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Conformational Analysis of Coordination Compounds. VIII. Structures and Thermodynamic Properties of Mixed (1,2-Ethanediamine)- and (1,3-Propanediamine)cobalt(III) Complexes

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Total energies, energy contributions, free enthalpies and conformer populations were calculated for ten conformers of $[Co(1,2\text{-ethanediamine})_2(1,3\text{-propanediamine})]^{3+}$ and twenty conformers of $[Co(1,2\text{-ethanediamine})(1,3\text{-propanediamine})_2]^{3+}$. Shapes of chelate rings and of coordination octahedra CoN_6 are discussed. Supplementary results on free enthalpies and conformer populations as well as a survey of shapes of coordination octahedra are given for $[Co(1,3\text{-propanediamine})_3]^{3+}$.

Lel:ob and fac:mer ratios were calculated for $[Co(2,3\text{-diaminobutane})_3]^{3+}$ and for $[Co(2,4\text{-diaminopentane})_3]^{3+}$ and compared with the available experimental results.

An attempt at *a priori* calculation of stability constants for Co(III) complexes of 1,2-ethanediamine and 1,3-propanediamine gave results of correct sequence. log β_3 for $[Co(tn)_3]^{3+}$ is estimated to 41.

Some features of ^{13}C NMR spectra of 1,2-ethanediamine-1,3-propanediamine complexes of Co(III) are commented in the light of the results of force field calculations.

A nomenclature is proposed for description of certain heteroconformational forms of octahedral tris(bidentate) complexes containing one six-membered chelate ring in the chair conformation.

A series of papers from this Laboratory has dealt with calculations of structure, energetics and thermodynamic functions of tris(diamine)cobalt(III) coordination complexes. The following systems** were treated: $Co(en)_3$ and $Co(bn)_3$;[1,2] $Co(ibn)_3$;[2,3] $Co(tn)_3$ and $Co(ptn)_3$;[4] and $Co(en)_2(bn)$.[2,3] In this paper we bring the series to an intermediate conclusion by reporting calculations on the systems $Co(en)_x(tn)_{3-x}$, $x=1$ and 2; and by supplementing the earlier papers in the series with thermodynamic calculations on $Co(tn)_3$, estimation of the fac:mer ratio for $Co(ptn)_3$, comments on the shapes of coordination octahedra for both systems, and on ^{13}C NMR spectra of $Co(tn)_3$. In addition, the first attempt to calculate stability constants by the Consistent Force Field (CFF) is reported.

NOMENCLATURE

We use essentially the same nomenclature as in our previous papers. For explanation see papers III[4] and IV.[1] A slight modification is introduced to describe structures with three conformationally or constitutionally different chelate rings one of which is a chair-tn. In such structures a six-membered tn ring can adopt one of two possible distinct chair orientations depicted in Fig. 1f and 1g of paper I,[5] which are distinguished by the sense of fold around the N---N line, the extent of which is determined by the dihedral angle D_1 defined in Paper III.[4] Carbons and most hydrogens of the chair can lie either on one or on the other side of the NMN plane, making the chair effectively proximal (p) to one of the remaining two rings, which is one the same side of the NMN plane, and distal (d) from the other, which is on the opposite side on the NMN plane, or *vice versa*.

If the two non-chair rings are of the same constitution, symbols p and d are used in conjunction with

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** *Abbreviations.* en = 1,2-ethanediamine; bn = *meso*- and racemic-2,3-butanediamine; ibn = 2-methyl-1,2-propanediamine; tn = 1,3-propanediamine; ptn = 2,4-pentanediamine. Charges of complex ions are omitted throughout the paper for clarity.

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the conformational labels. For example $M(tn)_3$ conformers which were named $trans_{(chair,lel)}$-chair lel ob and $cis_{(chair,lel)}$-chair lel ob in papers I[5] and III,[4] are now chair(p,ob) lel ob ≡ chair(d,lel) lel ob and chair(p,lel) lel ob ≡ chair(d,ob) lel ob, respectively, and conformers Nos. 7 and 8 of $M(en)_2(tn)$ (see Table 1) are lel ob chair(p,ob) ≡ lel ob chair(d,lel) and lel ob chair(p,lel) ≡ lel ob chair(d,ob), respectively.

If the two non-chair rings bear the same conformational label but differ in constitution, symbols p and d are used in conjunction with constitutional notation. Examples are $M(en)(tn)_2$ conformers having one chair-tn (Nos. 11 – 18 in Table 2).

As shown by the above examples, the p-d nomenclature can be applied to different situations in a simple and straightforward way, indicating clearly the mutual disposition among the chelate rings.

CALCULATIONS

The programme. An updated version of the CFF system as described earlier[6] was used.

Table 1. Conformers of $Co(en)_2(tn)$ and their energies, free enthalpies and populations.

No.	Conformer	Stat. wt.	E_b	E_θ	E_φ	E_{nb}	E_T	ΔE	G	ΔG	n
1	lel_2chair	1	2.68	17.42	12.75	−17.77	19.070	0.000	976.925	0.000	0.518
2.	lel_2lel	1	2.67	13.38	20.96	−13.32	23.690	4.620	980.561	3.636	0.120
3	lel_2ob	1	3.29	17.04	22.39	−8.72	34.002	14.932	990.050	13.125	0.003
4	ob_2chair	1	3.17	17.36	14.16	−10.70	24.004	4.934	982.454	5.529	0.056
5	ob_2lel	1	2.72	16.24	26.41	−10.33	35.036	15.966	992.801	15.876	0.001
6	ob_2ob	1	3.21	16.63	23.45	−9.32	33.964	14.894	990.245	13.320	0.002
7	lelobchair (p, ob)	1	2.88	17.84	13.71	−12.51	21.922	2.852	980.227	3.302	0.137
8	lelobchair (p,lel)	1	3.03	17.25	13.42	−11.42	22.282	3.212	980.337	3.412	0.131
9	leloblel	2	2.90	14.99	22.95	−10.60	30.255	11.185	984.303	7.378	0.026
10	lelobob	2	2.96	16.40	24.45	−9.85	33.970	14.900	987.888	10.963	0.006

Table 2. Conformers of $Co(en)(tn)_2$ and their energies, free enthalpies and populations.

No.	Conformer	Stat. wt.	E_b	E_θ	E_φ	E_{nb}	E_T	ΔE	G	ΔG	n
1	lel$chair_2$ *syn*	1	5.18	29.13	10.51	−7.81	36.999	1.351	1070.582	1.859	0.168
2	ob$chair_2$ *syn*	1	5.28	29.03	11.29	−7.22	38.367	2.719	1071.691	2.968	0.108
3.	lel$chair_2$ *anti*	1	6.03	29.64	7.03	−1.46	41.251	5.603	1074.507	5.784	0.035
4	ob$chair_2$ *anti*	1	6.76	29.97	9.37	−0.36	45.742	10.094	1076.584	7.861	0.015
5	lel$chair_2$ (C_1)	1	5.04	27.07	11.25	−7.70	35.648	0.000	1068.723	0.000	0.356
6	ob$chair_2$ (C_1)	1	5.27	28.22	11.22	−6.34	38.377	2.729	1071.424	2.701	0.120
7	$lellel_2$	1	4.44	17.10	26.15	−7.61	40.072	4.424	1073.161	4.438	0.059
8	$oblel_2$	1	5.32	22.11	27.18	−2.19	52.423	16.775	1083.167	14.444	0.001
9	$lelob_2$	1	5.73	21.49	28.58	−0.21	55.596	19,948	1088.748	20.025	0.000
10	$obob_2$	1	5.86	22.10	27.84	−0.12	55.683	20.035	1088.192	19.469	0.000
11	lelchair(p,en)lel	1	4.33	26.89	21.81	−7.88	45.148	9.500	1077.614	8.891	0.010
12	obchair(p,en)lel	1	4.42	28.04	21.36	−7.17	46.648	11.000	1079.639	10.916	0.004
13	lelchair(p,tn)lel	1	4.63	23.79	17.54	−6.73	39.230	3.582	1071.820	3.097	0.102
14	obchair(p,tn)lel	1	4.31	25.47	22.14	−6.53	45.269	9.621	1078.555	9.832	0.007
15	lelchair(p,en)ob	1	5.90	27.86	17.57	0.14	49.086	13.438	1082.716	13.993	0.001
16	obchair(p,en)ob	1	4.72	22.06	22.06	−5.82	48.823	13.175	1082.257	13.534	0.002
17	lelchair(p,tn)ob	1	5.03	24.76	19.63	−5.27	44.157	8.509	1078.163	9.440	0.008
18	obchair(p,tn)ob	1	5.81	25.64	18.97	−2.75	47.675	12.027	1080.573	11.850	0.003
19	lellelob	2	4.68	21.23	30.06	−2.60	53.375	17.727	1083.029	14.306	0.001
20	oblelob	2	4.73	22.98	31.10	−2.77	56.046	20.398	1087.394	18.671	0.000

Force field. The same functions and parameter values as in papers IV – VI [1–3] were used. They are given in paper IV.[1] The consequences of the very slight change from the force field used in paper III[4] will be discussed.

Choice of molecules. The systems $Co(en)_2(tn)$ and $Co(en)(tn)_2$ were selected for minimization and subsequent calculations. They have, respectively, ten and twenty distinct conformers for each absolute configuration; their shorthand names are given in Tables 1 and 2.

Thermodynamic functions were not calculated in the previous work on $Co(tn)_3$.[4] It is done here after renewed minimization in the present force field. The sixteen conformers are given in Table 3.

Initial structures. The $Co(en)_2(tn)$ and $Co(en)(tn)_2$ conformations were constructed from the various ring conformations found previously.[1,4] For $Co(tn)_3$ the resultant conformers of the previous work[4] were used.

Minimization. 20 steepest-descent iterations followed by 10 – 20 modified Newton steps sufficed in most cases to produce neat minima, with final gradient norms below 10^{-6} kJ mol^{-1} Å^{-1}.

Thermodynamics. Averaging over all internal degrees of freedom was carried out at 300 K. External motion was quenched. The methods and subroutines were described shortly in a former paper,[2] and the formulae were given in a review paper.[7]

RESULTS

Energy contributions, total energy, free enthalpy corrected with statistical weight, and conformer population from Boltzmann distribution are shown in Tables 1 – 3. Global minima are shown in the Fig. 1.

$Co(en)_2(tn)$ Series

From the calculated ΔG values (see Table 1) it is clear that the overall order of stability of the ten $Co(en)_2(tn)$ conformers is mainly influenced by the conformation of the 6-membered tn ring, chair being the most, and ob the least favourable. With one exception the general rule lel < ob holds for the five-membered en rings. Thus one conformer, lel$_2$chair, accounts for about half of the total. This is the conformation found in the crystal structure[8] of $[Co(en)_2(tn)]Br_3$. The two lelobchair conformers populate more than a quarter of the total. Incident-

Table 3. Conformers of $Co(tn)_3$ and $Co(meso\text{-}ptn)_3$, their energies, free enthalpies and populations.

No.	Conformer	Stat. wt.	E_b	E_θ	E_φ	E_{nb}	E_T	ΔE	G	ΔG	n
1	(C_3)chair$_3$	1	6.18	40.59	12.08	−8.60	50.250	0.000	1159.714	0.000	0.572
2	lel$_3$	1	6.27	18.90	32.91	−2.20	55.877	5.637	1165.961	6.247	0.046
3	lel$_2$chair	3	7.03	28.81	23.24	0.73	59.808	9.558	1166.796	7.082	0.033
4	(C_1)chair$_3$	3	7.97	43.03	11.85	−2.61	60.238	9.988	1164.693	4.979	0.077
5	*syn*-chair$_2$lel	6	8.31	36.49	15.23	2.02	62.043	11.793	1167.045	7.331	0.030
6	(C_1)-chair$_2$lel	12	8.24	36.89	13.57	3.74	62.434	12.184	1163.117	3.403	0.145
7	(C_1)-chair$_2$ob	12	6.33	39.68	21.03	−4.55	62.496	12.246	1164.599	4.885	0.080
8	*anti*-chair$_2$lel	6	7.69	39.99	12.73	3.52	63.920	13.670	1169.893	10.179	0.009
9	chair(p,ob)lelob	3	6.60	34.08	26.65	−0.33	66.996	16.746	1174.014	14.300	0.002
10	*anti*-chair$_2$ob	6	9.44	36.88	15.43	5.64	67.388	17.138	1172.042	12.328	0.004
11	ob$_2$chair	3	7.10	33.89	26.89	1.02	68.895	18.645	1176.113	16.399	0.001
12	*syn*-chair$_2$ob	6	9.56	39.37	14.83	7.86	71.604	21.354	1174.114	14.400	0.002
13	lel$_2$ob	3	6.03	28.37	37.06	1.99	73.449	23.199	1180.004	20.290	0.000
14	chair(p,lel)lelob	3	8.83	34.36	23.57	9.19	75.945	25.695	1182.198	22.484	0.000
15	ob$_3$	1	9.45	25.15	32.60	9.01	76.209	25.959	1186.247	26.533	0.000
16	ob$_2$lel	3	6.55	32.60	37.23	3.16	79.536	29.286	1187.101	27.387	0.000
$Co(meso\text{-}ptn)_3$ conformers											
1	(C_3)-chair$_3$ (fac)	1	7.09	41.53	11.72	−20.78	39.56	0.00	1575.619	0.000	0.918
2	(C_1)-chair$_3$ (mer)	3	9.06	43.05	11.95	−13.64	50.42	10.86	1581.654	6.035	0.082

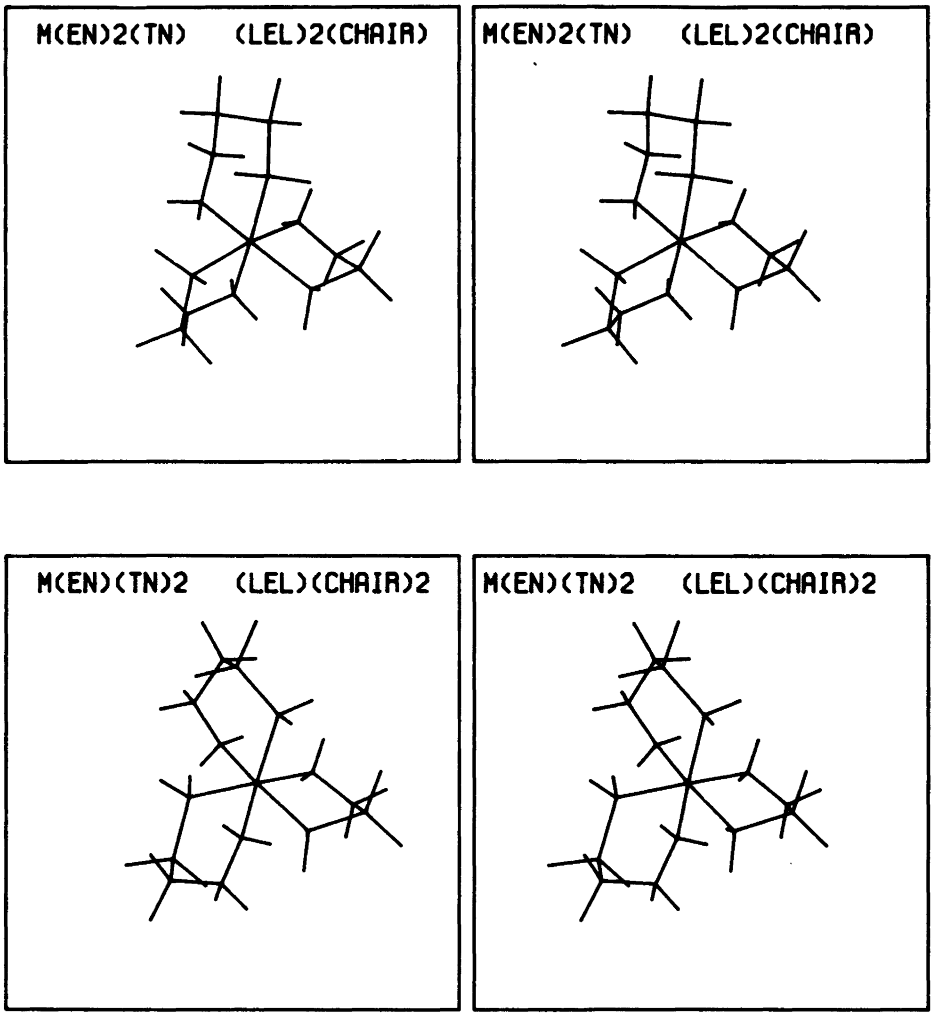

Fig. 1. Stereo drawings of (upper) Λ-[Co(en)$_2$(tn)] $\delta\delta$ chair (Conformer No. 1) and (lower) Λ-[Co(en)(tn)$_2$] δ(C$_1$)-chair$_2$ (Conformer No. 5). Global minima and the most populated conformers of the two systems are shown.

ally, one of them, the (p,ob) conformer, which is the second most populated one, is found in the crystal structure[9] of [Cr(en)$_2$(tn)]Br$_3$ · H_2O.

Close inspection of the results of energy minimization of the ten M(en)$_2$(tn) conformers disclosed that the equilibrium geometry of one of the conformers, the ob$_2$lel, was markedly unsymmetrical although the highest possible symmetry for this structure is C_2. Other similar structures of M(en)$_2$(tn) (lel$_2$lel, lel$_2$ob, and ob$_2$ob) acquired exact C_2 symmetry at equilibrium. This is the first example of the disappearance of symmetry in all our work on transition metal complexes.*

We have, therefore reinvestigated ob$_2$lel

*We have so far[1,2,4] investigated 110 different structures: 4 M(en)$_3$,[1] 16 M(tn)$_3$,[4] 10 M(ptn)$_3$,[4] 32 M(bn)$_3$,[1] 12 M(ibn)$_3$,[2] 6 M(bn)(en)$_2$,[2] together with 10 M(en)$_2$(tn) and 20 M(en)(tn)$_2$ presented in this paper. More than half of them possessed non-trivial elements of symmetry (16 of the structures belonging to D_3 point group, 9 to C_3 and 39 to C_2) *which were conserved or, more often, developed during minimizations. In other words, in all cases energy minimization led to equilibrium structures with highest possible symmetry.*

$M(en)_2(tn)$ by performing minimization from a number of different starting conformations some of which were obtained, for examply, by random displacements of the original cartesians up to the limits of the geometrical characteristics of ob_2lel. *All these attempts resulted in attainment of the same unsymmetrical equilibrium structure* characterized by the 3N-6 positive and 6 zero eigenvalues of the Hessian matrix (confirming its true minimum nature). Being aware of Ermer's cautionary remarks,[10] as a final effort we have constructed a ob_2lel $Co(en)_2(tn)$ structure with C_2 symmetry exact within the machine precision. Our usual minimization procedure (steepest descent plus modified Newton iterations) on this conformation gave the following results. Steepest-descent minimization conserved C_2 symmetry. When it practically cased to move, the ob_2lel $Co(en)_2(tn)$ conformation of C_2 symmetry thus obtained was 3.25 kJ/mol above the unsymmetrical minimum on the energy scale. The modified Newton procedure converged markedly slower than usual until the C_2 symmetry disappeared. Then it led rapidly to the unsymmetrical minimum. The Hessian matrix did remain positive definite throughout the modified Newton procedure. Our modified Newton algorithm always proceeds to a minimum irrespective of symmetry. In actual fact, this was also found during the development of a completely different potential energy function.[11]

We think that the unsymmetrical conformation is an artifact of our present force field. Fortunately, its free enthalpy is very high so that it hardly contributes to the equilibrium. Therefore we have given it the statistical weight 1 in Table 1 rather than the correct value 2. The difference could barely be noted in the last column of Table 1.

$Co(en)(tn)_2$ Series

The pattern of distribution of $Co(en)(tn)_2$ conformers on the ΔG scale (see Table 2) is much less obvious than that of $Co(en)_2(tn)$ conformers.

The most populated conformer is one of the lel $chair_2$, with 36 %. This conformation is actually found in the crystal structure[9] of $[Cr(en)(tn)_2]I_3 \cdot H_2O$. Altogether, $chair_2$ conformers contribute with more than 80 % of the total.

An attempt to compare six subclasses of 20 $Co(en)(tn)_2$ conformers (obtained on the basis of the conformation of the $M(tn)_2$ moiety) shows the same order of stability of tn rings (chair > lel > ob) as in the case of $Co(en)_2(tn)$.

Within the subclasses, distribution is a result of a complex balance between: conformation of the en ring (with two exceptions, lel-en is more favourable than ob-en), orientation of chair rings with respect to each other (C_1- and *syn*-chairs are more favourable than *anti*-chairs), and orientation of the chair with respect to other tn or en rings in the (chair,lel) and (chair,ob) subclasses (where a chair folded towards en is less favourable than a chair folded towards lel or ob tn).

A characteristic combination of interannular nonbonded contacts corresponds to each of these situations; this is reflected in the distribution of $Co(en)(tn)_2$ conformers on the ΔG scale.

Energy Contributions

As noted in previous papers, we find that the final energy of any conformer is the result of a delicate balancing of all energy contributions. No such contribution is solely responsible for the particular stability of any conformer. For example, conformers 1, 2 and 5 of $Co(en)_2(tn)$ have almost equal E_b but vastly different populations. It seems possible to state that a low E_{nb} is a necessary, but by no means sufficient, condition for high stability in both series.

Shapes of Chelate Rings in $Co(en)_2(tn)$ and $Co(en)(tn)_2$ Series

The ring puckering descriptor (τ) is defined[1] as a dihedral angle between a line connecting ligating nitrogen atoms and a line connecting methylene carbon atoms which are directly attached to the N atoms of the ring.

For each of 40 individual en chelate rings in $Co(en)_2(tn)$ and $Co(en)(tn)_2$ τ has a value which is always within the range found[1] for the corresponding rings in $Co(en)_3$ conformations.

The puckering of 24 chairs out of 50 tn chelate rings in $Co(en)_2(tn)$ and $Co(en)(tn)_2$ is characterized by having τ within the range found in $Co(tn)_3$ conformers containing chair-tn rings (see Ref. 4 and discussion to follow) and in experimentally observed chair-tn rings (Table 7 of Ref. 4).

The remaining 26 ob and lel conformations of tn are puckered in a symmetrical and an unsymmetrical fashion and, with two exceptions, fall into two distinct groups in remarkable similarity to ob- and lel-tn rings of $Co(tn)_3$ (Ref. 4 and the following discussion).

This shows that the puckering of en and tn rings is a result of some intraannular mechanism non-specifically (if at all) influenced by neighbouring chelate rings in the same coordination sphere.

Shapes of Coordination Octahedra in Co(en)$_2$(tn) Series

Twist angle (ω).[12] All ten Co(en)$_2$(tn) conformers show $\omega=(55.0\pm3.5)^\circ$ for en rings and $\omega=(58.0\pm2.0)^\circ$ for tn rings, just as found[1] for Co(en)$_3$ and its methyl substituted isomers. This trigonal distortion of the octahedron towards a trigonal prism is what elsewhere[12] is called azimuthal contraction.

Tilt angle (θ).[1,12] The descriptor θ is close to its octahedral value. Throughout the series one of the en rings is causing slight trigonal elongation, $\theta=(54.4\pm0.5)^\circ$, and the other slight trigonal compression $\theta=(55.5\pm1.5)^\circ$. The distribution of θ calculated from the tn rings is centered around the value for the regular octahedron $(54.8\pm1)^\circ$, but without any obvious pattern.

As a general remark we may say that the use of ω, θ and ψ (pitch angle[13]) descriptors to specify the departure of [MN$_6$] from regular octahedral symmetry is not as clarifying in the case of mixed ligand complexes studied in this work as it is in the case of homoconstitutional and homoconformational tris (chelate) structures, due to very irregular defor-

Table 4. Comparison of calculated and experimental conformers of M(eb)$_2$(tn) and M(en)(tn)$_2$*.

	Calc.[a]	Exp.[b]	Calc.[c]	Exp.[d]		Calc.[e]	Exp.[f]
ϕ_1	−41.1	−37.1(6)	−41.6	−42.1(17)	ϕ_1	35.7	26.0(9)
ϕ_2	60.2	59.1(10)	57.8	63.0(24)	ϕ_2	−58.3	−41.1(17)
ϕ_3	−69.7	−73.0(12)	−66.9	−68.2(27)	ϕ_3	72.5	59.1(27)
ϕ_4	68.5	68.4(12)	70.5	62.7(25)	ϕ_4	−70.8	−64.5(31)
ϕ_5	−58.3	−50.2(10)	−63.0	−49.6(17)	ϕ_5	55.7	52.1(28)
ϕ_6	40.3	32.8(6)	43.5	34.8(14)	ϕ_6	−34.6	−31.2(16)
ϕ_7	19.4	16.5(5)	17.8	16.1(13)	ϕ_7	39.2	39.6(10)
ϕ_8	−44.2	−41.1(8)	−43.6	−40.0(20)	ϕ_8	−61.9	−57.2(15)
ϕ_9	55.0	51.4(9)	56.5	48.4(23)	ϕ_9	73.0	65.1(18)
ϕ_{10}	−36.8	−36.2(8)	−39.3	−34.6(21)	ϕ_{10}	−68.2	−61.1(18)
ϕ_{11}	10.2	10.6(5)	12.5	10.8(14)	ϕ_{11}	54.2	48.6(16)
ϕ_{12}	−18.6	−20.5(6)	17.1	21.7(13)	ϕ_{12}	−36.1	−35.1(9)
ϕ_{13}	44.0	44.8(8)	−42.9	−43.3(18)	ϕ_{13}	19.7	14.8(8)
ϕ_{14}	−55.9	−51.0(9)	56.4	49.6(22)	ϕ_{14}	−44.3	−37.6(12)
ϕ_{15}	38.1	33.5(8)	−39.8	−32.8(20)	ϕ_{15}	54.7	45.6(15)
ϕ_{16}	−11.4	−7.6(5)	13.2	5.9(14)	ϕ_{16}	−36.3	−32.9(14)
τ_1	0.52	2.46	1.48	3.71	ϕ_{17}	9.7	9.8(9)
τ_2	−27.96	−26.49	−28.72	−25.23			
τ_3	28.40	26.66	−28.64	−26.85			
ω_1	−60.01	−57.48	−59.06	−58.00			
ω_2	−56.61	−55.15	−56.32	−53.76			
ω_3	−53.88	−49.05	−53.01	−52.87			
θ_1	54.59	53.77	54.25	55.84			
θ_2	54.10	55.49	54.27	53.93			
θ_3	54.63	56.07	54.59	53.69			
ψ_1	37.29	36.51	36.33	35.85			
ψ_2	31.96	34.62	32.45	28.69			
ψ_3	33.25	35.48	33.19	30.67			

[a]Calculated for lel ob chair(p,ob) conformer (No. 7 in Table 1). [b]Calculated from the positional parameters[9] for [Cr(en)$_2$(tn)]Br$_3$·H$_2$O. [c]Calculated for lel$_2$chair conformer (No. 1 in Table 1). [d]Calculated from the positional parameters[8] for [Co(en)$_2$(tn)]Br$_3$. [e]Calculated for lel chair$_2$(C$_1$) conformer (No. 5 in Table 2). [f]Calculated from the positional parameters[9] for [Cr(en)(tn)$_2$]I$_3$·H$_2$O. *Torsional angles, descriptors for ring puckering and shapes of coordination octahedra are given in the order tn−en−en, for M(en)$_2$(tn) and in the order tn−tn−en, for M(en)(tn)$_2$. For each ring the order is *e.g.* M−N, N−C, C−C, C−N, N−M.

mations of coordination octahedra in the former structures. Therefore, we do not present here a discussion of ω, θ and ψ descriptors for the twenty Co(en)(tn)$_2$ conformers.

Comparison with Crystal Structures

In Table 4 we present a comparison between the calculated and experimental shapes of chelate rings (in terms of torsional angles, ϕ, and ring puckering descriptor, τ) and shapes of coordination octahedra (in terms of descriptors ω, θ and ψ) for two M(en)$_2$(tn) and one M(en)(tn)$_2$ conformer. This comparison illustrates the limitations in the predictive power of the present force field method. As shown in Table 4, some calculated values of torsional angles are within three standard deviations of the experimental values (7 and 10 out of 16, and 7 out of 17, for the three crystal structures, respectively); others deviate from experimental values by 2.9–8.1, 4.6–13.4, and 4.7–17.2°, for Cr(en)$_2$(tn), Co(en)$_2$(tn) and Cr(en)(tn)$_2$, respectively. Considering that all three experimentally observed conformers are among those predicted to be the most stable, but that torsional angles are most susceptible to specific crystal packing forces, the agreement shown in Table 4 can be considered satisfactory. A similar comparison for M(ptn)$_3$ is given by Sato and Saito.[14] Optimization of the force field may improve the agreement between the calculated values for torsional angles and those derived from crystal structure data, but is hardly worthwhile undertaking for this particular reason alone.

Supplementary Data on Co(tn)$_3$ and Co(ptn)$_3$ Complexes

Equilibrium geometries and strain energies of Co(tn)$_3$ and Co(ptn)$_3$ conformers were presented in detail in Ref. 4. Here we give additional results on shapes of coordination octahedra and of chelate rings, and for Co(tn)$_3$ on equilibrium distribution.

Incidentally, the Co(2,4-ptn)$_3$ chair$_3$ (eq)$_6$ conformer, which we found[4] to be the lowest in energy, was later observed by Saito.[14] The measured structural data agree with the predicted.

Puckering of chelate rings. In Co(tn)$_3$ τ follows the same pattern as the dihedral angles D$_1$ and D$_2$ (defined in Ref. 4; see Table 7[4]) which would be expected. For chair rings in Co(tn)$_3$ $|\tau| = (0.0 \pm 2.5)°$ and for chair$_3$ (C$_3$) conformers of Co(2,4-ptn)$_3$ $|\tau| = (2.4 \pm 0.1)°$. For regular lel or ob rings in Co(tn)$_3$ series (rings with approximate C$_2$ symmetry) $|\tau| = (35.5 \pm 1.0)°$ and for unsymmetrically distorted lel or ob rings $|\tau| = (28.0 \pm 0.5)°$. A more narrow range is spanned in the case of the Co(2,4-ptn)$_3$ conformers studied before:[4] $|\tau| = (36.0 \pm 0.3)°$ for hexaequatorial lel$_3$ and ob$_3$ structures and $|\tau| = (31.5 \pm 0.3)°$ for corresponding eq$_3$ax$_3$ structures.

Twist angle (ω). For Co(tn)$_3$ only chair$_3$ conformers (Nos. 1 and 4) are twisted towards a trigonal antiprism (azimuthally expanded), $\omega = (63.6 \pm 0.6)°$. Other conformers show a wide irregular variation in ω, also among different rings of the same conformer, ranging from $\omega = 50°$ for a chair ring in *anti*-chair$_2$lel to the $\omega = 60°$ for most of the other conformers.

Among the conformations studied in the Co(2,4-ptn)$_3$ series there seems to be a clear-cut distinction between chair$_3$ conformers which are all twisted towards the antiprism (azimuthally expanded), $\omega = (64.3 \pm 0.2)°$, and either lel$_3$ or ob$_3$ conformers which are twisted towards the prism (azimuthally contracted), $\omega = (55.6 \pm 0.8)°$ for hexaequatorial and $\omega = (52.8 \pm 1.6)°$ for (eq)$_3$(ax)$_3$ conformation.

Tilt angle (θ). Trigonal elongation is present in all homoconformational structures of Co(tn)$_3$, $\theta = (54.0 \pm 0.5)°$. Heteroconformational forms of Co(tn)$_3$ show an irregular variation of the θ descriptor, among which ob rings tend to have $\theta > 54.8°$. All Co(2,4-ptn)$_3$ conformations studied before,[4] except lel$_3$ with axial methyl groups, are trigonally elongated. However, departure of the θ descriptor from its regular octahedral value is negligible.

Pitch angle (ψ). For Co(tn)$_3$ ψ has randomly distributed values in a wide range around the value corresponding to the regular octahedron, $\psi = 35.3°$.

In homoconformational chair$_3$ Co(tn)$_3$, the rings are in a more skew position with respect to the C_3 axis. In lel$_3$ and ob$_3$, ψ has almost the regular octahedral value. The same trend but slightly greater differences in ψ is found in homoconformational forms of Co(2,4-ptn)$_3$.

All these observations should be considered keeping in mind that some arbitrariness is introduced in defining ω for structures which are not strictly of C_3 symmetry, and in defining θ and ψ for structures which are not of D_3 symmetry.

Effect on Co(tn)$_3$ of a changed force field. In our previous paper on this system[4] we used a torsional angle concept different from the present: nine individual torsional angles around each C–C and

C–N bond, with K_φ one-ninth of the values used in later papers.[1–3] The new results are seen in Table 3. The differences from the former[4] are small and only of a quantitative nature. The most spectacular is that conformer No. 2 is now 5.6 rather than 3.4 kJ mol^{-1} above No. 1 on the energy scale. This difference suggests that the uncertainty of prediction of relative conformer energy with a force field of this type (without electrostatic interaction terms) is about 2 kJ mol^{-1}. The results emphasize that, for energy differences as small as these, it is imperative to evaluate the statistical sums when considering thermodynamics stability. The same conclusion was reached through a similar series of studies of conformations of disaccharides treated with a completely different set of potential energy functions.[11,15]

Equilibrium population in Co(tn)$_3$. Table 3 shows that the tris-chair of C_3 symmetry is dominating. The second most populated is the (C_1)-chair$_2$lel; it is clearly the high statistical weight which is responsible for the 15 % contribution of this conformer to the equilibrium mixture in spite of its rather high energy.

A note on other computations. Many authors have performed calculations similar to ours; references have been given before.[1,3,4] Since then a series of papers has been published by McDougall *et al.*,[16–18] in which the authors drew conclusions on relative thermodynamic stabilities of nickel(II) amine complexes. They used Boyd's program[19] modified by Snow.[20] That method leaves out the majority of the non-bonded interactions[16,20] and, as we have shown before,[4] this leads to erroneous relative energies. The criterion for energy minimum is very liberal and certainly not acceptable in CFF work. Furthermore, calculated energies are compared with measured enthalpies, no account being taken of the internal motion which contributes substantially to the enthalpy. As a modelling tool, therefore, the procedure is altogether rather incomplete.

Supplementary Data on Co(bn)$_3$ and Co(ptn)$_3$

Recently, Tapscott *et al.* published a study of the stereochemistry of tris(2,3-butanediamine)cobalt (III) complexes based on ^{13}C NMR measurements.[21] Some of their results confirm our earlier calculations.[1,2]

The average conformer ratios lel:ob for the Co(m-bn)$_3$ system are, as derived from the primary material of a former paper,[2] 0.89:0.11 for the fac and 0.85:0.15 for the mer isomer. The new data[21] are 86 and 92 % lel for the fac isomer in 0.2 M PO_4^{2-} and SO_4^{2-}, respectively, and 74–92 % lel for the lel isomer without complexing anions, the values being a little higher with PO_4^{3-} and SO_4^{2-} added.

For Co(m-bn)$_3$, the fac:mer ratios are[21] 0.36:0.64 and 0.22:0.78 in two different preparations; our calculated value is[2] 0.24:0.76.

For Co((±)-bn)$_3$, the lcl$_3$:lel$_2$ob:lelob$_2$:ob$_3$ distribution is[21] 0.60:0.28:0.12:0.00. The values derived from our previous material[1,2] are 0.47: 0.35:0.13: 0.05, pertaining to hexa-equatorial disposition of methyl groups.

After the completion of our former calculations[4] on Co(ptn)$_3$ a preparation of the mer isomer of Co(meso-ptn)$_3$ was reported.[22] This prompted us to carry out thermodynamic calculations on both isomers (fac and mer) of Co(meso-ptn)$_3$, the results of which are presented in Table 3. We predict a fac:mer ratio 0.92:0.08. Comparison of this result with the experiment[22] is, however, impossible as no quantitative data on the isomer ratio are given.

An Attempt at Stability Constants

Stability constants are known for Co(en)$_3$,[23,24] Co(en)$_2$(tn),[24] and, less precisely, for Co(en)(tn)$_2$.[24] It would be of principal interest to calculate differences in free enthalpy between not only conformers and isomers, as it has been demonstrated in this series of papers, but between molecules with different numbers and even types of atoms.

In a first attempt to do so, we tried to calculate absolute values of free enthalpy of the series Co(en)$_{3-x}$(tn)$_x$, $x=1,2,3$, relative to Co(en)$_3$. We note that our potential energy functions[1] for bond and angle deformations are scaled to zero energy for the minimum of the function, and that therefore the energy contributions E_b,E_θ and E_φ are measured relative to zero. For non-bonded interactions this is not so: the minima are at non-zero energies and are different for the different types of interaction. To bring them on a common basis we would therefore have to add, for each molecule, the depth of the minimum for each type of interaction multiplied by the number of times the interaction occurs in the molecule.

From plots of the non-bonded potential energy functions we read approximate values of ε and r^* and used them as initial values in an iterative pro-

Table 5. Conformers of en and their energies, free enthalpies and populations.

No.	Conformer	Stat. wt.	E_b	E_θ	E_φ	E_{nb}	E_T	ΔE	G	ΔG	n
1	aaa	1	0.19	0.65	0.00	0.97	1.813	0.064	214.291	5.428	0.025
2	aag	4	0.16	0.48	0.02	1.12	1.780	0.031	208.863	0.000	0.220
3	gag	2	0.14	0.29	0.05	1.27	1.749	0.000	212.037	3.174	0.061
4	gag′	2	0.14	0.29	0.03	1.34	1.801	0.052	210.393	1.530	0.119
5	aga	2	0.27	1.85	0.38	1.09	3.588	1.839	214.739	5.876	0.021
6	agg	4	0.24	1.42	0.65	1.67	3.990	2.241	211.355	2.492	0.081
7	agg′	4	0.19	0.63	0.03	0.95	1.791	0.042	209.203	0.340	0.192
8	ggg	2	0.21	1.02	0.84	2.11	4.718	2.429	214.749	5.886	0.021
9	ggg′	4	0.16	0.42	0.07	1.22	1.876	0.127	209.059	0.196	0.204
10	g′gg′	2	0.15	0.33	0.03	1.25	1.766	0.017	212.176	3.313	0.058

gram for the HP33E calculator, with parameters A, B and C of the Buckingham functions[1] as input, giving ε and r^* as output. A utility program[4] to the CFF system gave us the frequency of each interaction type for each type of molecule.

In order to calculate $\Delta G_{1,2,3}$ for the hypothetical processes

$$Co(en)_3 + x\text{tn} \rightleftarrows Co(en)_{3-x} + x\text{en}, x = 1,2,3,$$

we needed also free enthalpy values of en and tn. This entailed doing full conformational energy minimization, vibrational frequency calculation and statistical summation of 10 en and 25 tn conformers. The results of this sizeable computational effort are shown in Tables 5 and 6. The conformer nomencla-

Table 6. Conformers of tn and their energies, free enthalpies and populations.

No.	Conformer	Stat. wt.	E_b	E_θ	E_φ	E_{nb}	E_T	ΔE	G	ΔG	n
1	aaaa	1	0.27	0.73	0.00	0.22	1.226	0.108	282.057	3.697	0.027
2	aaag	4	0.24	0.57	0.02	0.38	1.210	0.092	278.360	0.000	0.119
3	gaag	1	0.22	0.40	0.04	0.53	1.190	0.072	283.252	4.892	0.017
4	gaag′	2	0.22	0.40	0.04	0.54	1.196	0.078	279.824	1.464	0.066
5	aaga	4	0.37	1.95	0.41	0.48	3.213	2.095	281.083	2.723	0.040
6	aagg	4	0.35	1.48	0.71	1.15	3.688	2.570	281.204	2.844	0.038
7	aagg′	4	0.28	0.72	0.02	0.16	1.189	0.071	278.668	0.308	0.105
8	gaga	4	0.34	1.83	0.39	0.69	3.247	2.129	280.870	2.510	0.043
9	gagg	4	0.32	1.35	0.69	1.36	3.719	2.601	280.987	2.627	0.041
10	gagg′	4	0.25	0.57	0.04	0.34	1.194	0.076	278.433	0.073	0.116
11	g′aga	4	0.33	1.74	0.47	0.56	3.113	1.995	280.748	2.388	0.045
12	g′agg	4	0.31	1.28	0.77	1.22	3.583	2.465	280.868	2.508	0.043
13	g′agg′	4	0.25	0.55	0.05	0.30	1.152	0.034	278.387	0.027	0.118
14	agga	2	0.49	3.78	0.47	0.32	5.059	3.941	287.812	9.452	0.003
15	aggg	4	0.45	3.50	0.55	0.81	5.302	4.184	284.210	5.850	0.011
16	aggg′	4	0.37	2.10	0.31	0.13	2.915	1.797	280.991	2.631	0.041
17	gggg	2	0.43	3.16	0.70	1.58	5.868	4.750	287.871	9.511	0.003
18	gggg′	4	0.35	1.68	0.54	0.82	3.395	2.277	281.109	2.749	0.039
19	g′ggg′	2	0.28	0.75	0.02	0.07	1.118	0.000	282.145	3.785	0.026
20	agg′a	2	0.56	4.05	8.03	1.35	13.991	12.873	295.071	16.711	0.000
21	agg′g	4	0.43	2.73	1.86	0.38	5.401	4.183	283.787	5.427	0.013
22	agg′g′	4	0.51	3.34	8.14	2.11	14.109	12.991	292.731	14.371	0.000
23	ggg′g	4	0.39	2.27	2.08	1.16	5.909	4.791	283.612	5.252	0.014
24	ggg′g′	2	0.47	2.96	8.31	2.20	13.932	12.814	294.004	15.644	0.000
25	g′gg′g	2	0.32	1.12	0.33	0.23	2.001	0.883	281.647	3.287	0.032

Table 7. Calculated and measured free enthalpies.

	$\bar{G}$	$\Sigma\varepsilon$	$\bar{G}_o$	$\bar{G}_o-\bar{G}_o(en_3)$	$\Delta G_{1,2,3}$	$\log\beta_3$	$RT\ln\beta_3$	$\Delta G-\Delta G(en_3)$
Coordination sphere								
en_3	886.509	123.375	1009.884	0.000		49.07	280.1	
en_2tn	975.296	148.201	1123.497	113.613	38.8	46.95	268.0	12.1
en tn_2	1066.165	175.163	1241.328	231.444	81.9	44.3	253.	27.
tn_3	1158.329	204.262	1362.591	352.707	128.3	[41.]	[234.]	[46.]
Free ligand								
en	265.112	7.057	212.684					
tn	273.249	13.709	287.373					

ture can be exemplified by No. 12 of the tn series, g′agg: lone-pair$_1$ minus-*gauche* to C_2, N_1 anti to C_3, C_1 *gauche* to N_2, C_2 *gauche* to lone-pair$_2$. The free enthalpies were calculated as for the complexes, that is with quenching of external motion. Details of structure and conformer population will be discussed in another context.

From the data for G and n of the four complexes and the two amines we calculated the mean free enthalpies, corrected by the entropies of mixing. They are given in Table 7 together with the non-bonded energy corrections, measured log β_3 and free enthalpy differences derived from log β_3. Values in square brackets are estimated by scaling ΔG_3 with a factor derived from $\Delta G_{1,2}$ and the unbracketed ΔG values.

The calculated ΔG_1 and ΔG_2 are three times the corresponding experimental values. Thus the stability of the tn chelates is underestimated by a factor of three, and this is of course unsatisfactory. On the other hand, we believe we may conclude that our approach is basically sound, and we feel certainly encouraged to improve on it. The most important among the obvious shortcomings are: inadequacy of potential energy function, nonoptimized parameter values, harmonic oscilator and small amplitude approximations in the statistical summation, and, worst of all, lack of water spheres on the complexes. At the present stage, these approximations are common to most studies published in this field.

A Note on ^{13}C NMR Spectra of Mixed en-tn Complexes

Some support for the dominance of one conformer in the cases of $Co(en)_2(tn)$ and $Co(tn)_3$, as opposed to a more balanced equilibrium for $Co(en)(tn)_2^{3+}$,

Table 8. Non-bonded distances (Å) between C-atoms of one tn ring and other chain atoms in $Co(en)(tn)_2$.*

	C_1	C_m	C_2	C_1^{en}	C_2^{en}	N_1	N_2	N_1^{en}	N_2^{en}
Conformer No. 1									
C_1	4.4	4.7	3.6	5.4	5.6	3.3	3.3	4.0	4.9
C_m	5.7	5.8	4.7	5.4	5.5	5.1	4.0	4.1	5.1
C_2	5.7	5.6	4.4	5.0	4.7	5.0	3.3	4.0	4.2
Conformer No. 5									
C_1	4.7	5.4	4.7	4.7	5.2	4.2	4.1	3.2	4.9
C_m	5.7	6.0	5.0	5.2	5.4	5.1	4.2	3.9	5.0
C_2	5.9	6.2	5.3	4.4	4.3	5.0	4.1	3.3	4.2

* Subscripts 1, 2, and m specify terminal carbons and the middle carbon of tn rings; superscript en designates chain atoms of en ring; numbering is illustrative.

may come from ^{13}C NMR measurements.[25] For $Co(en)_2(tn)$ and $Co(tn)_3$ only three ^{13}C resonances are found, assigned to one type of CH_2 in en and two types of CH_2 in tn. For $Co(en)(tn)_2$, two resonances are seen for CH_2 neighbouring NH_2 in tn. The two most prominent conformers are, according to the calculations, the lel chair$_2(C_1)$ and the lelchair$_2$ *syn*.

The assignments are supported by our calculations, as the non-bonded distances (see Table 8) from the middle carbon atom to all other chain atoms are almost the same in the two conformers, whereas there are substantial differences between the conformers in non-bonded distances involving the terminal carbon atoms of the tn rings. Since the relative differences in non-bonded distances such as those shown in Table 8 are likely to influence local paramagnetic shielding terms noticeably it is to be expected that observed chemical shifts of the terminal carbon atoms will be different in conformers 1 and 5. Furthermore, since chair conformations are so different in different conformers, it is not to be expected that ^{13}C NMR measurements can be used to differentiate between chair and twist-boat conformations in such complexes.

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