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Isomer Stabilities of Tartrate-Bridged Binuclear Complexes

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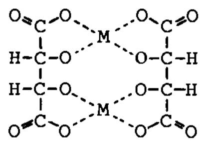
The seven possible isomers for a tetragonal coordination geometry and the twenty-four possible isomers for trigonal-bipyramidal and octahedral geometries are enumerated and described for binuclear tartrate-bridged complexes. Two geometrical parameters corresponding to the strain in the binuclear structure and to the ligand conformation energy have been evaluated as a function of the coordination geometry. Predictions of the relative energies of tartrate-bridged isomers made from these parameters agree with known stability differences when protonation of the tartrate ligand is also considered. An entropy factor of Rln2 contributes to the stabilities of the mixed-ligand isomers. This work indicates that tartrate-bridging may be used to induce known absolute configurations about metal ions for CD studies and for stereochemical correlations and to lock tartrate groups into known conformations for thermochemical determinations of conformational energies.

Introduction

Of the eleven X-ray structure determinations reported to date for tartrate complexes, ten have shown the presence of the binuclear structure



containing bridging tetradentate ligands.[1–6] The presence of binuclear species have also been indicated in several solution studies on metallotartrate systems.[2,7–13]

Since tartaric acid exhibits three isomeric forms (*d, l,* and *meso*), six possible isomers of these 2 :2 bridged complexes – *dd, ll, dl, d–meso, l-meso,* and *meso–meso* – are apparent. Examples of the first three isomers have been reported[2] and work in our laboratory indicates the probable existence of a *meso–meso* isomer also (a chromium(III) tartrate complex[14]). Observed stability differences between isomers of binuclear antimony(III) and vanadyl(IV) tartrates have been explained by qualitative ligand conformational arguments.[2] In the present paper, this conformational analysis is made quantitative and is extended to isomers and coordination geometries not previously considered. The effects on isomer stability of strain in the binuclear structure and entropy of ligand mixing are also evaluated.

Procedure

Nomenclature and Conventions

The absolute configuration of an individual dissymmetric carbon atom is designated by "*R*" or "*S*" following the rules of Cahn, *et al.;*[15] however, an entire tartrate group is labeled "*d*", "*l*", or "*meso*" according to whether it has the *(R,R),(S,S),* or *(R,S)* configuration.[2] The "Δ,Λ" designation for the absolute configuration of an octahedral chelate[16] is extended to include other coordination geometries in which two chelate rings exhibit a chirality. Where necessary, the prefixes α, β, and γ are used in assigning labels to similar isomers.

The dihedral angle for a group of atoms and/or points A–B–C–D is defined as the angle between A–B and C–D as viewed by sighting along B–C. This angle is positive if the near pair must be rotated clockwise to eclipse the far pair.

In general, the degree of ionization of the tartrate ligand is not considered. All point group symmetries assigned are for the ideal case with no distortion.

Isomer Counting

The binuclear structures are considered to be constructed from two "fragments", each containing a metal atom, two five-membered chelate rings, and two carbon–carbon half-bonds. The last elements are linked to combine two fragments to form a dimer. Each fragment contains two dissymmetric carbon atoms and a potentially dissymmetric metal atom. The fragments possible are enumerated by considering all unordered combinations of dissymmetric elements (Figure 1). All combinations of these fragments taken two at a time are then counted noting that two frag-

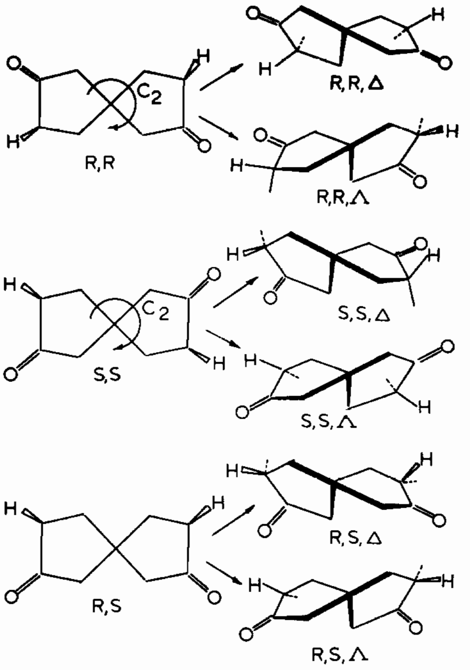
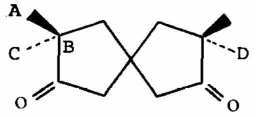


Figure 1. Component fragments for tartrate-bridged structures. The fragments on the left are for a tetragonal coordination geometry; those on the right are for a trigonal-bipyramidal or an octahedral geometry.

ments, neither having a vertical C_2 axis, may be joined in two ways differing by a rotation of 180 deg.

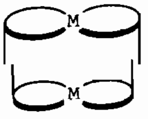
Stability Parameters

It is proposed that the relative energies of two tartrate-bridged isomers are determined by two parameters – the ligand conformation angle, φ, and the "strain angle", Θ. The first parameter, which has been discussed in qualitative terms previously,[2] is the dihedral angle between the vicinal hydrogen atoms of a tartrate group. A staggered (low energy) conformation is indicated by $\varphi = 60$ deg and an eclipsed conformation, by $\varphi = 0$ deg. If the "conformation half-angle" is defined as the dihedral angle between a carbon–hydrogen bond and the extension of a line joining the ends of two carbon–carbon half-bonds, *i.e.* the supplement of the dihedral angle for A–B–C–D in I, φ may be approximated for a binuclear structure by summing the half-angles for the component fragments.



I

The second parameter, Θ, is a measure of the strain induced when two fragments are joined to form a dimer. A completely strain-free structure can be formed only when the carbon–carbon half-bonds of the component fragments meet collinearly. The half-bonds can mismatch owing to differences in distance (II), longitudinal angle (III), or transverse angle (IV).



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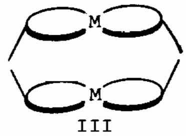

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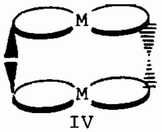
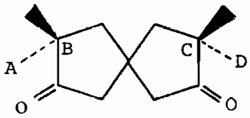


IV

Molecular models indicate that only the last type of mismatch causes any significant strain since any strain induced by the first two types may be relieved by rotation of the carboxyl group. The transverse angle is the dihedral angle between the carbon–carbon half-bonds on opposite sides of a fragment, *i.e.* the dihedral angle for A–B–C–D in V. Unless the transverse angles of two joined fragments are equal in magnitude and sign, there will be some strain in the dimer formed. The strain angle, Θ, of a binuclear structure is defined as the absolute value of the difference between the transverse angles of the component fragments. A value of zero for Θ indicates no strain and the dimer becomes more strained as Θ increases.



V

Calculations

Bond angles and bond lengths (Figure 2) have been taken as suitable mean values of those reported for several tartrate complexes.[2–4,6] Our calculations

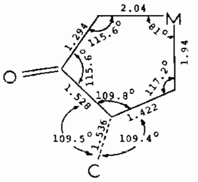
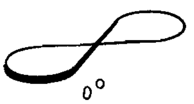


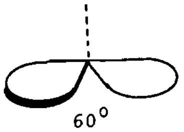
Figure 2. The bonding parameters used in the geometrical calculations.

show that moderate changes in the bonding parameters used do not significantly change the values calculated for the stability parameters and certainly do not affect any conclusions about relative isomer energies.

The rotation of two pentagonal rings relative to each other keeping two of the metal–ligand bonds approximately collinear generates the three coordination geometries which have been observed for tartrate complexes[1–6] – tetragonal (VI), trigonal bipyramidal (VII), and octahedral (VIII). Starting with the basic *(R,R)*, *(S,S)*, and *(R,S)* fragments shown in Figure 1 and using standard geometric formulae, transverse and conformation half-angles have been calculated for both *Δ* and *Λ* rotations from 0 to 120 deg. From these data, values of Θ and φ are calculated for rotations of 0, 60, and 90 deg for the various isomers.



VI



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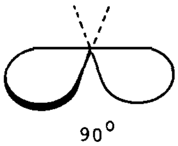

VIII

Results

Conformation half-angles and transverse angles calculated for the fragments as a function of the rotation angle are given in Tables I and II.

The three fragments for a tetragonal coordination geometry can be combined seven ways since the *(R,S)* fragment lacks a twofold rotation axis and can be joined to itself in two ways. Similarly, there are twenty-four possible combinations of the six fragments for a dissymmetric coordination since two of these fragments lack a C_2 axis. The isomers possible for tetragonal, octahedral, and trigonal-bipyramidal geometries are listed in Tables III–V with the calculated values of Θ and φ. Since the component fragments, point group symmetries, and arrangements of carboxyl and hydroxyl oxygen atoms in the coordination sphere are the same for corresponding octahedral and trigonal-bipyramidal isomers, this information is omitted from Table V.

In every case where a high value of the strain angle is given for an isomer in Tables III–V, molecular models indicate that isomer to be strained. Similarly, low values of Θ are found for isomers which models indicate to be relatively unstrained. With only one exception, the conformation angles calculated for isomers with relatively small strain ($\Theta \lesssim 40$ deg) agree well with those predicted from molecular models or determined by X-ray diffraction techniques.[2–6] The calculated value of 76 deg for φ for a tetragonal *dl* isomer (Table III) is somewhat larger than the value of 65 deg predicted from a model or the values of 59 and 57 deg observed for the racemic copper(II)[3] and vanadyl(IV)[17] complexes.

TABLE I. Calculated Conformation Half-Angles (deg).[a]

Geometry	Rotation Angle deg	*(R,R)* Fragmt *Δ*	*(R,R)* Fragmt *Λ*	*(S,S)* Fragmt *Δ*	*(S,S)* Fragmt *Λ*	*(R,S)* Fragmt *Δ(R)*	*(R,S)* Fragmt *Δ(S)*	*(R,S)* Fragmt *Λ(R)*	*(R,S)* Fragmt *Λ(S)*
Tetrag	0	19	19	–19	–19	38	–38	38	–38
	10	19	17	–17	–19	38	–35	35	–38
	20	19	15	–15	–19	38	–32	32	–38
	30	20	13	–13	–20	39	–28	28	–39
	40	21	11	–11	–21	40	–24	24	–40
	50	22	8	–8	–22	42	–20	20	–42
Trig-bipy	60	24	5	–5	–24	43	–15	15	–43
	70	27	2	–2	–27	46	–10	10	–46
	80	30	–1	1	–30	48	–5	5	–48
Octahed	90	35	–4	4	–35	51	1	–1	–51
	100	40	–7	7	–40	54	6	–6	–54
	110	46	–9	9	–46	57	12	–12	–57
	120	52	–12	12	–52	60	18	–18	–60

[a] The half-angles for the *(R,R)* and *(S,S)* fragments are the same for both sides of a fragment; those for the *R* and *S* sides of an *(R,S)* fragment are different.

TABLE II. Calculated Transverse Angles(deg).

Geometry	Rotation Angle deg	(R,R) Fragmt Δ	(R,R) Fragmt Λ	(S,S) Fragmt Δ	(S,S) Fragmt Λ	(R,S) Fragmt Δ	(R,S) Fragmt Λ
Tetrag	0	25	25	–25	–25	0	0
	10	19	32	–32	–19	–7	7
	20	13	40	–40	–13	–13	13
	30	8	47	–47	–8	–19	19
	40	3	54	–54	–3	–25	25
	50	–2	61	–61	2	–32	32
Trig-bipy	60	–7	68	–68	7	–38	38
	70	–12	76	–76	12	–45	45
	80	–18	83	–83	18	–52	52
Octahed	90	–24	90	–90	24	–59	59
	100	–32	98	–98	32	–67	67
	110	–40	105	–105	40	–75	75
	120	–49	113	–113	49	–82	82

TABLE III. Tetragonal Tartrate-Bridged Isomers with Component Fragments, Calculated Conformation Angles, Strain Angles, and Geometry.

Isomer[a]	Component Fragments	φ,deg	Θ,deg	Point Group	Geometry[b]
dd	*(R,R) + (R,R)*	+38	0	D_2	*trans,trans*
ll	*(S,S) + (S,S)*	–38			
dl	*(R,S) + (R,S)*	+76,–76	0	C_{2h}	*cis,cis*
d–meso	*(R,R) + (R,S)*	–19 *(meso)*,+57 *(d)*	25	C_1	*cis,trans*
l–meso	*(S,S) + (R,S)*	+19 *(meso)*,–57 *(l)*			
cis–meso–meso	*(R,S) + (R,S)*	0	0	C_{2v}	*cis,cis*
trans–meso–meso	*(R,R) + (S,S)*	0	50	C_{2h}	*trans,trans*

[a] Enantiomeric pairs are indicated by brackets. [b] Relative positions of the coordinated carboxyl and hydroxyl oxygen atoms about each of the two metal atoms in a dimer.

TABLE IV. Octahedral Tartrate-Bridged Isomers with Component Fragments, Calculated Conformation Angles, Strain Angles, and Geometry.

Isomer[a]	Component Fragments	φ,[b]deg	Θ,deg	Point Group	Geometry[c]
		dd and *ll* Isomers			
ΔΔ(dd)	*(R,R,Δ) + (R,R,Δ)*	+70	0	D_2	CC,CC
ΛΛ(ll)	*(S,S,Λ) + (S,S,Λ)*	–70			
ΛΛ(dd)	*(R,R,Λ) + (R,R,Λ)*	–8	0[d]	D_2	HH,HH
ΔΔ(ll)	*(S,S,Δ) + (S,S,Δ)*	+8			
ΔΛ(dd)	*(R,R,Δ) + (R,R,Λ)*	–	114	C_2	CC,HH
ΔΛ(ll)	*(S,S,Λ) + (S,S,Δ)*	–			
		dl Isomers			
ΔΔ(dl)	*(R,S,Δ) + (R,S,Δ)*	+2*(l)*,+102*(d)*	0	C_2	HC,HC
ΛΛ(dl)	*(R,S,Λ) + (R,S,Λ)*	–2*(d)*,–102*(l)*			
ΔΛ(dl)	*(R,S,Δ) + (R,S,Λ)*	–	118	C_i	HC,HC
		d–meso and *l–meso* Isomers			
ΔΔ(d–meso)	*(R,R,Δ) + (R,S,Δ)*	+86 *(d)*,+36*(meso)*	35	C_1	CC,HC
ΛΛ(l–meso)	*(S,S,Λ) + (R,S,Λ)*	–86*(l)*,–36*(meso)*			
ΛΛ(d–meso)	*(R,R,Λ) + (R,S,Λ)*	–55*(meso)*,–5*(d)*	31[d]	C_1	HH,HC
ΔΔ(l–meso)	*(S,S,Δ) + (R,S,Δ)*	+55*(meso)*,+5*(l)*			

TABLE IV. (Cont.)

Isomer[a]	Component Fragments	φ,[b]deg	Θ,deg	Point Group	Geometry[c]
α-ΔΛ(d–meso)	*(R,R,Δ) + (R,S,Λ)*	–	83	C_1	CC,HC
α-ΔΛ(l–meso)	*(S,S,Λ) + (R,S,Δ)*	–			
β-ΔΛ(d–meso)	*(R,R,Λ) + (R,S,Δ)*	–	149	C_1	HH,HC
β-ΔΛ(l–meso)	*(S,S,Δ) + (R,S,Λ)*	–			
		meso–meso Isomers			
α-ΔΛ(meso–meso)	*(R,R,Δ) + (S,S,Λ)*	0	48	C_{2h}	CC,CC
β-ΔΛ(meso–meso)	*(R,R,Λ) + (S,S,Δ)*	–	180[d]	C_{2h}	HH,HH
γ-ΔΛ(meso–meso)	*(R,S,Δ) + (R,S,Λ)*	–	118	C_i	HC,HC
α-ΔΔ(meso–meso)	*(R,R,Δ) + (S,S,Δ)*	+39	66	C_2	HH,CC
α-ΛΛ(meso–meso)	*(R,R,Λ) + (S,S,Λ)*	−39			
β-ΔΔ(meso–meso)	*(R,S,Δ) + (R,S,Δ)*	+52	0	C_2	HC,HC
β-ΛΛ(meso–meso)	*(R,S,Λ) + (R,S,Λ)*	−52			

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[a] Brackets indicate an enantiomeric pair. [b] Conformation angles are given only for isomers with strain angles less than 70 deg (arbitrary). For larger values of Θ, the calculations for φ become inexact. [c] The atoms *trans* to each other about each metal atom are given. "H" and "C" denote, respectively, hydroxyl and carboxyl oxygen atoms. [d] Short nonbonded contact.

TABLE V. Trigonal-Bipyramidal Tartrate-Bridged Isomers with Calculated Conformation Angles and Strain Angles.

Isomer[a]	φ,[b]deg	Θ,deg
	dd and *ll* Isomers	
ΔΔ(dd)	+48	0
ΛΛ(ll)	−48	
ΛΛ(dd)	+10	0[c]
ΔΔ(ll)	−10	
ΔΛ(dd)	–	75
ΔΛ(ll)	–	
	dl Isomers	
ΔΔ(dl)	+86*(d)*, −30*(l)*	0
ΛΛ(dl)	−86*(l)*, +30*(d)*	
ΔΛ(dl)	–	76
	d–meso and *l–meso* Isomers	
ΔΔ(d–meso)	+67*(d)*, +9*(meso)*	31
ΛΛ(l–meso)	−67*(l)*, −9*(meso)*	
ΛΛ(d–meso)	+20*(d)*, −38*(meso)*	30
ΔΔ(l–meso)	−20*(l)*, +38*(meso)*	
α–ΔΛ(d–meso)	+39*(d)*, −19*(meso)*	45
α–ΔΛ(l–meso)	−39*(l)*, +19*(meso)*	
β–ΔΛ(d–meso)	–	106
β–ΔΛ(l–meso)	–	
	meso–meso Isomers	
α-ΔΛ(meso–meso)	0	14
β-ΔΛ(meso–meso)	–	136
γ-ΔΛ(meso–meso)	–	76
α-ΔΔ(meso–meso)	+19	61
α-ΛΛ(meso–meso)	−19	
β-ΔΔ(meso–meso)	+28	0
β-ΛΛ(meso–meso)	−28	

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[a] Brackets indicate an enantiomeric pair. [b] Conformation angles are given only for isomers with strain angles less than 70 deg (arbitrary). For larger values of Θ, the calculations become inexact. [c] Short nonbonded contacts.

Discussion

Tetragonal Coordination Geometry (Table III)

The relative contributions of the strain angle and conformation angle to the energy of an isomer are difficult to assess. Certainly for a tetragonal geometry, a *dl* isomer is expected to have the lowest energy and is, in fact, the most stable of the bridged isomers in the tetragonal-pyramidal vanadyl(IV) system.[2] Moreover, only a *dl* complex has been isolated for square-planar copper(II).[3] That all of the *meso*-tartrate-containing tetragonal isomers are predicted to be either strained or to have unfavorable ligand conformations explains the apparent nonexistence of binuclear *meso*-tartrate complexes in both the vanadyl(IV)[2] and copper(II)[18] systems.

If the rotation barrier for a tartrate bridge can be assumed to be threefold symmetric and the same for both active and *meso* ligands, conformational energies of the tetragonal isomers in terms of V_0, the barrier height, can be calculated. From the equation $E = 1/2\ V_0\ (1 + \cos 3\varphi)$[19] and the values of φ in Table III, conformational energies of 0.3 V_0 *(dl),* 0.6 V_0 *(dd* and *ll),* 0.7 V_0 *(d–meso* and *l–meso),* and 2.0 V_0 *(meso–meso)* are calculated for one mole of dimeric molecules. Using the observed difference of 1.5 kcal/mol between the enthalpies of the *dd* and *dl* vanadyl(IV) tartrates[20] and the reported conformation angles of 42 and 39 deg for the *dd* isomer[2] ($E = 0.5\ V_0$) and 58 deg for the *dl* isomer[17] ($E = 0.0\ V_0$), we calculate a value of 3 kcal/mol for V_0.

Octahedral Coordination Geometry (Table IV)

Only one X-ray structure determination has been reported for an octahedral tartrate-bridged complex – that of copper(II) *d*-tartrate(2–) 3-hydrate.[6] The isomer found was $\Delta\Delta$ *(dd),* which is predicted from the values of the stability parameters to be the most favorable of the *dd* isomers. The same isomer has been proposed for two chromium(III) *d*-tartrate species with 2,2′-dipyridyl and 1,10-phenanthroline completing the coordination spheres, and the CD spectra of these complexes have been interpreted accordingly.[7,21]

Pressure-jump kinetic studies carried out by Hoffmann and coworkers[8,9] indicate the formation of binuclear nickel(II) tartrate complexes containing two ligands of the same enantiomeric form and $\Delta\Delta$ *(dd),* $\Lambda\Lambda$ *(ll)* bridged structures have been proposed. The absence of a racemic complex in these studies was attributed to strain as indicated by molecular models; however, apparently only the $\Delta\Lambda$ *(dl)* isomer, shown in Figure 2 of ref 9, was considered. There are clearly two other possible *dl* isomers, both of which are strain-free but contain nearly eclipsed bridging ligands.

The kinetic studies on nickel(II) tartrates also indicate no formation of a *meso-meso* dimer. This structure has been ruled out on the grounds that a *meso*-tartrate group does not allow bridging.[9] This conclusion is not in accordance with our results, which show both the β-$\Delta\Delta$ *(meso–meso)* and β-$\Lambda\Lambda$ *(meso–meso)* isomers to be strain-free and to have favorable ligand conformations. There is, however, another explanation for the observed absence of *meso–meso* nickel(II) tartrates. The complexes studied by Hoffmann and coworkers presumably contain tartrate(2–) ligands with the hydroxyl groups protonated. Molecular models indicate that in both the β-$\Delta\Delta$ *(meso–meso)* and β-$\Lambda\Lambda$ *(meso–meso)* isomers there will be a close contact between two of the hydroxyl protons. That nonbonded repulsions are expected in these protonated structures may also explain the absence of a binuclear complex in the crystal structure of octahedral copper(II) *meso*-tartrate(2–).[6] In our laboratory, we have prepared octahedral chromium(III) complexes with *meso*-tartrate(3–) and *meso*-tartrate (4–) ligands and these now appear to be bridged structures, although characterizations are still in progress.[14] Molecular models show that of the remaining octahedral tartrate-bridged isomers, only the already strained $\Delta\Lambda$ *(dl)* isomer should have similar close contacts between hydroxyl protons.

Trigonal-Bipyramidal Coordination Geometry (Table V)

Tartrate-bridged complexes with this geometry have been qualitatively discussed elsewhere.[2] The results in Table V are in complete accordance with the instabilities of trigonal-bipyramidal antimony(III) *dl* (disproportionates to *dd* and *ll*) and *meso–meso* binuclear tartrates and with the observed distortion of the coordination geometry (towards trigonal-bipyramidal) in the vanadyl(IV) *dd* complex.[2] As predicted, all of the crystal structures[2,4,5] of trigonal-bipyramidal *dd* complexes have shown only the $\Delta\Delta$ *(dd)* isomer.

Entropy Contributions

Solvation, vibration, and translation entropy differences should be negligible for a series of isomers having the same charge and metal ion. On the other hand, statistical factors may contribute significantly to the stabilities of mixed-tartrate *(dl, d–meso,* and *l–meso)* complexes. For these mixed isomers, entropy contributions of $R\ln 2$ are calculated from either the symmetry numbers[22] or the probabilities of formation.[23]

Conclusions

The stabilities of tatrate-bridged binuclear complexes have been quantitatively analyzed in terms of two geometrical parameters (the ligand conformation angle and the strain angle) and a statistical factor (the entropy of ligand mixing). The results of this analysis permit predictions of not only the most stable isomers in tartrate-bridged systems but also of their detailed geometries. Potential applications are given below.

1. The ability to accurately assign absolute configurations to dissymmetric metal ions in 2:2 tartrate-bridged complexes extends the applicability of tartrate compounds in circular dichroic[7,12,24,25] and chemical[26] correlations of absolute configuration.

2. We have illustrated the use of bridged complexes in thermochemical determinations of ligand conformational energies. Similar determinations have been made using other complex systems.[27]

3. Knowledge of the detailed conformations of bridging tartrate groups may permit the use of binuclear tartrate complexes as "conformational locks"[28] for studies on NMR correlations of ligand conformation.

Acknowledgements

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References and Footnotes

1 X-ray structure determinations reported to date are two for VO^{2+}, six for Sb^{3+}, and three for Cu^{2+}. Only copper(II) *meso*-tartrate(2–) 3-hydrate exhibits a nondimeric structure in the solid state.[6]

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