and trimethoxyborane were precisely controlled by metering valves and measured with a calibrated flow meter. The vapor pressure of $B(OCH_3)_3$ at room temperature was sufficient to provide the desired flow from a reservoir of the liquid. The microwave coupling heads could be positioned along $^1/_2$-in. o.d. Pyrex tubes from 2 to 20 cm upstream from the quenching traps. However, use of the quenching traps (from room temperature to −20 °C) did not significantly enhance the yield of the dimethoxy compound for any position of the discharge head. (The traps were eventually removed.) Cleanliness of the discharge tubes was an important constraint—contamination by dioctyl phthalate from the flow meters led to poor conversions. Some decomposition of the trimethoxy compound also occurred, and the yield of the dimethoxy species dropped drastically when a perceptible white deposit (B_2O_3) built up in the discharge region. The optimum flow conditions were about 5% of the trimethoxyborane in hydrogen, at a total pressure of 7–12 torr, with a linear flow rate of about 2–10 m/min. Increasing the flow rate to 20 m/min, even with the percent of $B(OCH_3)_3$ halved, and at the same total pressure, led to rather poor fractional conversions, indicating that the residence time is an important constraint. Mixtures of less than 5% $B(OCH_3)$ in H_2 gave good fractional yields, but above 5%, conversion dropped significantly. Our most successful runs ranged from 45 to 75% conversion to $HB(OCH_3)_2$, with little side products; the trimethoxy compound could be readily recovered. In all cases the microwave power was about 10–20 W/head; higher powers caused significant decomposition and production of large amounts of acetylene.

Production yields under our nearly optimum conditions—for three parallel streams—were as follows (μW power used $\lesssim 30$ W): $B(OCH_3)_3$ processed, 1.1×10^{-3} g/min; H_2 processed, 2.1×10^{-3} g/min; $HB(OCH_3)_2$ produced, 6.6×10^{-4} g/min; $B(OCH_3)_3$ recovered, $\sim 3 \times 10^{-4}$ g/min. No IR absorptions nor mass spectra were detected for $B_2(OCH_3)_4$.

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Registry No. Dimethoxyborane, 4542-61-4; trimethoxyborane, 121-43-7.

Contribution from the Department of Chemistry,
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Crystal and Molecular Structure of Sodium Hydrogen Bis(μ-*ms*-tartrato)-bis(2,2′-bipyridyl)dichromate(III) Heptahydrate: A Di-*ms*-tartrate-Bridged Binuclear Complex with a Short Intramolecular Hydrogen Bond

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and Charles F. Campana

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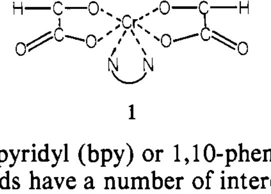
Binuclear ditartrate-bridged chromium(III) complexes (1)



1

containing 2,2′-bipyridyl (bpy) or 1,10-phenanthroline as the nonbridging ligands have a number of interesting features.[2,3]

Table I. Crystal and Intensity Data Collection Summary

mol formula	$C_{28}H_{35}O_{19}N_4NaCr_2$
fw	858.6
a, Å	12.890 (4)
b, Å	10.364 (3)
c, Å	24.996 (6)
β, deg	90.90 (2)
V, Å^3	3339 (2)
Z	4
space group	$P2_1/c$
ρ(calcd), g cm^{-3}	1.71
cryst dimens, mm	0.6 × 0.6 × 0.6
cryst shape	cubelike with faces {110} and {001}
radiation	Mo Kα (λ = 0.710 69 Å)
abs coeff, μ (Mo Kα), cm^{-1}	7.35
temp, °C	−40 ± 3
scan speed, deg min^{-1}	variable, 2.0-15.0
scan range	0.8° below 2θ (Kα_1) to 1.1° above 2θ (Kα_2)
bkgd counting time	0.5(scan time)
stds monitored	2 stds every 50 reflcns
2θ limits, deg	2.0-55.0
reflcns collected	$h,k,\pm l$
no. of reflcns collected	7769
unique reflcns	6444
unique data used	4017 with $F_o^2 > 3\sigma(F_o^2)$
R(*F*)	0.064
$R_w(F)$	0.050

They include the first binuclear systems shown to contain bridging *ms*-tartrate ligands (though systems containing bridging *ms*-tartrate derivatives are now known[4]). For many coordination geometries (but not for octahedral), *ms*-tartrate bridging gives an unfavorable ligand conformation.[5] Furthermore, the presence of strong intramolecular hydrogen bonding in these complexes is indicated[2] by an absence of deprotonation for the monoprotic species below pH 11 and by geometrical calculations which predict a close approach between hydroxyl oxygen atoms—a close approach which may be involved in the facile oxidative cleavage of the bridges by permanganate.[6] The *ms*-tartrate bipyridyl derivative also exhibits an unusual solution UV spectrum which has been explained in terms of different $\pi^* \leftarrow \pi$ transition energies for two chemically distinct pyridyl groups of the bipyridyl ligand.[2] Finally, these complexes are known or expected to exhibit large stereoselectivities.[2] Steric considerations[5] indicate stereospecific formation of only one diastereomer (or enantiomeric pair) among the several possible for each isomeric form of the tartrate ligand used. For the racemic-ligand system, the isomers are ΔΔ(*RR*,*RR*) and ΛΛ(*SS*,*SS*); for the meso-ligand system, β-ΔΔ(*RS*,*RS*) and β-ΛΛ(*RS*,*RS*).[7]

So that our predictions[2] of a binuclear structure, a close intramolecular approach between hydroxyl oxygen atoms, and stereospecific formation of one diastereomer could be confirmed, as well as for the elucidation of the stereochemical features in hopes of relating these to the unusual UV spectrum and to the ligand oxidation reactions, a crystal structure determination on sodium hydrogen bis(μ-*ms*-tartrato)-bis-

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[1] To whom correspondence should be addressed.

[2] Robbins, G. L.; Tapscott, R. E. *Inorg. Chem.* **1976**, *15*, 154. This paper gives incorrect absolute configuration designations for the enantiomers of tartrate. The designations should have been "*d* = *R*,*R*, *l* = *S*,*S*".

[3] Kaizaki, S.; Hidaka, J.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 988.

[4] Marcovich, D.; Tapscott, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 5712.

[5] Tapscott, R. E. *Inorg. Chim. Acta* **1974**, *10*, 183.

[6] Robbins, G. L.; Tapscott, R. E. *Inorg. Chem.* **1981**, *20*, 2343.

[7] These designations differ from those used in preceding papers[2,4] which give the isomers as ΔΔ(*dd*), ΛΛ(*ll*) and β-ΔΔ(*ms*-*ms*), β-ΛΛ(*ms*-*ms*). The change has been made in order to differentiate by absolute configuration (owing to our recent work with tartrate derivatives[4,8]) rather than by the sign of optical rotation.

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Table II. Final Positional Parameters for $Na[HCr_2(\mathit{ms}\text{-tart})_2(bpy)_2]\cdot 7H_2O$

atom	x	y	z
Cr(1)	0.30493 (6)	0.19133 (8)	0.31777 (3)
O(11)	0.2220 (3)	0.1029 (3)	0.3713 (2)
C(11)	0.1160 (3)	0.1369 (5)	0.3731 (2)
C(12)	0.0874 (4)	0.2123 (4)	0.3226 (2)
O(12)	−0.0041 (3)	0.2370 (4)	0.3119 (4)
O(13)	0.1643 (2)	0.2477 (3)	0.2936 (1)
O(21)	0.4286 (2)	0.1388 (3)	0.3535 (1)
C(21)	0.4538 (4)	0.2117 (5)	0.3990 (2)
C(22)	0.4000 (4)	0.3437 (5)	0.3951 (2)
O(22)	0.4271 (3)	0.4329 (3)	0.4246 (1)
O(23)	0.3272 (2)	0.3516 (3)	0.3591 (1)
Cr(2)	0.23943 (6)	0.19356 (8)	0.50623 (3)
O(31)	0.1140 (3)	0.3144 (3)	0.4708 (1)
C(31)	0.0869 (4)	0.2091 (5)	0.4249 (2)
C(32)	0.1404 (4)	0.3407 (4)	0.4291 (2)
O(32)	0.1108 (3)	0.4321 (3)	0.4006 (1)
O(33)	0.2153 (2)	0.3486 (3)	0.4639 (1)
O(41)	0.3223 (3)	0.1026 (3)	0.4538 (1)
C(41)	0.4278 (4)	0.1400 (5)	0.4511 (2)
C(42)	0.4563 (4)	0.2170 (4)	0.5019 (2)
O(42)	0.5469 (3)	0.2427 (3)	0.5119 (1)
O(43)	0.3785 (3)	0.2498 (3)	0.5310 (1)
N(1)	0.3179 (3)	0.0297 (4)	0.2698 (2)
C(13)	0.2943 (4)	−0.0896 (5)	0.2849 (2)
C(14)	0.3170 (4)	−0.1980 (5)	0.2554 (2)
C(15)	0.3691 (4)	−0.1794 (5)	0.2075 (2)
C(16)	0.3942 (4)	−0.0552 (5)	0.1913 (2)
C(17)	0.3685 (4)	0.0470 (5)	0.2236 (2)
N(2)	0.3695 (3)	0.2671 (4)	0.2501 (2)
C(23)	0.3864 (4)	0.3929 (5)	0.2410 (2)
C(24)	0.4316 (4)	0.4378 (5)	0.1955 (2)
C(25)	0.4599 (4)	0.3500 (5)	0.1565 (2)
C(26)	0.4414 (4)	0.2207 (5)	0.1641 (2)
C(27)	0.3951 (4)	0.1821 (5)	0.2108 (2)
N(3)	0.2368 (3)	0.0383 (4)	0.5575 (1)
C(33)	0.2616 (4)	−0.0838 (4)	0.5447 (2)
C(34)	0.2451 (4)	−0.1863 (5)	0.5788 (2)
C(35)	0.2029 (4)	−0.1627 (5)	0.6278 (2)
C(36)	0.1792 (4)	−0.0380 (5)	0.6427 (2)
C(37)	0.1972 (4)	0.0626 (5)	0.6062 (2)
N(4)	0.1739 (3)	0.2758 (4)	0.5727 (1)
C(43)	0.1479 (4)	0.4010 (5)	0.5779 (2)
C(44)	0.1208 (4)	0.4521 (5)	0.6272 (2)
C(45)	0.1245 (4)	0.3764 (5)	0.6718 (2)
C(46)	0.1497 (4)	0.2472 (5)	0.6664 (2)
C(47)	0.1726 (4)	0.1983 (5)	0.6167 (2)
Na	0.3300 (2)	0.5971 (2)	0.4627 (1)
O(51)	0.0475 (3)	0.8755 (3)	0.4581 (1)
O(52)	0.3681 (3)	0.5212 (3)	0.5496 (1)
O(53)	0.0416 (3)	0.5828 (4)	0.7673 (1)
O(54)	0.1526 (3)	0.6385 (4)	0.4765 (1)
O(55)	0.1074 (3)	0.7724 (3)	0.3553 (1)
O(56)	0.1314 (3)	0.5393 (4)	0.2843 (2)
O(57)	0.3004 (3)	0.6422 (4)	0.3704 (2)

(2,2′-bipyridyl)dichromate(III) heptahydrate, $Na[HCr_2(\mathit{ms}\text{-tart})_2(bpy)_2]\cdot 7H_2O$,[9] has been carried out. Though a large number of structures of (±)-tartrate-bridged binuclear complexes have been reported,[10] this is the first report of a structure for a *ms*-tartrate-bridged complex.

Experimental Section

Crystals of $Na[HCr_2(\mathit{ms}\text{-tart})_2(bpy)_2]\cdot 7H_2O$[2] were grown by slow cooling of a solution in a 20:1 mixture of water and ethanol. A low-temperature data collection, summarized in Table I, was carried out on a brown, cubelike crystal coated with epoxy to prevent dehydration. The apparatus used for data collection and the programs and scattering factor source employed in the direct methods structure solution and in the refinement are the same as those described elsewhere.[11] An empirical absorption correction based on psi scans was applied. No corrections for extinction were made.

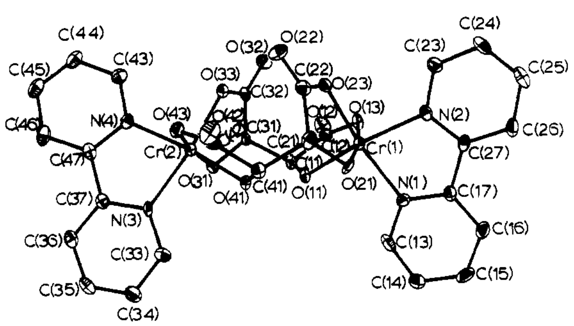

Figure 1. $[HCr_2(\mathit{ms}\text{-tart})_2(bpy)_2]^-$ anion as the β-ΛΛ(*RS*,*RS*) isomer. Thermal ellipsoids are plotted at the 50% probability level. Hydrogen atoms are not shown.

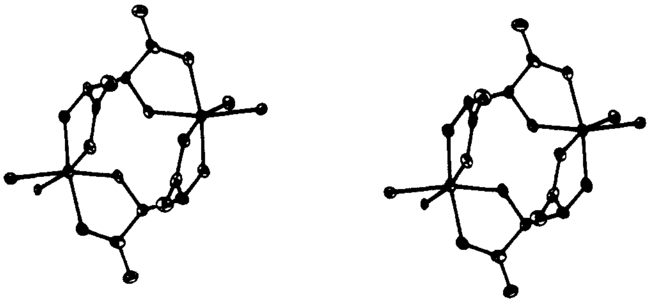

Figure 2. Stereoview of the ditartrate-bridged anion with hydrogen atoms and bipyridyl carbon atoms omitted for clarity.

After solution and partial refinement, hydrogen atoms were fixed on the anion with idealized angles and C–H bond lengths of 0.96 Å. All water hydrogen atoms were fixed at the values determined from a difference map except those on O(53). The positions of these last hydrogen atoms were idealized. A small difference peak was found approximately midway between the two hydroxyl oxygen atoms of the tartrate ligands O(41) and O(11); however, attempts to refine the position of a hydrogen atom, H(1B), placed at this location were unsuccessful. Accordingly a hydrogen atom was fixed midway between these two hydroxyl oxygen atoms. All hydrogen atoms were assigned fixed isotropic thermal parameters of $U_{iso} = 0.05$ Å^2. Nonhydrogen atoms were refined anisotropically. The reflections (011), (−1,0,2), (−7,7,9), (−12,2,16), (−10,3,17), (−5,8,18), and (−7,7,21), whose $|F_o - F_c|/\sigma$ values were greater than 5σ, were not included in the final two cycles of refinement. Final fractional coordinates for the nonhydrogen atoms are given in Table II, where the designations "O(51)"–"O(57)" denote oxygen atoms of water molecules. Tables of thermal parameters, hydrogen positions, complete interatomic distances and angles, selected least-squares planes, selected torsion angles, and observed and calculated structure factors are available as supplementary material.

Results and Discussion

The $[HCr_2(\mathit{ms}\text{-tart})_2(bpy)_2]^-$ anion is located in a general position with two independent tartrate ligands bridging two crystallographically nonequivalent chromium bipyridyl units; however, the complex has an idealized C_2 symmetry with the twofold axis passing between the two tartrate bridges. As expected,[2] the crystal contains a racemic mixture of β-ΛΛ-(*RS*,*RS*) and β-ΔΔ(*RS*,*RS*) isomers. The former isomer is shown in Figures 1 and 2. Selected interatomic distances and angles for this anion are reported in Table III.

As predicted from earlier studies,[2] there is a very close approach (2.418 (6) Å) between two hydroxyl oxygen atoms,

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(9) In a preceding paper,[2] the complexes were given names with the formal ligand charge denoted; however, owing to the apparent presence of strong interligand hydrogen bonding, the assignment of protons to specific ligands is not meaningful. In the present paper the terms "tartrato" and "tart" denote the $C_4H_2O_6$ group (which would be tetranegative if it were not associated with one or more protons).

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(11) Ortega, R. B.; Tapscott, R. E.; Campana, C. F. *Inorg. Chem.* **1982**, *21*, 672.

Table III. Selected Interatomic Distances (Å) and Angles (Deg) for Na[HCr$_2$(*ms*-tart)$_2$(bpy)$_2$]·7H$_2$O with Estimated Standard Deviations

Cr(1)-Cr(2)	4.799 (2)	Cr(1)-O(23)	1.975 (4)
O(11)-O(41)	2.418 (6)	Cr(2)-O(33)	1.946 (4)
O(11)-H(1B)	1.25[a]	Cr(1)-O(13)	1.989 (4)
O(41)-H(1B)	1.22[a]	Cr(2)-O(43)	1.975 (4)
Cr(1)-O(11)	1.954 (4)	Cr(1)-N(1)	2.069 (5)
Cr(2)-O(41)	1.947 (4)	Cr(2)-N(3)	2.057 (5)
Cr(1)-O(21)	1.894 (4)	Cr(1)-N(2)	2.053 (5)
Cr(2)-O(31)	1.932 (4)	Cr(2)-N(4)	2.061 (5)
O(11)-Cr(1)-O(13)	80.7 (1)	N(1)-Cr(1)-N(2)	78.1 (2)
O(41)-Cr(2)-O(43)	81.3 (1)	N(3)-Cr(2)-N(4)	79.0 (1)
O(21)-Cr(1)-O(23)	83.2 (1)	O(11)-H(1B)-O(41)	159[a]
O(31)-Cr(2)-O(33)	83.5 (1)		

[a] Calculated from the difference map peak position for H(1B), the bridging hydrogen atom.

O(11) and O(41), of different tartrate groups and there is very compelling evidence that there exists between these two oxygen atoms a strong and probably symmetric hydrogen bond. This is concluded from considerations of (1) the complex charge, which must be mononegative and therefore requires the presence of a proton, (2) the observation of a difference peak at distances of 1.25 and 1.22 Å from O(11) and O(41), (3) pH titration data[2] which show an unexpectedly low acidity for this complex, (4) the O(11)–O(41) distance which, though not the shortest O–O distance known,[12] is well below the range of 2.50–2.45 Å, which is believed to form the boundary between ordinary and symmetrical hydrogen bonds, [13] and (5) the observation that the Cr–O distances involving the presumably partially protonated hydroxy oxygen atoms (average 1.950 Å) are significantly longer than those involving unprotonated hydroxyl oxygen atoms (average 1.913 Å). An admittedly troubling aspect of this assignment, however, is the absence of any indication of hydrogen bonding in the IR spectra[2] even though other hydrogen-bonded complexes such as oximes with similar short O–O contacts exhibit characteristic O–H–O bending and stretching vibrations.[14]

As found in many other α-hydroxycarboxylate complexes,[10] the coordination distances involving ionized hydroxyl oxygen atoms are significantly shorter than those involving carboxyl oxygen atoms (Table III). The tartrate chain is well staggered with the average dihedral angle of the O–C–C–O fragments containing hydroxyl oxygen and aliphatic carbon atoms being −56.6°. The N–C–C–N torsional angles of 4.0 (5) and 12.2 (5)° for the bipyridyl groups near Cr(1) and Cr(2), respectively, are similar to those found in other bipyridyl complexes.[15]

The low symmetry of the complex, even when idealized, makes possible several interesting comparisons. There are two chemically distinct α-hydroxycarboxylate chelate rings, which can be designated as "O" or "N" depending on whether the coordinated hydroxyl oxygen atom of a ring is trans to an oxygen or a nitrogen atom in the coordination sphere. "N" rings contain hydroxyl oxygen atoms which are apparently involved in hydrogen bonding. The two ring types differ in the O–Cr–O bite angle (averages: "O" rings, 83.4°; "N" rings, 81.0°) and in conformation (average O–C–C–O dihedral angles involving one hydroxyl oxygen atom and one bonded carboxyl oxygen atom: "O" rings, +15.1°; "N" rings, −10.8° for the β-ΛΛ(*RS*,*RS*) enantiomer, where "O" chelate rings contain carbinols of *R* chirality and "N" chelate rings contain carbinols of *S* chirality). Though the UV spectra of the *ms*-tartrate bipyridyl complex has been explained in terms of two chemically distinct pyridyl groups,[2] the crystal structure results do not indicate any significant geometrical differences in the two types of pyridyl groups (trans to a carboxyl oxygen atom or trans to a hydroxyl oxygen atom). Corresponding bond lengths and bond angles and N–Cr coordination distances are the same within experimental error for the two chemically distinct pyridyl fragments.

Acknowledgment. This work was supported by grants from the Minority Biomedical Sciences Program (NIH-DRR 506 RR08139), the National Science Foundation (CH-780921) for purchase of the Syntex P3F and R3 diffractometer and computing systems, and the Research Allocations Committee of the University of New Mexico.

Registry No. NaH[Cr$_2$(*ms*-tart)$_2$(bpy)$_2$]·7H$_2$O, 81244-79-3.

Supplementary Material Available: Tables of thermal parameters hydrogen positions, complete interatomic distances and angles, selected least-squares planes, selected torsion angles, and observed and calculated structure factors (48 pages). Ordering information is given on any current masthead page.

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Electronic Spectra of Titanium(II), Vanadium(II), and Chromium(II) in Anhydrous Hydrogen Fluoride

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UV–visible spectra have been recorded for solutions in anhydrous hydrogen fluoride (AHF) of transition-metal, lanthanide, and actinide cations in "normal" oxidation states by treating suspensions in AHF of the appropriate sparingly soluble fluorides with Lewis acids of the HF system such as BF$_3$,[1] AsF$_5$,[2] or SbF$_5$.[3] Treatment of metallic uranium with HF–BF$_3$ yielded a stable solution containing U^{3+},[3] whereas the corresponding aqueous solution is unstable, with U^{3+} reducing H$_2$O.

This reaction with uranium has led to an extensive program in which d transition elements and lanthanides in the metallic state have been added to pure AHF or to AHF containing Lewis acids of different strengths. Many stable solutions have been obtained and spectra recorded. Frequently the elements have been in unusually low oxidation states, for which the formally corresponding aqueous spectra cannot be observed because the cations concerned reduce water.

This note reports the results of treating metallic Cr, V, and Ti with AHF acidified with Lewis acids. Stable solutions of Cr^{2+} and V^{2+} were obtained as expected with all the Lewis acids BF$_3$, AsF$_5$, and SbF$_5$. With Ti, an orange solution containing Ti^{2+} was prepared when the strong Lewis acid SbF$_5$ was used, even though Ti^{3+} might have been expected. Reaction of Ti with less acidic AHF solutions gave evidence of Ti^{3+} formation as will be discussed later. Work is proceeding currently on the characterization of solid residues from all of these solutions.

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[3] Baluka, M.; Edelstein, N.; O'Donnell, T. A. *Inorg. Chem.* **1981**, *20*, 3279.

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