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The stereochemistry and absolute configurations of the metal complexes of novel optically active NSSN system tetradentate ligands. Cobalt(III) complexes of S,S′-*bis*(*β*-aminoethyl)-*trans*-1,2-dithiocyclohexane. Crystal and molecular structure of s-*cis*[Co(adch)Cl_2]Cl · C_2H_5OH

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Abstract—A novel open-chain tetradentate ligand having the NSSN donor atom array, S,S′-*bis*(*β*-aminoethyl)-trans-1,2-dithiocyclohexane (adch), has been synthesized and the cobalt(III) complexes of $[Co(adch)X_2]^+$ ($X = Cl^-$, NO_2^-, NCS^-, $X_2 = CO_3^{2-}$) have been prepared. Only the s-*cis* geometric isomers have been formed. From the reaction between $Na_3[CO(CO_3)_3]$ and the racemic adch ligand, the RR–adch ligand is coordinated to the cobalt(III) ion stereospecifically to give the Λ-s-*cis*-($\delta\lambda\delta$)-$[Co(adch)Cl_2]^+$ enantiometer complex, while the SS-adch ligand stereospecifically to give the Δ-s-*cis*-($\lambda\delta\lambda$)-$[Co(adch)Cl_2]^+$ enantiometer complex, which have been observed in the crystal structure of the $[Co(adch)Cl_2]Cl_2 \cdot C_2H_5OH$ complex solved by single-crystal X-ray analysis. The unit cell contains both Λ and Δ complex isomer, two chloride ions and two ethanol molecules. The bond distances in Å: Co—S = 2.241 (2) and 2.232 (2), Co—N = 1.963 (5) and 1.959 (6), Co—Cl = 2.262 (2) and 2.250 (2). The coordination geometry about the cobalt atom is a distorted octahedron. © 1997 Elsevier Science Ltd

INTRODUCTION

Metal complexes of the flexible tetradentate ligands having the donor atom sequence nitrogen–sulfur–sulfur–nitrogen have been prepared for the stereochemical investigation of those metal complexes and more recently for the investigation of the binding site for the copper ion in the blue copper electron-transfer proteins [1].

In 1969 Worrell and Busch reported the synthesis of the flexible tetradentate ligand, 1,8-diamino-3,6-dithiaoctane ($H_2NCH_2CH_2SCH_2CH_2SCH_2CH_2NH_2$; eee). They observed only the symmetrical cis isomer in their preparation of the dichlorocobalt(III) complex of eec [2]. Bosnich *et al.* [3] synthesized the three homologous open-chain tetradentate ligands, 1,8-diamino-3,6-dithiaoctane (eee), 1,9-diamino-3,7-dithianone ($H_2N(CH_2)_2S(CH_2)_3S(CH_2)_2NH_2$; ete), 1,10-diamino-4,7-dithiadecane ($H_2N(CH_2)_3S(CH_2)_2S(CH_2)_3NH_2$; tet). In the dichlorocobalt(III) complexes of these ligands, ete yielded the trans and unsymmetrical cis isomers only, while tet gave the s-*cis* and uns–*cis* isomers. Worrell *et al.* [4] prepared the asymmetric ligand, (±)-4-methyl-1,8-diamino-3,6-dithiaoctane ($H_2N(CH_2)_2SCH(CH_3)CH_2S(CH_2)_2NH_2$; epe), which yielded the s-*cis*-$[Co(epe)Cl_2]^+$ isomer only. Bosnich and Phillip synthesized the stereoselective tetradentate ligand L-(−)-1,8-diamino-1,8-dimethyl-3,6-dithiaoctane ($H_2NCH(CH_3)CH_2S(CH_2)_2SCH_2CH(CH_3)NH_2$; pep), which gave only the s-*cis*-$[Co(pep)X_2]^+$ ($X = Cl^-$, Br^-, NCS^-, NO_2^-, and H_2O) [5]. The ligand 1,8-bis(2-pyridyl)-3,6-dithiaoctane (bpto) and cobalt(II) complex of bpto were

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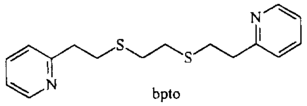
prepared by Castinieras *et al.* [6] and Braithwaite *et al.* [7] obtained the copper(II) complex of the tetradentate NSSN-type ligand 3,4-*bis*(2-aminoethylthio)-toluene (aett), μ-chloro-chlorobis[3,4-*bis*(2-aminoethylthio)toluene]dicopper(II) diperchlorate, which was shown to have a distorted octahedral structure at one copper center and a distorted square pyramidal at the other copper center by X-ray crystallographic study. The copper(II) complex of 1,6-bis(2-benzimidazolyl)-2,5-dithiahexane (bbdh), [Cu(bbdh)Cl]Cl, was shown to have a trigonal bipyramidal geometry at the copper(II) center by single crystal X-ray analysis [8]. On the other hand, the copper(II) complex of 1,5-*bis*(quinoline-8-yl)-1,5-dithiapentane (bqdtp), $[Cu(bqdtp)(NO_3)(OH_2)]NO_3$, was observed to have an elongated octahedron at the copper atom by X-ray study [9]. Bouwman *et al.* [10] reported the synthesis of the thiocyanato-bridged mixed-valence copper(I)–copper(II) complex of 1,6-*bis*(5′-methylimidazol-4′-yl)-2,5-dithiahexane (bmth). Prins *et al.* [11] synthesized the trinuclear copper(II) complexes with the ligand 1,9-*bis*(3-amino-4*H*-triazole-5-yl)-3,7-dithianonane (attn), $[Cu_3(attn)_2(H_2O)_2Cl_2]Cl_4(H_2O)_4$ and $Cu_3(attn)_2(ZnCl_4)_2](H_2O)_4$, in which the copper center is octahedral.

We are interested in synthesizing new NSSN-type tetradentate ligands which can coordinate to a metal ion stereoselectively. In this paper the synthesis of a novel NSSN-type tetradentate ligand S,S′-*bis*(β-aminoethyl)-trans-1,2-dithiocyclohexane (adch) and the cobalt(III) complex of this ligand, $[Co(adch)Cl_2]Cl$, are reported. The only cobalt(III) complex of the NSSN-type tetradentate ligand whose X-ray crystal structural determination has been reported so far in the literature is that of the cobalt(III) complex of ete [12]. In this work the X-ray crystal structural study of the s-*cis*-$[Co(adch)Cl_2]^+$ complex is reported, which will show the fact that the adch ligands are coordinated stereospecifically to the cobalt(III) ion.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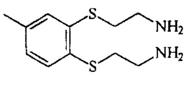
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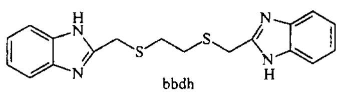
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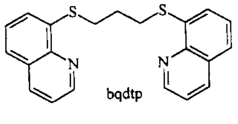
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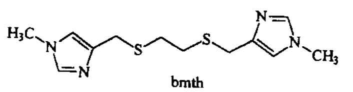
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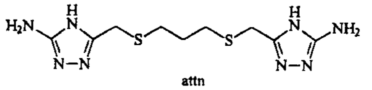
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EXPERIMENTAL

Physical measurements

The absorption spectra were measured using a Shimadzu UV-160A spectrophotometer. The NMR spectra were taken by means of a Bruker DPX-50 spectrophotometer. The IR spectra were obtained using a Nicolet Impact 400 FT-IR spectrophotometer.

X-ray crystallographic data were collected on an Enraf–Nonius CAD4 diffractometer. Data reduction and solution were performed on a Micro VAX using SHELXL-93 and VAX/SDP package of programs.

Reagents

The cyclohexene oxide, 2-bromoethylamine hydrobromide and lithium aluminium hydride were purchased from Aldrich and were used without further purification. All the solvents used were reagent grade and purified by conventional procedures prior to use.

Synthesis of S,S′-bis(*β-aminoethyl*)-trans-1,2-*dithiocyclohexane* (*adch*)

Trans-1,2-cyclohexanedithiol [13] (8 g, 5.4×10^{-2} mol) and NaOH (4.5 g, 0.11 mol) were dissolved in 60 cm^3 of distilled water and stirred for 20 min at 65°C. To this solution a solution (80 cm^3) of 2-bromoethylamine hydrobromide (22.1 g, 0.1 mol) and NaOH (4.3 g, 0.1 mol) was slowly added for 25 min. The resultant solution was refluxed for 12 h. It was cooled to room temperature and then filtered. The filtrate was concentrated to 50 cm^3 under reduced pressure. 20% NaOH solution (50 cm^3) was added to the solution, which was extracted with 50 cm^3 of $CHCl_3$ three times. The combined extracts were washed with 50 cm^3 of water twice. The washed solution was dried with $MgSO_4$ and concentrated under reduced pressure to get a yellow liquid. This liquid was dissolved in a mixed solution of ethanol and ethyl ether. The product was obtained as a white dihydrochloride salt by adding concentrated HCl to this solution. Yield: 11.2 g (68%). Analysis: Found C, 38.8; H, 7.9; N, 9.0; S, 20.1. Calc. for $C_{10}H_{24}N_2S_2Cl_2$; C, 39.1; H, 7.9; N, 9.1; S, 20.9%. ^1H NMR (D_2O, ppm): 3.1 (t, 4H), 2.8–2.7 (m, 4H), 2.6 (m, 2H), 2.0 (m, 2H), 1.5 (m, 2H), 1.3 (m, 2H), 1.2 (m, 2H); ^{13}C NMR (D_2O, ppm): 48.1 (CH_2N), 38.9 (CH_2S), 33.1 (CH), 27.3 ($CHCH_2$), 24.6 (CH_2).

Preparation of the s-cis-[Co(adch)Cl_2]Cl · C_2H_5OH

$Na_3[Co(CO_3)_3] \cdot 3H_2O$ [14] (1.81 g, 5 mmol) was dissolved in distilled water (10 cm^3), to which a solution of adch · 2HCL (1.54 g, 5 mmol) dissolved in 10 cm^3 of water was added. The resultant solution was stirred for 40 min at 65°C and filtered while hot. 5 cm^3 of concentrated HCl was added to the filtrate. After stirring for 10 min at room temperature, the solution was concentrated to 10 cm^3 under reduced pressure, and was then filtered. Ethanol and ethyl ether were added to the filtrate, which was stored in a refrigerator for 4 days. Deep blue crystals formed were filtered. The product was washed with ethanol and ethyl ether, and recrystallized from concentrated hydrochloric acid and ethanol. Yield: 0.9 g (40%). Analysis: Found C, 32.8; H, 6.4; N, 5.9; S, 13.7. Calc. for $Co(C_{10}H_{22}N_2S_2)Cl_3 \cdot C_2H_5OH$; C, 32.3; H, 6.3; N, 6.3; S, 14.4%. ^1H NMR (D_2O, ppm): 3.1–3.0 (m, 4H), 2.9–2.7 (m, 6H), 2.6–2.2 (m, 2H), 1.6 (m, 4H), 1.2–1.1 (m, 2H); ^{13}C NMR (D_2O, ppm): 53.1 (CH_2N), 42.7 (CH_2S), 39.0 (CH), 32.2 ($CHCH_2$), 23.9 (CH_2).

Preparation of the s-cis-[Co(adch)CO_3]Cl

Li_2CO_3 (5×10^{-2} g, 7.2×10^{-2} mol) and s-*cis*-[Co(adch)Cl_2]Cl (0.2 g, 0.5 mmol) were dissolved in 10 cm^3 of water was stirred for 10 min at 50°C. The solution was filtered while hot, and was concentrated to *ca* 1 cm^3 under reduced pressure. After adding ethanol and ethyl ether, the solution was allowed to stand 4 h at 0°C. The pink precipitates formed were filtered. The product was washed with ethanol and ethyl ether and dried in vacuum. Yield: 0.1 g (50%). Analysis: Found C, 31.8; H, 5.7; N, 6.8; S, 15.2. Calc. for $Co(C_{10}H_{22}N_2S_2)(CO_3)Cl \cdot H_2O$; C, 32.5; H, 5.9; N, 6.9; S, 15.8%. ^1H NMR (D_2O, ppm): 2.9–2.6 (m, 10H), 2.3–2.2 (m, 2H), 1.6 (m, 4H), 1.2 (m, 2H).

Preparation of the s-cis-[Co(adch)$(NO_2)_2$]Cl

A solution of $NaNO_2$ (7 mg, 0.1 mmol) and s-*cis*-[Co(adch)Cl_2]Cl (20 mg, 0.05 mmol) dissolved in 3 cm^3 of water was stirred for 5 min at 80°C. The solution was cooled to room temperature. After ethanol and ethyl ether, the resultant solution was allowed to stand 6 h at 0°C. The yellow–orange precipitates formed were filtered. The product was washed with ethanol and ethyl ether and dried in vacuum. Yield: 9 mg (43%). Analysis: Found C, 26.9; H, 5.7; N, 12.6; S, 13.9. Calc. for $Co(C_{10}H_{22}N_2S_2)(NO_2)_2Cl \cdot H_2O$; C, 27.4; H, 5.5; N, 12.8; S, 14.6%. ^1H NMR (D_2O, ppm): 3.1–2.7 (m, 10H), 2.4–2.3 (m, 2H), 1.7 (m, 4H), 1.3–1.2 (m, 2H).

Preparation of the s-cis-[Co(adch)$(NCS)_2$]Cl

A solution of NaSCN (0.23 g, 2.8 mmol) and s-*cis*-[Co(adch)Cl_2]Cl (0.56 g, 1.4 mmol) were dissolved in 20 cm^3 of water was stirred for 10 min at 80°C. The solution was filtered while hot. The filtrate was cooled to 0°C, at which temperature the solution was allowed to stand 5 h. The red–brown precipitates formed were filtered. The product was washed with acetone and ethyl ether and then dried *in vacuo*. Yield: 0.5 g (80%). Analysis: Found C, 31.4; H, 5.1; N, 12.4;, S, 27.4. Calc. for $Co(C_{10}H_{22}N_2S_2)(NCS)_2Cl \cdot H_2O$; C, 31.1; H, 5.2; N, 12.1; S, 27.7%. ^1H NMR (D_2O, ppm): 3.1–2.7 (m, 10H), 2.4–2.3 (m, 2H), 1.7 (m, 4H), 1.3–1.2 (m, 2H).

X-ray crystal determination for [CO(adch)Cl_2] · C_2H_5OH

A bar-shaped single crystal of [Co(adch)Cl_2] Cl · C_2H_5OH of good quality was selected for the structure determination. A crystal (0.25 × 0.5 × 0.05 mm) was mounted on Enraf–Nonius CAD4 diffractometer. X-ray data were collected using Mo–Kα radiation at room temperature. Cell parameters and orientation matrix for data collection were obtained from least squares refinement, using the setting angles of 25 reflections. The intensities of 3 standard reflections, recorded very 3 h of X-ray exposure, showed no systematic changes. Crystal and refinement data are noted in Table 1.

The intensity data were corrected for Lorentz and polarization effects. Empirical absorption corrections were also applied (DIFABS). The structure was solved by a combination of Patterson and difference Fourier methods (SHELXL93). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions ($d_{C\text{–}H} = 0.95$ Å) and were assigned an isotropic thermal parameter of 1.2 times that of attached atom. All the calculations except structure solution were carried with the Enraf–Nonius CAD4 SDP program package.

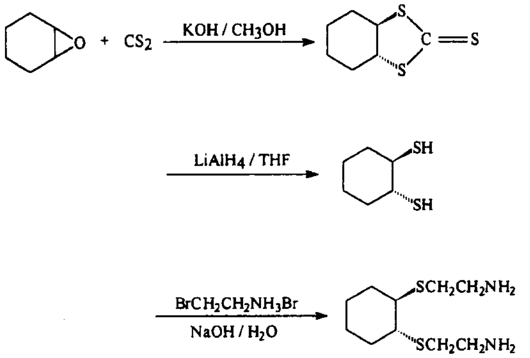
RESULTS AND DISCUSSION

The ligand S,S′-*bis*(β-aminoethyl)-*trans*-1,2-dithiocyclohexane (adch) has been prepared from the reaction between *trans*-1,2-cyclohexanedithiol and 2-bromoethylamine as depicted in Scheme 1. Though the ligand has two asymmetric centers, it has been obtained as a racemic mixture. The ^1H NMR spectrum of adch shows the methylene group protons at near 1.6 ppm and at near 2.0 ppm as multiplets, while the protons on the asymmetric carbon are shown at 2.7 ppm. The protons next to sulfur are shown at 2.8–2.9 ppm and those next to nitrogen at 3.1 ppm as triplets.

The dichlorocobalt(III) complex of adch, [Co (adch)Cl_2]Cl, has been prepared from the reaction between $Na_3(Co(CO_3)_3]$ with adch ligand and HCl. s-*cis*-[Co(adch)CO_3]$^+$, s-*cis*-[Co(adch)$(NO_2)_2$]$^+$, and s-*cis*-[Co(adch)$(NCS)_2$]$^+$ complexes have been obtained from the substitution reaction of s-*cis*-

Table 1. Crystal data and structural refinement for $[Co(adch)Cl_2]\cdot C_2H_5OH$

Empirical formula	C(12)H(28)C(13)CoN(2)OS(2)
Formula weight	445.76
Temperature (K)	293(2)
Wavelength (Å)	0.71073 Å
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 8.185(2)$ Å, $\alpha = 75.42(2)°$ $b = 9.576(2)$ Å, $\beta = 81.24(2)°$ $c = 12.845(3)$ Å, $\gamma = 77.48(2)°$
Volume (Å^3)	946.0(4)
Z	2
Density (calculated)	1.565 g/cm^3
Absorption coefficient	1.551 mm^{-1}
$F(000)$	464
Crystal size (mm)	0.25 × 0.5 × 0.05
θ Range for data collection (°)	1.65–24.97°
Index ranges	$0 \leqslant h \leqslant 9$, $10 \leqslant k \leqslant 11$, $-15 \leqslant l \leqslant 15$
Reflections collected	2152
Independent reflections	2006 [R(int) = 0.0269]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2006/0/190
Goodness-of-fit on F^2	1.093
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0546, wR2 = 0.1341
R indices (all data)	R1 = 0.0566, wR2 = 0.1359
Largest diff. peak and hole (e Å^{-3})	1.178 and −0.717



Scheme 1. Synthetic route to prepare adch ligand.

$[Co(adch)Cl_2]^+$ with, respectively, Li_2CO_3, $NaNO_2$, and NaSCN. Except for the carbonato complex, in which more than one equivalent amount of Li_2CO_3 were used to prepare the s-*cis*-$[Co(adch)CO_3]^+$ complex, two equivalent amounts of $NaNO_2$ and NaSCN were good enough to obtain, respectively, s-*cis*-$[Co(adch)(NO_2)_2]^+$ and s-*cis*-$[Co(adch)(NCS)_2]^+$ complexes.

The dichlorocobalt(III) complexes of the NSSN-type tetradentate ligands $[Co(NSSN)Cl_2]^+$, have been observed to show the $^1A_{1g} \rightarrow {}^1T_{1g}$ (Oh) electronic transition at 607–610, 537–545 and 630 nm for, respectively, s-*cis*, uns–*cis*, and trans geometric isomers [3–5]. Figure 1 shows the electronic absorption spectra for the four complexes of s-*cis*-$[Co(adch)X_2]^+$

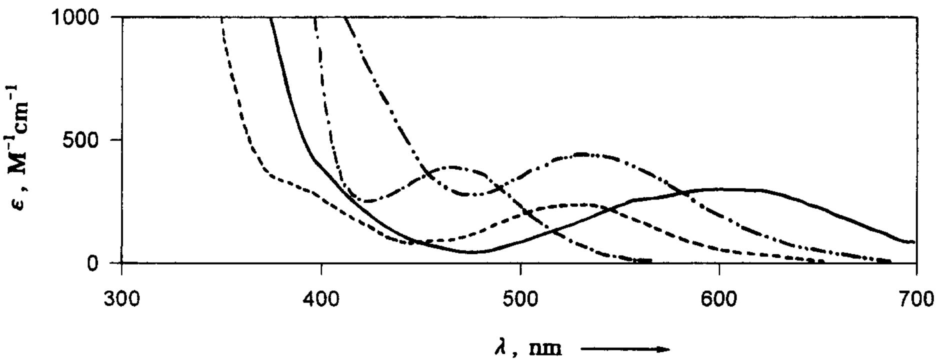


Fig. 1. Electronic absorption spectra of s-cis-$[Co(adch)Cl_2]^+$ (—), s-cis-$[Co(adch)CO_3]^+$ (- - -), s-cis-$[Co(adch)(NCS)_2]^+$ (– · · –), s-cis-$[Co(adch)(NO_2)_2]^+$ (– · –).

($X = Cl^-$, NO_2^-, NCS^-, and $X_2 = CO_3^{2-}$) prepared in this work. The complex $[Co(adch)Cl_2]^+$ shows the $^1A_{1g} \rightarrow {}^1T_{1g}$ (Oh) electronic transition at 608 nm, which suggest that this dichloro complex has the s-*cis* geometric configuration. The carbonato, dinitro, and diisothiocyanto cobalt(III) complexes of adch show the $^1A_{1g} \rightarrow {}^1T_{1g}$ (Oh) electronic transition at, respectively, 527, 468 and 531 nm, which are typical for the s-*cis* geometric isomers [3–5] (Table 2).

The crystal structure of the dichlorocobalt(III) complex of adch, s-*cis*-$[Co(adch)Cl_2]Cl \cdot C_2H_5OH$, has been determined. Table 1 shows the crystal data, while Table 3 indicates the bond distances and bond angles.

In Fig. 2, the Δ and Λ absolute configurations of the s-*cis*-$[Co(adch)Cl_2]^+$ cations, two chloride ions and two ethanol molecules are shown in the unit cell. Figures 3 and 4 show the structures of, respectively, Δ-s-*cis*-(λδλ)-$[Co(adch)Cl_2]^+$ and Λ-s-*cis*-(δλδ)-[Co

Table 2. Absorption data (λ_{max}) of s-*cis*-$[Co(L)X_2]^+$ Complexes (L = adch)

s-*cis*-complex	Color	L adch[a]	eee[b,c]	epe[d]	tet[c]
$[Co(L)Cl_2]^+$	blue	608 nm	610 nm	610 nm	570 nm
		545 sh	545 sh	550 sh	
		290	282		
$[Co(L)CO_3]^+$	pink	527	520	520	
		390 sh	390 sh	390 sh	
$[Co(L)(NCS)_2]^+$	red–brown	531	527		
$[Co(L)(NO_2)_2]^+$	orange–yellow	468	463	463	

[a] This work.
[b] Ref. [2].
[c] Ref. [3].
[d] Ref. [4].

Table 3. Bond distances (Å) and angles (°) for $[Co(adch)Cl_2]Cl \cdot C_2H_5OH$

Co(1)—N(2)	1.959(6)	N(2)—C(1)	1.466(9)
Co(1)—N(1)	1.963(5)	C(1)—C(2)	1.521(10)
Co(1)—S(2)	2.232(2)	C(3)—C(4)	1.514(11)
Co(1)—S(1)	2.241(2)	C(5)—C(10)	1.504(9)
Co(1)—Cl(2)	2.250(2)	C(5)—C(6)	1.523(10)
Co(1)—Cl(1)	2.262(2)	C(6)—C(7)	1.540(11)
S(1)—C(2)	1.814(7)	C(7)—C(8)	1.511(11)
S(1)—C(5)	1.835(7)	C(8)—C(9)	1.523(11)
S(2)—C(4)	1.821(8)	C(9)—C(10)	1.526(10)
S(2)—C(10)	1.835(7)	O(1)—C(11)	1.374(12)
N(1)—C(3)	1.468(9)	C(11)—C(12)	1.385(14)
N(2)—Co(1)—N(1)	177.2(3)	C(4)—S(2)—Co(1)	99.1(3)
N(2)—Co(1)—S(2)	94.6(2)	C(10)—S(2)—Co(1)	104.3(2)
N(1)—Co(1)—S(2)	87.0(2)	C(3)—N(1)—Co(1)	114.1(5)
N(2)—Co(1)—S(1)	86.4(2)	C(1)—N(2)—Co(1)	113.5(5)
N(1)—Co(1)—S(1)	95.9(2)	N(2)—C(1)—C(2)	107.5(6)
S(2)—Co(1)—S(1)	90.47(8)	C(1)—C(2)—S(1)	108.9(5)
N(2)—Co(1)—Cl(2)	90.1(2)	N(1)—C(3)—C(4)	108.6(6)
N(1)—Co(1)—Cl(2)	88.4(2)	C(3)—C(4)—S(2)	108.7(5)
S(2)—Co(1)—Cl(2)	174.86(8)	C(10)—C(5)—C(6)	110.2(6)
S(1)—Co(1)—Cl(2)	87.89(8)	C(10)—C(5)—S(1)	111.5(5)
N(2)—Co(1)—Cl(1)	88.7(2)	C(6)—C(5)—S(1)	113.2(5)
N(1)—Co(1)—Cl(1)	89.1(2)	C(5)—C(6)—C(7)	109.6(6)
S(2)—Co(1)—Cl(1)	88.96(8)	C(8)—C(7)—C(6)	118.8(7)
S(1)—Co(1)—Cl(1)	174.91(8)	C(7)—C(8)—C(9)	111.7(7)
Cl(2)—Co(1)—Cl(1)	93.09(9)	C(8)—C(9)—C(10)	109.2(6)
C(2)—S(1)—C(5)	103.0(3)	C(5)—C(10)—C(9)	110.6(6)
C(2)—S(1)—Co(1)	99.1(2)	C(5)—C(10)—S(2)	112.6(5)
C(5)—S(1)—Co(1)	104.7(2)	C(9)—C(10)—S(2)	111.9(5)
C(4)—S(2)—C(10)	102.1(4)	O(1)—C(11)—C(12)	116.7(10)

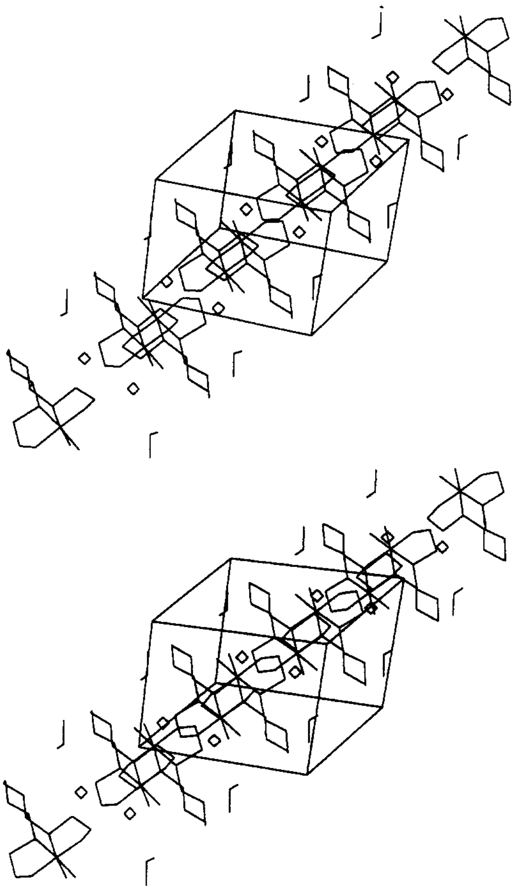


Fig. 2. Stereoview of contents of unit cell of [Co(adch)Cl_2]·C_2H_5OH.

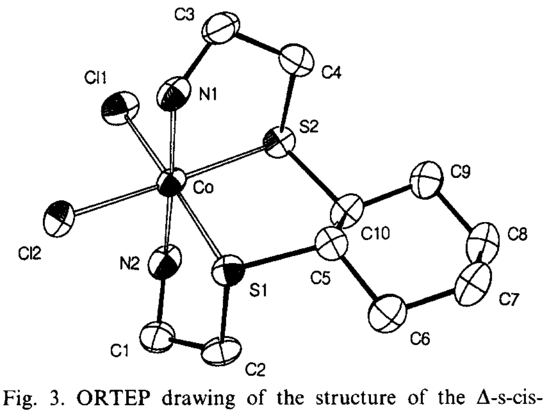


Fig. 3. ORTEP drawing of the structure of the Δ-s-cis-[Co(adch)Cl_2]$^+$ cation, in which the coordinated ligand is SS-adch only.

(adch)Cl_2]$^+$ isomers, in each of which the cobalt atom has a distorted octahedral structure with two nitrogen atoms in axial position, while two thioether sulfur atoms and two chloride ligands are *cis*-positioned in an equatorial plane.

In the Δ-s-*cis* configuration (Fig. 3) only the SS enantiometer of the adch ligand is coordinated stereospecifically to the cobalt(III) ion and the conformation of the central chelate ring is δ, which is the only conformation the SS-adch take. Such conformation causes the carbon atom adjacent to the nitrogen atom of the —$SCH_2CH_2NH_2$ rings to move away from the central chelate ring, and the nonbonded H—H interactions between the adjacent chelate ring protons and the central chelate ring protons are minimized [4]. In the Λ-s-*cis* configuration (Fig. 4), on the other hand, only the RR enantiometer of the adch ligand is coordinated stereospecifically to the cobalt(III) ion and the conformation of the central chelate ring is λ, which is the only conformation the RR–adch take. The adch ligand has been synthesized as a racemic mixture and has not been resolved. Although the racemic mixture of the adch ligand has been used to prepare the complex with the cobalt(III) ion, the SS and RR enantiometers have been coordinated stereospecifically to the cobalt(III) ion to give the complexes having, respectively, Δ and Λ absolute configurations.

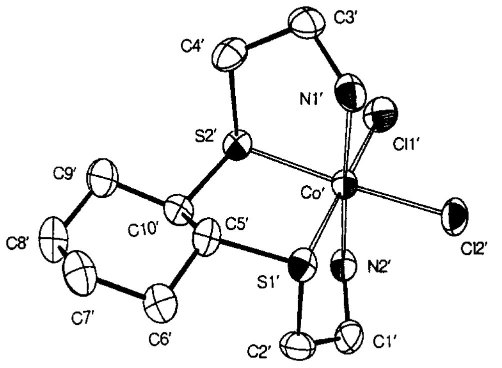
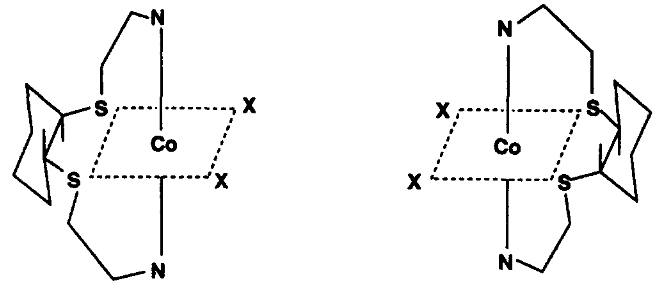


Fig. 4. ORTEP drawing of the structure of the Λ-s-cis-[Co(adch)Cl_2]$^+$ cation, in which the coordinated ligand is RR-adch only.

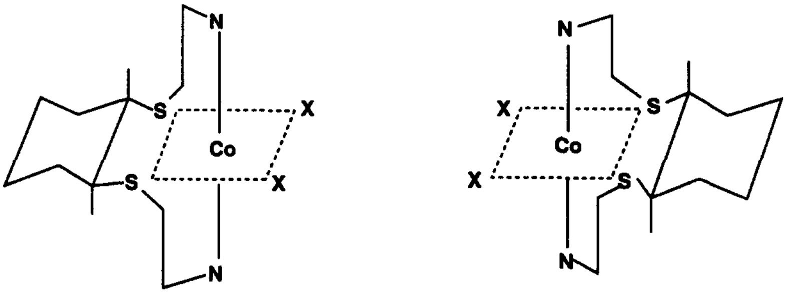
The Co—S bond lengths of the complex are 2.241 (2) and 2.232 (2) Å, while the Co—N bond lengths are 1.963 (5) and 1.959 (6) Å. Such bond lengths are very similar to those in [Co(ete)NO_2Cl]Cl whose crystal structure is known (Co—S: 2.24, 2.22 Å, Co—N: 1.96, 1.99 Å).

The bond angles around the sulfur atom suggest that there is considerable strain. The Co—S(1)—C(2,5) bond angles are 99.1 (2) and 104.7 (2)°, and the C(2)—S(1)—C(5) bond angle is 103.0 (3)°, which are smaller than expected for the tetrahedral geometry. Such small Co—S—C bond angles are expected when a five-membered chelate is formed [15]. If a six-membered chelate ring is formed in a complex such as [Co(ete)NO_2Cl]Cl, the Co—S—C bond angles are 114.6 (2) and 109.5 (2)° as expected for a tetrahedral geometry.

In this work the adch ligand has been observed to yield the s-*cis*-geometric isomer only, and, furthermore, has stereospecifically coordinated to the cobalt(III) ion to give the Λ-s-*cis*-($\delta\lambda\delta$) enantiometer for the RR–adch and the Δ-s-*cis*-($\lambda\delta\lambda$) enantiometer for the



A. Λ-Complex-RR-adch **B. Δ-Complex-SS-adch**



C. Λ-Complex-SS-adch **D. Δ-Complex-RR-adch**

Fig. 5. Possible absolute configurations and chelate ring conformations for the s-cis-[Co(adch)X_2]$^+$, in which the cyclohexane ring a chair conformation.

SS–adch, though the ligand used for the preparation of the complexes is a racemic mixture. Such stereospecificity may be understood considering the absolute configuration of the complex and the configuration and ring conformation of the ligand. Though the RR–adch ligand can take the λ central chelate ring conformation only and the SS–adch ligand the δ central chelate ring conformation only [16], there are still four possible optical isomers as shown in Table 3 and Fig. 5.

The outside —$SCH_2CH_2NH_2$ chelate ring can have either λ or δ chelate ring conformation, and the carbon atom next to nitrogen donor atom can be toward the central chelate ring (*endo*) or away from the central chelate ring (*exo*) [4,5]. For the endo isomer, however, the hydrogen–hydrogen nonbonded interaction will be increased, since the carbon atom next to the nitrogen atom is toward the central chelate ring, and thus the ring strain between the central chelate ring and the outside chelate rings is increased. Therefore, C and D in Fig. 5 and Table 4 will not be formed, and the RR– or SS–adch ligand can coordinate to the cobalt(III) ion stereospecifically to give, respectively, the Λ-s-*cis* or Δ-s-*cis* complex configuration. It is noted that, unlike the s-*cis*-cobalt(III) complexes of the triethylenetetetraamine-type tetradentate ligands 6,17], the s-*cis*-cobalt(III) complex of the adch has en isomerized to either the uns-*cis* or trans iso- sic solution.

Busch *et al.* [4] prepared s-*cis*-[Co(epe)Cl_2]$^+$ complex, which were resolved into optical isomers using antimonyl-*d*-tartrate. Although no X-ray data were given, they found out that L-epe were coordinated stereospecifically to give the Λ isomer and D-epe stereospecifically to give the Δ isomer. Since such stereospecific coordination have been observed in our work to prepare s-*cis*-[Co(adch)Cl_2]$^+$ complex *via* X-ray crystallographic study, resolution of this complex has not been attempted.

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