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The Formation and Reactivity of Sulfito Complexes of Tetraethylenepentamine-cobalt(III): X-ray Structure of $\alpha\alpha$-[Co(tetren)SO_3]ClO_4

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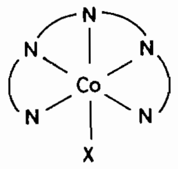
Abstract

The synthesis of complexes of the type Co(tetren)-OH_2^{3+} (tetren = tetraethylenepentamine) and their reactions with sulfite to produce O- and S-bonded isomers were studied in detail. The linkage isomerization reaction of $\alpha\beta$S-Co(tetren)OSO_2^+ to $\alpha\beta$S-Co(tetren)SO_3^+ is accompanied by a geometrical isomerization to $\alpha\alpha$-Co(tetren)SO_3^+. The latter species was isolated as pure crystals and an X-ray structure was determined. The structure data clearly show the strong *trans* effect of the sulfito ligand, which may account for the geometrical isomerization process.

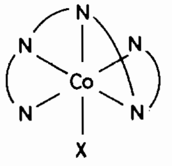
Introduction

The formation and reactivity of sulfito complexes in general, have received considerable attention in recent years [1–6]. Most fascinating is the very rapid formation of O-bonded sulfito complexes via SO_2 uptake by metal hydroxo species and the different reactions that such species can undergo, *viz.* acid-catalysed loss of SO_2, intramolecular electron transfer, and O- to S-bonded linkage isomerization. The latter reaction is only observed in a few extreme cases, *viz.* for the $\alpha\beta$S-Co(tetren)OSO_2^+ and *trans*-Co$(NH_3)_4$(CN)OSO_2 species [6, 7]. The reactivity of such sulfito complexes is of fundamental interest since such systems can be adopted as models for metal catalysed oxidation reactions of S(IV). With increasing chelation the redox component becomes less important such that for the pentadentate tetren (tetraethylenepentamine) complex no redox reaction occurs and the linkage isomerization can be studied.

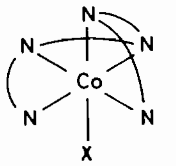
The treten ligand has four modes of coordination, *viz.*



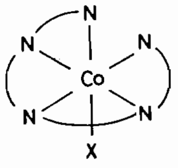
α α



β β



α β



β - trans

Of these structures the $\alpha\alpha$ configuration has a plane of symmetry, the $\alpha\beta$ and β-*trans* isomers can exist in 2 and 4 diastereoisomeric forms, respectively, and the $\beta\beta$ isomer can exist in only one form. The absolute configurations and conformations of three of the chloro complexes have been established by crystal structure determinations, *viz.* the $\alpha\beta$R, $\alpha\beta$S and $\alpha\alpha$ isomers [8–10]. The introduction of multidentate ligands in general [7–16] may lead to confusion in the literature with respect to the assignment of the different isomers. This is the case for the tetren complexes mentioned above [7–10, 13, 14]. House and Garner [13, 14] synthesized α- and β-Co(tetren)-$X^{(3-n)+}$ complexes, where $X = Cl^-$, OH^-, OH_2, NO_2^-, N_3^- and SCN^-. It was later shown [8] for the chloro complexes that the α isomer is in fact $\alpha\beta$R, and the β isomer $\alpha\beta$S. A significant observation is that in basic solution the $\alpha\beta$R isomer is substantially converted into the $\alpha\beta$S [8, 17] and the β isomer into the α [13]. From this one would conclude that $\alpha\beta$R is the β isomer and $\alpha\beta$S the α isomer, as suggested by Harris and co-workers [7]. Whatever the answer to

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this confusion may be, it is generally accepted that the $\alpha\beta$S species is produced in basic medium [7, 8, 17].

In the past it was usually assumed without conclusive evidence that during substitution reactions the configuration of the tetren ligand does not alter [7, 13, 14]. Our general interest in the formation and reactivity of O- and S-bonded sulfito complexes has led to a detailed investigation of the linkage isomerization reaction of $\alpha\beta$S-Co(tetren)OSO_2^+ [18]. Dash *et al.* [7] found that the isosbestic points did not remain well-defined at longer reaction times and a slow subsequent isomerization of presumably $\alpha\beta$S-Co(tetren)SO_3^+ to another tetren configuration was postulated. We have isolated the isomerization product and report the crystal structure of $\alpha\alpha$-[Co(tetren)SO_3]ClO_4 in this communication.

Experimental

Materials

$\alpha\beta$R- and $\alpha\beta$S-[Co(tetren)OH_2]$(ClO_4)_3$: a mixture of $\alpha\beta$R- and $\alpha\beta$S-[Co(tetren)Cl]$(ClO_4)_2$ was prepared according to the method of House and Garner [13, 14]. Approximately 5 cm^3 1 M LiOH was added dropwise to a stirred suspension of 2 g [Co(tetren)-Cl]$(ClO_4)_2$ in 10 cm^3 water until the pH remained constant at pH 8. Concentrated $HClO_4$ was now added to convert the produced hydroxo species into the aquo form (pH 2), and 0.86 g $AgClO_4$ was added to precipitate the released chloride as AgCl. The latter was filtered off and the solvent was removed from the filtrate by freeze drying. The residue was washed with three portions of 95% ethanol, and ether was added to the oily residue to produce a very hygroscopic orange powder. *Anal.** (theoretical values): C 17.1 (17.0); H 4.7 (4.5); N 12.5 (12.4); Cl 19.0 (18.8); Co 10.5 (10.4)%. Its UV–Vis spectrum is in good agreement with that reported in the literature [14]. This product undergoes a slow isomerization reaction in the solid state and after approx. six months it has a completely different spectrum, *viz.* 490 (76) and 346 nm (68 M^{-1} cm^{-1}). The ^1H NMR spectrum indicated a highly symmetric species, which can only be the $\alpha\alpha$ configuration.

$\alpha\alpha$-[Co(tetren)SO_3]$ClO_4 \cdot H_2O$: According to the method of Dash *et al.* [7] 0.22 g $Na_2S_2O_5$ was added to 1.1 g of a mixture of $\alpha\beta$R- and $\alpha\beta$S-[Co(tetren)-OH_2]$(ClO_4)_3$ in 10 cm^3 water, covered and left to stand at room temperature. After a week small yellow crystals began to appear. These were collected on a fritted glass funnel, washed with 95% ethanol and recrystallised from hot water (0.5 g/15 cm^3) to which 0.3 g $NaClO_4$ was added. Reddish-brown crystals formed. *Anal.* C 21.8 (21.6); H 5.4 (5.7); N 15.8 (15.7); S 7.1 (7.2)%. UV–Vis spectral data are compared to literature data in Table I.

TABLE I. UV–Vis Spectral Data for Sulfito Complexes of Co(tetren)

Complex	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})	Reference
$\alpha\beta$S-Co(tetren)OSO_2^+	330, 510	1928, 150	7
$\alpha\beta$S-Co(tetren)SO_3^+	281, 444	16900, 236	7
$\alpha\alpha$-Co(tetren)SO_3^+	289, 453	17500, 177	this work
Co(tetren)$SO_3^{+\,a}$	281, 445	>10000, ~260	this work

[a] Endproduct of linkage isomerization observed in solution – see 'Discussion'.

Chemicals of analytical reagent grade and doubly distilled water were used throughout this study. UV–Vis absorption spectra were recorded on a Perkin-Elmer 555 spectrophotometer. Reaction rates were measured on a Zeiss PMQ II spectrophotometer equipped with a thermostated high pressure cell [19]. Ambient pressure work was usually performed at 15 to 20 bar in this instrument.

Structure Determination

The reddish-brown crystals of [Co(tetren)SO_3]-ClO_4 were suitable for data collection.

Crystal data: $a = 14.576(9)$ Å; $b = 12.765(8)$ Å; $c = 9.544(6)$ Å; $\alpha = 91.52(8)°$; $\beta = 102.76(8)°$; $\gamma = 105.45(9)°$; $D_{exp} = 1.77$ g cm^{-3}; $Z = 4$; $\mu = 14.2$ cm^{-1} and space group $P\bar{1}$.

The three dimensional intensity data were collected on a Philips PW 1100 diffractometer, using graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) for θ values between 3° and 23°. A total of 4598 reflections were measured of which 4314 with $I > 3\sigma(I)$. Three reflections were used as standard and remeasured after every 60 reflections to check for any decomposition. A crystal with dimensions 0.3 × 0.3 × 0.25 mm was used for the data collection. Only Lorentz and polarization corrections were applied.

The structure was solved by using the X-ray 72 system of programs on a Univac 1100 computer. The cobalt atoms were located from a three-dimensional Patterson function. All the other non-hydrogen atoms were located from successive Fourier maps. The full-matrix least squares refinement using all the observed reflections and anisotropic thermal parameters for all the atoms yield a final R value of 0.056. Atomic scattering factors were taken from Cromer and Mann [20]. See also 'Supplementary Material'.

Results and Discussion

The UV–Vis absorption spectrum of the isolated Co(tetren)SO_3^+ species differs significantly from that

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*Chemical analyses carried out at Hoechst Analytical Laboratory, Frankfurt/Main, F.R.G.

TABLE II. Fractional Atomic Co-ordinates (× 10^4) and Thermal Parameters (× 10^2)

Atom	Molecule 1				Molecule 2			
	x	*y*	*z*	U_{eq} [a]	*x*	*y*	*z*	U_{eq} [a]
Co	2197.1(6)	6368.6(6)	1002.3(9)	2.3(1)	1950.9(6)	1281.8(6)	2150.6(9)	2.6(1)
N(1)	1223(4)	6690(4)	−580(6)	2.8(3)	1959(4)	1608(5)	147(6)	3.6(3)
N(2)	2938(4)	6211(4)	−459(6)	2.9(3)	3240(4)	1016(5)	2264(7)	3.7(3)
N(3)	2985(4)	7953(4)	1308(6)	2.8(3)	2718(5)	2825(4)	2948(6)	3.8(3)
N(4)	3181(4)	6168(4)	2711(6)	3.1(3)	1896(4)	1034(4)	4182(6)	3.7(3)
N(5)	1421(4)	6557(4)	2390(6)	3.1(3)	691(4)	1610(4)	1969(7)	3.7(3)
C(1)	1535(6)	6714(7)	−1992(8)	4.4(4)	2931(6)	1656(6)	186(8)	4.7(5)
C(2)	2257(5)	6024(6)	−1941(7)	4.1(4)	3399(6)	891(6)	765(9)	4.7(5)
C(3)	3815(5)	7194(5)	−302(8)	3.5(4)	4037(5)	1913(7)	3208(9)	4.8(5)
C(4)	3549(5)	8206(5)	163(8)	3.6(4)	3783(6)	2983(6)	3007(9)	4.8(5)
C(5)	3616(5)	8193(6)	2811(8)	3.6(4)	2503(6)	3039(6)	4378(8)	4.4(5)
C(6)	4007(5)	7210(6)	3195(8)	3.8(4)	2492(6)	2029(6)	5201(8)	4.3(4)
C(7)	2660(6)	5804(6)	3890(8)	4.3(4)	845(6)	723(6)	4261(9)	4.8(4)
C(8)	1909(5)	6451(6)	3924(8)	4.3(4)	299(6)	1424(7)	3313(10)	5.3(5)
S	1426(1)	4574(1)	600(2)	2.7(1)	1202(1)	−488(1)	1479(2)	2.7(1)
O(1)	2187(3)	4015(3)	502(5)	3.7(3)	1663(3)	−1084(4)	2633(5)	3.8(3)
O(2)	668(3)	4347(4)	−778(6)	4.3(3)	1372(4)	−839(4)	88(5)	4.0(3)
O(3)	949(3)	4154(4)	1780(6)	4.2(3)	140(3)	−741(4)	1373(6)	3.9(3)
Cl	5446(1)	5425(1)	2317(2)	3.6(1)	6475(1)	453(2)	3343(2)	4.1(1)
O(4)	6034(6)	6412(7)	1994(9)	10.4(6)	7406(5)	431(7)	3156(9)	10.0(6)
O(5)	5856(6)	4567(7)	2250(9)	9.7(6)	6483(6)	1561(5)	3545(8)	9.1(5)
O(6)	4503(4)	5160(5)	1341(6)	5.4(3)	5775(6)	−71(7)	2113(7)	10.1(6)
O(7)	5301(5)	5587(6)	3733(6)	6.9(4)	6294(6)	−76(5)	4598(6)	7.8(5)
O[b]	693(7)	2643(6)	−2880(9)	10.9(7)	480(10)	4176(12)	5026(15)	18.3(13)

[a] $U_{eq} = 1/3\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$. [b] Oxygen atom of the water molecule.

found by Dash *et al.* [7] which they believe to be the $\alpha\beta$S isomer since it was formed from the $\alpha\beta$S aquo complex. A systematic study of the linkage isomerization in solution was therefore undertaken. On addition of bisulfite to the Co(tetren)OH_2^{3+} species at $5 < pH < 7$, the Co(tetren)OSO_2^+ species is produced rapidly via SO_2 uptake [7]. This is followed by a linkage isomerization reaction to the S-bonded isomer, characterized by absorption maxima at 281 and 445 nm which are in good agreement with those reported by Dash *et al.* [7] (see Table I). However, the isosbestic points around 434 and 486 nm during this reaction showed continuous shifts of approximately 3 nm to lower and higher wavelengths, respectively. First-order plots were linear for at least two to three half-lives, but the resulting rate constants showed considerable scatter, a strong dependence on the starting material used and a high pH sensitivity. The results [18] were in reasonable agreement with those reported by Dash *et al.* [7]. The product produced at longer reaction times was identical to that isolated as pure crystals, *viz.* the $\alpha\alpha$ isomer. It follows that the linkage isomerization reaction is accompanied by stereochemical changes, which have shown to be very pH dependent [18] and can account for the scatter in the kinetic data [7, 18].

The structure of the $\alpha\alpha$-[Co(tetren)SO_3]ClO_4 species was solved with the aid of X-ray analysis. The final positional and thermal parameters with their standard deviations for the two crystallographic independent molecules are listed in Table II. The two independent [Co(tetren)SO_3]$^+$ ions are nearly equivalent as may be judged from the bond distances and angles given in Tables III and IV, respectively. Figure 1 gives a general view of one of the independent cations and also shows the numbering scheme of the atoms. It is clear that the $\alpha\alpha$-isomer was obtained. Figure 2 shows a stereoview of the [Co(tetren)SO_3]$^+$ ion.

The average Co–N bond distance is 1.985 Å compared to the 1.967 Å found in [Co(tetren)Cl]$^{2+}$ [10]. The Co–N(3) bond distance is slightly longer (in contrast with the Co–N(3) bond distance in [Co(tetren)Cl]$^{2+}$) than the other Co–N bond distances. It may be attributed to the stronger *trans* influence of the sulfite ligand. A similar effect was observed in the structures of $Co(NH_3)_5SO_3^+$ and *cis*-$Co(en)_2(SO_3)_2^-$ [21, 22]. This *trans*-influence [2] may in fact induce the $\alpha\beta \rightarrow \alpha\alpha$ isomerization process as observed in this study. All the C–N and C–C bond distances agree well with those found in [Co(tetren)Cl]$^{2+}$ [10].

TABLE III. Interatomic Distance (A) with Estimated Standard Deviations in Parenthesis

Bond	Molecule 1	Molecule 2
Co–N(1)	1.965(5)	1.970(6)
Co–N(2)	1.980(6)	1.978(6)
Co–N(3)	2.019(5)	2.020(5)
Co–N(4)	1.992(5)	1.988(6)
Co–N(5)	1.970(6)	1.963(7)
Co–S	2.247(2)	2.237(2)
N(1)–C(1)	1.513(10)	1.505(11)
C(1)–C(2)	1.537(13)	1.540(12)
C(2)–N(2)	1.510(8)	1.509(11)
N(2)–C(3)	1.510(8)	1.498(8)
C(3)–C(4)	1.525(11)	1.514(13)
C(4)–N(3)	1.500(10)	1.499(11)
N(3)–C(5)	1.497(8)	1.500(11)
C(5)–C(6)	1.532(11)	1.526(11)
C(6)–N(4)	1.517(8)	1.513(8)
N(4)–C(7)	1.509(10)	1.496(11)
C(7)–C(8)	1.541(13)	1.536(13)
C(8)–N(5)	1.507(9)	1.515(12)
S–O(1)	1.487(6)	1.495(5)
S–O(2)	1.484(5)	1.482(6)
S–O(3)	1.489(6)	1.475(5)
Cl–O(4)	1.408(8)	1.414(9)
Cl–O(5)	1.387(10)	1.420(8)
Cl–O(6)	1.428(5)	1.390(7)
Cl–O(7)	1.430(7)	1.430(7)

TABLE IV. Bond Angles (°) with Estimated Standard Deviations in Parenthesis

Atoms	Molecule 1	Molecule 2
Co–N(1)–C(1)	111.9(5)	111.7(4)
N(1)–C(1)–C(2)	109.1(6)	108.4(6)
C(1)–C(2)–N(2)	109.2(6)	109.1(7)
C(2)–N(2)–C(3)	112.9(5)	112.3(6)
N(2)–C(3)–C(4)	109.0(6)	109.2(6)
C(3)–C(4)–N(3)	109.8(6)	110.2(6)
C(4)–N(3)–C(5)	113.6(5)	114.2(6)
N(3)–C(5)–C(6)	108.2(5)	108.3(6)
C(5)–C(6)–N(4)	109.3(5)	108.3(6)
C(6)–N(4)–C(7)	111.8(5)	111.5(6)
N(4)–C(7)–C(8)	109.3(6)	109.7(6)
C(7)–C(8)–N(5)	108.1(6)	109.0(7)
C(8)–N(5)–Co	113.1(5)	112.9(5)
Co–S–O(1)	106.4(2)	105.2(2)
Co–S–O(2)	110.1(2)	111.9(2)
Co–S–O(3)	112.4(2)	111.4(2)
S–Co–N(3)	175.2(2)	173.6(2)
N(1)–Co–N(4)	174.6(2)	176.0(3)
N(2)–Co–N(5)	177.3(2)	176.8(3)
S–Co–N(1)	91.2(2)	92.2(2)
N(1)–Co–N(2)	86.7(2)	86.5(3)
N(3)–Co–N(5)	93.3(2)	92.4(3)
O(4)–Cl–O(5)	112.7(5)	108.0(5)
O(6)–Cl–O(7)	107.0(4)	111.1(4)
O(4)–Cl–O(7)	108.2(4)	109.7(5)
O(6)–Cl–O(5)	109.6(4)	110.8(5)

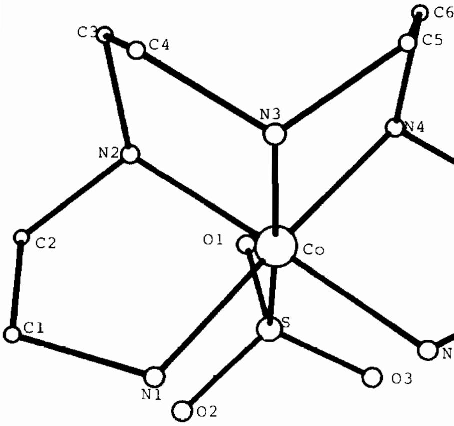

Fig. 1. A perspective view of the αα-Co(tetren)SO$_3^+$ ion showing also the system of numbering of the atoms.

The bond distances within the perchlorate ions are normal, see Table III. The closest contact between perchlorate oxygen atoms and atoms of the cation, is in the range of 3.02–3.4 Å. The oxygen atom of the water molecule is only weakly hydrogen bonded to a water molecule and an oxygen atom of the SO$_3$ group (2.82–2.97 Å).

The results of this study [18] clearly demonstrate how complex the chemistry and kinetic behaviour of a system involving a multidentate ligand can be when different geometrical and linkage isomers exist in equilibrium.

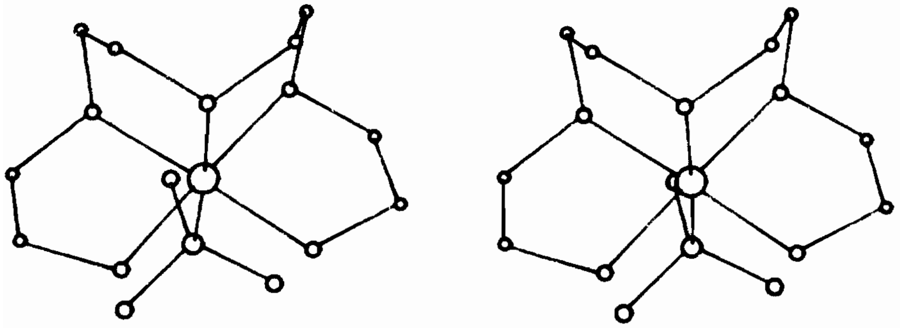

Fig. 2. Stereoview of αα-Co(tetren)SO$_3^+$.

Supplementary Material

A list of observed and calculated structure factors may be obtained from the authors.

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