THE COORDINATION BETWEEN SILVER NITRATE AND OPEN CHAIN POLYETHER [1]

Li, Yongxiu
Jiangxi University, Nanchang 330047, China

Ni, Zhaoai
Hangzhou University, Hangzhou 310028, China

ABSTRACT

A complex of silver nitrate with 1.8–bis(8′–quinolyloxy)–3.6–dioxaoctane (noted as ligand L) was synthesized. The results of element analysis show that it consists of the calculated values of $[Ag_4L_3](NO_3)_4$. It is clear from the IR, UV and ^{1}HNMR spectra that the ligand L coordinated to Ag^+ ion with its N and O atoms which connected with the terminal quinolyloxy group.

Key words: open chain polyether silver nitrate coordination

1 INTRODUCTION

The coordination between crown ether ligands and metal cations mainly depends on the ion-dipole inyeraction. The formation of crown ether-metal complex greatly relates to the correspondence between metal ionic diameter and the size of the cavity in the crown ether[1]. The ion-dipole interaction of silver ion with crown ether oxygen atom is not very strong, but Ag^+ and K^+ have similar ion diameters[2], so some research works on the coordination properties of silver ions with crown ether ligands, especially those containing N or S as the coordination atom, were reported[3,4]. Open chain crown ether is similar to the crown ether, in that their complexes can form ring-like structures similar to those of crown ether compounds[5,6]. Some of our previous work have been devoted to the coordination compounds of open chain polyether with rare earth elements[7,8], and the extraction behaviour of rare earth elements with open chain polyether[9]. In this paper, an open polyether, 1.8–bis(8′–quinolyloxy)–3.6–dioxaoctane, which contains two 8–quinoline groups as its terminal group, and its complex with silver nitrate were synthesized. Then, the composition and properties of the complex were investigated.

2 EXPERIMENTAL METHOD

The open chain crown ether L used in this paper was prepared by the method described in Refs[5,6] and the product was evaluated with ^{1}HNMR, IR and element analysis methods. Anhydrous ethyl acetate was obtained from ethyl acetate (A.R), which was dehydrated by a distillation method in which P_2O_5 was added as a desiccant. Silver nitrate was the analysis agent.

C.H.N were determined by a Carlo Erba element analysis instrument. Ag was measured by a GGX–2 atomic-absorption spectrophotometer. IR spectra were obtained by a Perkin-Elmer 683 spectrophotometer from KBr pellets or liquid membrane. Electronic absorption spectra were recorded with a UV–265 spectrophotometer. The ^{1}HNMR spectra were obtained using a FX–90Q spectrometer. TG–DTA analysis were performed on a PRT–1 heat balance and

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CDR-1 heat analysis instrument. The conductances of the solution of the complex were measured with a DDS-11A conductance instrument.

The solid complex was prepared by adding the solution of open chain polyether L in anhydrous ethyl acetate dropwise to an equal amount of solution of silver nitrate in anhydrous ethyl acetate while stirring. The concentration of both solutions was 0.02 mol / L. The mixture was stirred for 1 h, then allowed to stay for 24 h. The complex deposited from the solution was filtrated off, then washed several times with anhydrous ethyl acetate solution, and dried in a vacuum dryer containing P_2O_5 as a desiccant.

3 RESULT AND DISCUSSION

The synthetic complex is a yellow powder. The results of element analysis (listed in Table 1) indicate that it consists of the calculated values of $[Ag_4L_3](NO_3)_4$. This confirms the complex is a composition of $[Ag_4L_3](NO_3)_4$. The product does not dissolve in ethyl acetate solution, but dissolve slightly in acetone, ethanol and water. The complex was found to have greater solubility in chloroform, acetronitrate and DMSO solutions. The colour of solution, in which the complex is dissolved is yellow (similar to the colour of solid complex). Molar conductivity values determined in water, ethanol and chloroform solutions are 528, 156 and 8.4 $\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$ respectively. These results show that the complex is a 1:4 type electrolyte[10], in which four Ag+ and three ligand molecules L form a $[Ag_4L_3]^{4+}$ ion group.

The electronic spectra (shown in Fig. 1) show two absorption bands, at 248.2 and 305.8 nm for the corresponding $\pi-\pi^*$ electronic transition, and $n-\pi^*$ electronic transition respectively. The formation of the complex with silver nitrate causes 2.2 and 2.4 nm red-shifts, and the relative intensity for the latter transition decreases (intensity ratio of $A_{n-\pi^*} / A_{\pi-\pi^*} = 0.677$ for the free ligand L and 0.453 for the complex). This is a clear indication of coordination between the terminal group of L and Ag^+, especially between the N atoms of the terminal group and Ag^+.

Table 1 The element analyse results of complex (%)

Elements	C	H	N	Ag
found values	45.57	3.88	7.01	23.43
calculated values of $[Ag_4L_3](NO_3)_4[L]_3$	45.67	3.81	7.40	22.89

The IR spectra of the ligand L and its complex with silver nitrate are shown in Fig. 2, 3. The formation of the complex causes a pronounced change in IR absorption. Two wide bands, around 3,400 and 3,500 cm^{-1}, were

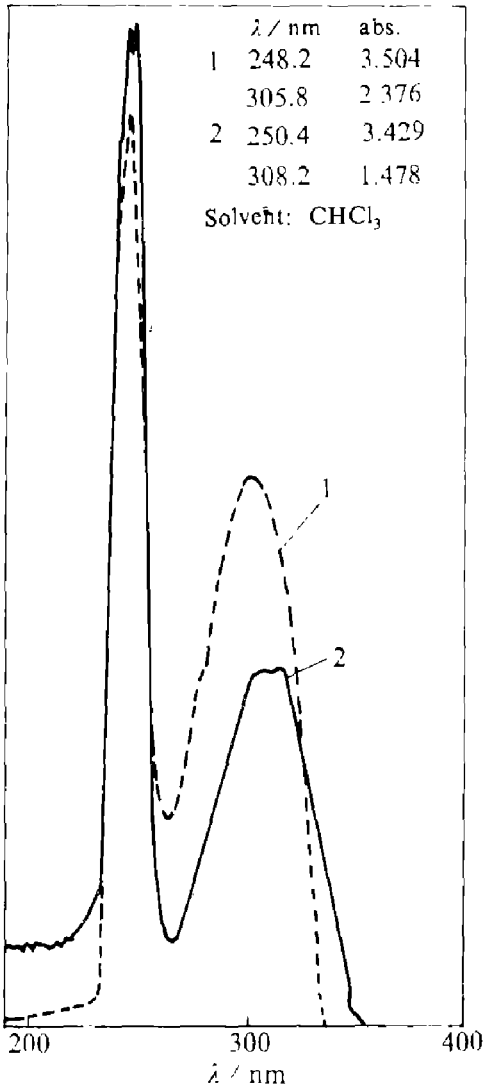


Fig. 1 UV spectra of the ligand L and its complex

combined to one wide band and the maximum absorption lies at 3,440 cm^{-1}. No significant shift was observed for the C–H stretching mode which appear around 3,050 and 2,930 and 2,880 cm^{-1} in the spectra, but the relative intensity undergo a significant decrease. This shows that the IR absorption activity was decreased by the formation of the complex with silver nitrate. The intensity of most of the IR absorption peaks (except for peak at 1,383 cm^{-1}), decreased, especially for Ar–O–R and R–O–R stretching modes which appear at 1,262 and 1,103 cm^{-1} respectively. On the other hand, the band shape around 1,103 cm^{-1} became narrower (from 1,080~ 1,130 cm^{-1} to 1,060~ 1,150 cm^{-1}). The absorption peaks of the quinoline and nitrate groups overlapped, it is difficult to determine the coordination type of NO^{3-}. There are four absorption peaks between 600~900 cm^{-1}. The strong peaks at 820 and 740 cm^{-1} must be the typical absorption peaks of coordinated NO^{3-}, but the strong absorption peak at 1,383 cm^{-1} is similar to the absorption peak of uncoordinated NO^{3-}. The latter result agrees with the measured molar conductivity value. It is suggested that the NO^{3-} lies in the outer portion of the complex, and no

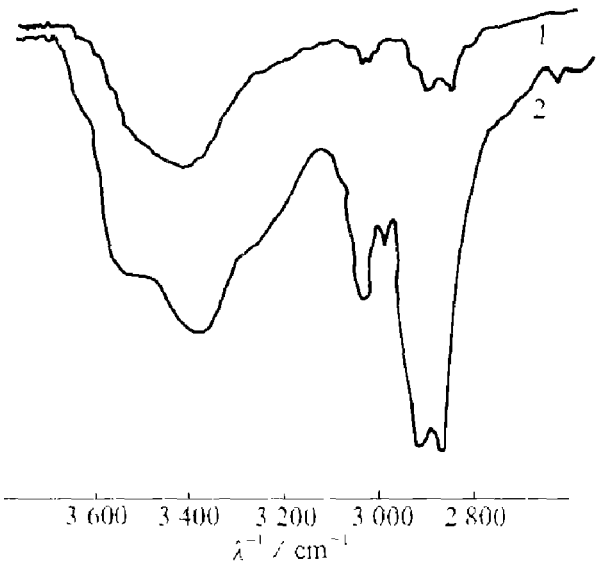


Fig. 2 IR spectra of L and its complex

1—complex(KBr pellet); 2—L(ligand membrane)

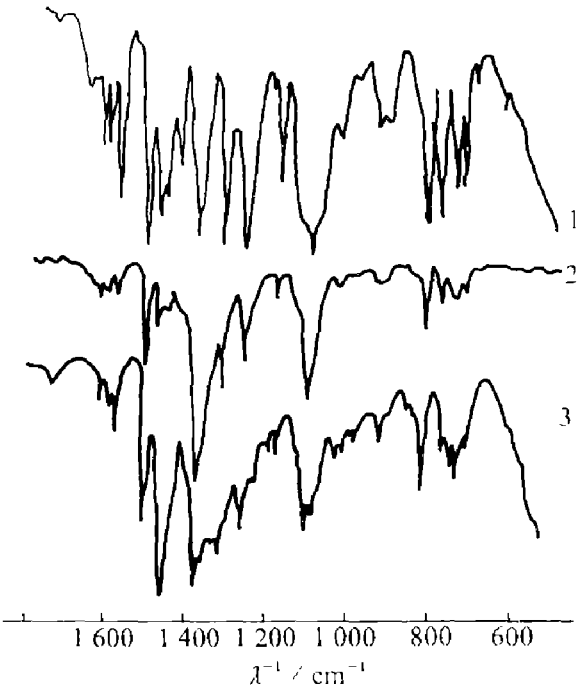


Fig. 3 IR spectra of L and its complex

1—L(ligand membrane); 2—complex(KBr pellet); 3—complex (paraffin menbrane)

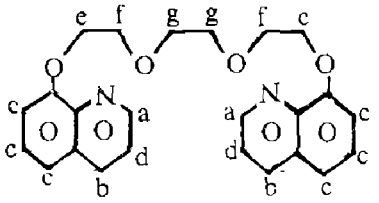
bond occurs between NO^{3-} group and Ag^{+} ion.

The ^{1}HNMR spectra of the ligand and its complex in deuterated acetone were obtained. The observed chemical shifts(δ ppm) of different protons in the open chain polyether, are listed in Table 2.

Table 2 Comparsion of δ of different protons in the ligand L and its complex

proton	*a*	*b*	*c*	*d*	*e*	*f*	*g*
ligand	8.844	8.247	7.440	7.185	4.346	3.989	3.749
complex	9.100	8.609	7.749	7.650	4.744	4.006	3.673
$-\delta$ ppm	0.256	0.357	0.309	0.469	0.398	0.017	−0.076

noted



solvent: $CD_3\overset{O}{\overset{\|}{C}}CD_3$

standard: TMS

Comparison of the chemical shift of the complex with that of ligand L shows that the downfield shift for the protons of positions *f* and *g* are quite small. This means that very weak bonding occurs between the alkane ether

oxygen atoms and Ag^+ ion. However, formation of the complex caused a significant downfield shift for the other protons, and the magnitude order of variation values of the chemical shifts was $d > b > c > a$. These results indicate that the bond arose from the aromatic ether oxygen atom and quinoline N atom in the ligand L. When coordinated with Ag, the ligand L uses the aromatic ether oxygen atom and quinoline N atom as coordination atoms. The increasing electron cloud density in the π–orbital of the quinoline ring is due to the anti-coordination of the electron in the d–orbital of Ag^+ to the π–orbital of the quinoline ring. This causes a downfield shift for the aromatic proton, and the maximum downfield shift is observed for the internal position proton d. The downfield shift of proton a (near the N atom) is smaller than that of protons d, b and c. This can be explained as the electron of the N→Ag σ–bond being partial to the Ag^+ ion, and this causes the electron density of the adjacent carbon atom to decrease. These facts show that the terminal 8–quinoline group plays an important role in the formation of the complex with Ag.

Fig. 4 shows the DTA curve of ligand L. There exist a wide endothermic peak around 247 ℃ and endothermic double peaks from 394 ℃ to 418 ℃. Fig. 5 shows the TG–DTA curves of the complex.

In Fig. 5 several endothermic peaks around 170, 197, 290 and 380 ℃, and a strong exothermic peak around 555 ℃ were observed. This suggested that some strong interactions exist between ligand L and Ag^+. The TG curve can be divided into three parts, 20～150 ℃, 150～400 ℃ and 400～600 ℃. No platform was found before 700 ℃. The total observed loss is 77.39 wt.–%, and consists of the calculated value 77.19% from the composition $[Ag_4L_3](NO_3)_4$.

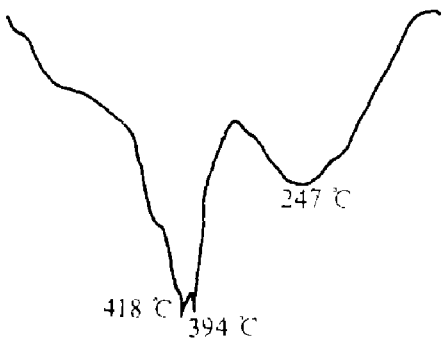


Fig. 4 DTA curve of L

N_2 sphere, rate of temperature increase: 10℃ / min

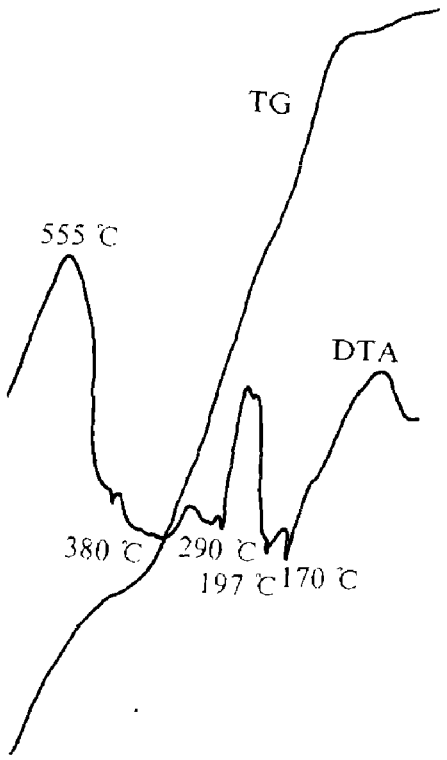


Fig. 5 TG–DTA curves of the complex

N_2 sphere, rate of temperature increase: 10℃ / min

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