Force Field Calculations on Cobalt(III) Complexes of Amine and Thioether Ligands

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A force field has been constructed to reproduce experimental structural features of a series of cobalt(III) complexes. A satisfactory agreement is obtained between computed enthalpy differences for isomers of tris(1,2-propanediamine)cobalt(III) and tris(*trans*-1,2-cyclohexanediamine)cobalt(III) and enthalpy differences determined experimentally from equilibrium studies. The force field tested in this way has been used in computations which form a basis for an explanation of the existence of only one geometric isomer of bis{di(2-aminoethyl)-sulfide}cobalt(III). By means of further force field calculations predictions are made on the relative stability of the eight different geometric isomers of bis{(2-aminoethyl)(3-aminopropyl)sulfide}cobalt-(III). The nomenclature describing the complicated stereochemistry of the latter system is elaborated.

A number of computer programs have been developed in recent years which provide an opportunity for an automatic search for the minimum energy geometry for a molecule or even for a crystal structure. In this paper we have used a program developed to include coordination compounds by Rasmussen and Niketic.[1] The computations presented here are extending other recent work dealing with force field calculations on coordination compounds[2–4] by including the thioether function as a ligator to cobalt(III). We have performed computations with two force fields. One of these is analogous to those used by others for coordination compounds, and it includes the thioether function. In the other force field the two lone pairs of a free thioethers sulfur are assigned properties, just like an atom, analogous to the way Allinger[5] introduced lone pairs on ether oxygen.

The first goal for the force field computations presented here is to explain why only the unsymmetrical *facial* isomer of bis{di(2-aminoethyl)sulfide}cobalt(III), $[Co(daes)_2]^{3+}$, exists.[6] In this isomer the two sulfur atoms are *cis* while the s-*fac* isomer has the sulfur atoms arranged *trans* and, so far, this isomer has escaped discovery. Secondly, we wish to make predictions about the relative stabilities of the eight geometric isomers of bis{(2-aminoethyl)(3-aminopropyl)sulfide}cobalt(III), $[Co(aeaps)_2]^{3+}$. This system is presently under study in this laboratory and it will later be possible to compare the computed properties with experimental results.

The force field has been constructed by varying the parameters to a best overall fit to experimental structures while it is mainly going to find use in calculating the relative energies of isomers. In order to test the calculated strain energies we have made comparisons with other strain energy calculations. A further test is made in comparing computed enthalpy differences between the geometric isomers of tris(1,2-propanediamine)cobalt(III), $[Co(pn)_3]^{3+}$, and of tris(*trans*-1,2-cyclohexanediamine)cobalt(III), $[Co(chxn)_3]^{3+}$, with the experimental enthalpy differences.

THE FORCE FIELD

The program used in this work has been described earlier.[1] It computes the total conformational energy as

$$E_T = E_l + E_\theta + E_\phi + E_{NB}$$

where $E_l = \sum \frac{1}{2} k_l (l - l_0)^2$ is the stretching energy summarized over all bonds, $E_\theta = \sum k_\theta (\theta - \theta_0)^2$ is the bending energy of the bond angles, $E_\phi = \sum_{i=1}^{9} 2\, k_\phi$ $(1 + \cos 3\, \phi_i)$ is the torsional energy connected to all bonds between tetrahedrally coordinated atoms for which each bond contributes with nine terms, finally $E_{NB} = \sum A \, \exp(-Br) - Cr^{-6}$ expresses the

Table 1. Parameters used in the energy minimization procedure. One force field assumes that sulfur lone pair electron density can be included in the form of ghost atoms (Lp). Another force field does not include Lp-parameters and this is constituted by the remaining parameters with the exception that l_0 for Co−S is changed to 2.20 Å and parameters for S-non-bonded interactions are substituted with the values in parentheses.

Bond stretching constants

Bond	k_l kJ/mol/Å^2	l_0 Å
Co − N	887	1.92
Co − S	669	2.24
Co − Cl	1013	2.26
N − H	2962	1.011
N − C	2343	1.47
C − H	2770	1.094
C − C	2653	1.512
S − Lp	2293	0.80
S − C	1933	1.82

Bond angle bending constants

Angle	k_θ kJ/mol/rad^2	θ_0 rad
H − N − H	126	1.911
H − C − H	167	1.911
C − N − H	167	1.911
C − C − H	146	1.911
C − S − C	343	1.658
N − C − H	167	1.911
C − C − C	251	1.911
N − C − C	418	1.911
N − Co − N	251	1.571
Co − N − H	167	1.911
Co − N − C	167	1.911
Co − S − C	167	1.571
Co − S − Lp	251	1.911
Lp − S − Lp	251	1.911
Lp − S − C	251	1.911
S − C − H	180	1.911
S − C − C	293	1.911
N − Co − S	251	1.571
S − Co − S	335	1.571
Cl − Co − N	167	1.571
Cl − Co − S	167	1.571
Cl − Co − Cl	167	1.571

Torsional parameters

Atoms involved	k_ϕ kJ/mol	Atoms involved	k_ϕ kJ/mol
C − C − C − S	2	H − N − C − S	1.3
C − C − C − C	1	H − N − C − C	0.5
C − C − C − N	1	Co − N − C − C	0.75
N − C − C − N	1	Co − N − C − H	0.9
H − C − C − C	1	H − C − S − Lp	2
H − C − C − H	1	H − C − S − C	2
H − C − C − N	1	H − C − S − Co	2
H − C − C − S	2	C − C − S − Lp	2
N − C − C − S	2	C − C − S − C	2
H − N − C − H	0.6	C − C − S − Co	2

The remaining torsion constants were set to 0.

Non-bonded parameters

Atom pair	A kJ/mol	B Å	C Å^6 kJ/mol
H·H	21.82	4.53	431
N·H	16.95	4.25	494
C·H	17.61	4.18	565
Co·H	42.68	3.88	2130
Co·C	34.35	3.62	2590
C·N	15.02	3.94	628
C·C	14.22	3.88	711
S·C	9.92(30.12)	3.62	749(2276)
S·H	12.30(37.32)	3.88	615(1866)
S·N	9.58(28.74)	3.67	665(2021)
Lp·H	13.77	4.69	222
Lp·Lp	8.66	4.85	113
Lp·C	11.09	4.31	293
Lp·N	10.66	4.38	259
Lp·S	7.74	4.00	326
Lp·Cl	25.36	4.06	975
Cl·H	39.92	3.94	1841
Cl·C	32.22	3.67	2263
Cl·N	31.38	3.72	2029

potential between all atom pairs not bound to each other or to a common atom.

Input parameters could partly be obtained from a number of already published force fields for cobalt(III) complexes.[2,4] They appear very different from each other and all are lacking the thioether functions. However, recently Allinger and co-workers[7,8] have included sulfur parameters in a force field and, mainly therefore, Allinger's force field was considered as a starting point the more so as it had already been extended[2] to cobalt(III) complexes. Allinger had no need to assume a lone pair on sulfur but for alchols and ethers it was necessary to introduce oxygen lone pairs in order to reproduce structures and energy differences with accuracy.[8] We have had no difficulty in reproducing

structures with a force field without sulfur lone pairs. However, certain energy differences between conformers were found to be unsatisfactory (vide infra). The lone pairs were included as phantom atoms having a position roughly 0.8 Å from the sulfur nucleus and directed away from the remaining atoms bound to sulfur. The sulfur — lone pair distance was assumed to follow Hooke's law with a force constant identical to that of S−H. The angle deformation around sulfur was treated similarly. The force constants involving lone pairs had no consequences for the computed geometries and energy differences so that the effect of a lone pair on sulfur in thioether complexes is solely to introduce a directional effect in the non-bonded interactions.

The non-bonded interactions were not varied to obtain better results but were taken from Allinger's table[9] of r^* and ε values except for heavier atoms. The parameters for the latter kind of atoms were obtained by extrapolation of the values in the table assuming a linear variation. In order to be used in the Buckingham potential functions demanded by the Rasmussen's program the following transformations were made:

$$A_{ij} = 346(\varepsilon_i \varepsilon_j)^{\frac{1}{2}} \qquad \times 10^4 \text{ kJ/mol}$$
$$B_{ij} = 1/(0.0736 \, (r_i^* + r_j^*))^{\frac{1}{2}} \quad \text{Å}$$
$$C_{ij} = 9.43 \, (r_i^* + r_j^*)^6 \, (\varepsilon_i \varepsilon_j)^{\frac{1}{2}} \quad \text{Å}^6 \text{ kJ/mol}$$

In order to keep the number of parameters to be varied as low as possible it was decided not to use cross terms, e.g. connecting bond stretching with bond angle deformation. This is a natural consequence of the high number of parameters introduced by the presence of the metal ion, but therefore, and because of the inclusion of the sulfur lone pair, the present force field has lost its close connection to Allinger's force field. In order to reproduce structural features described below the parameters were varied slightly to the final values given in Table 1.

TEST COMPUTATIONS

The derived force field has been tested in various ways. The results of these tests are important for judging the reliability of the results reported later and they are therefore mentioned in the following.

Table 2. A comparison between experimental and computed structural features for $[Co(daes)_2]^{3+}$. The experimental values are averages between the two halves ideally related by a two-fold axis. Units are Å and deg.

Property	Exp. value	Comp. value[c]	Comp. value[d]
Co−N[a]	1.964	1.974	1.969
Co−N	1.977	1.986	1.992
Co−S	2.243	2.248	2.245
N[a]−C[a]	1.485	1.494	1.491
N−C	1.482	1.491	1.488
C[a]−C[a]	1.498	1.525	1.525
C−C	1.490	1.522	1.521
C[a]−S	1.832	1.828	1.831
C−S	1.818	1.821	1.825
S−Co−S	90.2	90.8	88.9
N[a]−Co−S[b]	87.4	87.5	88.4
N−Co−S[b]	87.6	87.3	88.8
N[a]−Co−N[a]	95.0	94.2	93.5
Co−N[a]−C[a]	113.3	114.7	113.9
Co−N−C	116.0	115.8	114.9
Co−S−C[a]	98.7	99.9	98.3
Co−S−C	102.3	103.6	97.1
N−C−C−S[a]	45	42	43
N−C−C−S	49	50	50

[a] The ligand atoms belong to the chelate rings spanning a coordination edge of the CoS_2-plane. [b] The atom belongs to the same chelate ring as the other atoms in the symbol. [c] Computed with the force field including Lp (Table 1). [d] Computed with the force field not including Lp.

Thioethers. The parameterization model with sulfur lone pair phantom atoms included was based on dimethyl sulfide, thiacyclopentane and thiacyclohexane and test calculations were made in order to reproduce Allinger's structural results. After arriving at satisfactory structural agreements for the energy minimized molecules, the parameters derived at so far were kept unaltered in the remaining computations. The energy differences between conformers and isomers were then tested. The energy difference between axial and equatorial 2-methyl-, 3-methyl- and 4-methylthiacyclohexane were computed to be 6.8, 4.4 and 6.2 kJ/mol compared to Allinger's result 4.1, 4.6 and 6.6 kJ/mol. The simplicity of the present force field which neglects all cross energy terms has made it impossible to describe small ring systems like thiacyclobutane.

Cobalt(III) complexes. The pertinent parameters were obtained by fitting the computed structures of bis{di(2-aminoethyl)sulfide}cobalt(III) and *cis* dichlorido-1,9-diamino-3,7-dithianonanecobalt(III) to experimental[10,11] X-ray structures. The structure of the latter complex, $[Co(ete)Cl_2]^+$, has not been determined directly. Instead we have used the X-ray structure[11] of the nitrocomplex $[Co(ete)NO_2Cl]^+$ to fit the bond lengths and bond angles nearest sulfur.

The adjustment of the merely guessed start parameters to the structural features allowed for an excellent fit. A number of computed and experimental structural parameters are given in Table 2 and from a comparison it is obvious that the only discrepancy is found for the $C-C$ bond lengths which are found experimentally to be very short. The torsional angles give as usual a very sensitive measure of the agreement between computed and the experimental structures. The found deviations are considered small.

Table 3. An example of the agreement between averaged computed and experimental structural features is here shown for lel₂ob $[Co(chxn)_3]^{3+}$.

Property	Calc. value	Exp. value[16]
Co−N (Å)	1.99	1.97
N−C (Å)	1.49	1.49
(N)C−C(N) (Å)	1.51	1.50
N−Co−N (°)	84.5	84.5
N−C−C (°)	107.2	106.0
N−C−C−N (lel) (°)	49	53.8
N−C−C−N (ob) (°)	49	52.8

Good structural agreements have also been achieved for those isomers of tris(1,2-propanediamine)cobalt(III), $[Co(pn)_3]^{3+}$, and tris(*trans*-1,2-cyclohexanediamine)cobalt(III), $[Co(chxn)_3]^{3+}$, for which X-ray structures have been published.[12-16] In most cases the computed structure ended up having the highest possible symmetry although no symmetry restraint was applied. In Table 3 these results are exemplified for lel₂ob $[Co(chxn)_3]^{3+}$.

The computed conformational energies for the 12 diastereoisomeric $[Co(pn)_3]^{3+}$ and for the 4 diastereosiomeric $[Co(chxn)_3]^{3+}$ are listed in Table 4. The labeling of the 1,2-propanediamine complexes is elaborated in Ref. 17 and shall not be repeated here. The $[Co(chxn)_3]^{3+}$ system is less complicated than that of $[Co(pn)_3]^{3+}$ and the experimental results[18] are more reliable. The agreement between computed and experimental energy differences is surprisingly good considering that the enthalpies are determined for aqueous solutions while the force field computations assume isolated molecules in vacuum. Even better agreement can undoubtedly be achieved with more variations of the parameters, *e.g.* the non-bonded potentials. However, it is not the opinion of the present authors that the force field method should be considered more than semi-quantitative at this stage. We find that the computed results gathered in Tables 2−4 reproduce experimental properties with reasonable accuracy to justify the opinion that the computations reported later have a similar validity.

RESULTS AND DISCUSSION

The first task given to the force field calculations was to estimate the relative enthalpy of the *u-fac* and *s-fac* geometrical isomers of $[Co(daes)_2]^{3+}$. From considerations with Dreiding models the *mer* isomer was found too unlikely to be considered in these computations. The crystal structure analysis of the isolated *u-fac* isomer as the optically active chloride $(-)_D$-$[Co(daes)_2]Cl_3.2H_2O$ showed it to have the Δ-configuration with all the four chelate rings in λ-conformations.[10] The chelate rings are known from ¹H and ¹³C NMR to be flexible[6] and it is therefore necessary to perform energy minimization for the ten *u-fac* and the six *s-fac* conformers. The resulting energies for the 16 diastereoisomers are given in Table 5.

It is first of all gratifying that the isomer found in the X-ray structure has the lowest energy of all

Table 4. Calculated conformational energies in kJ/mol of the diastereoisomers of tris(1,2-propanediamine)-cobalt(III) and tris(*trans*-1,2-cyclohexanediamine)cobalt(III) and experimental[a] enthalpy differences calculated from equilibrium constants at 373 K assuming a statistical entropy term.

Isomer[b]	Strain energy	Relative energy	$\Delta H'^{\circ}$	Isomer[c]	Strain energy	Relative energy	$\Delta H'^{\circ}$
fac lel$_3$[d]	137.98						
mer lel$_3$	137.99	0	0	lel$_3$	275.16	0	0
fac lel$_2$ob	139.02						
mer lel$_2$ob	139.04						
mer lel$_2$ob	139.04	1.0	2.9	lel$_2$ob	279.14	3.98	4.34
mer lel$_2$ob	139.04						
fac lelob$_2$	140.31						
mer lelob$_2$	140.33						
mer lelob$_2$	140.33	2.3	5.5	lelob$_2$	282.24	7.08	7.13
mer lelob$_2$	140.33						
fac ob$_3$	139.81						
mer ob$_3$	139.81	1.8	6.7	ob$_3$	282.07	6.91	8.20

[a] The experimental enthalpies (kJ/mol) are those reported in Refs. 17 and 18. [b] The tris(1,2-propanediamine)cobalt-(III) system. [c] The tris(*trans*-1,2-cyclohexanediamine)cobalt(III) system. [d] For an introduction to the stereochemical notation used see Ref. 17.

the sixteen forms. The many isomers have strain energies which vary less than 20 kJ/mol and the most stable *s-fac* form has only 2.22 kJ/mol higher energy than the Δ-$\lambda\lambda\lambda\lambda$-*u-fac* form. However, when the probability of each of the sixteen conformers is calculated the probability of the *s-fac* forms adds up to only 4 % (at 300 K). This amount is near the detection limit for one isomer. We thus feel that the computations have demonstrated that there is a simple explanation to the isomer distribution of [Co(daes)$_2$]$^{3+}$ and that there is no need for assuming a binding interaction between the two sulfur atoms, a "*trans* effect" or a significant π-interaction between sulfur and cobalt. Thus thio-ether sulfur behaves structurally and spectro-scopically as an innocent ligator to cobalt(III).

The computations were first performed with the force field without lone pair. The results were very similar and the energy separation between the *u-fac* and *s-fac* isomers was even larger (Table 5). The Δ-$\lambda\lambda\lambda\lambda$ conformer was computed to be less stable than the Δ-$\delta\delta\delta\delta$ conformer with this force field. This may indeed be the correct order of the stabilities but the former conformer is found to exist in the crystal structure of $(-)_D$-Δ-*u-fac*-[Co(daes)$_2$]Cl$_3$.2H$_2$O. The force field with sulfur lone pairs is reproducing experimental features as well as the one without lone pairs and the resulting energy separation $E(\Delta$-$\lambda\lambda\lambda\lambda) < E(\Delta$-$\delta\delta\delta\delta)$ was found

Table 5. The conformational energies (kJ/mol) of the ten *u-fac* and the six *s-fac* forms of [Co(daes)$_2$]$^{3+}$ computed with lone pair (first column) and without. The missing energies indicate that the computations did not lead to minimum corresponding to this conformation.

Isomer		Strain energy	Strain energy
u-fac-Δ-$\lambda\lambda\lambda\lambda$[a]		173.2	120.6
Δ-$\lambda\lambda\lambda\lambda$		177.3	131.9
Δ-$\lambda\lambda\lambda\delta$		185.3	137.2
Δ-$\lambda\lambda\delta\delta$		176.7	128.1
Δ-$\delta\lambda\delta\lambda$		173.6	133.3
Δ-$\delta\lambda\lambda\delta$		183.1	139.8
Δ-$\lambda\delta\lambda\delta$			
Δ-$\lambda\delta\delta\delta$			
Δ-$\delta\lambda\delta\delta$		176.7	127.1
Δ-$\delta\delta\delta\delta$		174.5	117.5
s-fac	$\lambda\lambda\lambda\lambda$	186.9	132.6
	$\delta\lambda\lambda\delta$	179.3	140.4
	$\delta\lambda\delta\lambda$	183.8	144.3
	$\delta\delta\lambda\lambda$		140.5
	$\delta\lambda\lambda\lambda$	185.2	138.2
	$\lambda\delta\lambda\lambda$	192.1	142.6

[a] The ring conformations are in the order: (1) a chelate ring in the CoS$_2$-plane, (2) the other chelate ring of the same ligand, (3) the other chelate ring in the CoS$_2$-plane and (4) the remaining chelate ring.
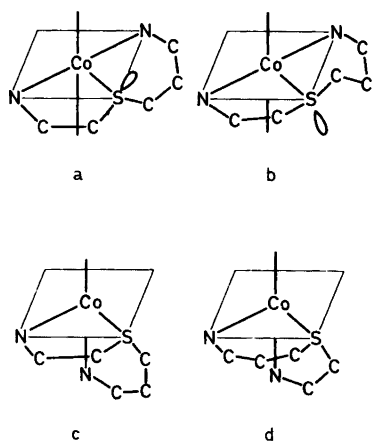
Fig. 1. Structures of mono{(2-aminoethyl)(3-amino-propyl)sulfide}cobalt(III) complexes. a, *mer*-[Co(*R*-aeaps)X₃]; b, *mer*-[Co(*S*-aeaps)X₃]; c, *fac*-[Co(*R*-aeaps)X₃]; d, *fac*-[Co(*S*-aeaps)X₃].

preferable with the experimental data presently available.

Not all possible conformers are found to appear as minima in the parameter space. This may be a consequence of the efficient minimization methods

Table 6. Minimized energy for the twelve ideal conformers of [Co(aeaps)Cl₃] having the sulfur atom of *R*-configuration.

Con-figuration around Co	Conformation of the five-membered ring	six-membered ring	Energy kJ
meridional λ		chair[a]	114.10
		skew-boat λ	112.19
		skew-boat δ	221.78[b]
	δ	chair[a]	103.38
		skew-boat λ	103.23
		skew-boat δ	128.35
facial λ		chair[a]	111.59
		skew-boat λ	103.51
		skew-boat δ	121.46
	δ	chair[a]	104.10
		skew-boat λ	117.56
		skew-boat δ	117.15

[a] The chair form of the six-membered ring might take two spacial structures. However, when the chirality of the sulfur atom is specified as *R* only one rigid chair form seems possible. [b] Not completely minimized.
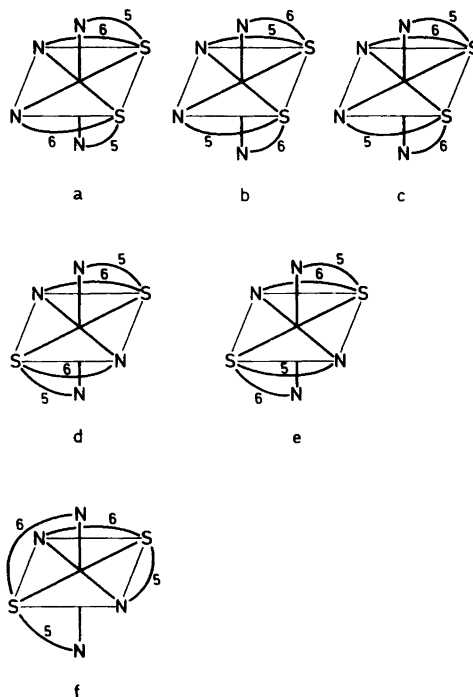
Fig. 2. Diastereoisomers of bis{(2-aminoethyl)(3-aminopropyl)sulfide}cobalt(III). a, Λ-*u-fac*-[Co(*S*-aeaps)₂]³⁺; b, Λ-*u-fac*-[Co(*R*-aeaps)₂]³⁺; c, Λ-*u-fac*-[Co(*R*-aeaps)(*S*-aeaps)]³⁺; d, *s-fac*-[Co(*R*-aeaps)-(*S*-aeaps)]³⁺; e, Λ(5,5)Δ(6,6)-*s-fac*-[Co(*S*-aeaps)₂]³⁺; f, This formula represents three forms all having Λ(5,5)Λ(6,6) configurations: Λ-*mer*-[Co(*S*-aeaps)₂]³⁺, Λ-*mer*-[Co(*R*-aeaps)₂]³⁺, and Λ-*mer*-[Co(*S*-aeaps)(*R*-aeaps)]³⁺.

which may have the effect that less well-defined minima are overlooked.

The second task for the force field computations is predictive rather than explanative. It is concerned with the relative energy of the isomers of bis{(2-aminoethyl)(3-aminopropyl)sulfide}cobalt-(III), [Co(aeaps)₂]³⁺. The system is presently under examination and the predictions are going to provide assistance in assignments of structures and to give an idea of the number of isomers to be expected.

The larger ring size of one of the chelate rings of a [Co(aeaps)X₃] complex (X₃ may be, for example, Cl₃) relative to the corresponding daes complex makes it feasible according to Dreiding models that the chelate may take a *meridional* configuration. The total number of isomers of [Co(aeaps)X₃] is

therefore four. These four diastereoisomers are shown in Fig. 1. All the isomers are chiral having the chirality connected to the sulfur atom which may take R or S absolute configurations.

The isomers of $[Co(aeaps)_2]^{3+}$ are most easily accounted for by (I) characterizing the geometric arrangement around the cobalt(III) ion in analogy with the nomenclature for symmetric tridentates

as *mer*, *s-fac* or *u-fac*, (ii) characterizing the chirality of the sulfur atoms as R and S, (iii) finally one may characterize the chiral distribution of chelate rings as Δ or Λ. In total there are eight diastereoisomers possible. They are shown in Fig. 2 with a labeling according to the above characterization scheme.

The chirality of most of the chiral complexes is fully specified by the use of the two first characteriza-

Table 7. Computed strain energy for some of the conformers of the eight diastereoisomeric $[Co(aeaps)_2]^{3+}$. The conformation of the ring is denoted λ, δ or ch, where ch is an abbreviation for chair (relevant for the six-membered rings only).

Ring distribution	Sulfur conf.	Ring conformations	Energy kJ/mol	
			a	*b*
Λ-*u-fac*	*R,R*	$(\lambda$-5, ch-6$)_2$	246	207
		$(\lambda$-5, λ-6$)_2$	227	194
		$(\lambda$-5, λ-6)(δ-5, ch-6)	229	195
		$(\lambda$-5, ch-6)(δ-5, ch-6)	244	206
		$(\delta$-5, ch-6$)_2$	233	196
		$(\lambda$-5, λ-6)(λ-5, ch-6)	240	203
Λ-*u-fac*	*R,S*	$(\lambda$-5, ch-6)(δ-5, ch-6)	244	210
		$(\lambda$-5, ch-6)(λ-5, ch-6)	243	210
		$(\lambda$-5, λ-6)(δ-5, δ-6)	231	199
		$(\lambda$-5, λ-6)(λ-5, ch-6)	226	197
		$(\delta$-5, ch-6)(λ-5, ch-6)	230	201
		$(\lambda$-5, λ-6)(δ-5, ch-6)	236	202
Λ-*u-fac*	*S,S*	$(\lambda$-5, ch-6$)_2$	233	197
		$(\delta$-5, ch-6$)_2$	242	211
		$(\delta$-5, δ-6$)_2$	230	198
		$(\delta$-5, ch-6)(λ-5, ch-6)	234	200
		$(\lambda$-5, ch-6)(δ-5, δ-6)	235	204
		$(\delta$-5, δ-6)(δ-5, ch-6)	231	198
s-fac	*R,R*	$(\lambda$-5, ch-6$)_2$	238	210
		$(\lambda$-5, λ-6$)_2$	245	219
		$(\lambda$-5, λ-6)(δ-5, ch-6)	247	220
		$(\delta$-5, ch-6$)_2$	239	213
s-fac	*R,S*	$(\lambda$-5, ch-6)(δ-5, ch-6)	246	221
		$(\lambda$-5, λ-6)(λ-5, ch-6)	245	218
		$(\lambda$-5, λ-6)(δ-5, δ-6)	241	214
		$(\delta$-5, ch-6)(λ-5, ch-6)	245	218
Λ(5,5)-*mer*	*R,R*	$(\lambda$-5, ch-6$)_2$	259	231
		$(\delta$-5, λ-6$)_2$	217	203
		$(\delta$-5, ch-6$)_2$	230	207
		$(\delta$-5, λ-6)(λ-5, δ-6)	229	210
Λ(5,5)-*mer*	*S,S*	$(\lambda$-5, ch-6$)_2$	230	207
		$(\delta$-5, ch-6$)_2$		230
		$(\lambda$-5, δ-6$)_2$	217	204
		$(\lambda$-5, ch-6)(λ-5, δ-6)	226	209
Δ(5,5)-*mer*	*S,R*	$(\lambda$-5, ch-6)(δ-5, ch-6)	239	215
		$(\lambda$-5, δ-6)(δ-5, ch-6)	226	211
		$(\lambda$-5, δ-6)(δ-5, λ-6)	218	205
		$(\delta$-5, ch-6)(λ-5, ch-6)	262	237

a Computed with Lp. *b* Computed without Lp.

tion principles. However, the two isomers *u-fac*-[Co(*R*-aeaps)(*S*-aeaps)]$^{3+}$ and *mer*-[Co(*R*-aeaps)-(*S*-aeaps)]$^{3+}$ are both enantiomeric and the third element of the characterization is necessary. For this "*meso u-fac* isomer" shown on Fig. 2, the standard procedure[19] for finding the absolute configuration shows that the three pairs of skew lines form Λ, Δ and Λ configurations resulting in an overall Λ configuration. This result could be specified as $\Lambda(5,5)$, $\Lambda(6,6)$ $\Delta(6,5)$, where 5 and 6 represent the line drawn from N to S in either a five-membered chelate ring or in a six-membered chelate ring. When the chiral *s-fac* isomer of Fig. 2 is considered this last specification is necessary when the Λ,Δ notation is used since there are only two pairs of skew lines of opposite chirality: $\Lambda(5,5)$ and $\Delta(6,6)$.

For the *mer* isomers shown in Fig. 2 one finds the configurations $\Lambda(6,6)\Lambda(5,5)\Delta(5,6)\Delta(6,5)$ and for these isomers it is obviously necessary to use the full scheme for the characterization.

For the force field computations it is necessary to further take into account the conformational isomerism exerted by each chelate ring. As it is the case for [Co(daes)$_2$]$^{3+}$ each diastereoisomer may populate a manifold of conformations. In case of [Co(aeaps)$_2$]$^{3+}$ the computations would be exceedingly expensive if the energy of all of these conformational isomers were to be calculated. Instead computations were carried out first for the twelve conformational combinations of the structural elements for [Co(aeaps)Cl$_3$] (Table 6) and those combinations having more strain energy than 112 kJ/mol were disregarded in the following computations for the bis complex. The final minimized energies for [Co(aeaps)$_2$]$^{3+}$ conformers are presented in Table 7. Both force fields predict that the *s-fac* isomers are less stable than the *u-fac* and *mer* isomers. The relative strain energies obtained with the two force fields are different. When the experimental work on this system has resulted in the isolation and characterization of the *u-fac* and *mer* diastereoisomers it is possible to determine the enthalpy differences by calorimetric measurements[20] of the heat evolved on addition of sulfide ions. So far one isomer has been characterized with certainty by means of X-ray crystallography as $(-)_D$-Λ-*u-fac*-$(\delta$-5, ch-6)(λ-5, ch-6)-[Co(*S*-aeaps)$_2$]-ClO$_4$S$_2$O$_6$·H$_2$O.[23] This is not the conformation for which we compute the least strain energy, however, it is one of the conformers of Λ-*u-fac*-*S,S* with lowest energy.

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