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Short Communication

Crystal Structure of the Silver 1,3-Propanediamine Complex $[Ag(NH_2CH_2CH_2CH_2NH_2)]ClO_4$

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The equilibrium studies of aqueous silver(I) and the bidentate amines 1,2-ethanediamine (en) and 1,3-propanediamine (tn) have lead to detection of dimeric species of the formula $Ag_2(en)_2^{2+}$ and $Ag_2(tn)_2^{2+}$, and formation of ring structures were suggested.[1,2] Further solubility experiments[3] indicated the existence of higher polymers, and a crystal structure investigation on $Ag(en)ClO_4$ showed that the complex in the solid state forms infinite chains with a bridging 1,2-ethanediamine ligand between two silver atoms. Solubility experiments on the stoichiometrically analogous 1,3-propanediamine salt $Ag(tn)ClO_4$ could not be carried out to be sufficient informative, partly on account of the stronger basic character of the 1,3-propanediamine. The crystal structure investigation given below shows that the formation of infinite chains of the complex also takes place here.

The $Ag(tn)ClO_4$ salt was prepared by addition of a 2.5 M aqueous solution of $AgClO_4$ to an equivalent amount of a 1 M solution of trimethylenediamine cooled in ice. The precipitated $Ag(tn)ClO_4$ was recrystallized from water. The crystals, mainly of poor quality, are orthorhombic needles along the *c*-axis and have developed faces (100) and (120). Reflection conditions taken from Weissenberg and Precession were $0kl: k+l=2n$ and $h0l: h=2n$. Data were collected on a Cad4 diffractometer (Table 1). The possible space groups were *Pnam* and $Pna2_1$ and one formular unit in the unit cell. The Patterson function and the centrosymmetric choice in Multan[5] gave most of the complex. The calculations carried out in space group *Pnam* showed chains of the complex along the *c*-axis having the silver atom in a symmetry center on the screw axis as shown in Fig. 1. Figure 2 shows the two different types of Ag(en) and Ag(tn) chains. The coordinates of the atoms are given in Table 2. The positions of the hydrogen atoms were calculated from the positions of the nitrogen and carbon atoms and were not refined. Selected distances and angles are given in Table 3 together with some of the results for the Ag(en) chain. Ag–N distances for two-coordinated

Table 1. Crystal data, and data collection and reduction characteristics, with standard deviations in parenthesis.

Formula	$Ag(NH_2CH_2CH_2CH_2NH_2)ClO_4$
Space group	*Pnam*(*Pnma* No. 62)
Mol. wt./g mol^{-1}	281.42
Cell parameters:	
a/Å	9.814(2)
b/Å	8.337(4)
c/Å	10.390(4)
Z	4
V/Å^3	850(1)
μ(Mo*K*α)/cm^{-1}	26.0
Crystal size/mm^3	$0.09 \times 0.09 \times 0.12$
No. of reflections:	
Independent	684
Observed [$F^2 > 2\sigma(F^2)$]	374
Used in calculations [$\sin\Theta/\lambda < 0.6$]	560
No. of parameters	60
R	0.040
w^{-1}	$\sigma^2(F) + 0.05\|F\|$
R_w	0.050

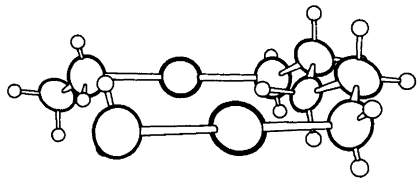

Fig. 1. Part of the Ag(tn) chain showing the positions of the calculated hydrogen atoms.

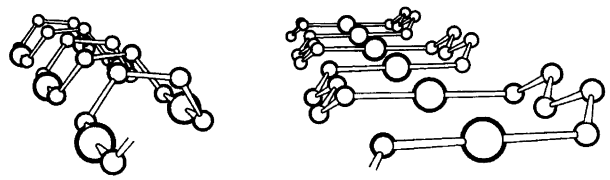

Fig. 2. The $[Ag(en^+)]_\infty$ and the $[Ag(tn^+)]_\infty$ chains.

Table 2. Fractional coordinates and equivalent isotropic parameters, with standard deviations in parenthesis.

Atom	*X*	*Y*	*Z*	PP	$100U/Å^2$
Ag	0	0	0	1.0	6.2
N	0.1420(8)	−0.1948(11)	0.0165(6)	1.0	6.1
C1	0.2314(8)	−0.1906(13)	0.1289(9)	1.0	6.0
C2	0.1486(13)	−0.1820(13)	0.25	1.0	4.2
Cl1	0.0718(7)	0.3584(7)	0.25	0.70	3.6
Cl2	0.1124(21)	0.3798(23)	0.25	0.30	6.8
O1	0.0278(16)	0.4433(19)	0.1368(17)	0.50	6.2
O2	0.0986(21)	0.4357(21)	0.1311(19)	0.50	9.3
O3	0.2309(31)	0.4159(34)	0.25	0.40	8.0
O4	0.4937(29)	0.2839(34)	0.25	0.45	8.8
O5	0.0887(32)	0.2083(30)	0.25	0.45	7.9
O6	0.1989(41)	0.2566(43)	0.25	0.35	9.2
O7	0.4355(46)	0.1256(52)	0.25	0.35	12.8

Table 3. Selected bond lengths and angles for the $Ag(tn)ClO_4$ complex and the $Ag(en)ClO_4$ complex.

$Ag(tn)ClO_4$		$Ag(en)ClO_4$	
Distances/Å			
Ag–N	2.146(8)	Ag–N1	2.171(11)
		Ag–N2	2.170(11)
N–C1	1.461(11)	N1–C2	1.500(16)
		N2–C1	1.492(11)
C1–C2	1.499(11)	C1–C2	1.504(15)
Angles/°			
N–Ag–N	180	N1–Ag–N2	175.8(3)
Ag–N–C1	115.8(6)	Ag–N1–C2	112.7(6)
		Ag–N2–C1	113.7(8)
N–C1–C2	110.3(7)	N1–C2–C1	112.9(11)
C1–C2–C1	114.1(9)	N2–C1–C2	112.9(9)

silver nitrogen complexes are found to vary between 2.08 and 2.21 Å according to 62 results taken from the Cambridge data file (1971–94), in good agreement with the result 2.15 Å found here.

The perchlorate ion is disordered with two chlorine atoms of different populations, Cl1 0.70 and Cl2 0.30, evaluated during the refinement and both situated in the symmetry plane 0.44 Å from each other. The oxygen atoms could partly be located through difference syntheses. The population and the temperature factors of the oxygen atoms were refined in the final calculations. The chains are linked together through the oxygen atoms in the two perchlorate ions mentioned above which have contact to nitrogen atoms. These distances vary from 3.10 to 3.33 Å. Calculations carried out in the space group $Pna2_1$ lead to a pseudo-centrosymmetric structure and consequently problems in refining. The XRAY system was used in the calculations.[6]

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