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Preparation and Crystal Structure of [Co(di(2-aminoethyl)sulfide Cl_3]

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Complexes containing flexible polydentate ligands, L, have long been of considerable interest to coordination chemists [1–13]. Such complexes often can be designed to function as stereospecific catalysts when incorporated into metal complexes of the from [MLX_n] containing good leaving ligands X. However, relatively few structural investigations have appeared on complexes with tridentate ligands or with N,S donor ligands. Therefore, we have prepared and structurally characterized the complex [Co(III)-(daes)Cl_3], where daes is the N,S tridentate ligand, di(2-aminoethyl)sulfide.

Experimental

^{1}H NMR spectra were measured on a Varian EM 390 instrument. Natural abundance ^{13}C NMR spectra were measured on a Varian CFT-20, all NMR shifts are reported in ppm relative to TMS. IR spectra were measured on a Perkin-Elmer 727B instrument. Elemental analyses were performed by Atlantic Microlabs, Inc. Except for mercaptoethylphthalimide which was prepared differently [14], organic syntheses followed the methods of Gabriel [15]. Spectral data not in the literature are reported below.

Preparation of Di(phthalimidoethyl)sulfide

This material was prepared as reported by Gabriel [15]. ^{1}H NMR ($CDCl_3$) 2.9(t), 7.75(d). ^{13}C NMR ($CDCl_3$) 29.46, 36.66, 123.39, 132.18, 134.01, 168.16. M.p. 98 °C (129 °C lit) [15].

Preparation of Di(2-aminoethyl)sulfide·2HCl

This material was prepared as reported by Gabriel [15]. ^{1}H NMR (D_2O) 2.9(t), 3.3(t). ^{13}C NMR (D_2O) 28.62, 39.06. IR (KBr) 2600–3200, 1980(m), 1580, 1480, 1405, 1380, 1310, 1240, 1120, 1080, 1035, 920, 880, 820(w), 790. M.p. 121–3 °C, (131 °C lit) [15]. Neutralization of the product with NaOH resulted in an oil, $bp_{0.2 mm}$ = 60–65 °C. ^{1}H NMR (D_2O) 2.7(m).

Preparation of cis-*Trinitro(di(2-aminoethyl)sulfide)-cobalt(III)*

The filtrate from the preparation di(2-aminoethyl)sulfide·2HCl was evaporated to dryness. The resulting residue was dissolved up in MeOH. $CoCl_2 \cdot 6H_2O$ (1.5 g) was added. The deep blue solution was aerated for 10 min and an aq. solution of $NaNO_2$ (0.3 g) was added. Aeration was continued for an additional 15 min. The yellow–orange precipitate formed was collected, washed with water and dried. ^{1}H NMR (DMSO-d_6) 2.85, 4.6(b). ^{13}C NMR (DMSO-d_6) 35.55, 43.53. *Anal.* Calcd. for $C_4H_{12}CoN_5O_6S$; C, 15.14; H, 3.79; N, 22.08. Found: C, 15.26; H, 3.93; N, 22.05%.

Preparation of cis-*Trichloro(di(2-aminoethyl)sulfide)-cobalt(III)*

The trinitro complex (0.5 g) in 10 ml conc. HCl was heated for 10 min. A blue–green solid precipitated. After the solution cooled, the solid was collected and washed with acetone. The green compound was recrystallized from conc. HCl. *Anal.* Calcd. for $C_4H_{12}Cl_3CoN_2S$: C, 16.83; H, 4.24; N, 9.8. Found: C, 16.84; H, 4.4; N, 10.26%; IR (KBr) 3250, 1600, 1400, 1310, 1260, 1140, 1020, 980 cm^{-1}.

Collection of X-ray Data

Crystals of [Co(daes)Cl_3] were grown from conc. HCl as intensely greeen prisms. A crystal with approximate dimensions 0.2 by 0.1 by 0.1 mm was mounted on a quartz fiber using epoxy cement so that the longest crystal dimension was approximately parallel to the fiber axis. Unit cell dimensions and orientation matrix were determined on a Nicolet R3 four-circle diffractometer at room temperature using Ni-filtered Cu K-alpha radiation. 14 reflections whose Bragg angles varied from 15.08 to 83.96° were centered by the machine and used in unconstrained least-squares refinement of the lattice parameters and orientation matrix. The unit cell parameters are a = 7.3945(9), b = 13.8321(21), c = 10.0400(14) Å, β = 101.88(1)°, volume = 1004.9(2) Å^3. Omega scans of several low-Bragg-angle reflections gave peak widths at half height of less than 0.3°, indicating a satisfactory mosaic spread for the crystal. The density, ρ_{ex} = 1.88(02) g/cm^3 was determined by flotation in $CHCl_3$ and $CHBr_3$ and is in agreement with ρ_c = 1.89 for z = 4. Axial photographs indicated that the crystals were monoclinic. The absence of

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TABLE I. Positional and Isotropic Thermal Parameters for an Independent Molecule of Co(daes)Cl_3.

Atom	x/A	y/B	z/C
Co	0.2734(0)	0.1950(1)	1.1255(0)
Cl_1	−0.0221(5)	0.1664(3)	1.0113(4)
Cl_2	0.3855(5)	0.1737(2)	0.9334(4)
Cl_3	0.2577(5)	0.3581(2)	1.0957(4)
N_1	0.5259(13)	0.2081(7)	1.2241(11)
C_2	0.6384(17)	0.1146(9)	1.2358(14)
C_3	0.5278(16)	0.0345(9)	1.2783(14)
S_4	0.2946(4)	0.0382(2)	1.1711(3)
C_5	0.1490(18)	0.0359(9)	1.2964(16)
C_6	0.1835(16)	0.1283(8)	1.3820(13)
N_7	0.1790(14)	0.2144(7)	1.2920(12)

all reflections with $h + k = 2n + 1$ and the absence of h0l reflections with $l = 2n + 1$ were consistent with the space group *Cc* (No. 9) [26].

Intensity data were collected using the $\theta/2\theta$ scan technique with a scan rate ranging from 3.91 to 29.3 min^{-1}. A scan width of 2° was sufficient to collect all of the peak intensity. Stationary background counted were measured at the beginning and at the end of each scan with a total background to scan time ratio of 1. No significant fluctuations were observed in the intensities of three standard reflections monitored every 97 reflections. Data with Bragg angle between 4 and 100° (550 total) were corrected for Lorentz and polarization effects but not for absorption. The standard deviation for each reflection was calculated on the basis of counting statistics. The data are stored with the editors.

Solution of the Structure

The structure was solved by the heavy atom technique. The cobalt atom was located from a three-dimensional patterson synthesis. Electron density maps based on the heavy atom phases revealed the positions of the chlorine and sulfur atoms and subsequent Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. The structure was refined anisotropically by least squares using all data with $F > \sigma(F)$. Hydrogen atom positions were then deduced from an electron density difference map but did not refine well. Hydrogen atom positions were then constrained to their calculated positions and only their isotropic thermal parameters allowed to vary. The final $R = 0.050$ and $R_w = 0.049$ ($w = 0.7366/(\sigma(F^2) + 0.004587F^2)$). Final positional and isotropic thermal parameters are given in Table I. Anisotropic thermal parameters can be found in supplemental material, stored with the editors.

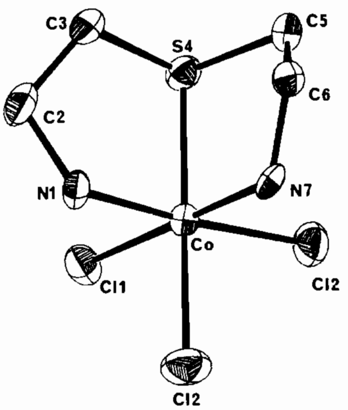

Fig. 1. ORTEP drawing of [Co(III)(daes)Cl_3]. The probability ellipsoids are shown at the 50% level. The atom labels in the figure are the same as those identifying the atoms in the tables.

Results and Discussion

Di(2-aminoethyl)sulfide was first prepared by Gabriel [15]. Gabriel's synthesis is a multi-step synthesis involving the preparation of mercaptoethylphthalide which is condensed with bromoethylphthalide to form di(phthalilimidoethyl)sulfide. This product is deprotected with hydrochloric acid. This procedure was followed except that mercaptoethylphthalide was made using thiourea and base hydrolysis [14] instead of potassium hydrosulphide. Gabriel's procedure is rather time consuming and therefore an alternative method using ethyleneimine and hydrogen sulfide has been reported [17]. This alternative was not used due to the toxicity of ethyleneimine.

Ligands with S donors form complexes with fewer isolated geometric isomers than ligands with exclusively N donors. Complexes of the type [$CoLX_3$] can have L in two geometric arrangements, *cis* and *trans*. Hydrolysis of *trans*-[Co(dien)Cl_3] [8–10] yields *cis*[Co(dien)$(H_2O)_3$]$^{3+}$ [10]. Only one isomer [Co(deas)Cl_3] has been isolated [13]. Both the [$Co(daes)_2$]$^{3+}$ [11, 12] and [$Rh(daes)_2$]$^{3+}$ [18], cations exist in the *u-fac* isomeric form.

The stereoselectivity of ligands containing the thioether moiety has been observed in tetradentate and pentadentate ligands. The complex [Co(eee)Cl_2]$^+$, where eee is 1,8-diamino-3,6-dithiaoctane, forms the *s-cis* isomer only [6]. Attempts to isomerize [Co(eee)Cl_2]$^+$ were unsuccessful. The nitrogen analogue, [Co(trien)Cl_2]$^+$ (trien is triethylenetetraamine) is known to exist in three geometrical forms that readily isomerize [7]. The complex [CoQCl]$^{2+}$, where Q is the pentadentate 7-methyl-4,10-dithia-1,7,13-triazatridecane, has the potential of existing in four geometrical isomers but only one isomer is observed [19].

TABLE II. Interatomic Distances and Angles for the Independent Molecule of $Co(daes)Cl_3$.

Interatomic distances (Å)

$Co-Cl_1$	2.283(4)	C_2N_1	1.529(15)
$Co-Cl_2$	2.270(4)	C_2-C_3	1.490(18)
$Co-Cl_3$	2.275(4)	C_3-S_4	1.835(12)
$Co-N_1$	1.933(9)	C_5-S_4	1.817(13)
$Co-S_4$	2.216(3)	C_5-C_6	1.531(19)
$Co-N_7$	1.959(11)	C_6-N_7	1.491(15)

Interatomic angles (deg)

$Cl_1-Co-Cl_2$	91.7(1)	$Co-N_1-C_2$	114.4
$Cl_1-Co-Cl_3$	95.0(1)	$Co-N_7-C_6$	107.8
$Cl_2-Co-Cl_3$	92.0(1)	C_3-S_4-Co	99.6(4)
Cl_2-Co-N_1	87.9(3)	C_5-S_4-Co	97.7(4)
Cl_3-Co-N_1	89.6(3)	$C_5-S_4-C_3$	102.3(7)
Cl_1-Co-S_4	87.3(1)	$N_1-C_2-C_3$	109.2(10)
Cl_2-Co-S_4	91.5(1)	$C_2-C_3-S_4$	108.4
Cl_1-Co-N_7	88.8(3)	$S_4-C_5-C_6$	108.7(8)
Cl_3-Co-N_7	87.7(3)	$C_5-C_6-N_7$	110.2(11)
N_1-Co-N_7	91.5(4)		
N_7-Co-S_4	88.8(3)		

The complexes discussed above all contain fused 5-membered rings. When the size of the chelate rings is increased to 6 the stereoselectivity is lost. The cobalt complexes of the series eee, 1,9-diamino-3,7-dithianonane (ete) and 1,10-diamino-4,7-dithiadecane (tet) have been extensively studied [20]. $[Co(ete)Cl_2]^+$ contains the fused ring system 5,6,5 and exists in the *trans* and *uns-cis* conformations. $[Co(tet)Cl_2]^+$ contains the fused ring system 6,5,6 and exists in the *u-cis* and *s-cis* isomers.

Based on spectral data Dikman predicted that $[Co(daes)Cl_3]$ existed in the *cis* form [13]. This has been confirmed by the X-ray structure reported in this paper. The molecular structure of $[Co(daes)Cl_3]$ is shown in Fig. 1 with interatomic distances and angles given in Table II. The arrangement of the donating atoms around cobalt is roughly octahedral with the ligand occupying a *cis* configuration. Co–N distances are different, being 1.933(9) Å and 1.959(11) Å for N(1) and N(7) respectively. The Co–N distances for $[Co(daes)_2]^{3+}$ [12], $[Co(ete)(NO_2)Cl]^+$ [21] and $[Co(gee)(NO_2)_2]^+$ [22] are in the range of 1.96–1.99 Å. The Co–S distance, 2.22 Å, and the Co–Cl distances, 2.27 Å average, are in the expected range. The angles between $S_4-Co-Cl_3$ and $N_1-Co-Cl_1$ are 175.7(3) and 175.4(4) respectively, a 4.3 and 4.6 degree deviation from 180. Similar distortions are seen in $[Co(ete)(NO_2)Cl]^+$ [21], $[Co(gee)(NO_2)_2]^+$ [22], and $[Co(daes)_2]^{3+}$ [12]. Thus there are no unusual structural features in $[Co(daes)Cl_3]$.

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