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A PRELIMINARY STUDY ON CONFORMATIONAL ANALYSIS OF ION PAIRS CONTAINING $[Co(en)_3]^{3+}$

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The conformational analysis was performed for the systems of the ion pairs, Λ-$[Co(en)_3]^{3+}$-ClO_4^--, -SO_4^{2-}-, -PO_4^{3-}-, and -$tart^{2-}$-nH_2O. The analysis of the Λ-$[Co(en)_3]^{3+}$-$tart^{2-}$-$25H_2O$ systems gave the results consistent with the experimental data of the stereoselective ion associations, in which the approximation of a dielectric constant dependent on inter-charge distance was made. The structures of Λ-$[Co(en)_3]^{3+}$-$tart^{2-}$ suggest that two hydroxyl groups of a tartrate ion play an important role.

There have been no examples of conformational analysis (strain-energy minimization) for the metal complex systems in which intermolecular electrostatic interactions have also been considered. Recently, Lifson et al. reported the study of the energetics of packing of the carboxylic acid crystals, where the van der Waals and electrostatic contributions to the overall lattice energy of each crystal, were presented and their relative importance was evaluated.1) Clementi et al. reported a series of Monte Carlo simulations of the water structure around Zn^{2+} and $Zn^{2+}\cdot CO_2$.2)

This paper presents a preliminary study on conformational analysis for some ion pairs between a metal complex ion and its counter ion. In energy minimization calculation, a modification of the MMI computer program3) was used, containing van der Waals and Coulomb potential functions of non-bonded interactions. The inter-ionic interaction in an ion pair is regarded to be a balance between van der Waals repulsion and electrostatic attraction. It was presumed that almost all charges of an ion are distributed to certain atoms on the surface, for example, twelve hydrogen atoms of amino groups in a $[Co(en)_3]^{3+}$ ion and four oxygen atoms (and/or their lone pairs of electrons) in a PO_4^{3-} ion. On the other hand, the partial atomic charges in a tartrate ion and a water molecule were computed mainly on the basis of empirical data of bond-dipole moments.4) The initial structure of each ion pair was prepared by the addition of a counter ion to a complex ion with reference to the crystal structure data.5) Then several water molecules were added to the ion pair, their oxygen and hydrogen atoms being positioned near the positively and negatively charged sites of the ion pair, respectively.

First, Λ-$[Co(en)_3]^{3+}$-XO_4^{n-}-$29H_2O$ systems were analyzed and the results are shown in Table 1. It can be seen that the electrostatic interaction energy is conspicuously large in each system. In case 1, the effective dielectric constant, ε in the electrostatic energy function was taken to be equal to 2, and in Case 2, ε was calculated from the function dependent on inter-charge distance, r,6) that is, ε has a constant value of 2 up to 3 Å, and then sharply increases with increasing distance, and from 4 to 10 Å, gradually approaches to 78.5 ($r \geq 10$ Å; $\varepsilon = 78.5$). The three systems converged, giving the similar structures. It is reasonable that the greater the charge on the oxy-anion, the more largely the system is stabilized.

Figure 1 shows an ion-pair structure ($XO_4^{n-} = PO_4^{3-}$) in Case 2, which is very similar to the corresponding one in Case 1. In this structure, the PO_4^{3-} ion is twisted about 60° from that proposed by Mason,7) about the threefold axis of the ion pair. It should be noted that a contribution from the energy of hydrogen-bond interaction has not been explicitly included in this empirical potential. Therefore, the structure might be somewhat changed by more detailed calculation.

Table 1. The final energy terms for the Λ-$[Co(en)_3]^{3+}$ - XO_4^{n-} - $29H_2O$ systems

		Bond Stretching	Angle Bending	Torsion	van der Waals	Electro-static	Total	
Case 1	ClO_4^-	15.1	37.5	70.2	-108.6	-359.5	-345.3	kJ/mol
	SO_4^{2-}	16.0	43.7	72.7	-95.0	-601.8	-564.4	
	PO_4^{3-}	19.9	56.8	73.9	-63.6	-774.2	-687.1	
Case 2	ClO_4^-	36.9	80.9	62.0	-46.1	-419.5	-285.8	
	SO_4^{2-}	35.3	108.9	69.0	-45.4	-532.3	-364.5	
	PO_4^{3-}	50.9	156.6	73.0	-31.6	-657.2	-408.4	

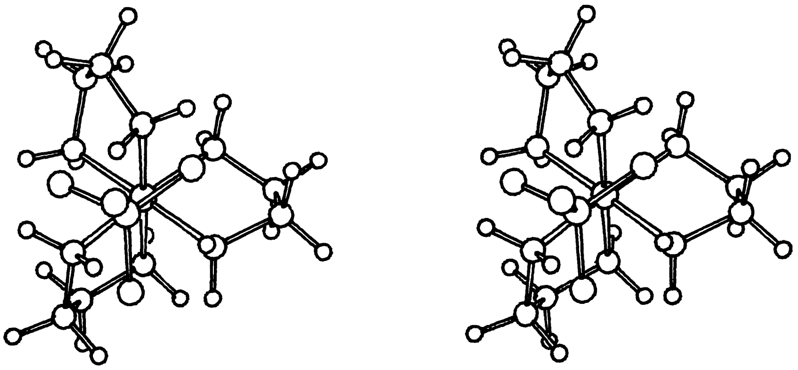

Fig.1. A stereopair showing Λ-$[Co(en)_3]^{3+}$ - PO_4^{3-} (- $29H_2O$) as viewed down the threefold axis of the ion pair. The surrounding water molecules are omitted for the simplicity.

Table 2 shows the analysis data on Λ-$[Co(en)_3]^{3+}$ - $tart^{2-}$ - $25H_2O$ systems. Yoneda and Taura reported that the ion-association constants for these systems in aqueous solutions are 13 ((+)tart^{2-}), 11 ((-)tart^{2-}), and 40 (meso-tart^{2-}).8) The results in Case 1 are incompatible with the experimental ones. It may be due to the overestimation of long-range electrostatic interactions. On the other hand, in Case 2, the estimation of them was improved and the calculated results were consistent with the experimental data of ion-association constants.

Figure 2 shows the ion-pair structures in the Λ-$[Co(en)_3]^{3+}$ - $tart^{2-}$ - $25H_2O$ systems (Case 2). (Each structure in Case 1 was very similar to the corresponding one in Case 2.) In all three systems, two hydroxyl groups of a tartrate ion are

Table 2. The final energy terms for the Λ-$[Co(en)_3]^{3+}$ - $tart^{2-}$ - $25H_2O$ systems

		Bond Stretching	Angle Bending	Torsion	van der Waals	Electro- static	Total	
Case 1	(+)	18.5	47.5	64.1	-51.2	-706.7	-627.9	kJ/mol
	(-)	17.2	47.8	61.4	-50.4	-695.6	-619.7	
	meso	17.2	62.3	62.2	-55.4	-679.6	-593.2	
Case 2	(+)	47.0	124.4	62.5	-50.8	-578.3	-395.2	
	(-)	49.2	156.3	65.7	-32.7	-629.0	-390.4	
	meso	47.4	156.8	65.3	-26.5	-716.7	-473.8	

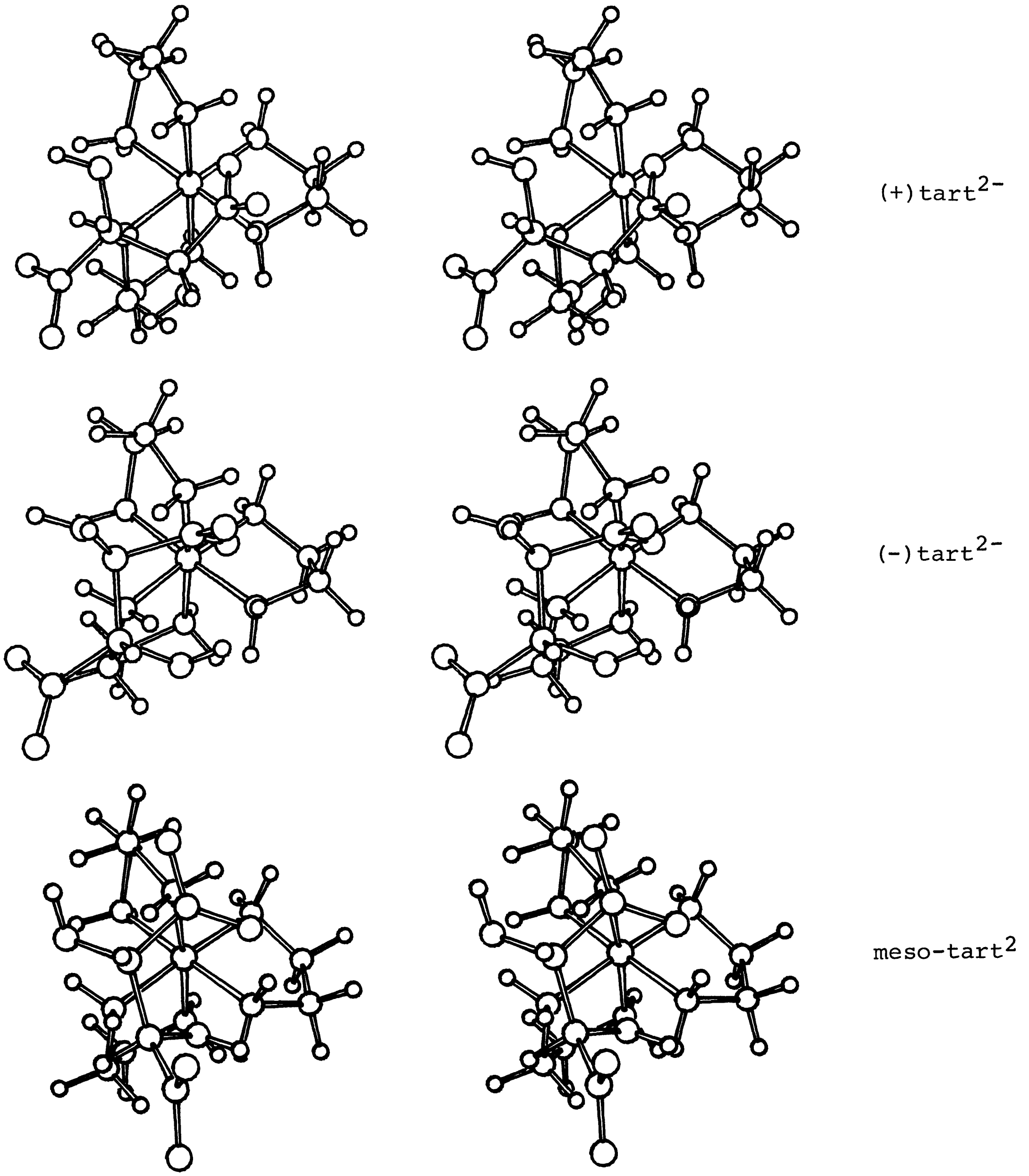

Fig.2. Stereopairs showing Λ-$[Co(en)_3]^{3+}$ - $tart^{2-}$ (- $25H_2O$) as viewed down the threefold axis of the cation. The surrounding water molecules are omitted for the simplicity.

considered to play an important role in the ion association since the distance between the hydroxyl oxygen and the nearest nitrogen atoms are 2.94 and 3.49 Å ((+)tart^{2-}), 3.05 and 3.32 Å ((-)tart^{2-}), and 2.72 and 3.09 Å (meso-tart^{2-}). The shortest distance between a nitrogen and a carboxylate oxygen atom is 2.91 Å ((+)tart^{2-}), 2.72 Å ((-)tart^{2-}), and 3.02 Å (meso-tart^{2-}). A few reports have already suggested that two hydroxyl and one carboxylate groups take part in the formation of these ion pairs[8,9] and furthermore the structure of Λ-[Co(en)$_3$]$^{3+}$-(+)tart^{2-} is similar to that in Λ-[Co(en)$_3$]Br·(+)tart·5H$_2$O the crystal structure of which Kushi et al. have determined.[5b] However, these ion-pair structures changed markedly when water molecules around tartrate ion were removed from the systems. That is, two carboxylate groups more strongly interact with the complex ion in all systems of both Λ-[Co(en)$_3$]$^{3+}$-tart^{2-}-9H$_2$O and Λ-[Co(en)$_3$]$^{3+}$-tart^{2-} (without water molecules), though the results obtained were energetically consistent with experimental information. These results suggest that it is important to take into consideration the interaction with solvent molecules in evaluating the state of dissolved ions or molecules.

The present conformational analysis estimates only the strain energy for the energy-minimized structure as significant. It is different from the method of "molecular dynamics" in which a number of energy states of a system are statistically treated. Now there is no guarantee that the final strain energy can be related to the thermodynamical property of each system. If the energy-minimized structure was a "local minimum" structure, such a comparison would have less meaning. This remains a subject for further study with the subjects for the determination of the initial structure and the approximation of the empirical potential.

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