

## QUANTUM CHEMISTRY COMPUTATION OF STABILITY CONSTANT OF COBALTHEXAMINE ION IN AQUEOUS SOLUTION. AN ATTEMPT

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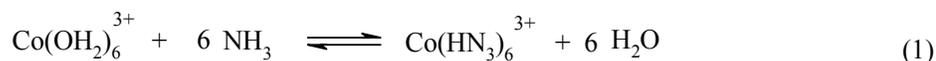
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Free enthalpy for formation of the cobalthexamine cation in aqueous solution was calculated by an ab initio method at the 3-21G level, with a polarisable continuum method (BemCalc) for hydration free enthalpies. The calculated  $\Delta G = -21.25$  kcal/mol compares favourably with  $\Delta G = -31.8$  kcal/mol from the experimental stability constant.

Computation of stability constants for transition metal complexes imply calculations of in vacuo formation energies of participants to the corresponding equilibrium, of hydration energies

and of various entropy effects. Here we attempt to compute the  $\Delta G$  corresponding to the stability constant of cobalthexamine cation in aqueous solution, i.e. to the equilibrium:



The experimental value of the stability constant (25°C),<sup>1</sup>  $K = 1.34 \cdot 10^{23}$ , corresponds to  $\Delta G = -31.8$  kcal/mol for the abovementioned equilibrium. Ab initio method at the 3-21G level<sup>2</sup> was used for internal energy calculations of the participants and the BemCalc method<sup>3-6</sup> for hydration free energies; the last yields good results for higher valence cation hydrations.

Although modern computational chemistry methods are rather successful in calculation of molecular stability and hydration effects, applications to stability constants of complex ions are rather rare. Stabilities of cobalt complexes were evaluated with a second order perturbational method based upon calculated electronic energy levels,<sup>7</sup> solvation of metal complexes was discussed on hand of relativistic effects in ZDO methods,<sup>8</sup> and, more recently, DFT-methods were used to calculate stability of spin states for some Co(II)- complexes.<sup>9</sup>

### METHODS

Internal energies,  $U_i$ , of the participants to equilibrium (1) are calculated by an ab initio method at the 3-21G level<sup>2</sup>. These  $U_i$  values, listed in kcal/mol in Tab. 1, are energies of formation out of free nuclei and electrons (at 0<sup>0</sup>K).

Hydration energies,  $G_i$ , were calculated by the BemCalc method<sup>3-6</sup> with a dielectric constant  $D_{\text{ext}} = 78.5$  for the exterior polarisable continuum (water) and  $D_{\text{int}} = 4$  for the polarising particles. Geometries, for BemCalc, are these calculated by our ab initio method, with Van der Waals radii 1.20 Å, 1.54 Å and 1.40 Å for the H, N and O atoms<sup>10,11</sup> and 0.61 Å, 0.645 Å for the  $\text{Co}^{3+}$  and  $\text{Fe}^{3+}$  cations. These central cations are actually not in direct contact with the polarisable continuum.

No corrections for zero point energies or translational, rotational and vibrational entropy effects were performed. As numbers of particles on both sides equilibrium (1) are equal and their

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structures similar, such corrections are expected largely to cancel. The  $\Delta G$  for equilibrium was

equated to the algebraic sums of internal energies,  $\Delta U_i$ , and hydration free enthalpies,  $\Delta G_i^h$ :

$$\Delta G = \Delta U_i + \Delta G_i^h \quad (2)$$

Table 1

Results of internal energy and hydration free enthalpy calculations

Particle	$\Delta U_i$	$\Delta G_i^h$
H <sub>2</sub> O	-47430.90	<b>-8.915</b>
NH <sub>3</sub>	-35060.00	<b>-1.600</b>
Co(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup>	-1072481.05	<b>-428.81</b>
Co(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>	-1146688.33	<b>-467.59</b>
Fe(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup>	-998207.41	<b>-423.60</b>
<b>Fe(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup></b>	<b>-1072416.07</b>	<b>-464.22</b>

$U_i$  - internal energies (vacuum),  $G_i^h$  - hydration free enthalpies, kcal/mol

## RESULTS

According to equation (2) and Tab. 1, the result for equilibrium (1) is  $\Delta G = -21.25$  kcal/mol which compares favourably to the experimental  $\Delta G = -38.8$  kcal/mol. For the corresponding equilibrium for the, unstable in water, ferihexammine cation Fe(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>, the computed value,  $\Delta G = -18.03$  kcal/mol, yields an about 200 times lower predicted stability constant than for the stable cobalthexammine cation.

For the in vacuo dissociation,  $ML_6^{3+} \leftrightarrow M^{3+} + 6 L$ , our ab initio 3-21G computations yield 847.8 kcal/mol for Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> and 822.4 kcal/mol for Fe(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>. The difference, 24.5 kcal/mol is in agreement with expectation for both electrostatic effect (smaller radius for Co<sup>3+</sup> than for Fe<sup>3+</sup>) and the classic ligand field effect (Co<sup>3+</sup> - d<sup>6</sup> electronic structure, Fe<sup>3+</sup> - d<sup>5</sup> electronic structure).

## CONCLUSIONS

The calculated free enthalpy,  $\Delta G$ , for the stability constant of Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> in aqueous solution compares favourably with the  $\Delta G$  corresponding to the experimental stability constant, albeit the rather low degree of sophistication of our theoretic calculations. This

encourages us to develop more exact methods for such computations, including the zero point energy and entropy corrections.

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