examination of lattice effects with EPR powder techniques and a variety of further studies are needed. Studies of the temperature dependence of these lattice effects and of the effect of host lattice cation variations are in progress. We have attempted to define some of the possible origins of lattice contributions both to systemize and to stimulate further work.

Appendix

The transformation of the anisotropic temperature factors to root-mean-square displacements along the principal axes of the thermal ellipsoids, given by Messmer and Amma[20] is incorrect. Their Table 4 should be replaced by Table III which refers the thermal ellipsoids to the crystal coordinates *a*, *b*, and *c*. A molecular coordinate system with *z* along the Co–Cl_1 bond, with *y* along the crystalline *b* axis which is approximately parallel to the Co–N_3 bond, and with *x* normal to the *yz* plane coincides with all the thermal ellipsoids of the molecular ion within experimental error and the correlation is indicated in Table III. This information is also illustrated in Figure 2. The fact that the non-symmetry-constrained principal axes of the ellipsoids for Cl_1, N_1, N_3, and N_4 coincide with the molecular axes lends strong credence to these parameters as real properties of the system.

Registry No. $[Cr(NH_3)_5Cl]Cl_2$, 13820-89-8; $[Cr(NH_3)_5Cl]Br_2$, 57255-92-2; $[Cr(NH_3)_5Cl]I_2$, 57255-93-3; $[Cr(NH_3)_5Cl](NO_3)_2$, 57255-94-4; $[Cr(NH_3)_5Br]Cl_2$, 57255-95-5; $[Cr(NH_3)_5Br]Br_2$, 13601-60-0; $[Cr(NH_3)_5Br]I_2$, 57255-96-6; $[Cr(NH_3)_5Br](NO_3)_2$, 57255-97-7; $[Co(NH_3)_5Cl]Cl_2$, 13859-51-3; $[Co(NH_3)_5Cl]Br_2$, 13601-43-9; $[Co(NH_3)_5Cl]I_2$, 37922-32-0; $[Co(NH_3)_5Cl](NO_3)_2$, 13842-33-6; $[Co(NH_3)_5Br]Cl_2$, 13601-38-2; $[Co(NH_3)_5Br]Br_2$, 14283-12-6; $[Co(NH_3)_5Br]I_2$, 14591-70-9; $[Co(NH_3)_5Br](NO_3)_2$, 21333-43-7.

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Tartrate-Bridged Chromium(III) Complexes. Synthesis and Characterization[1]

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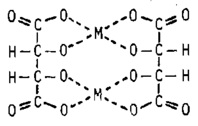
The syntheses and properties of the tartrate-bridged complexes $[Cr_2(tartH)_2L_2]$ and $Na[Cr_2(tart)(tartH)L_2]$ ("tart" = $C_4H_2O_6^{4-}$, "tartH" = $C_4H_3O_6^{3-}$, L = 1,10-phenanthroline or 2,2'-bipyridyl) having either two optically active or two meso bridging ligands are described. The results of formula weight determinations prove a binuclear structure. The *ms*-tartrate derivatives are the first *ms-ms* isomers to be reported for a tartrate-bridged complex and, as predicted from steric considerations, both octahedral coordinations in these *ms-ms* isomers have the same chirality (Δ or Λ). The *ms*-tartrato–bipyridyl complex has been resolved and a ΛΛ absolute configuration assigned to the $(+)_{589}$ enantiomer. Complexes containing two bridging groups of the same enantiomeric configuration are formed in preference to a complex with bridges of opposite chirality. Strong intramolecular hydrogen bonding probably accounts for the low acidity of the tartrato(4–)–tartrato(3–) compounds.

Introduction

The binuclear structure exhibited by a number of tartrate complexes[2–6] has been of interest owing, in part, to the large stereoselective effects observed in molecules having such a geometry[2,7,8] and to the exchange coupling found for some tartrate-bridged metal ion pairs.[9,10] Since varying combinations of tartrate isomers (*d* = *S*,*S*; *l* = *R*,*R*; meso = *R*,*S*) and, in some complexes, a dissymmetric coordination geometry may be present, an extensive isomerism is possible for tartrate-bridged complexes. The relative stabilities of the isomers have been explained in terms of the steric constraints of the binuclear structure and the conformations of the bridging tartrate groups and depend strongly on the coordination geometry.[2]

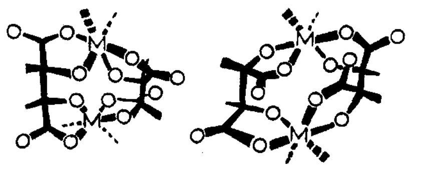


Of particular interest is the stereochemistry of binuclear tartrates containing octahedral metal ions since this geometry is sterically more favorable than tetragonal or trigonal bipyramidal coordinations, the coordination geometries of most of the previously studied tartrate-bridged structures,[3] for *ms*-tartrate bridging.[2,11] No binuclear metallotartrates containing meso bridges have heretofore been reported. Of the 24 isomers possible for tartrate-bridged octahedral complexes, the two enantiomeric pairs ΔΔ(*dd*), ΛΛ(*ll*) and β-ΔΔ(*ms-ms*), β-ΛΛ(*ms-ms*) (Figure 1)[12] are expected to be the energetically most stable.[2,11] The designation "β" distinguishes the more stable enantiomeric pair of bis(meso) isomers from the α pair which has the opposite orientation for the rotationally nonequivalent chiral (*R* and *S*) extremities of the meso bridges. A related structural variation is possible for mononuclear octahedral chelates with meso bidentates.[13]

α

β

In an initiation of a study of the stereochemistry of octa-



ΔΔ(dd) β-ΔΔ(meso-meso)

Figure 1. The isomers predicted to be the most sterically favorable for octahedral tartrate-bridged systems (one enantiomer shown for each). Ligands occupying the fifth and sixth coordination sites are unspecified.

hedral tartrate-bridged complexes, we have prepared *dd* and *ms-ms* binuclear chromium(III) tartrates with two tartrato(3−) bridges and also with one tartrato(3−) and one tartrato(4−) bridge. The remaining coordination sites on chromium(III) are occupied by 1,10-phenanthroline or 2,2′-bipyridyl. The mixed tartrato(3−)–tartrato(4−) *dd* complexes containing 1,10-phenanthroline (as the ammonium salt) and 2,2′-bipyridyl (as the barium salt) have been reported previously.[14] However, that binuclear structures had been assigned to these complexes only from the elemental analyses, CD and absorption spectra, and molecular model considerations[14] warranted a reinvestigation, in particular, a formula weight determination. The remaining complexes have not been previously reported.

Experimental Section

Syntheses. The preparations used herein are modifications of those reported[14] for Ba[Cr$_2$(*d*-tart)(*d*-tartH)(bipy)$_2$]$_2$ and NH$_4$[Cr$_2$(*d*-tart)(*d*-tartH)(phen)$_2$].

Bis(tartrato(3−)) Complexes. To a hot solution of sodium *d*-, *l*-, or mixed *d,l*-tartrate 2-hydrate (11.5 g, 0.050 mole) or of sodium *ms*-tartrate (9.7 g, 0.050 mole) in 150 ml 1:1 DMF–water was added trichloro(dimethylformamide)(2,2′-bipyridyl)chromium(III) ([CrCl$_3$(DMF)(bipy)]) (19.3 g, 0.050 mol) or trichloro(dimethylformamide)(1,10-phenanthroline)chromium(III) ([CrCl$_3$(DMF)(phen)]) (20.6 g, 0.050 mol).[15] The green mixtures were heated to 90°C while stirring to give red solutions (ca. 5 min) and then were allowed to sit on a steam bath for 24 hr during which time crystals separated. The precipitates, which were mixtures of the bis(tartrato(3−)) and tartrato(4−)–tartrato(3−) complexes, were collected after allowing the mixtures to sit overnight and were dissolved in hot solvent. The solvent used was water, methanol, 1:1 DMF–water, or 1:1 methanol–water depending on whether the complex was *ms*-tartrato–bipyridyl; *d*-, *l*-, or *dl*-tartrato–bipyridyl; *ms*-tartrato–phenanthroline; or *d*- or *l*-tartrato–phenanthroline, respectively. The solutions were acidified to pH <1 with hydrochloric acid to bring out the relatively insoluble bis(tartrato(3−)) complexes. The solids were collected, washed with absolute ethanol and ligroin, and air-dried (yields 55–75%). The compounds obtained were di-μ-*d*-tartrato(3−)-bis(2,2′-bipyridyl)dichromate(III) 3.5-hydrate ([Cr$_2$(*d*-tartH)$_2$(bipy)$_2$]·3.5H$_2$O); di-μ-*dl*-tartrato(3−)-bis(2,2′-bipyridyl)dichromate(III) 3.5-hydrate ([Cr$_2$(*dl*-tartH)$_2$(bipy)$_2$]·3.5H$_2$O); (±)-di-μ-*ms*-tartrato(3−)-bis(2,2′-bipyridyl)dichromate(III) 3-hydrate ((±)-[Cr$_2$(*ms*-tartH)$_2$(bipy)$_2$]·3H$_2$O); di-μ-*d*-tartrato(3−)-bis(1,10-phenanthroline)dichromate(III) 3.5-hydrate ([Cr$_2$(*d*-tartH)$_2$(phen)$_2$]·3.5H$_2$O); (±)-di-μ-*ms*-tartrato(3−)-bis(1,10-phenanthroline)dichromate(III) 3-hydrate ((±)-[Cr$_2$(*ms*-tartH)$_2$(phen)$_2$]·3H$_2$O); and the *l*-tartrato analogues.

Mixed-Ligand Tartrato(4−)–Tartrato(3−) Complexes. Sodium salts of the partially deprotonated complexes, with the exception noted below, were prepared by dissolving the bis(tartrato(3−)) complexes in water while adding sodium hydroxide to solubilize the compounds, adjusting the solutions to pH 7–7.5, concentrating the solutions on a rotary evaporator if necessary, and cooling the solutions overnight (3–5°C). The solids were collected, recrystallized from hot 1:1 methanol–water, and air dried. In the preparation of the *d*-tartrato–phenanthroline derivative, 1:1 DMF–water was used as the solvent in both the deprotonation and recrystallization steps. The salts sodium μ-*d*-tartrato(4−)-μ-*d*-tartrato(3−)-bis(2,2′-bipyridyl)dichromate(III) 5-hydrate (Na[Cr$_2$(*d*-tart)(*d*-tartH)(bipy)$_2$]·5H$_2$O); sodium (±)-μ-*ms*-tartrato(4−)-μ-*ms*-tartrato(3−)-bis(2,2′-bipyridyl)dichromate(III) 6-hydrate ((±)-Na[Cr$_2$(*ms*-tart)(*ms*-tartH)(bipy)$_2$]·6H$_2$O); sodium μ-*d*-tartrato(4−)-μ-*d*-tartrato-3−)-bis(1,10-phenanthroline)dichromate(III) 5-hydrate (Na[Cr$_2$-*d*-tart)(*d*-tartH)(phen)$_2$]·5H$_2$O); sodium (±)-μ-*ms*-tartrato(4−)-μ-*ms*-tartrato(3−)-bis(1,10-phenanthroline)dichromate(III) 7.5-hydrate ((±)-Na[Cr$_2$(*ms*-tart)(*ms*-tartH)(phen)$_2$]·7.5H$_2$O); and the *l*-tartrato analogues were obtained in 55–80% yields.

Addition of barium chloride solution in stoichiometric amounts to aqueous solutions of the sodium salts of the appropriate tartrato(4−)–tartrato(3−) complexes gave essentially quantitative yields of the relatively insoluble barium salts (±)-Ba[Cr$_2$(*ms*-tart)(*ms*-tartH)(bipy)$_2$]$_2$·21H$_2$O and (±)-Ba[Cr$_2$(*ms*-tart)(*ms*-tartH)(phen)$_2$]$_2$·12H$_2$O.

Resolution of the *ms*-Tartrato–Bipyridyl Complex. To a solution of (−)-quinine 2-hydrate (1.12 g, 3.10 mmol) in 80 ml of methanol were added 0.179 *M* aqueous H$_2$SO$_4$ (8.84 ml, 1.58 mmol) and Ba[Cr$_2$(*ms*-tart)(*ms*-tartH)(bipy)$_2$]$_2$·21H$_2$O (3.00 g, 1.55 mmol). After being stirred for 0.5 hr, the mixture was filtered to remove barium sulfate and reduced to 40 ml on a rotary evaporator. Addition of acetone brought out a solid which was put back into solution by heating and allowed to crystallize out on cooling. After three recrystallizations from methanol, the material was collected and dried in vacuo at 90°C to give 1.22 g (1.18 mmol) of the quinine salt. Anal. Calcd for [(−)-C$_{20}$H$_{25}$N$_2$O$_2$][Cr$_2$(*ms*-tart)(*ms*-tartH)(bipy)$_2$]: C, 55.71; H, 4.48; N, 8.12. Found: C, 53.96; H, 4.48; N, 8.26. The quinine salt was dissolved in water and the solution was acidified with 1 *M* HCl to give (+)$_{589}$-[Cr$_2$(*ms*-tartH)$_2$(bipy)$_2$]. The solid was put into solution with the addition of aqueous sodium hydroxide to give the deprotonated complex ($\Delta\epsilon = +4.78$ at 533 nm). Attempted resolutions employing quinidine, cinchonidine, α-(2-naphthyl)ethylamine, strychnine, brucine, and amphetamine gave solids with little or no enantiomer separation, as shown by CD of solutions of the precipitates in the visible region. Similarly, all attempts at resolving the *ms*-tartrato–phenanthroline complex failed.

Analyses. Water was determined by weight loss at 90°C in vacuo. Elemental analyses were carried out on the dehydrated compounds. The results are given in Table I.

Characterization. Formula weight determinations on the dehydrated sodium salts of the tartrato(4−)–tartrato(3−) complexes, excluding the *d*-tartrato–phenanthroline derivative, were carried out with a Mechrolab Model 301A vapor pressure osmometer. Aqueous solutions, 0.0133 to 0.0164 *m* in chromium(III), were employed. Various aggregates were assumed and corrections for nonideality and number of ions were applied as discussed elsewhere.[7]

pH titration curves for 1.62 m*M* solutions of the bis(tartrato(3−)) complexes in 1:1 DMF–water (to increase solubility) at 25°C were obtained with an Orion Model 801 pH meter calibrated with pH 6.865 and 4.008 NBS buffers. Carbonate-free aqueous sodium hydroxide was used as a titrant. No attempt was made to apply nonideality corrections in the calculations of the pK_a values.

Ir spectra of hydrated and dehydrated compounds were obtained on a Perkin-Elmer 621 spectrophotometer using cesium iodide pellets. All ir spectral pellets of the dehydrated materials were prepared from ground mixtures of cesium iodide and sample which had been dried for several hours in vacuo at 105°C and were formed in a hot pellet press. Spectra were also obtained for the sodium salts recrystallized several times from 99.8% deuterium oxide. The ir spectra of hydrated and anhydrous sodium bis(oxalato)-2,2′-bipyridylchromate(III) and sodium bis(oxalato)-1,10-phenanthrolinechromate(III)[16] were determined for comparison. Solution circular dichrographs and visible–uv spectra were recorded on a Cary Model 60 spectropolarimeter with circular dichroism attachment and a Cary Model 14RI spectrophotometer, respectively.

Results and Discussion

Syntheses and Properties. The preparations reported previously[14] for the *d*-tartrate complexes give a mixture of the protonated and deprotonated complexes as shown by pH titrations and elemental analyses. Accordingly the synthetic procedures were modified to give the pure protonated complexes first and then the sodium salts of the tartrato(4−)–tartrato(3−) complexes by deprotonation.

The uncharged, acidic bis(tartrato(3−)) complexes, [Cr$_2$(tartH)$_2$L$_2$] (L = bipy or phen), are relatively insoluble in pure water, sparingly soluble in 1:1 DMF–water, and highly soluble in concentrated aqueous acids (apparently owing to the formation of more highly protonated species). The sodium

Table I. Analysis and Appearance of Di-μ-Tartrato Chromium(III) Complexes

	Dehydrated compd								Hydrated compd			
	% Cr		% C		% H		% N			H_2O		
Compd	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Appearance	No.	% calcd	% found
$[Cr_2(d\text{-tartH})_2(bipy)_2]$	14.64	14.32	47.33	47.04	3.12	3.43	7.88	7.87	Red dichroic needles	3.5	8.15	8.23
$[Cr_2(dl\text{-tartH})_2(bipy)_2]$	14.64	*a*	47.33	47.24	3.12	3.22	7.88	7.89	Red dichroic needles	3.5	8.15	8.19
$(\pm)\text{-}[Cr_2(ms\text{-tartH})_2(bipy)_2]$	14.64	14.51	47.33	47.10	3.12	3.27	7.88	7.88	Brown powder	3	7.07	7.25
$(+)_{589}\text{-}[Cr_2(ms\text{-tartH})_2(bipy)_2]$	14.64	*a*	47.33	45.71	3.12	2.96	7.88	7.64	Brown powder	*a*	*a*	*a*
$[Cr_2(d\text{-tartH})_2(phen)_2]$	13.71	13.25	50.67	50.21	2.92	3.32	7.39	7.53	Gray-brown powder	3.5	7.67	7.64
$(\pm)\text{-}[Cr_2(ms\text{-tartH})_2(phen)_2]$	13.71	13.50	50.67	50.51	2.92	3.08	7.39	7.14	Purple-gray powder	3	6.65	6.80
$Na[Cr_2(d\text{-tart})(d\text{-tartH})(bipy)_2]$	14.20	14.20	45.91	45.77	2.89	3.02	7.65	7.47	Red dichroic plates	5	10.95	10.83
$(\pm)\text{-}Na[Cr_2(ms\text{-tart})(ms\text{-tartH})(bipy)_2]$	14.20	14.19	45.91	45.13	2.89	3.10	7.65	7.70	Brown powder	6	12.86	12.87
$Na[Cr_2(d\text{-tart})(d\text{-tartH})(phen)_2]$	13.32	13.51	49.24	49.33	2.71	3.21	7.18	7.69	Dark brown dichroic plates	5	10.35	10.15
$(\pm)\text{-}Na[Cr_2(ms\text{-tart})(ms\text{-tartH})(phen)_2]$	13.32	13.33	49.24	49.55	2.71	2.90	7.18	7.32	Light brown powder	7.5	14.79	14.89
$(\pm)\text{-}Ba[Cr_2(ms\text{-tart})(ms\text{-tartH})(bipy)_2]_2$	13.36	*a*	43.22	42.76	2.72	2.96	7.20	7.05	Red-brown powder	21	19.56	19.58
$(\pm)\text{-}Ba[Cr_2(ms\text{-tart})(ms\text{-tartH})(phen)_2]_2$	12.59	*a*	46.52	46.05	2.56	2.96	6.78	6.39	Green-brown powder	12	11.57	11.58

[a] Not determined.

salts of the deprotonated complexes containing bipyridyl have a relatively high water solubility; however, this is not the case for the phenanthroline derivatives. In particular, $Na[Cr_2(d\text{-tart})(d\text{-tartH})(phen)_2]$ gives a gel on mixing with water. The latter salt is, however, soluble in DMF and DMF–water mixtures, as are the other sodium salts. All of these complexes tend to hydrolyze in aqueous solution, particularly at higher temperatures and at higher pH. The hydrolyses are sufficiently slow, however, that aqueous solution studies can be made with little difficulty.

With the exceptions of $Na[Cr_2(ms\text{-tart})(ms\text{-tartH})(phen)_2]\cdot 7.5H_2O$ and $[Cr_2(ms\text{-tartH})_2(phen)_2]\cdot 3H_2O$, which changed reversibly from gray-brown to greenish-tan and from purple-gray to gray, respectively, no significant color changes occurred upon dehydration.

Formula Weights. Computations[7] employing the vapor pressure osmometry data and assuming a dimeric structure give formula weights for the sodium salts in excellent agreement (less than 3% deviation) with the expected values (Table II). Osmotic coefficients (Φ) of 0.99 are estimated from available data[17] for 1:1 electrolytes having concentrations of 0.00665 to 0.00821 *m*. Similar computations for tetramers (2:1 electrolytes, $\Phi_{est} = 0.96$) and hexamers (3:1 electrolytes, $\Phi_{est} = 0.90$) yield formula weights which deviate from expected values by 28 and 40%, respectively. These results show unambiguously that the complexes are binuclear.

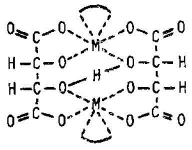
pH Titrations. The bis(tartrato(3–)) complexes are easily deprotonated in solution to give tartrato(4–)-tartrato(3–) compounds. The pK_a values determined in 1:1 DMF–water (Table II) differ little among the various complexes. That the *d*-tartrato complexes are more easily deprotonated than the *ms*-tartrato derivatives could be indicative of a stronger hydroxyl oxygen–metal coordination in the former compounds; however, the probable existence of intramolecular hydrogen bonding (vide infra) makes such a simple interpretation of the pK_a values suspect.

The pH titration curves give no evidence for removal of an additional proton to give the bis(tartrato(4–)) complexes below pH 11. This behavior is in marked contrast to the vanadyl(IV) di-μ-tartrato(4–) complexes which are easily formed at pH ~7.[7] Why the last proton, which is assumed to belong to a coordinated tartrate hydroxyl group, should exhibit such a low acidity is not immediately apparent. The pK_a difference between the first and second ionizations of a diprotic acid with equivalent proton sites (in this case, $[Cr_2(tartH)_2L_2]$) is expected to be no more than 5[18] while we find $pK_2 - pK_1 > 7$. However, a very probable explanation for the large differences between the dissociation constants of the last two potentially acidic protons becomes evident upon an examination of molecular models of these complexes. In both the *dd* (or *ll*) and *ms-ms* structures, hydroxyl oxygen atoms lie so close together that strong intramolecular hydrogen bonds are quite likely. In fact, if the hydroxyl oxygen atoms are assumed to be sp³ hybrids, the lone pairs of the nearest-neighbor hydroxyl oxygens will point toward one another.

Table II. Physical Properties of Di-μ-Tartrato Chromium(III) Complexes

	Formula wt of sodium salt		pK_a of protonated compd
	Calcd	Found	
$Na_nH_{2-n}[Cr_2(d\text{-tart})_2(bipy)_2]$	732	712	3.78
$Na_nH_{2-n}[Cr_2(d\text{-tart})_2(phen)_2]$	781	*a*	3.67
$Na_nH_{2-n}[Cr_2(ms\text{-tart})_2(bipy)_2]$	732	718	3.95
$Na_nH_{2-n}[Cr_2(ms\text{-tart})_2(phen)_2]$	781	767	4.04

[a] Not measured owing to solubility problems.



Geometrical calculations using the average bond parameters assumed in previously reported calculations[2] give predicted hydroxyl oxygen contacts of 2.5 and 2.0 Å in the *dd* and *ms-ms* complexes, respectively. It is noteworthy that these values are equal to or less than the 2.5 Å distance which seems to be an upper limit indicative of the formation of symmetric hydrogen bonds.[18] The distance calculated for the *ms-ms* isomer is somewhat variable owing to nonrigidity of the binuclear structure. Molecular models also indicate that only one intramolecular hydrogen bond between hydroxyl oxygen atoms can be formed at a time in the *dd* isomer, where there are two

Table III. Absorption and Circular Dichroic Spectral Data[a]

$Ba[Cr_2(d\text{-tart})(d\text{-tartH})(bipy)_2]_2$[b]				$Na[Cr_2(d\text{-tart})(d\text{-tartH})(bipy)_2]$				$(+)_{589}\text{-}Na[Cr_2(ms\text{-tart})(ms\text{-tartH})(bipy)_2]$			
Absorption		CD		Absorption		CD		Absorption		CD	
λ, nm	$\epsilon, M^{-1}\ cm^{-1}$	λ, nm	$\Delta\epsilon, M^{-1}\ cm^{-1}$	λ, nm	$\epsilon, M^{-1}\ cm^{-1}$	λ, nm	$\Delta\epsilon, M^{-1}\ cm^{-1}$	λ, nm	$\epsilon, M^{-1}\ cm^{-1}$	λ, nm	$\Delta\epsilon, M^{-1}\ cm^{-1}$
389	316	351	−0.78	387	365	354	−0.75	389	424	353	+1.58
410	229	398	+0.95	410	248	400	+0.91	410	313	403	−0.94
441	126			440	136			442	157		
546	123	544	−5.10	535	129	533.5	−5.03	540	109	533	+4.78

[a] Positions of band maxima are given with absorptivities or circular dichroisms per mole of binuclear complex (two chromium atoms).
[b] Taken from ref 14.

close contacts. The presence of intramolecular hydrogen bonding between adjacent hydroxyl groups of diprotic acids is known to decrease pK_1 and increase pK_2.[19-21] In the binuclear vanadyl(IV) tartrates, where the pK_a difference between the last two proton dissociations is small,[7] the distances between hydroxyl groups[22,23] and the orientations of lone pairs are such that intramolecular hydrogen bonding is much less likely.

Absolute Configurations. Of the several isomers possible for an octahedral bis(*ms*-tartrato) complex, the enantiomeric pair β-ΔΔ(*ms-ms*) and β-ΛΛ(*ms-ms*), having C_2 symmetry, is clearly favored by steric and conformational factors.[2] Moreover, with one exception, the remaining *ms-ms* isomers are expected to have symmetries which preclude optical isomerism. Formation of the (−)-quinine salt proves to be an ideal resolution method for the *ms*-tartrato–bipyridyl complex. Since the ir spectrum of the diastereomeric (−)-quinine salt does not change with recrystallization after the initial recrystallization and since the resolved product isolated exhibits absolute values of molar circular dichroism close to those determined for the very similar and optically pure *d*-tartrato complex (Table III), we conclude that the resolution using (−)-quinine gives an essentially optically pure product. This result contrasts with the negligible resolution of the *ms*-tartrato–bipyridyl complex obtained with a variety of resolving agents other than (−)-quinine and with our inability to resolve the corresponding phenanthroline derivative.

That the CD spectrum of $(+)_{589}\text{-}Na[Cr_2(ms\text{-tart})\text{-}ms\text{-tartH})(bipy)_2]$, which forms the less soluble (−)-quinine salt, is essentially the mirror image of the CD spectrum of the analogous *d*-tartrato complex (Table III) indicates that these two complexes have opposite absolute configurations about chromium(III). Moreover, since the *d*-tartrato binuclear complexes must be ΔΔ owing to steric constraints,[2,14,24] we may assign a ΛΛ absolute configuration to the $(+)_{589}$ isomer of the *ms*-tartrato complex.

CD spectral changes indicate that less than 1% of the resolved *ms*-tartrato–bipyridyl complex racemizes in pH 7.25 aqueous solution at room temperature during a 48-hr period. This complex is expected to be very stable toward intramolecular racemization since either simultaneous inversions must occur at the two chromium(III) sites or a sterically unfavorable[2] ΔΛ intermediate must be formed.

Ir Spectra. There have been relatively few ir spectral studies of α-hydroxycarboxylate complexes and nearly all of those reported[27] involve compounds with un-ionized hydroxyl groups. The following discussion first presents some general observations obtained from spectral comparisons and then advances a limited analysis of some selected regions of the ir spectra.

Our first observation is that the IR spectrum of $[Cr_2(dl\text{-tartH})_2(bipy)_2]\cdot 3.5H_2O$ is identical with that of the corresponding *d*-tartrate derivative. Since large structural differences and, therefore, significant ir spectral differences between *dl* and *dd* (or *ll*) binuclear tartrate-bridged complexes are expected,[2] we conclude that with the racemic ligand an equimolar mixture of *dd* and *ll* isomers is obtained.[27] The mixed-ligand *dl* complex is predicted to have a ligand conformational energy which is significantly higher than that of the *dd* and *ll* isomers for an octahedral coordination geometry.[2,11] In addition, spectral comparisons between hydrated and dehydrated compounds show no indication of any structural changes or decompositions upon dehydration. With the exceptions of intensity changes in water bands, the corresponding spectra are identical. Moreover, with the exceptions of the 500–600 and 3500 cm⁻¹ regions, there are no differences between spectra of protonated and deprotonated complexes. We also note that while the ir spectra of all of the tartrate complexes are roughly similar, there are some striking differences between the *d*-tartrate and *ms*-tartrate derivatives and that these variations do not depend on whether phenanthroline or bipyridyl is present. In fact the similarities between the ir spectra of the bipyridyl and phenanthroline *ms*-tartrates (Table IV) indicate that the isomer present is the same in both cases despite our inability to resolve the latter complex. For similar reasons, we conclude that the structures of the bipyridyl and phenanthroline *d*-tartrates are essentially the same although no formula weight determination was carried out on the latter owing to solubility problems.

Table IV. Some Selected Ir Spectral Bands and Assignments[a]

	Bis(oxalate)		Bis(*ms*-tartrate)		Bis(*d*-tartrate)	
Assignment	Phen	Bipy	Phen	Bipy	Phen	Bipy
			320	323	310	317
ν(CrO)	550	550	510 (?)	510 (?)	540 (vw)	540 (vw)
			548	548	578	578
			575 (vw)	575 (vw)		
			595	595		
ν(CC)			875	875	898	898
			900–950	900–950	924	923
ν(CO), hydroxyl			1090	1090	1120	1120
$\nu(CO_2)$	1380	1378	1360	1358	1355	1355

[a] Positions of band maxima are given in cm⁻¹ for the hydrated sodium salts with assignments of predominant vibrations.

Table IV gives the positions of some selected ir spectral band maxima and their tentative assignments. The broad band at 550 cm⁻¹ in the ir spectra of the complexes $Na[Cr(ox)_2(phen)]$ and $Na[Cr(ox)_2(bipy)]$, which can be assigned to a chromium–oxygen stretch,[28] gives rise to a number of broad, overlapping bands in the spectra of the tartrate complexes (Figure 2). With the possible exception of the 510-cm⁻¹ band of the *ms*-tartrate derivatives, which disappears completely upon protonation and which could correspond to a O–H–O symmetric stretch, the spectral features in the 500–600 cm⁻¹ region can be reliably assigned to chromium–oxygen stretches since (1) the positions and shapes are identical for complexes with the same tartrate isomer regardless of whether phenanthroline or bipyridyl is present and (2) all of the bands exhibit large relative intensity changes upon protonation (Figure 2). The carboxyl oxygen–chromium and un-ionized hydroxyl oxygen–chromium stretching modes are expected to couple strongly;[29] however, the force constant for an ionized hydroxyl oxygen–chromium bond may be higher since it is

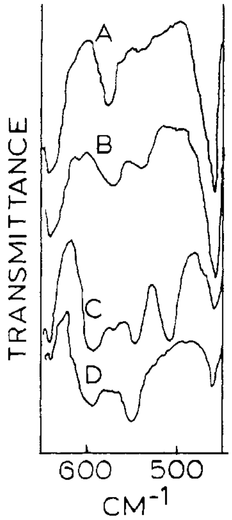


Figure 2. Ir spectra in the Cr–O stretching region of (A) Na[Cr_2(*d*-tart)(*d*tartH)(bipy)$_2$], (B) [Cr_2(*d*-tartH)$_2$(bipy)$_2$], (C) Na[Cr_2(*ms*-tart)(*ms*-tartH)(bipy)$_2$], and (D) [Cr_2(*ms*-tartH)$_2$(bipy)$_2$]. The spectra of the corresponding phenanthroline derivatives in this region are nearly identical.

known that in some α-hydroxy carboxylate complexes, metal ion coordination bonds involving ionized hydroxyl groups are very short, an observation indicative of a strong metal–ligand interaction.[3] The spectral changes upon protonation indicate that the bands at 595 cm^{-1} (*ms*-tartrate complexes) and at 578 cm^{-1} (*d*-tartrate), whose intensities decrease, may correspond primarily to metal–oxygen stretches involving ionized hydroxyl groups. The bands at 310–320 cm^{-1}, which are not present in spectra of the oxalate complexes, could also correspond to a metal–oxygen stretching mode;[29] however, these features exhibit no changes with protonation and their positions do depend on whether phenanthroline or bipyridyl is present.

The carbon–carbon stretching regions[29] are strikingly different for spectra of the two binuclear isomers (Table IV). The *d*-tartrate derivatives exhibit only two spectral bands in this region while the *ms*-tartrate spectra have a band at 875 cm^{-1} and a broad flattened feature in the region 900–950 cm^{-1} apparently owing to several overlapping peaks. The symmetry of a *ms*-*ms* binuclear complex (C_2) is lower than that of the *dd* isomer (D_2).[2] The hydroxyl carbon–oxygen and carboxyl stretching frequencies are similar to those observed in related compounds.[29–32] The lower hydroxyl carbon–oxygen stretching frequency in the *ms*-tartrate complexes may indicate a stronger hydroxyl oxygen coordination in these compounds.

Little information concerning the location and hydrogen bonding of the ligand OH group of the sodium salts is given by the ir spectral studies. The only spectral feature in the 1700–4000 cm^{-1} region attributable to an O–H stretch is a broad band with a maximum at 3450 cm^{-1} found in the spectra of all of the complexes. This band is reduced greatly in intensity upon dehydration; however, it cannot be caused to completely disappear even with special dehydration procedures (Figure 3). It may be that the maxima around 3450 cm^{-1} in the spectra of the dehydrated compounds correspond to residual water or to water picked up during pellet preparation and that the ligand hydroxyl stretching frequency is broadened and shifted by strong intramolecular hydrogen bonding so that it is obscured by the carbon–hydrogen bands in the region 2800–3100 cm^{-1} or even by the broad, intense carbonyl band centered at approximately 1630 cm^{-1}. Carefully prepared dehydrated samples of the chromium oxalate complexes, which contain no ligand hydroxyl groups, exhibit ir spectra with water bands at 3450 cm^{-1} of about the same intensity as those found in spectra of the dehydrated tartrate complexes. That the hydroxyl bands in the spectra of the dehydrated protonated complexes are more intense in all cases than the corresponding bands in the spectra of the dehydrated sodium salts indicates that at least one ligand hydroxyl stretching frequency in the protonated complexes lies at ca. 3450 cm^{-1} and is coincidental with the water band (Figure 3).

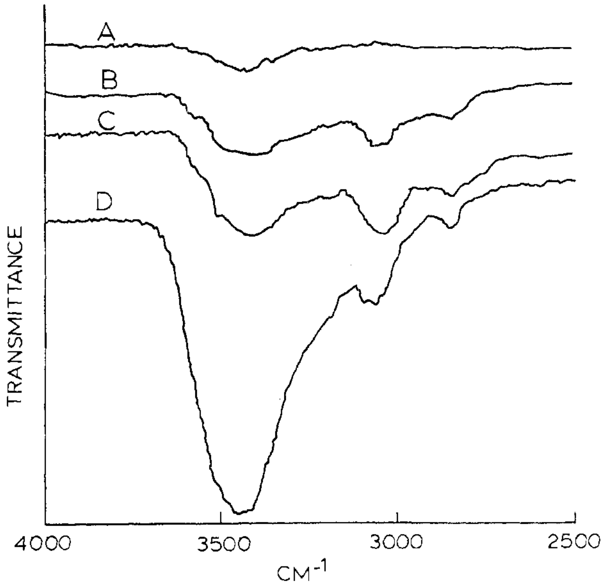


Figure 3. Ir spectra in the O–H stretching region of (A) cesium iodide matrix only, (B) dehydrated Na[Cr_2(*d*-tart)(*d*-tartH)(bipy)$_2$], (C) dehydrated [Cr_2(*d*-tartH)$_2$(bipy)$_2$], and (D) Na[Cr_2(*d*-tart)(*d*-tartH)(bipy)$_2$]·$5H_2O$. Features at 2800–3100 cm^{-1} are assigned as C–H stretching vibrations. The corresponding spectra of the other chromium(III) tartrate derivatives are almost identical.

Ir spectra of the dehydrated sodium salts recrystallized several times from deuterium oxide are identical with corresponding spectra obtained on nondeuterated compounds. It may be that ligand OD groups exchange with atmospheric water or that the ligand hydroxyl stretch is so obscured by other bands that spectral changes cannot be identified. Even with careful handling, the samples recrystallized from deuterium oxide rapidly exchange lattice deuterium oxide with atmospheric water during pellet preparation. Others have reported difficulty with deuterium loss from hydroxyl groups during infrared spectral data collection.[29]

Visible and Uv Absorption Spectra. Aqueous solution absorption spectra of the chromium(III) tartrates, in both the d–d and intraligand + charge-transfer spectral regions are essentially unaffected by the degree of protonation of the complexes. Similarly, the *ms*-tartrato–phenanthroline and *d*-tartrato–phenanthroline complexes, whether protonated or as the sodium salts, exhibit very similar spectra. On the other hand, in the higher energy region, there is a striking difference between absorption spectra of the *d*- and *ms*-tartrates containing bipyridyl. A spectrum of the former complex exhibits a single intense band at 33.0 kK, which can be assigned to an intraligand $\pi^* \leftarrow \pi$ transition,[33] while that of the latter contains two intense bands (and some ill-defined shoulders) at 33.2 and 36.1 kK (Figure 4).

The different number of bands in the $\pi^* \leftarrow \pi$ region of the spectra of the *dd* and *ms*-*ms* isomers of the tartrato–bipyridyl complexes can be explained. These complexes, as do the phenanthroline compounds, contain two coordinating oxygen atoms which lie trans to coordinated nitrogen atoms, and two coordinating oxygen atoms which lie above and below the plane of the heterocyclic ligand. Each member of the latter pair of "out-of-plane" oxygen atoms has the required symmetry to act as a π donor toward one of the metal t_{2g} orbitals which

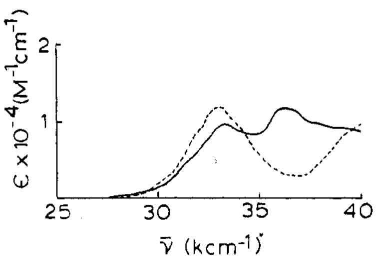


Figure 4. Uv spectra of Na$[Cr_2(d\text{-tart})(d\text{-tartH})(bipy)_2]$ (- - -) and Na$[Cr_2(ms\text{-tart})(ms\text{-tartH})(bipy)_2]$ (–) in aqueous solution, [Cr(III)] = 3 × 10^{-5} *M*. The molar absorptivities are given per mole of Cr(III). The spectra of the corresponding protonated complexes are nearly identical.

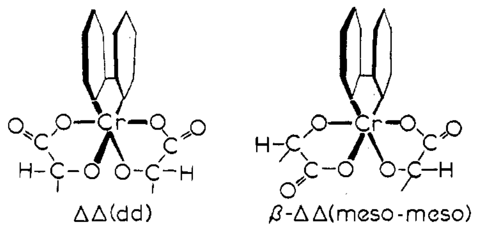
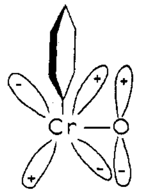


Figure 5. Coordination geometries in the *dd* and *ms-ms* isomers of the tartrato–bipyridyl complex.

is itself capable of π interaction with one of the pyridine rings.



The substitution of an ionized hydroxyl oxygen atom for an out-of-plane carboxyl oxygen atom upon going from the *dd* to the *ms-ms* complex (Figure 5) is expected to increase the π donation to one of the t_{2g} orbitals and, subsequently, to increase its interaction with the π orbitals of one of the pyridyl groups, which are nonequivalent in the *ms-ms* complex.[2] It is expected that this will result in an increase in the energy of the π* orbitals and a decrease in the energy of the π orbitals of the pyridyl moiety.[34] Indeed, it has been observed that the π* ← π transitions of bipyridyl ligands increase in energy as the positive charge on the central metal ion decreases.[34] We propose, therefore, that the two bands observed in the spectrum of the *ms*-tartrato–bipyridyl complex arise from separate π* ← π transitions in nonequivalent pyridyl groups.

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Registry No. $[Cr_2(d\text{-tartH})_2(bipy)_2]$, 57172-74-4; $[Cr_2(dl\text{-tartH})_2(bipy)_2]$, 57129-80-3; (±)-$[Cr_2(ms\text{-tartH})_2(bipy)_2]$, 57172-56-2; $(+)_{589}$-$[Cr_2(ms\text{-tartH})_2(bipy)_2]$, 57129-81-4; $[Cr_2(d\text{-tartH})_2(phen)_2]$, 57129-82-5; (±)-$[Cr_2(ms\text{-tartH})_2(phen)_2]$, 57172-57-3; Na$[Cr_2(d\text{-tart})(d\text{-tartH})(bipy)_2]$, 57129-83-6; (±)-Na$[Cr_2(ms\text{-tart})(ms\text{-tartH})(bipy)_2]$, 57129-84-7; Na$[Cr_2(d\text{-tart})(d\text{-tartH})(phen)_2]$, 57129-85-8; (±)-Na$[Cr_2(ms\text{-tart})(ms\text{-tartH})(phen)_2]$, 57129-86-9; (±)-Ba$[Cr_2(ms\text{-tart})(ms\text{-tartH})(bipy)_2]_2$, 57172-59-5; (±)-Ba$[Cr_2(ms\text{-tart})(ms\text{-tartH})(phen)_2]_2$, 57172-58-4; $[(-)\text{-}C_{20}H_{25}N_2O_2][Cr_2(ms\text{-tart})(ms\text{-tartH})(bipy)_2]$, 57172-75-5; $[CrCl_3(DMF)(bipy)]$, 23807-43-4; $[CrCl_3(DMF)(phen)]$, 23807-44-5.

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