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Conformational Analysis of Coordination Compounds. VI. Force Field Calculation of Thermodynamic Properties of Tris(diamine)cobalt(III) Coordination Complexes

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

An empirical force field developed to reproduce geometries of equilibrium conformers of tris-(diamine)cobalt(III) complexes is used to derive thermodynamic functions and equilibrium distributions through statistical methods. The programme is tested on a series of alkanes prior to application to the coordination compounds.

Differences in thermodynamic properties between different conformers are well reproduced. Good agreement is also obtained for differences between configurational isomers. Calculations of properties of complexes of different ligands fail to reproduce the observed trends.

The Consistent Force Field concept (CFF)[1] was developed to account simultaneously for equilibrium geometry, vibrational spectra, thermodynamic data and other properties of a family of related compounds. A version of the CFF system was constructed at this Department;[2] so far it has been applied to tris(diamine) complexes of Co(III) and Cr(III),[3-5] to mono- and disaccharides[6-9] and to haloalkanes.[10] For coordination complexes, until now only equilibrium geometries and differences in static potential energy were considered;[3-5] the normal coordinate analysis was tested on a chloropropane;[10] and the thermodynamic programmes to be described briefly in this paper were applied to sugars.[7-9]

From the start of this project in 1969 it was our intention to calculate thermodynamic functions of both robust and labile complexes. We cannot yet, with our programme, compare molecules with different numbers and types of atoms, and we therefore confine our interest to such tris(diamine) Co(III) complexes as have been studied before with our CFF system, and for which thermodynamic data for conformers and isomers are available.

Such data have been obtained in recent years, mainly with Bjerrum's classical equilibrium methods,[11-13] and by calorimetric measurements.[14]

We shall first describe our new general programme for calculation of thermodynamic data, and assess its reliability by calculations on simple alkanes. We shall then apply it to robust Co(III) complexes and see to which extent the force field developed entirely to reproduce geometry[3,4] can predict measured differences in thermodynamic properties.

THE PROGRAMME

Method. We use the standard statistical-mechanical methods, assuming that the molecule under treatment is in thermodynamic equilibrium with its surroundings and obeys Boltzmann statistics, and that its total energy is separable and that therefore its partition function can be factorized. We are interested in differences between conformers and isomers; accordingly we do not consider electronic

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and nuclear spin degrees of freedom, but only vibrational plus external degrees of freedom. For molecules in solution, generally the case in thermodynamic measurements on coordination compounds, we quench translational and rotational motion.

The formulae we use can be found in any standard textbook on statistical thermodynamics.[15-16] Further simplifying assumptions underlie our choice of formulae: for the rotational partition function we use the high-temperature approximation and treat the molecule as a quasi-rigid body, for the vibrational we assume harmonic vibrations. These simplifications are used almost universally although they are not always stated explicitly. Their validity is investigated in an extensive series of test calculations on alkanes reported in the Appendix. Subsequent work on sugars[7-9] would also serve to justify the approximations.

It will be seen that we give no special treatment of internal rotation, "free" and "restricted". Such motion is simply an internal vibration, usually of low frequency, and is treated as such. The concept of internal rotation was introduced at a time when it was almost impossible to either measure or calculate the lowest frequencies of vibrations. This is now done as a matter of routine, and we shall see that it gives perfectly good results to treat internal rotation as any other vibration.

Implementation. The new programmes are organized as one more overlay branch of the CFF system[2] and are fully compatible with the rest of the system. In this way no extra core store is required, and the user will sense no other change than the possibility of ordering thermodynamic output by specifying the value of just two control digits per molecule. The input manual available to users gives directions on how to choose this control parameter to get data at 298.15 and 313.15 K or at 100, 200, 300 and 400 K, and to include or exclude summation over external degrees of freedom. If summation over rotations is wanted, the symmetry number of the molecule (the order of its pure rotational group) must also be specified. Output consists of energy, enthalpy, free energy, free enthalpy, entropy and heat capacity. The static potential energy is added to the zero-point vibrational energy. As the product of the principal moments of inertia are needed for summation over rotations, we also diagonalize the inertia tensor and print moments of inertia and rotational constants; this gives us the possibility of comparing with the most important results of microwave and rotational-vibrational spectroscopy.

COORDINATION COMPOUNDS

Choice of substances. We choose those five-membered chelate ring systems whose structures have previously been described with the CFF system: $(en)_3$, $(rac\text{-}bn)_3$, $(m\text{-}bn)_3$, $(ibn)_3$ and $(rac\text{-}bn)(en)_2$ complexes of cobalt(III),[4,5] where the abbreviations are: en = 1,2-ethanediamine, bn = 2,3-butanediamine, ibn = 2-methyl-1,2-propanediamine, *rac* = *racem* (= *d* or *l*, or = *R,R* or *S,S*), *m* = *meso* (= *R,S*).

As mentioned before, we do not include translational and rotational motion when evaluating statistical sums for these large molecules in solution. This approach contrasts with the practice of De-Hayes and Busch.[17] The question of how reliable calculations on isolated molecules are when compared to measurements on solutions and on condensed phases in general is partly answered by reference to the comparable work on glucose,[6,7] maltose[8] and cellobiose,[9] where calculated properties nicely reproduce results from measurements on solutions. Earlier papers of the present series[3,4] show that crystal structures are reproduced, and there is an indication[18] that most internal vibrations do not change from crystalline to dissolved state.

We shall see how well the force field developed for a different purpose[3,4] can reproduce thermodynamic differences between conformers and between isomers.

$[Co(en)_3]^{3+}$, *lel-ob equilibrium.* The problem of the equilibrium distribution of the four conformers is the classical one of conformational analysis of chelate compounds since Corey and Bailar.[19] Their simple calculation of non-bonded H---H interaction energy gave $E(ob_3) - E(lel_3) \simeq 4.7$ kJ mol^{-1}. Very little extra insight has been provided by a host of later researchers, including ourselves.[4]

We shall here consider only free enthalpy, and not energy differences. Gollogly *et al.*,[20] using a rather special way of summing over vibrations, estimated free enthalpy differences for the four conformers. De Hayes[21] calculated proper statistical sums, but included translational and rotational terms as if the molecule were in the gaseous state. These results are shown, with our values, in Table 1. All ΔG values refer to $G(lel_3)$ as zero and are cor-

Table 1. Free enthalpy differences and equilibrium distributions of conformers of $[Co(en)_3]^{3+}$. Unit for ΔG is kJ mol^{-1}.

		lel_3	lel_2ob	$lelob_2$	ob_3	lel:ob	Ref.
Calc.	ΔG	0.00	0.15	0.75	1.50		33
	distr.	0.47	0.36	0.13	0.04	0.75:0.25	
Calc.	ΔG	0.00	−0.61	−0.05	1.42		34
	distr.	0.20	0.56	0.22	0.02	0.65:0.35	
Meas.	distr. 290 K					0.75:0.25	35
Calc.	ΔG 298 K	0.00	0.52	2.80	5.80		This work
	distr.	0.45	0.36	0.15	0.04	0.74:0.26	
Meas.	distr. 298 K	0.40	0.40	0.16	0.03	0.73:0.27	36
Calc.	ΔG 313 K	0.00	0.41	2.70	5.85		This work
	distr.	0.43	0.37	0.15	0.05	0.73:0.27	
Meas.	distr. 333 K					0.74:0.26	35
Meas.	distr. 366 K					0.79:0.21	35
Meas.	distr. 373 K	0.35	0.41	0.20	0.04	0.69:0.31	36
Calc.	ΔG 400 K	0.00	−0.20	2.13	6.13		This work
	distr.	0.36	0.39	0.19	0.06	0.69:0.31	

rected with the statistical weights which are 1, 3, 3 and 1 for the four conformers lel_3, lel_2ob, $lelob_2$ and ob_3.

Comparison can be made with equilibrium distributions derived from NMR measurements and chromatographic separations. Sudmeyer *et al.*[22] measured the 251 MHz ^1H NMR spectrum of $[Co(en)_3]^{3+}$ in D_2O using decoupling of ^{59}Co. Under some simplifying assumptions they derived from spin-coupling parameters, through the Karplus equation, the ratio of the gross population lel:ob at three temperatures. Harnung *et al.*[23] measured, by a chromatographic method, distributions in the system $[Co(pn)_3]^{3+}$, pn = 1,2-propanediamine, and derived from these data the distribution for $[Co(en)_3]^{3+}$ at 298 and 373 K. All of these experimental data are shown in Table 1. Our calculations reproduce very closely, also concerning temperature dependence, the distributions derived from chromatographic separation.[23] The distributions derived from NMR measurements,[22] being reproduced at ordinary temperature, show a temperature dependence which is unexpected and not accounted for, and which is at variance with that found by chromatography and in our calculations.

$[Co(rac\text{-}bn)_3]^{3+}$, stereospecificity. A synthesis of the tris-complex, carried out with the resolved amine, will result in complexes having all six methyl groups equatorially disposed. The two configurations Δ and Λ will form with the same statistical probability, but the ob-lel energy difference will change the equilibrium. This energy difference,

Table 2. Free enthalpies for isomers of $[Co(bn)_3]^{3+}$ complexes. Units are kJ mol^{-1}.

System	T/K	ΔG° [12,13]	G_{calc}	$\Delta\Delta G^{\circ}$	ΔG_{calc}	Error
d,l-bn	298	−292.3	1304.0			
l-bn	298	−295.9	1307.4			
	313	−297.1	1302.6			
m-bn	298	−259.2	1349.6			
	313	−260.2	1345.0			
ibn	298	−236.2	1336.2			
	313	−239.0	1331.2			
l-bn	298			−36.0	−44.2	6.2
−*m*-bn	313			−36.9	−42.4	5.5
l-bn	298			−59.7	−28.8	−30.9
−ibn	313			−58.1	−28.6	−29.5
m-bn	298			−23.7	13.4	−37.1
−ibn	313			−21.2	−13.8	−35.0
l-bn −*d,l*-bn	298			−3.6	3.4	−7.0

small though it is, will have some effect, as we can have only homoconformational geometry. With 2*S*,3*S*-bn, for example, we shall have, keeping all methyl groups equatorial, either $\Lambda\delta\delta\delta$ (lel_3) or $\Delta\delta\delta\delta$ (ob_3). At 298 K, we calculate a free enthalpy difference of 5.81 kJ mol^{-1} in favour of the former, which gives an equilibrium ratio for the Λ on Δ configurations of 0.91:0.09. This predicted difference is large enough for detection with a chromatographic method. We have found no report of such an experiment.

$[Co(m\text{-}bn)_3]^{3+}$, fac:mer *ratio.* We calculate the free enthalpies at 298 K for all 4 *fac* and 8 *mer* conformers[4] of this system. After correcting with the statistical weights, which are 1 for the fac lel_3 and fac ob_3 conformers and 3 for the rest, we calculate the entire equilibrium distribution spectrum. Summing over all fac and all mer conformers gives a fac:mer ratio of 0.24:0.76.

Kojima *et al.*[24] separated the equilibrium mixture prepared at room temperature on a Sephadex column and identified the products spectroscopically. Graphical integration of their Fig. 2 gives a fac:mer ratio of 0.42:0.58.

For the closely related system of $[Co(cis\text{-}chxn)_3]^{3+}$, chxn = cyclohexanediamine, Toftlund and Laier[25] separated the fac and mer isomers after equilibration at 363 K; they found a ratio of 0.41:0.59. Our force field thus overestimates the population of the mer isomers by 17 %.

$[Co(ibn)_3]^{3+}$, fac:mer *ratio.* In exactly the same way, we calculated a fac:mer ratio of 0.23:0.77. Graphic integration of Fig. 3 in the paper[26] of Kojima *et al.* gives a ratio of 0.26:0.74. The coincidence could hardly be better.

$[Co(bn)_3]^{3+}$, *stability constants.* A number of stability constants for these complexes are available. Bang measured β_3 at 298 and 313 K for Co(III) with *rac*-bn,[12] *m*-bn[12] and ibn,[13] and derived ΔG°, ΔH° and ΔS°.

With our methods we can calculate free enthalpies. Their absolute values are not of interest, but the differences for series of isomers can be compared with differences in the ΔG° values derived from stability constants. Table 2 shows such comparisons.

For *rac*-bn we average over the four conformers having six equatorial methyl groups,[4] and correct the free enthalpies with a term $-RT\ln 2$ to account for both Δ and Λ configurations, which will form in equal proportion under equilibrium conditions.

For *l*-bn we use averaged data for the eq_6lel_3 and eq_6ob_3 conformers of lowest energy, as the comparison is to be made with measurements on a preparation from optically pure amine.

The calculated data for the *m*-bn and ibn systems have been statistically averaged over all 12 iso- and conformers. Under equilibrium conditions both Δ and Λ configurations will be formed, and we therefore corrected the free enthalpies with the term $-RT\ln 2$.

Table 3. Differences in complexation enthalpy at 298 K. Units are kJ mol^{-1}.

System	H_{strain} [14]	$H°_{calc}$	ΔH_{strain}	$\Delta H°_{calc}$
Δ-$[Co(l\text{-bn})_3]^{3+}$	−5.0	1398.9		
rac-$[Co(m\text{-bn})_3]^{3+}$	20.9	1442.6		
rac-$[Co(ibn)_3]^{3+}$	41.1	1428.4		
l-bn − *m*-bn			−25.9	−43.7
l-bn − ibn			−46.1	−29.5
m-bn − ibn			−20.2	14.2

The comparisons show that we have here struck the limit of realibility, not of the method and programme, but of the present force field. The calculated sequence of stability is *d,l*-bn > *l*-bn > ibn > *m*-bn against the experimentally established *l*-bn > *d,l*-bn > *m*-bn > ibn.

$[Co(l\text{-}bn)(en)_2]^{3+}$, *stability constants.* Bang[13] also reported a ΔG for Λ- and Δ-$[Co(l\text{-bn})en_2]^{3+}$, in which the methyl group preference for equatorial positions causes the l-bn ring to adopt ob and lel conformations, respectively. He found a ΔG difference of 2.06 kJ mol^{-1}; our calculated value is 2.11 kJ mol^{-1}.

Enthalpies of complexation. Enthalpy differences were measured calorimetrically at 298 K by Bagger *et al.*;[14] a more accurate method than deriving the $\Delta H°$ from equilibrium data. Essentially they measured the heat evolved during sulfide decomposition of the complex. Results are shown in Table 3, together with calculated values. H_{strain} is[14] ΔH for the process $[Co(en)_3]^{3+}$ (aq) + 3 bn (aq) → $[Co(bn)_3]^{3+}$ (aq) + 3 en (aq).

Bang[13] also produced calorimetric data for Λ- and Δ-$[Co(l\text{-bn})(en)_2]^{3+}$ where the l-bn ring has ob and lel conformations, respectively. He derived H_{strain} $(\Lambda ob' - \Delta lel') = -0.6$ kJ mol^{-1}, a rather unexpected result. Our calculated value is 2.6 kJ mol^{-1}.

The comparisons show that, as for the free enthalpies, we have reached the limit of reliability of the force field.

Conclusion. We have demonstrated that it is practicable to calculate thermodynamic properties of series of coordination complexes. The agreement with measured data is encouraging for differences between conformers. For differences between isomers, caution should be exercised. When the differences are limited to configurations at the metal atom, the calculations show neat agreement; but when we try to reproduce differences between complexes with different amines we fail.

The remedy is a refinement of the force field on structures and frequencies of vibration. This is a major task now being undertaken.

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APPENDIX: TEST OF ALKANES

Choice of substances. Thermodynamic functions of alkanes are known to a very high degree of precision, and it is evident that we should be able to reproduce them to a fair degree of approximation. The small alkanes are very flexible, and in context with our applications to complexes of 2,3-butanediamines, which contain methyl groups with different degrees of restricted rotation, they are particularly interesting.

We choose two groups of molecules: methane, ethane, propane, isobutane, neopentane and cyclohexane; and butane and pentane. In the first group each molecule exists as only one conformer, in the second as two or more. n-Butane can take two conformations, *anti* (A) and *gauche* (G and −G), the second with a twofold statistical weight. Pentane takes four conformations: AA, AG = GA = −GA = A−G, GG = −G−G and −GG = G−G, with statistical weights 1,4, 2 and 2.

Force field. We use, without changes, the force field which was employed in our earlier work on coordination complexes.[4]

Initial geometries. All thirteen individual conformers were built by the CFF programme from standard values of bond lengths, valence angles and

Table 4. Comparison of calculated and measured alkane structures.

Property	No. of exp. data	Max. dev.	Mean dev.	Ref.
C–H	9	0.036 Å	0.022 Å	27–34
C–C	7	−0.016 Å	−0.013 Å	28–34
C–C–H	6	1.5°	0.7°	28, 30–33
C–C–C	4	2.0°	1.6°	29–30, 32–34
H–C–H	3	−2.0°	−1.0°	29, 31, 34
C–C–C–C	2	−3.5°	−1.3°	32, 34

torsional angles. For all but one, the initial energies and energy gradients indicated that energy minimization would be easy. For n-pentane −GG we found a few very large elements in the gradient vector. This was due to hydrogens of different methyl groups being placed closer to each other than the distance corresponding to the maximum of the Buckingham exp-6 function used for non-bonded interactions. This difficulty was overcome by twisting the methyl groups so that no H---H distance would be shorter than that corresponding to the function maximum, which is 0.85 Å.

Energy minimization. Up to 20 steepest descent and 10 modified Newton iterations were sufficient to get to minimum for all cases but two. For pentane −GG up to 40 Newton iterations had to be used. For neopentane the resultant conformer had a rather high energy gradient. The molecule was therefore "shaken" by adding cartesian coordinate increments generated with a random number routine, whereupon minimization proceeded satisfactorily. All final energy gradient norms were below 10^{-6} kJ mol^{-1} Å^{-1}.

Comparison of geometry. In view of the shortcomings of the present force field in reproducing structures of Co complexes,[3,4] it was to be expected that the calculated alkane conformations would deviate from the measured, particularly with respect to C–H and C–C bond lengths. Table 4 bears this out, in a comparison with published r_g structures found by electron diffraction (the r_a or r_α structure for angles). Another and very fast test of a structure is a comparison of calculated and measured moments of inertia or rotational constants. These are measured with microwave spectroscopy (the r_s structure), or infrared or Raman spectroscopy (the r_0 or r_e structure). A comparison of these properties is shown in Table 5.

The comparisons show that the calculated C–H bond lengths are consistently too short; this tends to give too small moments of inertia and too large rotational constants. C–C bond lengths are calculated too long; this gives moments of inertia and rotational constants with the opposite trend. These trends are well illustrated by the rotational constants in Table 5. Comparison, where possible, is made with spectroscopically determined A_0, B_0 and C_0.

Vibrational spectra. A reasonable reproduction of vibrational frequencies must be secured if statistical summation over internal vibrations is to have any meaning. Here we shall not go into details of vibrational analysis, but simply state that all frequencies are calculated 0–100 cm^{-1} too high, the extremes being exceptions. This is a welcome though slightly unexpected result from a force field

Table 5. Calculated and measured rotational constants of alkanes.

Molecule	Property	Calc.	Meas.	Diff.	Unit	Rel. diff. %	Ref.
Methane	B_0	5.2497	5.2406(11)	−0.0091	cm^{-1}	−0.174	35
Ethane	A_0	2.631	2.671(5)	0.040	cm^{-1}	1.50	36
	B_0	0.66370	0.66313(2)	−0.00057	cm^{-1}	−0.086	37
Propane	A_s	28475.77	29207.36(5)	732.41	MHz	2.51	38
(microwave)	B_s	8488.81	8446.07(5)	−42.74	MHz	−0.51	
	C_s	6768.23	7458.98(5)	−690.75	MHz	−8.12	
Isobutane	B_0	7713.78	7789.45(1)	−75.67	MHz	−0.97	39
Cyclohexane	B_0	0.142528	0.143429(2)	0.000901	cm^{-1}	0.63	40

Table 6. Calculated and correlated[41] thermodynamic functions of alkanes. All units are J mol^{-1} K^{-1}.

Substance	Temp. K	$(H_T^\circ - H_0^\circ)/T$ Calc.	Correl.	S_T° Calc.	Correl.	$C_{p,T}^\circ$ Calc.	Correl.
Methane	200	33.28	33.22	172.5	172.6	33.47	33.51
	400	34.72	34.73	197.3	197.4	40.56	40.63
Ethane	200	35.70	36.28	209.5	201.5	40.56	42.26
	400	43.26	44.81	243.9	246.5	63.33	66.23
Propane	200	40.64	42.72	242.6	245.1	52.73	52.89
	400	55.29	58.07	289.6	294.3	89.48	93.97
Isobutane	200	46.11	49.04	258.5	261.5	67.11	70.50
	400	68.71	73.18	319.7	326.9	117.36	123.93
Neopentane	200	51.44	56.19	261.8	258.4	82.40	80.54
	400	82.80	95.06	338.3	347.5	146.75	159.98
Butane	200	51.41	56.11	270.3	276.1	66.64	76.82
	400	71.86	77.36	331.4	342.5	115.79	123.22
Pentane	200	64.35	68.87	292.9	307.5	80.34	93.55
	400	88.74	95.14	372.1	389.2	142.15	152.55
Cyclohexane	400	73.3	76.9[42]	329.1	335.5[42]	142.3	149.9[42]

selected for a different purpose. There will be a tendency to overestimate the zero-point energy and underestimate vibrational contributions to thermodynamic function. These errors are more serious than those introduced by erroneous rotational constants.

Thermodynamic functions. We have chosen to compare our calculated values with a fairly recent compilation of correlated data for alkanes.[41] In Table 6 we present excerpts from our comparisons.

For n-butane and n-pentane, the calculated values of Table 6 are average values. Data for individual conformers are weighted according to their equilibrium distributions calculated from computed G values corrected with statistical weights. S values are corrected with the entropy of mixing.

The calculated equilibrium distributions can be compared with data derived from electron diffraction. For n-butane we calculate a ratio A:G = 0.63:0.37 at 300 K; Bradford *et al.*[32] found A:G = 0.54:0.46 with an uncertainty of 0.09; the nozzle temperature was about 30 °C. The derived ΔG(G − A) is (2.08 ± 0.92) kJ mol^{-1}; our calculated value at 300 K is 1.35 kJ mol^{-1}.

Also enthalpy differences may be compared. From Raman intensity data on n-butane in the range 399 − 500 K, Verma *et al.*[43] derived ΔH(G − A) = (4.08 ± 0.18) kJ mol^{-1}; the calculated value at 400 K is 2.80 kJ mol^{-1}. Similarly, for n-pentane Harada *et al.*[44] found ΔH(AG − AA) ≃ 2.5 kJ mol^{-1} for the range 160 − 300 K; the calculated value at 200 K is 2.9 kJ mol^{-1}. (Only less than 5 % GG and virtually no −GG conformers are present.)

Conclusion. We feel justified in claiming that the force field employed here, though not ideal, is sufficiently accurate to account for the main features of the structures and energetics of smaller alkanes, and that the approximations in the statistical-mechanical procedure are valid. We thus have reason to presume that an application to coordination complexes is meaningful.

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