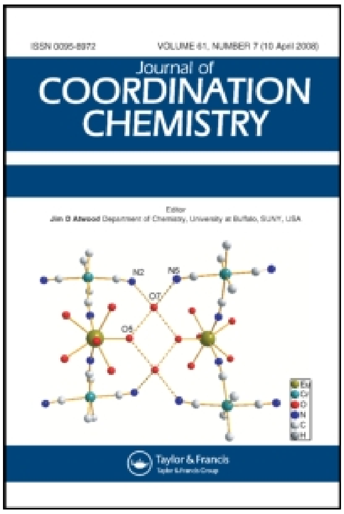

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MACROBICYCLIC d-METAL TRIS-DIOXIMATES OBTAINED BY CROSS-LINKING WITH p-BLOCK ELEMENTS. XV. CRYSTAL AND MOLECULAR STRUCTURES OF TWO MACROBICYCLIC TIN-CONTAINING COBALT(III) TRIS-DIOXIMATES

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The structure of the tin-containing clathrochelates cyclohexadione-1,2-dioximate $(NBu_4)[CoNx_3(SnCl_3)_2]$ (A) and dimethylglioximate $(NBu_4)[CoDm_3(SnBr_3)_2]\cdot H_2O$ (B) have been determined by X-ray methods. Crystal data: (A) is orthorhombic, space group $P2_12_12_1$ a = 16.566(4), b = 16.551(4), c = 16.560(4)Å, Z = 4; (B) is orthorhombic, space group $Pca2_1$, a = 16.271(3), b = 15.337(3), c = 18.572(4)Å, Z = 4. The cobalt(III) atoms are encapsulated by the clathrochelate ligands and surrounded by a distorted octahedral coordination polyhedron.

KEYWORDS: macrobicyclic complexes, X-ray structure, cobalt, oximes

INTRODUCTION

The majority of structures of macrobicyclic d-metal tris-dioximates solved by X-ray methods belong to boron-containing iron(II) complexes.[1–6] The structure of one tin-containing iron(II) complex was also solved.[7] Only for three cobalt(III) and one cobalt(II) clathrochelate tris-dioximates have structures been determined.[8–10] Obtaining further structural information on new macrobicyclic tin-containing cobalt(III) complexes would be of undoubted interest. This prompted the current study.

EXPERIMENTAL

$(NBu_4)[CoNx_3(SnCl_3)_2]$ (A) and $(NBu_4)[CoDm_3(SnBr_3)_2]$ (B), where Bu is an *n*-butyl residue, were synthesized in a way similar to that of corresponding

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diethylammonium salts[9] by adding tetrabutylammonium hydroxide to the reaction mixture. Single crystals of the complexes were obtained by slow evaporation of saturated solutions in acetonitryl:benzen (1:10) during several weeks.

Crystal Data

(A): $C_{34}H_{60}Cl_6CoN_7O_6Sn_2$, M = 1171.9, orthorhombic, at 153K; a = 16.566(4), b = 16.551(4), c = 16.560(4)Å, V = 4540(3)Å^3 (by least-squares refinement of diffractometer angles for 24 automatically centred reflections, λ = 0.71073Å), space group $P2_12_12_1$, Z = 4, D_c = 1.714 g cm^{-3}, $F(000)$ = 2360. Yellow plates; μ(MoKα) = 18.55 cm^{-1}.

(B): $C_{28}H_{56}Br_6CoN_7O_7Sn_2$, M = 1378.6, orthorhombic, at 153K; a = 16.271(3), b = 15.337(3), c = 18.572(4)Å, V = 4635(2)Å^3 (by least-squares refinement of diffractometer angles for 24 automatically centered reflections, λ = 0.71073Å), space group $Pca2_1$, Z = 4, D_c = 1.976 g cm^{-3}, $F(000)$ = 2664. Yellow, air-unstable prisms; μ(MoKα) = 66.41 cm^{-1}.

Data Collection and Refinement

Unit cell parameters and X-ray diffraction data were measured at 153 K (to protect against decomposition) with a four-circle automated Siemens P3/PC diffractometer (experimental details are given in Table 1). Intensities were corrected for Lorentz and polarization effects; absorption correction was applied only for (B) (DIFABS procedure).

Table 1 Structure determination data summary.

	(A)	(B)
Empirical Formula	$C_{34}H_{60}Cl_6CoN_7O_6Sn_2$	$C_{28}H_{56}Br_6CoN_7O_7Sn_2$
Space Group	$P2_12_12_1$	$Pca2_1$
Unit Cell Dimensions	a = 16.566(4)Å	16.271(3)Å
	b = 16.551(4)Å	15.337(3)Å
	c = 16.560(4)Å	18.572(4)Å
V	4540(3)Å	4635(3)Å^3
Z	4	4
Formula Weight	1171.9	1378.6
Density (calc.)	1.714 g cm^{-3}	1.976 g cm^{-3}
Wavelength Used	MoKα = 0.71073Å, graphite monochromated	
Absorption Coefficient	18.55 cm^{-1}	66.41 cm^{-1}
$F(000)$	2360	2664
2θ Range	4.0 to 54.0°	4.0 to 55.0°
Scan Type	ω/2θ	
Standard Reflections	2 measurement every 98 reflections	
Index Ranges	$0 \le h \le 17$	$0 \le h \le 21$
	$0 \le k$ 23	$0 \le k$ 18
	$0 \le l$ 23	$-24 \le l \le 0$
Independent reflections	4589	5049
Observed Reflections	2848 ($F > 6.0\sigma(F)$)	2236 ($F > 8.0\sigma(F)$)
Weigting Scheme	$w^{-1} = \sigma^2(F)$	$w^{-1} = \sigma^2(F) + 0.0004F^2$
Number of Parameters		
Final R Indices	R = 0.575, R_w = 0.586	R = 0.652, R_w = 0.739

Both structures were solved by direct methods. For (A) space group $P2_12_12_1$ was chosen, because in the possible cubic space group $P2_13$ both complex anion and tetrabutylammonium counterion are found to be highly disordered near a three-fold axis. The solvate water molecule was localized in (B) using a subsequent difference Fourier map.

All non-hydrogen atoms of the complex anion in (A) and the Sn, Co and Br atoms in (B) were refined anisotropically; other non-hydrogen atoms were treated in the isotropic approximation. All hydrogen atoms in (A) and the hydrogens of the tetrabutylammonium cation in (B) were placed in calculated positions and were refined isotropically (fixed U_{iso} = 0.04Å^2 for the hydrogens of (A) and 0.08Å^2 for the hydrogens of both counter ions in the riding model approximation. We failed to localize the hydrogens of the complex anion and the solvate water molecule in (B).

Details of refinement and results are given in Table 1. All calculations were performed on an IBM-PC/AT computer using the SHELXTL PLUS programs. The structure of complex anions (A) and (B) and corresponding tetrabutylammonium counter ions are shown in Figures 1–3. The coordinates of non-hydrogen atoms are given in Table 2 and 3; selected bond lengths and angles are listed in Table 4–7.

RESULTS AND DISCUSSION

Both compounds represent salts of calthrochelate cobalt(III) anions with a tetrabutylammonium cation (compound (B) crystallized as a monohydrate). The central Co(III) ion has in both structures a coordination polyhedron intermediate between an octahedron and a trigonal prism; the relative twist angle, φ, of the N(1), N(3),

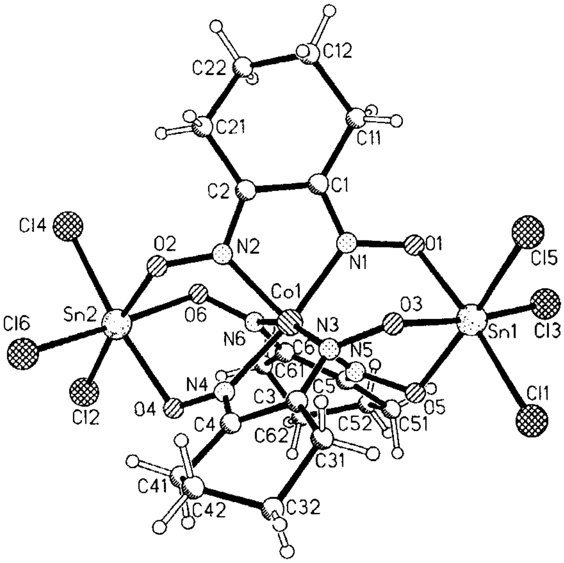

Figure 1 Perspective view of the $[CoNx_3(SnCl_3)_2]^-$ anion showing the labelling scheme used.

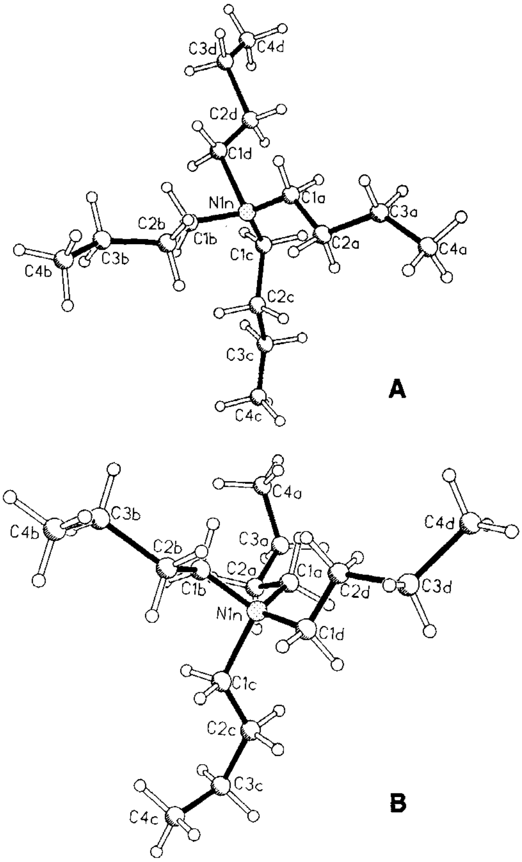

Figure 2 Perspective view of the NBu^{+}_{4} cation in (A) and (B) complexes with the labelling scheme used.

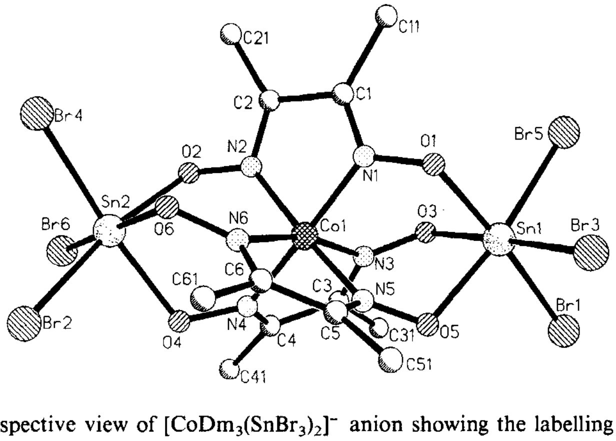

Figure 3 Perspective view of $[CoDm_3(SnBr_3)_2]^-$ anion showing the labelling scheme used.

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for (A).

	x/a	y/b	z/c	U(eq)
Sn(1)	3734(1)	3736(1)	3735(1)	35(1)*
Sn(2)	1213(1)	1217(1)	1214(1)	41(1)*
Co(1)	2475(2)	2470(2)	2474(2)	17(1)*
Cl(1)	5141(3)	3485(4)	3867(4)	60(2)*
Cl(2)	1370(6)	1218(6)	- 211(4)	97(3)
Cl(3)	3868(4)	5138(3)	3489(4)	56(2)*
Cl(4)	-216(3)	1381(5)	1212(5)	91(3)*
Cl(5)	3487(4)	3873(4)	5144(3)	56(2)*
Cl(6)	1202(5)	-221(4)	1378(5)	93(3)*
O(1)	2517(8)	3927(7)	3447(7)	40(3)*
O(2)	1228(7)	1249(6)	2504(6)	27(3)*
O(3)	3447(6)	2520(8)	3927(6)	33(3)*
O(4)	2500(6)	1228(6)	1258(6)	25(3)*
O(5)	3921(6)	3445(6)	2516(7)	29(3)*
O(6)	1246(6)	2492(6)	1232(6)	24(3)*
N(1)	2089(8)	3261(7)	3215(8)	22(3)*
N(2)	1479(8)	1942(8)	2776(8)	23(3)*
N(3)	3215(8)	2093(8)	3269(8)	20(3)*
N(4)	2780(8)	1488(8)	1954(8)	23(3)*
N(5)	3250(8)	3223(9)	2069(7)	23(3)*
N(6)	1962(8)	2797(8)	1488(9)	27(3)*
C(1)	1404(9)	3090(9)	3581(9)	27(4)*
C(11)	1043(11)	3614(11)	4204(10)	42(4)*
C(12)	248(14)	3215(13)	4596(13)	63(5)*
C(2)	1044(10)	2352(9)	3287(9)	29(4)*
C(21)	209(12)	2121(11)	3553(13)	48(4)*
C(22)	- 207(11)	2876(15)	3895(15)	63(5)*
C(3)	3575(10)	1423(10)	3103(9)	31(4)*
C(31)	4209(10)	1033(10)	3614(11)	38(4)*
C(32)	4582(13)	259(14)	3232(14)	61(5)*
C(4)	3274(10)	1037(10)	2347(9)	29(4)*
C(41)	3542(12)	221(12)	2122(10)	44(4)*
C(42)	3902(16)	- 202(12)	2859(13)	67(4)*
C(5)	3109(9)	3565(9)	1410(9)	23(4)*
C(51)	3611(11)	4217(10)	1044(10)	35(4)*
C(52)	3211(15)	4579(14)	260(14)	67(5)*
C(6)	2342(11)	3280(10)	1049(9)	32(4)*
C(61)	2115(10)	3536(12)	196(10)	40(4)*
C(62)	2856(13)	3886(16)	-209(12)	65(4)*
N(1N)	3945(25)	999(25)	-993(24)	170(8)
C(1A)	4011(25)	1519(25)	-407(23)	155(8)
C(2A)	4567(17)	1433(17)	194(16)	84(6)
C(3A)	4645(20)	2070(19)	834(19)	106(7)
C(4A)	5212(19)	2168(19)	1462(18)	105(7)
C(1B)	3557(29)	245(25)	-901(25)	164(9)
C(2B)	3502(20)	-238(19)	-347(19)	103(7)
C(3B)	2957(19)	-904(19)	-321(19)	100(7)
C(4B)	2779(24)	-1489(24)	255(23)	160(9)
C(1C)	4560(24)	1018(26)	-1480(26)	160(8)
C(2C)	5176(19)	439(19)	-1400(20)	109(7)
C(3C)	5874(22)	316(23)	-2055(22)	130(8)
C(4C)	6455(20)	-201(20)	-2145(21)	117(8)
C(1D)	3125(37)	1300(37)	-1716(38)	347(9)
C(2D)	3078(17)	1983(17)	-1937(18)	86(7)
C(3D)	2237(38)	2263(37)	-2394(39)	373(10)
C(4D)	2219(19)	2833(17)	-2831(18)	99(7)

*Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3 Atomic coordinates (× 10^4) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$) for (B).

	x/a	*y/b*	*z/c*	*U(eq)*
Sn(1)	1825(1)	1198(1)	5969(3)	21(1)*
Sn(2)	1847(1)	-2872(1)	4047(3)	25(1)*
Co(1)	1830(3)	-829(3)	5000	19(1)*
Br(1)	1857(3)	2658(2)	5359(3)	41(1)*
Br(2)	3189(2)	-3410(2)	3537(3)	42(1)*
Br(3)	2958(2)	1597(3)	6890(3)	36(1)*
Br(4)	1425(2)	-4268(2)	4688(3)	43(1)*
Br(5)	619(2)	1548(3)	6806(3)	31(1)*
Br(6)	989(2)	-3092(3)	2941(3)	40(1)*
O(1)	1841(14)	-67(14)	6406(12)	31(5)
O(2)	822(11)	-2214(13)	4466(11)	18(5)
O(3)	946(12)	774(14)	5171(11)	22(5)
O(4)	2244(12)	-1634(13)	3643(11)	18(5)
O(5)	2713(11)	735(13)	5234(11)	19(5)
O(6)	2465(12)	-2583(12)	5006(11)	20(5)
N(1)	1511(12)	-700(14)	5962(13)	6(5)
N(2)	984(13)	-1634(15)	4972(13)	13(6)
N(3)	1234(14)	175(16)	4722(15)	20(6)
N(4)	1921(13)	0932(13)	3957(12)	7(5)
N(5)	2752(15)	-114(16)	5178(14)	21(6)
N(6)	2633(15)	-1730(16)	5115(13)	19(6)
C(1)	933(18)	-1178(22)	6184(16)	23(8)
C(2)	630(19)	-1812(22)	5582(18)	27(8)
C(3)	1184(17)	298(20)	4031(18)	21(7)
C(4)	1570(19)	-406(21)	3614(19)	24(8)
C(5)	3440(17)	-573(21)	5373(18)	23(8)
C(6)	3363(19)	-1472(22)	5286(19)	28(8)
C(11)	578(22)	-1169(25)	6994(20)	39(10)
C(21)	21(22)	-2535(25)	5756(21)	44(11)
C(31)	850(20)	1127(22)	3720(19)	31(8)
C(41)	1420(21)	-455(21)	2730(19)	29(9)
C(51)	4152(19)	-53(23)	5644(18)	31(9)
C(61)	4099(25)	-2114(29)	5340(25)	58(12)
N(1N)	3171(19)	3702(19)	3312(16)	40(7)
C(1A)	2302(27)	4145(31)	3264(24)	70(14)
C(2A)	1801(33)	4013(40)	2634(33)	107(20)
C(3A)	913(31)	4237(33)	2759(29)	80(16)
C(4A)	545(37)	3571(41)	3160(32)	121(23)
C(1B)	3086(29)	2774(33)	3372(30)	85(16)
C(2B)	3744(30)	2201(33)	3643(32)	87(16)
C(3B)	3505(24)	1215(26)	3625(25)	54(11)
C(4B)	4240(33)	691(37)	3766(34)	111(21)
C(1C)	3644(32)	3785(34)	2555(29)	81(16)
C(2C)	3796(56)	4500(49)	2247(39)	163(33)
C(3C)	4039(22)	4633(24)	1497(19)	35(9)
C(4C)	4691(38)	4127(40)	1333(40)	141(26)
C(1D)	3735(31)	4123(35)	3821(26)	79(16)
C(2D)	3390(35)	4091(39)	4413(32)	102(21)
C(3D)	3961(39)	4596(42)	5070(34)	122(24)
C(4D)	3437(56)	4877(66)	5746(50)	274(60)
O(1W)	8104(45)	2896(52)	1574(43)	112(27)

*Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4 Selected bond lengths (Å) for (A).

Sn(1)-Cl(1)	2.377(5)	Sn(1)-Cl(3)	2.366(5)
Sn(1)-Cl(5)	2.380(5)	Sn(1)-O(1)	2.097(14)
Sn(1)-O(3)	2.093(13)	Sn(1)-O(5)	2.099(12)
Sn(2)-Cl(2)	2.375(6)	Sn(2)-Cl(4)	2.382(6)
Sn(2)-Cl(6)	2.396(6)	Sn(2)-O(2)	2.138(11)
Sn(2)-O(4)	2.134(10)	Sn(2)-O(6)	2.111(10)
Co(1)-N(1)	1.905(13)	Co(1)-N(2)	1.933(14)
Co(1)-N(3)	1.904(13)	Co(1)-N(4)	1.907(13)
Co(1)-N(5)	1.911(14)	Co(1)-N(6)	1.918(14)
O(1)-N(1)	1.365(17)	O(2)-N(2)	1.301(16)
O(3)-N(3)	1.355(17)	O(4)-N(4)	1.315(17)
O(5)-N(5)	1.386(17)	O(6)-N(6)	1.357(17)
N(1)-C(1)	1.318(20)	N(2)-C(2)	1.302(20)
N(3)-C(3)	1.289(21)	N(4)-C(4)	1.284(21)
N(5)-C(5)	1.251(19)	N(6)-C(6)	1.251(21)
C(1)-C(11)	1.475(23)	C(1)-C(2)	1.443(22)
C(11)-C(12)	1.610(29)	C(12)-C(22)	1.494(32)
C(2)-C(21)	1.501(25)	C(21)-C(22)	1.533(30)
C(3)-C(31)	1.496(24)	C(3)-C(4)	1.491(22)
C(31)-C(32)	1.557(28)	C(32)-C(42)	1.494(33)
C(4)-C(41)	1.470(25)	C(41)-C(42)	1.528(29)
C(5)-C(51)	1.491(22)	C(5)-C(6)	1.482(23)
C(51)-C(52)	1.576(29)	C(52)-C(62)	1.504(34)
C(6)-C(61)	1.521(23)	C(61)-C(62)	1.514(28)

Table 5 Selected bond angles (°) for (A).

Cl(1)-Sn(1)-Cl(3)	95.5(2)	Cl(1)-Sn(1)-Cl(5)	95.5(2)
Cl(3)-Sn(1)-Cl(5)	95.2(2)	Cl(1)-Sn(1)-O(1)	172.1(3)
Cl(3)-Sn(1)-O(1)	84.4(3)	O(1)-Sn(1)-O(1)	92.4(4)
Cl(1)-Sn(1)-O(3)	92.3(3)	Cl(3)-Sn(1)-O(3)	172.1(3)
Cl(5)-Sn(1)-O(3)	84.4(3)	O(1)-Sn(1)-O(3)	87.7(4)
Cl(1)-Sn(1)-O(5)	84.5(3)	Cl(3)-Sn(1)-O(5)	92.6(3)
Cl(5)-Sn(1)-O(5)	172.1(3)	O(1)-Sn(1)-O(5)	87.6(4)
O(3)-Sn(1)-O(5)	87.7(4)	Cl(2)-Sn(2)-Cl(4)	96.2(3)
Cl(2)-Sn(2)-Cl(6)	96.5(3)	Cl(4)-Sn(2)-Cl(6)	96.1(3)
Cl(2)-Sn(2)-O(2)	172.9(4)	Cl(4)-Sn(2)-O(2)	90.6(4)
Cl(6)-Sn(2)-O(2)	84.9(3)	Cl(2)-Sn(2)-O(4)	85.6(4)
Cl(4)-Sn(2)-O(4)	172.7(4)	Cl(6)-Sn(2)-O(4)	90.7(4)
O(2)-Sn(2)-O(4)	87.4(4)	Cl(2)-Sn(2)-O(6)	90.6(4)
Cl(4)-Sn(2)-O(6)	85.0(3)	Cl(6)-Sn(2)-O(6)	172.6(4)
O(2)-Sn(2)-O(6)	87.8(4)	O(4)-Sn(2)-O(6)	88.0(4)
N(1)-Co(1)-N(2)	81.8(5)	N(1)-Co(1)-N(3)	89.7(6)
N(2)-Co(1)-N(3)	102.8(6)	N(1)-Co(1)-N(4)	164.8(6)
N(2)-Co(1)-N(4)	87.6(6)	N(3)-Co(1)-N(4)	82.1(6)
N(1)-Co(1)-N(5)	90.2(6)	N(2)-Co(1)-N(5)	163.6(6)
N(3)-Co(1)-N(5)	91.4(6)	N(4)-Co(1)-N(5)	102.7(6)
N(1)-Co(1)-N(6)	101.8(6)	N(2)-Co(1)-N(6)	88.3(6)
N(3)-Co(1)-N(6)	165.1(6)	N(4)-Co(1)-N(6)	88.6(6)
N(5)-Co(1)-N(6)	79.3(6)	Sn(1)-O(1)-N(1)	116.2(9)
Sn(2)-O(2)-N(2)	111.8(8)	Sn(1)-O(3)-N(3)	116.3(9)
Sn(2)-O(4)-N(4)	112.6(8)	Sn(1)-O(5)-N(5)	117.2(8)
Sn(2)-O(6)-N(6)	113.6(8)	Co(1)-N(1)-O(1)	124.3(10)
Co(1)-N(1)-C(1)	115.9(10)	O(1)-N(1)-C(1)	119.4(13)

Table 5 *Continued*

Co(1)-N(2)-O(2)	125.6(10)	Co(1)-N(2)-C(2)	113.9(11)
O(2)-N(2)-C(2)	120.5(13)	Co(1)-N(3)-O(3)	124.6(10)
Co(1)-N(3)-C(3)	115.6(11)	O(3)-N(3)-C(3)	119.3(13)
Co(1)-N(4)-O(4)	125.5(10)	Co(1)-N(4)-C(4)	115.8(11)
O(4)-N(4)-C(4)	118.6(13)	Co(1)-N(5)-O(5)	121.7(9)
Co(1)-N(5)-C(5)	118.4(11)	O(5)-N(5)-C(5)	119.7(13)
Co(1)-N(6)-O(6)	123.3(10)	Co(1)-N(6)-C(6)	116.9(12)
O(6)-N(6)-C(6)	119.7(14)	N(1)-C(1)-C(11)	123.0(14)
N(1)-C(1)-C(2)	112.5(13)	C(11)-C(1)-C(2)	124.5(14)
C(1)-C(11)-C(12)	111.9(15)	C(11)-C(12)-C(22)	104.7(16)
N(2)-C(2)-C(1)	115.5(14)	N(2)-C(2)-C(21)	124.6(15)
C(1)-C(2)-C(21)	119.8(14)	C(2)-C(21)-C(22)	108.4(15)
C(12)-C(22)-C(21)	111.5(17)	N(3)-C(3)-C(31)	125.1(15)
N(3)-C(3)-C(4)	113.2(14)	C(31)-C(3)-C(4)	121.7(14)
C(3)-C(31)-C(32)	113.8(15)	C(31)-C(32)-C(42)	106.8(17)
N(4)-C(4)-C(3)	112.9(14)	N(4)-C(4)-C(41)	126.7(15)
C(3)-C(4)-C(41)	120.4(14)	C(4)-C(41)-C(42)	109.6(15)
C(32)-C(42)-C(41)	113.0(18)	N(5)-C(5)-C(51)	125.3(14)
N(5)-C(5)-C(6)	111.6(13)	C(51)-C(5)-C(6)	123.0(13)
C(5)-C(51)-C(52)	112.0(15)	C(51)-C(52)-C(62)	107.5(18)
N(6)-C(6)-C(5)	113.6(14)	N(6)-C(6)-C(61)	126.4(16)
C(5)-C(6)-C(61)	119.8(14)	C(6)-C(61)-C(62)	108.5(15)
C(52)-C(62)-C(61)	112.3(17)		

N(5) and N(2), N(4), N(6) bases is 41.0° in (A) and 45.1° in (B), being similar to other tin-containing cobalt(III) and iron(II) dioximates (Table 8). These values are more close to the octahedral case (φ = 60°), than was found for an analogous iron(II) complex (37.5°) and for a boron-containing cobalt(III) complex (31.2°).

The φ angle for complex (B) is about 2.8° greater than that of H[CoDm$_3$(SnCl$_3$)$_2$]. This fact may be connected to steric hindrance between bromine atoms and methyl substituents in dioxime fragments.

Table 6 Selected bond lengths (Å) for (B).

Sn(1)-Br(1)	2.511(5)	Sn(1)-Br(3)	2.588(6)
Sn(1)-Br(5)	2.561(5)	Sn(l)-O(1)	2.103(22)
Sn(1)-O(3)	2.161(20)	Sn(1)-O(5)	2.110(19)
Sn(2)-Br(2)	2.520(5)	Sn(2)-Br(4)	2.544(5)
Sn(2)-Br(6)	2.507(7)	Sn(2)-O(2)	2.099(19)
Sn(2)-O(4)	2.142(20)	Sn(2)-O(6)	2.093(21)
Co(1)-N(1)	1.872(23)	Co(1)-N(2)	1.849(23)
Co(1)-N(3)	1.891(25)	Co(1)-N(4)	1.948(22)
Co(1)-N(5)	1.888(25)	Co(1)-N(6)	1.913(24)
O(1)-N(1)	1.381(31)	O(2)-N(2)	1.322(31)
O(3)-N(3)	1.326(33)	O(4)-N(4)	1.334(29)
O(5)-N(5)	1.307(32)	O(6)-N(6)	1.352(31)
N(1)-C(1)	1.261(37)	N(2)-C(2)	1.299(41)
N(3)-C(3)	1.301(43)	N(4)-C(4)	1.177(39)
N(5)-C(5)	1.371(39)	N(6)-C(6)	1.292(39)
C(1)-C(2)	1.562(46)	C(1)-C(11)	1.612(47)
C(2)-C(21)	1.522(50)	C(3)-C(4)	1.469(45)
C(3)-C(31)	1.498(46)	C(4)-C(41)	1.660(50)
C(5)-C(6)	1.394(48)	C(5)-C(51)	1.494(45)
C(6)-C(61)	1.554(53)		

Table 7 Selected bond angles (°) for (B).

Br(1)-Sn(1)-Br(3)	94.2(2)	Br(1)-Sn(1)-Br(5)	95.9(2)
Br(3)-Sn(1)-Br(5)	95.5(2)	Br(1)-Sn(1)-O(1)	175.4(6)
Br(3)-Sn(1)-O(1)	87.4(6)	Br(5)-Sn(1)-O(1)	88.2(6)
Br(1)-Sn(1)-O(3)	88.4(6)	Br(3)-Sn(1)-O(3)	175.1(6)
Br(5)-Sn(1)-O(3)	88.4(5)	O(1)-Sn(1)-O(3)	89.8(8)
Br(1)-Sn(1)-O(5)	89.6(6)	Br(3)-Sn(1)-O(5)	91.1(5)
Br(5)-Sn(1)-O(5)	171.0(5)	O(1)-Sn(1)-O(5)	86.0(8)
O(3)-Sn(1)-O(5)	84.7(8)	Br(2)-Sn(2)-Br(4)	97.7(2)
Br(2)-Sn(2)-Br(6)	97.5(2)	Br(4)-Sn(2)-Br(6)	96.9(2)
Br(2)-Sn(2)-O(2)	170.2(6)	Br(4)-Sn(2)-O(2)	91.0(6)
Br(6)-Sn(2)-O(2)	85.8(6)	Br(2)-Sn(2)-O(4)	84.1(5)
Br(4)-Sn(2)-O(4)	172.6(6)	Br(6)-Sn(2)-O(4)	90.0(6)
O(2)-Sn(2)-O(4)	86.8(7)	Br(2)-Sn(2)-O(6)	88.4(6)
Br(4)-Sn(2)-O(6)	84.8(6)	Br(6)-Sn(2)-O(6)	173.5(6)
O(2)-Sn(2)-O(6)	88.0(8)	O(4)-Sn(2)-O(6)	88.0(8)
N(1)-Co(1)-N(2)	83.7(10)	N(1)-Co(1)-N(3)	91.8(10)
N(2)-Co(1)-N(3)	98.8(10)	N(1)-Co(1)-N(4)	168.1(9)
N(2)-Co(1)-N(4)	88.5(10)	N(3)-Co(1)-N(4)	80.4(10)
N(1)-Co(1)-N(5)	89.5(10)	N(2)-Co(1)-N(5)	169.8(11)
N(3)-Co(1)-N(5)	89.0(11)	N(4)-Co(1)-N(5)	99.3(10)
N(1)-Co(1)-N(6)	99.2(10)	N(2)-Co(1)-N(6)	91.7(10)
N(3)-Co(1)-N(6)	165.6(11)	N(4)-Co(1)-N(6)	90.1(10)
N(5)-Co(1)-N(6)	81.8(11)	Sn(1)-O(1)-N(1)	114.4(16)
Sn(2)-O(2)-N(2)	115.4(15)	Sn(1)-O(3)-N(3)	113.9(15)
Sn(2)-O(4)-N(4)	116.3(15)	Sn(1)-O(5)-N(5)	114.8(16)
Sn(2)-O(6)-N(6)	115.4(16)	Co(1)-N(1)-O(1)	122.4(16)
Co(1)-N(1)-C(1)	117.2(20)	O(1)-N(1)-C(1)	120.3(24)
Co(1)-N(2)-O(2)	128.2(17)	Co(1)-N(2)-C(2)	116.5(21)
O(2)-N(2)-C(2)	112.9(24)	Co(1)-N(3)-O(3)	125.1(20)
Co(1)-N(3)-C(3)	114.8(21)	O(3)-N(3)-C(3)	119.8(24)
Co(1)-N(4)-O(4)	122.0(16)	Co(1)-N(4)-C(4)	116.6(22)
O(4)-N(4)-C(4)	120.5(26)	Co(1)-N(5)-O(5)	123.7(18)
Co(1)-N(5)-C(5)	113.3(20)	O(5)-N(5)-C(5)	122.0(24)
Co(1)-N(6)-O(6)	123.0(17)	Co(1)-N(6)-C(6)	115.7(21)
O(6)-N(6)-C(6)	121.2(25)	N(1)-C(1)-C(2)	111.4(26)
N(1)-C(1)-C(11)	124.5(28)	C(2)-C(1)-C(11)	124.1(27)
N(2)-C(2)-C(1)	110.6(27)	N(2)-C(2)-C(21)	128.9(30)
C(1)-C(2)-C(21)	120.4(28)	N(3)-C(3)-C(4)	112.8(27)
N(3)-C(3)-C(31)	121.8(28)	C(4)-C(3)-C(31)	125.1(30)
N(4)-C(4)-C(3)	115.1(31)	N(4)-C(4)-C(41)	125.2(29)
C(3)-C(4)-C(41)	119.5(27)	N(5)-C(5)-C(6)	113.9(26)
N(5)-C(5)-C(51)	116.6(28)	C(6)-C(5)-C(51)	129.5(28)
N(6)-C(6)-C(5)	114.4(28)	N(6)-C(6)-C(61)	122.1(31)
C(5)-C(6)-C(61)	123.4(29)		

One of the reasons for the larger octahedral distortion may be the lower ionic radius of Co(III) in comparison to Fe(II); the average Co-N bond lengths 1.913Å in (A) and 1.893Å in (B) are shorter than the average Fe-N bond length 1.923Å in the abovementioned complex (standard[11] values for Co(III)-N and Fe(II)-N bond lengths in six-coordinate dioximate complexes are 1.890 and 1.901Å respectively). The difference between complexes (A) and (B) may be defined by different conformational flexibilities of corresponding dioximate ligands. Chelate rings in anion (A) are less folded than in anion (B); deviation of oxime carbon atoms from corresponding N-Co-N planes amounts to ±0.06 and 0.16Å, respectively (although

Table 8 Data for coordination polyhedron geometries of clathrochelate tris-dioximates.

Complex	a, Å	h, Å	α,°	φ,°	Reference
[CoDm$_3$(BF)$_2$](BF$_4$)	1.89		39.8	31.2	8
H[CoDm$_3$(SnCl$_3$)$_2$]·2C$_6$H$_6$	1.90	2.18	40.2	42.3	9
(NBu$_4$)[CoNx$_3$(SnBr$_3$)$_2$]	1.89	2.20	40.7	39.9	10
(NBu$_4$)[CoNx$_3$(SnCl$_3$)$_2$] (A)	1.91	2.24	40.5	41.0	this work
(NBu$_4$)[CoDm$_3$(SnBr$_3$)$_2$]·H$_2$O (B)	1.89	2.18	41.0	45.1	this work
[FeNx$_3$(SnCl$_3$)$_2$]$^{2-}$ (C)	1.92	2.23	39.5	37.5	7

both kinds of rings are in fact substantially flattened). Nevertheless, the bite angles α in the complex (A) and (B) are very close one to another (average values are 40.5 and 41.0°, respectively; they ca 39.5° in the iron complex and in the other complexes of cobalt(III), Table 8). The cyclohexane rings of the dioximate ligands in complex anion (A) have an intermediate conformation with both carbon β-atoms displaced from the mid-plane of the remaining atoms in opposite directions; the atoms C(12), C(32) and C(52) deviate from the corresponding planes by ca 0.3Å, and atoms C(22), C(42) and C(62) by ca 0.5Å.

The coordination polyhedra of tin atoms are slightly distorted octahedra as in other complexes. Distortions manifest themselves mainly by an increase of Hal-Sn-Hal angles (95.2–96.5(2)° in (A) and 94.2–97.7(2)° in (B)), whereas O-Sn-O angle are decreased (to 87.4–88.0(4)° in (A) and to 84.7–89.8(8)° in (B)). Average Sn-Cl and Sn-O bond lengths in (A) (2.379 and 2.112Å, respectively) are close to those found in other tin-containing complexes. The average Sn-Br and Sn-O distances in (B) are 2.539 and 2.188Å, respectively. The Co(III) ion does not deviate much from the Sn-Sn axis in both complexes (the Sn...Co...Sn angle is 179.7° in (A) and 179.3° in (B)). Non-bonded Co...Sn distances are 3.609 and 3.621Å in (A) and 3.592 and 3.599Å in (B).

Tetrabutylammonium cations have different conformations in (A) and (B). In (A), all four *n*-butyl residues have a *trans-trans* conformation, but in the (B) two of these residues have a *trans-gauche* conformation (torsion angles around C(2a)-C(3a) and C(2c)-C(3c) are close to 60°. The water molecule in the structure (B) does not have any obvious contacts with surrounding atoms, such as might suggest hydrogen bonding.

The geometry of the coordination polyhedron in all solved tin-containing iron(II) and cobalt(III) tris-dioximate structures is close to octahedral and practically independent of the nature of dioxime residues and tin-containing caps. Clearly, the larger size of tin-containing fragments is an important cause.

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SUPPLEMENTARY MATERIAL

A summary of data collection and refinement parameters, tables of bond lengths and angles, hydrogen atom parameters, anisotropic temperature factors and lists of observed and calculated structure factors are available from Prof. Y.Z. Voloshin on request.

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