

A Calorimetric Study of the Relative Strain Enthalpies in Some C-Methyl-substituted Tris(ethylenediamine)cobalt(III) Complexes

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Strain enthalpies for a series of complexes have been determined from calorimetric measurements of decomposition reactions with sodium sulfide in aqueous solution. The experimental data are correlated with the stereochemistry of the complexes and are compared with some theoretical results from the literature.

In recent decades metal complexes with chelate rings have been extensively studied by application of the methods of conformational analysis.¹

One chief objective for these studies has been to evaluate the relative strain energies of geometrical and conformational isomers of octahedral complexes with three diamine ligands.

The concept of strain in a molecule has a long history in chemistry² and although its definition is rather vague it has proved to be very useful.

In theoretical approaches the strain energy (or conformational energy) is often treated as a sum of four potentials, representing bond length distortion strain, bond angle distortion strain ("Baeyer strain"), torsional energy of rotation about bonds ("Pitzer strain"), and nonbonded interactions.

Energy differences obtained from such calculations, where entropy is not taken into account, may be equated with enthalpy differences, ΔH , since at constant pressure, P ,

$$\Delta H = \Delta E + P\Delta V \approx \Delta E$$

where ΔV , the volume change between isomers, normally is considered to be negligible.

In the present experimental approach we have attempted to obtain the relative strain

enthalpies of some tris(diamine)cobalt(III) complexes by calorimetry.

We have looked at the effect of C-methyl-substitution in the five-membered chelate rings of 1,2-ethanediamine, a theme which has been treated theoretically in a recent paper from our laboratory.³

NOMENCLATURE

The diamine ligands used are abbreviated as follows: 1,2-ethane-diamine (or ethylenediamine) = en, $(-)_D$ -(*R,R*)-1,2-dimethyl-1,2-ethanediamine (or *l*-butanediamine) = lbn, (*R,S*)-1,2-dimethyl-1,2-ethanediamine (or *meso*-butanediamine) = mbn, and 1,1-dimethyl-1,2-ethanediamine (or isobutanediamine) = ibn.

An unspecified diamine is designated by aa. For simplicity the complexes are sometimes referred to by the numbers I—X (see Table 2).

The Greek letters Δ , Λ , δ , and λ are used to specify configurations and conformations as recommended by IUPAC;⁴ ξ is used instead of δ and λ if the ring conformation is unspecified.

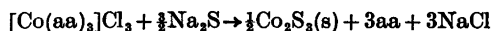
A five-membered ring in an octahedral tris(diamine) complex is puckered and may have its C—C axis either almost parallel or oblique relative to the C_2 -axis (or pseudo C_2 -axis) of the complex; these two situations are denoted *lel* and *ob*.⁵ A C-methyl-substituent in the ring may be either equatorially or axially oriented, and these two possibilities are indicated by *eq* and *ax*.

METHOD

The experimental basis of the method employed was in part adopted from the literature.⁶⁻⁸ It amounts to measuring the heat of reaction for the decomposition of the amine

complexes by excess sodium sulfide in aqueous solution.

If a solution of $[\text{Co}(\text{aa})_3]\text{Cl}_3$ is added to a solution of Na_2S , the complex ion will decompose quantitatively in a reaction with the following stoichiometry



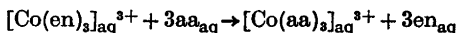
We have determined ΔH for such reactions by calorimetry at 25.0°C.

The experimental ΔH -values, ΔH_{exp} , for the tris(diamine) complexes I–X are taken as indications of their relative strain enthalpies.

For lack of an obvious, "strainfree" reference molecule we have chosen to normalize our results relative to $[\text{Co}(\text{en})_3]^{3+}$ by defining a strain parameter, H_{strain} , as

$$H_{\text{strain}} \equiv \{\Delta H_{\text{exp}} \text{ for } [\text{Co}(\text{en})_3]^{3+}\} - \{\Delta H_{\text{exp}} \text{ for } [\text{Co}(\text{aa})_3]^{3+}\}$$

This means that H_{strain} equals ΔH for the hypothetical process



in dilute aqueous solution.

Evidently, H_{strain} includes differences in solvation enthalpies in addition to the differences in strain enthalpy. But in the interpretation of our results we have assumed solvational differences to be negligible. Recent experimental results⁹ support the validity of this approximation if the argument is restricted to 1,2-ethanediamine and its *C*-alkyl-substituted derivatives.

EXPERIMENTAL

Calorimeter. The calorimeter used (Type 8721-1 from LKB-Instruments, Sweden) is of the constant environment-temperature type, designed for work at atmospheric pressure. It has a thin-walled 100 ml Pyrex glass reaction vessel with a built-in thermistor as temperature sensor. A gold stirrer also serves as a holder for a 1 ml cylindrical ampoule. The breaking of the ampoule against a sapphire-tipped rod is accomplished by activating a motor-driven mechanism. The reaction vessel is contained in a chromium plated brass case which is submerged in a water thermostat with a temperature constancy better than 10^{-3} K.

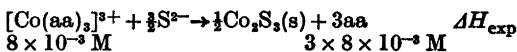
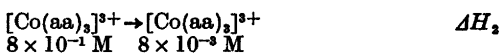
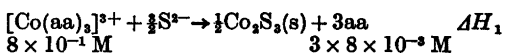
Temperature *vs.* time curves were registered by a Beckman ten-inch potentiometric record-

er (Full scale deflection 0.15 K; reading accuracy $\pm 6 \times 10^{-4}$ K).

Calibrations were performed on the system after each reaction using a built-in electrical heater.

In order to check the experimental uncertainty of the set-up, the heat of solution of a recommended¹⁰ test substance, tris(hydroxymethyl)aminomethane (200 mg in 100 ml 0.1 M HCl), was determined at 25.0°C. The result from five runs was 29.68 ± 0.10 kJ mol⁻¹ to be compared with the very accurately determined value¹⁰ of 29.70 ± 0.025 kJ mol⁻¹.

Thermochemical experiments. The quantity ΔH_{exp} at 25.0°C for a certain complex, $[\text{Co}(\text{aa})_3]\text{Cl}_3$, was determined in two steps from a molar reaction enthalpy, ΔH_1 , and a molar solution enthalpy, ΔH_2 .



$$\Delta H_{\text{exp}} = \Delta H_1 - \Delta H_2$$

For determinations of ΔH_1 and ΔH_2 , the ampoule always contained 0.8 mmol accurately weighed complex chloride in 1 ml aqueous solution. The reaction vessel was filled with 100 ml 80 mM aqueous Na_2S to obtain ΔH_1 , and with 100 ml H_2O to obtain ΔH_2 .

It was checked by spectrophotometry that the decomposition was quantitative under the conditions used.

Some typical temperature curves for sulfide reactions are presented in Fig. 1. The temperature change was evaluated by a graphical procedure based on "Dickinson's method".¹¹

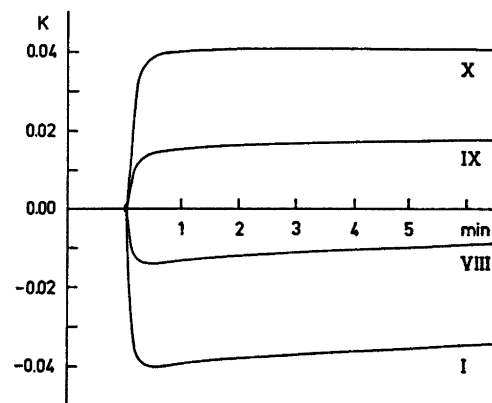


Fig. 1. Temperature *vs.* time curves for the sulfide reactions of complexes I, VIII, IX, and X.

Table 1.

		Molecular weight (see text)	ΔH_1 kJ mol ⁻¹	ΔH_2 kJ mol ⁻¹
I	<i>rac</i> -[Co(en) ₃] ³⁺	409	21.51 21.63 21.30 21.63	3.10 3.10
II	Δ -[Co(en) ₂ (lbn)] ³⁺	387	22.05 21.76	2.38
III	Δ -[Co(en)(lbn) ₂] ³⁺	432	25.94 26.23	2.13
IV	Δ -[Co(lbn) ₃] ³⁺	448	24.35 24.60	1.13
V	<i>rac</i> -[Co(en) ₂ (mbn)] ³⁺	399	12.43 12.22	3.18
VI	<i>rac</i> -[Co(en)(mbn) ₂] ³⁺	415	5.56 5.86	3.93
VII	<i>rac</i> -[Co(mbn) ₃] ³⁺	457	0.62 0.59	3.10
VIII	<i>rac</i> -[Co(en) ₂ (lbn)] ³⁺	382	7.07 7.47	2.75
IX	<i>rac</i> -[Co(en)(lbn) ₂] ³⁺	437	-7.91 -7.82	2.59
X	<i>rac</i> -[Co(lbn) ₃] ³⁺	499	-20.83 -20.92	1.80

The results from determinations of ΔH_1 and ΔH_2 are given in Table 1.

Preparation of complexes. The complexes were prepared in aqueous solution by aerial oxidation of CoCl₂·6H₂O, the pertinent amine(s), and HCl (molar ratio 1:3:1) in the presence of active charcoal.

Purification and separation was carried out by descending paper chromatography using Whatman 3 MM paper with a mixture of water saturated butanol and butylchloride (98 vol %:2 vol %) as eluent.

The general procedure has previously been described in more detail.¹²

Analyses. The molecular weights of the chlorides, [Co(aa)₃]Cl₃·nH₂O, given in Table 1 were obtained from cobalt analyses on the samples actually used in the calorimetric experiments. These determinations were performed in the following way. The complexes were fumed to dryness with conc. H₂SO₄; after dilution with water cobalt(II) in the resulting clear solutions was determined by

addition of excess EDTA and back-titration with zinc(II) following the method of Kiss.¹³

The number of methyl-substituents relative to the number of ring protons was in each case verified by the integrated ¹H NMR spectra.

Description of the samples. All the complexes were isolated as the chlorides, [Co(aa)₃]Cl₃·nH₂O.

Samples II, III, and IV each consist of only one geometrical isomer, as defined by their formulae in Table 2.

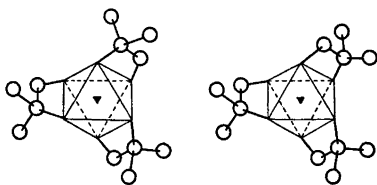
I, V, and VIII each consist of one Δ/Δ -pair.

VII and X are equilibrium mixtures of the two possible Δ/Δ -pairs. This is illustrated for the lbn case in Fig. 2; the situation is analogous for mbn, where one ring carbon has *R*-configuration and the other has *S*-configuration.

VI and IX are equilibrium mixtures of the three possible Δ/Δ -pairs. See Fig. 3.

Table 2.

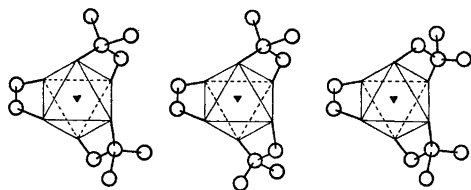
		ΔH_{exp} kJ mol ⁻¹	H_{strain} kJ mol ⁻¹	Number of axial CH ₃ -groups
I	<i>rac</i> -[Co(en) ₃ ξξξ] ³⁺	18.4	0	0
II	Δ -[Co(en) ₂ (lbn)ξξλ] ³⁺	19.5	-1.1	0
III	Δ -[Co(en)(lbn) ₂ ξλλ] ³⁺	24.0	-5.6	0
IV	Δ -[Co(lbn) ₃ λλλ] ³⁺	23.4	-5.0	0
V	<i>rac</i> -[Co(en) ₂ (mbn)ξξξ] ³⁺	9.2	9.2	1
VI	<i>rac</i> -[Co(en)(mbn) ₂ ξξξ] ³⁺	1.8	16.6	2
VII	<i>rac</i> -[Co(mbn) ₃ ξξξ] ³⁺	-2.5	20.9	3
VIII	<i>rac</i> -[Co(en) ₂ (lbn)ξξξ] ³⁺	4.5	13.9	1
IX	<i>rac</i> -[Co(en)(lbn) ₂ ξξξ] ³⁺	-10.5	28.9	2
X	<i>rac</i> -[Co(lbn) ₃ ξξξ] ³⁺	-22.7	41.1	3

Fig. 2. Possible geometrical isomers of Δ -[Co(lbn)₃ξξξ]³⁺ (only carbon atoms are shown).

RESULTS AND DISCUSSION

The final results are given in Table 2, and the experimental values of the strain parameter are presented diagrammatically in Fig. 4.

By examination of molecular models it clearly appears that in tris(diamine) complexes with five-membered rings the axial methyl-substituents must be subject to a considerable steric hindrance, which in part is caused by interactions with neighbouring rings. It is also apparent from models that equatorial substituents, which point away from the rest of the molecule, hardly will affect the molecular strain.

Fig. 3. Possible geometrical isomers of Δ -[Co(en)(lbn)₂ξξξ]³⁺ (only carbon atoms are shown).

These simple considerations are sufficient to rationalize the main features of the pattern observed in Fig. 4.

In chelate rings with mbn or lbn one methyl group will always adopt axial orientation in λ - as well as δ -conformation (see Table 3), and in accordance with this the molecular strain enthalpy, H_{strain} , increases with increasing number of mbn or lbn ligands.

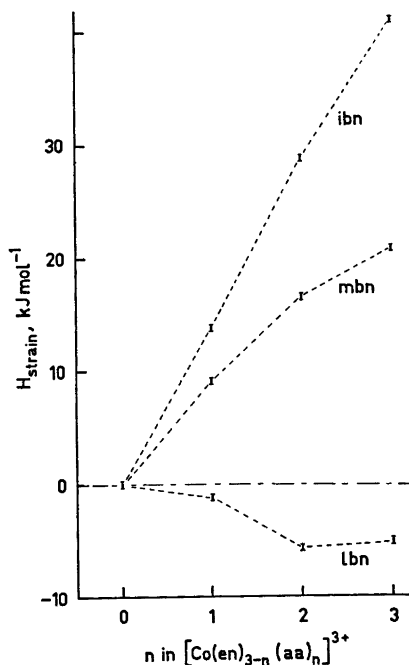


Fig. 4. The experimental strain enthalpies of complexes I–X in diagrammatical representation. Uncertainties are indicated.

Table 3. Key to structures of diamine ligands.

λ -configuration		λ -configuration
δ -conformation		
en	<i>ob</i>	<i>lel</i>
lbn	<i>ob/2 ax</i>	<i>lel/2 eq</i>
mbn	<i>ob/1 eq, 1 ax</i>	<i>lel/1 eq, 1 ax</i>
ibn	<i>ob/1 eq, 1 ax</i>	<i>lel/1 eq, 1 ax</i>
λ -conformation		
en	<i>lel</i>	<i>ob</i>
lbn	<i>lel/2 eq</i>	<i>ob/2 ax</i>
mbn	<i>lel/1 eq, 1 ax</i>	<i>ob/1 eq, 1 ax</i>
ibn	<i>lel/1 eq, 1 ax</i>	<i>ob/1 eq, 1 ax</i>

In the three lbn complexes studied all methyl groups are equatorial; this explains that H_{strain} is close to zero in these cases.

Corey and Bailar⁵ stated that in tris(1-methyl-1,2-ethanediamine) complexes the energy difference between a ring conformation with an axial methyl group and a conformation with an equatorial methyl group probably is in excess of 8 kJ mol⁻¹ per CH₃-group.

Niketić and Woldbye³ arrived at 9.2 kJ mol⁻¹ per CH₃-group for the *ax*-*eq* difference in lbn complexes.

For comparison the data in Table 2 yields *ca.* 8 kJ mol⁻¹ in mbn rings and *ca.* 14 kJ mol⁻¹ in ibn rings for the average value of H_{strain} per axial CH₃-group.

So far the experimental results have been discussed in terms of the orientation of methyl groups. For a more detailed analysis differences between *lel* and *ob* conformations should also be taken into account.^{1,9}

It is generally accepted that in, *e.g.*, [Co(en)₃]³⁺ a *lel* conformation is energetically favoured relative to an *ob* conformation, and an evaluation by Corey and Bailar⁵ led to *ca.* 2.5 kJ mol⁻¹ per ring for this *ob*-*lel* strain enthalpy difference.

Studies by Sudmeier *et al.*¹⁰ indicate that in solution [Co(en)₃lel₂ob]³⁺ is the most abundant form as a result of combined enthalpy and entropy effects. This might explain the fact that the experimental strain enthalpy for [Co(en)₃]³⁺ is found to be higher than for, *e.g.*, [Co(lbn)₃lel₃]³⁺. But it should be noted that equatorial *C*-methyl-substitution in itself

may lower the strain enthalpy, as it was shown in a theoretical study of [CoCl₄(en)]⁻.¹⁵

In the discussion given here it has been assumed that ring conformations are either λ or δ . Although this assumption may seem reasonable it should be remembered that for the present some intermediate compromise between λ and δ cannot be excluded in all cases.

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