X-Ray Crystal Structure of Silver(I) Complex with 1,3-Bis(8-quinolylthio)propane

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Synopsis. An X-ray crystal structure has been determined for a silver(I) complex with 1,3-bis(8-quinolylthio)propane (BQTP), Ag(BQTP)NO_3. Since a conformational sequence of *sc-ap-ap-sc*, inherently preferred by the S-C-C-C-S backbone, is kept in the silver(I) complex, BQTP does not coordinate to a single metal ion, but forms polymeric complexes. Crystal data: monoclinic, space group $P2_1/c$, a=27.011(8), b=7.962(1), c=20.270(5) Å, β=110.41(3)°, V=4086(2) Å^3, Z=8, R=0.037 for 5211 reflections.

Acyclic ligands derived from 1,3-bis(8-quinolyloxy)-propane (BQOP) show high Li^+-selectivity as a neutral carrier in cation transport through liquid membranes.[1] An X-ray crystallographic study of Li(BQOP)ClO_4 (**1**) has demonstrated that Li^+ (0.76 for hexa-coordination; hereinafter, numerals in parentheses denote ionic radii in Å) is best fit to the inherent cavity of BQOP and that unfavorable distortion would be expected upon coordination to larger ions, such as Na^+ (1.0) and K^+ (1.4).[2]

The sulfur analogue, 1,3-bis(8-quinolylthio)propane (BQTP) was proposed as a linear quadridentate ligand for metal ions like Cu^+, Cu^{2+}, Ni^{2+}, Pd^{2+}, and Pt^{2+} (0.6 to 0.7).[3] We found, however, that a larger ion of Ag^+ (1.1) also forms a stable complex with BQTP, and that the resulting cationic complex is extracted with counter anions into organic solvents, as in the cases of cyclic and acyclic polythioethers.[4] The difference in the behavior between BQOP and BQTP has prompted us to analyze the X-ray crystal structure of Ag(BQTP)NO_3 (**2**).

Experimental

BQTP was prepared as described previously.[3] Although the melting point had been reported to be 68 °C, it was actually 88 °C. Single crystals of **2** were obtained by slow evaporation of an acetonitrile solution of silver nitrate and BQTP. Upon exposure to sunlight, the complex slowly decomposed to give metallic silver.

Three-dimensional intensity data were collected on a

Table 1. Atomic Coordinates (×10^4) and Equivalent Isotropic Temperature Factors (Å^2×10) with esd in Parentheses

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
Ag1	4905.5(1)	10063.6(5)	3079.9(2)	37.9(1)	C104	8042(2)	9897(7)	1479(3)	45(2)
N1	4010(1)	9251(5)	2482(2)	39(1)	C105	7911(2)	9512(8)	218(3)	53(2)
C2	3805(2)	9350(8)	1792(3)	51(2)	C106	8111(2)	9600(9)	−311(3)	63(2)
C3	3280(2)	8896(9)	1389(3)	64(2)	C107	8649(2)	9970(8)	−168(3)	51(2)
C4	2965(2)	8309(8)	1744(3)	59(2)	C108	8985(2)	10299(6)	507(2)	34(1)
C5	2849(2)	7646(8)	2870(4)	60(2)	C109	8784(2)	10306(6)	1069(2)	32(1)
C6	3054(2)	7523(8)	3582(4)	61(2)	C110	8241(2)	9894(6)	925(3)	39(2)
C7	3576(2)	8014(8)	3946(3)	53(2)	S111	9663.3(5)	10603(2)	645.0(6)	33.7(3)
C8	3890(2)	8591(6)	3589(3)	39(2)	C112	9934(2)	8568(6)	1027(3)	39(2)
C9	3692(2)	8726(6)	2843(3)	39(2)	C113	9678(2)	7081(6)	570(2)	39(2)
C10	3161(2)	8235(7)	2481(3)	48(2)	N101′	9168(1)	6273(5)	2685(2)	38(1)
S11	4551.7(5)	9146(2)	4113.6(6)	38.3(4)	C102′	8952(2)	6722(7)	3151(3)	49(2)
C12	4820(2)	7031(7)	4324(2)	41(2)	C103′	8405(2)	6648(9)	3021(3)	61(2)
C13	4826(2)	6140(6)	3663(3)	40(2)	C104′	8077(2)	6124(9)	2381(4)	61(2)
N1′	4193(1)	4294(5)	1439(2)	38(1)	C105′	7964(2)	5108(9)	1174(4)	64(2)
C2′	3963(2)	4583(8)	752(3)	56(2)	C106′	8177(2)	4643(8)	698(3)	60(2)
C3′	3409(2)	4551(9)	410(3)	64(2)	C107′	8733(2)	4667(7)	868(3)	46(2)
C4′	3093(2)	4247(9)	791(3)	64(2)	C108′	9059(2)	5181(6)	1522(3)	34(1)
C5′	3008(2)	3663(8)	1946(3)	56(2)	C109′	8845(2)	5730(6)	2042(3)	37(1)
C6′	3243(2)	3307(8)	2638(3)	55(2)	C110′	8285(2)	5639(7)	1856(3)	49(2)
C7′	3796(2)	3197(7)	2940(3)	45(2)	S111′	9757.9(4)	5120(1)	1759.4(6)	28.7(3)
C8′	4110(2)	3508(5)	2542(2)	32(1)	C112′	9875(2)	5433(6)	930(2)	36(1)
C9′	3877(2)	3933(6)	1826(2)	33(1)	N201	3617(2)	3989(9)	4684(3)	70(2)
C10′	3317(2)	3960(7)	1523(3)	46(2)	O202	3189(2)	3550(10)	4305(3)	119(3)
S11′	4808.5(4)	3276(1)	2921.1(6)	29.7(3)	O203	3989(2)	3430(12)	4597(3)	143(4)
C12′	4947(2)	4276(6)	3777(2)	36(1)	O204	3659(4)	5009(11)	5128(4)	179(5)
Ag101	9937.4(1)	11963.7(5)	1976.9(2)	37.0(1)	N205	8597(2)	10999(9)	3977(3)	74(2)
N101	9099(1)	10755(5)	1734(2)	36(1)	O206	8174(2)	10714(12)	3910(4)	143(4)
C102	8881(2)	10790(7)	2235(2)	42(2)	O207	8985(2)	10533(13)	4296(4)	172(4)
C103	8362(2)	10367(8)	2130(3)	49(2)	O208	8635(4)	12274(11)	3622(4)	164(5)

$B_{eq}=4/3\sum_i\sum_j\beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 2. Selected Bond Distances and Angles for $Ag(BQTP)NO_3$

	Bond distance/Å		
Ag1–N1	2.384(4)	Ag101–N101	2.349(4)
Ag1–S11	2.689(2)	Ag101–S111	2.760(2)
Ag1–N1′(i)	2.369(4)	Ag101–N101′(iii)	2.336(4)
Ag1–S11′(i)	2.801(2)	Ag101–S111′(iii)	2.815(2)
Ag1–S11′(ii)	2.580(2)	Ag101–S111′(ii)	2.568(2)
	Bond angle/°		
N1–Ag1–S11	75.6(1)	N101–Ag101–S111	74.0(1)
N1–Ag1–N1′(i)	148.7(1)	N101–Ag101–N101′(iii)	142.0(1)
N1–Ag1–S11′(i)	89.0(1)	N101–Ag101–S111′(iii)	86.1(1)
N1–Ag1–S11′(ii)	99.6(1)	N101–Ag101–S111′(ii)	104.7(1)
S11–Ag1–N1′(i)	101.7(1)	S111–Ag101–N101′(iii)	95.3(1)
S11–Ag1–S11′(i)	133.6(1)	S111–Ag101–S111′(iii)	25.4(1)
S11–Ag1–S11′(ii)	108.6(1)	S111–Ag101–S111′(ii)	104.2(1)
N1′(i)–Ag1–S11′(i)	70.2(1)	N101′(iii)–Ag101–S111′(iii)	70.5(1)
N1′(i)–Ag1–S11′(ii)	110.6(1)	N101′(ii)–Ag101–S111′(iii)	113.2(1)
S11′(i)–Ag1–S11′(ii)	117.0(1)	S111′(ii)–Ag101–S111′(iii)	130.1(1)

(i) $1-x$, $1/2+y$, $1/2-z$; (ii) x, $1+y$, z; (iii) $2-x$, $1/2+y$, $1/2-z$.

Rigaku AFC-5R diffractometer with graphite-monochromatized Cu $K\alpha$ radiation (λ=1.54178 Å). Crystallographic details are summarized as follows: formula=$AgC_{21}H_{18}N_3O_3S_2$, FW=532.38, monoclinic, space group $P2_1/c$, a=27.011(8), b=7.962(1), c=20.270(5) Å, β=110.41(3)°, V=4086(2) Å^3, Z=8, D_c=1.73 g cm^{-3}, crystal size 0.4×0.1×0.05 mm, μ(Cu $K\alpha$)=101.7 cm^{-1}, scan mode ω–2θ, $2\theta_{max}$=120°, number of observed reflections with $F_o>3\sigma(F_o)$=5211, R=0.037, R_w=0.048.

The intensity data were corrected for both Lorentz and polarization effects. The structure was solved by the conventional heavy-atom method, and then refined by a block-diagonal least-squares method to minimize $\Sigma(w|\Delta F|^2)$, where $w=[\sigma^2(F_o)+0.00083|F_o|^2]^{-1}$ for the observed reflections with $w^{1/2}|\Delta F|<4$, and w=0 for others. Hydrogen atoms were located in a difference density map. The temperature factors of H atoms were set equal to B_{eq}'s of the bonded atoms. Absorption corrections were applied after an isotropic least-squares refinement using an empirical method based on the difference between the observed and calculated structure factors.[5] Computations using the PLUTO and XPACK86 Shionogi programs were performed on a FACOM M-730/10 computer at Shionogi Research Laboratories. The final positional parameters for non-hydrogen atoms are given in Table 1; the selected bond lengths and angles with their estimated standard deviations are given in Table 2. Tables of the observed and calculated structure factors, atomic coordinates and equivalent isotropic temperature factors for all of the atoms, anisotropic thermal parameters for non-hydrogen atoms, bond lengths, and angles have been deposited as Document No. 9017 at the Office of the Editor of Bull. Chem. Soc. Jpn.

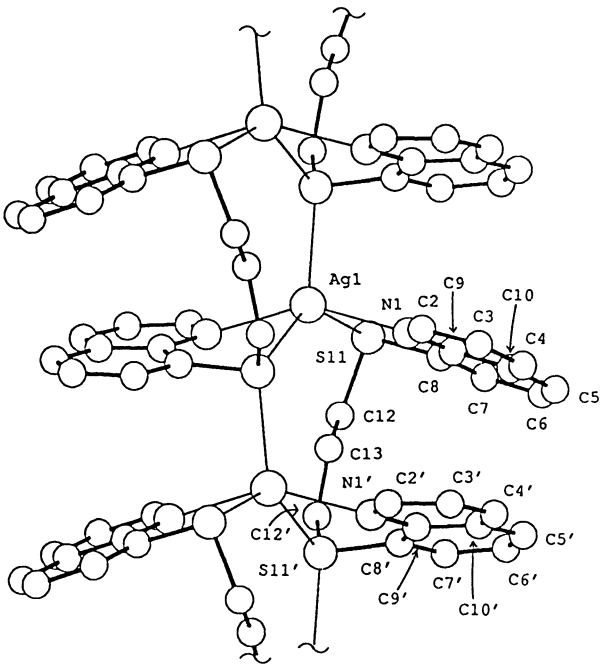

Fig. 1. X-Ray crystal structure of $Ag(BQTP)NO_3$ with atom-numbering system. The polymeric structure including Ag1 is presented. Another polymeric chain containing Ag101 has almost the same structure.

Results and Discussion

In an asymmetric unit, two independent complexes (Ag1–C12′ and Ag101–C112′) are included together with two nitrate ions (N201–O204 and N205–O208). These complexes are similar to each other, and are infinite polymers that extend along the b-axis. Figure 1 shows the molecular structure and the atom numbering system of the complex including Ag1.

In both complexes, BQTP acts as two bidentate ligands to coordinate to two symmetry-related Ag atoms in an unequivalent manner; S11′ is 0.11 Å more distant from Ag than S11, and further coordinates to a third symmetry-related Ag atom. In other words, both Ag1 and Ag101 atoms are penta-coordinate with N1 and S11 of a first ligand, N1′ and S11′ of a second, and S11′ of a third. The coordination geometry around the Ag atoms is described as being trigonal bipyramid with three S atoms in basal and two N atoms in apical positions. Ag1 deviates from the basal plane by 0.130 Å, whereas Ag101 does so by 0.079 Å. Two quinoline rings within a single ligand are nearly parallel (dihedral angles of 17.3 and 16.7° for the polymeric complexes containing Ag1 and Ag101, respectively). The bond

lengths and angles within the quinoline rings, except for ∠C7–C8–S11 and ∠C9–C8–S11, are practically the same as those of 8,8′-diquinolyl disulfide.[6] Compared with those in disulfide, ∠C7–C8–S11 decreases and ∠C9–C8–S11 increases to become close to 120°. The NO_3^- ions have no interaction with metal complexes. Since the constituent atoms possess considerably large temperature factors, the bond lengths and angles are less reliable. The difference in the molecular structures of **1** and **2** stems from that in the conformation of the backbones connecting two quinoline rings, E–C–C–C–E(E=S or O): *sc-ap-ap-sc* for BQTP(E=S), whereas *ap-sc-sc-ap* for BQOP(E=O).

Recent structural studies have demonstrated the essential differences in the conformational propensities between free polythioethers and polyethers in the solid state.[7] For acyclic ethylene-linked chains, CS–CC bonds generally adopt a synclinal placement, while the CO–CC bonds typically avoid it as much as possible. The synclinal placement is stabilized at OC–CO, but destabilized at SC–CS. According to our knowledge, no crystal-structural data exist concerning the acyclic trimethylene-linked chains, though a ^{1}H NMR spectroscopic study has suggested the preference of SC–CC for an antiperiplanar placement.[8] In summary, the inherent conformational sequence for S–C–C–C–S is *sc-ap-ap-sc*. This conformation of BQTP is maintained upon complexation with silver ions. Hence, BQTP does not coordinate to a single Ag^+ ion, but acts as two bidentate ligands to two different metal centers together with bridging at S11′.

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