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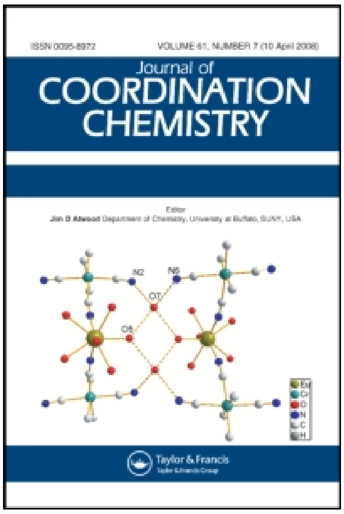

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Why does spontaneous resolution take place? (empirical force-field calculations)

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WHY DOES SPONTANEOUS RESOLUTION TAKE PLACE? (EMPIRICAL FORCE-FIELD CALCULATIONS)

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Empirical force-field calculations were performed on $[Ag\{Co(aet)(en)_2\}](NO_3)_3$ (aet = $H_2NCH_2CH_2S^-$) systems to further understand the occurrence of spontaneous resolution [1]. Results of the calculations reveal that the ΛΛΛΛ strand is more stable than the ΛΔΛΔ strand. Furthermore, the spontaneously crystallized system ΛΛΛΛ, with six constitutional repeating units (CRUs), ΛΛΛΛΛΛ, was more stable than the hetero-chiral system, ΔΔΔΔ, with the same six units as above. In addition, the calculations revealed that electrostatic interactions contributed most of the stability to the system.

Keywords: Spontaneous crystallization; Calculations; Absolute configurations

INTRODUCTION

Spontaneous resolution has long been noted in connection with optical resolution and the relative determination of absolute configurations of metal complexes [2]. In general, optical isomers crystallize in racemates. Spontaneous crystallization or spontaneous resolution, in which a crystal consists of only optically active isomers, is atypical. Shimura *et al*. examined the spontaneous resolution of cobalt(III) complexes and clarified their mechanisms using solubility measurements [3]. Tange and Yoshikawa [4] showed that crystal growth of *l*-$[Co(ox)(en)_2]Cl$ is inhibited in the presence of *d*-$[Co(ox)(en)_2]^+$, and force-field calculations revealed that the homo-chiral system is more stable than the hetero-chiral system. Recently, Katsuki *et al*. reported the spontaneous resolution of nickel(II) complexes [5].

In order to further understand spontaneous crystallization, a single-stranded $\{Co(III)–Ag(I)\}_n$ polymeric complex, $[Ag\{Co(aet)(en)_2\}](NO_3)_3$ (Fig. 1), that is spontaneously resolved upon crystallization was evaluated in the present study.

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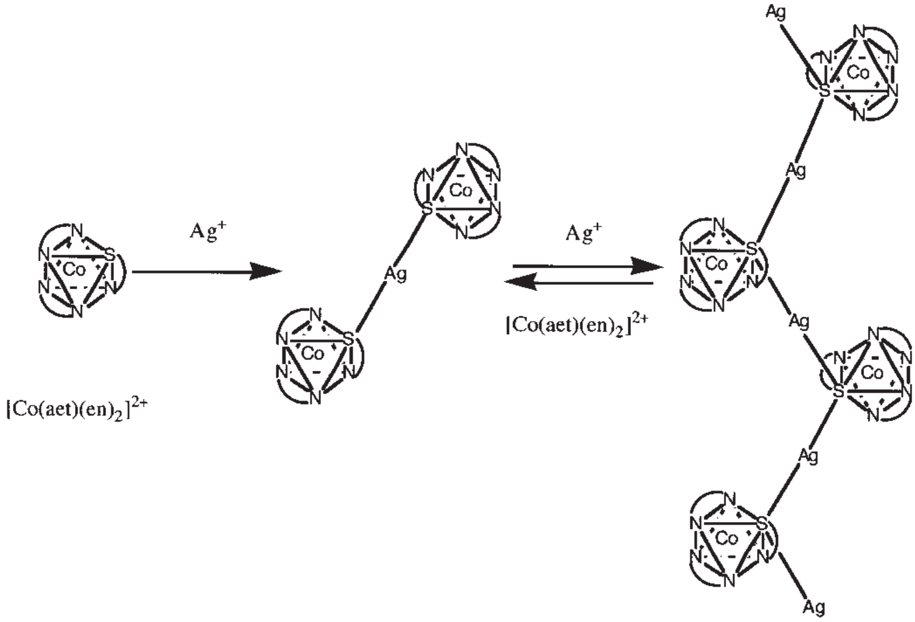

FIGURE 1 Formation and depolymerization of a single strand polymer.

The mononuclear complex $[Co(aet)(en)_2](NO_3)_2$ reacts with $AgNO_3$ forming a sulfur-bridged Co(III)–Ag(I)–Co(III) trinuclear complex, $[Ag\{Co(aet)(en)_2\}_2](NO_3)_5$. Further reaction of this trinuclear complex with $AgNO_3$ leads to the formation of a single-stranded $\{Co(III)–Ag(I)\}_n$ polymeric complex, $[Ag\{Co(aet)(en)_2\}](NO_3)_3$. The components A and B of the constitutional repeating unit (CRU)–$(A–B)_n$– are defined as $[Co(aet)(en)_2]^{2+}$ and Ag(I), respectively, in the present complex system. The absolute configurations of A are identical in the present spontaneously crystallized system.

The empirical force-field method was used to calculate the strain energies of molecules using empirical parameters [6]. The structure was optimized to obtain a structure with a minimum strain energy. The total strain energy of a system is expressed by the following equation:

$$E(\text{total}) = E(\text{bond}) + E(\text{angle}) + E(vdW) + E(\text{torsion}) + E(\text{charge})$$

where *E*(bond) is the strain energy due to bond stretching, *E*(angle) is the strain energy due to bond–angle deformations, *E*(*vdW*) is the energy of van der Waals interactions, *E*(torsion) is the strain energy due to dihedral–angle deformations and *E*(charge) is the energy of electrostatic interactions.

CALCULATIONS

The following systems were considered in the calculations.

1. Four isolated CRUs where the absolute configurations of a series of $[Co(aet)(en)_2]^{2+}$ were $\Lambda\Lambda\Lambda\Lambda$ and $\Lambda\Delta\Lambda\Delta$ (Fig. 2).

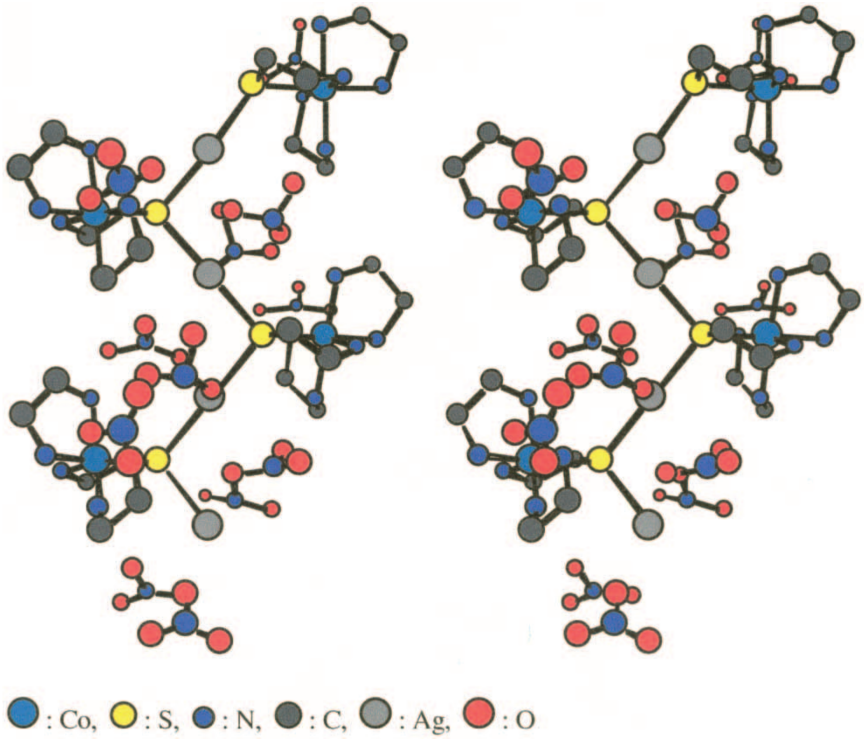

FIGURE 2 Stereoview of system **1**.

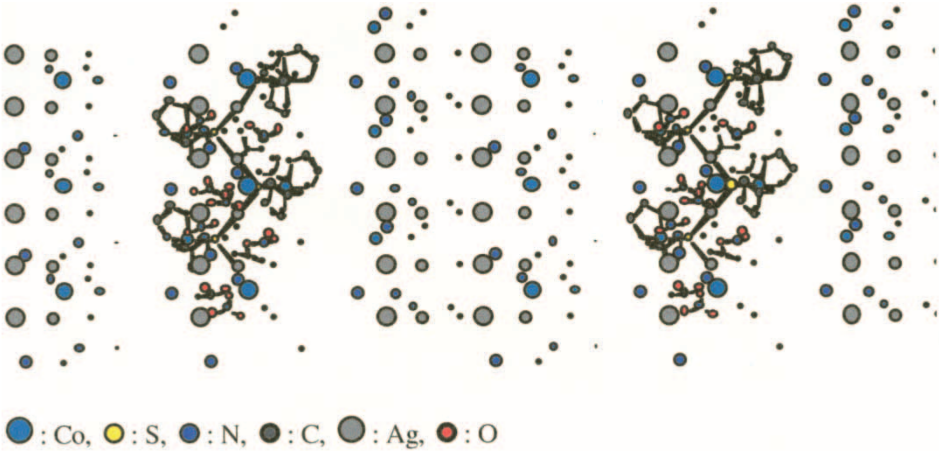

FIGURE 3 Stereoview of system **2**.

2. Four CRUs (absolute configurations of $[Co(aet)(en)_2]^{2+}$; ΛΛΛΛ and ΔΔΔΔ) surrounded by eight sets of six CRUs (absolute configurations of $[Co(aet)(en)_2]^{2+}$; ΛΛΛΛΛΛ) (Fig. 3).

Calculations were carried out using the modified MM2 (Molecular Mechanics Version 2) program [6]. The values used for the force constants and parameters are listed in

TABLE I Parameters for force field potential function in MM2

Force constants for bond stretching

Bond type	K_s (mdyn/Å)	r_θ (Å)	*Bond type*	K_s (mdyn/Å)	r_θ (Å)
C–C	5.0	1.51	Co–S	1.75	2.28
C–H	5.0	1.09	Ag–S	1.0	2.54
C–N	6.0	1.485	C–S	3.21	1.84
N–H	5.6	1.03	N–O	5.62	1.24
Co–N	1.75	1.96	O–LP	4.6	0.5

Force constants for bond–angle deformation

Bond–angle type	K_s (mdyn/Å rad^{-2})	θ_0 (°)	*Bond–angle type*	K_s (mdyn/Å rad^{-2})	θ_0 (°)
C–C–H	0.694	109.47	Co–S–C	0.480	96.60
H–C–H	0.605	109.47	Co–S–Ag	0.480	107.00
C–C–N	0.694	109.47	S–Ag–S	0.030	173.14
C–N–H	0.278	109.47	Ag–S–Ag	0.480	106.77
N–C–H	0.485	109.47	C–C–S	0.694	109.47
H–N–H	0.417	109.47	S–C–H	0.485	109.47
N–Co–N	0.400	90.0, 180.0	O–N–O	0.540	120.00
Co–N–C	0.278	109.47	LP–O–LP	0.240	120.00
Co–N–H	0.278	109.47	N–O–LP	0.300	109.47
N–Co–S	0.400	90.0, 180.0			

Force constants for torsional deformation

Torsional type	V_3 (kcal/mol)	*Torsional type*	V_3 (kcal/mol)
H–C–C–H	0.217	C–C–S–Ag	0.367
C¯C–N–H	0.217	H–C–S–Ag	0.320
H–C–N–H	0.144	N–C–C–S	0.180
N–C–C–H	0.327	S–C–C–H	0.217
N–C–C–N	0.164	C–C–S–Co	0.367
C–C–N–Co	0.109	H–C–S–Co	0.320
H–C–N–Co	0.217	O–N–O–LP	0.000

Table I. The initial coordinates were obtained from X-ray structure analysis [1]. Three NO_3^- ions were used as counter ions for each CRU. To maintain the framework, Ag, Co and $N_{nitrate}$ were fixed at the optimized structure. The electric charge was distributed on each atom as the partial atomic charge for the calculation of electrostatic interactions [Ag, 0.500; Co, 1.000; H_{amine}, 0.150; $N_{nitrate}$, 0.008; LP, −0.112].

RESULTS AND DISCUSSION

The results of the calculations for system **1** are presented in Table II. These calculations revealed that the $\Lambda\Lambda\Lambda\Lambda$ strand was more stable ($-533.60\,\mathrm{kcal\,mol^{-1}}$) than the $\Lambda\Delta\Lambda\Delta$ strand ($-509.61\,\mathrm{kcal\,mol^{-1}}$).

Table III summarizes the results of the calculations on system **2**. The calculations revealed that the spontaneously crystallized system, $\Lambda\Lambda\Lambda\Lambda$ with six CRUs ($\Lambda\Lambda\Lambda\Lambda\Lambda\Lambda$) is more stable than the hetero-chiral system. Systems (i)–(iii) are independent of one another. Calculations revealed that the $\Lambda\Lambda\Lambda\Lambda$ system was lower in energy than the optimized $\Delta\Delta\Delta\Delta$ system by $3\,\mathrm{kcal\,mol^{-1}}$ (ii); however, the difference in (i) was much larger, $78\,\mathrm{kcal\,mol^{-1}}$. This difference arises mainly from the charge interactions in the (i)–(ii)–(iii) system. The *E*(*vdW*) of systems (i) and (iii) is extremely large, as these are nonrealistic systems, but that of the (i)–(ii)–(iii) system is cancelled out. In the current evaluation, the energy of the electrostatic

TABLE II Final strain energy (kcal/mol) for each structure of system **1**

	ΛΛΛΛ	ΛΔΛΔ
E(bond)	25.64	30.65
E(angle)	33.23	34.37
E(*vdW*)	−7.07	−8.65
E(torsion)	11.14	18.79
E(charge)	−596.54	−584.77
E(total)	−533.60	−509.61

TABLE III Strain energy (kcal/mol) for ΛΛΛΛ and ΔΔΔΔ with six CRUs (ΛΛΛΛΛΛ)

	(i) *Total*	(ii) ΛΛΛΛ	(iii) *Six CRUs*	(i)–(ii)–(iii)
E(bond)	36.34	36.34	0.00	0.00
E(angle)	41.63	41.63	0.00	0.00
E(*vdW*)	25 201.88	5.23	25 201.23	−4.58
E(torsion)	11.14	11.14	0.00	0.00
E(charge)	4199.64	−603.53	4538.97	264.20
E(total)	29 490.62	−509.19	29 740.20	259.61
	(i) *Total*	(ii) ΔΔΔΔ	(iii) *Six CRUs*	(i)–(ii)–(iii)
E(bond)	37.51	37.51	0.00	0.00
E(angle)	46.63	46.63	0.00	0.00
E(*vdW*)	25 194.78	4.01	25 201.23	−10.46
E(torsion)	12.19	12.19	0.00	0.00
E(charge)	4277.88	−606.48	4538.97	345.39
E(total)	29 568.98	−506.15	29 740.20	334.93

interactions made the greatest contribution to the stability of the system. The stereoview of system **2** is shown in Fig. 3.

Thus, the strain energy calculations for both systems **1** and **2** show that a homochiral, spontaneously crystallized system, is more stable than a hetero-chiral system.

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