Stereochemically Nonrigid Six-Coordinate Molecules. Crystal Structure of Tris(tropolonato)aluminum(III)

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Abstract: The crystal structure of tris(tropolonato)aluminum(III) was determined by single crystal X-ray techniques from diffractometer data. Crystals are monoclinic, space group $C2/c$, with $a = 10.855$ (12), $b = 10.214$ (6), $c = 17.719$ (13) Å, and $\beta = 112.71$ (10)° with four molecules per cell and with observed and calculated densities of 1.43 g/cm^3. Structure refinement by least squares led to a conventional R of 0.040. The complex has $C_2(2)$ space group imposed molecular symmetry, but the departure from idealized $D_3(32)$ symmetry is slight. The tropolonato ligands are bent slightly in the vicinity of the aluminum atoms with resultant angles (AlO_2–C_7H_5 dihedral angles) of 6.24° for the ligand on the $C_2(2)$ axis and 3.73° for the other unique ligand. The most significant feature of the AlO_6 coordination sphere is the 48.1 (13)° twist angle ϕ (projection of the "bite" angle in the C_3 direction) which compares with 60° for a regular octahedron; the relevance of ϕ to trigonal twist rearrangement barriers in metal tropolonates is discussed. Data associated with the tropolonato ligand are examined in some detail and compared with analogous data from other crystal structure determinations of metal tropolonates. This comparison fully substantiates the characterization of the tropolone ion as an inflexible ligand (excepting, of course, the bending phenomenon). Even the "bite" (O–O separation) is fairly constant in the metal chelates (2.53 (1) Å average) despite large variations in the metal atom radius, electronic structure, and coordination number.

In the early period of mechanistic analyses of intramolecular rearrangements in stereochemically nonrigid molecules, only idealized models were considered for the ground state and for the transition state or reaction intermediate.[1] In five-coordinate molecules, the Berry[2] mechanism based on the close interrelationships of the D_{3h} trigonal bipyramid and C_{4v} square pyramid was used[1,3] in discussing rearrangements. The only model proffered for rearrangements in six-coordinate molecules was based on the relationships between the regular octahedron and the trigonal prism.[7–10] Such simple models have proved very effective in rationalizing vast bodies of data, particularly in five-coordinate complexes.[1,3] Alternatives were not seriously considered, although in most discussions there was an implicit recognition of departures from the idealized physical motion in real molecules, especially those whose ground state geometry did not closely approximate the idealized polyhedra. More explicit general discussions of physical alternatives have now appeared,[11,12] and Gielen and Van Lauten[13] and others[14,15] have considered the maximum number of *permutational* mechanisms for certain idealized polyhedra. More recently, rearrangement mechanisms that are different from the classic, idealized models have been established. For example, nmr studies have shown that a novel mechanism,[14] "the tetrahedral jump," is operative in a class of six-coordinate molecules *in which the ground state geometry significantly departs from a regular octahedron.*[16] Also, a class of HML_4 hydrides proved nonrigid,[15] and these hydrides *do not have trigonal bipyramidal geometry but rather a pseudotetrahedral geometry.*[17–20] Rearrangements in this class of five-coordinate molecules cannot be realistically viewed in terms of the classical Berry motion.[15] Thus, assessment of the bond distances and angles in the ground state of a nonrigid molecule is becoming of substantial importance in the more detailed characterization of the *physical* motion that effects the rearrangement. The combined approach of solution nmr studies and X-ray analysis of the crystalline state has already been effectively employed by Cotton and coworkers in studies of nonrigid organometallic molecules.[21]

Most six-coordinate tris chelates have relatively high barriers to racemization or isomerization reactions, and these reactions appear to proceed largely by intramolecular bond breaking processes.[10,22–25] However, Pignolet, Lewis, and Holm[26,27] have presented rather

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(1) E. L. Muetterties, *Rec. Chem. Progr.*, **31**, 51 (1970).

(2) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

(3) For reviews see ref 4–6.

(4) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

(5) E. L. Muetterties, *ibid.*, **3**, 266 (1970).

(6) K. Mislow, *ibid.*, **3**, 321 (1970).

(7) W. G. Gehman, Ph.D. Thesis, The Pennsylvania State University, 1954.

(8) L. Seiden, Ph.D. Thesis, Northwestern University, 1957.

(9) J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958).

(10) E. L. Muetterties, *J. Amer. Chem. Soc.*, **90**, 5097 (1968).

(11) (a) E. L. Muetterties and W. Mahler, *Inorg. Chem.*, **4**, 1520 (1965); (b) E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 4115 (1969).

(12) I. Ugi, D. Marquarding, H. Klusacek, G. Gokel, and P. Gillespie, *Angew. Chem., Int. Ed. Engl.*, **9**, 703 (1970).

(13) M. Gielen and N. Van Lauten, *Bull. Soc. Chim. Belg.*, **79**, 679 (1970).

(14) P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Amer. Chem. Soc.*, **93**, 4701 (1971).

(15) P. Meakin, E. L. Muetterties, and J. P. Jesson, *ibid.*, **94**, 5271 (1972).

(16) L. J. Guggenberger, D. D. Titus, M. T. Flood, R. E. Marsh, A. A. Orio, and H. B. Gray, *ibid.*, **94**, 1135 (1972).

(17) R. W. Baker and P. Pauling, *Chem. Commun.*, 1495 (1969).

(18) B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, **9**, 2403 (1970).

(19) R. W. Baker, B. Ilmaier, P. J. Pauling, and R. S. Nyholm, *Chem. Commun.*, 322 (1971).

(20) D. D. Titus, A. A. Orio, R. E. Marsh, and H. B. Gray, *ibid.*, 322 (1971).

(21) "Stereochemically Nonrigid Organometallic Molecules," series; *cf.* F. A. Cotton, B. G. DeBoer, and T. J. Marks, *J. Amer. Chem. Soc.*, **93**, 5069 (1971), and references therein.

(22) J. G. Gordon, II, and R. H. Holm, *ibid.*, **92**, 5319 (1970).

(23) J. R. Hutchison, J. G. Gordon, II, and R. H. Holm, *Inorg. Chem.*, **10**, 1004 (1971).

(24) R. C. Fay, A. Y. Girgis, and U. Klabunde, *J. Amer. Chem. Soc.*, **92**, 7056 (1970).

(25) A. Y. Girgis and R. C. Fay, *ibid.*, **92**, 7061 (1970).

(26) L. H. Pignolet, R. A. Lewis, and R. H. Holm, *ibid.*, **93**, 360 (1971).

(27) L. H. Pignolet, R. A. Lewis, and R. H. Holm, *Inorg. Chem.*, **11**, 99 (1972).

convincing evidence that certain tris chelates with ligating sulfur atoms do rearrange *via* a trigonal twist process about the threefold or pseudo-threefold axis. The notable features of these chelates are a short ligand bite and a ground state geometry nearly intermediate between a trigonal prism and a trigonal antiprism.[26,28] The twist angles, ϕ, defined by projection of metal–ligand vectors on a plane normal to the C_3 or pseudo-C_3 axis, range from 33 to 41° as compared to 0 and 60° for the trigonal prism and trigonal antiprism, respectively.[26,28] Such intermediate twist angles may well account for the relatively low energy barrier to a trigonal twist rearrangement about the C_3 (cis) or pseudo-C_3 (trans) axis. Recently, a detailed nmr analysis[29] of certain metal tris tropolonates has given strong support to a twist mechanism for the very rapid rearrangements of these molecules in solution. The rigid character of the ligand and the short ligand bite literally sets these complexes apart from the β-diketonate analogs[22–25] which do not exhibit this fast rearrangement *via* the twist mechanism. Additionally, it has been noted that due to the short ligand bite the twist angles in the aluminum and cobalt tropolonates might be intermediate between those for the trigonal prism and the trigonal antiprism;[30] however, the cobalt(III) derivative of tropolone has near trigonal antiprismatic geometry with a twist angle of ~55°.[31] A further assessment of the effect of twist angle on rearrangement barriers in these tropolonates requires additional structural data, and for this reason, the crystal structure of the aluminum derivative of tropolone has been analyzed.

Experimental Section

Tris(tropolonato)aluminum(III) was prepared from tropolone and aluminum(III) chloride.[32] Attempts to grow suitable crystals of this complex from organic solvents were unsuccessful. Large crystals were obtained by the following procedure. The complex was dissolved in a minimum of liquid sulfur dioxide, then a small amount of methanol was added, and the solution was filtered into a tenfold excess of methanol. The initial crops of crystals that formed as the solution warmed to ~25° were removed by filtration. On standing for about 1 day, crystals (primarily plates) formed. From these, a relatively equidimensional crystal (0.32 × 0.31 × 0.27 mm) was selected and was used in all subsequent X-ray studies.

Preliminary X-ray study of the crystal by photographic techniques established a monoclinic lattice of either $C2/c$ or Cc space group symmetry (hkl, $h + k = 2n$, and $h0l$, $l = 2n$). A check of second harmonic generation in a thin layer of powdered tris(tropolonato)aluminum(III) was made with a laser beam (source, Nd:glass). This test was negative, supporting the centrosymmetric $C2/c$ space group assignment,[33] and every detail of the following structural analysis supported the selection of the $C2/c$ space group. Cell dimensions of $a = 10.855\,(12)$, $b = 10.214\,(6)$, $c = 17.710\,(13)$ Å, and $\beta = 112.71\,(10)°$ were obtained from a least-squares refinement of the angular positions measured for eleven centered reflections on the diffractometer. The observed and calculated densities for four molecules per unit cell are 1.43 g/cm^3. The molecule has space group imposed $C_2(2)$ point symmetry.

The crystal was mounted on a Picker four-circle diffractometer with the 402 reflection coincident with the diffractometer ϕ axis. Data were measured with Zr-filtered Mo Kα radiation at a takeoff angle of 3.0° using θ–2θ scan technique with a scan speed of 1°/min and a scan range of 1.5° plus Kα_1–Kα_2 separation. A counting period of 15 sec before and after each peak was employed to establish background. A standard reflection was repeated every 50 reflections. These standard reflections showed random variation throughout with an average variation of about 2%. Attenuation was used for counting rates in excess of 10,000 cps. A total of 1510 reflections (max sin θ/λ of 0.58) were collected, including the symmetry equivalent $hk0$ and the $\bar{h}k0$ which were averaged.

Net intensities were reduced to relative square amplitudes, $|F_o|^2$, through use of standard Lorentz and polarization factors. Structure factors which were less than the standard deviations[34] were considered unobserved and were given zero weight in the refinement. In this way 1434 (115 listed as unobserved) of the reflections were retained for the structure analysis giving a data/parameter ratio of 8 (with hydrogen atoms included). No absorption correction was made. The error due to absorption was less than 2% in F_o based on an experimental check of equivalent reflections. This was expected since the crystal was essentially equidimensional with a linear absorption coefficient for Mo Kα radiation of 1.57 cm^{-1}. In later stages of refinement, secondary extinction effects were apparent in systematic differences with F_o less than F_c for strong reflections. An extinction correction was applied after the method of Zachariasen[35] according to $F_{cor} = F_{\mathrm{uncor}}(1 + \beta C I_{\mathrm{obsd}})$; a β of 1.0 was used for all the data and C was refined with the other parameters.

The aluminum atom was initially located on the twofold axis from a Patterson function. The oxygen atom positions were found from Patterson superpositions using the minimum function. The aluminum and three unique oxygen atom positions were then used to calculate an electron density map from which six of the eleven unique carbon atoms were located (R at this stage was 0.461). The remaining carbon atoms were added in two steps, and a calculation with anisotropic thermal parameters yielded an $R(\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ value of 0.077 and $wR\{[\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2}\}$ value of 0.111. Hydrogen atom positions were calculated using a 1.0-Å C–H separation and bisection of the appropriate CCC angles. All calculated positions (eight unique hydrogen atoms) coincided closely with electron density maxima (0.2 to 0.4 electron) in the difference Fourier. These hydrogen atom positions with isotropic thermal parameters were refined, and the refinement converged at R of 0.044. The refined hydrogen positions were close to the observed positions. The secondary extinction correction was made and then a final refinement was applied varying all parameters (isotropic thermal parameters for the hydrogen atoms). After several least-squares cycles, the refinement converged at an R of 0.040 (0.047 including rejected reflections) and wR of 0.035 (0.041 including rejects). In the final refinement, thirteen reflections were listed as unobserved because inspection of the intensity plots clearly indicated bad background approximations; all peak profiles were conveniently scaled and plotted on a Calcomp plotter with the background approximation. The standard deviation of an observation of unit weight for 1319 pieces of "observed" data and 159 variables was 1.314.

Atomic scattering factors for neutral atoms were used.[36a] The real and imaginary parts of the anomalous scattering effect were included for the aluminum atom.[36b] The refinement minimized the function $\Sigma w(|F_o| - |F_c|)^2$.[37]

In all of the following tables, the standard deviations of the least significant digits are in parentheses. The error estimates include the covariances except for distances and angles involving atoms on the twofold axis where only the variances were used. Averages of angles and distances are taken where statistically and chemically

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(28) D. L. Johnston, W. L. Rohrbaugh, and W. D. Horrocks, Jr., *Inorg. Chem.*, 10, 1474 (1971).

(29) (a) S. S. Eaton and R. H. Holm, *J. Amer. Chem. Soc.*, 93, 4313 (1971); (b) S. S. Eaton, J. R. Hutchison, R. H. Holm, and E. L. Muetterties, *ibid.*, 94, 6411 (1972).

(30) (a) A twist angle of ~40° has been estimated[29] from the molecular parameters reported[30b] for tris(tropolonato)iron(III). (b) T. A. Hamor and D. J. Watkin, *Chem. Commun.*, 440 (1969).

(31) A. P. Gaughan and R. Eisenberg, private communication. The data were obtained at a stage of refinement with $R = 11\%$ for a monochloroform solvate of tris(tropolonato)cobalt(III).

(32) E. L. Muetterties and C. M, Wright, *J. Amer. Chem. Soc.*, **86**, 5132 (1964).

(33) S. K. Kurtz and T. T. Perry, *J. Appl. Phys.*, 39, 3978 (1968).

(34) L. J. Guggenberger, *Inorg. Chem.*, 7, 2260 (1968).

(35) W. H. Zachariasen, H. A. Plettinger, and M. Marezio, *Acta Crystallogr.*, **16**, 1144 (1963).

(36) (a) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *ibid.*, **17**, 1040 (1964); (b) D. H. Templeton, "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 216.

(37) Computer programs used in addition to various local programs were Prewitt's least-squares program SFLS5, Johnson's plotting program ORTEP, the Busing–Levy error function program ORFFE, and the Fourier program FOUR written originally by Dr. C. J. Fritchie, Jr.

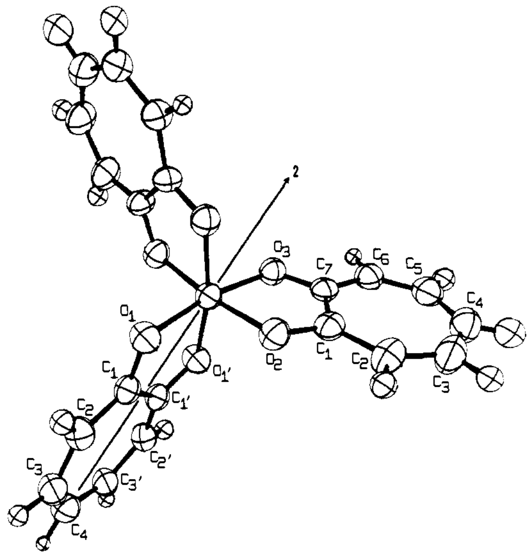

Figure 1. Molecular structure of tris(tropolonato)aluminum(III) illustrating the appropriate thermal ellipsoids and labeling scheme. The view is in the direction of the idealized threefold axis. The A ligand is on the twofold axis and the unique B ligand is the other labeled ligand.

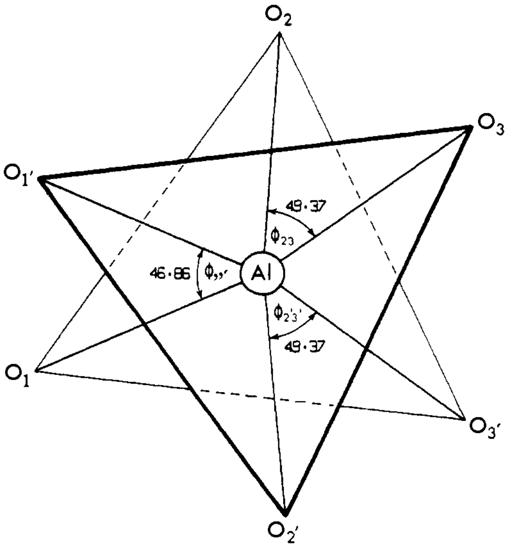

Figure 2. A projected view of the aluminum–oxygen coordination sphere illustrating the twist angles (ϕ).

meaningful; the estimated errors for these were calculated according to $[\Sigma(d_i - \bar{d})^2/n(n-1)]^{1/2}$ where d_i and $\bar{d}$ are the functions and mean function, respectively. The labeling sequence for the atoms follows that of Figure 1 with the hydrogen atoms identified by the carbon atoms to which they are bonded. Ligand A refers to the tropolonato ligand that lies on the twofold axis, and ligands B and B′ are related by the twofold rotational axis. The primed atoms are related to the unprimed atoms by the $C_2(2)$ operation.

Results and Discussion

The AlO_6 Coordination Sphere. Final positional parameters are listed in Table I and thermal parameters in Table II. A table of the observed and calculated structure factors (× 10) is available.[38]

Table I. Positional Parameters for Tris(tropolonato)aluminum(III)[a]

Atom	Ligand	x	y	z
Al		0	0.10057 (8)	0.75
O_1	A	0.08107 (13)	0.23881 (8)	0.71570 (8)
O_2	B	0.15426 (13)	0.08858 (13)	0.84755 (8)
O_3	B	−0.06471 (13)	−0.02467 (12)	0.80409 (8)
C_1	A	0.04930 (17)	0.35442 (18)	0.73173 (11)
C_2	A	0.11282 (19)	0.46415 (19)	0.71611 (12)
C_3	A	0.09270 (21)	0.59558 (20)	0.72599 (13)
C_4	A	0	0.65521 (31)	0.75
C_1	B	0.14407 (18)	0.01210 (19)	0.90274 (11)
C_2	B	0.25121 (22)	−0.00030 (24)	0.97782 (13)
C_3	B	0.26138 (26)	−0.07337 (26)	1.04605 (14)
C_4	B	0.17093 (26)	−0.15344 (25)	1.05884 (15)
C_5	B	0.04470 (26)	−0.18315 (21)	1.00381 (14)
C_6	B	−0.02405 (22)	−0.14122 (20)	0.92441 (13)
C_7	B	0.01605 (20)	−0.05395 (18)	0.87750 (12)
H_2	A	0.1852 (23)	0.4406 (22)	0.6964 (13)
H_3	A	0.1537 (21)	0.6508 (21)	0.7114 (12)
H_4	A	0	0.7494 (29)	0.75
H_2	B	0.3304 (25)	0.0523 (22)	0.9811 (14)
H_3	B	0.3501 (25)	−0.0702 (22)	1.0893 (15)
H_4	B	0.1953 (26)	−0.1928 (27)	1.1151 (18)
H_5	B	−0.0087 (24)	−0.2392 (22)	1.0234 (14)
H_6	B	−0.1124 (20)	−0.1723 (20)	0.8948 (13)

[a] Estimated errors in the least significant digits are in parentheses here and in all other tables. The refined secondary extinction parameter C is 0.48 (7) × 10^{-6}.

The structure of tris(tropolonato)aluminum(III) is depicted in Figure 1 with atom labeling following the scheme described in the Experimental Section. Parameters associated with the AlO_6 coordination sphere are listed in Table III; average values are given for chemically similar distances and angles. Relevant dihedral angles are given in Table IV. No significant differences were found in the Al–O distances. There are three distinct sets of polyhedral edges with associated sets of angles (Table III). The three short edges and associated small OAlO angles are those bridged by the ligand and reflect the rigid, short bite of the tropolonate ion. Opposite to the sets of short edges and angles are the sets of three edges and three angles which are the largest of the groups as a consequence of a symmetrical compensation in the coordination sphere to the abnormally short ligand bite.

There is crystallographically imposed $C_2(2)$ point symmetry for the molecule; however, the departure from $D_3(32)$ point symmetry, which should prevail in the solution state,[39] is not large. Deviation from D_3 microsymmetry in the AlO_6 coordination sphere is reflected in two interrelated parameters (see Figure 2). The dihedral angle between the $O_1O_2O_3$ and $O_{1'}O_{2'}O_3$ is 2.29°, and the twist angles (ϕ) are not equivalent (Figure 2 and Table IV). The genesis of the smaller $\phi_{11'}$ angle is probably packing effects; as noted below, ligand A is more severely bent than the B and B′ ligands suggesting more severe intermolecular nonbonding interactions for the unique ligand. The average twist angle of 48.1 (13)° is substantially lower than the 60° for the idealized trigonal antiprism, and this facet of the molecular structure is discussed later in the context of

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(38) Listings of the observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Regular unobserved reflections are indicated by asterisks and reflections called unobserved because of bad background measurements are identified by B's. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 22036, by referring to code number JACS-72-8046. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

(39) For the closely related tris(tropolonato)iron(III) complex, the crystals are trigonal, space group $R\bar{3}c$, and the molecule has $D_3(32)$ point symmetry in the solid state.[30b]

Table II. Final Thermal Parameters for Tris(tropolonato)aluminum(III)[a]

Atom	Ligand	β_{11} or B, Å^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
A1		738 (9)	695 (9)	276 (4)	0	198 (5)	0
O_1	A	921 (16)	760 (15)	380 (7)	58 (11)	363 (9)	16 (7)
O_2	B	822 (15)	935 (16)	292 (6)	−116 (12)	194 (8)	9 (7)
O_3	B	785 (14)	815 (15)	287 (6)	−69 (11)	156 (8)	12 (7)
C_1	A	625 (18)	743 (20)	238 (7)	37 (16)	129 (10)	21 (9)
C_2	A	717 (20)	840 (23)	323 (9)	−14 (17)	185 (11)	56 (11)
C_3	A	921 (24)	834 (24)	314 (9)	−137 (19)	126 (12)	67 (11)
C_4	A	1182 (38)	723 (32)	327 (13)	0	120 (18)	0
C_1	B	802 (21)	786 (21)	286 (9)	87 (17)	211 (11)	−53 (10)
C_2	B	878 (23)	1234 (27)	311 (10)	33 (21)	130 (13)	−11 (13)
C_3	B	1116 (29)	1384 (31)	285 (10)	256 (25)	97 (14)	28 (14)
C_4	B	1386 (33)	1180 (29)	316 (10)	283 (26)	255 (15)	72 (13)
C_5	B	1567 (33)	811 (23)	386 (11)	92 (22)	454 (16)	39 (13)
C_6	B	1105 (26)	757 (21)	328 (9)	5 (19)	300 (13)	−17 (11)
C_7	B	838 (21)	641 (18)	285 (8)	64 (16)	233 (11)	−53 (10)
H_2	A	1.87 (45)					
H_3	A	1.39 (45)					
H_4	A	0.80 (59)					
H_2	B	2.15 (52)					
H_3	B	2.08 (49)					
H_4	B	3.53 (57)					
H_5	B	2.41 (52)					
H_6	B	1.16 (42)					

[a] Anisotropic thermal parameters are ×10^5 and of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Bond Distances and Angles in the Coordination Sphere of Tris(tropolonato)aluminum(III)[a]

Type	Ligand	Length, Å	Type	Ligand	Angle, deg
A1–O_1	A	1.884 (1)	O_1AlO_3	A,B	169.30 (6)
Al–O_2	B	1.890 (1)	$O_2AlO_{2'}$	B,B′	172.57 (7)
Al–O_3	B	1.889 (1)			
		1.888 (2)			170.9 (16)
		Polyhedral Edges Spanned by Ligand			
O_1–$O_{1'}$	A	2.495 (3)	$O_1AlO_{1'}$	A	82.92 (5)
O_2–O_3	B	2.484 (3)	O_2AlO_3	B	82.20 (6)
		2.490 (6)			82.6 (4)
		Edges Opposite to Ligand			
O_1–$O_{2'}$	A,B′	2.815 (3)	$O_1AlO_{2'}$	A,B′	96.50 (5)
O_3–$O_{3'}$	B,B′	2.779 (3)	$O_3AlO_{3'}$	B,B′	94.73 (5)
		2.797 (18)			95.6 (9)
		Remaining Edges			
O_1–O_2	A,B	2.647 (3)	O_1AlO_2	A,B	89.08 (6)
O_1–$O_{3'}$	A,B′	2.711 (2)	$O_1AlO_{3'}$	A,B′	91.87 (5)
O_2–$O_{3'}$	B,B′	2.735 (3)	$O_2AlO_{3'}$	B,B′	92.75 (5)
		2.698 (26)			91.2 (11)
O–O av of 7		2.667 (50)	OAlO av of 7		90.0 (21)
Polyh ht[b]		2.13 (5)	ϕ[c]		48.1 (13)

[a] Error estimate of the means explained in Experimental Section [b] The polyhedral height is the average distance between planes defined by $O_1O_2O_{3'}$ and $O_{1'}O_{2'}O_3$. [c] Average twist angle.

rearrangement reactions. This is the most important, albeit expected,[29] structural feature in the AlO_6 coordination sphere.

The Tropolonato Ligands. The bond distance and angle data for the ligand atoms are relatively accurate. Because of this and certain systematics in ligand parameters, these data are discussed in some detail and compared with earlier X-ray studies of metal tropolonates.[30b,40–45]

The C_7H_5 rings are nearly planar. Atom displacements from the mean planes are listed in Table V; the maxima carbon atom displacement is 0.049 Å in ligand A and 0.012 Å in ligand B. The displacements in ligand A are significantly larger than those found in sodium tropolonate[41] and in tris(tropolonato)iron(III).[30b] Displacements are even larger from the mean C_7O_2 plane with maximum heavy atom displacements of 0.101 Å in ligand A and 0.018 Å in ligand B. These maximum values are rather large as compared with 0.009 Å in FeT_3[30b] (T = tropolone ion), 0.06 Å in T_3SnCl for the one ligand that is significantly distorted,[44] and 0.07 Å in $ThT_4\cdot DMF$ for the most severely distorted ligand.[45]

The departure from molecular $D_3(32)$ symmetry in

(40) Y. Sasad and I. Nitta, *Acta Crystallogr.*, 9, 205 (1956).

(41) R. Shino, *ibid.*, 14, 42 (1961).

(42) J. M. Robertson, *J. Chem. Soc.*, 1222 (1951).

(43) W. M. Macintyre, J. M. Robertson, and R. F. Zahrobsky, *Proc. Roy. Soc., Ser. A*, 289, 161 (1966).

(44) V. W. Day and J. L. Hoard, *J. Amer. Chem. Soc.*, 92, 3627 (1970).

(45) J. J. Park, D. M. Collins, and J. L. Hoard, *ibid.*, 92, 3636 (1970).

Table IV. Dihedral Angles[a] in Tris(tropolonato)aluminum(III)

Plane A	Plane B	Dihedral angle, deg
$AlO_1O_{1'}$	Plane 1	6.24
AlO_2O_3	Plane 2	3.73
$AlO_1O_{1'}$	AlO_2O_3	83.47
AlO_2O_3	$AlO_{2'}O_{3'}$	85.35
Plane 1	Plane 2	82.11
Plane 3	Plane 4	82.92
Plane 1	Plane 3	1.61
Plane 3	Plane 4	0.35
AlO_1CNT1	$AlO_{1'}CNT1$	46.86($\phi_{11'}$)
AlO_2CNT1	AlO_3CNT1	49.17(ϕ'_{23})
$AlO_{3'}CNT1$	$AlO_{2'}CNT1$	49.57($\phi'_{2'3'}$)
$AlO_{2'}CNT2$	AlO_3CNT2	49.57(ϕ''_{23})
$AlO_{3'}CNT2$	$AlO_{2'}CNT2$	49.17($\phi''_{2'3'}$)
$\phi_{23} = \phi_{2'3'}$		49.37[d]
$O_1O_1O_{3'}$	$O_3O_{2'}O_{1'}$	2.29

[a] Planes defined in Table V. [b] CNT1–centroid based on O_1, O_2, and $O_{3'}$. [c] CNT2–centroid based on $O_{1'}$, $O_{2'}$, and O_3. [d] $\phi_{23} = (\phi'_{23} + \phi''_{23})/2$.

Table V. Atomic Displacements from the Ligand Least-Squares Planes in Tris(tropolonato)aluminum(III)

Equations for the least-squares planes[a]

Plane 1: $0.3494X + 0.0Y + 0.9370Z - 9.689 = 0$
Plane 2: $-0.5370X + 0.7690Y + 0.3468Z - 7.673 = 0$
Plane 3: $0.3755X + 0.0Y + 0.9268Z - 9.430 = 0$
Plane 4: $-0.5390X + 0.7656Y + 0.3513Z - 7.761 = 0$

		Displacements from the plane, Å			
Atom	Ligand label	Plane 1	Plane 2	Plane 3	Plane 4
Al		0.000	0.120	0.000	0.094
O_1	A	−0.136		−0.101*	
$O_{1'}$	A	0.136		0.101*	
O_2	B		0.037		0.017*
O_3	B		0.018		0.003*
C_1	A	−0.049*		−0.029*	
C_2	A	−0.010*		0.034*	
C_3	A	0.041*		0.076*	
C_4	A	0.000*		0.000*	
$C_{3'}$	A	−0.041*		−0.076*	
$C_{2'}$	A	0.010*		−0.034*	
$C_{1'}$	A	0.049*		0.029*	
C_1	B		0.011*		−0.001*
C_2	B		−0.010*		−0.018*
C_3	B		−0.006*		−0.005*
C_4	B		0.012*		0.018*
C_5	B		0.001*		0.006*
C_6	B		−0.011*		−0.013*
C_7	B		0.003*		−0.007*
H_2	A	0.00		0.08	
H_3	A	0.08		0.14	
H_4	A	0.00		0.00	
$H_{3'}$	A	−0.08		−0.14	
$H_{2'}$	A	−0.00		−0.08	
H_2	B		−0.03		−0.04
H_3	B		−0.09		−0.09
H_4	B		0.09		0.10
H_5	B		0.05		0.06
H_6	B		−0.02		−0.02

[a] The planes are in Cartesian coordinates, Å (a, b, c^*). Asterisk denotes atoms included in the plane calculations.

the aluminum chelate primarily arises from a bending of the chelate rings as represented by the dihedral angle between the AlO_2 and C_7 planes (Table IV). This bending is really a twisting (ligand A) or a combination of twisting and folding (ligand B) as evidenced by the oxygen atom displacements from planes 1 and 2 in Table V. The folding is at the O–O edge while the twisting of the AlO_2 and C_7 planes is with respect to the local ligand $C_2(2)$ axis. Twisting and folding of this character is insignificant or small in FeT_3[30b] and for some of the ligands in $ThT_4 \cdot DMF$[44] but large (23.5°) in one ligand in $ThT_4 \cdot DMF$.[44] This last, large fold was decisively ascribed to packing effects through identification of major nonbonding interactions involving this ligand.[44] Packing effects are probably the source of the twisting and departure from planarity in ligand A of tris(tropolonato)aluminum(III), but inspection of the intermolecular nonbonding distances showed no simple distinctions between ligands A and B in the aluminum complex (*vide infra*).

Bond lengths and angles in the tropolonato ligands are given in Table VI. Table VII gives a listing of mean distances in various metal derivatives of tropolone since certain consistent features from the cumulative data provide documentation for several important features of the tropolonato ligand. The key features in the bond distances for the tropolonato ligand in AlT_3 are the following.

(1) There is no discernible bond alternation around the tropolone ring.

(2) The C_1–C_7 type distances are significantly longer (~0.07 Å) than the other C–C distances.

(3) There appears to be a sequential decrease in C–C bond distances proceeding from the carbon atoms vicinal to oxygen to the central C_4 ring atom.

(4) Overall, the parameters in AlT_3 differ only slightly from those found for other metal tropolonates

Table VI. Bond Lengths and Angles in the Tropolonato Ligands[a]

Type	Ligand		Type	Ligand	
		Interatomic Distances (Å)			
O_1–C_1	A	1.292 (2)	C_3–C_4	A	1.377 (3)
O_3–C_7	B	1.292 (2)	C_3–C_4	B	1.362 (4)
O_2–C_1	B	1.289 (2)	C_4–C_5	B	1.374 (3)
		1.291 (1)			1.371 (5)
C_2–$C_{1'}$	A	1.449 (3)	C–C av of 11		1.396 (9)
C_1–C_7	B	1.451 (3)	C_2–H_2	A	1.00 (2)
		1.450 (1)	C_3–H_3	A	0.98 (2)
			C_4–H_4	A	0.96 (3)
C_1–C_2	A	1.398 (3)	C_2–H_2	B	1.00 (2)
C_1–C_2	B	1.394 (3)	C_3–H_3	B	0.97 (2)
C_6–C_7	B	1.398 (3)	C_4–H_4	B	1.01 (3)
		1.397 (1)	C_5–H_5	B	0.97 (2)
			C_6–H_6	B	0.95 (2)
C_2–C_3	A	1.382 (3)			0.98 (1)
C_2–C_3	B	1.388 (3)			
C_5–C_6	B	1.381 (3)			
		1.384 (2)			
		Interatomic Angles (deg)			
			$C_3H_4C_{3'}$	A	127.48 (23)
AlO_1C_1	A	114.61 (11)	$C_3C_4C_5$	B	126.86 (24)
AlO_2C_1	B	115.30 (12)			
AlO_3C_7	B	115.25 (12)			127.17 (31)
		115.05 (22)	CCC av of 11		128.5 (5)
$O_1C_1C_2$	A	119.67 (16)	$H_2C_2C_1$	A	112.8 (13)
$O_2C_1C_2$	B	119.62 (19)	$H_3C_3C_2$	A	111.8 (12)
$O_3C_7C_6$	B	119.99 (18)	$H_2C_2C_1$	B	113.0 (13)
			$H_3C_3C_2$	B	112.9 (14)
		119.76 (12)	$H_5C_5C_6$	B	112.6 (14)
$O_1C_1C_{1'}$	A	113.83 (13)	$H_6C_6C_7$	B	111.4 (9)
$O_2C_1C_7$	B	113.61 (16)			112.4 (3)
$O_3C_7C_1$	B	113.54 (16)			
		113.66 (9)	$H_2C_2C_3$	A	117.4 (13)
			$H_3C_3C_4$	A	118.5 (12)
$C_{1'}C_1C_2$	A	126.45 (14)	$H_2C_2C_3$	B	117.5 (13)
$C_6C_7C_1$	B	126.46 (18)	$H_3C_3C_4$	B	116.5 (14)
$C_7C_1C_2$	B	126.78 (19)	$H_5C_5C_4$	B	116.6 (14)
		126.56 (11)	$H_6C_6C_5$	B	119.4 (8)
$C_1C_2C_3$	A	129.75 (20)			117.6 (5)
$C_2C_3C_4$	A	129.72 (22)			
$C_1C_2C_3$	B	129.49 (22)	$H_4C_4C_3$	A	116.3 (15)
$C_2C_3C_4$	B	130.35 (23)	$H_4C_4C_3$	B	118.2 (16)
$C_4C_5C_6$	B	130.74 (23)	$H_4C_4C_5$	B	114.9 (15)
$C_5C_6C_7$	B	129.28 (21)			
					116.5 (10)
		129.89 (22)	HCC av of 15		115.3 (7)

[a] Error estimates of the means explained in Experimental Section.

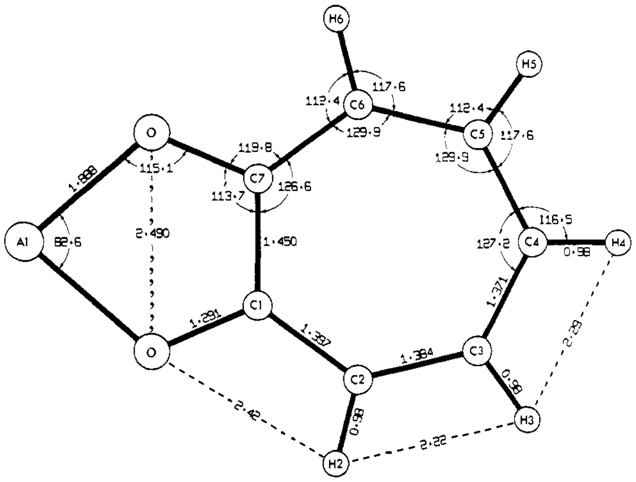

Figure 3. Average tropolonato ligand in tris(tropolonato)aluminum(III).

(Table VII). The characterization of the tropolonato ligand as a rigid moiety seems fully justified.

(5) The carbon–hydrogen distances are identical within the accuracy of the determination.

Additional amplification seems warranted for several of these points. There was some question from the earlier work[40,42,43] about the single-double bond alteration around the ring. It seems clear from this and other recent work[30b,44,45] that there is no alternation around the ring; *i.e.*, the ligand has C_{2v} symmetry within the estimated errors. In the valence bond language this does not limit the number of resonance hybrids but only requires a statistical distribution about the ligand twofold axis. The longer C_1–C_7 distance is surely statistically significant and is a feature of all metal tropolonates (Table VII). The implication is that there is less aromatic character to this bond which is not surprising in view of the types of resonance hybrids possible for this ligand.

The continuous decrease in bond lengths (C_1–C_2 > C_2–C_3 > C_3–C_4) in the ring is more difficult to assess. If the σ's are reliable, a point can be made that the observed differences are larger than expected for a normal distribution (based on a χ^2 test). Examination of all distances by type in a purely statistical sense leads us to believe that the C_1–C_2 (C_6–C_7) distance is possibly significantly larger than C_2–C_3 (C_5–C_6) and C_3–C_4 (C_4–C_5) and the differences in the latter sets are not statistically significant. Examination of Table VII shows that the C_1–C_2 (C_6–C_7) distance is consistently[47] the largest of the three types of C–C distances, but the C_2–C_3 (C_5–C_6) distance is next largest only in about half the cases and it is not significantly different from the C_3–C_4 (C_4–C_5) set in any of the determinations. Although we suspect at least part of the sequential decrease in AlT_3 may be real, the best assessment, consistent with all other studies (except CuT_2[47]) of metal tropolonates, seems to be that the C_1–C_2 (C_6–C_7) distance is larger than the C_2–C_3 (C_5–C_6) and C_3–C_4 (C_4–C_5) sets which are equivalent.

Inspection of Table VII clearly shows that the variations in the tropolonato ligand distances are surprisingly small. This is really quite striking because the molecules represented in the table have coordination numbers of 4, 6, 7, and 9, with a substantial range of metal ion radii and electronic configuration; NaT does not even have a chelate structure. The range of intramolecular O–O separation (ligand bite) in the chelates is quite narrow, 2.490 to 2.593 Å. Clearly the tropolonato ligand can adjust internal parameters only to a very minor degree for maximal overlap with metal ion orbitals.

The angle data for the tropolonato ligand are summarized in Table VI, and a composite tropolonato ligand with averaged parameters is depicted in Figure 3. The values for the internal angles merely reflect the differences in bond lengths already discussed. Of special note are the HCC angles which vary systematically

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(46) R. M. Wing and R. L. Schlupp, *Inorg. Chem.*, 9, 471 (1970).

(47) We are ignoring the seemingly anomalous result for CuT_2 where bond alternation was observed.[42,43]

Table VII. Comparison of Distance Parameters in the Tropolonato (T) Ligand in Metal Tropolonates[a]

Compd	O–O[b]	M–O	C–O	C_1–C_7	C–C[c]	C_1–C_2 C_6–C_7	C_2–C_3 C_5–C_6	C_3–C_4 C_4–C_5	Ref
NaT[d]	2.650 (5)	2.4–2.6	1.278 (4)	1.487 (3)	1.401	1.426 (3)	1.390 (5)	1.388 (8)	41
FeT_3	2.522 (4)[e]	2.008 (3)	1.294 (5)	1.463 (7)	1.387	1.397 (7)	1.385 (7)	1.379 (7)	30b
CuT_2	2.57 (1)	1.91 (3)	1.30 (1)	1.44 (1)	1.41	1.41 (4)	1.41 (4)	1.40 (4)	43
T_3SnCl	2.548 (6)	2.050–2.168	1.287 (8)	1.453 (15)	1.399	1.412 (8)	1.392 (8)	1.393 (12)	45
T_3SnOH	2.538 (1)	2.057–2.220	1.285 (14)	1.458 (0)	1.384	1.396 (12)	1.377 (12)	1.380 (7)	45
$T_4Th \cdot DMF$	2.521 (7)–2.564 (7)	2.436–2.519	1.277 (3)	1.471 (7)	1.392	1.407 (12)	1.385 (7)	1.383 (10)	44
AlT_3	2.490 (6)	1.888 (2)	1.291 (1)	1.450 (1)	1.384	1.397 (1)	1.384 (2)	1.371 (5)	
$(C_7H_7)^+$[f]					1.4 (1)				46
Averages[g]			1.285 (3)	1.464 (6)	1.391 (3)	1.406 (5)	1.385 (2)	1.382 (3)	

[a] Mean distance with estimated errors of least significant digits in parentheses. [b] Ligand bite. [c] Exclusive of C_1–C_7 in the tropolonates. [d] The errors for this complex are our estimates based on the differences between the differential synthesis and least-squares refinements. [e] Calculated from the OFeO angle given in ref 30b. [f] $(C_7H_7)^+Ni[S_2C_2(CF_3)_2]_2^-$ with tropylium ion disordered. [g] The CuT_2 and $(C_7H_7)^+$ data were excluded in the averages

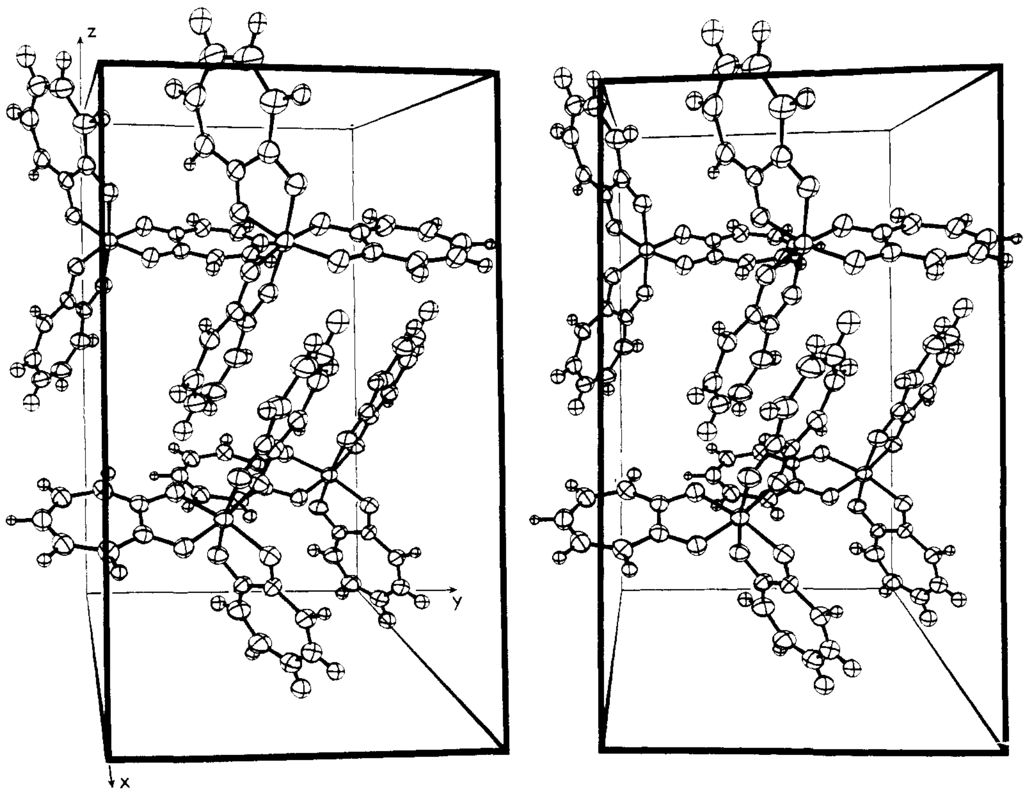

Figure 4. A stereoview of one unit cell of the tris(tropolonato)aluminum(III) structure.

around the ring in such a way that the angles towards the aluminum and oxygen atoms are smaller than those opening the other way (112.4 (3) *vs.* 117.6 (5)°, Table VI). This means that the hydrogen atoms are uniformly displaced toward the oxygen atoms of the ligand. This angle alternation which mirrors through the Al–C_4 axis and is present in both ligands seems to be real. It is probably a composite reflection of (a) minimization of H–H repulsions, (b) minor H_2–O and H_6–O bonding interactions (London type), and (c) maximization of σ bonding in the ring. The latter effect can arise because the angles between the orbitals of the sp^2 hybridized carbon atoms do not match the seven-membered tropolone ring angles exactly (all CCC > 126°) so that the hybrid can rotate about the p_z direction to maximize the overlap with vicinal sp^2 carbon atoms. The vicinal H–H and O–H separations are shown in Figure 3. The $H_4C_4C_3$ and $H_4C_4C_5$ angles are different in ligand B with the former some 3.3° larger; this may result from intramolecular contacts since differences are also observed in the C_3–C_4 and C_4–C_5 bond lengths (0.012 Å or 3σ). Distances and angles involving the hydrogen atoms were not tabulated for other metal tropolonates,[30b, 40–45] although hydrogen atoms were included as fixed contributions in the $T_4Th \cdot DMF$[44] and T_3SnOH[45] structures.

A final difference map was synthesized, but there were no unusual features. For the unique A ligand, electron densities of 0.1 electron were evident only in the regions between the CO, CC, and CH bonds. This finding is probably fortuitous since a similar mapping in the plane of the other ligand (B) showed a poor correlation of electron density with ligand bonds. In any case we do not have sufficient high-angle data to do bond mapping.

Crystal Structure and Thermal Motion. A stereoview of the crystal structure of tris(tropolonato)aluminum(III) is given in Figure 4. The discrete molecules are separated by normal van der Waals forces. All intermolecular contacts were examined; the shortest of these are listed in Table VIII. The shortest heavy–heavy, heavy–light, and light–light atom contacts are 3.238, 2.576, and 2.520 Å, respectively (marked by asterisks in Table VIII).

Table VIII. Selected[a] Nonbonding Separations, Å

Intramolecular		Intermolecular		
Type	Distance	Type	Distance	Second atom at
Al–C_1	2.692	O_1–H_{4B}*	2.576	$x, \bar{y}, z - {}^1/_2$
Al–C_5	2.704	O_1–H_{3A}	2.810	${}^1/_2 - x, y - {}^1/_2, {}^3/_2 - z$
Al–C_7	2.705	O_1–C_{4B}	3.394	${}^1/_2 - x, y - {}^1/_2, {}^3/_2 - z$
O_1–C_{2A}	2.327	O_2–H_{2A}*	2.641	${}^1/_2 - x, y - {}^1/_2, {}^3/_2 - z$
O_2–C_{2B}	2.319	O_2–H_{3A}	2.742	${}^1/_2 - x, y - {}^1{}_{.2}, {}^3/_2 - z$
O_3–C_{6B}	2.329	O_2–C_{2A}	3.388	${}^1/_2 - x, y - {}^1/_2, {}^3/_2 - z$
C_{1A}–C_{3A}	2.517	O_3–H_{2A}*	2.672	$x - {}^1/_2, y - {}^1/_2, z$
C_{3A}–$C_{3A'}$	2.469	O_3–H_{4A}	2.694	$x, y - 1, z$
H_{2A}–H_{3A}	2.207	O_3–C_{2A}*	3.238	$x - {}^1/_2, y - {}^1/_2, z$
H_{5B}–H_{6B}	2.222	C_{3A}–H_{3B}	2.818	$x - {}^1/_2, {}^1/_2 - y, z - {}^1/_2$
O_1–H_{2A}	2.437	C_{4A}–H_{3B}	2.815	${}^1/_2 - x, {}^1/_2 - y, {}^4/_2 - z$
O_2–H_{2B}	2.428	C_{7B}–H_{4A}	2.977	$x, y - 1, z$
O_3–H_{6B}	2.401	H_{2A}–H_{4B}	2.934	$x, \bar{y}, z - {}^1/_2$
H_{2A}–C_{1A}	2.013	H_{3A}–H_{6B}*	2.520	$\bar{x}, 1 + y, {}^3/_2 - z$
H_{4A}–$C_{3A'}$	1.998	H_{3A}–H_{4B}	2.903	${}^1/_2 - x, {}^1/_2 - y, {}^4/_2 - z$
H_{4B}–C_{5B}	2.019	H_{2B}–H_{5B}*	2.672	${}^1/_2 + x, {}^1/_2 + y, z$
H_{6B}–C_{7B}	1.957			

[a] Excluded are the O–O intramolecular separations noted in Table III. Asterisks denote shortest intermolecular separations.

Figures 1 and 4 show the thermal ellipsoids plotted at the 50% probability level. The rms amplitudes of vibration are given in Table IX. The important features of the thermal motion are (a) the aluminum atom is isotropic, (b) the motion is essentially the same for both types of ligands, and (c) the motion increases continuously proceeding out from the aluminum atom. The thermal vibrations are surprisingly isotropic in character, especially in view of the length of the ligands and their tendency to fold along the O–O direction.

Table IX. Root-Mean-Square Amplitudes of Vibration (Å) for Tris(tropolonato)aluminum(III)

Atom	Ligand	Minimum	Intermediate	Maximum
Al		0.1850 (13)	0.1916 (13)	0.1970 (13)
O_1	A	0.1744 (21)	0.2003 (20)	0.2402 (19)
O_2	B	0.1923 (20)	0.2000 (20)	0.2309 (19)
O_3	B	0.1930 (19)	0.1979 (20)	0.2176 (19)
C_1	A	0.1738 (28)	0.1861 (27)	0.1995 (26)
C_2	A	0.1888 (28)	0.1985 (28)	0.2226 (28)
C_3	A	0.1921 (30)	0.1988 (30)	0.2511 (30)
C_4	A	0.1955 (43)	0.2049 (42)	0.2673 (43)
C_1	B	0.1739 (29)	0.2030 (28)	0.2180 (28)
C_2	B	0.1972 (32)	0.2295 (30)	0.2563 (28)
C_3	B	0.1891 (34)	0.2417 (31)	0.2892 (32)
C_4	B	0.2024 (32)	0.2301 (31)	0.2868 (33)
C_5	B	0.1991 (31)	0.2058 (30)	0.2857 (30)
C_6	B	0.1937 (28)	0.2029 (29)	0.2384 (28)
C_7	B	0.1640 (30)	0.2021 (28)	0.2096 (27)

Significance of the Twist Angle. The structure determining features favoring a trigonal prism or trigonal antiprism in six-coordinate metal chelates are still somewhat obscure although ligand bite, nature of the ligating atoms, and availability of d electrons on the metal are important elements. Six-coordinate tris chelate structures with ligating oxygen atoms generally are based on the octahedron, although in many, if not most, of these chelates the ligating oxygen atoms tend not to assume the vertex positions of a regular octahedron because of constraints imposed by ligand structural characteristics. *In every such case the actual geometry will necessarily represent a displacement of ligating atoms from octahedral vertex positions toward trigonal prismatic vertex positions if the $D_3(32)$ symmetry is maintained.* All parameters associated with tris(tropolonato)aluminum(III) point to a displacement toward the trigonal prism. One parameter is the twist angle which is reduced from the trigonal antiprismatic value of 60 to 48.1 (13)°. Stiefel and Brown[48] have identified another parameter, called the compression ratio, which is a measure of the departure from a regular octahedral disposition of ligating atoms and from a trigonal prismatic arrangement.[49] The compression ratio is s/h, where s is a polyhedral edge and h is the polyhedral height. The limits cited by Stiefel and Brown[48] apply strictly to nonchelate structures and are based on the premise that the limiting idealized trigonal prism has square faces. For a more realistic assessment of the compression ratio in the chelate, tris(tropolonato)aluminum(III), we have calculated the limiting ratios for an idealized trigonal prism (D_{3h}) and an idealized trigonal antiprism (D_3) respecting the constraint of the fixed tropolonato bite (2.490 Å) and using the Al–O distance from this work (1.888 Å) as shown in Table X.

Table X. Twist Angles and Compression Ratios for Tris(tropolonato)aluminum(III) in the Crystalline State and in Idealized Geometries

Geometry	ϕ, deg	s, Å	h, Å	s/h
Trigonal prism	0	2.457	2.490	0.987
$(C_7H_5O_2)_3Al$	48.1	2.698	2.131	1.266
Trigonal antiprism	60	2.839	1.875	1.514

The observed compression ratio is midway between the limits. Note that the short bite leads to an untenable compression for the trigonal antiprism (*i.e.*, short O_1–$O_{2'}$ type distance results). Thus the two parameters, ϕ and s/h, for the aluminum complex point to a geometry that is almost midway between the trigonal prism and trigonal antiprism.

The six-coordinate metal tris tropolonates are distinguished from the analogous tris β-diketones by a facile rearrangement process,[29] especially notable in the cobalt(III) derivatives, and by the evidence that points strongly to a trigonal twist mechanism (rotation about C_3 or pseudo-C_3 axis) rather than an M–O bond breaking process implicated in the β-diketonates. What feature in the metal tropolonates leads to this qualitative distinction? Certainly electronic effects, although difficult to objectively and quantitatively

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(48) E. I. Stiefel and G. F. Brown, *Inorg. Chem.*, **11**, 434 (1972).

(49) The compression radio as defined by Stiefel and Brown[48] is 1.00 for the trigonal prism with square faces and 1.22 for the trigonal antiprism. There may be, however, a flaw in their argument that the trigonal prism with square faces is a fundamental limiting polyhedron in six-coordination. There is as yet no sound theoretical basis to set a square face criterion for trigonal prismatic geometry especially in chelates. Trigonal prismatic geometries with rectangular faces are, of course, realistic possibilities especially for metal ions with a relatively large radius and chelate ligands with the ligand bite fixed and abnormally small (or the converse of short radii and large ligand bites).

assess, cannot be the sole cause of the differentiation. As emphasized in the first general studies[32,50] of the tropolonato ligand in coordination chemistry, the unique features are the rigid, planar character of the ligand and the relatively fixed, short ligand bite. The rigid character of the ligand may be a contributing factor to the intramolecular, nonbond breaking rearrangement reactions in the metal tropolonates since M–O bond breaking and ligand reorientation is necessarily more energy demanding in the tropolonato ligand than in the more flexible β-diketonate ligands.[51] However, this facet alone seems insufficient to explain the stereochemical nonrigidity of the tropolonates. We believe, as others have proposed,[29] that the answer lies partially in the ground state geometry of the complex. The distortion toward the trigonal prismatic configuration[29,52] probably alters the potential energy surface so as to provide a relatively low energy pathway to rearrangement through a twisting about the threefold or pseudo-threefold axis of the chelate molecule. We note that the metal oxygen overlap is probably reduced (at least altered) in both the antiprismatic and prismatic geometries from values accessible in a regular octahedron or with a ligand that has a larger bite than the tropolonato ligand, but this is rather difficult to quantitatively assess. Perhaps most importantly, the energy level for the trigonal prismatic state may be lowered in those complexes with a short, fixed ligand bite; the M–O bond length to polyhedral edge ratio for the aluminum complex is, in fact, identical with the optimal 0.76 value[44,45] for the trigonal prism.

Cobalt(III) has an ionic radius very similar to aluminum, yet the twist angle in this transition metal is substantially larger ($\sim 55°$); energy minimization at this angle for a d^6 electronic configuration has been rationalized by angular overlap calculations by Larsen, *et al.*[50] Hence the abnormally low barriers to intramolecular rearrangements in the cobalt derivatives remain somewhat of a mystery. The rhodium(III) analogs show no evidence of stereochemical nonrigidity (nmr time scale) yet the larger radius for this metal ion would make a smaller twist angle rather likely for the chelate (note, however, that ϕ and metal–ligand distance are not uniquely related even with a fixed ligand bite[29b,52]). Thus, subtle electronic factors (*e.g.*, factors that lead to lower M–O force constants) are of substantive importance in the intramolecular rearrangements of these transition metal tropolonates. In the six-coordinate d^0 and d^{10} derivatives of tropolones, twist angle correlation with barriers is consistent. The rearrangement barriers[53] in group III and IV follow the orders Al > Ga > In and Si > Ge, respectively, which parallels ionic radius increase and the *probable* twist angle decrease.

The nmr studies[29] of metal tropolonates that strongly implicated a twist mechanism for the low temperature rearrangements were not based on tropolone since the parent symmetrical ligand can provide no stereochemical change information in the resonance experiments. All studies[29] employed a ligand with an isopropyl or isopropenyl substituent at the α position of the tropolone ring. Such a bulky substituent could substantially alter the geometrical parameters from those of the parent tris tropolonates. To examine this possibility, a precise model of tris(tropolonato)aluminum(III) was modified by placing an isopropyl group at an α position.[54] Measurement[55] of nonbonding distances involving the isopropyl hydrogen atoms showed none of such magnitude as to suggest, for example, a substantial change in twist angles.[55] Furthermore, a trigonal prismatic model with this α-isopropyltropolonato ligand showed no ligand repulsion features that would clearly render the trigonal prismatic state energetically distinct for the parent and the substituted ligands.[55,56]

We conclude that detailed parameters for ground state geometries of stereochemically nonrigid molecules can provide important information concerning the ordering of rearrangement barriers and the physical nature of the rearrangement process although electronic perturbations can in some cases yield the inevitable exceptions at least to qualitative orderings. There is a certain

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(50) (a) E. L. Muetterties and C. M. Wright, *J. Amer. Chem. Soc.*, 87, 4706 (1965); (b) E. L. Muetterties, *ibid.*, 88, 305 (1966); (c) E. L. Muetterties, H. Roesky, and C. M. Wright, *ibid.*, 88, 4856 (1966); (d) E. L. Muetterties and C. W. Alegranti, *ibid.*, 91, 4420 (1969).

(51) It should again[29] be noted that the cogent stereochemical arguments for a twist rearrangement in the metal tropolonates cannot distinguish the former from the "gray area" between nonbond breaking and bond breaking mechanism wherein, for example, the twist motion may initiate weakening and possibly scission of an M–O bond but with trigonal twist follow through with retention of stereochemical correlation between "vacant" metal site and the "free" ligating atom. A further point relevant to this subject is that the nmr delineation of nonbond breaking processes through nonloss of central atom–ligand–atom spin–spin correlation breaks down in chelate systems unless the unlikely situation prevails in which the lifetime of the metal–ligand separation is long with respect to the nuclear relaxation times.

(52) E. Larsen, G. N. LaMar, B. E. Wagner, J. E. Parks, and R. H. Holm, *Inorg. Chem.*, 11, 2652 (1972).

(53) S. S. Eaton, R. H. Holm, and E. L. Muetterties, to be published.

(54) This model accentuated any such interaction since the HCC angles of $Al(O_2C_7H_5)_3$ were used for the isopropyl group placement.

(55) By adjusting the rotational configurations of isopropyl groups to maximize isopropyl H–H interligand repulsion, the minimum H–H separation is about 2.0 Å. However, any orientations that lead to interligand separations less than 2.5 Å also yield short intraligand H–O and H–H separations. Thus, interligand repulsions based on the isopropyl hydrogen atoms should not have significant effect upon the twist angle in *cis*-tris(α-isopropyltropolonato)aluminum(III). There are notable intraligand O–H and H–H (isopropyl hydrogen atom and the β hydrogen atom of the tropolone ring) repulsions based on any orientation of the isopropyl group with respect to the ring with the exception of the one orientation in which the hydrogen atom of the secondary carbon atom is nearly coplanar with the tropolone ring and nearest to the β hydrogen. Intraligand separations in this orientation are ~ 2.5 for two H–O interactions and one H–H interaction (in this orientation interligand H–H separations are minimally ~ 2.5 Å). These intraligand repulsions would be substantially eased by small changes in the C_r–C_r–C_i (r = ring and i = isopropyl) and the adjacent H–C_r–C_r angles and in the C_r–C_r bond distances from those found for the tropolone ligand in AlT_3. For the cis D_3 trigonal prismatic isomer of tris(α-isopropyltropolonato)aluminum(III), interligand H–H separations range from ~ 2.0 to 2.5 Å depending upon relative CH_3 orientations if the isopropyl group is essentially aligned, as described above, to minimize intraligand O–H and H–H repulsions. Again, however, small adjustments in the C_r–C_r–C_i and H–C_r–C_r angles and in C_r–C_r distances could place the minimal isopropyl H–H interligand separations at a larger, more reasonable level. This stereoisomer would not appear to suffer unduly from nonbonding repulsions and seems to be a reasonable transition state, or reaction intermediate, in the intramolecular rearrangement of tris(α-isopropyltropolonato)aluminum(III). Similar arguments validly apply to the trans isomer. Thus we would not expect significant differences due to structural effects in the barriers to the twist rearrangement in AlT_3 or the analogous complexes based on α-isopropenyl- or α-isopropyltropolone.

(56) An accurate model of tris(tropolonato)aluminum(III) was made such that the tropolonato ligands could be swiveled on the Al–C_1 axis. Considering only the degree of motion required to get to a D_{3h} or C_{2v} trigonal prism ("Bailar" or "Ráy and Dutt" type of intermediate), there seems little basis to select a twist on the C_3 axis over a twist on an imaginary C_3 axis. Perhaps the C_{2v} type of intermediate is at a higher energy level than D_{3h} because overlap is less extensive in the former isomeric state. The nmr studies of the tris(α-isopropyl- and α-isopropenyltropolonato)aluminum complexes clearly show that the dominating low temperature process does not involve a twist on an imaginary C_3 axis.

formal analogy here to the situation that prevails for the nonrigid pyramidal molecules that exhibit a wide range of barriers to pyramidal inversion:[57] the barriers are generally very sensitive to the pyramidal XMX angles.

Acknowledgment. We are indebted to Mr. L. Lardear who constructed the precision molecular models.

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[57] See review by A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, 9, 400 (1970).

Negative Ion Mass Spectra of Nido Carboranes

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Abstract: The negative ion mass spectra of 2,3-dicarbahexaborane(8), 2-methyl-*nido*-2,3-dicarbahexaborane(8), and 2,3-dimethyl-*nido*-2,3-dicarbahexaborane(8) have been investigated. Evidence has been found to show that formation of negative ions in these nido carboranes occurs predominantly *via* resonance capture and dissociative resonance capture mechanisms. With the aid of deuterium labeling experiments, a diagnostic fragmentation giving a P − 1 anion which is specific for loss of a bridge hydrogen has been found. Discrete and narrow electron energy ranges for electron capture have been determined and the electron energy dependence on ion intensities and fragmentations in the lower voltage regions have been studied.

In organoboron chemistry where a wide variety of stable anions and anionic intermediates have been known for years, it is remarkable that so few of these negative ions have been studied in the gas phase. The few reported studies have been mainly on boron hydrides.[2–6] In contrast, there have been numerous positive ion gas mass spectral studies of organoboron compounds, including carboranes.[5] Yet, the postulation of stable cations and cationic intermediates in organoboron chemistry, especially carborane chemistry, is extremely rare. For this reason, there are severe limitations on the potential for direct correlation between the positive ions produced in a mass spectrometer and the chemistry of carboranes or any other type of compounds where anions and anionic intermediates predominate. The study of these gas-phase anions with a mass spectrometer and the application of this technique hopefully will provide additional information on the well-known anionic intermediates in the chemistry of carboranes.

Experimental Section

All mass spectra were run on a Hitachi RMU-6E mass spectrometer in the negative mode at source temperatures ranging between 80 and 100°. The low voltage spectra were run with a repeller voltage of zero, filament emission range between 10 and 25 μA, and a trap current of approximately zero. The accelerating voltage used was either 1.8 or 3.6 kV and the electron multiplier voltage was 1.5 kV. Sample pressures ranged between 1 and 5×10^{-6} Torr, in the ion source. The electron energy was calibrated using literature values for the *m/e* 16 peak (O^-) maxima from CO_2 (4.4; 8.2 eV), CO (10.1 eV), N_2O (2.2 eV), and NO (8.15 eV).[7] No peaks are reported whose calculated relative monoisotopic intensity is <0.1% of the base peak. For each reported spectrum, a check was made for peaks higher than the parent ion. There were no other indications of ion-molecule reactions, such as nonlinear ion intensity variations with sample pressures.

The syntheses of **1**, **2**, **3** and the deuterium-labeled derivatives of **1** have all been reported.[8] The purity of all compounds was checked by infrared analysis on either a Beckman IR-5 or a Perkin-Elmer 137 spectrophotometer and by positive ion mass spectrometry. The highest mass checked for impurities was usually twice the mass of the parent ion. When needed, purification was effected by one of two methods: gas chromatography (a 30% Kel-F on firebrick column operating at about 60° was used) or a cold column distillation. Handling of chemicals was carried out using conventional high-vacuum apparatus.

Results and Discussion

$C_2B_4H_8$ (1). In a previous communication[9] we reported a portion of the mass spectra of 2,3-dicarbahexaborane (8) (**1**) at 70 and 8 eV. The major gas-phase anions produced in these spectra were shown to be *m/e* 75 ($C_2B_4H_7^-$), *m/e* 73 ($C_2B_4H_5^-$), and *m/e* 61 ($C_2B_3H_4^-$). The latter two ions have been correlated with the photochemical and thermal reaction products of $C_2B_4H_8$.[9] We have continued our study of $C_2B_4H_8$ by investigating the relationship of the energy of the bombarding electrons and intensities of these three major fragment ions. This type of information is particularly important in this case for three main reasons. (1) In contrast to positive ion mass spectrometry, there is a tremendous variation in ion intensity with electron energy in the low-voltage region (<15 eV). (2) The major ions are all characterized by narrow and intense low-voltage ion current maxima over narrow energy ranges. These low-voltage maxima rep-

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[2] D. F. Munro, J. E. Ahnell, and W. S. Koski, *J. Phys. Chem.*, 72, 2682 (1968).

[3] R. E. Enrione and R. Rosen, *Inorg. Chim. Acta*, 1, 1169 (1967).

[4] R. M. Reese, V. H. Dibeler, and F. L. Mohler, *J. Res. Nat. Bur. Stand.*, 57, 367 (1956).

[5] For a review and primary references, see J. F. Ditter, F. J. Gerlart, and R. E. Williams, *Advan. in Chem. Ser.*, No. 72, 191 (1969).

[6] R. C. Dunbar, *J. Amer. Chem. Soc.*, 93, 4167 (1971).

[7] L. G. Christophorou and R. N. Compton, *Health Phys.*, 13, 1277 (1967).

[8] (a) T. P. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, 3, 1686 (1964); (b) T. Onak and G. B. Dunks, *ibid.*, 5, 439 (1966); (c) J. R. Spielman, R. Warren, G. B. Dunks, J. E. Scott, Jr., and T. Onak, *ibid.*, 7, 216 (1968).

[9] C. L. Brown, K. P. Gross, and T. P. Onak, *Chem. Commun.*, 78 (1972).