balance[16] between strain and conversion of a terminal hydrogen to a bridge using an adjacent vacant orbital is apparently fairly even in B_2H_4. Both polarization functions and correlation corrections are usually required to exhibit the correct relative energies of isomers in this situation. When both of these effects are included, the instability of the nonclassical nonplanar 2010 (C_{2v}) structure over the classical nonplanar 0012 (D_{2d}) structure is reduced from 32.6 to 1.5 kcal/mol. The formation of the two hydrogen bridges does increase the BB overlap and population as compared with values for the 0012 (D_{2d}) isomer (Table III). However, the Mulliken charges of bridge and terminal hydrogen atoms are distorted by the change from one boron neighbor (terminal) to two boron neighbors (bridge). Hence, care must be used in relating these charges to the chemistry.

Because of the complexity of the potential energy surface we do not present a detailed reaction pathway between the two most stable isomers. Study of this pathway is left to the future.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8210536) for support of this research. Support of the computing center through Grant PCM 77 11398 is also acknowledged.

Registry No. B_2H_4, 18099-45-1.

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Notes

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Characterization and Structure of $[H_7O_3]^+[As(catecholate)_3]^-\cdot p$-Dioxane

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Although the "hydronium" salt of the catecholate (cat) complex of arsenic, $H[As(C_6H_4O_2)_3]\cdot nH_2O$, has been known since early in this century,[1] its structure has remained uncharacterized. It was originally assumed to be a bis chelate complex with a monodentate protonated-catechol ligand and a coordinated water ligand,[2] although a tris chelate structure was also considered. The latter formulation was strengthened when the complex anion was resolved into enantiomers with use of alkaloid bases.[3] The kinetics of the loss of optical rotation of acidic solutions of the complex were later studied,[4] and in the pH region below the acid dissociation constant for the complex ($pK_a = 2.75$) it was concluded that the apparent racemization was due to hydrolysis. Circular dichroism studies of the resolved complexes[5,6] supported the formulation as a tris chelate (at least for the potassium salt). Finally, the crystal structure of the resolved potassium salt $(-)_{585}$-$K[As(cat)_3]\cdot 1.5H_2O$ showed this structure to be a tris chelate complex in the Δ conformation.[7]

The nature of the "hydronium" salt has remained a mystery, particularly since the salt is a relatively weak acid that slowly hydrolyzes under acidic conditions. In principle, this interaction could range from a strong hydrogen bond, leaving the tris complex relatively undistorted, to actual protonation of a catechol oxygen, resulting in a phenolate mode of coordination for one of the catechol ligands, as has been observed in other catechol complexes.[8,9] We present here a structural characterization of the salt $[H_7O_3]^+[As(cat)_3]^-\cdot p$-diox ($p$-diox = p-dioxane), which clearly establishes the tris(catecholate) formulation as a hydronium tight ion pair.

Experimental Section

Arsenic was used in the form of $As_2O_5\cdot xH_2O$ (Mallinckrodt). It was analyzed for arsenic by the procedure of Vogel,[10] found to be 86.4% As_2O_5 by weight, and used as obtained. Catechol (Crown-Zellerbach) was recrystallized from benzene. Elemental analyses were performed by the Microanalytical Laboratory, Department of Chemistry, University of California, Berkeley, CA.

The complex was prepared with use of a scaled-down version of the procedure of Ryschkewitsch and Garret.[11] Crystallization was carried out by dissolving 200 mg of crude product in a solution of 10:1 p-dioxane/H_2O. Slow evaporation led to the formation of large platelike crystals of acceptable quality. Anal. Calcd for $[H_7O_3][As(C_6H_4O_2)_3]\cdot C_4H_8O_2$: C, 48.72; H, 5.02; As, 13.81. Found: C, 48.87; H, 4.99; As, 14.8.

Table I. Crystallographic Data

formula	$[H_7O_3][As(C_6H_4O_2)_3]\cdot C_4H_8O_2$	space group	$P2_1/c$
mol wt	542.2	Z	4
a, Å	16.299 (1)	ρ_{calcd}, g cm^{-3}	1.490
b, Å	14.457 (1)	ρ_{obsd}, g cm^{-3}	1.49 (1)
c, Å	10.320 (1)	radiation (λ, Å)	Mo Kα (0.71073)
β, deg	98.81 (1)	abs coeff, μ, cm^{-1}	14.55
V, Å^3	2410.0 (6)		
		cryst dimens, mm	0.45 × 0.25 × 0.21

Data Collection[a]	
h,k,l ranges	±19,±17,0–12
2θ range, deg	3–50
no. of reflecns	8829
no. of unique reflecns	4261
R for averaging intens, %	2.1
Refinement	
no. of reflecns with $F_o^2 > 3\sigma(F_o^2)$, n_{obsd}	2815
no. of variables, n_{var}	312
extinction coeff	2.8 (2) × 10^{-7}
R, %	2.94
R_w, %	3.75
goodness of fit (GOF)[b]	1.92

[a] At ambient temperature (23 °C); for details see ref 12. [b] GOF = $[\sum w(|F_o| - |F_c|)^2/(n_{obsd} - n_{var})]^{1/2}$.

X-ray Crystallography

Crystal fragments suitable for X-ray diffraction were cleaved from the large crystals and mounted on glass fibers with epoxy. A thin coating of epoxy was applied to the crystal to prevent its decomposition in air. Crystal density was measured by flotation in hexane/CCl_4. Crystal quality assessment and initial space group and lattice constant determinations were made from precession photographs. The cell volume and

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Table II. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B, Å^2
As	0.26021 (2)	0.07563 (2)	0.00574 (3)	3.648 (6)
O1	0.1587 (1)	0.0764 (1)	0.0649 (2)	4.01 (5)
O2	0.2204 (1)	0.1700 (1)	-0.1048 (2)	4.10 (5)
O3	0.2995 (1)	0.1541 (1)	0.1396 (2)	4.05 (5)
O4	0.3604 (1)	0.0834 (1)	-0.0503 (2)	4.29 (5)
O5	0.2905 (1)	-0.0216 (1)	0.1153 (2)	4.04 (5)
O6	0.2243 (1)	-0.0053 (1)	-0.1251 (2)	4.05 (5)
O1W	0.2415 (1)	0.1632 (2)	-0.3688 (2)	6.81 (7)
O2W	0.1569 (1)	0.0012 (2)	0.3083 (2)	6.65 (7)
O3WA	0.2656 (2)	0.0251 (3)	-0.5127 (3)	7.9 (1)
O3WB	0.2805 (5)	0.0943 (6)	-0.5644 (8)	7.1 (2)*
O1D	0.0156 (1)	0.0499 (2)	0.3907 (2)	5.23 (6)
O2D	0.4185 (2)	0.0130 (2)	0.4804 (3)	13.3 (1)
C1D	-0.0473 (2)	-0.0177 (2)	0.3784 (3)	5.27 (9)
C2D	0.0270 (2)	0.0894 (2)	0.5184 (3)	5.78 (9)
C3D	0.5287 (3)	-0.0383 (5)	0.4065 (6)	19.7 (2)
C4D	0.4558 (3)	-0.0417 (4)	0.4000 (5)	15.6 (2)
C11	0.1023 (2)	0.1270 (2)	-0.0180 (3)	3.38 (6)
C12	0.1358 (2)	0.1786 (2)	-0.1094 (3)	3.53 (6)
C13	0.0863 (2)	0.2318 (2)	-0.1988 (3)	4.19 (7)
C14	0.0023 (2)	0.2318 (2)	-0.1967 (3)	4.97 (8)
C15	-0.0315 (2)	0.1812 (2)	-0.1067 (3)	5.19 (8)
C16	0.0185 (2)	0.1271 (2)	-0.0144 (3)	4.28 (7)
C21	0.3837 (2)	0.1654 (2)	0.1450 (3)	3.87 (7)
C22	0.4167 (2)	0.1261 (2)	0.0425 (3)	3.94 (7)
C23	0.5000 (2)	0.1306 (2)	0.0380 (3)	4.89 (8)
C24	0.5501 (2)	0.1778 (3)	0.1378 (3)	6.05 (9)
C25	0.5168 (2)	0.2171 (3)	0.2378 (4)	6.14 (9)
C26	0.4326 (2)	0.2115 (2)	0.2441 (3)	4.91 (8)
C31	0.2689 (2)	-0.1016 (2)	0.0522 (3)	3.65 (7)
C32	0.2309 (2)	-0.0930 (2)	-0.0791 (3)	3.60 (7)
C33	0.2037 (2)	-0.1686 (2)	-0.1504 (3)	4.35 (7)
C34	0.2157 (2)	-0.2547 (2)	-0.0924 (3)	5.27 (8)
C35	0.2541 (2)	-0.2629 (3)	0.0339 (3)	5.15 (9)
C36	0.2807 (2)	-0.1867 (2)	0.1078 (3)	4.37 (7)

[a] Atoms marked with an asterisk were refined with isotropic thermal parameters. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

density (assuming $Z = 4$) supported the formulation of the salt as determined by elemental analysis. Lattice constants and other crystal data are presented in Table I. A redundant set of intensity data related by the crystallographic mirror plane was collected ($\pm h,\pm k,+l$).[12] The crystal orientation remained constant (angular deviation of standards less than 0.1°) through 92% of the data collection, but the crystal orientation had to be redetermined for collection of the last 8% of the data. During the 146 h of X-ray exposure the intensity of three standards measured every 2 h decreased by 4.2% and a linear decay correction was applied. ψ scans collected near $\chi = 90°$ showed a range in transmission coefficients of about 11%, and an empirical absorption correction, based on the ψ-scan data, was applied to all the data. Averaging the data resulted in 4261 unique reflections, with an agreement factor for the averaged intensities of 2.1%. This value was assigned to the factor p in the weighting scheme used during the structure refinement.[12]

Structure Solution and Refinement

The structure was solved by conventional methods, the structure being refined on only the 2815 data with $F_o^2 > 3\sigma(F_o^2)$. Catechol and dioxane hydrogens were assigned idealized positions with isotropic thermal factors. Other hydrogen atoms were assigned positions corresponding to peaks in the ΔF map and were not refined. The central atom of the disordered oxonium cation was modeled by two alternate positions (labeled O3WA and O3WB in Table II and Figure 2) with occupancies of 70 and 30%. A single proton position was assigned to a persistent peak in the ΔF map between O3WA, O3WB, and O2D. Refinement was concluded when the largest shift/error was 18%. Final agreement factors for refinement of 310 atom parameters, scale factor, and extinction coefficient[13] are $R = 2.94\%$ and $R_w = 3.78\%$. The largest peaks in the final ΔF map had densities of less than 0.35 e/Å^3 (comparable to a hydrogen atom) and were located near the disordered atoms O3WA and C3D.

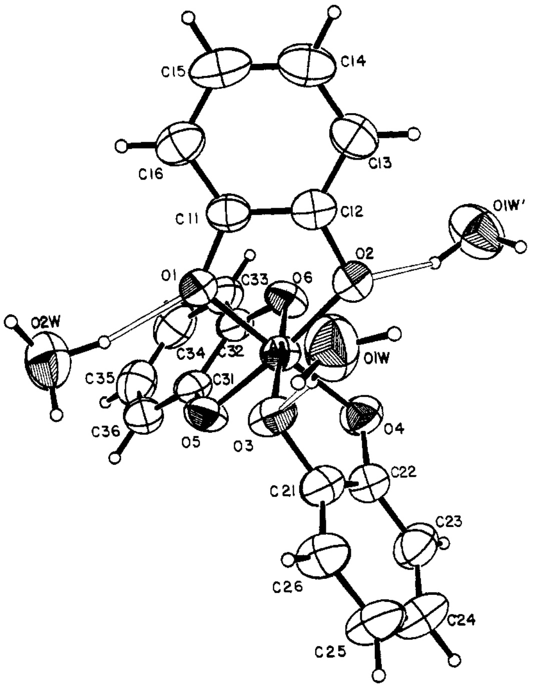

Figure 1. ORTEP drawing of the As(cat)$_3^-$ moiety, including the hydrogen bonds to O1W and O2W. Ellipsoids are drawn at the 50% probability level.

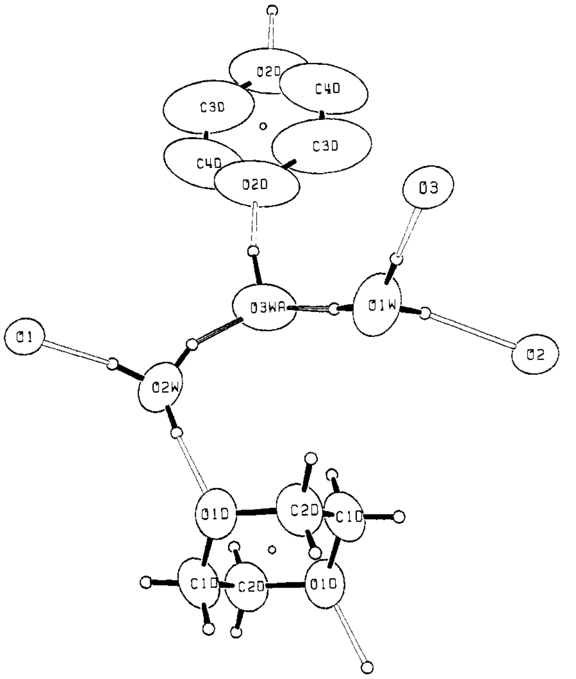

Figure 2. ORTEP drawing of the $H_7O_3^+$ cation and its hydrogen bonding to the dioxane molecules and the catechol oxygens of the As(cat)$_3^-$ complex. O3WB has been omitted for clarity. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are shown with a 0.1-Å radius at the positions of peaks in the ΔF map.

Discussion

Atomic coordinates and bond lengths and angles are presented in Tables II and III. Hydrogen atom parameters, anisotropic thermal parameters, least-squares planes, and structure factors are deposited as supplementary material (Tables IV–VII).

[As(cat)$_3$]$^-$. The [As(cat)$_3$]$^-$ complex in the hydronium salt (Figure 1) shows remarkably little structural perturbation from

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[12] Data collection parameters and data reduction programs are as described in: Eigenbrot, C. W., Jr.; Raymond, K. N. *Inorg. Chem.* **1982**, *21*, 2653.

[13] Stout, G. H.; Jensen, L. H. "X-ray Structure Determination"; Macmillan: New York, 1968; p 412, eq 17.16.

Table III. Distances (Å) and Angles (deg) in $[H_7O_3][As(cat)_3]\cdot C_9H_8O_2$[a]

$[As(cat)_3]^-$ Complex

atom 1	atom 2	dist	av	atom 1	atom 2	dist	av
As	O1	1.849 (1)		O4	C22	1.370 (2)	
As	O2	1.839 (1)		O5	C31	1.355 (3)	
As	O3	1.830 (1)		O6	C32	1.359 (3)	
As	O(H-bonded)		1.839 (8)	O	C(all)		1.368 (8)
As	O4	1.817 (1)		C*n*1[b]	C*n*2		1.390 (12)
As	O5	1.830 (2)		C*n*2	C*n*3		1.368 (4)
As	O6	1.819 (1)		C*n*3	C*n*4		1.386 (9)
As	O(all)		1.831 (11)	C*n*4	C*n*5		1.364 (4)
O1	C11	1.370 (2)					
O2	C12	1.377 (2)					
O3	C21	1.375 (2)					
O	C(H-bonded)		1.374 (3)				

atom 1	atom 2	atom 3	angle	av	atom 1	atom 2	atom 3	angle	av
O1	As	O2	87.21 (6)		O1	As	O3	88.52 (6)	
O3	As	O4	88.53 (6)		O1	As	O5	88.36 (6)	
O5	As	O6	89.08 (7)		O1	As	O6	92.68 (7)	
O	As	O(bite)		88.3 (8)	O2	As	O4	90.32 (6)	
					O2	As	O6	88.87 (7)	
O1	As	O4	176.05 (7)		O3	As	O5	89.16 (7)	
O2	As	O5	175.03 (6)		O4	As	O5	94.22 (7)	
O3	As	O6	177.84 (7)		O4	As	O6	90.35 (7)	
O	As	O(trans)		176 (1)	O	As	O		90 (2)
					As	O	C		110.1 (2)
					O	C*n*1	C*n*2		115.1 (2)
					O	C*n*1	C*n*6		124.1 (4)
					C	C	C		120.0 (3)

$[H_7O_3]^+$ Cation

atom 1	atom 2	dist	atom 1	atom 2	dist
O1W	O3W	2.564 (4)	O1W	O3WB	2.424 (8)
O2W	O3WA	2.382 (3)	O2W	O3WB	2.609 (7)

atom 1	atom 2	atom 3	av	atom 1	atom 2	atom 3	av
O1W	O3WA	O2W	113.6 (1)	O1W	O3WB	O2W	110.7 (3)

Hydrogen Bonding

atom 1	atom 2	dist	atom 1	atom 2	dist
O1W	O2	2.800 (2)	O2W	O1D	2.670 (3)
O1W	O3	2.818 (3)	O3WA	O2D	2.509 (4)
O2W	O1	2.744 (2)	O3WB	O2D	2.520 (8)

atom 1	atom 2	atom 3	angle	av	atom 1	atom 2	atom 3	angle	av
As	O1	O2W	115.82 (7)		O1	O2W	O3WA	122.75 (10)	
As	O2	O1W	119.52 (8)		O1	O2W	O3WB	97.97 (17)	
As	O3	O1W	119.22 (7)		O3WA	O2W	O1D	106.86 (11)	
As	O(cat)	OW		118 (2)	O3WB	O2W	O1D	109.83 (18)	
O2	O1W	O3	91.55 (7)		O	O2W	O		109 (8)
O2	O1W	O3WA	130.11 (11)		O1W	O3WA	O2W	113.65 (14)	
O3	O1W	O3WA	132.54 (10)		O1W	O3WA	O2D	108.21 (14)	
O2	O1W	O3WB	155.79 (20)		O2W	O3WA	O2D	126.31 (16)	
O3	O1W	O3WB	106.62 (19)		O	O3WA	O		116 (8)
O	O1W	O		123 (22)	O1W	O3WB	O2W	110.68 (27)	
					O1W	O3WB	O2D	112.45 (28)	
					O2W	O3WB	O2D	116.59 (32)	
					O	O3WB	O		113 (3)

[a] Standard deviations are calculated as the greater of $\sigma(\bar{x}) = [(1/n(n-1))\sum_{i=1}^{n}(x_i - \bar{x})^2]^{1/2}$ or $\sigma(\bar{x}) = [\sum_{i=1}^{n} 1/\sigma_i^2]^{-1/2}$. [b] The *n* stands for catechol ring 1, 2, or 3. Only the average geometry of all three rings is reported.

that of the potassium salt;[7] the symmetry of the complex is approximately D_3. As in the earlier structure, hydrogen bonding plays a role. Three of the catecholate oxygens are involved in H-bonding: O1···O2W = 2.744 (2) Å; O2···O1W = 2.800 (2) Å; O3···O1W = 2.818 (3) Å. The average As–O distance for hydrogen-bonded oxygens is 1.839 (10) Å compared to 1.822 (7) Å for those not H-bonded. This difference is relatively small, *less* than that seen in other tris(catecholate) structures exhibiting strong H-bonding.[9,14] There is no indication of a tendency toward protonation or dissociation of the ligands. The average As–O distance is about that expected from the ionic radii of As(V) and O^{2-}.[15]

The twist angle[16] of 55.6° and the ligand bite are essentially the same as reported for the potassium salt and fit very well with the trend established for tris(catecholate) complexes. Consideration of the tris(catecholate) structures involving d^0, d^5 (high spin), and d^{10} metals results in an empirical expression for the twist angle (ϕ) as a function of the bite (b = O–O/M–O): ϕ =

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(14) Cooper, S. R.; Koh, Y. B.; Raymond, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 5092.

(15) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751.

(16) The twist angle is defined as the chelate O–M–O angle in a planar projection of the molecule viewed down the threefold axis. The angle is 60° for an ideal octahedron and 0° for a trigonal prism.

(113°)*b* − 102°.[17] The value calculated for this structure, based on a bite of 1.292, is 55.4°.

The bond length alternation in the C–C distances of catechol rings seen in other complexes also occurs here (Table III); each ring also exhibits a slight bending along the O–O vector. The dihedral angles between the O–As–O plane and the catechol planes are 14.7 and 11.2° for the ligands involved in H-bonding, while the third ligand shows an angle of only 4.3°. The bending along the O–O vector is not due simply to steric effects or hydrogen bonding; ligand O1···O2, which is hydrogen bonded on both oxygens, has the largest dihedral angle, but the hydrogen bonds are on *opposite* sides of the plane.[18-21]

$H_7O_3{}^+$ Cation. There are many structural reports on oxonium ($H_{2n+1}O_n{}^+$) cations.[22-28] The most common is the $H_5O_2{}^+$ aggregate,[24] which has been characterized by neutron diffraction. However, $H_7O_3{}^+$ [27-29] and $H_9O_4{}^+{}_{24}$ structures have also been reported. The structure and environment of the cation in this compound are shown in Figure 2 and show a distinct $H_7O_3{}^+$ unit. The proton positions have not been well determined, but presumably the structure is the same as that found for $H_7O_3{}^+$ cations characterized by neutron diffraction. The O–O bond lengths and O–O–O angles in this $H_7O_3{}^+$ salt are consistent with earlier reports. A recent tabulation of data from neutron diffraction studies of hydrogen bonding in crystalline hydrates sets the average OH–O distance at 2.8 (1) Å.[30]

The asymmetric unit also contains two unique half *p*-dioxane molecules. These are centered at two inversion centers (0, 0, $^1/_2$ and $^1/_2$, 0, $^1/_2$). The first dioxane (O1D···C2D) fits in the packing arrangement very nicely. The bond distances and angles are nominal, and the torsion angles average 56.8°. It is hydrogen bonded to O2W. The second dioxane molecule exhibits very large thermal motion. It appears that this is coupled with the disorder of O3WA/B, to which it is hydrogen bonded. The bond distances are consequently poor, and the torsion angles are anomalously low (25.6°). Models assuming disorder, with alternate chair conformations, were not successful in improving the fit to the data; the structure does not allow sufficient room for a well-ordered, hydrogen-bonded arrangement for this conformer.

Conclusion

This structure exemplifies the stability of the $[M(cat)_3]^{n-}$ coordination complex, particularly for a formal +5 ion. Structures have been reported containing cations ranging from amines to simple alkali metals to the oxonium ion (the present case). Conditions for the crystallizations are equally varied. For trivalent metal ions such as Fe^{3+}, full complexation by the weakly acidic catechol ligand occurs only at high pH (0.1 M KOH has been a typical host solution[18]) while for the oxoanions of metals (or metalloids) in very high oxidation states the complexation reaction occurs in acid as

$$MO_4{}^{n-} + 3H_2cat + 2H^+ \rightarrow [M(cat)_3]^{2-n} + 4H_2O$$

Examples of the latter are As(V), Mo(VI), P(V), Si(IV), V(IV), and Ti(IV). The structural features of the resultant $[M(cat)_3]^{n-}$ complexes are remarkably consistent and predictable (e.g. the twist angle from assumed M–O and O–O distances). The present structure, though originally formulated as a protonated complex with an alternate mode of coordination, is no exception. Even under extremely acidic conditions, the complex retains a fully coordinated tris(catecholato) structure with essentially D_3 symmetry.

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Registry No. $[H_7O_3][As(C_6H_4O_2)_3]\cdot p$-dioxane, 100447-63-0.

Supplementary Material Available: Hydrogen atom parameters for $[H_7O_3][As(cat)_3]\cdot C_4H_8O_2$ (Table IV), temperature factor expressions (*B*'s) (Table V), least-squares planes (Table VI), and structure factors for $[H_7O_3][As(cat)_3]\cdot p$-$C_4H_8O_2$ (Table VII) (27 pages). Ordering information is given on any current masthead page.

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(17) Borgias, B. A.; Barclay, S. J.; Raymond, K. N. *J. Coord. Chem.*, in press.

(18) It appears that this bend is a consequence of (1) the tetrahedral (sp^3) hybridization of the oxygen atoms (stabilized by hydrogen bonding), (2) the rigid As–O bonds, and (3) the constraints imposed by the octahedral packing of the oxygen atoms around the As. In fact, the M–O–C bond angle tends to be about 110° for all metal catecholates, while the O–C1–C2 angle is always compressed with respect to the ideal 120° angle (112° in $[P(cat)_3]^-$ to 118° in $[Fe(cat)_3]^{3-}$).[19,20] In free catechol the O–O distance is 2.72 Å compared to the shorter distances found in most of the metal complexes, and the O–C1–C2 angle is about 120°.[21] The bend arises from rotation of the oxygen–metal vector out of the plane of the catecholate ligand in order to accommodate the constraints described above. For example, consider the O–M–O geometry if the whole metal–chelate moiety is assumed to be planar and the ligand geometry is assumed to be the same as the free ligand. Such a hypothetical structure results in a calculated M–O distance of 2.15 Å and an O–M–O angle of 81.1°. In order to fit metals of smaller size the ligand distorts and a rotation of the O–M vector out of the ligand plane occurs, resulting in a dihedral angle between the O–M–O and ligand planes.

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Anisotropic Exchange in Bibridged Copper(II) Dimers: A Topological Approach

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The magnetostructural correlations represented quite an important step in the history of molecular magnetism.[2] They allowed one to specify the main factors governing the sign and the magnitude of the isotropic interaction between two metal ions. They are at the origin of several concepts that have been utilized to design polymetallic systems exhibiting predictable magnetic properties.[3] The best established correlation concerns bibridged copper(II) dimers, particularly the bis(μ-hydroxo) complexes.[4]

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