

**ELECTROOXIDATION OF SILVER(I) NITRATE AND SILVER(I) PERCHLORATE IN THE PRESENCE OF 4,4'-DIMETHYL-2,2'-BIPYRIDYL; 2,2',2''-TERPYRIDYL; 5,5'-DIBUTYL-2,2'-BIPYRIDYL AND 2,2'-BIQUINOLYL IN ACETONITRILE**

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**Abstract.** Electrooxidation of silver(I) nitrate and silver(I) perchlorate in the presence of 4,4'-dimethyl-2,2'-bipyridyl and 2,2',2''-terpyridyl enable the preparation and isolation of  $AgL_2$  type complexes where silver is stabilised in  $Ag^{2+}$  state. Whereas the ligands 5,5'-dibutyl-1,2,2'-bipyridyl and 2,2'-biquinolyl, though give indications where silver(I) is converted to silver(II) state, but the isolation of complexes was not successful. Particularly for 2,2'-biquinolyl, which due to its low solubility in acetonitrile created hindrance even in obtaining conclusive evidence in terms of coulometric determinations for silver(I) to silver(II) conversion.

The study on silver(I) salts in the presence of 2,2'-bipyridyl (bipy),<sup>1</sup> using the basic technique exploited for the oxidation of organic compounds in nonaqueous solvents as reviewed by Weinberg and Weinberg,<sup>2</sup> prompted us to use ligands, 4,4'-dimethyl-2,2'-bipyridyl (dime-bipy), 2,2',2''-terpyridyl (terpy), 5,5'-dibutyl-2,2'-bipyridyl (dibut-bipy), and 2,2'-biquinolyl (biqu), capable of chelating satisfactorily with silver(I), by anodic polarography leading to controlled potential electrolysis corresponding to specific oxidation steps. Since the anodic range available is about 3 V vs S.C.E., the complexation with suitable ligands would permit oxidation of transition metal ions depending upon  $\beta$  and  $\beta_2$  values for respective systems. The present work is restricted only to silver(I) salts in an effort to collect data for the metal with various ligands capable of  $\pi$ -bonding.

### Experimental

The apparatus used for both the polarographic and controlled potential coulometric studies was basically the same as described earlier and comprised a potentiostat based on a design described by Hickling,<sup>3</sup> a reference voltage scanner capable of scanning between two voltages in the range +5.0 to -5.0 V in either direction at rates of scan varying between 1-1.5 mV/min, a potentiometric recorder with sensitivity of 1 mV, 10 mV and 100 mV for a full scale deflection alongwith chart speeds varying from 0.6 to 600 in/hr, and one of the two cells depending upon the mode of operation. Single compartment cell was used for polarographic studies and three compartment cell for controlled potential electrolysis. Rotating platinum microelectrode (R.P.E.) as described by Nernst and Merriam<sup>4</sup> was used for polarography. Tetra-n-butylammonium perchlorate (TBAP) was prepared<sup>5,6</sup> for use as a supporting electrolyte in 0.1M in acetonitrile which was dried to only 50 p.p.m. of water content.

Studies were carried out in a dry box filled with oxygen-free nitrogen maintained at R.H. 5-8% at  $20 \pm 1^\circ$ , since the acetonitrile solvent was capable of absorbing about 56 p.p.m. water in 3 hr, the normal

time required for each set of experiment.

It is well known<sup>8,9</sup> that the ohmic drop between the working electrode and reference electrode in high resistance system is not completely compensated for in three electrode resistance-compensating potentiostat, even though the current flowing in the reference cell is zero. Although theoretical calculations<sup>8,10</sup> have been made for the ohmic drop occurring in the vicinity of a D.M.E. The problem is much more complicated when a R.P.E. is employed and theoretical calculation is not possible. To evaluate the magnitude of this effect, polarograms of silver(I) nitrate were obtained where the distance between the tip of the reference electrode and R.P.E. was varied, while the other parameters were kept constant. This attempt led to the conclusion that if the distance between reference electrode tip and R.P.E. is kept from 0.5 to 1.0 mm approximately, the ohmic drop correction was negligible under the particular cell conditions used.

**Determination of Silver(II).** A novel method was developed for the determination of small amounts of silver(II). The method described by Dutta<sup>7</sup> involving the oxidation of iodide by silver(II) was found to be unsuitable because silver(II) complexes with polypyridyls were found to give an incomplete reaction with potassium iodide solution in the cold. It was thought that this was due to the adsorption of iodine onto the surface of the crystals and that this prevented further reaction. This difficulty was apparently overcome by refluxing the solution, however, using a water condenser, some iodine was lost and further it was difficult to remove all traces of iodine from the condenser. The method described here used bromide ion as the reductant, the liberated bromine being readily removed from the reaction mixture.

The apparatus used for silver(II) determination is shown in Fig. 1 and consists of a 50 ml pear-shaped distillation flask fitted with a nitrogen inlet and reflux condenser leading to a trap 'A' containing potassium iodide solution. A second safety trap contained a solution of potassium iodide to which was added a few drops of starch solution.

An accurately weighed amount of silver(II) complex (usually about 50 mg) was introduced into the pear-shaped flask together with about 10 ml de-

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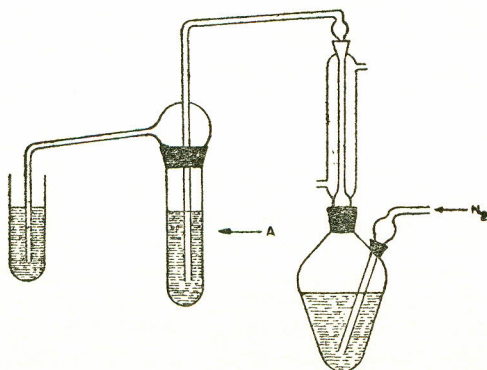


Fig. 1

oxygenated water and about 100 mg analar grade potassium bromide. The oxygen-free nitrogen supply was switched on and the solution was heated to boiling using a microburner and refluxed for about 5 min. At this stage most of the bromine had passed over into the iodide trap, the last traces of bromine in the reaction vessel were removed by increasing the nitrogen flow and switching off the water supply to the condenser until steam just began to condense into the delivery tube. With the water supply restored, the nitrogen flow was continued for another minute.

The iodine solution was transferred to a 100 ml conical flask together with washings from the delivery arm and titrated against a standardised 0.01N solution of thiosulphate contained in a weighed burette using starch solution as indicator. A known weight of Analar grade potassium bromate was placed in the reaction vessel to which was added an excess of analar  $KBr$  and 10 ml 0.5N sulphuric acid. The bromine thus produced was transferred to the iodide trap by the procedure described above and the resulting iodine titrated by weight against the 0.01N thiosulphate solution.

The use of 0.01N solution of thiosulphate together with the weight titration technique allowed small quantities of silver(II) complexes to be accurately analysed.

**Isolation and Analysis of 4,4'-Dimethyl-2,2'-bipyridyl Complex.** After each electrolysis for silver(I) salts in the presence of dime-bipy, the anolyte was immediately transferred to a round-bottom flask and the solvent was removed under vacuum at room temperature. The residue consisted of excess of ligand, (TBAP) and the silver(II) complex. Impurities were successfully removed by selecting dry ethyl acetate for washing, whereas every unwanted species, except the complex was soluble. About seven washings were required to obtain a pure product. The product was dried in vacuum for 2 hr at 30°C and stored in desiccator over phosphorous pentoxide. The technique<sup>1</sup> of pushing out of the complex by adding silver(I) salt in anolyte was successful in this case as well. But evaporation method was preferred, since the technique gave better yield. The C, H, N and  $Ag^{2+}$  analysis of the product obtained from silver(I) nitrate and silver(I) perchlorate are given as follows alongwith the theoretical values for  $[Ag(dime-bipy)_2]NO_3ClO_4$  and  $[Ag(dime-bipy)_2](ClO_4)_2$ .

	C(%)	H(%)	N(%)	$Ag^{2+}$ (%)
$Ag(dime-bipy)_2$	Calcd:45.19	3.79	10.98	16.91
$NO_3ClO_4$	Found:45.18	3.77	9.88	16.6
$Ag(dime-bipy)_2$	Calcd:42.69	3.58	8.30	15.97
$(ClO_4)_2$	Found:42.29	3.59	8.19	15.6

The products were isolated from the anolyte (of silver(I) salts in the presence of bipy) in the same way as used for silver(II)/dime-bipy, except that the solvent used for washing was chloroform instead of ethyl acetate. The process of adding silver(I) salt in anolyte for pushing out silver(II) complex were not successful for terpy which were exploited quite successfully for silver(II)/bipy<sup>1</sup> and silver(II) dime-bipy as mentioned earlier. The C, H, N and  $Ag^{2+}$  analysis of the products obtained from silver(I) nitrate and silver(I) perchlorate in the presence of terpy alongwith the theoretical values are given as follows:

	C(%)	H(%)	N(%)	$Ag^{2+}$ (%)
$Ag(terpy)_2$	Calcd:46.59	2.87	10.87	13.95
$(ClO_4)_2$	Found:45.8	2.9	10.8	13.7
$Ag(terpy)_2$	Calcd:48.96	3.01	13.32	14.66
$ClO_4.NO_3$	Found:46.6	3.3	10.8	13.5

## Results and Discussion

**Anodic Polarography of Polypridyls.** Since polarograms for silver(I) nitrate and silver(I) perchlorate were obtained<sup>1</sup> it was concluded<sup>1</sup> that silver(I) is not oxidised to silver(II) in the absence of ligands. The anodic polarography of these polypridyls alone was therefore, carried out first, to make sure that ligands themselves do not get oxidised within the anodic range, and if so, to determine the extent of the interference which might be expected. A small wave was observed at a half wave potential ( $E_{\frac{1}{2}}$ ) of 2.04 V for dime-bipy, the limiting current being about 0.3  $\mu A$ . Several polarograms were obtained at different concentrations of the ligand (up to 10 mM and it was found that the limiting current was independent of concentration for the particular electrode, as has already been noted in the case of 2,2'-bipyridyl.<sup>1</sup> The anodic polarography of dibut-bipy and terpy gave somewhat smaller limiting currents ( $i_L$ ), i.e. about 0.2  $\mu A$ ; the  $E_{\frac{1}{2}}$  were 2.0 V and 1.9 V respectively. Again the limiting currents were found to be independent of concentration. But, the polarographic study of biqu was limited to solutions having concentrations in the range 1-2 mM due to the low solubility of this ligand in acetonitrile. The limiting current for biqu was found to be only 0.1  $\mu A$  and half-wave potential was about 1.9 V; a value similar to terpy.

The observation of small limiting current for all these ligands remain constant over a wide range of concentration. The use of graphite electrode<sup>11</sup> might solve the mystery of this  $i_L$  which could possibly be due to platinum-to-ligand complexation. Nothing, however, has been recorded in the literature regarding this phenomenon.

*Anodic Polarography of Silver(I) Salts in the Presence of Polypyridyls.* The main purpose of the polarographic study was to determine the anodic potentials required for the electrooxidation of silver(I) complexes as a preliminary to preparative scale electrolyses.

Silver(I) nitrate and silver(I) perchlorate in the presence of polypyridyls using 0.1 M TBAP as supporting electrolyte, and scanning at 0.4 V/min. gives  $i_L$  varying with concentrations (Table 1).

Two well-defined waves were observed in case of silver nitrate-polypyridyl systems; for the silver perchlorate-polypyridyl systems the second wave is usually complicated by a maximum which is followed by a marked drop in current. Because of this effect, values of  $i_L$  for second wave is not quoted in Table 1, and half-waves are only approximate. Values for the  $i_L$  of the first wave for these systems are again small compared to the values expected for a one-electron change based on the total metal present. In the case of silver(I) nitrate-bipy<sup>1</sup> system, this effect was explained in terms of the involvement of the intermediate species, Ag (bipy)<sup>+</sup>. Unfortunately, stability constant data are not available to enable similar calculations to be made of the intermediate complexes associated with the silver(I)/ polypyridyl systems. However, it is found in all cases, that the  $i_L$  is reduced to low values when ligand is in excess in qualitative agreement with the dependence of limiting current on the concentration of an intermediate species. In the case of silver(I) salt-biquinolyl system, the values of the  $i_L$  appear to be much smaller than the corresponding values for bipy system; this may be due to a higher ratio of the successive stability constant ( $K_2/K_1$ ) for 2,2'-biquinolyl system which would lead to a reduction

TABLE 1. ANODIC POLAROGRAPHY OF SILVER(I) SALTS IN THE PRESENCE OF LIGANDS.

	$C_M^*$ (mM)	$C_L^*$ (mM)	$i_L$ ( $\mu$ A)	$E_{1/2}^{(I)}$ (V)	$E_{1/2}^{(II)}$ (V)	Ligand
Silver perchlorate	2.85	6.09	0.9	1.40	2.0	Dime bipy
	2.85	14.38	0.3	1.41	1.9	
	3.69	6.09	0.6	1.40	2.0	
Silver nitrate	1.62	1.70	0.4	1.31	1.91	Terpy
	1.11	20.20	0.1	—	1.93	
	4.00	1.70	0.7	1.29	1.95	
Silver perchlorate	0.92	1.74	0.2	1.30	2.0	Terpy
	0.92	15.33	0.0	—	1.9	
	3.56	6.12	0.4	1.30	1.9	
Silver perchlorate	3.00	10.04	0.2	1.42	2.05	Dibut-bipy
	3.00	19.87	0.4	1.41	2.03	
	3.00	47.35	0.1	1.43	2.04	
Silver nitrate	0.52	2.01	0.3	1.76	2.15	Biquinolyl
	3.01	3.00	1.2	1.76	2.02	
	2.02	4.00	0.7	1.75	2.05	

\*  $C_M$  = Total concn of metal salt \*  $C_L$  = Total concn of ligand

in the concentration of the intermediate species. The half-wave potential of the first anodic wave with the nature of the ligand as follows: 2,2'-biquinolyl (1.74 V), 5,5'-dibutyl-2,2' bipyridyl (1.42 V), 4,4'-dimethyl-2,2'-bipyridyl (1.40V), and 2,2',2''-terpyridyl (1.30 V).

*Electrolysis of Silver Nitrate and Silver perchlorate in the Presence of 4,4'-Dimethyl-2,2'-dipyridyl at its Half-wave Potential.* Controlled potential electrolysis corresponding to the first wave were carried out for silver nitrate and silver perchlorate in the presence of dime-bipy. Metal salt-ligand ratio was 1:2, which enabled the smooth coulometric determinations as no product covered the working electrode. In all cases there was almost one-electron oxidation (Table 2) indicating that the first polarographic wave corresponds to the oxidation of silver(I) to silver(II).

The C, H, N and Ag<sup>2+</sup> analysis for the dark red crystals dec. at 200° obtained from silver(I) nitrate corresponds to the theoretical analysis for the compound Ag (dime-bipy)<sub>2</sub> NO<sub>3</sub>ClO<sub>4</sub>. The spectrum of the above product showed in ionic nitrate band at 1387 cm<sup>-1</sup> and a strong, broad band at 1092 cm<sup>-1</sup> corresponding to ionic perchlorate, indicating the presence of nitrate and perchlorate anions. The diffuse reflectance spectrum gave a single absorption band at 19,417 cm<sup>-1</sup> which probably is associated with the d-d transition of the d<sup>9</sup> configuration. The mass spectrum gave a maximum mass number of 184.1002 corresponding to the mass of the 4,4'-dimethyl-2,2'-bipyridyl molecule. It appears that the complex is decomposed under the conditions used to obtain the mass spectrum (ion source temperature 220°, electron energy 70 eV). However, the result is useful in confirming that the ligand is not oxidised.

The C, H, N and Ag<sup>2+</sup> analysis for the red crystals (m.p. 162-162°) obtained from silver(I) perchlorate corresponds to the theoretical values for the compound Ag(dime-bipy)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>. The IR spectrum of the product showed a strong broad band at 1090 cm<sup>-1</sup> indicating the presence of an ionic perchlorate group. The diffuse reflectance spectrum gave a single absorption band at somewhat higher frequency (20,576 cm<sup>-1</sup>) compared to the mixed nitrate-perchlorate complex. The mass spectrum gave again, only the number corresponding to ligand alone.

*Electrolysis of Silver Nitrate and Silver Perchlorate in the Presence of 2,2',2''-Terpyridyl at its Half-Wave Potential.* Controlled potential electrolysis corresponding to the first wave were carried out for silver nitrate and silver perchlorate in the presence of terpy. Preparation and coulometric determinations were obtained simultaneously where metal salt-ligand ratio was 1:2. This ratio was sufficient for keeping the working electrode clean throughout the electrolysis. Coulometric determinations for silver nitrate as well as silver perchlorate gave convincingly one electron change for silver(I) to silver(II) process (Table 3).

The C, H, N, and Ag<sup>2+</sup> analysis for the product obtained from silver nitrate-terpy system was anticipated to correspond to the complex having 1:1 terpy to silver ratio as reported by Morgan and Burstall<sup>1,2</sup> who claim to have isolated [Ag(terpy)]NO<sub>3</sub>. Further, comparison with the product obtained from the oxidation of silver(I) nitrate in the presence of bipy

and dime-bipy, a mixed anion complex was expected. However, the analytical data are consistent with the formulation  $\text{Ag(terpy)}_2(\text{ClO}_4)_2$ . The IR spectrum of the product gave neither an ionic nitrate band in the region of  $1380\text{ cm}^{-1}$ , nor a covalent nitrate band in the region of  $125\text{ cm}^{-1}$ . Strong bands in the region of  $1000\text{--}1200\text{ cm}^{-1}$  and at  $920\text{ cm}^{-1}$  were also absent. These bands are characteristic of coordinated perchlorate group as described by Wickenden and Krause<sup>13</sup> but a strong and broad band in the region of  $1090\text{ cm}^{-1}$  was observed, indicating the presence of ionic perchlorate group.

The C, H, N, and  $\text{Ag}^{2+}$  analysis for silver(II) complex obtained from silver(I) perchlorate-terpy system is very close to the analysis of the complex obtained from silver(I) nitrate-terpy system, i.e. for the product having molecular formula  $\text{Ag(terpy)}_2(\text{ClO}_4)_2$ . The IR spectrum also supports this formulation, as a broad and strong band in the region of  $1090\text{ cm}^{-1}$  was observed, which is characteristic of ionic perchlorate. Disappointingly, mass spectrum gave again the maximum mass of 233.0953 corresponding to the mass of terpy molecule only, as has been observed for dime-bipy complexes.

Although the products obtained from silver nitrate and silver perchlorate gave the same analysis, there were differences in physical properties of the two complexes. For example, the product obtained from silver nitrate-terpy solutions gave dark-red plate-shaped crystals (m.p.  $216\text{--}220^\circ$ ), whereas the silver perchlorate-terpy solutions gave dark-red needle-shaped crystals m.p.  $208\text{--}215^\circ\text{C}$ ). The diffuse reflectance spectra showed a single absorption band at about  $19,000\text{ cm}^{-1}$  for the product obtained from silver nitrate compared to a band at  $18,200\text{ cm}^{-1}$  for the complex prepared from silver perchlorate. These data indicate possible existence of different isomers.

The complex bis(terpy)silver(II) diperchlorate suggests the possibility of six coordinated complex formation, whereas terpy acts as a tridentate ligand but structural data would be required to support the structure. It may, however, be noted that a three-dimensional X-ray analysis of silver(II) dipicolinate monohydrate<sup>14</sup> has shown it to have a distorted octahedral structure in which each ligand is tridentate.

*Electrolysis of Silver Perchlorate in the Presence of Dibut-Bipy at its first Half-wave potential.* Preparative

TABLE 2. COULOMETRY OF SILVER(I) SALTS-DIME-BIPY SOLUTIONS.

Wt. of silver salt (g)	Potential applied (V)	Initial current (mA)	Electrolysis time (min)	Current used (Coulomb)	Molecular ratios	Electron/mole
Ligand: $\text{AgClO}_4$						
$\text{AgClO}_4$						
0.0253	1.38	2.97	92	12.140	2:1	1.03
0.0507	1.35	40	28	22.930	2:1	0.97
Ligand: $\text{AgNO}_3$						
$\text{AgNO}_3$						
0.0368	1.46	80	20	19.568	2:1	0.94
0.0365	1.50	90	15	19.780	2:1	0.95

TABLE 3. COULOMETRY OF SILVER(I) SALTS-TERPY SOLUTIONS.

Wt of Silver salts (g)	Potential applied (V)	Initial current (mA)	Electrolysis time (min)	Current used (Coulomb)	Molecular ratio of Terpy: Silver Salt	Electron/mole
Terpy: $\text{AgClO}_4$						
$\text{AgClO}_4$						
0.0104	1.20	2.25	60	4.830	2:1	1.00
0.0452	1.25	22	40	21.729	2:1	1.03
Terpy: $\text{AgNO}_3$						
$\text{AgNO}_3$						
0.0330	1.30	18.5	25	17.650	2:1	0.94
0.0322	1.35	22	21	19.946	2:1	1.06

TABLE 4 COULOMETRY OF SILVER(I) PERCHLORATE/DIBUT-BIPY SOLUTIONS.

Wt of $\text{AgClO}_4$ (g)	Potential applied (V)	Initial current (mA)	Electrolysis time (min)	Current used (Coulomb)	Molecular ratio of Ligand: $\text{AgClO}_4$	Electron/mole
0.0311	1.4	8.3	96	16.500	3:1	1.14
0.0598	1.5	40	32	27.340	3:1	0.98

TABLE 5. SOLVENTS USED FOR ISOLATION OF DIBUT-BIPY SILVER(II) COMPLEX.

Solvent	Observation
Acetone	Completely soluble
Ethyl acetate	Completely soluble
Chloroform	Immediately dissolved
Ether	Colour of the product fades gradually
Carbon tetrachloride	Decolourised
Nitromethane	Immediately decolourised
Methanol	Immediately decolourised
Benzene	Reddish brown viscous liquid settled down at the bottom of the test tube, stirred and decanted benzene. Repeated this treatment four times. Reddish brown liquid obtained which decolourised on drying under vacuum.

scale electrolyses were carried out at a fixed potential (in the range 1.4–1.5 V) corresponding to the first wave of the silver (I) perchlorate 5,5'-dibut-bipy system with 0.1M tetra-n-butylammonium perchlorate as supporting electrolyte. Table 4 gives details of the electrolyses and the calculated number of electrons involved per molecule in the electrode reaction. As in all other silver(I) polypyridyl systems, the results confirmed that a one-electron oxidation process occurred at potentials corresponding to the first polarographic wave.

Repeated attempts to isolate the product obtained from these electrolyses were unsuccessful. The oxidised solution was dark red-brown characteristic of silver(II)-polypyridyl complexes. A portion of this solution was treated with silver(I) salt but no silver(II) complex was precipitated, the colour of the anolyte remaining unaltered. Next, the solvent was removed under vacuum from the remainder of the solution until a viscous reddish brown residue containing an excess of supporting electrolyte and excess of 5,5'-dibutyl-2,2'-bipyridyl remained in the solution. The reddish brown residue gave iodine with aqueous potassium iodide solution indicating presence of silver(II). To isolate the product from the residue, a variety of solvents were used but without success. Table 5 gives a summary of the techniques used.

*Electrolysis of Silver Nitrate in the Presence of 2,2'-biquinolyl at its Half-wave Potential.* Controlled potential electrolysis of silver (I) nitrate solutions in the presence of 2,2'-biquinolyl using 0.1M TBAP as the supporting electrolyte was attempted. The potential used was 1.74 V which corresponded to the half-wave potential of the first anodic wave. However, it was found that, for this system, the initial current rapidly fell to very low levels apparently due to a deposit which formed on the electrode sur-

face. Previous difficulties of this nature were overcome by the addition of an excess of ligand which prevented the deposition of the product on to the electrode surface. Unfortunately, for the present system, the low solubility of the ligand in acetonitrile did not permit this technique to be applied and coulometric determinations therefore, were not possible.

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