7)	4.2	C(1B)	−794(11)	4560(9)	1299(14)	8.1
O(14)	1112(5)	3132(3)	2356(7)	4.3	C(20)	−2826(11)	2729(6)	−1027(13)	6.5
O(15)	63(5)	4801(4)	2700(7)	4.8	C(21)	−3378(8)	2152(5)	−227(10)	4.5
O(21)	−2719(5)	1530(3)	166(7)	4.6	C(22)	−4567(8)	2364(5)	64(12)	4.9
O(22)	−4804(5)	1153(3)	994(7)	4.2	C(23)	−5194(7)	1853(5)	617(10)	4.3
O(23)	−3481(5)	−195(3)	2284(7)	4.6	C(24)	−6476(9)	2131(7)	787(15)	6.8
O(24)	−1427(5)	264(3)	1504(7)	4.6	C(25)	−3275(11)	−1322(6)	3725(14)	7.0
O(25)	−3556(5)	−75(4)	−916(8)	5.1	C(26)	−2735(9)	−709(5)	2978(10)	4.5
C(10)	3922(8)	4843(6)	1105(11)	5.3	C(27)	−1494(9)	−788(5)	3014(12)	5.3
C(11)	3247(7)	4865(5)	2452(10)	3.9	C(28)	−916(8)	−308(5)	2300(11)	4.7
C(12)	3458(7)	5422(5)	3780(10)	4.2	C(29)	437(8)	−471(6)	2371(13)	6.0
C(13)	2842(7)	5537(4)	5048(10)	4.0	C(2A)	−2660(9)	1397(6)	3504(12)	5.4
C(14)	3115(10)	6220(6)	6441(12)	6.0	C(2B)	−3597(13)	118(10)	−2491(16)	9.1

Table 4. Selected Interatomic Distances and Angles for *trans*-[Cr(CH_2Cl)(acac)$_2$(H_2O)]·EtOH

Bond length (l/Å)			
Cr-O(1)	1.968(5)	Cr-O(2)	1.943(5)
Cr-O(3)	1.954(5)	Cr-O(4)	1.951(5)
Cr-O(5)	2.134(6)	Cr-C(1)	2.06(1)
C(1)-Cl	1.73(1)		
O(6)-C(2)[a]	1.47(2)	C(2)-C(3)[a]	1.38(3)
Bond angle (ϕ/°)			
O(1)-Cr-O(2)	90.8(2)	O(1)-Cr-O(3)	177.9(2)
O(1)-Cr-O(4)	89.3(2)	O(1)-Cr-O(5)	89.8(2)
O(1)-Cr-C(1)	90.7(3)	O(2)-Cr-O(3)	88.5(2)
O(2)-Cr-O(4)	174.9(2)	O(2)-Cr-O(5)	87.8(2)
O(2)-Cr-C(1)	97.1(3)	O(3)-Cr-O(4)	91.4(2)
O(3)-Cr-O(5)	88.3(2)	O(3)-Cr-C(1)	91.3(3)
O(4)-Cr-O(5)	87.1(2)	O(4)-Cr-C(1)	88.1(3)
O(5)-Cr-C(1)	175.1(3)		
Cr-C(1)-Cl	119.6(5)		
O(6)-C(2)-C(3)[a]	112(1)		

a) O(6), C(2), and C(3) denote the oxygen, methylene carbon, and methyl carbon atoms of EtOH solvate, respectively.

Table 5. Selected Interatomic Distances and Angles for *trans*-[Cr(CH_2Cl)(acac)$_2$(MeOH)]

Bond length (l/Å)			
Molecule 1		Molecule 2	
Cr(1)-O(11)	1.941(6)	Cr(2)-O(21)	1.959(7)
Cr(1)-O(12)	1.946(5)	Cr(2)-O(22)	1.974(5)
Cr(1)-O(13)	1.973(7)	Cr(2)-O(23)	1.953(7)
Cr(1)-O(14)	1.953(5)	Cr(2)-O(24)	1.944(6)
Cr(1)-O(15)	2.156(6)	Cr(2)-O(25)	2.138(6)
Cr(1)-C(1A)	2.049(9)	Cr(2)-C(2A)	2.052(9)
C(1A)-Cl(1)	1.794(9)	C(2A)-Cl(2)	1.77(1)
O(15)-C(1B)	1.42(1)	O(25)-C(2B)	1.42(2)
Bond angle (ϕ/°)			
Molecule 1		Molecule 2	
O(11)-Cr(1)-O(12)	90.9(2)	O(21)-Cr(2)-O(22)	90.1(3)
O(11)-Cr(1)-O(13)	177.9(2)	O(21)-Cr(2)-O(23)	175.0(2)
O(11)-Cr(1)-O(14)	88.9(3)	O(21)-Cr(2)-O(24)	87.4(3)
O(11)-Cr(1)-O(15)	89.6(2)	O(21)-Cr(2)-O(25)	90.7(3)
O(11)-Cr(1)-C(1A)	89.6(3)	O(21)-Cr(2)-C(2A)	91.8(4)
O(12)-Cr(1)-O(13)	89.7(2)	O(22)-Cr(2)-O(23)	91.0(3)
O(12)-Cr(1)-O(14)	175.3(2)	O(22)-Cr(2)-O(24)	176.8(3)
O(12)-Cr(1)-O(15)	85.5(2)	O(22)-Cr(2)-O(25)	87.8(2)
O(12)-Cr(1)-C(1A)	92.8(3)	O(22)-Cr(2)-C(2A)	93.0(3)
O(13)-Cr(1)-O(14)	90.3(3)	O(23)-Cr(2)-O(24)	91.3(3)
O(13)-Cr(1)-O(15)	88.4(2)	O(23)-Cr(2)-O(25)	84.5(3)
O(13)-Cr(1)-C(1A)	92.5(3)	O(23)-Cr(2)-C(2A)	93.0(4)
O(14)-Cr(1)-O(15)	89.8(2)	O(24)-Cr(2)-O(25)	90.2(2)
O(14)-Cr(1)-C(1A)	91.9(3)	O(24)-Cr(2)-C(2A)	89.1(3)
O(15)-Cr(1)-C(1A)	178.0(3)	O(25)-Cr(2)-C(2A)	177.4(4)
Cr(1)-C(1A)-Cl(1)	114.3(5)	Cr(2)-C(2A)-Cl(2)	116.7(5)
Cr(1)-O(15)-C(1B)	127.9(7)	Cr(2)-O(25)-C(2B)	126.7(8)

$acac^-$ chelates) and the plane 2 (the least-squares plane which is defined by the two oxygen atoms of a $acac^-$ chelate and three skeletal carbon atoms of the $acac^-$ chelate). The values of the dihedral angles are 164.7(1)° for the pyridine complex,[2] 169.4(3)—173.5(4)° for the methanol complex, and 174.1(4) and 173.6(5)° for the aqua complex. The bending of the $acac^-$ chelates is again due to the interaction of molecules in the crystal. In the aqua and methanol complexes, it is seen that the nearest intermolecular non-bonding distances between two methyl groups of different molecules are close to or slightly shorter than the sum

Table 6. Average Interatomic Distances in the acac$^-$ Chelate Rings of *trans*-[CrR(acac)$_2$L] (R=$CHCl_2$, CH_2Cl; L=H_2O, MeOH, py) and Related Complexes

Complex	Bond length (l/Å)			
	Cr-O	O-C	C-C(methine)	C-C(methyl)
trans-[Cr(CH_2Cl)(acac)$_2$(H_2O)][a]	1.954(5)	1.274(7)	1.39(1)	1.52(2)
trans-[Cr(CH_2Cl)(acac)$_2$(MeOH)][a]	1.955(7)	1.27(1)	1.38(2)	1.52(2)
trans-[Cr(CH_2Cl)(acac)$_2$(py)][b]	1.960(3)	1.266(5)	1.400(7)	1.506(7)
trans-[Cr($CHCl_2$)(acac)$_2$(py)][b]	1.955(6)	1.29(1)	1.38(2)	1.54(2)
[Cr(acac)$_3$][c]	1.951(7)	1.26(2)	1.39(2)	1.52(2)
	1.962(5)	1.27(1)	1.38(1)	1.51(1)
[Cr(acac)$_2$(tn)]$^+$[d]	1.96(1)	1.28(2)	1.39(2)	1.53(2)
[Cr(acac)$_2$(μ-OMe)]$_2$[e]	1.965(5)	1.267(8)	1.38(1)	1.51(1)
[Cr^{II}(acac)$_2$][f]	1.982(3)	1.274(5)	1.399(6)	1.518(6)

a) This work. b) Ref. 2. c) Refs. 24 and 25. d) Ref. 26. e) Ref. 27. f) Ref. 28.

of the van der Waals radii for the methyl groups. In the aqua complex, there is an additional interaction between a chloromethyl group and the nearest methyl group of an ethanol. The inclination of the chloromethyl group may come from this repulsion.

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1) Abbreviations used in this paper: Hacac, 2,4-pentanedione; MeOH, methanol; py, pyridine; EtOH, ethanol; tn, 1,3-diaminopropane.

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