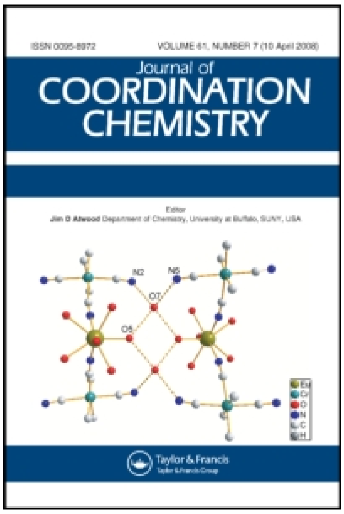

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Hon, P. K. and Pfluger, C. E.(1973) 'THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIS (ACETYLACETONATO)-ALUMINUM(III) AND -COBALT(III)', Journal of Coordination Chemistry, 3: 1, 67 — 76
To link to this Article: DOI: 10.1080/00958977308073789
URL: http://dx.doi.org/10.1080/00958977308073789

J. Coord. Chem., 1973, Vol. 3, pp. 67–76

THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIS (ACETYLACETONATO)-ALUMINUM(III) AND -COBALT(III)

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(*Received July* 11, 1972; *in final form October* 16, 1972)

The structures of tris(acetylacetonato)–Al(III) and –Co(III), $M(CH_3COCHCOCH_3)_3$, have been determined by 3-dimensional single crystal X-ray diffraction methods. These isomorphous complexes belong to the monoclinic crystal system and contain four molecules in the space group $P2_1/c$. The unit cell dimensions of tris(acetylacetonato)Al(III) are: $a = 14.069 \pm 0.009$ Å, $b = 7.568 \pm 0.005$ Å, $c = 16.377 \pm 0.010$ Å, $\beta = 99°00' \pm 5'$. The unit cell dimensions of tris(acetylacetonato)Co(III) are: $a = 13.951 \pm 0.009$ Å, $b = 7.470 \pm 0.005$ Å, $c = 16.222 \pm 0.011$ Å, $\beta = 98°29' \pm 5'$. 1505 photographically recorded reflections for the Co complex and 1569 reflections for the Al complex were evaluated by microphotometer techniques. Refinement was by least squares methods to a conventional unweighted R factor of 0.07 for the Al complex and 0.08 for the Co complex. The structures consist of discrete molecules held together by van der Waals forces. Distortions of the octahedral configuration of O atoms about the Co atom are very similar to that found for tris(acetylacetonato)Mn(III), whereas the distortions in tris(acetylacetonato)Al(III) from octahedral symmetry are significantly less. Comparisons with previously determined tris(acetylacetonato)metal(III) compounds are made.

INTRODUCTION

The early crystal studies of Astbury[1] indicated that the trisacetylacetonates of Al(III), Cr(III), Mn(III), Co(III) and one polymorph of Ga(III) formed a monoclinic isomorphic set. It has also been shown that the trisacetylacetonates of Fe(III),[2] the α-form of V(III)[3] and presumably one polymorph of Ga(III)[1] are othorhombic and isomorphic. In addition, the trisacetylacetonate of V(III) also crystallizes in a monoclinic β-form which is not isomorphous with the above monoclinic set.[3] This availability of a large number of tris(acetylacetonato)metal(III) complexes (acetylacetonato hereafter abbreviated as AcAc) makes it a suitable series for a systematic structural study to attempt to obtain some experimental information concerning the effect of changing the metal ion as well as possibly the effect of changing the crystal class, and thus the molecular packing, on the structure. Accurate structures of tris(AcAc)–Mn(III),[4] –Cr(III),[5,6] –Fe(III),[7] and the two forms of –V(III)[3] have been reported.* Earlier reports on the structures of the Co(III)[8] and Cr(III)[9] complexes have been shown to be in error.[5] We report here the structure of the transition metal(III) complex, tris(AcAc)Co(III), and the structure of the non-transition metal(III) complex, tris(AcAc)Al(III).

EXPERIMENTAL

Both tris(acetylacetonato)–aluminum(III) and –cobalt(III) were prepared by adding a slight excess of carefully purified acetylacetone to the corresponding freshly prepared metal(III) hydroxide in water.[10] Spectral and microanalysis of the complexes which had been recrystallized from a benzene-petroleum ether mixture indicated them to be of excellent purity.[18]

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* Note added in proof: Prof. E. C. Lingafelter has kindly pointed out that there is a distinct possibility that the structure of $Mn(AcAc)_3$ reported by Morosin and Brathovde[4] is actually that of $Co(AcAc)_3$. This possibility was mentioned at the XIVth International Conference on Coordination Chemistry held June 22–28, 1972, in Toronto, Canada, and should be kept in mind in reading this paper when reference is made to the $Mn(AcAc)_3$ results. A redetermination of this structure is underway by other workers which of course will eventually clear up this uncertainty.

In both cases crystals of suitable size were grown by slow room temperature evaporation of a saturated solution of the complex in a mixture of benzene and petroleum ether. Crystals grown in this manner were monoclinic prisms elongated in the direction subsequently designated as the "*b*" axis. Accurate lattice parameters were determined from powdered specimens at 23° C using the double scanning diffractometry method reported by King and Vassamillet.[11]

Systematic absences of ($h0l$) for $l = 2n + 1$ and of ($0k0$) for $k = 2n + 1$ obtained from indexed Weissenberg and precession photographs confirmed the space group pf $P2_1/c$ for both complexes as had been reported previously by other workers.[8,9] The densities for both complexes were taken from the literature.[1,8] The results are summarized in Table I.

TABLE I

Unit-cell dimensions and space groups for:

tris(acetylacetonato)aluminum(III)	tris(acetylacetonato)cobalt(III)
a = 14.069 ± 0.010 Å	a = 13.951 ± 0.009 Å
b = 7.568 ± 0.005 Å	b = 7.470 ± 0.005 Å
c = 16.377 ± 0.011 Å	c = 16.222 ± 0.011 Å
β = 99°00′ ± 5′	β = 98°29′ ± 5′
Density (obs.) = 1.27 g/cm³ (1)	Density (obs.) = 1.43 g/cm³ (8)
Density (calc.) = 1.250 g/cm³	Density (calc.) = 1.436 g/cm³
Space Group = $P2_1/c$	Space Group = $P2_1/c$
Z = 4 molecules/unit cell	Z = 4 molecules/unit cell

For the Al(III) complex, three crystals mounted along different rotation axes were used in gathering the intensities. The first crystal, rotated about its a-axis, had the dimensions 0.17 × 0.27 × 0·23 mm (crystal dimensions are given in the order a, b, c in all cases) and was used to record the $0kl$ net. The second crystal, rotated about its b-axis, had the dimensions 0.27 × 0.81 × 0.22 mm and was used to record the $h0l$, $h1l$, $h2l$ and $h3l$ nets. The third crystal, rotated about its c-axis, had the dimensions 0.26 × 0.29 × 0.16 mm and was used to record the nets $hk0$ through $hk5$. All intensities were recorded on Ilford Industrial G X-Ray Film by the multiple film pack equi-inclination Weissenberg technique using manganese filtered Fe Kα radiation (λ = 1.9373 Å). The intensities of all reflections, except those of the $hk4$ net, which were measured using a Nonius Model I microdensitometer, were measured by vertically scanning each reflection with a National Spectrographic Laboratory, Inc. "SpecReader" microdensitometer equipped with a recorder readout in optical densities. The area of the recorder tracing of each scanned reflection of each film of each multiple film pack was integrated by means of a K & E 4236M compensating polar planimeter. The total number of non-equivalent reflections evaluated was 1569 comprising approximately 85% of the possible reflections within the iron sphere of diffraction. Although tris(AcAc)Al(III) has a linear absorption coefficient for Fe Kα radiation of only 26.0 cm^{-1}, approximate absorption corrections were applied by assuming the second crystal to be cylindrical with a diameter of 0.245 mm and the other two crystals to be spherical having diameters of 0.22 and 0.24 mm respectively.

For the cobalt complex, one crystal having the dimensions 0.16 × 0.65 × 0.24 mm was used to gather all of the three dimensional intensity data. The $h0l$ through $h3l$ nets were recorded using the multiple film pack equi-inclination Weissenberg method and cobalt Kα radiation (λ = 1.7902 Å). Timed precession photographs and Mo Kα radiation were used to record the $hk0$ and $0kl$ nets. The intensities of 1505 reflections were evaluated using a modified Nonius Model I microdensitometer and the peak maximization method of Hoss.[12] No absorption corrections were applied (μ=26.8 cm^{-1} for CoKα and 10.9 cm^{-1} for MoKα). Absorption errors in the Weissenberg gathered data although low are not negligible. It is estimated that the maximum error in these observed structure factors because of the neglect of absorption corrections is approximately 4.5%.

The intensities for each complex were corrected for Lorentz and polarization effects in the usual manner. All reflections, after conversion to observed structure factors, F_o, were put on the same relative scale by intercomparison of reflections common to the various recorded nets, F_o for multiple determined reflections being taken as the average. Atomic scattering factors of the neutral atoms used in the calculation of structure factors were taken from the International Tables for X-Ray Crystallography, Volume III.[13] A listing of observed and calculated structure factors may be obtained from the authors upon request. All calculations were performed on an IBM 7094 computer at the University of Illinois Computer Center and an IBM 360/50 computer at the Syracuse University Computer Center.

Determination of the Structure

Although the structures of other isomorphous members of this tris(AcAc)M(III) series had been reported, Patterson projections onto the (010) for both the Al(III) and Co(III) complexes were calculated. A comparison of the two projections clearly revealed the metal-metal vectors and confirmed the previously determined *x* and *z* heavy atom coordinates.[4,5] Applying signs based on the cobalt atom position to the observed structure factors (F_o) of tris(AcAc)Co(III), a three-dimensional Fourier map was calculated which unambiguously revealed all of the non-hydrogen atoms and indicated the structure to be very similar to that reported for tris(AcAc)Mn(III)[4] and tris(AcAc)Cr(III).[5] Positional and isotropic thermal motion parameter refinement of all non-hydrogen atoms was carried out for both structures using least squares methods. All observed reflections were given unit weight. Convergence was very rapid to a conventional *R* factor of 0.12 for both structures. At this point a difference map was calculated in an attempt to locate hydrogens. Only the acetylacetone ring hydrogens could be located with certainty. Residual electron density about the methyl groups suggested that these hydrogens were disordered, a fact which has since been found to be the case for tris(AcAc)Cr(III).[6] For the final structure refinement, disorder was not considered, the hydrogens simply being placed in positions which gave good overlap with areas of high electron density. Their positions were included in fixed atom contributions in all subsequent refinement cycles. Several cycles of positional and anisotropic thermal motion refinement of all non-hydrogen atoms produced un-unweighted *R* factors (omitting unobserved reflections) of 0.08 for the aluminum complex and 0.07 for the cobalt complex. No extinction corrections were made nor was it considered necessary. Only two reflections, the 200 and the 002 of tris(AcAc)Co(III), were possibly effected by extinc-

TABLE II

Final heavy atom coordinates with estimated standard deviations (X 10^4)

Atom	tris(acetylacetonato)Al(III) *x*	*y*	*z*	tris(acetylacetonato)Co(III) *x*	*y*	*z*
metal	0.2411(2)	0.2687(4)	0.4691(1)	0.2420(1)	0.2701(3)	0.4688(1)
O(1)	0.1209(4)	0.3415(8)	0.4111(3)	0.1226(5)	0.3436(13)	0.4071(4)
O(2)	0.1847(4)	0.1924(8)	0.5608(3)	0.1933(5)	0.1907(12)	0.5644(4)
O(3)	0.3641(4)	0.1959(7)	0.5243(3)	0.3640(5)	0.1847(12)	0.5183(4)
O(4)	0.2968(4)	0.3464(8)	0.3770(3)	0.3022(5)	0.3574(12)	0.3803(4)
O(5)	0.2232(4)	0.0404(7)	0.4254(3)	0.2177(5)	0.0319(13)	0.4265(4)
O(6)	0.2581(4)	0.4991(7)	0.5141(3)	0.2528(5)	0.5068(14)	0.5163(4)
C(1)	0.0376(8)	0.3175(15)	0.4325(6)	0.0428(8)	0.3171(21)	0.4330(7)
C(12)	0.0189(7)	0.2418(20)	0.5060(7)	0.0269(8)	0.2361(26)	0.5068(8)
C(2)	0.0939(7)	0.1829(15)	0.5672(6)	0.1020(9)	0.1884(22)	0.5682(7)
C(X1)	−0.0461(8)	0.3847(20)	0.3664(7)	−0.0445(9)	0.3759(27)	0.3696(8)
C(X2)	0.0726(8)	0.1075(19)	0.6494(7)	0.0781(10)	0.1094(27)	0.6534(8)
C(3)	0.4283(6)	0.2985(16)	0.5632(6)	0.4274(7)	0.2900(22)	0.5596(6)
C(36)	0.4192(7)	0.4738(15)	0.5805(6)	0.4157(8)	0.4675(25)	0.5796(7)
C(6)	0.3327(7)	0.5608(12)	0.5589(5)	0.3302(8)	0.5620(23)	0.5573(6)
C(X3)	0.5276(7)	0.2043(17)	0.5925(7)	0.5276(8)	0.1986(23)	0.5887(8)
C(X6)	0.3250(8)	0.7530(15)	0.5863(7)	0.3210(11)	0.7523(26)	0.5889(8)
C(4)	0.3026(6)	0.2597(16)	0.3116(5)	0.3076(7)	0.2678(23)	0.3161(6)
C(45)	0.2731(7)	0.0827(15)	0.2994(6)	0.2764(9)	0.0917(18)	0.3005(6)
C(5)	0.2363(6)	−0.0149(11)	0.3537(5)	0.2357(8)	−0.0124(22)	0.3546(6)
C(X4)	0.3502(8)	0.3640(17)	0.2457(6)	0.3540(9)	0.3675(23)	0.2487(7)
C(X5)	0.2109(7)	−0.2073(14)	0.3356(6)	0.2092(9)	−0.2055(25)	0.3343(8)

tion, however the difficulty in accurately determining these extremely intense reflections is also a possible reason for the observed discrepancy between the observed and calculated structure factors. These two reflections were also omitted from the final calculation of R. The initial least squares refinements were made using the block diagonal program UCLALSI furnished by Trueblood *et al.*,[14] whereas the final refinements were made using Busing, Martin and Levy's ORFLS.[15] The final values of the positional

TABLE III

Anisotropic temperature factors (X 10^4) with estimated standard deviations (X 10^4)
Anisotropic thermal parameters are of the form:
$\exp[-(h^2\beta 11 + k^2\beta 22 + l^2\beta 33 + hk\beta 12 + hl\beta 13 + kl\beta 23)]$

tris(acetylacetonato)Al(III)						
Atom	$\beta 11$	$\beta 22$	$\beta 33$	$\beta 12$	$\beta 13$	$\beta 23$
Al	49(2)	105(6)	24(1)	−24(5)	8(2)	−10(5)
O(1)	59(4)	199(15)	31(3)	−51(13)	−23(5)	−23(12)
O(2)	66(4)	168(14)	25(2)	−33(12)	16(5)	−33(12)
O(3)	46(3)	144(13)	39(3)	−69(11)	2(5)	5(12)
O(4)	82(5)	153(13)	26(2)	23(13)	46(5)	8(11)
O(5)	69(4)	78(11)	35(3)	15(11)	16(5)	59(12)
O(6)	62(4)	100(12)	39(3)	−26(11)	10(5)	72(12)
C(1)	54(7)	314(30)	41(5)	−57(24)	−40(10)	27(23)
C(12)	43(7)	551(53)	41(5)	−3(29)	−5(9)	−36(29)
C(2)	62(6)	271(28)	42(4)	48(21)	43(9)	32(21)
C(X1)	75(9)	517(44)	58(6)	−142(33)	−53(12)	86(30)
C(X2)	94(9)	378(39)	44(5)	59(31)	36(12)	−61(27)
C(3)	43(6)	284(31)	33(4)	−41(21)	23(8)	−67(22)
C(36)	61(7)	159(25)	52(5)	1(23)	18(10)	39(25)
C(6)	86(8)	69(18)	32(4)	9(20)	35(9)	−12(18)
C(X3)	53(7)	263(33)	73(6)	−108(25)	1(10)	0(27)
C(X6)	89(9)	149(23)	56(6)	−8(25)	20(12)	10(26)
C(4)	45(5)	209(28)	25(4)	−22(21)	14(7)	−44(22)
C(45)	59(7)	162(25)	42(5)	−21(22)	16(10)	44(25)
C(5)	37(5)	64(17)	40(4)	−21(16)	−5(8)	2(18)
C(X4)	90(8)	204(32)	42(5)	41(27)	26(10)	−5(24)
C(X5)	60(6)	126(24)	47(5)	−27(20)	−9(9)	11(21)

tris(acetylacetonato)Co(III)						
Atom	$\beta 11$	$\beta 22$	$\beta 33$	$\beta 12$	$\beta 13$	$\beta 23$
Co	55(1)	146(6)	31(1)	−23(4)	7(1)	−5(4)
O(1)	41(4)	159(28)	28(3)	−25(18)	−25(6)	−9(15)
O(2)	46(4)	119(25)	20(3)	−5(17)	10(5)	−1(13)
O(3)	33(4)	57(20)	40(3)	−20(15)	−10(6)	−6(15)
O(4)	63(5)	106(24)	18(3)	−4(19)	26(6)	9(13)
O(5)	58(5)	104(24)	30(3)	44(19)	13(6)	90(15)
O(6)	42(4)	150(25)	33(3)	−11(18)	0(6)	96(16)
C(1)	46(7)	142(41)	36(5)	−14(28)	−20(10)	58(25)
C(12)	41(7)	316(61)	50(6)	−6(32)	9(11)	9(33)
C(2)	64(8)	202(49)	30(5)	26(32)	37(10)	−11(25)
C(X1)	51(9)	325(62)	53(6)	−61(36)	−41(11)	36(33)
C(X2)	85(10)	379(69)	33(6)	69(43)	38(12)	−31(31)
C(3)	30(6)	140(41)	27(4)	−77(26)	18(8)	−54(24)
C(36)	50(7)	140(45)	43(6)	−46(33)	15(10)	58(29)
C(6)	55(7)	152(43)	25(4)	6(32)	26(9)	−22(24)
C(X3)	41(6)	249(56)	47(6)	−113(30)	−16(10)	14(30)
C(X6)	106(11)	127(38)	42(6)	2(46)	29(13)	42(30)
C(4)	43(6)	125(36)	29(5)	15(30)	15(8)	−91(24)
C(45)	70(7)	160(27)	25(4)	34(29)	18(9)	8(21)
C(5)	40(6)	100(37)	29(4)	−30(28)	−16(9)	36(24)
C(X4)	77(9)	221(49)	26(5)	47(37)	20(10)	0(26)
C(X5)	54(7)	202(58)	40(6)	7(33)	−10(10)	−16(30)

and anisotropic thermal parameters are given in Tables II and III. The labeling scheme for the molecule, which is identical to that used by Morosin,[5] may be seen in the stereodrawing of Figure 1. Bond lengths and bond angles are listed in Table IV and V respectively.

DISCUSSION OF THE STRUCTURE

The bond lengths and bond angles of equivalent atoms of both structures are in good agreement as can be seen from Tables IV and V. The somewhat shortened bond lengths of the acetylacetone ring carbons (1.38 Å average) are due to the expected delocalization of the π electrons. The ring carbon to methyl carbon bonds have an average length of 1.54 Å which agrees well with the accepted value for a single carbon-carbon bond. The deviations from this average value are similar to that found for the manganese(III) complex[4] and can likewise be explained on the basis of nearest neighbor interactions.[4] Figure 1 is an ORTEP[16] stereo drawing of an isolated tris(acetylacetonato)Al(III) molecule from which the directions of the thermal ellipsoids can be more clearly seen. Upon viewing this drawing, it is noted that the left hand acetylacetone ring, which lies essentially perpendicular to the crystallographic b axis, is vibrating somewhat more anisotropically than the remainder of the molecule. This motion is rather similar to that found for tris(AcAc)Cr(III)[5] and is very likely due to the manner in which the molecules are packed as the packing interactions for this ring are not only

TABLE IV

Bond lengths in Ångstroms with estimated standard deviations (esd)

tris(acetylacetonato)Al(III) (Bond)	(Å)	(esd)	tris(acetylacetonato)Co(III) (Bond)	(Å)	(esd)
Al—O1	1.887	0.006	Co—O1	1.894	0.008
Al—O2	1.894	0.006	Co—O2	1.878	0.007
Al—O3	1.904	0.006	Co—O3	1.884	0.007
Al—O4	1.899	0.005	Co—O4	1.884	0.007
Al—O5	1.873	0.007	Co—O5	1.919	0.008
Al—O6	1.893	0.006	Co—O6	1.926	0.009
Ave =	1.892	(.006)	Ave =	1.898	(.008)
O1—C1	1.288	0.010	O1—C1	1.262	0.013
O2—C2	1.299	0.011	O2—C2	1.283	0.014
O3—C3	1.282	0.010	O3—C3	1.294	0.015
O4—C4	1.270	0.010	O4—C4	1.249	0.014
O5—C5	1.287	0.011	O5—C5	1.273	0.013
O6—C6	1.272	0.010	O6—C6	1.252	0.014
Ave =	1.283	(.010)	Ave =	1.296	(.014)
C1—C12	1.395	0.016	C1—C12	1.389	0.019
C12—C2	1.409	0.014	C12—C2	1.381	0.018
C4—C45	1.407	0.014	C4—C45	1.398	0.018
C45—C5	1.322	0.015	C45—C5	1.357	0.017
C6—C36	1.380	0.014	C6—C36	1.388	0.019
C36—C3	1.366	0.014	C36—C3	1.381	0.019
Ave =	1.380	(.014)	Ave =	1.382	(.018)
C1—CX1	1.555	0.015	C1—CX1	1.538	0.018
C2—CX2	1.535	0.015	C2—CX2	1.584	0.018
C3—CX3	1.575	0.016	C3—CX3	1.565	0.017
C4—CX4	1.569	0.015	C4—CX4	1.541	0.018
C5—CX5	1.518	0.014	C5—CX5	1.513	0.019
C6—CX6	1.531	0.014	C6—CX6	1.522	0.019
Ave =	1.547	(.015)	Ave =	1.544	(.019)

TABLE V

Bond angles in degrees with estimated standard deviations (esd)

tris(acetylacetonato)Al(III) (Bonds)	(angle)	(esd)	tris(acetylacetonato)Co(III) (Bonds)	(angle)	(esd)
O1—Al—O2	92.0	0.2	O1—Co—O2	97.5	0.3
O3—Al—O6	91.9	0.2	O3—Co—O6	97.4	0.3
O4—Al—O5	91.7	0.2	O4—Co—O5	97.1	0.3
Ave =	91.8	(0.2)	Ave =	97.3	(0.3)
O1—Al—O3	178.1	0.2	O1—Co—O3	173.1	0.3
O2—Al—O4	179.6	0.2	O2—Co—O4	174.2	0.3
O6—Al—O5	179.3	0.2	O6—Co—O5	173.6	0.3
Ave =	179.0	(0.2)	Ave =	173.6	(0.3)
O1—Al—O4	87.6	0.2	O1—Co—O4	87.3	0.3
O1—Al—O5	91.2	0.3	O1—Co—O5	89.1	0.3
O1—Al—O6	88.6	0.2	O1—Co—O6	87.5	0.3
O2—Al—O3	89.8	0.2	O2—Co—O3	87.5	0.3
O2—Al—O5	88.5	0.2	O2—Co—O5	86.4	0.3
O2—A1—06	90.9	0.2	O2—Co—O6	88.6	0.3
O3—Al—O4	90.5	0.2	O3—Co—O4	88.0	0.3
O3—Al—05	88.4	0.2	O3—Co—O5	86.5	0.3
O4—Al—O6	88.9	0.2	O4—Co—O6	88.3	0.3
Ave =	89.4	(0.2)	Ave =	87.6	(0.3)
Al—O1—C1	127.2	0.7	Co—O1—C1	121.9	0.8
Al—O2—C2	128.3	0.7	Co—O2—C2	121.7	0.8
Al—O3—C3	125.3	0.6	Co—O3—C3	121.3	0.6
Al—O4—C4	126.8	0.7	Co—O4—C4	122.6	0.8
Al—O5—C5	128.2	0.7	Co—O5—C5	121.4	0.7
Al—O6—C6	127.2	0.7	Co—O6—C6	121.7	0.9
Ave =	127.2	(0.7)	Ave =	121.8	(0.8)
O1—C1—C12	126.5	0.8	O1—C1—C12	128.0	0.9
O2—C2—C12	124.1	0.9	O2—C2—C12	127.9	1.1
O3—C3—C36	127.5	0.9	O3—C3—C36	127.7	1.2
O4—C4—C45	123.7	0.8	O4—C4—C45	126.8	0.7
O5—C5—C45	124.0	0.9	O5—C5—C45	126.9	1.1
O6—C6—C36	126.0	0.9	O6—C6—C36	127.8	1.0
Ave =	125.3	(0.9)	Ave =	127.5	(1.0)
C1—C12—C2	121.5	0.9	C1—C12—C2	122.2	1.3
C3—C36—C6	121.1	0.8	C3—C36—C6	123.7	1.0
C4—C45—C5	125.0	0.8	C4—C45—C5	124.9	0.8
Ave =	122.6	(0.8)	Ave =	123.6	(1.0)
O1—C1—CX1	112.8	0.8	O1—C1—CX1	112.6	0.8
O2—C2—CX2	114.9	1.0	O2—C2—CX2	112.6	1.0
O3—C3—CX3	113.6	0.8	O3—C3—CX3	113.7	0.8
O4—C4—CX4	114.3	0.8	O4—C4—CX4	114.6	0.9
O5—C5—CX5	115.2	0.9	O5—C5—CX5	111.9	1.0
O6—C6—CX6	115.3	0.9	O6—C6—CX6	112.2	1.0
Ave =	114.4	(0.9)	Ave =	112.9	(1.0)

TABLE V (*continued*)

tris(acetylacetonato)Al(III) (Bond)	(angle)	(esd)	tris(acetylacetonato)Co(III) (Bonds	(angle)	(esd)
C12—C1—CX1	120.7	0.8	C12—C1—CX1	119.3	0.8
C12—C2—CX2	120.9	0.9	C12—C2—CX2	119.3	1.1
C36—C3—CX3	118.9	1.0	C36—C3—CX3	119.9	1.3
C36—C6—CX6	118.6	0.8	C36—C6—CX6	118.6	1.0
C45—C4—CX4	121.9	0.8	C45—C4—CX4	118.6	0.9
C45—C5—CX5	120.7	0.9	C45—C5—CX5	121.2	0.9
Ave =	120.3	(0.9)	Ave =	119.5	(1.0)

the weakest for the molecule, but are also at a minimum in the direction of the *b* axis.

Since a considerable number of reasonably accurate tris(AcAc)metal(III) structures have now been determined, it is of interest to compare their structural features, especially those features associated with the six ogygens and the metal atom. Estimated error in the atomic coordinates of these atoms is such that the value of one estimated standard deviation (1 esd) in metal-oxygen bond distances is approximately 0.007 Å for all structures. A comparison of the coordination octahedron in this series of tris(AcAc)metal (III)complexes is shown in Figure 2 and several features can be noted. One, both tris(AcAc)-Cr(III) and -Al(III) have reasonably undistorted coordination octahedra, that is little distortion from octahedral symmetry; two, the distorted oxygen coordination octahedron of tris(AcAc)Co(III) is very similar to that of tris(AcAc)Mn(III); three, the oxygen coordination octahedra of tris(AcAc)-Fe(III) and the two forms of -V(III) are very similar in the type and extent of distortions present; four, the distortion in the Co(III) and Mn(III) complexes is essentially the opposite of that found for the Fe(III) and V(III) complexes, that is whereas the "bite" oxygen–oxygen separations are long and the other oxygen–oxygen separations are short for the Co(III) and Mn(III) complexes, the "bite" oxygen–oxygen separations are short and other oxygen–oxygen separations are long in the Fe(III) and V(III) complexes. Table VI lists the average values for various structural parameters of the coordination octahedra from which the type and extent of the distortions from octachedral symmetry are more readily seen and compared. The reproducibility of these structure determinations is quite good as is evidenced by the excellent agreement between the two average tris (AcAc)Cr(III) structures which were determined independently by two separate groups.[5,6] Also the agreement between the average structures of the two crystal-

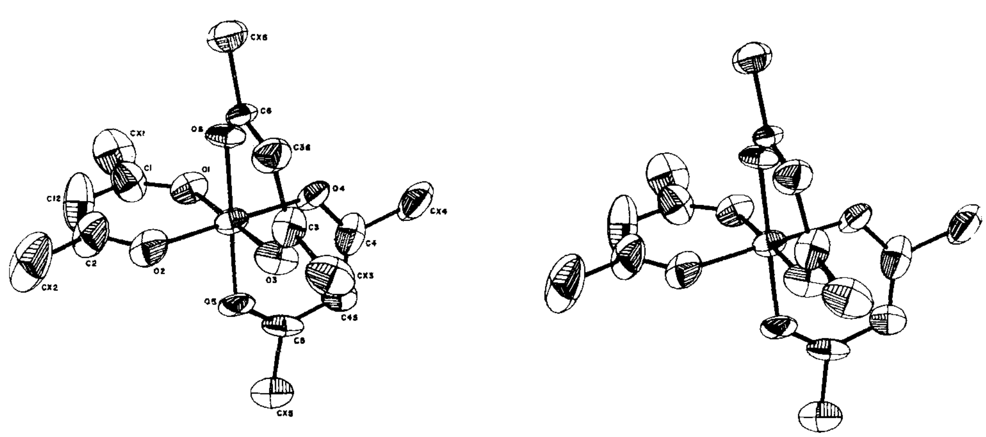

FIGURE 1 Stereo drawing of an isolated molecule of tris(acetylacetonato)Al(III). View is essentially down the *c* axis.

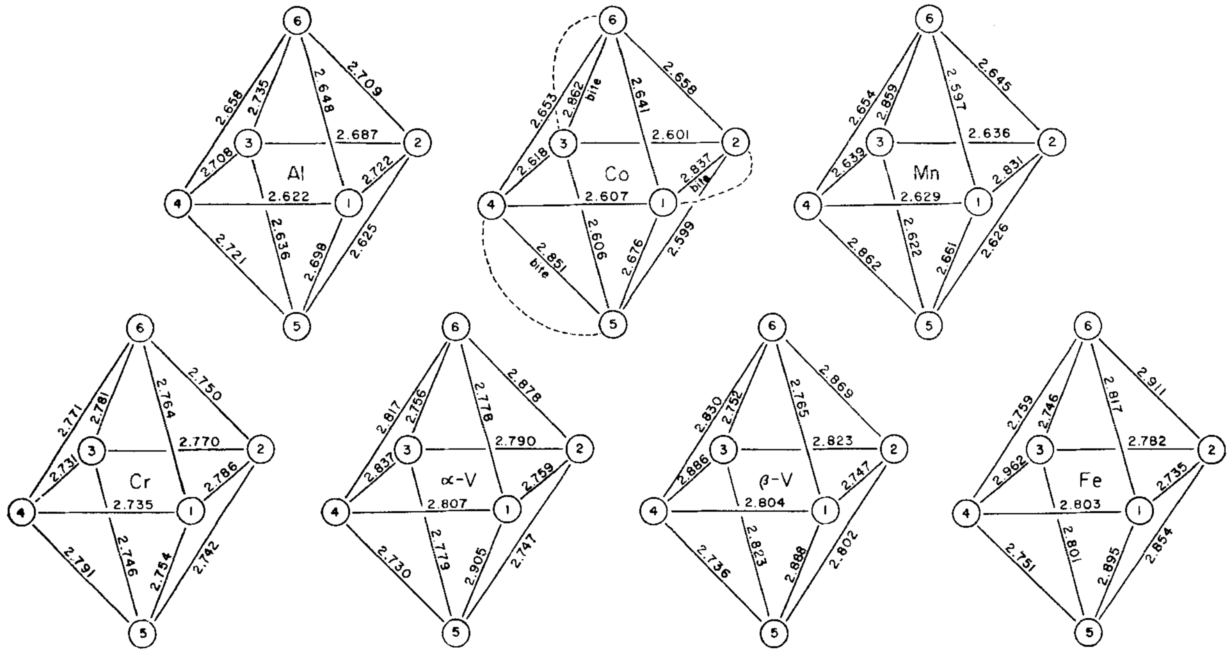

FIGURE 2 Comparison of the dimensions of the oxygen octahedra of various tris(acetylacetonato)metal(III) complexes.

line forms of tris(AcAc)V(III) (α- and β-forms) is very good indicating that the observed distortions are the results of effects other than crystal packing, that is, predominantly intra-molecular forces rather than inter-molecular forces must be involved.

A plot of the "bite" oxygen–oxygen separations versus the experimentally determined average metal–oxygen bond distance for each member of the tris(AcAc)M(III) series (Figure 3) reveals a remarkably good linear correlation for all members except aluminum. The aluminum complex with metal–oxygen bond lengths very similar to the complexes of Co(III) and Mn(III) does not possess their significant distortions to the coordination octahedron (see Figure 2 and Table VI) but rather is reasonably close to an undistorted octahedron. This "anamolous" behavior may be the result of significantly greater ionic character in the Al–O bond, arising because of the higher charge density

TABLE VI

Average values for various structural parameters of tris(acetylacetonato)metal(III) complexes.

metal ion	"bite" O—O separation (Å)	other O—O separations (Å)	metal—O distance (Å)	O—M—O chelate angle (°)
Al	2.726	2.666	1.892	91.84
Co	2.850	2.629	1.898	97.32
Mn	2.851	2.634	1.901	97.16
Cr[a]	2.786	2.751	1.952	91.09
Cr[b]	2.789	2.753	1.953	91.13
Fe	2.744	2.843	1.992	87.1
V (α)	2.748	2.815	1.979	88.0
V (β)	2.745	2.832	1.982	87.3

[a]Values from Morosin's determination.[5]
[b]Values from Marsh's determination.[6]

on the Al^{3+} ion, the result being greater electrostatic repulsions between oxygens thus forcing them into a more perfect octahedron. It is difficult to explain the observed dependence of the distortions of the coordination octahedron of the transition metal acetylacetonate complexes on the metal–oxygen bond length. It appears, however, that the bonding in the transition metal series is similar and probably more covalent. A simple model in which the configuration of the coordination octahedron is the equilibrium configuration due to the electrostatic repulsions of the oxygens on the one hand and the acetylacetone ligand force constants (acting similar to a spring) on the other hand fails as it does not predict the increase in 'bite" with decreasing M–O distance, but rather predicts the opposite. It appears possible that other charges on the acetylacetone ring, especially the negative charge on the central carbon, may be responsible. Crystal packing can be ruled out on the basis of the structural results of the two crystal forms of tris(AcAc)V(III) as was shown earlier. Calculations are presently being attempted using various electrostatic models in which all charges in the molecules are considered in an attempt to explain these unusual findings. It should be mentioned that Lingafelter and Braun[17] have also plotted "bite" oxygen–oxygen separations versus crystal radius/charge ratios (r/Q) for many acetylacetonate complexes. The correlation found was rather poor, however they observed a general tread of increasing "bite" with increasing r/Q, the opposite of which we have found. A closer examination of their curve indicates that for a group of complexes of *one* oxidation state, a reasonable fit is obtained if the line is drawn essentially perpendicular to the overall line, in agreement with our findings.

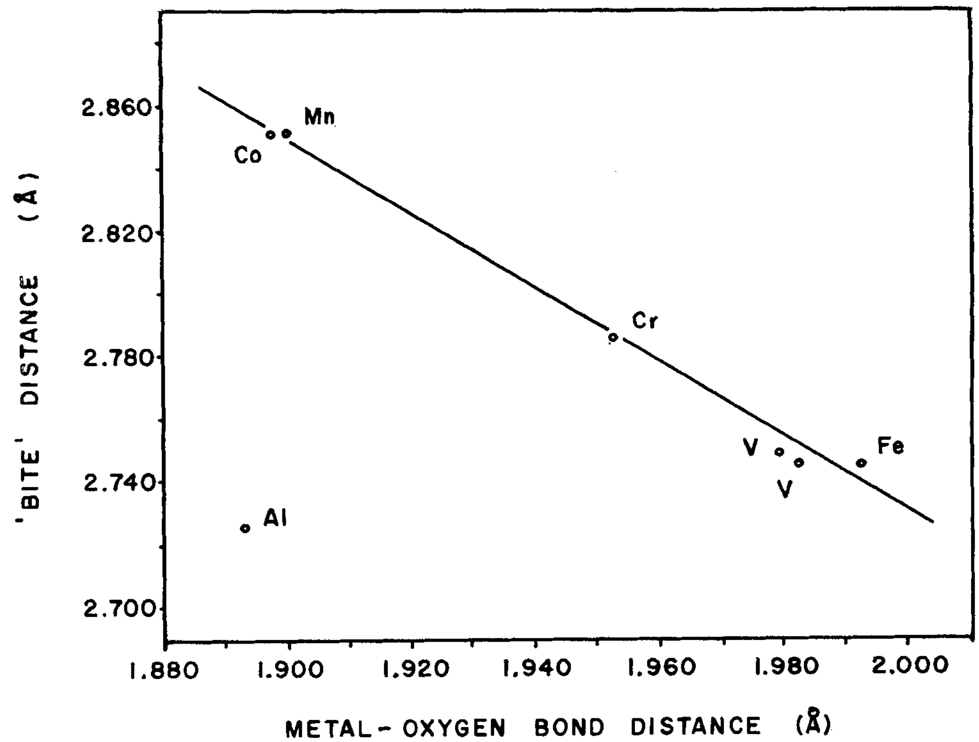

FIGURE 3 "Bite" oxygen-oxygen separations versus average metal-oxygen bond distances.

We wish to acknowledge early support by NSF Grant GP-255 for this project.

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