**Table IV.** Comparison of Theoretical Statistical Constants with Normalized Experimental Equilibrium Constants

| Equilibrium | Log (statistical) | Log (normalized experimental)$^a$ Graphical | Log (normalized experimental)$^a$ Computer |
|---|---|---|---|
| $^3/_4PdBr_4{}^{2-} + {}^1/_4PdCl_4{}^{2-} = PdBr_3Cl^{2-}$ | 0.60 | 0.39 | 0.64 |
| $^1/_2PdBr_4{}^{2-} + {}^1/_2PdCl_4{}^{2-} = PdBr_2Cl_2{}^{2-}$ | 0.78 | 0.43 | 0.64 |
| $^1/_4PdBr_4{}^{2-} + {}^3/_4PdCl_4{}^{2-} = PdBrCl_3{}^{2-}$ | 0.60 | 0.46 | 0.71 |

$^a$ Log (normalized experimental) = $\log {}^{\dagger}\beta_n - (n/4) \log {}^{\dagger}\beta_4$, where $n$ (=1, 2, 3) is the number of chlorides in the product.

verts the system in the opposite sense from what occurred with palladium.

The study of mixed-ligand complexes not only gives information about the nature of the mixed-ligand complexes but is possibly the best means of obtaining information on the relative stabilities of complex systems. As an example, it is almost impossible to decide upon the relative stabilities of the halide complexes of palladium by going to the literature.[10] Using measurements of the type performed in this investigation one has the advantage of evaluating the constants under identical conditions and the relative stabilities are obtained by determining only half of the number of constants that are required by the conventional approach.[6]

Clearly many other systems should be studied in order to understand the relative stabilities of ligand complexes in various solvents. Studies of mixed-ligand complexes should prove most valuable.

**Registry No.** $PdCl_4{}^{2-}$, 14349-67-8; $PdBr_4{}^{2-}$, 14127-70-9; $PdClBr_3{}^{2-}$, 36673-40-2; $PdCl_2Br_2{}^{2-}$, 36673-07-9; $PdCl_3Br^{2-}$, 36655-12-6.

(10) L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964; Supplement No. 1, 1971.

---

Contribution from the Chemistry Department, New Mexico
State University, Las Cruces, New Mexico 88001

# Cobalt(III) Complexes of Linear Tetramines. VI. Stereochemistry of Dichloro(4,8-diaza-2,10-undecanediamine)cobalt(III) Complexes

PATRICIA C. HARRINGTON,[1] SIEGFRIED LINKE, and M. DALE ALEXANDER*

*Received June 6, 1972*

The ligand 4,8-diaza-2,10-undecanediamine (diMe-2,3,2) has been prepared as an isomeric mixture containing the *RS* (meso) isomer and the *RR,SS* racemate. The pure *SS* isomer has been prepared, also. The ligand is a dimethyl derivative of 3,7-diaza-1,9-nonanediamine (2,3,2). *cis*- and *trans*-dichloro(4,8-diaza-2,10-undecanediamine)cobalt(III) complexes have been isolated containing the optically active ligand while only a *trans*-dichloro complex has been prepared containing the meso ligand. The optically active ligand coordinates stereospecifically in both the cis and trans complexes such that the *SS* ligand coordinates with the secondary nitrogen atoms exhibiting the *RR* configuration in both complexes. In the case of the cis complex the Λ-β topography is produced. The *RS* (meso) ligand coordinates in the trans complex with the secondary nitrogen atoms in the *SR* configuration.

## Introduction

Transition metal complexes of the tetramine ligand 3,7-diaza-1,9-nonanediamine, $NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2 \cdot NH_2$ (2,3,2), have been under investigation in our laboratory and others in recent years.[2-10] A notable result of these investigations is the isolation of three isomers of the *trans*-$[Co(2,3,2)Cl_2]^+$ complex which differ in the configuration of the asymmetric secondary nitrogen atoms, *RS* (meso), *RR*, and *SS*.[4-6] There is good evidence that the *RS* (meso) isomer is thermodynamically more stable than the optically active isomers (*RR* and *SS*) since the latter isomerize to the former in methanolic solution, and the former is prepared by the air oxidation technique.[4,11] This behavior is consistent with predictions based upon the assumption that the conformational behavior of the six-membered chelate ring of the complex parallels that of cyclohexane. In the *RS* (meso) isomer the six-membered ring can assume the chair conformation with the aminoethyl groups occupying equatorial positions on the ring allowing the primary amines to coordinate readily to positions coplanar with the six-membered ring (Figure 1a). In the case of the *RR* (*SS*) isomer if the ring assumes the chair conformation, one aminoethyl group occupies an axial site on the ring and its primary amine function cannot readily coordinate to a position coplanar with the ring but instead can coordinate only to a position perpendicular to the ring yielding a cis-β topography (Figure 1b). In order for this primary amine to coordinate readily in a

---

(1) NDEA predoctoral fellow.

(2) H. G. Hamilton, Jr., and M. D. Alexander, *Inorg. Chem.*, 5, 2060 (1966).

(3) B. Bosnich, R. D. Gillard, E. D. McKenzie, and G. A. Webb, *J. Chem. Soc. A*, 1331 (1966).

(4) H. G. Hamilton, Jr., and M. D. Alexander, *J. Amer. Chem. Soc.*, 89, 5065 (1967).

(5) R. Niththyananthan and M. L. Tobe, *Inorg. Chem.*, 8, 1589 (1969).

(6) G. R. Brubaker and D. P. Schaefer, *Inorg. Nucl. Chem. Lett.*, 6, 237 (1970).

(7) G. R. Brubaker and D. P. Schaefer, *Inorg. Chem.*, 9, 2372 (1970).

(8) G. R. Brubaker and D. P. Schaefer, *Inorg. Chem.*, 10, 811 (1971).

(9) G. R. Brubaker and D. P. Schaefer, *Inorg. Chem.*, 10, 968 (1971).

(10) M. D. Alexander, P. C. Harrington, and A. Van Heuvelen, *J. Phys. Chem.*, 75, 3355 (1971).

(11) M. D. Alexander and P. C. Harrington, unpublished results.

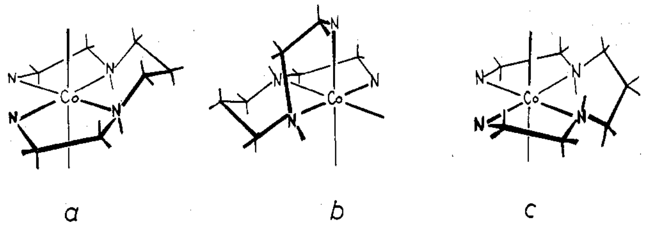


**Figure 1.** Structures of 2,3,2, complexes: (a) trans topography with *RS* nitrogen configuration; (b) cis-β topography with *RR* nitrogen configuration; (c) trans topography with *RR* nitrogen configuration.

trans fashion, the six-membered ring must assume a skew-boat (or twist) conformation (Figure 1c). That the *RS* (meso) isomer is the more stable of the two is good evidence for the chair conformation being preferred over the skew boat as is the case for cyclohexane. All cis complexes of 2,3,2 which have been prepared are believed to exhibit β topographies with *RR* (*SS*) nitrogen configurations providing further evidence for this conclusion.

In order to gain additional insight into the interplay of asymmetric nitrogen configuration, chelate ring conformations, and overall topographical behavior in complexes involving fused-ring systems we have undertaken a thorough investigation of a dimethyl derivative of 2,3,2, namely, 4,8-diaza-2,10-undecanediamine, $NH_2CH(CH_3)CH_2NH(CH_2)_3$-$NHCH_2CH(CH_3)NH_2$ (diMe-2,3,2). The direction of the investigation has been to determine how constraints placed upon the five-membered rings by the methyl groups affect the conformational behavior of the six-membered ring, the configurational behavior of the secondary nitrogen atoms, and the topographical behavior of the ligand in complex formation. The results of this investigation, which have proved quite informative in light of previous work with 2,3,2, are the subject of this paper.

## Experimental Section

**Synthesis of 4,8-Diaza-2,10-undecanediamine. Method I.** To 600 ml of a constantly stirred aqueous potassium hydroxide solution (1.5 *M* KOH), cooled in an ice-salt bath, was added 67.5 g of alanine. Carbobenzoxy chloride (CbzCl) (142 g) was added over a period of ~2 hr. The solution was stirred and cooled throughout the addition. The reaction mixture was allowed to stand at room temperature for another 2 hr and then acidified with dilute hydrochloric acid. The resulting precipitate was filtered, washed with cold water, and air-dried. The product, carbobenzoxyalanine (Cbz-ala), was purified by dissolution in acetone followed by precipitation by the addition of water and subsequently by recrystallization from benzene; yield 119 g (68%); mp (uncor) 110–112°; lit. mp 114–115°.

To 118 g of Cbz-ala in 500 ml of dry ethyl acetate was added 85 g of recrystallized *p*-nitrophenol slowly over a 20-min period. The mixture was stirred and cooled to ~0°. Dicyclohexylcarbodiimide (DCC) (103 g) in 250 ml of dry ethyl acetate was added over a period of ~1 hr. The mixture was cooled in ice for 30 min more and then allowed to warm to room temperature and stand there for approximately 1 hr. The thick precipitate of *N,N'*-dicyclohexylurea was filtered and washed several times with ethyl acetate. The filtrate and washings were evaporated to dryness and the product, carbobenzoxyalanine *p*-nitrophenyl ester, was recrystallized from ethyl acetate by the addition of petroleum ether (bp 30–60°); yield 154 g (89%); mp (uncor) 95–96°; lit. mp 91–93°.

Trimethylenediamine (11.1 g) was dissolved in 500 ml of dry dimethylformamide (DMF). The solution was stirred and cooled to 0°. The solid *p*-nitrophenyl ester (114 g) was added slowly. After the addition was complete, the mixture was stirred at 0° for 1 hr and then overnight at room temperature. The reaction mixture was poured into 2 l. of water and the product was extracted with chloroform (five 200-ml portions). Some solid in the chloroform layer was filtered and thoroughly washed with $CHCl_3$. The combined chloroform extracts and washings were washed with the following solutions: five times with 10% $NaHCO_3$, once with $H_2O$, once with 1 *N* HCl, and twice with $H_2O$. The chloroform solution was nearly colorless after this treatment. The solution was filtered and dried overnight over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator and the product was recrystallized from methanol. The product, 2,10-bis(carbobenzoxyamino)-4,8-diaza-3,9-undecanedione, was dried overnight *in vacuo* at 30°; yield 48 g (66%); mp (uncor) 176–178°; lit. mp 174–176°. *Anal.* Calcd for $C_{25}H_{32}N_4O_6$: C, 61.97; H, 6.64; N, 11.57. Found: C, 62.00; H, 6.67; N, 11.86.

The bis(carbobenzoxyamino) compound (45 g) prepared above was placed in a 500-ml flask equipped with a drying tube and a dropping funnel. A 36% solution of hydrogen bromide in glacial acetic acid (350 ml) was added dropwise and the reaction mixture was stirred constantly. Carbon dioxide began to evolve after a short time. After stirring overnight a clear solution resulted. Dry ether (1000 ml) was added to the solution and the resulting white precipitate was filtered off. The white solid was dissolved in a minimum amount of water and 40% sodium hydroxide was added, with cooling, until the solution was strongly basic. The product, 2,10-diamino-4,8-diaza-3,9-undecanedione, was extracted into chloroform and the $CHCl_3$ solution was dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator leaving the product as a yellowish oil. The oil was used directly in the next step without further purification.

The product from above (20 g) was dissolved in 100 ml of dry tetrahydrofuran (THF) and added dropwise to a cooled, constantly stirred mixture of lithium aluminum hydride (10 g) in 100 ml of dry THF. After the addition was complete the mixture was refluxed overnight. The reaction mixture was cooled in an ice-salt bath and then carefully quenched by the dropwise addition of 30 ml of water. A 5 *N* sodium hydroxide solution (30 ml) was then added and the white precipitate of aluminum hydroxide was filtered off. The filtered solid was washed with THF then stirred with two 200-ml portions of THF. The combined filtrate and washings were evaporated on a rotary evaporator. The residue, the desired product (4,8-diaza-2,10-undecanediamine) was then fractionally distilled; bp 105–120° (0.35 mm); yield 9.8 g (56%). *Anal.* Calcd for $C_9H_{24}N_2$: C, 57.40; H, 12.85. Found: C, 57.14; H, 12.61.

**Method II.** A solution of 2-bromopropionyl bromide (216 g) in 80 ml of benzene was added dropwise to a solution of trimethylenediamine (37 g) in 500 ml of a 5 *N* aqueous sodium hydroxide solution. The mixture was cooled in an ice-salt bath and stirred vigorously. The resulting precipitate, *N,N'*-bis(2-bromopropionyl)propanediamine, was filtered and washed several times with water. It was recrystallized from ethanol and dried overnight *in vacuo*; yield 142 g (82%); mp (uncor) 160–162.5°.

The *N,N'*-bis(2-bromopropionyl)propanediamine (142 g) was dissolved in a solution of methanol and 28% ammonium hydroxide. The solution was allowed to stand for 1 week and then evaporated to dryness on a rotary evaporator. The product, 2,10-diamino-4,7-diazaundecane-3,9-dione, which was a pale yellow oil, was used in the next step without further purification. The remainder of the procedure is identical with that of method I.

**Synthesis of (*SS*)-4,8-Diaza-2,10-undecanediamine.** The resolved ligand was prepared *via* method I described above except that (*S*)-alanine was employed as the starting material. Pmr spectra were obtained for the resolved products G and H (see Scheme I) and are in complete accord with their unresolved counterparts; yield (final step) 5 g (33%); $[\alpha]^{21.8}D$ 27.4°.

**Preparation of *cis*-[Co((*RR,SS*)-diMe-2,3,2)Cl$_2$]Cl and *trans*-[Co((*RS*)-diMe-2,3,2)Cl$_2$]ClO$_4$ *via* Cobalt(II) Oxidation.** The ligand diMe-2,3,2 (9.2 g) was added to 300 ml of an aqueous solution containing 11.9 g of cobalt(II) chloride hexahydrate and the solution was aerated for 24 hr. After the addition of concentrated hydrochloric acid (10 ml), the solution was evaporated to dryness. The tarry solid was taken up in a minimum amount of water and absorbed on a large Dowex 50W-X8 (100–200 mesh) ion-exchange column. The compact band at the top was washed with water and then eluted with 1 *M* hydrochloric acid. A pink band consisting of cobalt(II) came off the column very rapidly. Green *trans*-[Co((*RS*)-diMe-2,3,2)-$Cl_2]^+$ was eluted off the column with 1 *M* HCl and was crystallized as the sparingly soluble perchlorate salt by addition of perchloric acid to the eluent. Red-purple *cis*-[Co((*RR,SS*)-diMe-2,3,2)Cl-$(H_2O)]^{2+}$ was eluted off with 2 *M* HCl. The *cis*-dichloro complex was obtained as the chloride salt by evaporating the chloroaquo solution to dryness. The complexes were dried overnight *in vacuo* at 30°. *Anal.* Calcd for $CoC_9H_{24}N_4Cl_3O_4$ (trans complex): C, 25.88; H, 5.80. Found: C, 25.91; H, 5.53. Calcd. for $CoC_9H_{24}N_4Cl_3$ (cis complex): C, 30.56; H, 6.85. Found: C, 30.31; H, 7.00.

**Preparation of *cis*-[Co((*SS*)-diMe-2,3,2)Cl$_2$]Cl *via* Cobalt(II) Oxidation.** A procedure analogous to that described above for the preparation of the unresolved dichloro complexes was employed except that (*SS*)-diMe-2,3,2 was substituted for the unresolved ligand. The predominant purple band from the cation-exchange column was collected and evaporated to dryness. The violet solid was dried overnight *in vacuo* at 30°; yield 6.1 g (69%). *Anal.* Calcd for $CoC_9H_{24}N_4Cl_3$: C, 30.56; H, 6.85. Found: C, 29.57; H, 6.74.

**Preparation of *trans*-[Co((*SS*)-diMe-2,3,2)$Cl_2$]$ClO_4$ from *cis*-[Co((*SS*)-diMe-2,3,2)$Cl_2$]Cl.** To a 0.02 *M* hydrogen chloride methanol solution was added *cis*-[Co((*SS*)-diMe-2,3,2)$Cl_2$]Cl. Within a short time the color of the solution began to change from violet to green. Visible spectra were recorded during the course of the reaction. When no further change in the visible spectrum was observed the *trans*-dichloro complex was crystallized by the addition of sodium perchlorate. The experiment just described was repeated in neutral methanol solution. The infrared spectra of the *trans*-dichloro perchlorates obtained in the two experiments were identical. *Anal.* Calcd for $CoC_9H_{24}N_4Cl_3O_4$: C, 25.88; H, 5.80. Found: C, 26.12; H, 5.63.

**Aquation of *trans*-[Co((*RS*)-diMe-2,3,2)$Cl_2$]$ClO_4$.** The aquation of the *trans*-(*RS*)-dichloro isomer in 1 *M* nitric acid containing ~0.01 mol of complex was followed spectrophotometrically. At the point where no further spectral change was observed the aquation product mixture was absorbed on a short Dowex 50W-X8 cation-exchange column and eluted with 1 *M* nitric acid. Four bands were observed to separate on the column: a small rapidly moving green band, a second slower moving green band which eventually split into two unequal components, and finally a red band which had to be eluted from the column with 3 *M* nitric acid. Each of the separated aquation products was collected and the visible absorption spectrum was recorded.

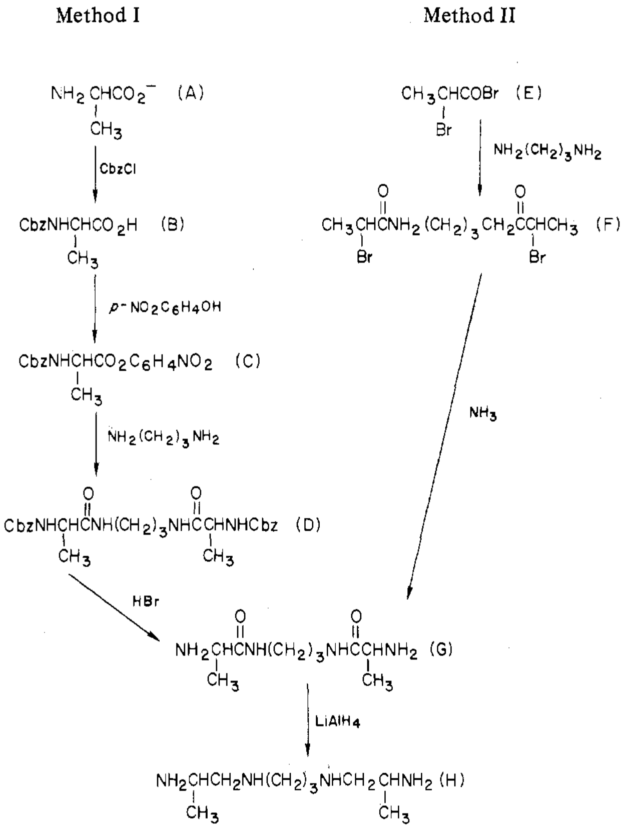
**Measurements.** Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrophotometer. Nujol mulls supported on sodium chloride plates were employed. Visible absorption spectra were obtained on a Cary 14 recording spectrophotometer using 1-, 5-, or 10-cm silica cells. Solution spectra were obtained in absolute methanol containing approximately 0.01 mol of complex. The visible absorption spectrum of solid *cis*-dichloro complex finely ground in Nujol and supported on filter paper was obtained. Circular dichroism spectra were recorded on a Cary Model 60 spectropolarimeter equipped with a Cary Model 6002 circular dichroism accessory. The solutions employed each contained approximately 0.02 *M* of complex. The CD spectrum of the optically active *trans*-dichloro complex was recorded in methanol solution and that of the *cis*-dichloro isomer was recorded in hydrogen chloride saturated methanol. Protron magnetic resonance spectra were recorded on a JEOLCO PS100 100-MHz nmr spectrometer. Spectra were obtained in 99.5% DMSO-$d_6$ with 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as the internal standard. The pmr spectrum of *trans*-[Co((*SS*)-diMe-2,3,2)-$Cl_2$]$ClO_4$ in DMSO-$d_6$ solution was recorded immediately after dissolution since the complex was observed to undergo a slow reaction with the solvent. The HDO and DMSO peaks are omitted from the spectra for simplicity.

**Elemental Analyses.** Elemental analyses were performed by Chemalytics Inc., Tempe, Ariz.

## Results and Discussion

The two methods employed in the synthesis of diMe-2,3,2 are shown in Scheme I. Both racemic alanine and (*S*)-alanine were employed as starting materials in method I, while only racemic bromopropionyl bromide was used as a starting material in method II. Since for either method the reaction in which the two asymmetric carbons are incorporated into the same molecule should exhibit no pronounced stereoselectivity, the products of the reaction for both methods should contain all three optical isomers *RR*, *SS*, and *RS* (meso) when racemic starting materials are used. The subsequent reactions should lack stereoselectivity, also. If separation of the *RS* (meso) isomer from the *RR* and *SS* isomers of the final product, diMe-2,3,2 were to have been effected in the syntheses, then the separation most likely would have resulted from solubility differences of optical isomers in solid precursors somewhere along the synthetic routes. In each of the two methods there is only one such solid precursor (D or F). Each of these was obtained in good yield (66% for D and 82% for E) providing strong evidence of the presence of all isomers in these precursors, and, hence, in the final product. Further evidence in support of this conclusion is that no differences were observed in the coordination chemistry of diMe-2,3,2 prepared by the two methods. One would predict that by using (*S*)-alanine as the starting material in method I the *SS* isomer of the tetramine should be produced. As will be seen subsequently, this prediction is borne out.

**Scheme I**



The usual air oxidation technique used to prepare dichloro(tetramine)cobalt(III) complexes produces *cis*-[Co((*SS*)-diMe-2,3,2)$Cl_2$]Cl when the optically active (*SS*) form of diMe-2,3,2 is employed as the tetramine. Elemental analysis is in accord with the formulation, and the cis structure is confirmed *via* visible absorption spectral data. The methanol solution spectrum exhibits a single maximum at the same position as the solid-state spectrum supporting the notion that the complex exhibits the same formulation and structure in solution and in the solid state. The position and intensity of the band in the solution spectrum ($\lambda_{max}$ 540 nm; $\epsilon$ 90) are nearly the same as that of *cis*-$\beta$-[Co(2,3,2)$Cl_2$]Cl as well as other known *cis*-dichloro(tetramine)cobalt(III) complexes. (For *cis*-$\beta$-[Co(2,3,2)$Cl_2$]$Cl_2$ $\lambda_{max}$ is 540 nm and $\epsilon$ is 103.[12])

When an acidic methanol solution of *cis*-[Co((*SS*)-diMe-2,3,2)$Cl_2$]$^+$ is allowed to stand, the spectral change depicted in Figure 2 occurs. The spectrum of the solution at the conclusion of the change is very similar to the spectra of known *trans*-dichloro(tetramine)cobalt(III) complexes, and, thus, isomerization is indicated. The trans complex can be isolated as the sparingly soluble perchlorate salt *trans*-[Co((*SS*)-diMe-2,3,2)$Cl_2$]$ClO_4$. Elemental analysis is in accord with this formulation.

[12] H. G. Hamilton, Jr., Ph.D. Dissertation, New Mexico State University, 1968.

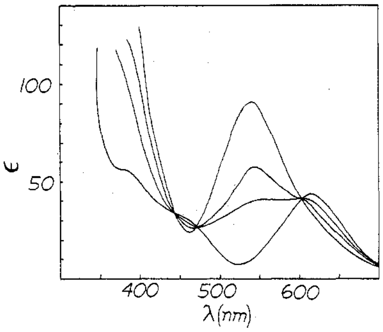


**Figure 2.** Spectra taken during the course of isomerization of *cis*-$[Co((SS)\text{-diMe-}2,3,2)Cl_2]^+$ to *trans*-$[Co((SS)\text{-diMe-}2,3,2)Cl_2]^+$ in acidic methanol.

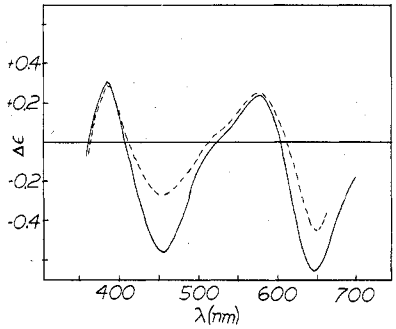


**Figure 3.** CD spectra of *trans*-$[Co((SS)\text{-diMe-}2,3,2)Cl_2]^+$ (—) and *trans*-$(RR)$-$[Co(2,3,2)Cl_2]^+$ (– – –).

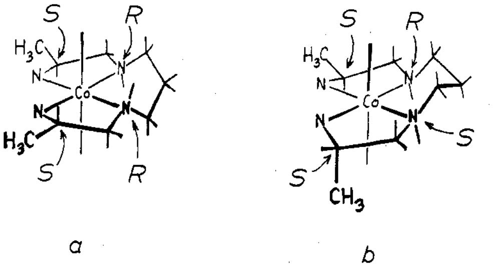


**Figure 4.** Possible structures of *trans*-$[Co((SS)\text{-diMe-}2,3,2)Cl_2]^+$: (a) six-membered ring in skew-boat conformation; (b) six-membered ring in chair conformation.

The CD spectrum of the complex is shown in Figure 3. Also shown is that of *trans*-(*RR*)-$[Co(2,3,2)Cl_2]^+$ where the *RR* notation refers to the configuration of the secondary nitrogen atoms.[6] Note the marked similarity between the two CD spectra. The structure of the 2,3,2 complex is believed to be that shown in Figure 1c.[9] The similarity between the CD spectra of the two complexes strongly suggests that the backbones of (*SS*)-diMe-2,3,2 and 2,3,2 are in the same configuration in the two complexes. Not surprisingly, this places the methyl groups of (*SS*)-diMe-2,3,2 at equatorial sites on the five-membered rings as shown in Figure 4a. Thus, if this structural assignment is correct, the methyl groups occupy equivalent sites. The pmr spectrum (Figure 5) is in accord with this since the spectrum exhibits a single methyl doublet.

An alternative structure for the *trans*-$[Co((SS)\text{-diMe-}2,3,2)Cl_2]^+$ complex has the six-membered ring in the chair conformation and the five-membered rings in conformations of opposite chirality with one of the methyl groups occupying an axial position (Figure 4b). Neither the CD spectrum nor the pmr spectrum of the complex is consistent with this structure, however. One would not expect the CD spectrum of the *trans*-(*RR*)-$[Co(2,3,2)Cl_2]^+$ complex and that of the (*SS*)-diMe-2,3,2 complex to be so similar if the latter exhibits this structure, since the optical activity in the former is due to chelate ring conformations while that for the (*SS*)-diMe-2,3,2 complex would be due primarily to the asymmetric carbon centers. As to the pmr spectrum, the axial methyl group should exhibit a significantly different chemical shift than the equatorial methyl group and a single methyl doublet should not be observed.

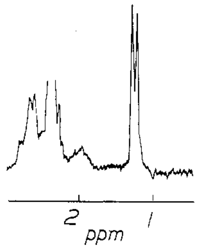


**Figure 5.** Pmr spectrum of *trans*-$[Co((SS)\text{-diMe-}2,3,2)Cl_2]^+$.

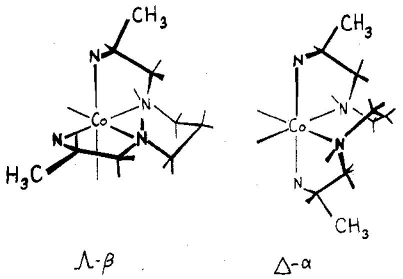


**Figure 6.** Structures of Λ-*cis*-β-$[Co((SS)\text{-diMe-}2,3,2)Cl_2]^+$ and Δ-*cis*-α-$[Co((SS)\text{-diMe-}2,3,2)Cl_2]^+$.

In an effort to determine if the *trans*-dichloro complex obtained through the isomerization of the *cis*-$[Co((SS)\text{-diMe-}2,3,2)Cl_2]^+$ complex would undergo a further structural change, the perchlorate salt of the complex was dissolved in slightly basic methanol; the solution was allowed to stand for several hours; and the complex was then recrystallized as the perchlorate salt by addition of perchloric acid. Under such conditions nitrogen configurational change would have been possible. However, the complex so obtained exhibited properties, such as its ir spectrum, indistinguishable from the initial *trans*-dichloro complex.

The nitrogen configuration in the complex, if our structural assignment is correct, is *RR;* and the complex is designated *trans*-$(R_NR_N)$-$[Co((SS)\text{-diMe-}2,3,2)Cl_2]^+$.

The isomerization

*cis*-$[Co((SS)\text{-diMe-}2,3,2)Cl_2]^+ \rightarrow$ *trans*-$[Co((SS)\text{-diMe-}2,3,2)Cl_2]^+$

was carried out in strongly acidic methanol under which conditions no nitrogen configurational change should occur. Therefore, the *RR* nitrogen configuration is assigned to the cis complex, also. For such a configuration the most probable structures are Λ-cis-β and Δ-*cis*-α as shown in Figure 6. In both structures the methyl groups occupy equatorial sites on the five-membered rings, and, therefore, the carbon and nitrogen configurations are compatible. From the observed behavior of 2,3,2 complexes, the β structure would be expected to be the more stable. In the pmr spectrum of the *cis*-dichloro complex there appear to be two overlapping methyl doublets (Figure 7). This is a strong indication that the isomer does indeed exhibit the β topography since for the β topography the two methyl groups are in different environments while for the α topography the methyl groups are in equivalent environments. Moreover, the number of peaks in the -NH, $-NH_2$ region (4–8 ppm) is consistent with the different site symmetries for all the N protons in the cis-β structure. For the α topography pairs of N protons are related by a two-

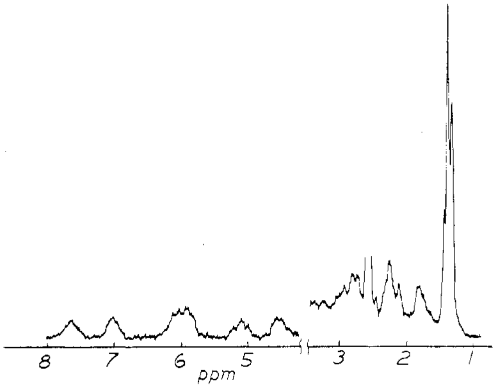


**Figure 7.** Pmr spectrum of *cis*-[Co((*SS*)-diMe-2,3,2)$Cl_2$]$^+$.

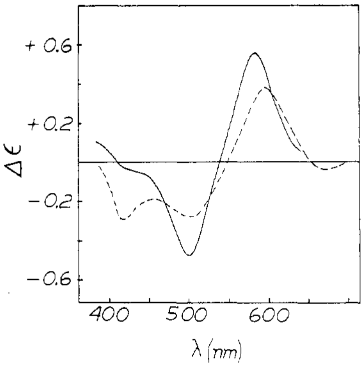


**Figure 8.** CD spectra of *cis*-[Co((*SS*)-diMe-2,3,2)$Cl_2$]$^+$ (– –) and Λ-*cis*-β-(*RR*)-[Co(2,3,2)($H_2O$)Cl]$^{2+}$ (—).

fold rotational axis which should result in no more than three NH peaks of equal intensity. We see that the pmr data are in strong support of the β structure for the complex. The CD data are in accord with this assignment, also. For a β topography the Λ configuration should be exhibited. Figure 8 shows the CD spectrum of Λ-*cis*-β-[Co(2,3,2)Cl($H_2O$)]$^{2+}$, the structure and configuration of which have been assigned by other investigators.[13,14] Also shown is the CD spectrum of the *cis*-dichloro complex in question. The splitting of the $^1T_1$ excited state should be similar for the two complexes. Note the marked similarity between the CD spectra of the two in the $^1A_1 \rightarrow {}^1T_1$ spectral region. Also note that the dominant band in this region, which has been used to assign absolute configurations,[14,15] is of the same sign in each. Consequently, the CD data are indicative of the Λ absolute configuration and are consistent with the assignment of the β topography.

The ligand obtained from racemic alanine is believed to be a mixture of the *RS* (meso) isomer and the *RR,SS* racemate. The coordination chemistry of the ligand is consistent with this. When the synthetic procedure used to prepare *cis*-[Co((*SS*)-diMe-2,3,2)$Cl_2$]$^+$ is carried out using the isomeric mixture of the tetramine, rather than the *SS* isomer, a *cis*-dichloro complex is obtained which exhibits solution properties, such as its pmr spectrum and its visible absorption spectrum, indistinguishable from those of *cis*-β-[Co((*SS*)-diMe-2,3,2)$Cl_2$]$^+$. In addition to this complex a nearly equal amount of a *trans*-dichloro complex is obtained. Properties of the perchlorate salt of the complex, such as ir, visible, and pmr spectra, are all different from those of *trans*-[Co((*SS*)-diMe-2,3,2)$Cl_2$]$ClO_4$ although the visible spectra of the two are similar. The ir and visible spectra of the two are shown in Figures 9 and 10. Therefore, we believe this isomer to be *trans*-[Co((*RS*)-diMe-2,3,2)$Cl_2$]$ClO_4$. We would have predicted that the *RS* (meso) isomer of the ligand would form a stable *trans*-dichloro complex since for this isomer the methyl groups can occupy equatorial sites on the five-membered rings and the six-membered ring can be in the chair conformation, and, thus, we assign this structure to the trans complex (Figure 11). Note that the nitrogen configuration is *SR* (meso).

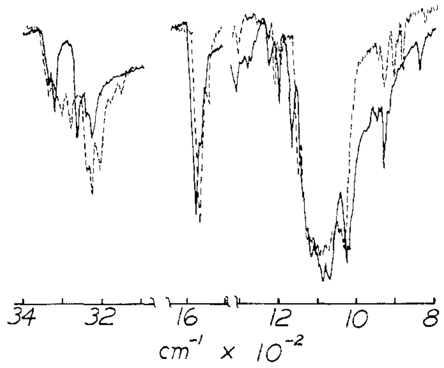


**Figure 9.** Ir spectra of *trans*-[Co((*SS*)-diMe-2,3,2)$Cl_2$]$^+$ (—) and *trans*-[Co((*RS*)-diMe-2,3,2)$Cl_2$]$^+$ (– –).

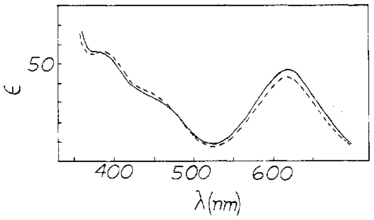


**Figure 10.** Visible absorption spectra of *trans*-[Co((*SS*)-diMe-2,3,2)-$Cl_2$]$^+$ (——) and *trans*-[Co((*RS*)-diMe-2,3,2)$Cl_2$]$^+$ (– –).

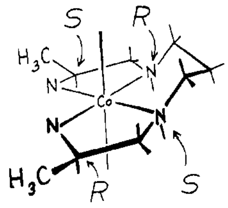


**Figure 11.** Structure of *trans*-($S_NR_N$)-[Co((*RS*)-diMe-2,3,2)$Cl_2$]$^+$.

The pmr is consistent with such a structure since a single methyl doublet is observed (Figure 12). Other experimental evidence supports this structure, also. The two coordination sites perpendicular to the amine plane are nonequivalent for trans complexes containing the *RS* (meso) ligand; and, thus, for the case of two different ligands coordinating at these positions, two geometrical isomers are possible. When the complex believed to be *trans*-($S_NR_N$)-[Co((*RS*)-diMe-2,3,2)$Cl_2$]$ClO_4$ is allowed to aquate in strongly acidic aqueous solution, several complexes can be isolated *via* cation-exchange chromatography among which are unreacted *trans*-($S_NR_N$)-[Co((*RS*)-diMe-2,3,2)$Cl_2$]$^+$ and two complexes which elute at similar rates but much more slowly than the *trans*-dichloro complex. These two complexes exhibit very similar visible absorption spectra with a maximum at 592 nm in each case. The spectra are very similar to known *trans*-chloroaquo(tetramine)cobalt(III) complexes (for *trans*-

---

[13] D. P. Schaefer, Ph.D. Thesis, Illinois Institute of Technology, 1970.

[14] G. R. Brubaker, D. P. Schaefer, J. H. Worrell, and J. I. Legg., *Coord. Chem. Rev.*, 7, 161 (1971).

[15] A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).

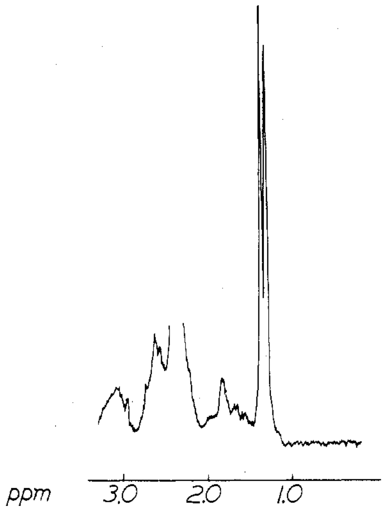


**Figure 12.** Pmr spectrum of *trans*-[Co((*RS*)-diMe-2,3,2)Cl$_2$]$^+$.

[Co(en)$_2$(H$_2$O)Cl]$^{2+}$ $\lambda_{max}$ is 590[16]) and are quite dissimilar to the spectra of *cis*- and *trans*-diaquo complexes. Thus, the aquation of the *trans*-dichloro complex is in accord with the assigned structure.

## Conclusion

The optically active isomers of diMe-2,3,2 coordinate stereospecifically in both *trans*- and *cis*-dichloro complexes. In the case of the trans structure there is strong evidence that the *SS* isomer yields a *RR* nitrogen configuration with the five-membered rings both in $\delta$ conformations and the six-membered ring in the $\lambda$ skew-boat conformation. It is significant to note that the ligand appears to prefer to coordinate such as to yield a skew-boat six-membered ring with two equatorial methyl groups on the five-membered rings than to coordinate with the six-membered ring in the chair conformation and one of the methyl groups occupying an axial site on its ring.

For the cis structure the data indicate that the *SS* ligand yields a $\Lambda$-cis-$\beta$ configuration with the six-membered ring in the chair conformation.

The *RS* (meso) isomer of the ligand coordinates stereospecifically, also, yielding the *trans-meso*-dichloro complex.

We see that the stereochemical behavior of the diMe-2,3,2 isomers is strongly in accord with the notions concerning the coordination chemistry of 2,3,2.

**Registry No.** 4,8-Diaza-2,10-undecanediamine, 36748-48-8; (*S,S*)-4,8-diaza-2,10-undecanediamine, 36749-49-2; *cis*-[Co((*R,R,S,S*)-diMe-2,3,2)Cl$_2$]Cl, 36841-26-6; *trans*-[Co((*R,S*)-diMe-2,3,2)Cl$_2$]ClO$_4$, 36841-27-7; *cis*-[Co((*S,S*)-diMe-2,3,2)Cl$_2$]Cl, 36841-28-8; *trans*-[Co((*S,S*)-diMe-2,3,2)Cl$_2$]-ClO$_4$, 36841-30-2.

**Acknowledgment.** The authors are grateful to the National Science Foundation for support of this research through Grant GP-28686. We also wish to acknowledge the Research Corp. and the National Science Foundation for grants through which the Cary 60 spectropolarimeter and JEOLCO PS100 nmr spectrometer were purchased.

[16] M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4367 (1961).

---

Contribution from the Department of Chemistry, State University
of New York at Buffalo, Buffalo, New York 14214

# The Preparation and Characterization of the Dianion of the New Dithiolate Cyclopentadienedithiocarboxylate and Its Zinc and Copper Complexes

PAUL C. SAVINO and ROBERT D. BEREMAN*

*Received June 12, 1972*

The disodium salt of cyclopentadienedithiocarboxylic acid, Na$_2$S$_2$CC$_5$H$_4$, can be prepared from sodium cyclopentadienide and carbon disulfide in tetrahydrofuran. The salt is obtained as a 1:1 complex with either tetrahydrofuran or acetonitrile depending on the recrystallization solvent. Nuclear magnetic resonance studies indicate that a large amount of negative charge resides in the ring system. This novel 1,1-dithiolate reacts in acetonitrile with copper(II) bromide or zinc(II) bromide to form 2:1 ligand to metal complexes which can be isolated as the tetraethylammonium salts. Optical spectra coupled with electron spin resonance studies on the copper complex in the analogous zinc matrix and in a frozen glass indicate a very covalent out-of-plane metal–sulfur $\pi$ bond.

## Introduction

During the past decade, there has been a great deal of interest in sulfur complexes of transition elements.[1,2] Attention recently has centered on thiolate ligands which are of interest because of their bioinorganic importance (*i.e.*, in nitrogenase model systems) and on dithiolate complexes because of their extensive uses in a wide variety of practical applications.[2]

Gompper and Kutter[3] speculated that the dianion of cyclopentadienedithiocarboxylic acid (I) was an intermediate in organic preparations but it was never isolated. This dianion represents a unique dithiolate ligand because of its potential electronic properties. For this reason, we have undertaken a detailed characterization of the disodium salt of I and the preparation and characterization of zinc and copper complexes of I.

## Experimental Section

**Materials.** Sodium hydride was obtained as a 50% dispersion in oil from Research Organic-Inorganic Chemical Corp. Carbon disulfide was dried over 4A molecular sieves. Acetonitrile was refluxed over and distilled repeatedly from phosphorus pentoxide. Tetrahydrofuran was distilled from LiAlH$_4$. Cyclopentadiene was prepared by the thermal cracking of dicyclopentadiene. Acetonitrile-$d_3$ was obtained from Norell Chemical Co. and dried over

---

[1] J. A. McCleverty, *Progr. Inorg. Chem.*, 10, 49 (1968).
[2] D. Coucouvanis, *Progr. Inorg. Chem.*, 11, 233 (1970).
[3] R. Gompper and E. Kutter, *Chem. Ber.*, 98, 2825 (1965).