The Crystal and Molecular Structure of Bis(2-methyl-8-quinolinolato)aluminum(III)-μ-oxo-bis(2-methyl-8-quinolinolato)aluminum(III)

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Abstract: The crystal and molecular structure of the compound $Al_2O(C_{10}H_8NO)_4$ has been determined by three-dimensional single-crystal X-ray diffraction techniques. The crystals of the compound are orthorhombic (Pbca) with $a = 19.09 \pm 0.01$ Å, $b = 17.04 \pm 0.01$ Å, and $c = 21.08 \pm 0.01$ Å. The observed density, 1.363 g/cm^3, agrees well with the calculated density 1.362 g/cm^3 for $Z = 8$. The structure was refined by full-matrix least-squares methods to a conventional R value of 8.9% over 3821 independent nonzero reflections which were collected by film techniques. The compound consists of two trigonal-bipyramidal pentacoordinated aluminum atoms joined together by an oxo bridge; the Al–O–Al bridge is linear and the Al–O distance in the oxo bridge (1.68 Å) is extremely short. The remaining four coordination positions around each of the aluminum atoms are occupied by two molecules of the bidentate ligand, 2-methyl-8-quinolinol. The presence of the methyl groups contributes to the unusual stability of the compound.

The reagent 2-methyl-8-quinolinol is useful for the determination of many transition metal ions in the presence of aluminum(III). This reagent has been used since 1944, when it was first reported that 2-methyl-8-quinolinol did not form a precipitate with aluminum(III).[1] For many years the behavior of 2-methyl-8-quinolinol with aluminum(III) was considered to be anomalous, since it was found that it did react with gallium(III) and beryllium(II) to form insoluble precipitates. The accepted explanation for the apparent nonreactivity of the 2-methyl derivative is that the ligand could not replace the water molecules that solvated the aluminum(III) ion because of steric interactions between the 2-methyl group and the water molecules.[2] Structural information on the complexes of aluminum(III), gallium(III), and beryllium(II) with 2-methyl-8-quinolinol and with 8-quinolinol is necessary for evaluating the proposed steric effects. We have synthesized several complexes of 2-methyl-8-quinolinol and aluminum(III) in nonaqueous media.[3] It was found that several of these compounds were unstable in air and decomposed extensively on exposure to X-rays. We report below the structure of one of the most stable compounds that was synthesized.[4]

Experimental Section

The compound $Al_2O(C_{10}H_8NO)_4$ was obtained by the reaction of anhydrous aluminum chloride with 2-methyl-8-quinolinol in dry chloroform. Crystals that were suitable for X-ray analysis were obtained from a mixture of chloroform and carbon disulfide. The unit cell dimensions and the space group were determined from oscillation and Weissenberg photographs with Cu Kα radiation (λ 1.5418 Å). Sodium chloride calibration lines were added to the edges of the Weissenberg photographs for calibration purposes. The crystal was orthorhombic and its unit cell dimensions found at 25° are: $a = 19.09 \pm 0.01$ Å, $b = 17.04 \pm 0.01$ Å, $c = 21.08 \pm 0.01$ Å. The standard deviations in the cell dimensions were estimated from the reproducibility of the measurements. From the systematic absences ($hk0$, $h = 2n + 1$; $h0l$, $l = 2n + 1$; and $0kl$, $k = 2n + 1$), it was deduced that the space group was Pbca. The observed density determined by the flotation method was 1.363 g/cm^3; the calculated value based on $Z = 8$ formula units was 1.362 g/cm^3. In the centrosymmetric space group with $Z = 8$, all atoms may occupy general positions.

Intensity data for reciprocal lattice levels $h0l$–$h11l$ were collected by the multiple-film equiinclination Weissenberg technique with a crystal of approximate dimensions 0.08 × 0.25 × 0.49 mm. Another crystal of approximate dimensions 0.08 × 0.62 × 0.62 mm was used for the $hk0$ –$hk12$ levels. Nickel-filtered Cu Kα radiation was employed and the intensities were estimated visually by comparison with a calibrated strip. Lorentz–polarization and spot-shape corrections were applied in the usual manner. No corrections for absorption were made since $\mu = 13.3$ cm^{-1}. The total number of independent reflections that were measured was 6100; of these, 3821 were nonzero reflections. The maximum value of $\sin \theta/\lambda$ was 0.64. Atom scattering factors given in "International Tables" were used for all atoms.[5]

Solution and Refinement of Structure

A sharpened three-dimensional Patterson synthesis showed two extremely high peaks at $U, V, W = (0, 0, {}^1/_2)$ and $(0, {}^1/_2, {}^1/_4)$. These peaks indicated that the center of the molecule might be located at $x, y, z = (0, {}^1/_4, {}^1/_8)$. The initial trial structure that was assumed for the molecule was the dihydroxo-bridged dimer $[Al(C_{10}H_8NO)_2(OH)]_2$, which had hexacoordinated aluminum atoms.[3] This erroneous assumption and the absence of any heavy atoms contributed to the failure of further attempts to interpret the Patterson function. An approximate idea of the orientation of the molecule, however, was deduced.

Normalized structure factors (E values) were computed by the program FAME.[6] Table I shows the experimental and theoretical values for several functions of E. These results confirm the presence of a centrosymmetric space group. The program FAME calculated a Σ_2 list and also assigned symbols to several of the largest E values having the greatest number of Σ_2 interactions, which were used as a starting set. Table II shows these reflections. The first three reflections in Table II were used as origin-determining reflections. The sign of reflection (8, 4, 8) was calculated by use of the Σ_1 formula (the value of $|E|_{4,2,4} = 2.98$). The symbols A, B, and C were assigned as phases to the three remaining reflections in Table II.

Two thousand reflections for which $|E| > 0.74$ were

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[1] L. L. Merritt and J. K. Walker, *Ind. Eng. Chem., Anal. Ed.*, 16, 387 (1944).

[2] H. Irving, E. J. Butler, and M. E. Ring, *J. Chem. Soc.*, 1489 (1949).

[3] P. R. Scherer and Q. Fernando, *Anal. Chem.*, 40, 1938 (1968).

[4] Y. Kushi and Q. Fernando, *Chem. Commun.*, 555 (1969).

(5) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 202–205.

(6) The four programs FAME, MAGIC, LINK, and SYMPL, written by R. Dewar and A. Stone of the University of Chicago, were used for the application of the symbolic addition method of Karle and Hauptman to any centric space group.

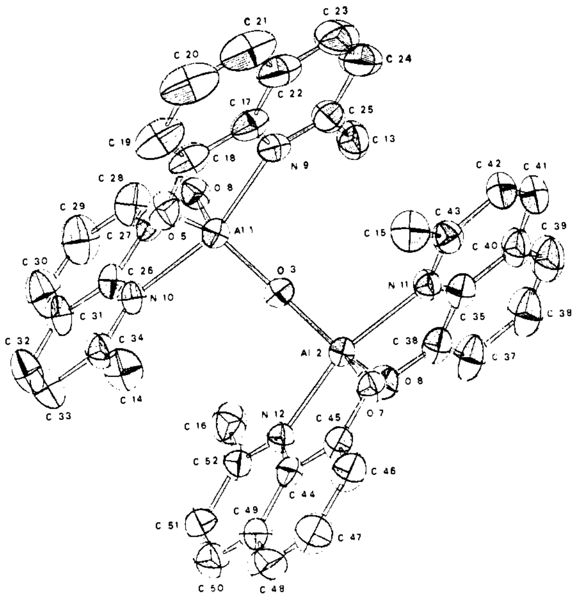

Figure 1. Projection of the $Al_2O(C_{10}H_8NO)_4$ molecule along [010].

Table I. Statistical Distributions and Averages, Experimental and Theoretical

	Experimental	Centro-symmetric	Noncentro-symmetric
$<\|E\|>$	0.657	0.798	0.886
$<\|E\|^2>$	0.983	1.000	1.000
$<\|E^2 - 1\|>$	1.163	0.968	0.736
$\|E\| > 1.0$	25.91%	32.00%	37.00%
$\|E\| > 2.0$	6.00%	5.00%	1.80%
$\|E\| > 3.0$	1.17%	0.30%	0.01%

Table II. Basic Phase Assignment Used in Application of the Symbolic Addition Procedure

h	k	l	Sign	$\|E\|$
3	2	4	+	4.08
12	1	14	+	4.86
8	4	7	+	3.42
10	3	13	A	3.03
5	2	3	B	3.03
7	3	6	C	4.00
8	4	8	+	5.42

arranged in descending order of magnitude in order to apply the Σ_2 formula. This was accomplished by the program MAGIC.[6] Starting with seven known signs (Table II) the program calculated in the first iteration, signs for 34 new reflections with a probability greater than 0.990. In the second iteration, 200 new signs were determined, and in the third iteration, 485 new signs (probability >0.990) were determined. Hence a total of 726 reflections with known signs were obtained in 4 min with the CDC-6400 computer with a 64K memory. The program also showed that the symbols A, B, and C were −, +, and −, respectively. An E map calculated with 726 terms revealed all the atoms in the structure, with the exclusion of the hydrogen atoms. It was apparent from this E map that the hydroxo-bridged trial structure with two hexacoordinated aluminum atoms was incorrect. The structure, from the E map, appeared to be a μ-oxo-bridged dimer with pentacoordinated aluminum atoms. A structure factor calculation with the coordinates of all the atoms in the molecule (51 atoms) gave a conventional R value of 48% for all the F_o data. A three-dimensional Fourier map was calculated next, and the atomic coordinates from this map gave an R value of 28%. Four cycles of full-matrix least-squares refinement with the program ORFLS[7] with isotropic temperature factors reduced the R value to 12%. The quantity minimized was $[\Sigma w(F_o - F_c)^2]^{1/2}$ with unit weight assigned to each reflection. Refinement of the structure with Cruickshank's weighting scheme,[8] the weighting factors being given by $w = 1/(a + |F_o| + c|F_o|^2)$, where $a = 20.0$ and $c = 0.004$, together with anisotropic temperature factors, gave, after three cycles, an R factor of 8.9% for 3821 nonzero terms. The largest shifts in the final refinement cycle were 0.004 Å for atom C(48) and 0.003 Å for atom C(44). No corrections for extinction were applied, and all hydrogen atoms in the molecule were neglected in the structure factor calculations.[9] The atomic positional and anisotropic thermal parameters are given in Table III.

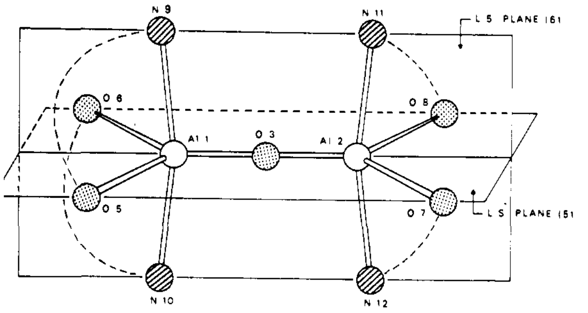

Figure 2. A perspective view of the coordination polyhedra around the aluminum atoms.

It is of interest to compare the analytical data for this compound which were reported earlier.[3] *Anal.* C, 67.72; H, 4.68; N, 7.81; density, 1.363 g/cm^3; mol wt (calculated from cell dimensions), 704. On the basis of the incorrect formula $Al_2(OH)_2(C_{10}H_8NO)_4$, the following values were calculated. *Anal.* C, 66.66; H, 4.75; N, 7.77; density, 1.372 g/cm^3; mol wt, 720.7. On the basis of the correct formula $Al_2O(C_{10}H_8NO)_4$, the following data are obtained. *Anal.* C, 68.37; H, 4.59; N, 7.97; density, 1.362 g/cm^3; mol wt, 702.7.

Description and Discussion of Structure

The structure consists of discrete molecules of $Al_2O(C_{10}H_8NO)_4$ as shown in Figure 1, which was plotted with the program ORTEP.[10] The molecule does not have a center of symmetry, but it has approximately D2 (222) symmetry (Figure 2). The oxygen atom of the μ-oxo bridge is located at the intersection of three twofold axes. The two aluminum atoms and the oxygen lie on one of these twofold axes. The coordination around each of the aluminum atoms is trigonal bipyramidal. Three oxygen atoms and the aluminum atom form the equatorial plane and two nitrogen atoms occupy the apical positions. Two molecules of the bi-

(7) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least Squares Program," U. S. Atomic Energy Commission Publication ORNL-TM-305, 1962.

(8) D. W. J. Cruickshank, "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," R. Pepinsky, J. M. Robertson, and J. C. Speakman, Ed., Pergamon Press, New York, N. Y., 1961, p 45.

(9) For detailed paper, extended version, or supplementary material, order document No. NAPS-00590 from ASIS National Auxiliary Publications Service, c/o CCM Information Corp., 909 Third Ave., New York, N. Y. 10022, remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

(10) C. K. Johnson, "ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structures," U. S. Atomic Energy Commission Publication ORNL-3794, 1966.

Table III. Positional and Thermal Parameters[a]

Atom	x	y	z	$\beta_{11} \times 10^5$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Al(1)	0.4388(1)	0.2528(1)	0.3215(1)	164(4)	180(5)	155(4)	−7(4)	−14(3)	3(4)
Al(2)	0.5589(1)	0.2616(1)	0.4374(1)	146(4)	203(5)	148(4)	3(4)	−12(3)	−1(4)
O(3)	0.4991(2)	0.2589(3)	0.3792(2)	196(11)	422(19)	146(9)	−24(12)	−21(8)	2(12)
O(5)	0.3933(2)	0.3386(2)	0.2930(2)	254(14)	289(17)	266(14)	95(12)	−17(11)	46(13)
O(6)	0.4166(2)	0.1582(2)	0.2873(2)	201(11)	230(14)	184(10)	−39(10)	19(9)	−15(10)
O(7)	0.5901(2)	0.3557(2)	0.4668(2)	177(11)	268(15)	208(11)	−19(10)	3(9)	−67(11)
O(8)	0.5950(2)	0.1729(2)	0.4715(2)	239(13)	259(15)	208(12)	49(11)	2(10)	21(11)
N(9)	0.5033(3)	0.2755(3)	0.2438(2)	236(14)	256(17)	137(11)	−34(13)	−11(10)	3(12)
N(10)	0.3499(2)	0.2294(3)	0.3779(2)	170(12)	212(16)	194(12)	9(11)	4(10)	−2(12)
N(11)	0.6479(2)	0.2533(3)	0.3801(2)	164(12)	255(16)	174(11)	22(12)	5(10)	−13(13)
N(12)	0.4926(2)	0.2670(3)	0.5140(2)	157(13)	333(20)	170(12)	37(13)	5(10)	35(13)
C(13)	0.5775(3)	0.1581(4)	0.2457(4)	219(19)	409(28)	280(20)	49(19)	13(16)	−37(21)
C(14)	0.3427(4)	0.3513(4)	0.4385(4)	326(24)	258(23)	339(23)	9(19)	32(19)	−113(20)
C(15)	0.6400(4)	0.3789(4)	0.3242(4)	319(23)	253(23)	302(21)	−7(19)	−4(18)	48(19)
C(16)	0.4359(4)	0.1402(4)	0.5035(4)	252(20)	417(29)	312(22)	−73(21)	−17(18)	85(22)
C(17)	0.4840(3)	0.3460(4)	0.2182(3)	299(21)	264(22)	176(15)	−101(18)	−57(14)	28(16)
C(18)	0.4227(4)	0.3790(4)	0.2463(3)	364(24)	269(22)	195(16)	−13(19)	−73(16)	24(18)
C(19)	0.3974(5)	0.4488(4)	0.2220(4)	546(35)	232(23)	298(22)	26(23)	−136(23)	47(20)
C(20)	0.4323(6)	0.4858(4)	0.1709(4)	739(48)	281(28)	298(25)	−38(31)	−121(30)	65(23)
C(21)	0.4915(5)	0.4551(5)	0.1442(4)	663(43)	322(29)	263(23)	−210(29)	−125(26)	74(23)
C(22)	0.5177(4)	0.3829(5)	0.1679(3)	423(29)	441(32)	174(17)	−152(25)	−52(19)	48(20)
C(23)	0.5758(5)	0.3412(6)	0.1417(4)	415(33)	661(45)	212(19)	−209(32)	39(21)	82(26)
C(24)	0.5951(4)	0.2684(5)	0.1669(3)	383(27)	595(42)	181(16)	−164(28)	24(17)	−9(22)
C(25)	0.5580(3)	0.2364(4)	0.2192(3)	231(18)	352(25)	192(14)	−47(19)	5(14)	−49(17)
C(26)	0.3271(3)	0.1558(3)	0.3643(3)	158(14)	213(18)	209(15)	4(14)	−12(13)	16(15)
C(27)	0.3658(3)	0.1171(3)	0.3157(3)	189(16)	210(19)	195(15)	−19(14)	−38(13)	12(14)
C(28)	0.3482(4)	0.0413(4)	0.2991(4)	294(23)	216(21)	336(22)	−44(18)	−20(18)	0(19)
C(29)	0.2907(4)	0.0046(4)	0.3304(4)	310(26)	340(29)	450(29)	−124(22)	1(24)	−27(25)
C(30)	0.2530(4)	0.0413(5)	0.3769(4)	275(23)	416(31)	423(28)	−128(22)	55(22)	−8(25)
C(31)	0.2710(3)	0.1190(4)	0.3950(3)	176(17)	315(24)	288(20)	−45(16)	21(15)	8(19)
C(32)	0.2375(4)	0.1620(5)	0.4434(4)	217(21)	474(34)	370(24)	−42(21)	98(19)	−6(25)
C(33)	0.2605(4)	0.2370(4)	0.4568(4)	250(21)	445(32)	310(21)	20(21)	81(17)	−3(22)
C(34)	0.3173(3)	0.2701(4)	0.4230(3)	202(17)	321(24)	240(17)	32(16)	18(14)	−37(17)
C(35)	0.6783(3)	0.1829(3)	0.3903(3)	182(16)	210(19)	221(16)	13(15)	−29(14)	−46(15)
C(36)	0.6490(3)	0.1388(3)	0.4413(3)	188(17)	247(21)	239(17)	22(15)	−41(14)	−48(16)
C(37)	0.6780(4)	0.0674(4)	0.4574(4)	248(21)	273(24)	380(24)	51(18)	−74(19)	−52(20)
C(38)	0.7346(4)	0.0373(4)	0.4192(4)	294(25)	342(29)	439(28)	111(22)	−42(22)	−83(25)
C(39)	0.7611(4)	0.0780(5)	0.3693(4)	257(22)	414(32)	384(26)	121(22)	−16(20)	−55(25)
C(40)	0.7343(3)	0.1535(4)	0.3541(3)	189(18)	324(24)	274(19)	55(17)	−16(15)	−67(19)
C(41)	0.7582(3)	0.2016(5)	0.3044(4)	178(19)	529(34)	273(19)	32(21)	21(17)	−26(22)
C(42)	0.7293(3)	0.2748(4)	0.2958(3)	188(18)	485(32)	251(19)	−5(20)	15(15)	−32(21)
C(43)	0.6735(3)	0.3004(3)	0.3350(3)	203(17)	268(22)	194(15)	−39(15)	2(14)	8(15)
C(44)	0.5026(3)	0.3371(4)	0.5436(3)	185(16)	406(26)	157(14)	86(17)	−28(12)	1(17)
C(45)	0.5561(3)	0.3855(3)	0.5162(3)	185(16)	286(21)	195(15)	20(16)	−46(14)	−28(16)
C(46)	0.5683(4)	0.4583(4)	0.5412(4)	278(22)	339(25)	293(21)	78(19)	−67(18)	−140(20)
C(47)	0.5306(4)	0.4847(5)	0.5958(4)	336(26)	445(33)	314(23)	69(24)	−39(21)	−107(24)
C(48)	0.4810(4)	0.4372(5)	0.6236(4)	384(28)	534(37)	219(20)	210(26)	−41(20)	−98(23)
C(49)	0.4666(4)	0.3623(4)	0.5986(3)	255(20)	515(34)	175(16)	179(22)	−11(15)	−6(20)
C(50)	0.4181(4)	0.3065(5)	0.6228(4)	270(22)	616(42)	235(21)	139(25)	35(18)	71(25)
C(51)	0.4073(4)	0.2381(5)	0.5930(4)	237(21)	684(45)	236(19)	49(25)	27(16)	87(26)
C(52)	0.4459(3)	0.2166(4)	0.5369(3)	168(16)	423(27)	233(17)	14(18)	−4(14)	109(19)

[a] The anisotropic temperature factors listed are defined as $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

dentate ligand, 2-methyl-8-quinolinol, are therefore coordinated to each of the aluminum atoms.

The bond distances and bond angles in the molecule are summarized in Tables IV and V. There are two types of Al–O bonds; the first type is 1.68 Å (between aluminum and the oxygen of the μ-oxo bridge), and the second type is 1.81 Å (between aluminum and the oxygen of the 2-methyl-8-quinolinolato group). The short Al–O distance is between Al^{3+} and O^{2-}, whereas the long Al–O distance is between Al^{3+} and O^{-}. (The superscripts denote the formal charges on these atoms.) In tetracoordinated aluminum complexes the average Al–O distance is 1.785 Å, and in hexacoordinated complexes the average Al–O distance[11] is 1.91 Å. In a pentacoordinated aluminum complex the Al–O distance ranged from 1.80 to 1.94 Å.[12] In the μ-oxo-bridged compound, one of the Al–O distances (1.81 Å) is in the range found previously for a pentacoordinated complex whereas the other Al–O distance (1.68 Å) is the shortest Al–O distance reported to date. The average Al–N distance (2.09 Å) is within the range of 2.00 and 2.18 Å, reported in the compounds aluminum borohydride–trimethylamine[13] and bis(trimethylamine)alane,[14] respectively.

The average value of the N–Al–N angle is 163°, which clearly indicates that the nitrogen atoms do not lie on the perpendicular drawn through the aluminum atom to the plane formed by the three oxygen atoms. The Al–O–Al angle is 178°, and these three atoms that form the μ-oxo bridge lie approximately on a straight line. Although there are no other M–O–M bridges, where M is a nontransition metal ion, the Al–O–Al angle may be

[11] "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, 1962, p 262.

[12] M. Bonamico, *Chem. Commun.*, 135 (1966).

[13] N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, *ibid.*, 286 (1966).

[14] C. W. Hertsch, C. E. Nordman, and R. W. Parry, *Inorg. Chem.*, 2, 508 (1963).

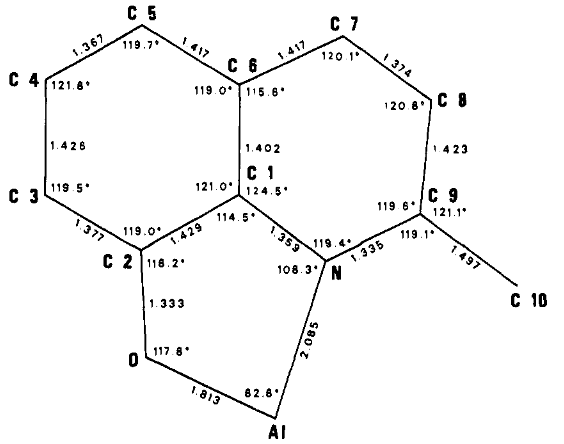

Figure 3. The average bond distances and bond angles in the 2-methyl-8-quinolinolato group. The carbon atom numering in this figure is independent of the previous numbering system, since this figure represents the average of four 2-methyl-8-quinolinolato groups.

Table IV. Bond Distances (Å) in $Al_2O(C_{10}H_8NO)_4$

Al(1)–Al(2)	3.354(3)	C(20)–C(21)	1.366(13)
Al(1)–O(3)	1.676(4)	C(21)–C(22)	1.420(11)
Al(1)–O(5)	1.804(5)	C(22)–C(23)	1.429(12)
Al(1)–O(6)	1.817(5)	C(23)–C(24)	1.399(12)
Al(1)–N(9)	2.086(5)	C(24)–C(25)	1.419(9)
Al(1)–N(10)	2.110(5)	C(26)–C(27)	1.426(8)
Al(2)–O(3)	1.678(4)	C(26)–C(31)	1.400(8)
Al(2)–O(7)	1.820(5)	C(27)–C(28)	1.379(8)
Al(2)–O(8)	1.809(5)	C(28)–C(29)	1.426(10)
Al(2)–N(11)	2.090(5)	C(29)–C(30)	1.367(11)
Al(2)–N(12)	2.054(5)	C(30)–C(31)	1.419(10)
		C(31)–C(32)	1.409(10)
O(5)–C(18)	1.324(8)	C(32)–C(33)	1.381(10)
O(6)–C(27)	1.337(7)	C(33)–C(34)	1.414(9)
O(7)–C(45)	1.326(7)		
O(8)–C(36)	1.345(7)	C(35)–C(36)	1.426(9)
		C(35)–C(40)	1.405(8)
N(9)–C(17)	1.367(8)	C(36)–C(37)	1.378(8)
N(9)–C(25)	1.342(8)	C(37)–C(38)	1.442(10)
N(10)–C(26)	1.358(7)	C(38)–C(39)	1.358(11)
N(10)–C(34)	1.332(8)	C(39)–C(40)	1.422(10)
N(11)–C(35)	1.350(7)	C(40)–C(41)	1.407(10)
N(11)–C(43)	1.336(8)	C(41)–C(42)	1.376(10)
N(12)–C(44)	1.360(8)	C(42)–C(43)	1.417(9)
N(12)–C(52)	1.329(8)		
		C(44)–C(45)	1.435(9)
C(13)–C(25)	1.494(9)	C(44)–C(49)	1.414(9)
C(14)–C(34)	1.502(9)	C(45)–C(46)	1.368(8)
C(15)–C(43)	1.499(9)	C(46)–C(47)	1.429(10)
C(16)–C(52)	1.492(10)	C(47)–C(48)	1.376(12)
		C(48)–C(49)	1.407(11)
C(17)–C(18)	1.427(10)	C(49)–C(50)	1.423(11)
C(17)–C(22)	1.390(9)	C(50)–C(51)	1.340(11)
C(18)–C(19)	1.383(9)	C(51)–C(52)	1.441(10)
C(19)–C(20)	1.414(12)		

compared with M–O–M angles, where M is a transition metal. For instance, the Mn–O–Mn angle is 178° in μ-oxo-phthalocyanatopyridinemanganese(III);[15] and the Fe–O–Fe angle is 139° in μ-oxo-bis(salicylidene–ethylenediaminepyridine)iron(III),[16] and 165° in the compound (HEDTA)Fe–O–Fe(HEDTA).[17] Any description of the bonding in the μ-oxo-bridged aluminum complex must explain the short Al–O distance and the almost linear Al–O–Al bridge.

In the coordination polyhedron of aluminum there are three types of N–Al–O angles. The first type, N–Al–O (μ-oxo), has an average value of 98.5°; for the second type, N–Al–O in which the Al atom is in the chelate ring, the average value of the angle is 82.8°; in the third type, the average value of the N–Al–O angle is 88.5°. The O–Al–O angles fall into two groups. In one group, the angle O–Al–O (μ-oxo) has an average value of 120.8°, and in the second group the average O–Al–O angle is 118.4°. A short Al–O (μ-oxo) distance and the five-membered chelate ring formation give rise to the above effects.

Table VI shows the properties of six important least-squares planes in the molecule. The planes 1–4 represent the four chelated 2-methyl-8-quinolinolato groups. The two aluminum atoms and the five coordinated oxygen atoms lie on plane 5. The four nitrogen atoms and the Al–O–Al bridge lie on plane 6. The maximum deviation of an atom from plane 6 is 0.3 Å, and from plane 5 is 0.1 Å. Planes 5 and 6 are perpendicular to each other. The deviations of the atoms from the least-squares planes of the chelated 2-methyl-8-quinolinol molecules are very small and are given in Table VII. The angles between each of the planes of the four chelated 2-methyl-8-quinolinolato groups and plane 5 vary between 85.6 and 88.4°. With plane 6, the dihedral angles formed by the four planes vary between 63.0 and 66.7°. The angle between the planes of two 2-methyl-8-quinolinolato groups which are coordinated to the same aluminum atom is 51.0° in one-half of the molecule and 50.2° in the other. Also the pairs of planes 1 and 3, and 2 and 4, are almost parallel, the dihedral angles between them being 3.7 and 7.5°.

There are four independent 2-methyl-8-quinolinolato groups in the molecule. Figure 3 shows the average values of the bond distances and bond angles in these groups. The bond distances in the metal chelate ring can be compared with the corresponding distances in the copper(II) chelate of 8-quinolinol. The C–O distance (1.33 Å) compares well with the values 1.32 and 1.33 Å obtained for the α[18] and β[19] forms of the copper(II) chelate of 8-quinolinol. The C–N distance (1.36 Å) in the aluminium chelate is comparable with 1.37 and 1.36 Å which are the C–N distances in copper(II) chelates. The C–C distance (1.43 Å) in the aluminum chelate ring agrees with the values 1.43 and 1.42 Å in the copper(II) chelate rings. Hence, the methyl group in the 2 position does not affect the bond distances in the chelate ring. However, the distance between the carbon atom of the 2-methyl group and the ring carbon is 1.50 Å, which is significantly shorter than 1.54 Å.

The introduction of the aluminum atom with a residual positive charge into the chelate ring has delocalized the electrons in the quinoline nucleus. This is apparent from the bond distances in the ring system which are alternately long and short (Figure 3). It is also of interest to compare these bond distances with the values calculated by self-consistent field molecular orbital theory for the quinoline molecule.[20] Figure 4 shows that the agreement between the calculated bond distances and the experimental values is quite good. It is surprising that the additional presence of the chelate ring as well as a methyl group in the 2 position has no noticeable

(15) L. H. Vogt, Jr., A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **6**, 1725 (1967).

(16) M. Gerloch, E. D. McKenzie, and A. Towl, *Nature*, **220**, 906 (1968).

(17) S. J. Lippard, H. Schugar, and C. Walling, *Inorg. Chem.*, **6**, 1825 (1967).

(18) R. C. Hoy and R. H. Morris, *Acta Cryst.*, **22**, 476 (1967).

(19) G. J. Palenik, *ibid.*, **17**, 687 (1964).

(20) K. Nishimoto and L. S. Forster, *Theor. Chim. Acta*, **4**, 155 (1966).

Table V. Bond Angles in $Al_2O(C_{10}H_8NO)_4$

Al(1)-O(3)-Al(2)	178.0(3)	C(23)-C(24)-C(25)	120.3(8)
N(9)-Al(1)-O(3)	98.8(2)	C(24)-C(25)-N(9)	119.8(6)
N(9)-Al(1)-O(5)	86.6(2)	C(25)-N(9)-C(17)	119.6(5)
N(9)-Al(1)-O(6)	89.5(2)	C(24)-C(25)-C(13)	120.6(7)
N(9)-Al(1)-N(10)	162.2(2)	C(13)-C(25)-N(9)	119.5(6)
O(3)-Al(1)-O(6)	120.2(2)	C(26)-C(27)-C(28)	119.3(6)
O(3)-Al(1)-O(5)	121.5(2)	C(27)-C(28)-C(29)	118.7(7)
O(3)-Al(1)-N(10)	98.9(2)	C(28)-C(29)-C(30)	122.5(7)
N(10)-Al(1)-O(5)	87.4(2)	C(29)-C(30)-C(31)	119.4(7)
N(10)-Al(1)-O(6)	82.4(2)	C(30)-C(31)-C(26)	118.7(6)
O(5)-Al(1)-O(6)	118.3(2)	C(31)-C(26)-C(27)	121.4(5)
N(11)-Al(2)-O(3)	97.4(2)	N(10)-C(26)-C(31)	124.2(6)
N(11)-Al(2)-O(7)	89.5(2)	C(26)-C(31)-C(32)	116.6(6)
N(11)-Al(2)-O(8)	82.2(2)	C(31)-C(32)-C(33)	119.0(6)
N(11)-Al(2)-N(12)	163.5(2)	C(32)-C(33)-C(34)	120.7(7)
O(3)-Al(2)-O(7)	119.7(2)	C(33)-C(34)-N(10)	120.7(6)
O(3)-Al(2)-O(8)	121.8(2)	C(34)-N(10)-C(26)	118.8(5)
O(3)-Al(2)-N(12)	99.0(2)	N(10)-C(34)-C(14)	118.9(6)
N(12)-Al(2)-O(7)	83.9(2)	C(14)-C(34)-C(33)	120.4(6)
N(12)-Al(2)-O(8)	87.7(2)	C(35)-C(36)-C(37)	119.6(6)
O(7)-Al(2)-O(8)	118.5(2)	C(36)-C(37)-C(38)	118.5(7)
Al(1)-O(5)-C(18)	117.7(4)	C(37)-C(38)-C(39)	122.1(7)
O(5)-C(18)-C(17)	116.8(5)	C(38)-C(39)-C(40)	120.1(7)
C(18)-C(17)-N(9)	113.8(5)	C(39)-C(40)-C(35)	118.3(7)
C(17)-N(9)-Al(1)	108.2(4)	C(40)-C(35)-C(36)	121.2(5)
Al(1)-O(6)-C(27)	117.2(4)	N(11)-C(35)-C(40)	123.9(6)
O(6)-C(27)-C(26)	117.0(5)	C(35)-C(40)-C(41)	116.4(6)
C(27)-C(26)-N(10)	114.4(5)	C(40)-C(41)-C(42)	119.6(6)
C(26)-N(10)-Al(1)	108.3(4)	C(41)-C(42)-C(43)	120.3(7)
Al(2)-N(11)-C(35)	108.5(4)	C(42)-C(43)-N(11)	120.3(6)
N(11)-C(35)-C(36)	114.9(5)	C(43)-N(11)-C(35)	119.4(5)
C(35)-C(36)-O(8)	115.5(5)	N(11)-C(43)-C(15)	119.2(6)
C(36)-O(8)-Al(2)	117.7(4)	C(15)-C(43)-C(42)	120.5(6)
Al(2)-N(12)-C(44)	108.3(4)	C(44)-C(45)-C(46)	119.1(6)
N(12)-C(44)-C(45)	114.8(5)	C(45)-C(46)-C(47)	120.7(7)
C(44)-C(45)-O(7)	116.4(5)	C(46)-C(47)-C(48)	120.3(7)
C(45)-O(7)-Al(2)	116.4(4)	C(47)-C(48)-C(49)	120.5(7)
C(17)-C(18)-C(19)	118.1(7)	C(48)-C(49)-C(44)	119.2(7)
C(18)-C(19)-C(20)	120.1(8)	C(49)-C(44)-C(45)	120.1(6)
C(19)-C(20)-C(21)	122.2(7)	N(12)-C(44)-C(49)	125.1(6)
C(20)-C(21)-C(22)	118.6(8)	C(44)-C(49)-C(50)	114.0(7)
C(21)-C(22)-C(17)	119.8(8)	C(49)-C(50)-C(51)	120.9(7)
C(22)-C(17)-C(18)	121.2(6)	C(50)-C(51)-C(52)	121.8(7)
N(9)-C(17)-C(22)	124.9(7)	C(51)-C(52)-N(12)	118.4(7)
C(17)-C(22)-C(23)	115.5(7)	C(52)-N(12)-C(44)	119.7(5)
C(22)-C(23)-C(24)	119.8(7)	N(12)-C(52)-C(16)	118.7(6)
		C(16)-C(52)-C(51)	122.9(6)

Table VIA. Six Important Least-Squares Planes[a]

	Equations of the least-squares planes[a]
LS plane 1	$0.6004X + 0.4863Y + 0.6348Z = 1.1130$
LS plane 2	$0.6263X - 0.3730Y + 0.6846Z = 8.1950$
LS plane 3	$0.6267X + 0.4302Y + 0.6497Z = 1.4791$
LS plane 4	$0.6996X - 0.4117Y + 0.5840Z = 1.1053$
LS plane 5	$-0.7220X - 0.0650Y + 0.6888Z = -1.6488$
LS plane 6	$-0.0744X + 0.9970Y + 0.0208Z = 3.8234$

[a] Where X, Y, Z are the atom coordinates in Å.

effect on the bond distances in the quinoline ring. It has been observed recently that the coordination of a negatively charged group, $NiBr_3^-$, to the quinoline nitrogen atom resulted in a negligible effect on the quinoline structure.[21]

Table VII shows a number of selected intramolecular nonbonded contacts between the 2-methyl carbon atoms and neighboring atoms. The 2-methyl carbon atoms have two short intramolecular contacts. The shorter contact is the C–O distance (3.16–3.22 Å) and the longer contact is the C–LS plane (3.36–3.54) Å. These short intramolecular contacts of the methyl groups help to preserve the rigidity of the molecule. The extraordinary stability of the compound in air can also be attributed to the presence of the methyl groups. The aluminum atom is completely surrounded by the organic moieties which prevent the approach of any attacking agent.

Table VIII gives all van der Waals contacts which are less than 3.6 Å. Figure 5 shows a boundary projection of the crystal structure ($y = 0$ to $y = {}^1/_2$). Table IX and Figure 5 show that there are many intermolecular contacts in the yz plane whereas only a few occur in the x direction. The crystal habit shows that the a axis is not elongated as expected from the packing of the molecules in the unit cell.

The structure of the compound $Al_2O(C_{10}H_8NO)_4$ which has been described above is of interest for several reasons. Pentacoordinated complexes of aluminum are rare, although in principle aluminum can have coordination numbers of 4, 5, or 6 with equal facility. The structures of only three other pentacoordinated complexes of aluminum have been conclusively established.[11,13,22] Although compounds with oxo-bridged nontransition metals are known, there are none in which

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(21) W. de W. Horrocks, Jr., D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, 7, 2303 (1968).

(22) G. J. Palenik, *Acta Cryst.*, 17, 1573 (1964).

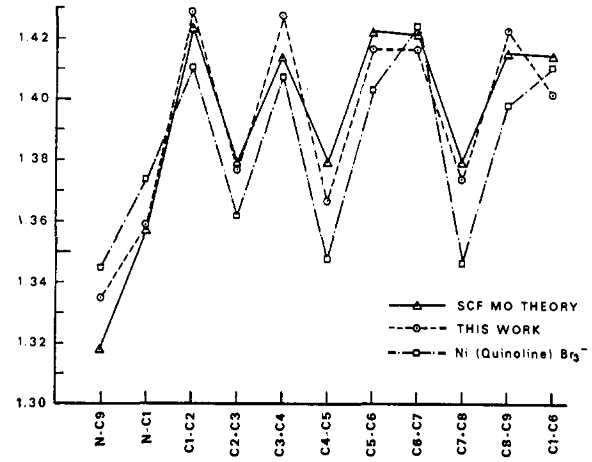

Figure 4. Comparison of the bond distances observed experimentally and calculated on the basis of SCF–MO theory.

Table VIB. Distances (Å) of the Atoms from Their Least-Squares Planes

LS plane 1		LS plane 3		LS plane 5	
Al(1)	0.127	Al(2)	−0.196	Al(1)	−0.011
O(5)	−0.065	O(8)	0.053	Al(2)	0.007
N(9)	0.014	N(11)	0.023	O(3)	−0.011
C(13)	−0.083	C(15)	0.084	O(5)	0.108
C(17)	0.035	C(35)	0.011	O(6)	−0.097
C(18)	−0.018	C(36)	0.035	O(7)	−0.100
C(19)	−0.055	C(37)	0.079	O(8)	0.103
C(20)	−0.032	C(38)	0.012		
C(21)	0.035	C(39)	−0.056	N(9)	−2.053[a]
C(22)	0.054	C(40)	−0.031	N(10)	2.059[a]
C(23)	0.023	C(41)	−0.073	N(11)	−2.042[a]
C(24)	−0.022	C(42)	0.000	N(12)	2.027[a]
C(25)	−0.012	C(43)	0.057		
LS plane 2		LS plane 4		LS plane 6	
Al(1)	0.084	Al(2)	−0.040	Al(1)	−0.010
O(6)	−0.074	O(7)	0.079	Al(2)	0.019
N(10)	−0.017	N(12)	−0.020	O(3)	0.033
C(14)	−0.003	C(16)	−0.017	N(9)	0.249
C(26)	−0.018	C(44)	−0.014	N(10)	−0.257
C(27)	−0.010	C(45)	0.024	N(11)	−0.273
C(28)	0.022	C(46)	−0.017	N(12)	0.239
C(29)	0.019	C(47)	−0.033		
C(30)	0.006	C(48)	−0.020	O(5)	1.499[a]
C(31)	−0.011	C(49)	0.005	O(6)	−1.601[a]
C(32)	0.013	C(50)	0.047	O(7)	1.587[a]
C(33)	0.005	C(51)	0.016	O(8)	−1.524[a]
C(34)	−0.014	C(52)	−0.009		

[a] These atoms are not included in the LS plane calculation.

Table VIC. Angles between Least-Squares Planes

LS plane 1–LS plane 2	51.0	LS plane 3–LS plane 4	50.2
LS plane 1–LS plane 3	3.7	LS plane 3–LS plane 5	88.1
LS plane 1–LS plane 4	53.8	LS plane 3–LS plane 6	66.7
LS plane 1–LS plane 5	88.4	LS plane 4–LS plane 5	85.6
LS plane 1–LS plane 6	63.0	LS plane 4–LS plane 6	63.2
LS plane 2–LS plane 3	47.4	LS plane 5–LS plane 6	89.8
LS plane 2–LS plane 4	7.5		
LS plane 2–LS plane 5	87.5		
LS plane 2–LS plane 6	66.2		

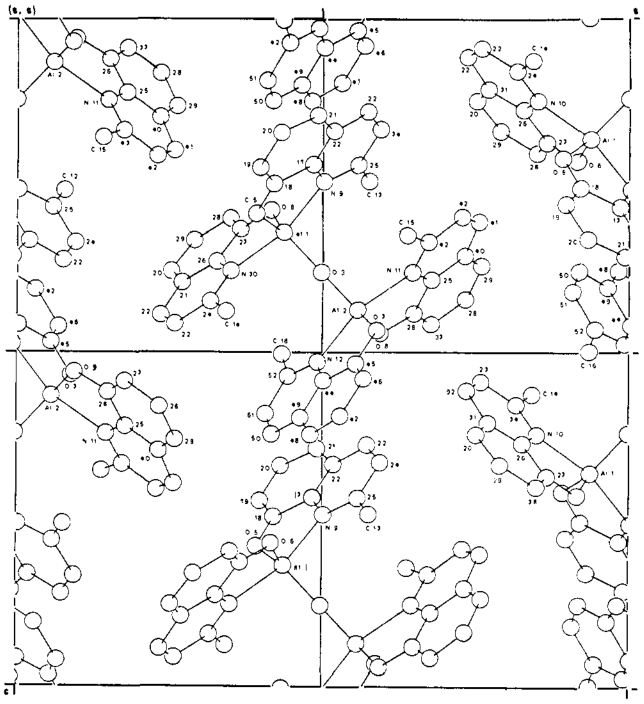

Figure 5. Projection of the contents of half the unit cell down the [010] axis.

Table VII. Selected Intramolecular Nonbonded Contacts (Å)

C(13)–Al(1)	3.488(7)	C(13)–N(11)	3.531(9)
C(14)–Al(1)	3.502(7)	C(14)–N(12)	3.576(9)
C(15)–Al(2)	3.476(7)	C(15)–N(9)	3.576(9)
C(16)–Al(2)	3.426(7)	C(16)–N(10)	3.466(9)
C(13)–O(3)	3.621(8)	C(13)–C(43)	3.577(9)
C(14)–O(3)	3.599(8)	C(14)–C(52)	3.666(10)
C(15)–O(3)	3.572(8)	C(15)–C(25)	3.640(10)
C(16)–O(3)	3.523(8)	C(16)–C(34)	3.593(10)
C(13)–O(6)	3.194(8)	C(13)–LS plane 3	3.358[a]
C(14)–O(5)	3.224(9)	C(14)–LS plane 4	3.543[a]
C(15)–O(7)	3.178(9)	C(15)–LS plane 1	3.514[a]
C(16)–O(8)	3.160(8)	C(16)–LS plane 2	3.391[a]

[a] See Table VI.

Table VIII. Intermolecular Contacts Less Than 3.60 Å

Atom in molecule at x, y, z	Distance, Å	Atom	Neighboring molecule
O(7)	3.406(8)	C(32)	0.5 + x, 0.5 − y, 1.0 − z
C(39)	3.589(11)	C(50)	0.5 + x, 0.5 − y, 1.0 − z
C(41)	3.418(10)	C(50)	0.5 + x, 0.5 − y, 1.0 − z
C(20)	3.427(11)	C(13)	1.0 − x, 0.5 + y, 0.5 − z
C(21)	3.589(11)	C(28)	1.0 − x, 0.5 + y, 0.5 − z
C(46)	3.442(14)	C(46)	1.0 − x, 1.0 − y, 1.0 − z
C(46)	3.585(11)	C(47)	1.0 − x, 1.0 − y, 1.0 − z
C(16)	3.545(11)	C(21)	x, 0.5 − y, 0.5 + z
C(48)	3.557(10)	C(13)	x, 0.5 − y, 0.5 + z
C(49)	3.513(9)	C(25)	x, 0.5 − y, 0.5 + z
C(50)	3.519(9)	O(6)	x, 0.5 − y, 0.5 + z
C(50)	3.332(9)	N(9)	x, 0.5 − y, 0.5 + z
C(50)	3.518(10)	C(17)	x, 0.5 − y, 0.5 + z
C(50)	3.434(10)	C(25)	x, 0.5 − y, 0.5 + z
C(51)	3.341(9)	C(17)	x, 0.5 − y, 0.5 + z
C(51)	3.344(10)	C(22)	x, 0.5 − y, 0.5 + z
C(52)	3.520(9)	C(22)	x, 0.5 − y, 0.5 + z
C(52)	3.466(11)	C(23)	x, 0.5 − y, 0.5 + z
C(41)	3.562(9)	C(27)	0.5 + x, y, 0.5 − z

a linear oxo bridge has been found. There can be no doubt that the unoccupied d orbitals of the aluminum atoms are involved in the bonding. A complete description of the bonding in the coordination polyhedron of the aluminum atom would be of importance in understanding the spectral and magnetic properties of this class of compounds.

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