

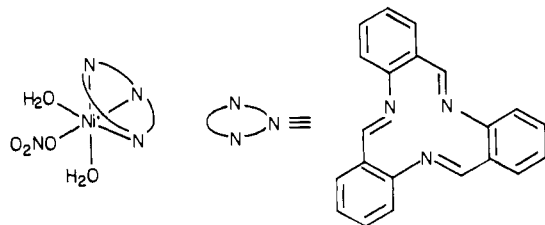
Methyl-Substituted Tribenzo[*b,f,j*][1,5,9]triazacyclododecine with Copper(II) Ion: A Dynamic Jahn-Teller Effect

Robert I. Sheldon,^{1a} Alan J. Jircitano,^{1a} Mark A. Beno,^{1b} Jack M. Williams,^{1b} and
Kristin Bowman Mertes*^{1a}

Contribution from the Department of Chemistry, University of Kansas, Lawrence, Kansas 66045,
and The Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439.
Received August 2, 1982

Abstract: The tridentate macrocyclic ligand (MeTRI) derived from the Schiff base condensation of 2-amino-5-methylbenzaldehyde forms a bis complex with copper(II) that exhibits a dynamic Jahn-Teller distortion. The complex crystallizes in the cubic space group *Pa*3 with $a = 16.445$ (5) Å at 105 K and $Z = 4$. The structures were determined at 298 and 105 K. D_3 site symmetry at the copper ion is achieved by its coordination to two MeTRI ligands. The immediate coordination sphere of the copper ion consists of six symmetry-equivalent nitrogen atoms (Cu-N = 2.058 (6) Å). Although no phase transition was observed at low temperature, the coordinated nitrogen atoms exhibited the large thermal anisotropies often associated with a dynamic Jahn-Teller distortion.

Macrocyclic ligands are noted for often imparting to their complexes exciting and unusual chemistry, which can be evidenced in increased stabilities with respect to ligand dissociation or uncommon metal ion oxidation states. As an example, consider the nickel(II) complex of the cyclic tridentate ligand derived from *o*-aminobenzaldehyde, tribenzo[*b,f,j*][1,5,9]triazacyclododecine (TRI).²⁻⁴ Too small to completely surround the metal ion, the ligand instead occupies three of the octahedral coordination sites:³



Despite the fact that the ligand does not completely encircle the metal ion, the complex is extremely inert toward substitution to the extent that salts of $\text{Ni}(\text{TRI})(\text{H}_2\text{O})_3^{2+}$ can be resolved into optical isomers.⁴ Furthermore, the optically pure compounds are inert toward racemization. This stabilization phenomenon has been termed "multiple juxtapositional fixedness" by Busch and co-workers.⁵ Complexes of TRI have been reported for nickel(II),^{2-4,6,7} cobalt(II),^{8,9} and vanadyl ion,¹⁰ but attempts to isolate copper(II) TRI complexes have thus far proven unsuccessful.^{6,11,12}

Thus the isolation of a copper(II) complex of a similar tridentate ligand (MeTRI) derived from 2-amino-5-methylbenzaldehyde was indeed serendipitous. Without question, however, the most interesting aspect of the complex is the high site symmetry of the bis(MeTRI) complex determined by X-ray crystallographic

Table I. Crystal Data for $[\text{Cu}(\text{MeTRI})_2][\text{BF}_4]_2$

formula	$\text{CuB}_2\text{F}_8\text{N}_6\text{C}_{48}\text{H}_{42}$	$\text{CuB}_2\text{F}_8\text{N}_6\text{C}_{48}\text{H}_{42}$
M_r	940.08	940.08
space group	<i>Pa</i> 3	<i>Pa</i> 3
unit cell: a , Å	16.621 (7)	16.445 (5)
Z	4	4
ρ_{calcd} , g cm ⁻³	1.360	1.404
ρ_{obsd} (flotation CCl ₄ /C ₆ H ₁₄)	1.35 (1)	
crystal dimens, mm	0.6 × 0.6 × 0.5	0.6 × 0.6 × 0.6
temp, K	298	105
radiatn	Mo K α	Mo K α
diffractometer	Syntex P2 ₁	Syntex P2 ₁
μ , cm ⁻¹	5.74	5.93
check reflections	6,0,0; 0,4,8; 6,0,4	6,0,0; 6,0,4; 2,3,4; 0,4,8; 2,4,0; 1,7,1
2θ range, deg	2.0-45.0	4.0-40.0
no. of indep reflections	1011	705
no. with $I > 3\sigma(I)$	755	548
final R_1	0.090	0.062
final R_2	0.113	0.056

methods. The observed D_3 symmetry requires an E_1 ground state in contradiction to the Jahn-Teller theorem, which prohibits orbitally degenerate ground states. Although the highest symmetry that should be possible for d^9 copper(II) complexes is tetragonal, a number of higher site symmetries, notably T_h and D_3 , have been observed as a result of time-averaged distortions arising from electronic-vibronic coupling.^{13,14} These dynamic Jahn-Teller distortions have been studied by a variety of techniques including EPR and X-ray crystallography.^{13,14} It has also been established that by lowering the temperature, the dynamic distortions can be "frozen out". The results of two crystallographic structure determinations for $[\text{Cu}(\text{MeTRI})_2][\text{BF}_4]_2$, at 298 and 105 K, are reported herein.

Experimental Section

Physical Measurements. Infrared spectra were recorded from 4000 to 400 cm⁻¹ on a Perkin-Elmer Model 421 grating spectrophotometer as KBr pellets.

Synthesis of $[\text{Cu}(\text{MeTRI})_2][\text{BF}_4]_2$. All chemicals used were reagent grade. The copper(II) complex was prepared by using the diacid salt of the tetrameric condensate of 2-amino-5-methylbenzaldehyde, $[\text{H}_2(\text{Me}-$

- (1) (a) University of Kansas. (b) Argonne National Laboratory.
- (2) Melson, G. A.; Busch, D. H. *J. Am. Chem. Soc.* **1965**, *87*, 1706-1710.
- (3) Fleischer, E. B.; Klem, E. *Inorg. Chem.* **1965**, *4*, 637-642.
- (4) Taylor, L. T.; Busch, D. H. *J. Am. Chem. Soc.* **1967**, *89*, 5372-5376.
- (5) Busch, D. H.; Farmery, K.; Goedken, V.; Katovic, V.; Melnyk, A. C.; Sperati, C. R.; Tokel, N. *Adv. Chem. Ser.* **1971**, No. 100, 44-78.
- (6) Taylor, L. T.; Vergez, S. C.; Busch, D. H. *J. Am. Chem. Soc.* **1966**, *88*, 3170-3171.
- (7) Taylor, L. T.; Busch, D. H. *Inorg. Chem.* **1969**, *8*, 1366-1371.
- (8) Cummings, S. C.; Busch, D. H. *J. Am. Chem. Soc.* **1970**, *92*, 1924-1929.
- (9) Wing, R. M.; Eiss, R. *J. Am. Chem. Soc.* **1970**, *92*, 1929-1934.
- (10) Hawley, G.; Blinn, E. L. *Inorg. Chem.* **1975**, *14*, 2865-2867.
- (11) Melson, G. A.; Busch, D. H. *Proc. Chem. Soc.* **1963**, 223-224.
- (12) Melson, G. A.; Busch, D. H. *J. Am. Chem. Soc.* **1964**, *86*, 4834-4837.

(13) Hathaway, B.; Duggan M.; Murphy, A.; Mullane, J.; Power, C.; Walsh, A.; Walsh, B. *Coord. Chem. Rev.* **1981**, *36*, 267-324 and references within.

(14) Bertini, I.; Gatteschi, D.; Scozzafava, A. *Coord. Chem. Rev.* **1979**, *29*, 67-84 and references within.

TAAB)] $[\text{BF}_4]_2$.¹⁵ A solution of the diacid salt (0.4 g, 0.6 mmol) in 5 mL of methanol was heated to reflux. The color of the solution changed slowly from deep red to pale yellow after refluxing for 1 h. $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.13 g, 0.6 mmol) was added to this solution as a solid followed by refluxing for 12 h. The resulting dark green solution was filtered to give an orange powder, $[\text{Cu}(\text{MeTRI})_2][\text{BF}_4]_2$, which was rinsed with methanol and ether; yield 15% based on the diacid salt. (The major product of the reaction, $[\text{Cu}(\text{MeTAAB})][\text{BF}_4]$, could be isolated from the remaining green filtrate.) Crystals suitable for X-ray analysis were obtained by slow evaporation of an acetonitrile solution of the complex; IR (cm^{-1}) 3025, 2920, 1624, 1568, 1495, 1370, 1300, 1254, 1219, 1070, 877, 828.

X-ray Data. Preliminary precession photographs indicated cubic symmetry ($m\bar{3}$) with the systematic absence $0kl$, $k \neq 2n$, indicative of space group $Pa\bar{3}$. That the crystals showed no evidence of extinction when examined under a polarizing microscope further corroborated the presence of cubic symmetry. Unit cell parameters were obtained by a least-squares fit of 15 reflections well distributed in reciprocal space. Data were collected as previously described for both room temperature¹⁶ and low-temperature (105 K)¹⁷ data sets with Syntex P2₁ diffractometers. Crystal data information is listed in Table I. Room temperature data were collected for one-half of an octant (1.5 data sets for hkl , $k \geq h$) and low-temperature data for a full octant. Symmetry-related reflections were averaged. Check reflections monitored every 97 reflections showed slight decay for which a decay correction was applied. No absorption correction was made for room temperature data. The low-temperature data were corrected for absorption; however, the variation in the transmission factor was less than 2%.

Solution and Refinement. The structure was determined from the room temperature data set. The position of the copper ion was located from a three-dimensional Patterson synthesis at the special position ($1/2, 1/2, 1/2$) at the center of symmetry on the 3-fold axis. Subsequent Fourier maps revealed the positions of the remaining non-hydrogen atoms. The BF_4^- anion was located with B and F(1) on the 3-fold axis. The remaining fluorides were related to F(2) by the 3-fold rotation. During initial refinement, the B and F(1) atoms shifted to chemically unreasonable positions, with unusually large thermal parameters. The disorder in the ion could not be fit to various models attempted, however, so the positions of the B and F(1) were fixed, and the thermal parameters of B and F(2) were allowed to vary anisotropically. F(1) gave an anisotropic thermal parameter that spread electron density along the 3-fold axis, so it was varied isotropically. Hydrogen atom positions were calculated at a distance of 1.0 Å from their atom of attachment or located from a difference map. Thermal parameters were fixed at 1.0 Å² greater than the isotropic thermal parameter of the atom of attachment. Hydrogen atoms were then included as fixed contributions. Refinement was performed as previously described,^{15,16} converging at $R_1 = 0.090$ and $R_2 = 0.113$ where $R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$. A final difference map showed a small residual electron density at special positions.

For the low-temperature data set the final positional and thermal parameters from the room temperature data were refined. The disorder problem in the anion disappeared; thus the positional and anisotropic thermal parameters of the entire anion were refined. Again hydrogen atoms were included as fixed contributions. Refinement converged at $R_1 = 0.062$ and $R_2 = 0.056$. In order to rule out the presence of a lower symmetry, the structure was also refined in $Pbca$, the space group that results upon deletion of the 3-fold axis from $Pa\bar{3}$. Refinement proceeded to convergence at $R_1 = 0.063$ and $R_2 = 0.056$ in the orthorhombic space group. The structural parameters for the complex obtained from the orthorhombic space group were essentially identical within error limits with those of the cubic analogue, indicating that the symmetry is indeed cubic. Final positional parameters for non-hydrogen atoms are listed in Table II. Structure factor calculations, anisotropic thermal parameters for non-hydrogen atoms, and positional and thermal parameters for hydrogen atoms are available as supplementary material. Results from both data sets are included in these and subsequent tables for comparison purposes.

Results and Discussion

The isolation of a copper(II) complex with the tridentate macrocycle derived from 2-amino-5-methylbenzaldehyde was clearly unexpected due to the previous unsuccessful attempts to achieve such a complex with unsubstituted *o*-aminobenz-

Table II. Final Positional Parameters for $[\text{Cu}(\text{MeTRI})_2][\text{BF}_4]_2$

atom	x	y	z
A. Data at 298 K			
Cu	0.5000	0.5000	0.5000
N	0.5115 (4)	0.3780 (4)	0.4694 (4)
C(1)	0.4834 (5)	0.3234 (5)	0.5286 (5)
C(2)	0.5279 (5)	0.2534 (6)	0.5509 (6)
C(3)	0.5012 (6)	0.2015 (6)	0.6083 (6)
C(4)	0.4202 (7)	0.2176 (6)	0.6447 (6)
C(5)	0.3890 (7)	0.1555 (6)	0.7065 (7)
C(6)	0.3761 (5)	0.2815 (5)	0.6218 (5)
C(7)	0.4060 (5)	0.3362 (5)	0.5657 (5)
C(8)	0.3534 (5)	0.4055 (6)	0.5407 (6)
B	0.1400	0.1400	0.1400
F(1)	0.1880	0.1880	0.1880
F(2)	0.1606 (6)	0.1628 (8)	0.0703 (6)
B. Data at 105 K			
Cu	0.5000	0.5000	0.5000
N	0.5107 (4)	0.3788 (4)	0.4705 (4)
C(1)	0.4821 (5)	0.3226 (5)	0.5300 (5)
C(2)	0.5281 (5)	0.2543 (6)	0.5521 (5)
C(3)	0.4977 (6)	0.2000 (5)	0.6105 (5)
C(4)	0.4214 (6)	0.2125 (6)	0.6449 (5)
C(5)	0.3868 (5)	0.1516 (5)	0.7066 (5)
C(6)	0.3757 (5)	0.2793 (5)	0.6220 (5)
C(7)	0.4063 (5)	0.3366 (5)	0.5658 (5)
C(8)	0.3526 (5)	0.4044 (6)	0.5403 (5)
B	0.1325 (9)	0.1325 (9)	0.1325 (9)
F(1)	0.1838 (6)	0.1838 (6)	0.1838 (6)
F(2)	0.1604 (4)	0.1535 (5)	0.0600 (4)

Table III. Interatomic Distances (Å) for $[\text{Cu}(\text{MeTRI})_2][\text{BF}_4]_2$

	298 K	105 K	298 K	105 K
Cu-N	2.100 (7)	2.058 (6)	C(6)-C(7)	1.394 (12)
N-C(1)	1.417 (11)	1.426 (10)	C(7)-C(1)	1.443 (12)
C(1)-C(2)	1.428 (13)	1.403 (12)	C(7)-C(8)	1.504 (13)
C(2)-C(3)	1.360 (14)	1.403 (12)	C(8)-N'	1.238 (12)
C(3)-C(4)	1.499 (15)	1.392 (13)	B-F(1)	1.382 ^a
C(4)-C(5)	1.546 (15)	1.534 (12)	B-F(2)	1.267 ^a
C(4)-C(6)	1.346 (13)	1.384 (12)		1.323 (8)

^a Due to extreme disorder associated with these atoms, they were assigned fixed positions.

aldehyde.^{6,11,12} Also somewhat unusual was that $[\text{Cu}(\text{MeTRI})_2][\text{BF}_4]_2$ is obtained from the reaction of the diacid salt, $[\text{H}_2\text{MeTAAB}][\text{BF}_4]_2$, with copper(II) along with the anticipated $[\text{Cu}(\text{MeTAAB})][\text{BF}_4]$. Studies involving the unsubstituted analogue, $[\text{H}_2\text{TAAB}][\text{BF}_4]_2$, have indicated that once formed, the diacid salt is not readily susceptible to degradation from the tetrameric condensate,¹⁸ with the exception of the reaction of the diacid salt with K_2PtCl_4 under aqueous conditions.¹⁹ The diacid salt has in the past, therefore, been used as a TAAB rather than a TRI precursor. The color change that occurs upon refluxing the methyl-substituted diacid salt $[\text{H}_2\text{MeTAAB}][\text{BF}_4]_2$ indicates that degradation probably occurs even before the addition of $\text{Cu}(\text{OAc})_2$. As a result $\text{Cu}(\text{MeTRI})_2^{2+}$ and $\text{Cu}(\text{MeTAAB})_2^{2+}$ ¹⁵ are both isolated from the methanol solution, with the less soluble $[\text{Cu}(\text{MeTRI})_2][\text{BF}_4]_2$ precipitating out of solution first.

The structural parameters from the low-temperature data only will be those referred to in the discussion unless otherwise specified. Bond lengths and angles are reported in Tables III and IV, respectively. The numbering scheme for the cation is shown in Figure 1, an overhead stereoview of the molecule. Figure 2 is a stereo side view of the molecule.

D_3 site symmetry at the copper ion is achieved by its coordination to two MeTRI ligands. The immediate coordination sphere consists of six symmetry-equivalent nitrogen atoms ($\text{Cu}-\text{N} = 2.058$ (6) Å), related by a center of symmetry at the copper and a 3-fold

(15) Jircitano, A. J.; Sheldon, R. I.; Mertes, K. B. *J. Am. Chem. Soc.* **1983**, preceding paper in this issue.

(16) Mertes, K. B. *Inorg. Chem.* **1978**, *17*, 49-52.

(17) Beno, M. A.; Williams, J. A.; Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 1485-1492.

(18) Skuratowicz, J. S.; Madden, I. L.; Busch, D. H. *Inorg. Chem.* **1977**, *16*, 1721-1725.

(19) Timken, M. D.; Sheldon, R. I.; Rohly, W. G.; Mertes, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 4716-4720.

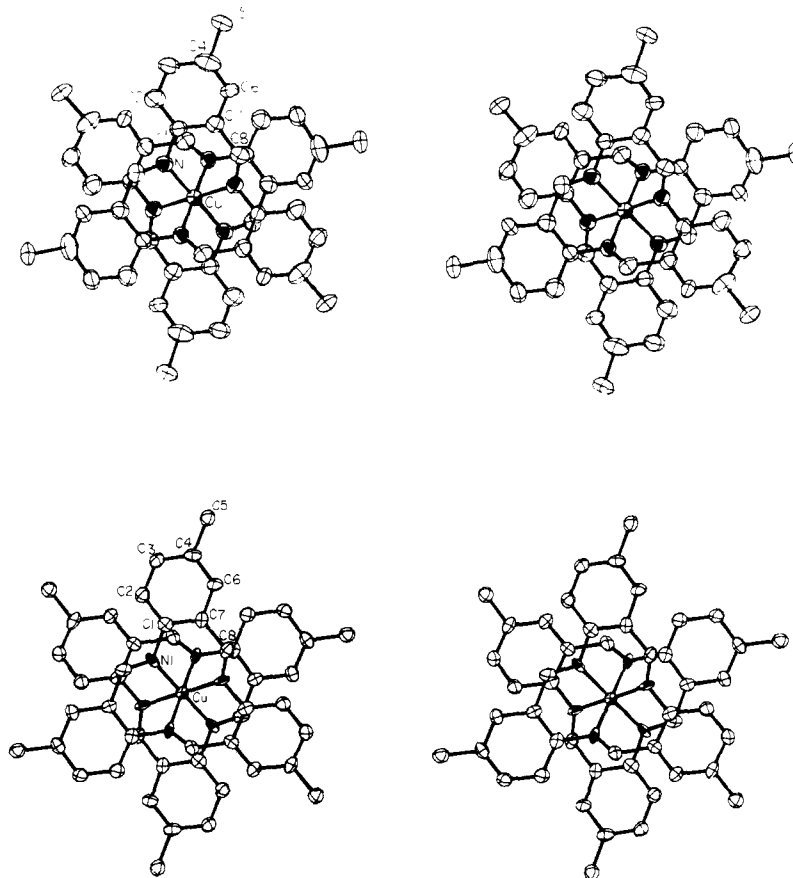


Figure 1. Stereo drawing of the $\text{Cu}(\text{TRI})_2^{2+}$ cation as viewed down the 3-fold rotation axis. Thermal ellipsoids are of 50% probability. Top drawing is from the room temperature data, while the bottom drawing is from the low-temperature data.

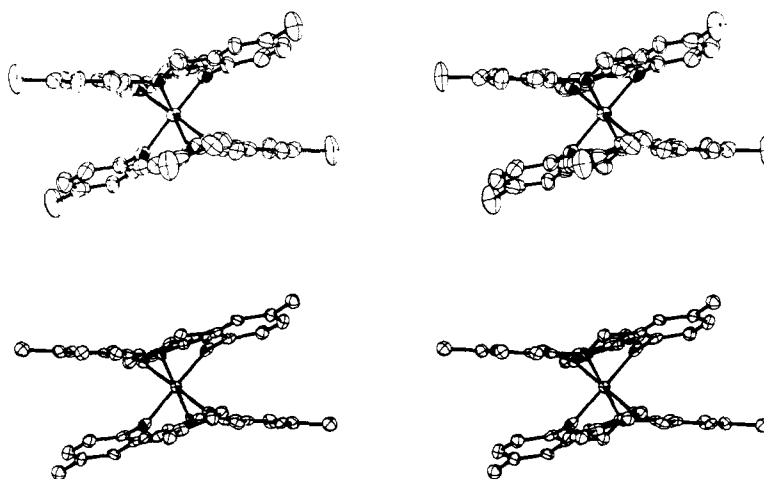


Figure 2. Stereoview of the $\text{Cu}(\text{TRI})_2^{2+}$ cation as viewed normal to the 3-fold axis. Thermal ellipsoids are of 50% probability. The top drawing is from the room temperature data, the bottom from the low-temperature data.

rotation axis. The geometry about the metal ion is distorted octahedral, with trigonal elongation along the C_3 axis. The $\text{N}-\text{Cu}-\text{N}'$ angles for a given TRI ligand are $82.8(3)^\circ$, while the corresponding interligand angles, $\text{N}-\text{Cu}-\text{N}''$, are $97.2(3)^\circ$. Acute intraligand $\text{N}-\text{M}-\text{N}$ angles are found in TRI complexes such as $[\text{Ni}(\text{TRI})(\text{H}_2\text{O})_2(\text{NO}_3)](\text{NO}_3)$ ($85.2(1)^\circ$)² and $[\text{Co}(\text{TRI})_2][\text{I}]_3 \cdot 3\text{H}_2\text{O}$ ($86.3(10)^\circ$)⁹ and are undoubtedly a consequence of the small cavity size in the tridentate ligand. The entire complex thus consists of the copper ion, two parallel MeTRI "crowns" separated by a distance of 2.66 \AA (as calculated from the centers of the N_3 planes), and two BF_4^- anions. Both the ligands and anions are related by inversion through the copper ion.

One of the most interesting aspects of the structure centers about the D_3 site symmetry of the copper ion, which results in

an orbitally degenerate E_1 ground state. The presence of high site symmetry in copper(II) complexes in apparent violation of the Jahn-Teller Theory is usually attributed to time-averaged distortions arising from electronic-vibronic coupling.^{13,14} The vibronic potential energy surface of these systems can be considered to consist of three energy minima corresponding to tetragonal distortions along each of the three orthogonal axes, respectively. The potential energy barrier between these wells in a dynamic Jahn-Teller situation will be less than the thermal energy, kT . Consequently, the wells will be equally occupied and the complex will display the unexpectedly high symmetry due to dynamic distortions among the three available tetragonal distortions.^{13,14} Temperature-dependent crystallographic studies of complexes exhibiting these dynamic Jahn-Teller effects have shown that

Table IV. Bond Angles (deg) for [Cu(MeTRI)₂][BF₄]₂

	298 K	105 K
N-Cu-N' ^a	82.9 (3)	82.8 (3)
N-Cu-N'' ^a	97.1 (3)	97.2 (3)
Cu-N-C(1)	114.8 (5)	115.9 (5)
Cu-N'-C(8)	124.2 (6)	124.4 (6)
N-C(1)-C(7)	119.8 (7)	118.4 (7)
N-C(1)-C(2)	122.1 (8)	121.3 (8)
C(7)-C(1)-C(2)	118.1 (8)	120.3 (8)
C(1)-C(2)-C(3)	122.0 (8)	119.6 (8)
C(2)-C(3)-C(4)	117.6 (9)	120.5 (8)
C(3)-C(4)-C(5)	116.8 (9)	120.4 (8)
C(3)-C(4)-C(6)	121.0 (8)	119.7 (8)
C(5)-C(4)-C(6)	122.1 (9)	119.8 (8)
C(4)-C(6)-C(7)	120.6 (8)	120.9 (8)
C(6)-C(7)-C(1)	120.5 (8)	118.9 (8)
C(6)-C(7)-C(8)	118.5 (8)	118.3 (8)
C(1)-C(7)-C(8)	120.8 (8)	122.4 (8)
C(7)-C(8)-N'	125.1 (8)	123.5 (8)
F(1)-B-F(2)	101.5 ^b	99.8 (11)
F(2)-B-F(2')	116.1 ^b	117.2 (6)

^a N' refers to N related by rotation of 2π/3; N'' refers to N related by rotation of 2π/3 followed by inversion through Cu.

^b Due to the extreme disorder in these atoms, they were assigned fixed positions.

phase transitions to lower symmetries often occur as the temperature is lowered.^{13,14} Also, marked anisotropies in the thermal parameters along the metal-ligand vector are expected.²⁰⁻²⁵ In static systems the bending modes of the metal-ligand bond are anticipated to be of lower energy than the stretching modes, so that anisotropy should manifest itself in higher root-mean-square displacements perpendicular to the metal-ligand bond. In the dynamic systems the opposite energy situation exists so that abnormally large root-mean-square displacements should be along the metal-ligand vector.^{13,14}

Although the data obtained from the low-temperature structure indicate no phase change has occurred, distinct anisotropies in the thermal ellipsoids of the coordinated nitrogen atoms are observed. Indeed, the nitrogen atoms appear as cigar-shaped ellipsoids along the Cu-N vector, as is clearly evident from the ORTEP diagram in Figure 1, with root-mean-square displacements along the principal axes of 0.10 (2), 0.15 (2), and 0.21 (1) Å. The largest displacement lies almost along the Cu-N vector as evidenced by its angle with said vector of 10 (9)°. The room temperature data show considerably less anisotropy in the thermal parameters, with root-mean-square displacements of 0.17 (1), 0.19 (1), and 0.22 (1) Å, the largest displacement making an angle of 39 (12)° with the Cu-N vector. Definite anisotropies have been observed in other structures where a dynamic Jahn-Teller distortion is evidenced;²⁰⁻²⁵ for example, tris(ethylenediamine)copper(II) sulfate shows root-mean-square displacements of 0.191 (3), 0.211 (4), and 0.232 (3) Å, the last lying nearly along the Cu-N vector.²⁰ Clearly, the 0.22-Å displacement, which is observed in the Cu(TRI)₂²⁺ structure along the Cu-N vector at 105 K, is quite large, particularly considering the low temperature. In the other structures cited²⁰⁻²⁵ a 0.02-Å elongation was considered as meaningful. Two additional factors may have con-

tributed to the extreme anisotropy at low temperature. Firstly, due to the rapid cooling process (approximately 1 h), a phase transition could have been prevented due to a "freezing in" of the disordered structure. It is also possible that 105 K is nearing a phase transition, which could account for the extreme anisotropies of the nitrogen atoms. Nonetheless the current data would certainly seem to indicate a dynamic Jahn-Teller effect is operable for Cu(MeTRI)₂²⁺. Such an occurrence is not necessarily unexpected, since it has also been observed for other bis complexes of tridentate ligands.^{21,26} The observation of dynamic Jahn-Teller effects in such complexes can possibly be attributed to the highly symmetrical stereochemistry of the ligand in which there may not be an energetically preferred pathway for distortion.

In a comparison of the structural aspects of this complex with that of Co(TRI)₂³⁺ several differences are noted. The first becomes evident upon an examination of the stereochemistry of the complex, which is a function of the mode of progression of the repeating units (benzo and azomethine groups) in the two macrocycles. When viewed along the 3-fold axis, the meso form occurs when the two macrocyclic rings progress in the same direction, resulting in a centrosymmetric complex as seen in Figure 1, while in the racemic form, the groups progress in the opposite direction, giving rise to optical isomers. Thus while Cu(MeTRI)₂²⁺ was isolated in the meso form, Co(TRI)₂³⁺ was resolved into its optical isomers, and the structure was completed on one of the racemic forms.⁹ In the racemic form, due to the eclipsed nature of the ligand coordination, the contacts between the benzo groups in the two macrocycles are maximized. The benzo groups in [Co(TRI)₂]³⁺ are spaced by a mean distance of 3.2 Å, while the closest C-C contacts between rings average 2.9 Å (sum of the van der Waals radii = 3.30-3.40 Å²⁷). The torsional distortion about the 3-fold axis tends to increase the overlap of the benzo groups in the cobalt structure, which led the authors to conclude that the interaction between TRI ligands is attractive rather than repulsive.⁹ In meso-[Cu(MeTRI)₂]²⁺, the staggering of the rings effectively minimizes contacts. The closest C-C approach between ligands is 3.504 (12) Å for C(1)-C(8)'. Although the observed interplanar distance between the two MeTRI ligands of 2.66 Å is longer than that observed in [Co(TRI)₂]³⁺ (2.36 Å), the distance is less than that in 2,2'-paracyclophane (3.09 Å), in which the π systems of the overlapping benzene rings are known to interact.²⁸ The inner-ring π systems in [Cu(MeTRI)₂]²⁺ may thus be undergoing some interactions.

Acknowledgment. K.B.M. acknowledges the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of Kansas General Research Allocation No. 3780-XO-0038 for support of this work. Work at Argonne National Laboratory is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Material Science, under Contract W-31-109-Eng-38. The authors also express their gratitude to Professor Byungkook Lee, who has provided a revised and improved X-ray crystallographic program package.

Registry No. [Cu(MeTRI)₂][BF₄]₂, 85135-55-3; [H₂(MeTAAB)]-[BF₄]₂, 85135-57-5; [Cu(MeTAAB)]-[BF₄]₂, 85135-59-7.

Supplementary Material Available: Table i, listing of observed and calculated structure factors for [Cu(TRI)₂][BF₄]₂; Table ii, final anisotropic thermal parameters, and Table iii, final hydrogen atom positional and thermal parameters (10 pages). Ordering information is given on any current masthead page.

- (20) Cullen, D. L.; Lingafelter, E. C. *Inorg. Chem.* **1970**, *9*, 1858-1864.
 (21) Ammeter, J. H.; Burgi, H. B.; Camp, E.; Meyer-Sandrin, V.; Jensen, W. P. *Inorg. Chem.* **1979**, *18*, 733-750.
 (22) Bertini, I.; Dapporto, P.; Gatteschi, D.; Scozzafava, A. *J. Chem. Soc., Dalton Trans.* **1979**, 1409-1414.
 (23) Cavalca, L.; Nardelli, M.; Grazioli, D. *Gazz. Chim. Ital.* **1956**, *86*, 1041-1044.
 (24) Van Driel, M.; Verweel, H. J. Z. *Kristallogr.* **1936**, *95*, 300-314.
 (25) Cullen, D. L.; Lingafelter, E. C. *Inorg. Chem.* **1971**, *10*, 1264-1268.

- (26) Burgi, H. B., cited as private communication in ref 12.
 (27) Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*; Harper and Row: New York, 1978; pp 232-233.
 (28) Cram, D. J.; Steinberg, H. *J. Am. Chem. Soc.* **1951**, *73*, 5691-5704.