Solution Structures and Isomer Distributions of Bis(β-diketonato) Complexes of Titanium(IV) and Cobalt(III)

Peter Comba,* Holger Jakob, Bernhard Nuber, and Bernhard K. Keppler

Anorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270,
69120 Heidelberg, Germany

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Force field parameters for β-diketonates coordinated to titanium(IV) and cobalt(III) were developed based on published structural data and the cobalt(III) X-ray structures of *cis*-$[Co(acac)_2(NH_3)_2]I \cdot H_2O$ (acac = 2,4-pentanedionate) and $[Co(acac)_2(en)]ClO_4$ (en = ethane-1,2-diamine). *cis*-$[Co(acac)_2(NH_3)_2]I \cdot H_2O$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.714(3)$ Å, $b = 9.885(3)$ Å, $c = 10.449(4)$ Å, $\alpha = 69.12(3)°$, $\beta = 67.83(3)°$, $\gamma = 65.48(2)°$, and $Z = 2$, and the structure was refined to $R_w = 4.2\%$. $[Co(acac)_2(en)]ClO_4$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.756(7)$ Å, $b = 7.389(2)$ Å, $c = 19.76(1)$ Å, $\beta = 102.55(4)°$, and $Z = 4$, and the structure was refined to $R_w = 4.2\%$. There is good agreement between calculated and experimental structural data, including an appreciable trans effect in the titanium(IV) structures. A full conformational analysis of various cobalt(III) and titanium(IV) systems leads to calculated isomer distributions that are in satisfactory agreement with the experimental data derived from ^1H-NMR spectroscopy.

Introduction

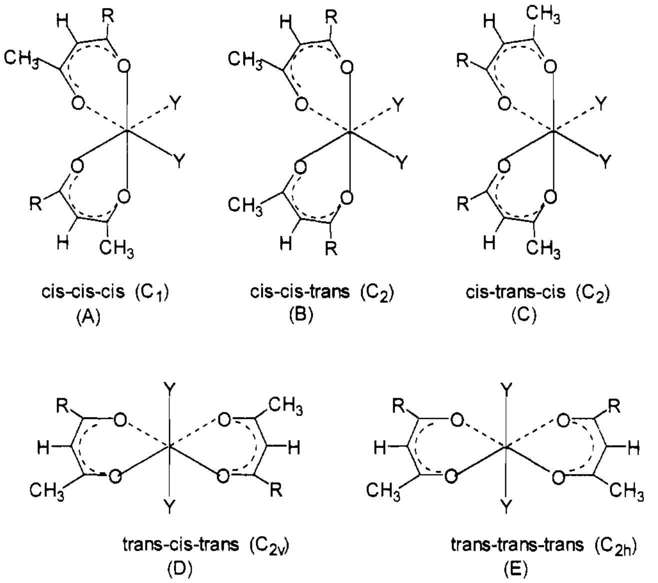
Budotitane (INN; $[Ti(bzac)_2(OEt)_2]$; bzac = 1-phenylbutane-1,3-dionate, OEt = ethoxide) is a promising drug which is under clinical tests for cancer chemotherapy.[1] There are no crystal structural data available for budotitane or analogues with other monodentate ligands. This is probably due to the fact that no isomerically pure fractions may be isolated from the isomeric mixture that exists in solution. For $[M(RR'ac)_2Y_2]$ (RR'ac = 1,3-disubstituted β-diketonate) there are three *cis*- and two *trans* isomers (see Chart 1).

Solution NMR data and the crystal structure of $[Ti(bbac)_2(OEt)_2]$ (bbac = 1,3-diphenylpropane-1,3-dionate) indicate that in solution an equilibrium mixture of the three *cis* isomers is obtained.[1] It was argued on a qualitative basis that the *cis*-configurations are more strained but preferred by electronic effects ($p\pi$-$d\pi$ (t_{2g}) bonding of the β-diketonato ligands).[1,2]

Molecular mechanics (MM) has been widely used for the computation of molecular structures and isomer distributions.[3,4] Clearly, the MM model cannot account for effects that have a specific electronic origin, such as selective stabilization of certain isomers via π-bonding. However, it was hoped to get some qualitative information on a putative stabilization of the *cis*-configuration via electronic effects by a quantitative evaluation of steric effects of all isomers of various bis(β-diketonato) complexes and a comparison of the distributions based on the strain energies with experimental data of titanium(IV) (empty t_{2g} set) and cobalt(III) (filled t_{2g} set) β-diketonato complexes. Also, MM allows a quantitative analysis of the isomer distribution and a determination of the concurrent molecular structures within the set of the experimentally observed *cis* isomers.

We have developed a force field for β-diketonato complexes of titanium(IV) and cobalt(III), based on a published force field for transition metal complexes,[5] and refined and tested it with published structural data and two new crystal structures which are also presented. MM calculations have then been used to determine isomer ratios and solution structures of a series of bis(β-diketonato)titanium(IV) and -cobalt(III) complexes.

Chart 1



cis-cis-cis (C_1) (A)

cis-cis-trans (C_2) (B)

cis-trans-cis (C_2) (C)

trans-cis-trans (C_{2v}) (D)

trans-trans-trans (C_{2h}) (E)

Experimental Section

Caution! Perchlorate salts of metal complexes are potentially explosive and should be handled with care.

Materials. All commercially available reagents were of analytical grade, and solvents were dried with standard methods, when necessary. $K[Co(CO_3)_2(en)] \cdot H_2O$ (en = ethane-1,2-diamine),[6] *trans*-$Na[Co(acac)_2(NO_2)_2]$ (acac = 2,4-pentanedionate),[7,8] *trans*-$[Co(acac)_2(NH_3)_2]I$,[9] *cis*-$[Co(acac)_2(NH_3)_2]I$,[9] and $[Co(acac)_2(en)]ClO_4$[9] were obtained as described in the literature. X-ray quality single crystals of *cis*-$[Co(acac)_2(NH_3)_2]I \cdot H_2O$ and $[Co(acac)_2(en)]ClO_4$ were isolated from saturated aqueous solutions of the purified products.

Bis(1-phenylbutane-1,3-dionato)(diamino-1,2-ethane)cobalt(III) Perchlorate ($[Co(bzac)_2(en)]ClO_4$, Isomer Mixture). An aqueous solution (50 mL) of benzoylacetone (1-phenyl-1,3-butanedione; 3.89 g, 24 mmol)

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Table 1. ^{1}H- and ^{13}C-NMR Data for $[M(RR'ac)_2X_2]^{n+}$ ^{a}

compound	δ(^{1}H)	δ(^{13}C)
$[Ti(bzac)_2(OET)_2]$	2.25 CH_3 cis–cis–cis	
	2.02 CH_3 cis–cis–cis	
	2.06 CH_3 cis–cis–trans	
	2.26 CH_3 cis–trans–cis	
$[Co(acac)_2(NH_3)_2]^+$	5.62 C–H	
	2.12 CH_3	
	2.10 CH_3	
$[Co(acac)_2(en)]^+$	5.61 C–H	
	2.68 CH_2	
	2.22 CH_3	
	2.09 CH_3	
$[Co(bzac)_2(en)]^+$	8.09–7.35 arom H	
	6.43 C–H	26.67 CH_3
	6.41 C–H	26.72 CH_3
	6.36 C–H	45.25 CH_2
	6.34 C–H	95.42 C–H
	3.39–3.27 CH_2	95.76 C–H
	2.39 CH_3	127.61–137.4 arom C
	2.37 CH_3	184–193.8 carbonyl C
	2.31 CH_3	
	2.27 CH_3	

Chart 2

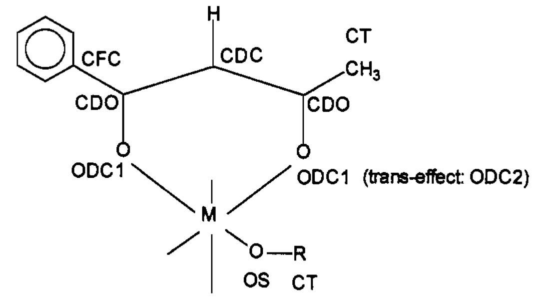

Table 2. Force Field Parameters Used for β-Diketonate Complexes

bonding interaction	force const, mdyn Å^{-1}	equilibrium value, Å
Ti4–ODC1	1.500	1.980
Ti4–ODC2	1.500	2.040
Ti4–OS	0.500	1.722
Co3–ODC1	1.400	1.880
CDC1,2–CDC	7.400	1.275
CDO–CDC	7.400	1.377
CDC–H	5.000	0.970
CDO–CT	5.000	1.500
CDO–CFC	5.000	1.470
CT–OS	0.500	1.340

valence angle interaction	force const, mdyn rad^{-1}	equilibrium value, rad
CT–CDO–ODC1,2	0.350	2.094
CFC–CDO–ODC1,2	0.350	2.094
CT–CDO–CDC	0.350	2.094
CFC–CDO–CDC	0.350	2.094
CDO–CFC–CA	0.350	2.094
CDO–CT–H	0.350	1.909
CDC–CDO–ODC1,2	0.970	2.094
CDO–CDC–H	0.970	2.094
CDO–CDC–CDO	0.970	2.094
OS–CT–CT	0.450	1.911
OS–CT–H	0.360	1.909
Ti4–ODC1,2–CDO	0.600	2.094
Ti4–OS–CT	0.050	1.915
Co3–ODC1,2–CDO	0.600	2.094
L–M–L (M=Ti4,Co3)	0.000	

torsion angle interaction	force const, mdyn rad^{-1}	equilibrium multiplicity	offset, rad
–CDO–CDO–	0.030	2	1.571
–CDC–CDC–	0.030	2	1.571
–CDO–CFC–	0.030	2	1.571
–CDO–CT–	0.005	6	0.524
–CT–OS–	0.008	3	0.000

out-of-plane interaction	force const, mdyn Å^{-1}
CDO–CDC–ODC1,2–CFC	0.500
CDO–CDC–ODC1,2–CT	0.500
CDC–CDO–CDO–H	0.500

Table 3. Crystal Data

	$[Co(acac)_2en]ClO_4$	$[Co(acac)_2(NH_3)_2]I\cdot H_2O$
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	12.756(7)	9.714
b, Å	7.389(2)	9.885
c, Å	19.76(1)	10.449
α, deg	90.0	69.12(3)
β, deg	102.55(4)	67.83(3)
γ, deg	90.0	65.48(2)
V, Å^3	1817.9	821.3
ρ, g cm^{-3}	1.52	1.98
formula	$C_{12}H_{22}N_2CoO_8Cl$	$C_{10}H_{22}N_2CoO_5I$
fw	1666.79	980.35
Z	4	2
μ, mm^{-1}	1.13	2.92
temp, K	293	293
λ, Å	0.71073	0.71073
R; R_w^{a}	0.044; 0.042	0.048; 0.042

^{a} $R = \sum(\|F_o\| - |F_c\|)/\sum|F_o|$; $R_w = \sum\|F_o| - |F_c\|w^{1/2}/\sum|F_o|w^{1/2}$.

and KOH (1.34 g, 24 mmol) was added to a stirred aqueous solution (50 mL) of $K[Co(CO_3)_2(en)]$ (3.0 g, 12 mmol). After 2 days at ambient temperature, the pH was adjusted to 5 ($HClO_4$). After removal of $KClO_4$ that precipitated overnight, the solution was sorbed onto a column of SP Sephadex C25 cation-exchange resin (K^+-form, 2.5 × 30 cm), washed with water and eluated as a single band with aqueous $NaClO_4$ (no isomer separation was observed with $NaClO_4$ concentrations between 0.1 and 1.0 M). H_2O and part of the $NaClO_4$ were removed by rotavaporation (40 °C) and filtration. The remaining $NaClO_4$ was removed by three successive extractions of the cobalt(III) complex with EtOH, succeeded by filtration and removal of the solvent.

Isomer distributions of $[Co(acac)_2(NH_3)_2]^+$ and $[Co(bzac)_2(en)]^+$ were determined via ^{1}H-NMR spectroscopy (see Table 1 for NMR data). Side products were removed via cation exchange chromatography (SP Sephadex C25), and the whole fractions containing the relevant complexes (isomer mixtures) and inert salt were isolated as solids via removal of the solvent at reduced pressure and dissolved in CD_3OD.

Physical Methods. ^{1}H- (200 MHz) and ^{13}C-NMR (50.32 MHz) spectra were recorded on a Bruker AS200 instrument. A Varian Cary 1E spectrophotometer was used for electronic spectroscopy. Elemental analyses were obtained from the microanalytical laboratory of the chemical institutes of the University of Heidelberg.

Molecular Mechanics Calculations. Force field calculations were performed with MOMECPC.[10] Parameters not specified in an earlier publication[5] are given in Table 2 (for nomenclature, see Chart 2).

Crystal Structure Determinations. For both structures, cell constant were determined by a least-squares fit to the setting parameters of 25 independent reflections. Data were measured on a Siemens Syntex, Nicolet R3 diffractometer within the limit $3.0 \le 2\theta \le 52.5°$ with Mo Kα radiation (λ = 0.7107 Å) and a graphite monochromator, operating in the ω-scan mode. Data reduction and Lorentz, polarization, and absorption corrections were applied with Patterson–Fourier methods. The structures were solved by direct methods and refined by full-matrix least-squares analysis, both using SHELXTL PLUS.[12] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at calculated sites (C–H = 0.97 Å). Scattering factors were taken from the literature.[13] The crystal data are given in Table 3. Non-hydrogen atomic coordinates are listed in Table 4, the atomic nomenclature is defined in Figure 1, and Table 5 gives selected bond lengths and angles. Listings of hydrogen atom coordinates, anisotropic thermal parameters, full lists

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Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)

	x	*y*	*z*	U_{eq}[a]
		$[Co(acac)_2en]ClO_4$		
Co(1)	2642(1)	1831(1)	934(1)	43(1)
O(1)	1483(2)	2770(4)	263(2)	51(1)
O(2)	2642(2)	−478(4)	527(2)	50(1)
C(1)	77(4)	2906(7)	−732(2)	75(2)
C(2)	974(3)	1885(7)	−262(2)	53(2)
C(3)	1194(4)	126(8)	−418(2)	64(2)
C(4)	2004(4)	−941(7)	−37(2)	51(2)
C(5)	2198(4)	−2830(7)	−272(3)	77(2)
O(3)	1688(2)	926(4)	1469(2)	51(1)
O(4)	2802(2)	4147(4)	1338(1)	49(1)
C(6)	746(4)	778(7)	2360(3)	74(2)
C(7)	1422(3)	1828(8)	1960(2)	50(2)
C(8)	1717(4)	3578(7)	2142(2)	53(2)
C(9)	2365(3)	4646(6)	1833(2)	44(2)
C(10)	2631(4)	6565(6)	2063(2)	63(2)
N(1)	3866(3)	978(5)	1624(2)	48(1)
N(2)	3684(3)	2631(5)	416(2)	50(1)
C(11)	4868(3)	1776(7)	1484(2)	55(2)
C(12)	4735(3)	1761(7)	703(2)	57(2)
Cl(1)	5972(1)	6757(2)	1388(1)	60(1)
O(11)	6617(3)	8086(5)	1149(2)	88(2)
O(12)	6608(3)	5302(6)	1724(2)	100(2)
O(13)	5182(3)	6126(6)	812(2)	99(2)
O(14)	5456(3)	7555(5)	1889(2)	92(2)
		$[Co(acac)_2(NH_3)_2]I\cdot H_2O$		
I(1)	982(1)	286(1)	2343(1)	62(1)
Co(1)	7417(1)	7382(1)	5119(1)	35(1)
O(1)	7517(5)	5392(5)	5217(5)	43(2)
O(2)	6491(5)	8403(5)	3583(5)	43(2)
O(3)	5347(5)	7728(5)	6353(5)	43(2)
O(4)	8467(5)	6432(5)	6570(5)	40(2)
N(1)	7326(6)	9389(6)	5135(6)	44(3)
N(2)	9502(5)	7029(6)	3766(6)	44(3)
C(1)	7384(8)	3414(7)	4546(8)	59(4)
C(2)	7164(7)	5095(7)	4301(7)	42(3)
C(3)	6627(8)	6144(8)	3166(7)	47(4)
C(4)	6300(7)	7731(8)	2848(7)	43(3)
C(5)	5697(8)	8753(8)	1588(7)	57(4)
C(6)	3321(8)	7736(9)	8494(8)	66(4)
C(7)	5042(7)	7363(7)	7705(8)	44(3)
C(8)	6147(7)	6665(8)	8483(8)	50(4)
C(9)	7771(7)	6237(7)	7897(7)	40(3)
C(10)	8842(8)	5492(8)	8876(7)	56(4)
O(5)	230(14)	1567(13)	9202(11)	116(9)

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

of bond lengths, bond angles, torsion angles, and the complete crystal data table have been deposited.

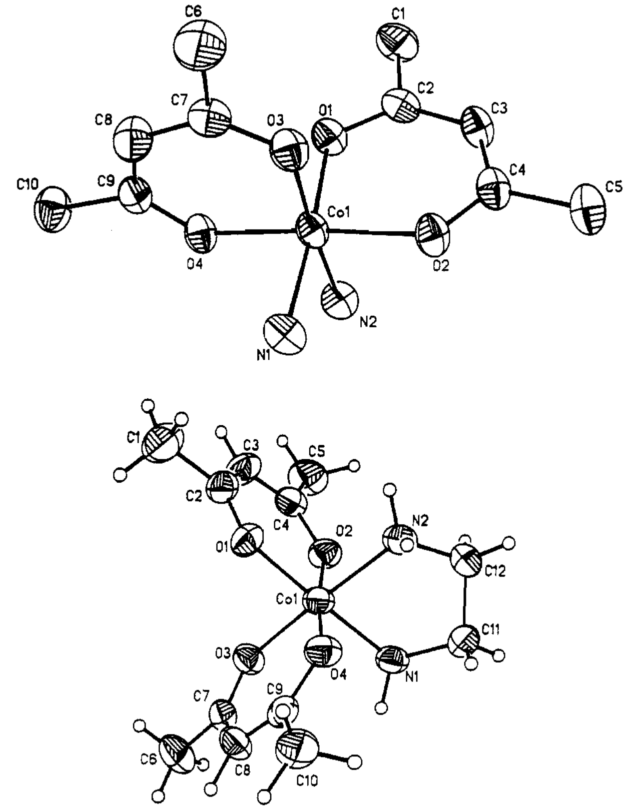

Figure 1. ORTEP[11] plots of (a) $[Co(acac)_2(NH_3)_2]I\cdot H_2O$ and (b) $[Co(acac)_2en]ClO_4$. Key: acac = 2,4-pentanedionate, $CH_3C(O)CHC(O)CH_3$; en = ethane-1,2-diamine, $H_2NCH_2CH_2NH_2$.

Table 5. Selected Bond Lengths (Å) and Angles (deg)

	$Co(acac)_2en]ClO_4$	$[Co(acac)_2(NH_3)_2]I\cdot H_2O$
Co–O(1)	1.890(3)	1.896(5)
Co–O(2)	1.887(3)	1.893(5)
Co–O(3)	1.899(3)	1.899(4)
Co–O(4)	1.880(3)	1.892(5)
Co–N(1)	1.942(3)	1.955(6)
Co–N(2)	1.937(4)	1.957(4)
O(1)–Co–O(2)	96.0(1)	96.3(2)
O(1)–Co–O(3)	91.2(1)	90.1(2)
O(2)–Co–O(3)	88.8(1)	87.4(2)
O(3)–Co–O(4)	96.2(1)	96.2(2)
N(1)–Co–N(2)	86.0(1)	92.3(2)
Co–O(1)–C(2)	124.3(3)	123.0(4)
C(2)–C(3)–C(4)	125.3(4)	125.9(9)
C(4)–O(2)–Co	123.8(3)	124.6(4)
O(1)–C(2)–C(1)	115.3(4)	114.5(6)
C(1)–C(2)–C(3)	119.8(4)	119.6(8)
C(3)–C(4)–C(5)	120.8(4)	120.6(8)
O(2)–C(4)–C(5)	113.6(4)	115.7(7)
C(4)–O(2)–Co	123.8(3)	124.6(4)

Results and Discussion

Structural Aspects. In *cis*-$[Co(acac)_2(NH_3)_2]^+$ and $[Co(acac)_2(en)]^+$, two pentane-2,4-dionato (acac) ligands each are coordinated to cobalt(III), with two amines coordinated in *cis*-disposition completing the distorted octahedral coordination sphere. The geometries of the acac chelates are very similar in both cases with Co–O ca. 1.89 Å and a bite angle of 96° and are comparable to those of other cobalt(III) complexes with acac chelates.[14,15] The coordination geometries of the cobalt(III)–diamine fragments are in terms of the *gauche* conformation of the Co–en chelate and the N–Co–N bite angles (92.3, 86.0)° for the diammine and en complexes, respectively) as expected from comparable structures.[16,17] The 92.3° angle in the diammonia complex—well reproduced by the force field calculations (93.6°)—indicates that the repulsive forces between the ammonia ligands are rather strong. The two unidentate ligands are twisted out of the plane perpendicular to the *trans* disposed oxygen atoms. The tetrahedral twist angle θ in this plane, defined as the angle between the two planes N(1)–Co–N(2) and O(1)–Co–O(3), of 7.5° is well reproduced by the molecular mechanics calculations (8.5°). There is a similar but smaller distortion in the en complex (θ_{exp} = 7°, θ_{calc} = 8°). The Co–N distances of the en complex are with $Co–N_{av}$ = 1.94 Å a little shorter than those for cobalt(III) hexaamines (corresponding values for $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ are ca. 1.96 Å each[16–18]). The somewhat longer Co–N distance in the diammine complex (1.96 Å) is likely to be a result of the above mentioned repulsion. Delocalization of negative charge of the acac ligands to the cobalt center and/or π-donation

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are expected to reduce the Co–N bond strength.[5] However, the small extent of repulsion excerted by the acac ligands obviously leads to the short Co–N bond distances observed here. Another possible explanation for the Co–N bond length differences in the two complexes involves an enhanced basicity induced by alkyl-substituted amines.[19] Usually, increased σ-donor strengths are counterbalanced by enhanced repulsion. In the present case, the comparably small repulsion due to the acac ligands (see above) leads to the relatively short Co–N bonds observed in the case of $[Co(acac)_2en]^+$.

In contrast to the cobalt(III) complexes the M–O distances in β-diketonato chelates of titanium(IV) are usually not symmetrical.[1,20,21] π-Donation of acac and substituted analogues to the metal center has been proposed as an explanation of selective *cis*-coordination geometry in $[Ti(RR'ac)_2X_2]^{n+}$. This hypothesis is based on the assumptions that (i) the *trans*-isomers are less strained (see relevant discussion ahead) and that (ii) the β-diketonates rather than the X groups (usually oxo, alkoxo, or halogeno ligands) are bonded more efficiently, i.e. they are the *trans*-directing group[1,2]—the more general question whether the *trans* influence shall be discussed as a π-bonding or as a σ-effect is not relevant here.[22,23] From a structural point of view there are two important observations to note: (i) The supposedly symmetrical $[Ti(acac)_3]^+$ cation[21] has Ti–O bonds scattered between 1.925 and 1.956 Å, suggesting that environmental effects (crystal lattice) are rather important, and *cis*-$[Ti(RR'ac)_2(OR)_2]^{n+}$ complexes[1,20] display relatively short Ti–OR bonds (ca. 1.8 Å) and longer Ti–O(RR'ac) bonds with Ti–O distances *trans* to OR distinctly longer than the bonds *cis* to OR (2.06 vs 2.00 Å).[1,20] Concurrently, the bonding within the acac backbone is slightly asymmetrical, suggesting some loss of electron delocalization.

Force Fields. A meaningful parametrization of titanium(IV) β-diketonates was rather difficult since neither titanium(IV) nor acac-type ligands have been parametrized so far in our MM model, since the *trans* influence needs an increased parameter set and since only few relevant structures are available. We therefore have first parameterized β-diketonates coordinated to cobalt(III), for which a well established force field is available, and then developed the corresponding titanium(IV) force field. The cobalt(III) β-diketonato force field was fitted to three X-ray structures. For Co–N the parameters for mixed amine-carboxylates[5] were used. There is excellent agreement between the calculated and experimental geometries (see Table 6). Parameters of the calculated structure of $[Co(bzac)_2(en)]^+$ (most stable isomer, see below) are also included in Table 6.

The titanium(IV) β-diketonato force field was developed on the basis of three experimental structures. As indicated a *trans* influence excerted by the oxo and alcoxo ligands had to be included. This was achieved via definition of different atom types for acac-type oxygen atoms *cis* or *trans* to the *trans*-directing ligands. With modern molecular modeling packages,[10] this may be done automatically. The results of the structure optimizations, presented in Table 6 (also included is the most stable isomer—see ahead—of $[Ti(bzac)_2(OEt)_2]$), are satisfactory.

Table 6. Selected Observed and Calculated Structural Parameters of Titanium(IV) and Cobalt(III) β-Diketonate Complexes[a]

compound	parameter	obsd[b]	calcd[b]
$[Co(acac)_3]^c$	Co3–ODC1	1.89	1.89
	ODC1–CDO	1.27	1.28
	CDO–CT	1.50	1.51
	CDO–CDC	1.38	1.39
	ODC1–Co3–ODC1	97	95
	Co3–ODC1–CDO	124	125
	ODC1–CDO–CDC	126	125
	CDO–CDC–CDO	125	125
$[Co(acac)_2(en)]^{+\,d}$	Co3–ODC1	1.89^e	$1.89;^e$ 1.89^f
	Co3–N	1.94	1.95; 1.95
	OCD1–Co3–OCD1	96	94; 94
	N–Co3–ODC1	177; 89	177, 90; 174, 92
$[Co(acac)_2(NH_3)_2]^{+\,d}$	Co3–ODC1	1.90^g	$1.89;^g$ 1.89^h
	Co3–N	1.96	1.95; 1.95
	ODC1–Co3–ODC1	96	94; 94
	N–Co3–ODC1	177; 89	174, 90
$[Co(bzac)_2(en)]^{+\,d}$	Co3–ODC1		1.89^i
	Co3–N		1.95
	ODC1–Co3–OCD1		94
	ODC1–Co3–N		175.90
$[Ti(acac)_3]^{+\,j}$	Ti4–ODC1	1.94	1.97
	ODC1–Ti4–ODC1	85	92
$[Ti(acac)_2O]_2^k$	$Ti4–O^{oxo}$	1.81; 1.83	1.79
	Ti–ODC1	1.98; 1.97	1.98
	Ti4–ODC2	2.04; 2.06	2.04
	$O^{oxo}–Ti4–O^{oxo}$	82; 83	89
	OCD1–Ti4–ODC2	83	90
	$Ti4–O^{oxo}–Ti4$	96	91
$[Ti(bzac)_2OEt]_2^d$	Ti4–ODC1		1.98^b
	Ti4–ODC2		2.04
	Ti4–OS		1.80
	ODC1–Ti4–ODC2		89
	OS–Ti4–OS		95
$[Ti(bbac)_2OEt]_2$	Ti4–ODC1	1.99^b	1.98^b
	Ti4–ODC2	2.06	2.04
	Ti4–OS	1.79	1.79
	ODC1–Ti4–ODC2	82	87
	OS–Ti4–OS	98	95

[a] For nomenclature see Figure 1 and Chart 2. [b] Averages; Å for distances and deg for angles. [c] X-ray.[15] [d] This work. [e] Δλ isomer. [f] Δδ isomer. [g] Λ *cis* isomer. [h] *trans*. [i] Δδ *cis–cis–cis*. [j] X-ray.[20] [k] X-ray[20] (two different crystal structures). [l] X-ray.[1] *cis–cis–cis* isomer.

Isomer Distributions. Cobalt(III). MM has been used extensively in the field of cobalt(III) complexes (mainly with amines),[3,4] and isomer distributions may generally be predicted within ca. 5%.[3] In a comparison of experimental data with strain energies three aspects have to be considered: (i) Environmental effects (solvation, ion-pairing) are not included in the calculations. (ii) Entropy effects are usually neglected with the exception of statistic effects. (iii) Cobalt(III) complexes are inert and thus thermodynamic equilibration requires special procedures. The more general points (i) and (ii) have been discussed extensively,[3] and with the necessary precaution in terms of experimental setup and not overly conservative error limits, they do not cause a particular problem. Equilibration of cobalt(III) complexes is usually achieved in presence of charcoal.[24,25] With mixed-ligand systems such as the ones described here some decomposition of the mixed-ligand complexes at the expense of corresponding homoleptic compounds (stable hexaamines in the present case) might occur. $[Co(acac)_2(NH_3)_2]^+$ was prepared in presence of charcoal,[9] and therefore the product mixture is expected to be at the thermodynamic equilibrium. However, in the case of $[Co(bzac)_2(en)]^+$ it cannot be excluded that the mixture of the three isomers obtained is the result of at least some kinetic control. All attempts to equilibrate the product mixture produced major amounts of $[Co(en)_3]^{3+}$. Also, the inherent instability of $[Co(bzac)_2(en)]^+$ resulted in product mixtures contaminated with some side products (mainly free ligand) leading to some overlapping signals and therefore preventing an unambiguous analysis of the isomer distribution. Thus, the calculated equilibrium distribution of $[Co(bzac)_2(en)]^+$, which according to numerous examples, including the ones presented in here, is expected to be correct within a 5% error limit[3] could not be tested

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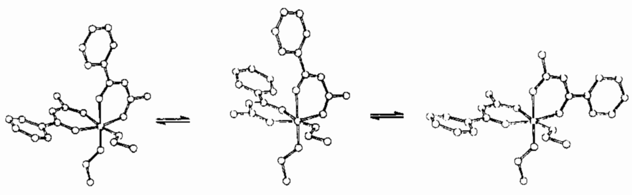

(A) cis-cis-cis (B) cis-cis-trans (C) cis-trans-cis

Figure 2. ORTEP[11] plots of the calculated structures of the three stable *cis* isomers of Budotitane.

Table 7. Observed and Calculated Isomer Distributions

compound	isomer	% calcd	% obsd
$[Co(acac)_2(NH_3)_2]^+$	*cis*	69	73
	trans	31	27
$[Co(bzac)_2(en)]^+$	A	51	52
	B	22	48
	C	26	
$[Ti(bzac)_2(OEt)_2]$	A	57	60[a]
	B	17	19
	C	26	21
	D	0	0
	E	0	0
$[Ti(bbac)_2(OEt)_2$	*cis*	100	100[a]
	trans	0	0

[a] Reference 1.

unambiguously by experiment. Calculated and experimentally determined isomer distributions are given in Table 7.

Titanium(IV). Isomerization is no problem with the labile titanium(IV) complexes studied here.[1,2,26] The quality of the predicted isomer distributions in comparison to the corresponding experimental data, also given in Table 7, indicates that the calculated ratios of the similar cobalt(III) systems are meaningful.

Of some interest is the comparison of the relative strain energies of isomers with *cis*- and *trans*-disposed β-diketonato ligands. We believe that in general strain energy differences may only be correlated with relative stabilities (ΔH) of coordination compounds with similar chromophores; i.e., stability differences due to electronic effects are not explicitly included in the molecular mechanics approach.[3] The fact that in the present examples the *trans* geometries are, in contrast to earlier, purely qualitative arguments,[1,2] sterically less favored (Table 7) does not indicate that electronic effects are not also present. However, they are not or at least not the only and most important product determining factor. The fact that steric interactions are a key feature for the relative stabilities of the β-diketonato complexes is supported by the observation that for both *low*-spin d^6 Co(III) and d^0 Ti(IV) the experimentally determined isomer abundances exhibit similar tendencies. The isomer mixtures discussed here are therefore an excellent example to demonstrate the utility of force field calculations for the estimation of "steric crowding". The fact that naively one might expect the *cis* isomers to be sterically less favored is paralleled by the observation that the strain induced in the coordination sphere of the *trans* isomers may not be attributed to any single interaction in the molecular mechanics results, and this is a rather general feature in molecular modeling.[27]

Conclusion

One of the main motivations for the present study was the need for some structural information on budotitane. In general, a well established force field allows molecular structures to be calculated via strain energy minimization.[3] The parameters presented here have been tested successfully with six structures involving β-diketonato ligands, three of them including Ti(IV). For the evaluation of solution structures it is generally an advantage to include nonstructural experimental results.[28] These might involve spectroscopic[19,28,29] or thermodynamic data[27,28] as in the present case. The generally good agreement between experimentally observed isomer abundances and the calculated values obtained with our force field indicates that the structures of budotitane presented in Table 6 and Figure 2 are accurately representing the solution geometries.

Supplementary Material Available: Listings of H atom coordinates, thermal parameters, bond distances and bond angles, and complete crystal data for $[Co(acac)_2(NH_3)_2]I\cdot H_2O$ and $[Co(acac)_2(en)](ClO_4)$ (9 pages). Ordering information is given on any current masthead page.

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