

## A conductometric study of the complex formation between copper (I) perchlorate and some organic ligands in acetonitrile

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Received 16 April 1998, revised 28 September 1998

Copper (I) perchlorate solutions of different concentrations in acetonitrile have been conductometrically titrated with solutions of thiourea (TU), N,N-dimethylthiourea (DMTU), N-phenylthiourea (NPTU), N, N-diphenylthiourea (DPTU), 1,10-phenanthroline (PHEN), 2,2'-bipyridyl (BPY) and triethylphosphite (TEP) at 298 K. The plots of conductivity versus moles of ligand added show significant decrease in conductivity followed by a region of almost constant conductivity. The fall of conductivity in the cases of thiourea and substituted thioureas is linear while in all the other cases it is non-linear. From these plots knowledge about the stoichiometry of the complexes formed between copper (I) perchlorate and various ligands has been derived. A complex of stoichiometry 1:2 is observed between copper (I) perchlorate and 1, 10-phenanthroline and 2, 2'-bipyridyl and 1:4 complex with triethylphosphite. Copper (I) perchlorate, however, forms complexes with thiourea and substituted thioureas, the stoichiometry of which strongly depends upon the concentrations of copper (I) perchlorate as well as of the ligands used for the titration. With N-phenylthiourea and N,N-diphenylthiourea, the complex formed has copper (I) perchlorate to ligand ratio as 1:2 under the present conditions employed, while with thiourea and N,N-dimethylthiourea, the stoichiometry of the complexes formed between copper (I) perchlorate and ligands is either 1:2 or 1:3 or 1:4 depending upon the conditions.

Copper (I) state is unstable and rarely studied. Copper (I) perchlorate tetraacetonitrile ( $\text{CuClO}_4 \cdot 4\text{CH}_3\text{CN}$ ) is an interesting copper (I) complex which remains stable in the solid form as well as in solutions of acetonitrile ( $\text{CH}_3\text{CN}$ ), benzonitrile ( $\text{C}_6\text{H}_5\text{CN}$ ), triethylphosphite (TEP) and also upto a certain mole fraction of these solvents with other organic solvents<sup>1-4</sup>. The solutions of this complex, however, are unstable in many organic solvents. In acetonitrile, it behaves as fully dissociated<sup>1,2</sup> 1:1 electrolyte producing  $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$  as cation and  $\text{ClO}_4^-$  as anion. The limiting equivalent conductance ( $\Lambda_0$ ) for this complex in acetonitrile is  $168.3 \text{ S cm}^2 \text{ mol}^{-1}$  which makes it a very strong electrolyte in acetonitrile. This complex salt has been extensively investigated in acetonitrile and its binary mixtures with several other organic solvents using <sup>63</sup>Cu NMR<sup>3,4</sup> conductance<sup>2,5,6</sup>, transport number<sup>7,8</sup>, viscosity<sup>9</sup> and ultrasonic velocity measurements<sup>10,11</sup>. Some strong organic ligands like thiourea, substituted thioureas, 1,10-phenanthroline, 2,2'-bipyridyl and triethylphosphite are expected to form very stable

ionic copper (I) complexes with copper (I) perchlorate. No exact knowledge about the formation of these complexes is available. The stoichiometry of these ionic copper (I) complexes is also not known though the stoichiometry of some other non-ionic copper (I) halide complexes with many other ligands is well known<sup>12-14</sup>. In the present studies attempts have been made to investigate the stoichiometry of these copper (I) perchlorate complexes using conductometric titration method.

### Materials and Methods

$\text{CuClO}_4 \cdot 4\text{CH}_3\text{CN}$  was prepared by the method already reported<sup>15-16</sup>. Acetonitrile (Merck 99% pure) was purified/dried by the method given earlier<sup>17-18</sup>. The purified acetonitrile had density  $0.77685 \text{ g cm}^{-3}$ , viscosity  $0.341 \text{ cP}$ , dielectric constant 36.0 and conductivity  $1-3 \times 10^{-7} \text{ S cm}^{-1}$  at 298 K. Thiourea (TU) (99% from New India chemical Enterprises, Cochin) N-phenylthiourea (NPTU), (Fluka) N,N-diphenylthiourea (DPTU) (99% from BDH), N,N-

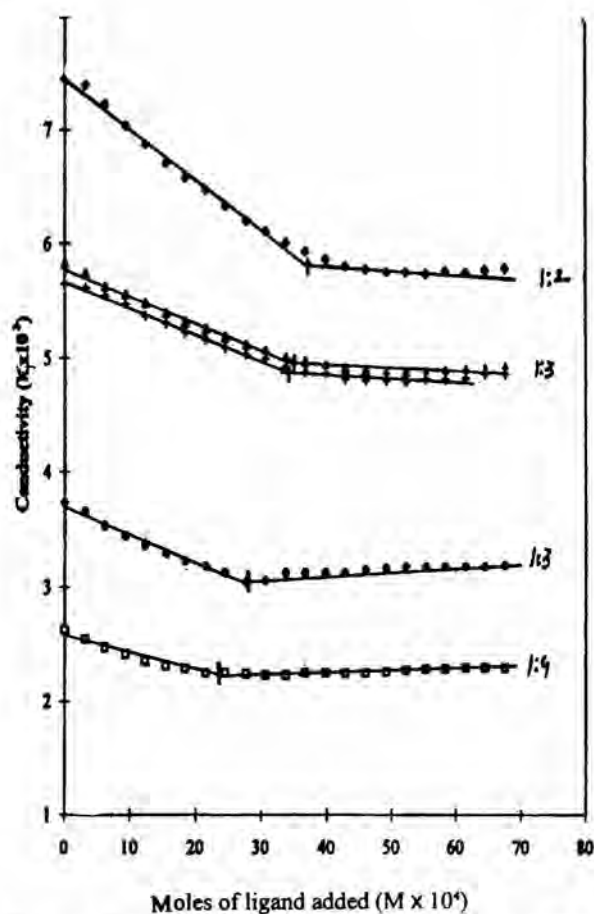


Fig. 1 -- Plot of conductivity ( $\kappa \times 10^3$ ) vs. moles of ligand added ( $M \times 10^4$ ) in the titration of  $\text{CuClO}_4$  with thiourea (TU) in acetonitrile at 298 K.

◆ 0.0714M	$\text{CuClO}_4$	0.307 M	TU
△ 0.0514M	$\text{CuClO}_4$	0.219 M	TU
+ 0.0506M	$\text{CuClO}_4$	0.220 M	TU
● 0.0381M	$\text{CuClO}_4$	0.237 M	TU
□ 0.0247M	$\text{CuClO}_4$	0.201 M	TU

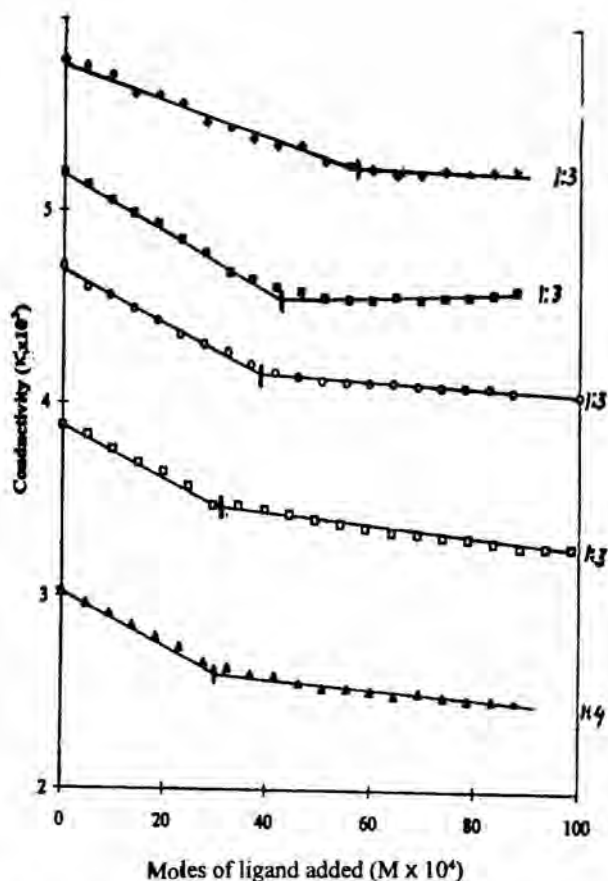


Fig. 2 - Plot of conductivity ( $\kappa \times 10^3$ ) vs. moles of ligand added ( $M \times 10^4$ ) in the titration of  $\text{CuClO}_4$  with N,N-dimethylthiourea (DMTU) in acetonitrile at 298 K.

◆ 0.0537M	$\text{CuClO}_4$	0.468 M	DMTU
■ 0.0465M	$\text{CuClO}_4$	0.463 M	DMTU
○ 0.0446M	$\text{CuClO}_4$	0.459 M	DMTU
□ 0.0325M	$\text{CuClO}_4$	0.493 M	DMTU
▲ 0.0247M	$\text{CuClO}_4$	0.421 M	DMTU

dimethylthiourea (DMTU) (99.8% from Merck Chuchardt), 1,10-phenanthroline monohydrate (PHEN) (99.5% from Loba), 2, 2'-bipyridyl (BPY) (99.5% from Qualigens) and triethylphosphite (TEP) (97% from Fulka) were used as received. For each conductometric titration 5-6 solutions of varying concentrations of copper (I) perchlorate were used. These solutions were prepared by dissolving known amounts of  $\text{CuClO}_4 \cdot 4\text{CH}_3\text{CN}$  and dissolving them in a known quantity of acetonitrile. Same number of stock solutions of a given ligand with appropriate concentrations (5 to 10 times stronger than  $\text{CuClO}_4$ ) were also prepared in acetonitrile. 35  $\text{cm}^3$  of copper (I) perchlorate solutions in each case were taken

in the conductivity cell placed in a water thermostat bath kept at  $298 \pm 0.01$  K for 10-15 minutes and to this solution, 0.5  $\text{cm}^3$  of the ligand solution from a microburette was added. This solution in the cell was thoroughly mixed, kept for 5-10 minutes in the thermostat bath and its conductance was measured. The addition of ligand solution (0.5  $\text{cm}^3$  each time) was continued till the molar ratio of copper (I) perchlorate to ligand sufficiently exceeded a value of 1:4. The measured conductance was corrected for "solvent correction" and for the "volume correction". The cell constant was determined by using aqueous KCl solutions and following the method reported by Fuoss and coworkers<sup>19</sup>. The conductivity ( $\kappa$ ) of the solu-

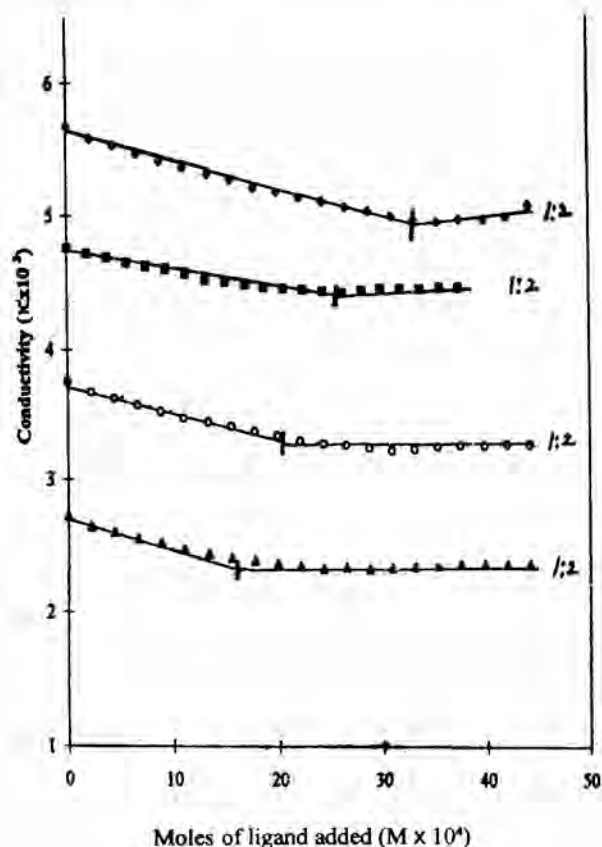


Fig. 3- Plot of conductivity ( $\kappa \times 10^3$ ) vs. moles of ligand added ( $M \times 10^4$ ) in the titration of  $\text{CuClO}_4$  with N-phenylthiourea (NPTU) in acetonitrile at 298 K.

◆	0.056M	$\text{CuClO}_4$	0.221 M	NPTU
■	0.047M	$\text{CuClO}_4$	0.187 M	NPTU
○	0.0373M	$\text{CuClO}_4$	0.117 M	NPTU
▲	0.027M	$\text{CuClO}_4$	0.159 M	NPTU

tion was calculated by multiplying the corrected conductance with the cell constant. In the case of each ligand 4-6 titrations were performed using independent stock solutions of copper (I) perchlorate as well as of the ligands.

### Results and Discussion

The plots of conductivity ( $\kappa$ ) of various solutions as a function of moles ( $M$ ) of ligands added in each case are given in Figs 1-7. It is interesting to note that the conductivity in each case decreases significantly by the increase in moles of the ligand. In the cases of thiourea and substituted thioureas the decrease in conductivity with the increase in moles of

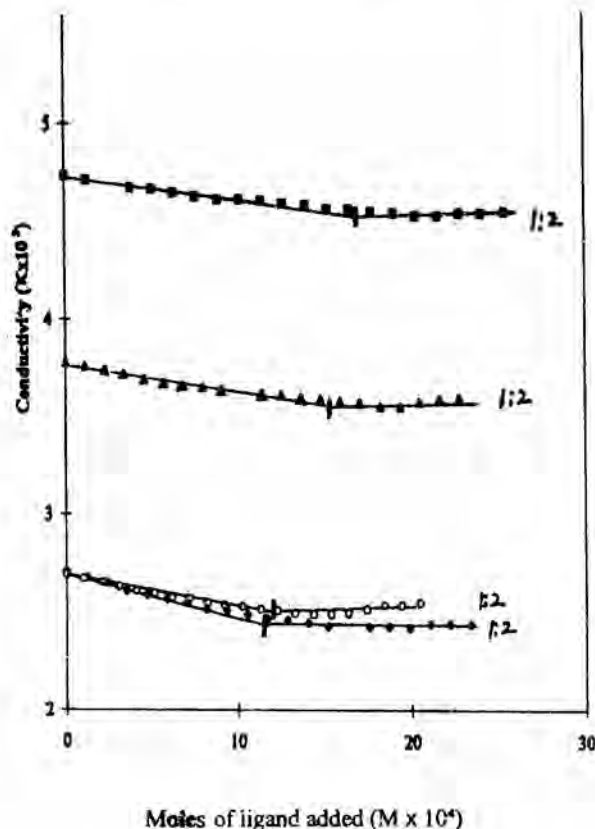


Fig. 4- Plot of conductivity ( $\kappa \times 10^3$ ) vs. moles of ligand added ( $M \times 10^4$ ) in the titration of  $\text{CuClO}_4$  with N, N-diphenylthiourea (DPTU) in acetonitrile at 298 K.

■	0.0409M	$\text{CuClO}_4$	0.127 M	DPTU
▲	0.0317M	$\text{CuClO}_4$	0.114 M	DPTU
○	0.0217M	$\text{CuClO}_4$	0.117 M	DPTU
◆	0.0204M	$\text{CuClO}_4$	0.1025 M	DPTU

ligand is almost linear while in the cases of 1, 10-phenanthroline, 2, 2'-bipyridyl and trithylphosphite the decrease is very sharp and is non-linear. The results indicate very strong effect of the later ligands for complex formation with copper (I) perchlorate. In all the cases after the complex formation is complete, the conductivity of the solutions becomes almost constant and further increase in the moles of the ligand does not change the conductivity. The point at which the conductivity becomes almost constant corresponds to the stoichiometry of the complex in each case. In Figs 1-7, the marked line indicates the moles ( $M$ ) of ligand corresponding to the stoichiometry of the complex formed. In the case of 1, 10-

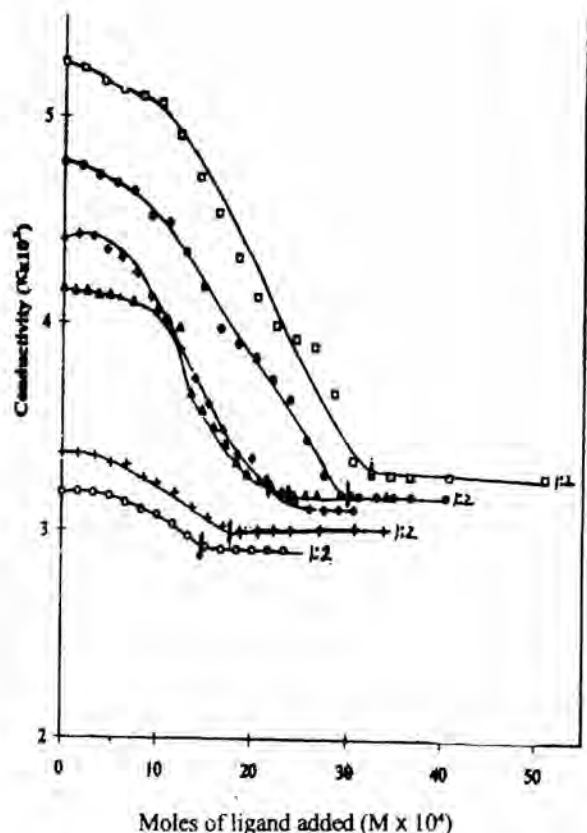


Fig. 5 - Plot of conductivity ( $\kappa \times 10^3$ ) vs. moles of ligand added ( $M \times 10^4$ ) in the titration of  $\text{CuClO}_4$  with 1, 10-phenanthroline (PHEN) in acetonitrile at 298 K.

□	0.0490M	$\text{CuClO}_4$	0.204 M	PHEN
●	0.0433M	$\text{CuClO}_4$	0.184 M	PHEN
◆	0.0383M	$\text{CuClO}_4$	0.307 M	PHEN
△	0.0363M	$\text{CuClO}_4$	0.243 M	PHEN
+	0.0285M	$\text{CuClO}_4$	0.340 M	PHEN
○	0.0244M	$\text{CuClO}_4$	0.334 M	PHEN

phenanthroline and 2, 2'-bipyridyl, the stoichiometry of the complex between copper (I) perchlorate at all concentrations used corresponds to a value of 1:2. Some evidence<sup>20</sup> for the 1:2 complex formation between copper (I) salts and between 1, 10-phenanthroline and 2, 2'-bipyridyl is also available in the literature from spectrophotometric methods. In the case of triethylphosphite at all concentrations of copper (I) perchlorate used, the stoichiometry of the complex is 1:4. The evidence of this comes from our <sup>63</sup>Cu NMR<sup>3,4</sup> studies, where coupling between <sup>63</sup>Cu and <sup>31</sup>P nuclei takes place. The splitting of <sup>63</sup>Cu NMR line into five peaks at all proportions of

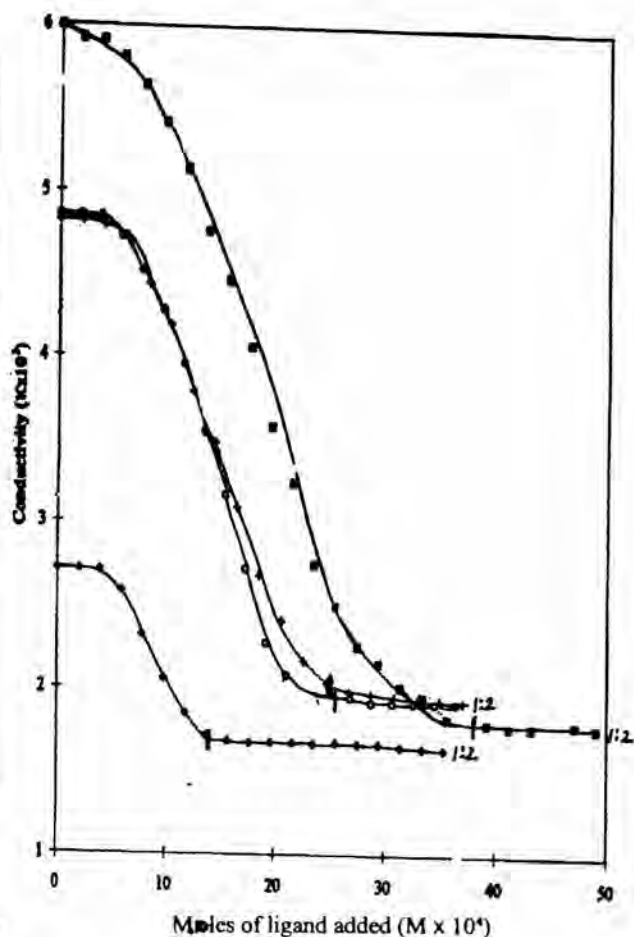


Fig. 6 - Plot of conductivity ( $\kappa \times 10^3$ ) vs. moles of 2,2-bipyridyl (BPL) in acetonitrile at 298 K.

■	0.0583M	$\text{CuClO}_4$	0.393 M	BPL
○	0.0429M	$\text{CuClO}_4$	0.384 M	BPL
+	0.0428M	$\text{CuClO}_4$	0.412 M	BPL
◆	0.0221M	$\text{CuClO}_4$	0.393 M	BPL

triethylphosphite clearly indicates a stoichiometry of 1:4 between copper (I) perchlorate and triethylphosphite.

The stoichiometry of copper (I) perchlorate complex with thiourea and substituted thioureas, is strongly affected by the concentrations of the copper (I) perchlorate and the ligand used (Figs 1-4). When solutions of 0.0714 M  $\text{CuClO}_4$  is titrated with 0.37 M thiourea solution, the complex formed is 1:2, when the solution of  $\text{CuClO}_4$  between 0.038 to 0.05 M is titrated with 0.2 to 0.3 M thiourea, the complex formed is 1:3 and when  $\text{CuClO}_4$  solution of concen-



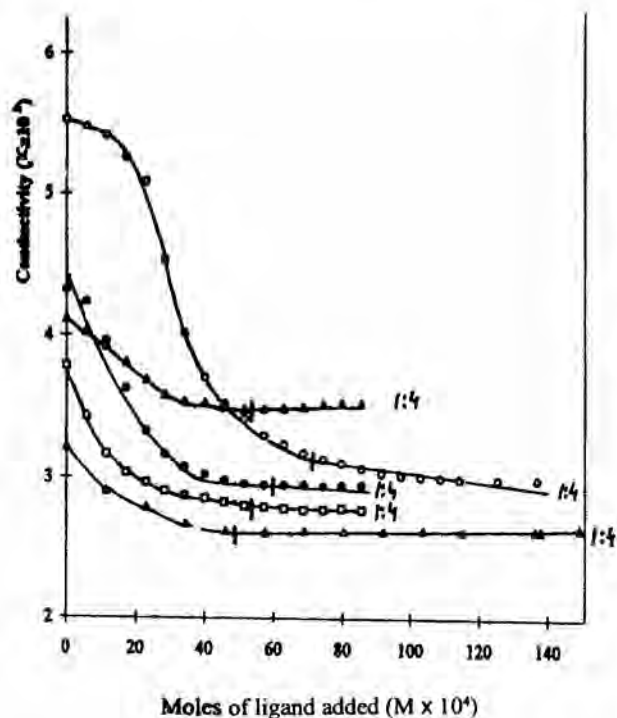


Fig. 7 - Plot of conductivity ( $\kappa \times 10^3$ ) vs. moles of triethylphosphite (TEP) in acetonitrile at 298K.

○	0.0517M	CuClO <sub>4</sub>	Pure	TEP
●	0.0435M	CuClO <sub>4</sub>	Pure	TEP
▲	0.0396M	CuClO <sub>4</sub>	Pure	TEP
□	0.0320M	CuClO <sub>4</sub>	Pure	TEP
△	0.0308M	CuClO <sub>4</sub>	Pure	TEP

tration 0.025 M is titrated with thiourea solution of concentration 0.2 M, 1:4 complex is formed. The results show that when relatively low concentrations of CuClO<sub>4</sub> and thiourea are employed, the complex formed has higher copper (I) perchlorate to thiourea stoichiometry (Fig 1). The complexes formed with N, N-dimethylthiourea also show a similar behaviour as with thiourea. In this case also 1:2 or 1:3 or 1:4 complexes are formed between copper (I) perchlorate and the ligand at various concentrations. With N-phenylthiourea and N, N-diphenylthiourea the stoichiometry of the complex formed under the conditions employed is 1:2. The steric hindrance due to bulky groups in these two cases, in the present

work, may restrict the stoichiometry only to 1:2 complex.

### Acknowledgement

DSG thanks the CSIR, New Delhi for the research grant under the research project 1(1412)/96-EMR-II.

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