Cobalt(III) Complexes with Quadridentate Ligands. XII.[1] Crystal Structure of *cis*-α-Salicylato(triethylenetetramine)cobalt(III) Chloride Pentahydrate

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The structure of the *cis*-α-salicylato(triethylenetetramine)cobalt(III) ion was confirmed by an X-ray crystallographic analysis. The conformation of the triethylenetetramine part of this complex was slightly different from the *cis*-α-glycinato(triethylenetetramine)cobalt(III) ion. A comparison of the stability of the this *cis*-α-salicylato complex with that of the *cis*-α-glycinato complex on the cation-exchange resin and in water, respectively, are described. The signals of the ^{1}H NMR and ^{13}C NMR spectra were assigned based on the crystal structure.

In this series we have reported on the preparation and chemical properties of *cis*-β_1 and *cis*-β_2-(trien)cobalt(III) complexes with bidentate ligands (e.g. salicylato,[2] thiosalicylato,[3] and salicylaldehydato[4]) (trien=triethylenetetramine=1,4,7,10-tetraazadecane). These complexes exists in three isomeric forms as *cis*-α, *cis*-β_1, and *cis*-β_2. Concerning the *cis*-α-isomer of these mixed-ligand cobalt(III) complexes with bidentate ligands and trien, the preparation of oxalato[5] and glycinato complexes[6—10] has been reported, and the structures of glycinato complexes have been confirmed by an X-ray analysis. Recently, we reported on the preparation and properties of the title complex and its structure speculated from those of *cis*-β-isomers.[1] We have exerted considerable effort concerning the crystal structure determination of these isomers for an investigation of the detailed properties. However, bad crystal habits hamper the establishment of their stereochemistry.

This report describes the structure determination of the title complex by an X-ray crystallographic analysis, a comparison of the stability with that of the *cis*-α-glycinato(trien)cobalt(III) complex and detailed NMR spectral studies.

Experimental

Material. *cis*-α-Salicylato(trien)cobalt(III) chloride pentahydrate (**1**) was synthesized according to a similar method described in a previous paper[1] as follows: A ethanol solution (40 cm^3) of trien (14.6 g, 0.1 mol) was added to an aqueous solution (30 cm^3) of $CoCl_2 \cdot 6H_2O$ (23.8 g, 0.1 mol) at room temperature. This was an exothermic reaction in which the color of reaction mixture changed to brown from violet. Sodium salicylate (16.0 g, 0.1 mol) was then added to the reaction mixture, and air was introduced for 4 h. The russet solution was warmed to 70 °C for 5 h and then concentrated on a rotary evaporator. The residue was dissolved in methanol, and the solution was passed through a column chromatograph on alumina, then Sephadex LH-20, in order to remove impurities and NaCl. The methanol eluate was concentrated to dryness on a rotary evaporator. The russet solid (26.3 g) was obtained. Pure *cis*-α (8.4 g, 23%), *cis*-β_1 (1.9 g, 5%), and *cis*-β_2-isomers (14.0 g, 37%) were isolated from this crude solid according to reported methods.[1,2] Recrystallization of the *cis*-α-isomer from aqueous acetone formed single crystals suitable for X-ray crystallographic analysis.

NMR Spectra. The ^{1}H and ^{13}C NMR spectra were recorded on an EX-400 spectrometer (JEOL).

Isomerization and Ratio of Isomer. Isomerization experiments using a cation-exchange resin (Dowex 50W-X2) were carried out with the complex (0.2 g) in water (100 cm^3). After the solution was sorbed on the resin (100 cm^3), the resin was stirred at room temperature, and then extracted with 0.3 mol dm^{-3} NaCl. The extract was concentrated, and the resulting NaCl was removed by passing through a Sephadex LH-20 column chromatograph. The methanol eluate was concentrated to dryness on a rotary evaporator. A solid (0.15 g) was obtained, this solid was used for isomerization measurements. The ratios of the *cis*-α, *cis*-β_1 and *cis*-β_2-isomers of the reaction mixture and isomerization mixture were determined according to the peak heights of the methylene carbons of the trien ligand of the ^{13}C NMR spectra.

X-Ray Crystallography. A deep-purple plate having approximate dimensions of 0.3×0.2×0.03 mm was selected. A Rigaku AFC5R diffractometer was employed for an X-ray crystallographic analysis with graphite-monochromatized Cu $K\alpha_1$ radiation (λ=1.5406 Å). The crystal belongs to a triclinic system, and the space group is $P\bar{1}$. Table 1 shows the crystal data. Lattice parameters were determined from a least-squares fit of the 2θ values of 25 reflections over the range $35° < 2\theta < 40°$. A total of 3040 independent reflections were collected up to 2θ=120°. Three standard reflections were monitored during data collection. No significant fluctuation was observed. A correction for the absorption was made using an empirical method based on psi scan data. An XTAL system[11] was used for the crystallographic calculations. The structure was solved by the heavy-atom method and refined based on the 2585 observed reflections with $F_o \geq 3\sigma$ (F_o). A full-matrix least-squares method using unit weights was employed for the refinement. The thermal motions of non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at positions calculated from the standard geometry, and the equivalent isotropic thermal parameter of the bonding atom was applied to each hydrogen atom. The parameters of the hydrogen atoms were not refined, but were reset after each refinement cycle.

Table 1. Crystal Data

Formula	$[Co(C_7H_4O_3)(C_6H_{18}N_4)]Cl{\cdot}5H_2O$
Formula weight	466.81
Crystal dimensions/mm	0.30×0.20×0.03
Crystal system	Triclinic
Lattice parameters	
a/Å	12.451(7)
b/Å	13.210(7)
c/Å	7.083(2)
α/°	101.87(4)
β/°	99.90(5)
γ/°	111.12(4)
V/Å^3	1024(1)
Space Group	$P\bar{1}$
Z value	2
D_{calcd}/cm^{-3}	1.514 g
μ (Cu $K\alpha_1$)/cm^{-1}	83.90
No. of observation	2585
Residuals: $R^{a)}$; R_w	0.091; 0.102

a) The large R value otained since the complex **1** was brittle crystal, so more or repeated observation interfered.

Results and Discussion

The positional parameters for non-hydrogen atoms are given in Table 2. The numbering of atoms and the conformation of complex **1** is shown in Fig. 1. The asymmetric unit comprises of a cobalt ion, a dianion form of salicylic acid, a trien, a chloride ion, and five molecules of water (Fig. 2). Water molecules participate in some hydrogen bondings with complex **1**, as shown in Table 3. One of the carboxylate oxygen (O(9)) behaves as an acceptor of three hydrogen bonds from the amino groups. The phenoxide oxygen (O(10)) is an acceptor of a hydrogen atom of the water molecule

Table 2. Atomic Coordinates and Thermal Parameters of Non-Hydrogen Atoms for Complex **1**

Atom	x/a	y/b	z/c	$B_{\text{eq}}$$^{a)}$
Co	0.3842(1)	0.6429(1)	0.2056(2)	2.6
C(1)	0.3014(8)	0.3940(7)	0.2485(13)	2.0
C(2)	0.2548(8)	0.2756(8)	0.2190(15)	2.8
C(3)	0.1435(9)	0.2168(8)	0.2371(17)	3.4
C(4)	0.0745(9)	0.2751(9)	0.2862(17)	3.2
C(5)	0.1132(8)	0.3871(8)	0.3061(15)	2.9
C(6)	0.2277(7)	0.4495(7)	0.2840(12)	1.9
C(7)	0.4271(8)	0.4490(7)	0.2445(12)	2.0
C(8)	0.4704(5)	0.5532(5)	0.2391(9)	2.4
C(9)	0.4920(5)	0.3970(5)	0.2431(10)	2.8
C(10)	0.2574(5)	0.5599(5)	0.2991(9)	2.3
N(11)	0.3041(6)	0.5495(6)	−0.0721(11)	1.9
C(12)	0.2334(9)	0.5970(8)	−0.1819(14)	2.6
C(13)	0.1964(8)	0.6677(9)	−0.0278(16)	3.1
N(14)	0.3013(6)	0.7386(6)	0.1487(11)	2.2
C(15)	0.3865(8)	0.8452(7)	0.1228(14)	2.5
C(16)	0.4844(8)	0.8247(8)	0.0458(14)	2.7
N(17)	0.5187(6)	0.7448(6)	0.1352(11)	2.2
C(18)	0.6221(8)	0.7993(8)	0.3200(15)	2.4
C(19)	0.5777(9)	0.8356(8)	0.4932(15)	2.7
C(20)	0.4672(6)	0.7384(6)	0.4824(11)	2.0
Cl	0.3105(3)	0.8813(2)	0.6114(4)	3.7
O(21)	0.2021(8)	1.0058(7)	0.9126(13)	5.5
O(22)	0.9489(8)	0.9215(8)	0.3065(14)	5.7
O(23)	0.1606(8)	0.9176(9)	0.2257(14)	6.5
O(24)	0.0938(8)	0.6466(8)	0.4073(16)	6.9
O(25)	0.9007(9)	0.6780(8)	0.1989(16)	6.5

a) $B_{\text{eq}}=8/3\,\pi^2(U_{11}+U_{22}+U_{33})$.

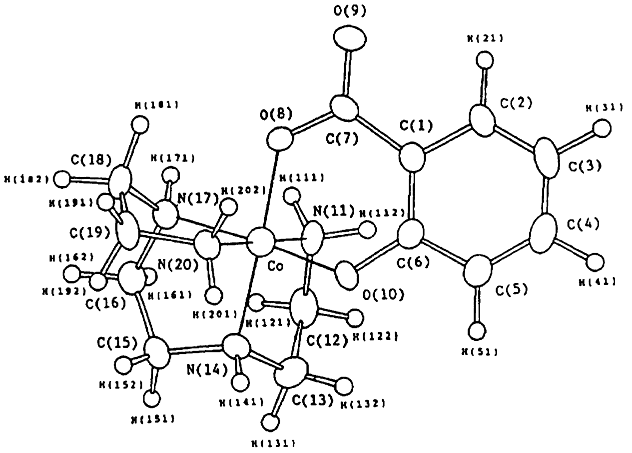

Fig. 1. Numbering of atoms of complex **1**.

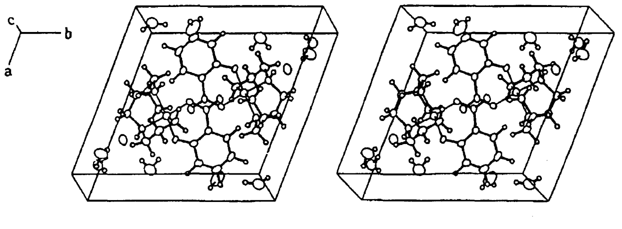

Fig. 2. Stereoview of molecular arrangement of complex **1** in the unit cell.

Table 3. Distances for Hydrogen Bonds for Complex **1**

Intermolecular hydrogen bonds			
Donor	Acceptor	Symmetry operation	Distance between heteroatoms (Å)
N(11)–H(111)	···O(9)	$(1-x, 1-y, 1-z)$	2.92(1)
N(11)–H(112)	···O(25)	$(1-x, 1-y, -z)$	2.99(1)
N(14)–H(141)	···Cl	(x, y, z)	3.39(1)
N(17)–H(171)	···O(9)	$(1-x, 1-y, -z)$	2.89(1)
N(20)–H(201)	···Cl	(x, y, z)	3.28(1)
N(20)–H(202)	···O(9)	$(1-x, 1-y, 1-z)$	3.00(1)
Hydrogen bonds for molecules with water			
Donor	Acceptor	Symmetry operation	Distance between heteroatoms (Å)
O(21)–H(211)	···Cl	(x, y, z)	3.20(1)
O(21)–H(212)	···O(23)	$(x, y, 1+z)$	2.75(1)
O(22)–H(221)	···O(25)	(x, y, z)	2.95(1)
O(22)–H(222)	···O(21)	$(1-x, 2-y, 1-z)$	2.79(2)
O(23)–H(231)	···Cl	(x, y, z)	3.26(1)
O(23)–H(232)	···O(22)	$(-x, y, z)$	2.81(2)
O(24)–H(241)	···O(10)	(x, y, z)	2.81(1)
O(24)–H(242)	···Cl	(x, y, z)	3.13(1)
O(25)–H(251)	···O(24)	$(1+x, y, z)$	2.81(2)

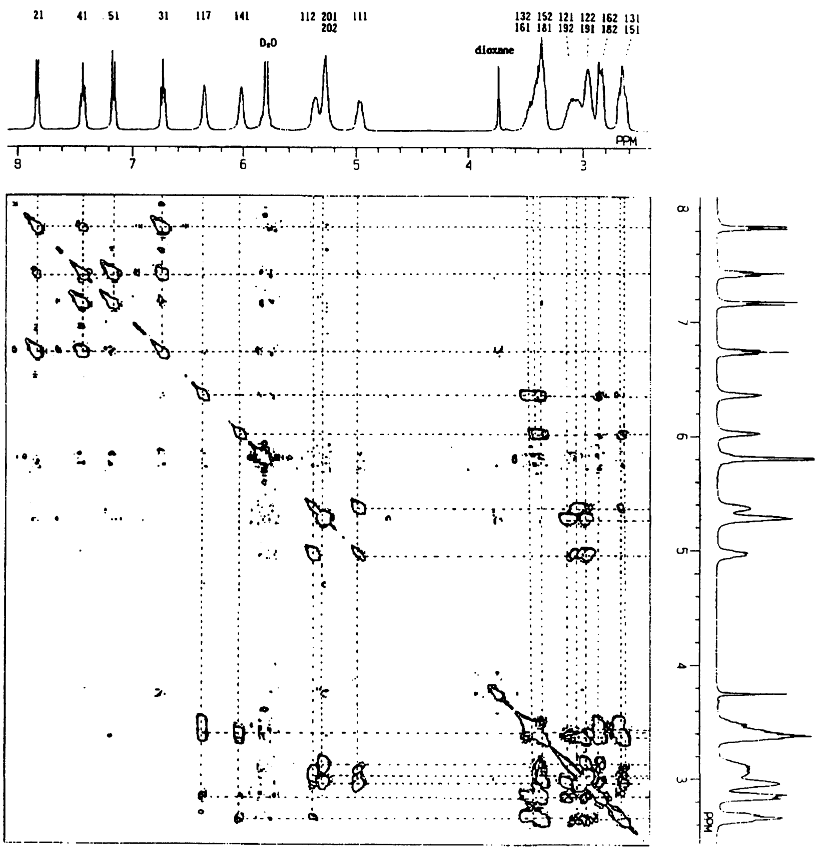

Fig. 3. ^{1}H–^{1}H COSY spectrum of complex **1**. Solvent and standard. 1.8 mol dm^{-3} D_2SO_4, internal DSS.

(O(24)). Selected bond lengths and angles of complex **1** are listed in Tables 4 and 5, respectively. A comparison of selected torsion angles between complex **1** and *cis*-α-glycinato(trien)cobalt(III) complex[10] is listed in Table 6. The cobalt ion is coordinated by six atoms, i.e., two oxygen atoms of salicylic acid and the four nitrogen atoms of trien. The cobalt–oxygen distances (1.88(1)—1.89(1) Å) are slightly shorter than the cobalt–nitrogen distances (1.95(1)—1.96(1) Å). The carboxylate moiety of salicylic acid derivates slightly from the plane of the benzene ring. C(7) is 0.16(2) Å and O(9) is 0.41(2) Å distant from the benzene plane, while O(8) is on the plane. The torsion angles are C(6)–C(1)–C(7)–O(8) and C(6)–C(1)–C(7)–O(9) are −13°(1) and 169°(1), respectively. Though the conformation of the trien molecule is staggered, it is rather distorted. The torsion angles deviate from ±60° by 12—34°. These conformations are probably caused by the coordination and hydrogen bonding. They are sufficiently strong to compensate for the decrease of the resonance energy between the benzene ring and the carboxylate moiety, as well as the increase in the steric repulsions between the hydrogen atoms of the trien molecule. These results could also be explained based on the fact that the conformation of the trien molecule of complex **1** was slightly different from that of the *cis*-α-glycinato(trien)cobalt(III) complex, as shown in Table 6.

Salicylato(trien)cobalt(III) complexes were prepared at pH 7.4. The ratios of the *cis*-α, *cis*-β_1, and *cis*-β_2-isomers of the reaction mixture were about 10 : 3 : 10. This result showed that complex **1** was stable in a near-neutral solution. Although isomerization of complex **1** in water could not be observed, the *cis*-β_1-isomer changed to the *cis*-β_2-isomer. The *cis*-α and *cis*-β_1-isomers of these salicylato complexes on the cation-exchange resin, however, were complatly isomerized to the *cis*-β_2-isomer at room temperature for 5 d, respectively. D. A. Buckingham et al.[9] reported that the equilibration of the *cis*-α, *cis*-β_1, and *cis*-β_2-glycinato(trien)cobalt(III) cations on activated charcoal gave the same products. The ratio was *cis*-α (2.3%), *cis*-β_1 (4.5%), and *cis*-β_2-isomer (93.2%). However, in the isomerization of the *cis*-α and *cis*-β_1-isomers of the salycilato complex under various conditions, the *cis*-α-isomer could not be observed. The difference between the *cis*-α-salicylato and *cis*-α-glycinato complex seems to be a different conformation, due to anion ligands.

Table 4. Selected Bond Lengths (Å) for the Non-Hydrogen Atoms for Complex **1**

Co–O(8)	1.89(1)
Co–O(10)	1.88(1)
Co–N(11)	1.96(1)
Co–N(14)	1.96(1)
Co–N(17)	1.95(1)
Co–N(20)	1.96(1)
N(11)–C(12)	1.46(1)
C(12)–C(13)	1.53(2)
C(13)–N(14)	1.49(1)
N(14)–C(15)	1.50(1)
C(15)–C(16)	1.50(2)
C(16)–N(17)	1.48(1)
N(17)–C(18)	1.50(1)
C(18)–C(19)	1.49(2)
C(19)–N(20)	1.48(1)

Table 5. Selected Bond Angles (°) for the Non-Hydrogen Atoms for Complex **1**

O(8)–Co–O(10)	95.3(3)
O(8)–Co–N(11)	90.6(3)
O(8)–Co–N(14)	174.4(3)
O(8)–Co–N(17)	88.2(3)
O(8)–Co–N(20)	89.3(3)
O(10)–Co–N(11)	92.6(3)
O(10)–Co–N(14)	89.5(3)
O(10)–Co–N(17)	173.0(3)
O(10)–Co–N(20)	88.5(3)
N(11)–Co–N(14)	86.3(3)
N(11)–Co–N(17)	93.4(3)
N(11)–Co–N(20)	178.9(4)
N(14)–Co–N(17)	87.3(4)
N(14)–Co–N(20)	93.7(3)
N(17)–Co–N(20)	85.5(3)
Co–O(8)–C(7)	126.5(6)
Co–O(10) –C(6)	121.5(6)
Co–N(11) –C(12)	112.5(6)
N(11)–C(12)–C(13)	107.0(8)
C(12)–C(13)–N(14)	109.4(8)
Co–N(14)–C(13)	106.9(6)
Co–N(14)–C(15)	110.0(6)
C(13)–N(14)–C(15)	115.0(8)
N(14)–C(15)–C(16)	110.4(8)
C(15)–C(16)–N(17)	110.7(9)
Co–N(17)–C(16)	110.6(6)
Co–N(17)–C(18)	107.1(6)
C(16)–N(17)–C(18)	115.3(7)
N(17)–C(18)–C(19)	108.3(8)
C(18)–C(19)–N(20)	107.0(7)
Co–N(20)–C(19)	111.7(6)

The ^{1}H and ^{13}C NMR spectra of complex **1** were measured in 1.8 mol cm^{-3} D$_2$SO$_4$. In the ^{1}H NMR spectrum, the five signals at $\delta = 2.60$—3.55 were assigned

Table 6. Comparison of Selected Torsion Angles (Å) between Complex **1** and *cis*-α-Glycinato(trien)-cobalt(III) Complex [Torsion angles (Å) of glycinato complex[10]]

Co–N(11)–C(12)–C(13)	−27(1) [−26.4]
N(11)–C(12)–C(13)–N(14)	45(1) [45.2]
C(12)–C(13)–N(14)–Co	−42(1) [−39.7]
Co–N(14)–C(15)–C(16)	28(1) [28.1]
N(14)–C(15)–C(16)–N(17)	−37(1) [−39.0]
C(15)–C(16)–N(17)–Co	28(1) [28.1]
Co–N(17)–C(18)–C(19)	−45(1) [−43.3]
N(17)–C(18)–C(19)–N(20)	48(1) [45.2]
C(18)–C(19)–N(20)–Co	−29(1) [−26.1]

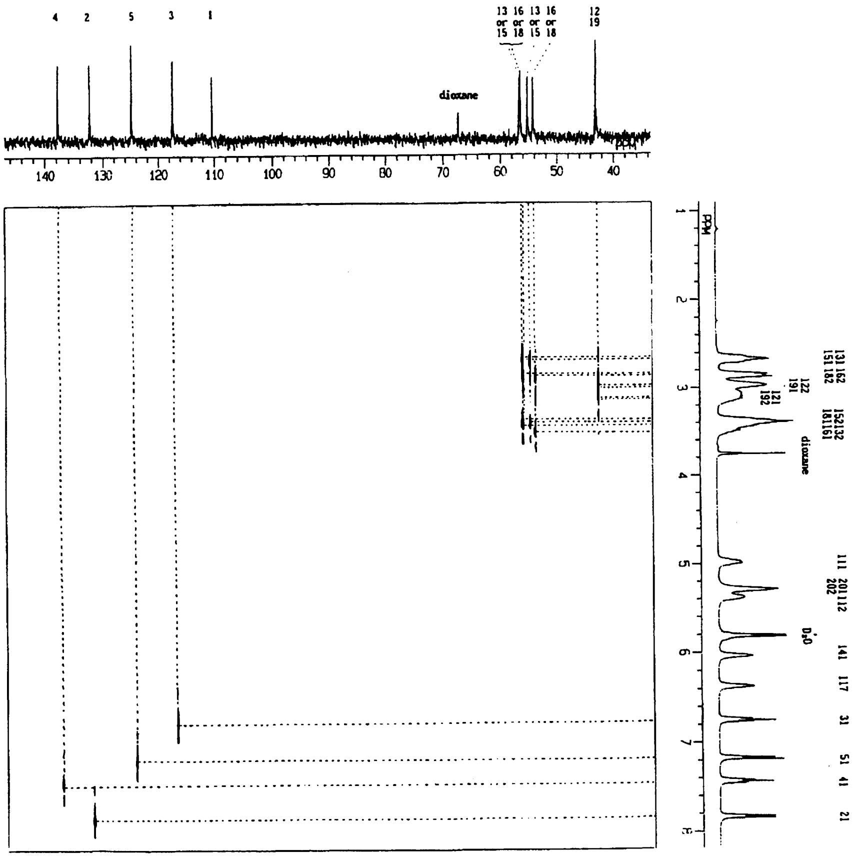

Fig. 4. ^{13}C–^{1}H COSY spectrum of complex **1**. Solvent and standard. 1.8 mol dm^{-3} D_2SO_4, internal DSS and dioxane (δ=67.4).

to the methylene protons of the coordinated trien ligand. The middle-field five signals of the broad singlet at δ=4.95, 5.28, 5.36, 6.05, and 6.37 in the intensity ratio of 1 : 2 : 1 : 1 : 1 were assigned to primary and secondary amine protons of the coordinated trien ligand, respectively. The lower field four sharp signals at δ=6.75, 7.16, 7.44, and 7.83 were assigned to the aromatic protons of the salicylato ligand.

An experiment concerning the Dreiding model based on the definitive crystal structure of **1** and X-ray crystallogrophic analytical data indicated that the dihedral angle between protons of H(111)–H(122), H(131)–H(141), H(141)–H(151), H(162)–H(171), H(171)–H(182), and H(191)–H(201) have about 90°, respectively. Therefore, in the ^{1}H–^{1}H correlation spectroscopy (COSY) spectrum (Fig. 3) of **1**, the relationships between these protons were not clarified. On the other hand, the correlation clarified between the primary or secondary amine protons and methylene protons, which have dihedral angle of about 15° or 120°. In the five signals due to amine protons, the relationship between the signals at δ=4.95 and 5.36 were clarified. These signals could thus be assigned to the primary amine proton, and the higher signals (δ=4.95) can be explained by the fact that the H(111) is closely located above the face of the carbonyl group of the salicylato ligand. The H(111) signal shows an upfield shift due to magnetic anisotropic effects of the carbonyl group. The different chemical shifts of the secondary amine protons are also considered to be due to the fact that the H(141) is at a position *trans* to the coordinated carbonyl oxygen. Thus, the signals of complex **1** were assigned as shown in Fig. 3. In the ^{13}C–^{1}H COSY spectrum of **1**, although the NH side methylene carbons could not be clearly assigned, other NH_2 side methylene carbons and aromatic carbons were assigned, as shown in Fig. 4.

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