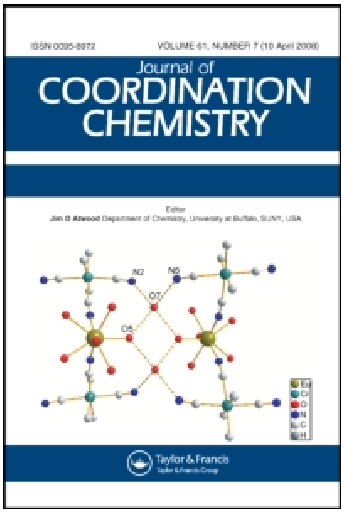

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STRUCTURAL CHEMISTRY OF GALLIUM(II1). CRYSTAL STRUCTURES OF K_3 [Ga(catecholate)$_3$)]·1.5H_2O AND [Ga(benzohydroxamate)$_3$]·H_2O·CH_3 CH_2OH

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STRUCTURAL CHEMISTRY OF GALLIUM(III). CRYSTAL STRUCTURES OF $K_3[Ga(catecholate)_3)].1.5H_2O$ AND $[Ga(benzohydroxamate)_3].H_2O.CH_3CH_2OH$.

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Although Ga(III) has been used extensively as a substitute for Fe(III) in microbial iron chelating agents or their analogues, there are some striking differences in their *in vivo* behaviour. A search for a structural difference is reported here, in which the structures of $K_3[Ga(C_6H_4O_2)_3]\cdot 1.5\ H_2O$, **1**, and $[Ga(C_7H_6NO_2)_3]\cdot H_2O\cdot CH_3CH_2OH$, **2**, have been determined by single crystal X-ray diffraction. Colorless crystals of **1** are monoclinic, space group *C2/c* with $a = 20.679(1)$ Å, $b = 15.868(1)$ Å, $c = 12.350(1)$ Å, $\beta = 91.90(1)°$, $V = 4050(1)$ Å. For eight formula units per cell, $d_{calc} = 1.766$, and $d_{obs} = 1.77(2)$ g cm^{-3}. Refinement of 268 variables on 4181 reflections resulted in agreement factors of $R = 3.24\%$, and $R_w = 3.87\%$. Crystals of **2** are triclinic, space group $P\bar{1}$, and have $a = 10.267(1)$ Å, $b = 11.388(2)$ Å, $c = 13.027(1)$ Å, $\alpha = 71.48(1)°$), $\beta = 73.32(1)°$, $\gamma = 60.72(1)°$, and $V = 1243.6(3)$ Å^3. For two formula units of **2** per unit cell, $d_{calc} = 1.448$ g cm^{-3} and $d_{obs} = 1.44(1)$ g cm^{-3}. Of 5696 unique reflections, 3426 were used to refine 307 variables, with the resulting agreement factors: $R = 4.0\%$ and $R_w = 5.4\%$. For **1** the average Ga–O distance is 1.984(6) Å with an average O-Ga-O_{ring} angle of 83.8(1)°. The twist angle is 48.8(1)°. For **2** the average Ga–O(N) and Ga–O(C) distances are 1.952(10) Å and 1.986 (13) Å, respectively. The average O-Ga-O_{ring} angle is 81.7(1)°, and the twist angle is 46(1)°. The structural similarities of the Fe(III0 and Ga(III) complexes do not point to any difference in stability or biological recognition.

Keywords: Gallium, catechol, benzohydroxamic acid, structures, synthesis

INTRODUCTION

The hydrolyic behaviour and aqueous chemistry of the Ga^{3+} ion is similar to that of the ferric ion. In fact, useful extrapolations of properties have been made between the two ions. For instance, diamagnetic gallium analogs of the microbial iron chelates (siderophores) have been useful in NMR studies,[1–3] since the native ferric ion complexes are paramagnetic. In reverse, the knowledge gained from studies of ferric ion transport has been applied to the development of ^{67}Ga radiopharmaceuticals.[4] The basis for this replacement of Fe^{3+} by Ga^{3+} lies in the physical and chemical similarities of the two ions. Both have the same charge and similar ionic radii in six-coordinate complexes (0.645 Å for Fe^{3+} compared to 0.620 Å for Ga^{3+}).[5] Neither ion is perturbed by crystal field effects. The ferric ion configuration is high-spin d^5 while the gallium is diamagnetic d^{10}. Moreover, since neither have any crystal field stabilization and both have similar ionic radii, they are similar in their ligand exchange rates. The size and kinetic similarity makes gallium better than aluminum as an iron analog; aluminum has significantly slower ligand exchange kinetics because it is smaller.

One notable difference in the properties of Ga^{3+} and Fe^{3+} is that while the Fe^{3+}/Fe^{2+} redox system is very important in biological systems, the absence of a stable divalent state for gallium removes from consideration any processes that involve one

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electron reduction of Ga^{3+}. This feature has been used to advantage in probing the mechanisms of siderophore mediated microbial iron transport.[6,7] The rationale behind these experiments is that if reduction of the metal is required for release from the siderophore, then uptake of the gallium analogue will be inhibited, even though it may be "recognized" by the receptor site. For the tricatechoylamide siderophore enterobactin, the Ga^{3+} substituted analogue is *not* taken up by *E. coli*[6] even though the Sc^{3+} and In^{3+} analogues are.[8] This is a puzzling difference which partially motivates the present study.

There are some significant differences in the stabilities of Ga^{3+} and Fe^{3+} complexes. The formation constants of a series of catecholate complexes have been determined in our laboratory and the gallium complexes consistently are found to be less stable than the analogous ferric complexes.[9,10] The stabilities of the benzohydroxamate complexes show a similar disparity.[11,12] The gallium analogue of the siderophore ferrioxamine-B is not only less stable than the ferric complex,[11] but also undergoes base hydrolysis more readily.[13] A comparison of these stability constants, and others [14,15] where data for both the Ga^{3+} and Fe^{3+} complexes are available, is presented in Table I.

These differences in the properties of Ga^{3+} and Fe^{3+} complexes prompted this structural study of gallium complexes with catecholate and benzohydroxamate ligands. Structures of both $[Fe(catecholate)_3]^{3-}$ and $[Fe(benzohydroxamate)_3]$ have previously been reported.[16,17] We report here the crystal structures of $K_3[Ga(catecholate)_3] \cdot 1.5\ H_2O$ (**1**) and $[Ga(benzohydroxamate)_3] \cdot H_2O \cdot C_2H_5OH$(**2**), and compare them with the structures of the iron analogues in order to evaluate the importance of structure on the observed differences in activity and stability.

TABLE I
Comparison of Fe^{3+} and Ga^{3+} stability constants.

		$\log \beta_{110}$[a]	
Ligand	Fe^{3+}	Ga^{3+}	refs.
MECAMS[b]	41	38	9,10
3,4-LICAMS[c]	41	38.5	9,10
HDFO[d]	30.6	27.6	11,13
EDTA	25.1	21.0	15,14
EHPG[e]	33.9	33.6	15,14
HBED[f]	39.68	39.57	15,14
		$\log \beta_{130}$[a]	
Ligand	Fe^{3+}	Ga^{3+}	
DMBS[g]	40.3	38	9,10
acac[h]	26.3	23.7	15
oxalate	18.5	15.1	15
oxinate	36.9	40.5	15
Ferron[i]	25.2	29.6	15
BHA[j]	27.8	25.3	11,12

[a] $\beta_{110} = [ML]/[M][L]$; $\beta_{130} = [ML_3]/[M][L]^3$; [b] *N,N',N''*-tris-(2,3-dihydroxy-5-sulfobenzoyl)-1,3,5-triaminomethylbenzene; [c] *N,N',N''*-(2,3-dihydroxy-5-sulfobenzoyl)-1,5,10-triazadecane; [d] desferriferrioxamine-B; [e] *N,N'*-ethylene-bis-(*o*-hydroxyphenylglycine); [f] *N,N'*-bis (2-hydroxybenzyl)ethylenediamine-*N,N'*-diacetic acid; [g] *N,N*-dimethyl-2,3-dihydroxy-5-sulfonatobenzamide; [h] acetylacetonate; [i] 8-hydroxy-7-iodo-5-quinolinesulfonic acid; [j] benzohydroxamic acid.

EXPERIMENTAL

Syntheses

$K_3[Ga(catecholate)_3]\cdot 1.5H_2O$ (1). Washed $Ga(OH)_3$ gel (3 mmol, precipitated by neutralizing an HCl solution of dissolved Ga ingots; Alfa) was slurried in 25 cm^3 degassed H_2O with catechol (Crown-Zellerbach; 30 mmol). Degassed KOH (60 mmol) was added, and the mixture immediately dissolved. The reaction was stirred overnight and dried (rotovap) to about 5 cm^3. This was added to 100 cm^3 of ethanol and refrigerated, yielding a white precipitate (about 90% yield). The IR spectrum is essentially identical to that of the ferric complex. Since KOH solutions[16] of the complex are very air sensitive, the complex was precipitated from 0.01 M cold aqueous KOH by addition of an equivalent volume of EtOH. The resulting mixture was heated until the precipitate redissolved, and then cooled slowly overnight in a covered Dewar. This procedure was carried out in air without any oxidation of the ligand occurring, and yielded feathery crystalline conglomerates. These were well-formed at their extremities, from which single-crystal fragments were cleaved and mounted on glass fibres with epoxy for further diffraction work. The density (1.77 g cm^{-3} measured by flotation in $CHBr_3$/toulene) and the space group and lattice constants determined from precession photographs indicated that the crystals were isomorphous with the iron complex.

TABLE II
Crystal data

Compound	1	2
Formula	$K_3Ga(C_6H_4O_2)_3\cdot 1.5H_2O$	$Ga(C_7H_6NO_2)_3\cdot H_2O\cdot C_2H_5OH$
FW	538.3	542.2
Space group	$C2/c$	$P\bar{1}$
Z	8	2
Cell constants[a]		
a, Å	20.679(2)	10.267(1)
b, Å	15.868(1)	11.388(2)
c, Å	12.350(1)	13.027(1)
α, deg	90	71.48(1)
β, deg	91.900(8)	73.32(1)
γ, deg	90	60.72(1)
V, Å^3	4050(1)	1243.6(3)
2θ range for cell constants, deg	28-36	24-25
ρ_{obs}, g cm^{-3}	1.77(1)	1.44(1)
ρ_{calc}, g cm^{-3}	1.766	1.448
μ(MoK$_\alpha$), cm^{-1}	20.80	11.50
F_{000}	2168	560
Dimensions, mm	0.25 × 0.22 × 0.18	0.22 × 0.19 × 0.17
2θ range for data collection, deg	3-62	3-55
Reflections measured, h_{max}, k_{max}, l_{max}	+29, ±22, ±17	±13, ±14, ±16
No. reflections measured	12970	11385
No. unique reflections[b]	6584	5696
R_I for averaging, %	2.7	3.5
No. reflections with $F^2 > 3\sigma(F^2)$	4181	3426
Secondary extinction coeff.	$1.6(2)\times 10^{-7}$	—
R, %	3.24	4.00
R_w, %	3.87	5.36
GOF	1.128	1.76
No. variables	268	307

[a] Determined from least squares refinement of 24 high angle reflections at ambient temperature, 23°, with MoK_α radiation. [b] After averaging the mirror related forms for **1** and the inversion related forms for **2**.

[Ga(benzohydroxamate)$_3$]·H_2O·EtOH (2). An acidic solution of $GaCl_3$ was combined with a 2% excess of benzohydroxamic acid (Aldrich) in aqueous solution. The pH was raised to about 8 with aqueous KOH and the product precipitated as a white powder. The product was recrystallized as the solvated species from ethanol/water by slow evaporation at room temperature.

Anal. Calcd. for $[Ga(C_7H_6NO_2)_3]\cdot H_2O\cdot C_2H_5OH$: C, 50.92; H, 4.79; N, 7.74; Ga, 12.92%. *Found:* C, 50.75; H, 4.70; N, 7.78; Ga, 14.0%.

Excellent single crystals were obtained from the ethanol/water recrystallization, although they became cloudy upon standing in air due to loss of solvent. Therefore crystals were wedged into thin-walled capillaries along with some of the mother-liquor for photographic examination and data collection.

X-ray Crystallograpahy

Crystal quality assessment and space group determination were carried out by precession photography. These studies showed that **1** is isomorphous with the Cr(III), Fe(III)[16] and V(III)[18] homologues, and suggested that the space group for **2** is either *P*1 or *P*$\bar{1}$. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer, using

TABLE III
Atomic coordinates for **1**.

Atom	*x*	*y*	*z*	B_{eqv}(Å^2)[a]
Ga	0.32441(1)	0.01801(2)	0.10385(2)	2.092(5)
K1	0.06868(3)	0.41645(4)	0.11884(5)	3.09(1)
K2	0.30868(3)	0.13594(4)	0.36199(5)	3.02(1)
K3	0.26193(3)	0.40969(5)	0.15862(5)	3.57(1)
OW1	0.00000(0)	0.5154(2)	0.2500(0)	3.20(6)
OW2	0.27024(21)	0.2979(2)	0.3524(3)	11.0(1)
O1	0.323032(9)	0.1160(1)	0.0047(1)	2.62(4)
O2	0.38914(9)	−0.03381(1)	0.0112(1)	2.54(4)
O3	0.25494(10)	−0.0397(1)	0.0158(2)	2.99(4)
O4	0.25240(9)	0.0513(1)	0.1956(1)	2.60(4)
O5	0.38376(9)	0.0908(1)	0.1916(1)	2.27(3)
O6	0.34343(10)	−0.0817(1)	0.1993(1)	2.79(4)
C11	0.3492(1)	0.1837(2)	0.0516(2)	2.30(5)
C12	0.3836(1)	0.1701(2)	0.1507(2)	2.15(5)
C13	0.4147(1)	0.2374(20)	0.2023(2)	2.89(6)
C14	0.4130(2)	0.3176(2)	0.1555(3)	3.28(6)
C15	0.3810(2)	0.3300(2)	0.0582(3)	3.30(6)
C16	0.3479(1)	0.2635(2)	0.0069(2)	2.85(6)
C21	0.4088(1)	−0.1085(2)	0.0500(2)	2.22(5)
C22	0.3837(1)	−0.1349(2)	0.1499(2)	2.41(5)
C23	0.4015(2)	−0.2135(2)	0.1912(2)	3.35(6)
C24	0.4441(2)	−0.2648(2)	0.1358(3)	3.89(7)
C25	0.4685(2)	−0.2386(2)	0.0392(3)	3.67(7)
C26	0.4504(1)	−0.1609(2)	−0.0037(2)	2.91(6)
C31	0.1969(1)	−0.0252(2)	0.0574(2)	2.36(5)
C32	0.1953(1)	0.0254(2)	0.1523(2)	2.30(5)
C33	0.1364(1)	0.0432(2)	0.1964(2)	3.16(6)
C34	0.0792(2)	0.0098(2)	0.1500(3)	4.03(7)
C35	0.0809(2)	−0.0416(2)	0.0607(3)	3.73(7)
C36	0.1396(1)	−0.0591(2)	0.0147(3)	3.15(6)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:
(4/3) • [a^2*β(1,1) + b^2*β(2,2) + c^2*β(3,3) ab(cos gamma)*β(1,2) + ac(cos beta)*β(1,3) + bc(cos alpha)*β(2,3)]

graphite monochromated MoK_α radiation as previously described.[19] After Lorentz-polarization, decay, and absorption corrections, the redundant data sets were averaged. The agreement factors for the averaged data were 2.7% and 3.5% for **1** and **2**, respectively. These values were used as the factor p in the weighting scheme[19] to prevent overweighting strong reflections. Crystal data are summarized in Table II.

$K_3[Ga(catecholate)_3]\cdot 1.5H_2O$. The structure of **1** is similar to the Fe(III) and Cr(III) isomorphs. The hydrogen atoms from the ordered water molecules were located by difference Fourier maps after refinement. The catecholate H atoms were assigned idealized positions and temperature factors.[20] Attempts were made to model the disordered water molecule OW2 (also disordered in the Fe^{3+} and Cr^{3+},[16] and V^{3+} structures[18]) without success. The final least-squares refinement on all parameters plus an extinction coefficient,[21] resulted in $R = 3.24\%$, and $R_w = 3.87\%$, with the goodness of

TABLE VII
Atomic coordinates for **2**.

Atom	x	y	z	B_{eqv}(Å^2)^a
Ga	0.22583(4)	0.26143(4)	0.33356(3)	2.644(8)
O1	0.1010(3)	0.3784(2)	0.4380(2)	3.71(7)
O2	0.3011(2)	0.4069(2)	0.2719(2)	3.23(6)
O3	0.1106(2)	0.1536(2)	0.3975(2)	3.24(6)
O4	0.0876(2)	0.3474(2)	0.2256(2)	3.30(6)
O5	0.3780(3)	0.1391(2)	0.4310(2)	3.35(7)
O6	0.3857(3)	0.1511(2)	0.2284(2)	3.16(6)
N1	0.1268(3)	0.4935(3)	0.4083(3)	3.64(8)
N2	−0.0019(3)	0.2005(3)	0.3374(3)	3.10(8)
N3	0.5073(3)	0.0583(3)	0.3698(3)	3.74(9)
C1	0.2279(4)	0.5042(3)	0.3239(3)	2.87(9)
C2	−0.0080(4)	0.2989(3)	0.2490(3)	2.92(9)
C3	0.5055(4)	0.0672(3)	0.2677(3)	3.05(9)
C4	0.2541(4)	0.6273(3)	0.2935(3)	3.32(9)
C5	0.3784(5)	0.6303(4)	0.2171(4)	5.3(1)
C6	0.4030(6)	0.7449(5)	0.1870(5)	7.3(2)
C7	0.3064(6)	0.8588(4)	0.2319(5)	7.1(2)
C8	0.1902(6)	0.8527(4)	0.3122(5)	6.6(2)
C9	0.1610(5)	0.7399(4)	0.3421(4)	5.5(1)
C10	−0.1182(4)	0.3474(4)	0.1759(3)	3.3(1)
C11	−0.1427(4)	0.4702(4)	0.0992(4)	4.2(1)
C12	−0.2355(5)	0.5136(5)	0.0233(4)	5.3(1)
C13	−0.3054(5)	0.4406(6)	0.0217(4)	6.0(2)
C14	−0.2853(5)	0.3214(5)	0.0982(4)	6.4(1)
C15	−0.1920(5)	0.2736(4)	0.1752(4)	5.1(1)
C16	0.6406(4)	−0.0200(4)	0.2015(3)	4.0(1)
C17	0.6302(5)	−0.0285(5)	0.1044(4)	6.4(2)
C18	0.7535(7)	−0.1121(6)	0.0407(4)	8.5(2)
C19	0.8869(6)	−0.1810(6)	0.0727(5)	8.8(2)
C20	0.8980(8)	−0.173(1)	0.1652(6)	19.4(3)
C21	0.7768(7)	−0.0880(8)	0.2295(5)	13.3(3)
O7	0.8001(3)	0.0796(3)	0.4348(2)	4.70(8)
O8,1	0.5094(8)	0.2306(7)	0.5322(6)	6.6(2)^b
O8,2	0.5148(8)	0.2797(7)	0.4766(6)	8.8(2)^b
C22	0.311(1)	0.3910(9)	0.6274(9)	14.0(3)^b
C23	0.460(1)	0.366(1)	0.5475(9)	16.0(4)^b

^{a}Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:
$(4/3) * [a^2*\beta(1,1) + b^2*\beta(2,2) + c^2*\beta(3,3)\ ab(\cos \text{gamma})*\beta(1,2) + ac(\cos \text{beta})*\beta(1,3) + bc(\cos \text{alpha})*\beta(2,3)]$. ^{b}Atoms refined isotropically.

TABLE XI
Bond lengths and angles for **1**.

Bond lengths (Å)

Ligand 1		Ligand 2		Ligand 3		Avg[a]
Ga-O1	1.979(2)	Ga-O2	1.969(2)	Ga-O3	1.995(1)	1.986(6)
Ga-O5	1.982(2)	Ga-O6	2.005(2)	Ga-O4	1.973(2)	
O1-C11	1.351(3)	O2-C21	1.337(3)	O3-C31	1.342(3)	1.346(3)
O5-C12	1.355(3)	O6-C22	1.346(3)	O4-C32	1.344(3)	
C11-C12	1.411(3)	C21-C22	1.418(3)	C31-C32	1.422(4)	1.417(3)
C12-C13	1.391(4)	C22-C23	1.392(4)	C32-C33	1.381(4)	1.386(2)
C11-C16	1.382(4)	C21-C26	1.382(3)	C31-C36	1.389(4)	
C13-C14	1.397(4)	C23-C24	1.396(4)	C33-C34	1.402(4)	1.394(3)
C15-C16	1.398(4)	C25-C26	1.388(4)	C35-C36	1.385(4)	
C14-C15	1.366(4)	C24-C25	1.374	C34-C35	1.373	1.371(3)

Angles (°)

	O1-Ga-O5	83.89(7)	O1-Ga-O6	170.97(8)	
	O2-Ga-O6	83.61(7)	O2-Ga-O4	170.41(8)	
	O3-Ga-O4	83.83(7)	O3-Ga-O5	170.82(8)	
	Avg O-Ga-O_{ring}	83.78(5)	Avg O-Ga-O_{trans}	170.7(2)	
O1-Ga-O2	89.09(7)	O1-Ga-O4	97.32(8)	O4-Ga-O5	89.72(7)
O1-Ga-O3	90.45(8)	O2-Ga-O5	98.09(8)	O4-Ga-O6	90.61(8)
O2-Ga-O3	89.01(8)	O3-Ga-O6	94.71(8)	O5-Ga-O6	91.87(7)
Avg	89.5(5)	Avg	96.7(10)	Avg	90.7(7)

Ligand 1		Ligand 2		Ligand 3		Avg
Ga-O1-C11	110.5(2)	Ga-O2-C21	111.4(2)	Ga-O3-C31	110.5(2)	110.6(3)
Ga-O5-C12	110.1(1)	Ga-O6-C22	109.9(2)	Ga-O4-C32	111.0(2)	
O1-C11-C12	117.0(2)	O2-C21-C22	117.3(2)	O3-C31-C32	117.2(2)	117.2(1)
O5-C12-C11	117.4(2)	O6-C22-C21	117.4(2)	O4-C32-C31	117.2(2)	
O1-C11-C16	123.7(2)	O2-C21-C26	123.2(2)	O3-C31-C36	123.4(2)	123.5(1)
O5-C12-C13	123.1(2)	O6-C22-C23	123.7(2)	O4-C32-C33	123.7(2)	
C11-C12-C13	119.4(2)	C21-C22-C23	118.9(3)	C31-C32-C33	119.0(3)	119.2(1)
C12-C11-C16	119.3(3)	C22-C21-C26	119.5(3)	C32-C31-C36	119.3(3)	
C12-C13-C14	120.3(3)	C22-C23-C24	120.4(3)	C32-C33-C34	120.3(3)	120.6(1)
C11-C16-C15	120.5(3)	C21-C26-C25	121.0(3)	C31-C36-C35	120.9(3)	
C13-C14-C15	120.0(3)	C23-C24-C25	120.3(3)	C33-C34-C35	120.6(3)	120.1(1)
C16-C15-C14	120.3(3)	C26-C25-C24	119.9(3)	C36-C35-C34	119.7(3)	

[a] Average calculated assuming D_3 symmetry; standard deviations calculated as $\sigma(\bar{x}) = \left[\sum_{i=1}^{n} (x_i-\bar{x})^2/n(n-1)\right]^{1/2}$ or $\sigma(\bar{x}) = \left[\sum_{i=1}^{n} 1/\sigma_i^2\right]^{-1/2}$, whichever is greater.

fit (GOF) equal to 1.128 for 4181 reflections with $F_o^2 > 3\sigma(F_o^2)$. The largest residual electron density in the final difference Fourier map (0.82 e/Å^3) was located 0.38 Å from OW2. Final positional parameters for the non-hydrogen atoms are listed in Table III. Anisotropic thermal parameters, hydrogen atom parameters, and observed and calculated structure factor amplitudes (Tables IV to VI) are available as supplementary material from the authors upon request.

[Ga(benzohydroxamate)$_3$]·H_2O·C_2H_5OH. The structure of **2** was solved by standard heavy-atom procedures and refined as above. Hydrogen atoms were located from the

ΔF map at densities of 0.3 to 0.7 e/Å^3 and were assigned idealized positions. The ethanol molecule was disordered, and refined using a model with two alternate positions for the oxygen atom, with refined ocupancies of 0.46 to 0.54. Hydrogens for the ethanol were not resolvable by ΔF, and were not included in the structure model. Anisotropic refinement of all non-hydrogen atoms except those from the ethanol converged with $R = 0.040$ and $R_w = 0.054$, with a GOF of 1.76. The largest residual peaks were 0.5–0.7 e/Å^3 located in the region of the ethanol molecule and C20. Comparison of F_0 vs F_c as a function of F_o, setting angle, and Miller indices showed minor disagreement only among the very weak reflections. Atomic coordinates are given in Table VII, anisotropic thermal parameters, hydrogen atom parameters, and observed and calculated structure factor amplitudes (Tables VIII to X) are available as supplementary material.

DISCUSSION

$K_3[Ga(catecholate)_3]\cdot 1.5\ H_2O$. Individual bond lengths and angles of **1** are tabulated in Table XI. The complex (Figure 1) is isostructural with the Cr(III), Fe(III)[16] and the V(III) complexes.[18] In fact, the present structure shows the characteristic bond length alteration in the catecholate rings and bending of the catechol ligands across the oxygen-oxygen vector [the angles defined by the centroid of the catechol ring, the midpoint of the O-O vector and the Ga atom are 9.5(3)°, 6.1(3)°, and 2.5(3)°]. The average Ga-O distance, 1.984(6) Å, is essentially the same as the average Cr-O distance, 1.986(4) Å; the Cr^{3+} ionic radius is 0.64 Å.[5] However a wider range of distances is spanned in the Ga^{3+} structure, 1.969(2)-2.005(2)Å, than in the Cr^{3+} structure, 1.973(3)-1.998(3) Å. The average Ga-O distance is 0.031 Å shorter than the average Fe-O distance, 2.015(6) Å, about as expected from their ionic radii. The average O-M-O$_{\text{ring}}$ angle in the Ga^{3-} complex, 83.8(1)°, is slightly larger than in the Cr^{3+} structure, 83.6(1)°, and significantly larger than the same angle in the Fe^{3+} complex [81.3(1)°]. While the bond lengths of the Ga^{3+} and Cr^{3+} complexes are nearly identical, there is a significant difference in the trigonal twist angle (Table XII). This arises from the crystal

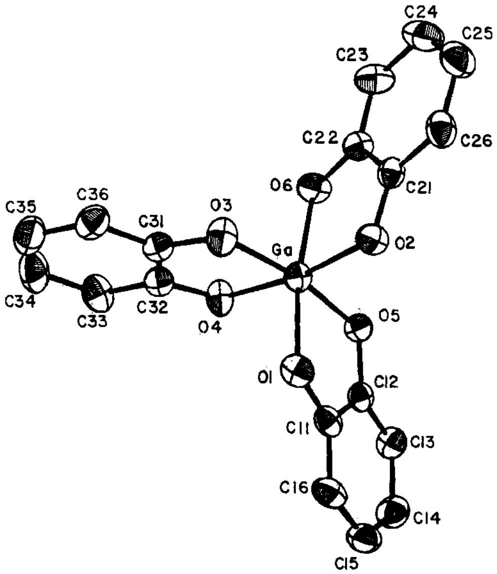


FIGURE 1 Molecular structure and labeling scheme for **1**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

TABLE XII
Coordination parameters for $M(cat)_3^{n-}$ complexes.

	M-O (Å)	O-M-O (deg)	O-O (Å)	Ligand bite[a]	Trigonal twist[b] (deg)
P(V)	1.714(8)	91.4(2)	2.454(5)	1.432	58.9
Si(IV)	1.784(15)	88 (1)	2.490(6)	1.396	55.9
As(V)[c]	1.843(5)	88.2(5)	2.565(7)	1.392	55.2
As(V)[d]	1.831(5)	88.3(6)	2.550(5)	1.393	55.6
Mn(IV)[e]	1.882(5)	85.5(3)	2.556(8)	1.358	52.3
Mn(IV)[f]	1.906(1)	85.2(1)	2.582(6)	1.355	51.8
Cr(III)	1.986(4)	83.6(1)	2.646(6)	1.333	50.0
Ga(III)	1.984(6)	83.78(5)	2.649(1)	1.335	48.8
V(III)	2.013(9)	81.3(3)	2.624(4)	1.304	45.6
Ti(IV)	1.966(12)	80.3(1)	2.537(6)	1.290	43.5
Fe(III)	2.015(6)	81.26(7)	2.625(2)	1.303	44.7
V(IV)	1.942(8)	80.7(1)	2.515(4)	1.295	38.6

[a] Ligand site defined as the ratio O-O/M-O. [b] Trigonal twist calculated as the average projection angle for $O\text{-}M\text{-}O_{ring}$ as viewed down the pseudo threefold axis of the complex. [c] Potassium salt, Ref. 23. [d] Hydronium $(H_7O_3^+)$ salt, Ref. 24. [e] Sodium salt, Ref. 26. [f] Potassium salt, Ref. 27.

field stabilization of the Cr^{3+} complex which favours ideal octahedral geometry. In addition, the twist angles and bite distances follow the correlation already established for catechol complexes.[16] Figure 2 shows a plot of this relationship for other *tris*-catecholate structures known to date: P(V),[22] As(V),[23,24] Si(IV),[25] Mn(IV),[26,27] Ti(IV),[28] and V(III) and V(IV).[18] The deviation of the V(IV) structure from the established trend has not been discussed previously. It is remarkable that even though the Ti(IV) and V(IV) structures are very similar (both experience very similar hydrogen bonding to triethylammonium cations), the V twist angle is unexpectedly small.

It is apparent from this structure that there is little *structural* basis for the different properties of the Ga^{3+} and Fe^{3+} catecholate complexes. The bond lengths are as

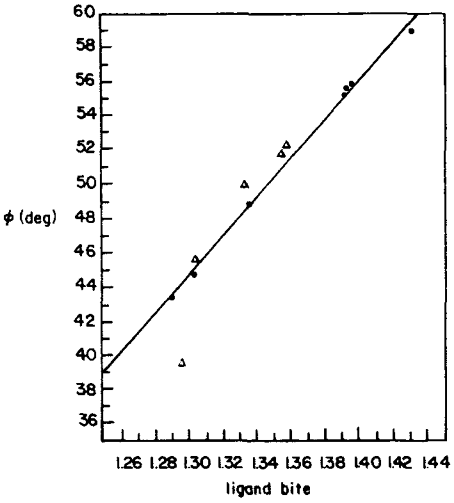


FIGURE 2 Twist angle ϕ in $M(cat)_3^{n-}$ complexes plotted as a function of the ligand bite (b). The line is a linear least-squares fit of the d^0, d^5 and d^{10} complexes (shown by ●), such that $\phi = 113°b-102°$. Other d^n electronic configuration are denoted by Δ.

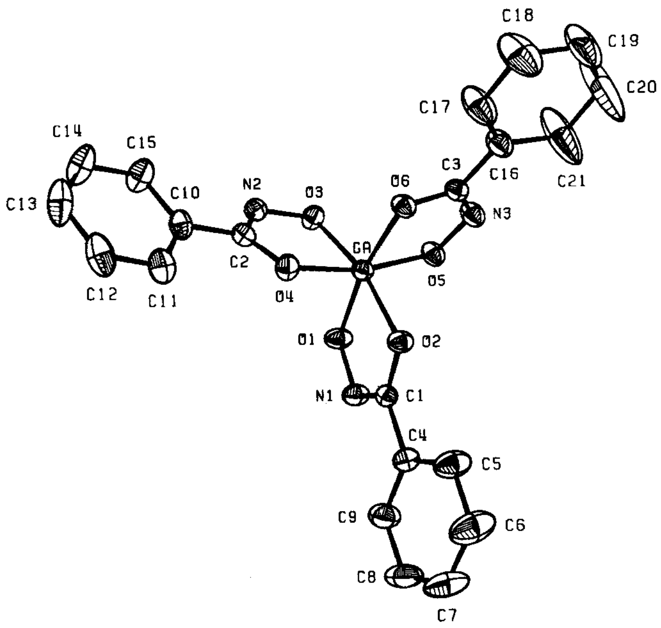


FIGURE 3 Molecular structure and labeling scheme for **2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

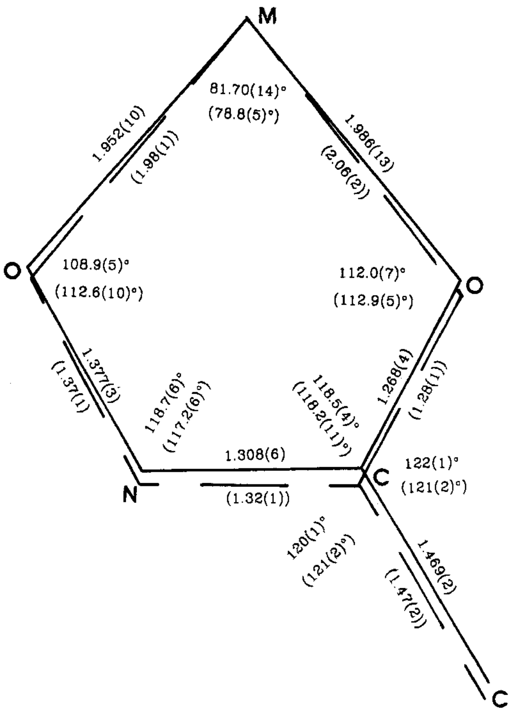


FIGURE 4 Comparison of the average metal-chelate bonding parameters for **2** and the Fe^{3+} analog. The broken line structure and values in parentheses refer to the Fe^{3+} structure.

TABLE XIII
Bond lengths and angles for **2**.

Bond Lengths (Å)

Ligand 1		Ligand 2		Ligand 3		Average
Ga-O1	1.936(2)	Ga-O3	1.951(2)	Ga-O5	1.969(2)	1.952(10)
Ga-O2	2.009(2)	Ga-O4	1.965(2)	Ga-O6	1.984(2)	1.986(13)
	Δ -0.073		Δ -0.014		Δ -0.015	-0.034
O1-N1	1.377(3)	O3-N2	1.372(3)	O5-N3	1.381(3)	1.377(3)
O2-C1	1.274(3)	O4-C2	1.270(3)	O6-C3	1.261(3)	1.268(4)
C1-N1	1.297(4)	C2-N2	1.319(4)	C3-N3	1.307(4)	1.308(6)
C1-C4	1.466(4)	C2-C10	1.471(4)	C3-C16	1.471(4)	1.469(2)

Average phenyl C-C 1.362(8)

Angles (deg)

O1-Ga-O2	81.68(8)	O1-Ga-O6	168.49(9)
O3-Ga-O4	81.96(8)	O3-Ga-O2	167.74(8)
O5-Ga-O6	81.47(8)	O5-Ga-O4	167.72(8)
Avg O-Ga-O$_{ring}$	81.70(14)	Avg O-Ga-O$_{trans}$	168.0(2)

O1-Ga-O3	89.01(9)	O1-Ga-O4	98.12(9)	O2-Ga-O4	91.43(8)
O1-Ga-O5	92.43(9)	O3-Ga-O6	101.00(9)	O2-Ga-O6	89.16(8)
O3-Ga-O5	92.92(8)	O5-Ga-O2	96.31(9)	O4-Ga-O6	89.16(8)
Avg	91.2(11)	Avg	98.5(12)	Avg	89.9(7)

Ligand 1		Ligand 2		Ligand 3		Average
Ga-O1-N1	109.3(2)	Ga-O3-N2	109.2(2)	Ga-O5-N3	108.1(2)	108.9(5)
Ga-O2-C1	111.0(2)	Ga-O4-C2	112.4(2)	Ga-O6-C3	112.6(2)	112.0(7)
O1-N1-C1	119.2(2)	O3-N2-C2	117.8(2)	O5-N3-C3	119.1(2)	118.7(6)
O2-C1-N1	118.7(3)	O4-C2-N2	118.5(3)	O6-C3-N3	118.4(3)	118.5(4)
N1-C1-C4	118.5(3)	N2-C2-C10	121.0(3)	N3-C3-C16	120.2(3)	119.9(10)
O2-C1-C4	122.8(3)	O4-C2-C10	120.4(3)	O6-C3-C16	121.4(3)	121.5(10)

Average phenyl C-C-C 120.0(3)

expected from simple considerations of ionic radii, implying no unexpected bonding interactions. Perhaps the most notable difference is in the twist angle of the complexes. This follows a steady trend that depends in part on the size of the ion, and it is possible that such a feature is critical in determining the "fit" of the complex in the siderophore receptor site. Overall, however, the structure argues well for the supposed *similarity* of Ga^{3+} and Fe^{3+} complexes.

[Ga(benzohydroxamate)$_3$]$\cdot H_2O\cdot C_2H_5OH$. The crystal structure of complex **2** (Figure 3), while not isomorphous with the analogous Fe^{3+} structure,[17] possesses the same *cis* (or *fac*) coordination geometry. Table XIII lists the bond lengths and angles for **2**. Figure 4 compares the structures of the chelates in the two complexes. Several important differences are noted:

1) The average M-O distance in the gallium complex is 0.055 Å shorter than in the iron complex — twice the 0.025 Å difference expected on the basis of the change in ionic radii.

2) The M-O bonds to the "carbonyl" and the "nitroxide" oxygens are more similar in the gallium complex, where they differ by only 0.034 Å, than in the ferric complex where they differ by 0.08 Å.

TABLE XIV
Hydrogen bonds in Ga(benz)$_3$ and Fe(benz)$_3$.

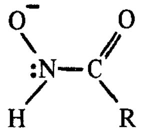
Ga(benz)$_3$				Fe(benz)$_3$			
(Å)	Bond	H-Bond	(Å)	(Å)	Bond	H-Bond	(Å)
1.951(2)	Ga-O3 ...	O7	2.783(3)	1.98	Fe-O3 ...	W(12)	2.96
1.969(2)	Ga-O5 ...	O8,1	2.813(7)	1.98	Fe-O3 ...	W(22)	2.63
1.969(2)	Gal-O5 ...	O8,2	2.858(8)	1.99	Fe-O5 ...	W(3)	2.78
1.952(10)				1.98	Avg Fe-O(N)		
				2.08	Fe-O2 ...	N3	2.74
				2.04	Fe-O6 ...	W(3)	2.99
				2.06	Avg Fe-O(C)		
1.319(4)	C2-N2 ...	O7	2.790(3)	1.32	C1-N1 ...	W(1)	2.72
1.308(9)	Avg C-N			1.31	C2-N2 ...	W(12)	2.65
				1.31	C2-N2 ...	W(22)	2.80
				1.34	C3-N3 ...	O2	2.74
				1.32	Avg C-N		

3) The Ga- and Fe-O(N) bonds differ by only 0.03 Å while the Ga- and Fe-O(C) bonds differ by 0.07 Å.

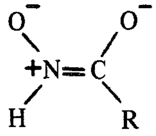
Thus, there is an apparent difference in the bonding of the metals to the two different oxygens types. Note that the bonds to the "ionic" nitroxide oxygens accurately reflect the different metal ionic radii, while the bonds to the carbonyl oxygens do not (the difference is nearly three times that expected from the ionic radii). Possible causes for these structural differences are discussed below.

Hydrogen bonding effects can be an important consideration in comparing these structures because they are not isomorphous. Table XIV lists the strongest hydrogen bond contacts in both structures. The gallium complex shows variations in the M-O bond length which clearly correlate with hydrogen bonding. The Ga-O3 and Ga-O5 distances, both affected by H-bonds, are longer than Ga-O1, and the difference between the M-carbonyl and M-nitroxide bonds is small. The low precision of the Fe^{3+} structure somewhat obscures the analogous correlations, but the *differences* between the carbonyl and nitroxide bonds do correlate with the H-bonding. Hydrogen bonding to the nitroxide oxygen results in more similar M-O bond lengths, while H-bonding to the carbonyl oxygens increases the difference. A direct consequence of hydrogen bonding to the carbonyl oxygens in the Fe^{3+} structure is to increase the difference in the M-O(C) bond lengths, providing at least a partial explanation for the 0.07 Å difference observed in point (3) above.

The different properties and structural details of the Ga^{3+} and Fe^{3+} complexes could also be a consequence of stabilization of different resonance forms of the hydroxamate ligand. Structures I and II below show the two limiting resonance forms of the hydroxamate ligand.



I



II

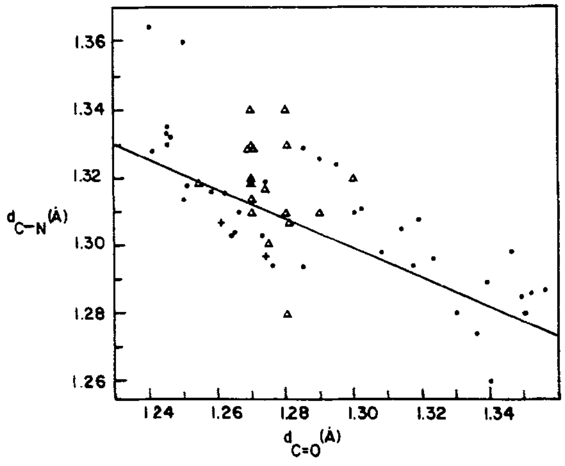


FIGURE 5 Plot of the C-N distance as a function of the C=O distance in hydroxamic acids and metal hydroxamate complexes. The line is a linear least-squares fit of the data. Data from Fe^{3+} structures are represented with a Δ, while data from the Ga^{3+} structure are shown as +. Data from the hydroxamic acids are shown as ●.

Structure I has no formal charge on the carbonyl oxygen or the nitrogen atom. This decreases the electrostatic contributions to the M-O(C) bonding. Significant contribution to the overall molecular orbital from resonance form I results in a short C=O distance and a long C-N distance. Resonance form II will have opposite effects. This form might be expected for metals with high formal charges, and will result in weaker N-H hydrogen bonding, since the strength of hydrogen bonds decreases with decreasing electronegativity of the H-bonded atoms. Inspection of Table XIV bears out this last expectation. The only H-bonded nitrogen in the gallium structure also has the longest C-N distance. In the Fe^{3+} structure, all three ligands are H-bonded through N-H, and the average C-N distance is comparable to the longest in the Ga^{3+} structure. These results suggest more contribution to the molecular bonding in the Fe^{3+} structure from resonance form II than in the Ga^{3+} structure, where form I may be more important.

A simple comparison of ligand bond lengths in the Fe^{3+} and Ga^{3+} structures does not satisfactorily categorise the dominant resonance form of the ligand in these complexes. The Ga^{3+} complex has shorter C=O *and* C-N bonds than the Fe^{3+} complex. Figure 5 plots the correlation between the C-N and C=O bond distances (which are listed in Table XV) in M-hydroxamate complexes and free hydroxamic acid structures.[17,29–55] At either extreme are the free hydroxamic acids, with structures corresponding to resonance form I, and the covalently bound alkyl ethers of hydroxamic acids, with resonance form II. There is a clear inverse relationship, as expected, between these bond lengths. The Ga^{3+} and Fe^{3+} structures discussed here fall into this region. However, while the correlation shown in Figure 5 indicates that the hydroxamate ligands *do* vary in a consistent manner between the canonical forms I and II, there is no clear relationship between the resonance form of the ligand and the mode of bonding to the metal. It must be concluded that the small difference in M-O(C) and M-O(N) bonding observed in the structures are not due to differences in the M-O interaction or the hybridization of the ligand.

TABLE XV
Structural parameters of hydroxamic acids (HA) and M(hydroxamate)$_n$ complexes

Complex	$\frac{\text{M-O(C)}}{\text{M-O(N)}}$	C=0 (Å)	C-N (Å)	$\frac{\text{C-N}}{\text{C=0}}$	Ref.
[(CH$_3$)$_2$CHN(OH)CO(CH$_2$)$_3$]$_2$		1.241(2)	1.328(2)	1.070(3)	28
Trichostatin A		1.240(9)	1.364(10	1.100(16)	29
Aceto-HA		1.245(6)	1.333(6)	1.070(10)	30
N-methyl-*p*-tolyl HA		1.246(2)	1.332(2)	1.069(3)	31
Salicyl HA		1.258(4)	1.316(4)	1.046(7)	32
syn-ethylbenzohydroxamic acid		1.33(2)	1.28(2)	0.96(3)	33
anti-ethylbenzohydroxamic acid		1.34(2)	1.26(2)	0.94(3)	33
Methylacetohydroxamic acid		1.336(3)	1.274(5)	0.954(6)	34
Cl P(benzoHA)$_2$	1.038(2)	1.356(3)	1.287(3)	0.949(4)	35
	1.044(2)	1.349(4)	1.285(3)	0.952(5)	
	1.038(2)	1.352(4)	1.286(3)	0.950(5)	
	1.046(2)	1.339(4)	1.289(3)	0.963(5)	
F$_2$B(N-methylacetoHA$^-$)	0.999	1.346	1.298	0.964	36
Cl$_2$Sn(*N*-phenylbenzoHA$^-$)$_2$	1.021(13)	1.25(3)	1.36(3)	1.09(5)	37
	1.068(16)	1.30(3)	1.31(2)	1.01(4)	
Me$_2$Sn(*N*-methylacetoHA$^-$)$_2$	1.127(4)	1.264(7)	1.303(6)	1.031(10)	38
	1.121(4)	1.250(6)	1.314(8)	1.051(11)	
Ph$_3$Sn(*N*-phenylbenzoHA$^-$)	1.104(4)	1.265(9)	1.304(9)	1.031(14)	39
(en)Zn(benzoHA$^-$)$_2$·(BHA)	1.035(2)	1.271(4)	1.312(4)	1.032(6)	40
	1.026(2)	1.251(4)	1.318(4)	1.054(6)	
		1.242(4)	1.322(5)	1.064(7)	
[O$_2$Mo(benzohydroximate)$_2$]$^{2-}$	1.096(7)	1.280(14)	1.188(16)	0.928(23)	41
	1.064(8)	1.328(13)	1.388(13)	1.045(20)	
	1.096(9)	1.294(13)	1.251(14)	0.967(21)	
	1.084(9)	1.307(13)	1.353(15)	1.035(22)	
[(CH$_3$)$_2$NOMoO(benzoHA$^-$)(benzohydroximate)]	1.061(3)	1.285(5)	1.329(4)	1.034(7)	41
	1.002(3)	1.323(5)	1.296(6)	0.980(8)	
[O$_2$Mo(benzoHA)$_2$]	1.108(6)	1.266(8)	1.310(8)	1.035(13)	42
	1.079(6)	1.262(8)	1.316(8)	1.043(13)	
[O$_2$Mo(benzoHA)$_2$]	1.062(15)	1.26(3)	1.38(3)	1.10(5)	43
	1.111(15)	1.29(3)	1.36(3)	1.05(5)	
(ϕ_3P)$_2$Pt(benzohydroximate)	1.004(11)	1.35(3)	1.28(3)	0.95	44
(ϕ_3P)CORh(*N*-phenyl-benzoHA)	1.026(3)	1.302(6)	1.311(7)	1.007(10)	45
Hf(*N*-phenyl-benzoHA)	1.078(5)	1.273(10)	1.372(10)	1.078(16)	46
	1.064(5)	1.264(10)	1.374(10)	1.087(16)	
	1.061(5)	1.267(10)	1.377(10)	1.087(16)	
	1.065(5)	1.261(10)	1.377(10)	1.092(11)	
trans-Cr(benzoHA)$_3$	1.007(2)	1.276(4)	1.294(4)	1.014(6)	47
	1.020(2)	1.273(4)	1.303(5)	1.023(6)	
	1.011(2)	1.271(4)	1.318(5)	1.037(7)	
trans-Cr(benzohydroximate)$_3$	0.990(2)	1.317(3)	1.294(3)	0.982(4)	48
	1.028(2)	1.319(3)	1.308(3)	0.989(4)	
	1.031(2)	1.314(3)	1.305(3)	0.993(4)	
cis-Cr(benzohydroximate)$_3$	1.006(2)	1.308(4)	1.298(4)	0.995(6)	
Ferrichrome A	1.025(20)	1.30(2)	1.32(2)	1.02(3)	49
	1.036(20)	1.28(2)	1.31(2)	1.02(3)	
	1.030(20)	1.27(2)	1.33(2)	1.05(3)	
Ferrichrome A (135 K)	1.027(4)	1.269(7)	1.329(7)	1.047(11)	50
	1.026(4)	1.270(7)	1.324(7)	1.046(11)	
	1.027(4)	1.254(7)	1.319(7)	1.052(11)	
Alumichrome A (135 K)	1.011(3)	1.295(4)	1.324(5)	1.022(7)	
	1.017(3)	1.290(5)	1.326(5)	1.028(8)	
	1.011(3)	1.285(6)	1.294(6)	1.008(9)	
Ferrixoamine E	1.061(4)	1.270(6)	1.314(5)	1.085(9)	51
	1.054(3)	1.275(6)	1.301(5)	1.088(9)	
	1.042(3)	1.2821(6)	1.307(5)	1.075(9)	
Ferrichrome	1.02(1)	1.27(2)	1.32(3)	1.04(3)	52
	1.02(1)	1.28(2)	1.28(2)	1.00(3)	
	1.04(1)	1.29(2)	1.31(2)	1.02(3)	

TABLE XV Cont'd.

Fe(*N*,*N*′,*N*″-triacetylfusarinine)	1.02(1)	1.27(2)	1.34(2)	1.06(3)	53
	1.04(1)	1.28(2)	1.33(2)	1.04(3)	
	1.05(1)	1.27(2)	1.39(2)	1.09(3)	
[Fe_2(pimelyl-bis-*N*-isoPr-HA)$_2$(μ-OCH_3)$_2$]	1.023(2)	1.274(2)	1.317(2)	1.034(3)	54
	1.011(2)	1.270(2)	1.319(2)	1.038(3)	
Fe(benzoHA)$_3$	1.06(1)	1.30(1)	1.32(2)	1.02(2)	15
	1.04(1)	1.27(1)	1.31(1)	1.04(2)	
	1.03(1)	1.28(2)	1.34(2)	1.05(3)	
Ga(benzoHA)$_3$	1.038(2)	1.274(3)	1.297(4)	1.018(5)	this work
	1.007(2)	1.270(3)	1.319(4)	1.038(5)	
	1.008(2)	1.261(3)	1.307(4)	1.036(5)	

The structures reported here contribute to the growing body of gallium structural chemistry. The geometries of both gallium complexes compare relatively well with the corresponding ferric analogs and support the premise that Ga^{3+} is a good structural analogue for the ferric ion. Therefore, neither structure provides a convincing basis for the observed difference in biological transport of Ga^{3+} and Fe^{3+} catecholate or hydroxamate complexes.

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SUPPLEMENTARY MATERIAL

Table IV[anisotropic thermal parameters for **1**], Table V[hydrogen atom parameters for **1**], Table VI[structure factor table of **1**], Table VIII[anisotropic thermal parameters for **2**], Table IX[hydrogen atom parameters for **2**], Table X[structure factor table for **2**] (61 pages). Copies are available from the Editor upon request.

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19. C.W. Eigenbrot, Jr. and K.N. Raymond, *Inorg. Chem.*, **21,** 2650 (1982). In the case of a **1** a modified procedure was followed in that the maximum scan time was progressively increased for successive θ_{min}-θ_{max} shells in order to maximize the time spent collecting higher angle data. Time in seconds for θ_{min}-θ_{max} ranges are as follows: 30(1.5°-15°), 60 (15°-22.5°), 120 (22.5°-30°) and 200 (30°-31°). In the last shell approximately 58% of the reflections were considered "observed". Crystal orientations monitored every 250 reflections, orientation redetermined if setting angles deviation greater than 0.1°. Intensity standards monitored every 2 hr of X-ray exposure time. No decay observed for **1**. For **2** there was an isotropic decrease of ~10% over 183 hr, and a linear decay correction was made. Azimuthal ψ scans recorded near $\psi = 90°$ showed significant variations for both **1** and **2**. Absorption corrections based upon the exact crystal shape and the empirical formula were performed.
20. C-H distance = 0.95 Å, $B_h = B_{eq} + 1$, where B_{eq} is the equivalent isotropic thermal factor of the atom to which the hydrogen is bonded.
21. The expression used for the extinction coefficient is Eq. 17.16 from G.H. Stout and L.H. Jensen, *X-Ray Structure Determination* (Macmillan, New York, 1968), p. 412.
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