JOURNAL OF MATERIALS SCIENCE 30 (1995) 447–451

D.C. conduction phenomenon and spectrum of a novel bis(7-formyl-8-hydroxyquinoline) zinc complex

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A novel bis(7-formyl-8-hydroxyquinoline)zinc complex was prepared from 7-formyl-8-hydroxyquinoline. This compound was characterized on the basis of elemental analysis, i.r., ^{1}H nuclear magnetic resonance, magnetic moment and conductivity measurements. The compound was a non-conductor in dimethylformamide. A tentative structure for this compound is suggested. The electrical conductivity at various temperatures for an annealing time of 1 h has been measured. The activation energy of this compound is found to be 0.68 eV. Conduction parameters including the Schottky coefficient (β_S), Schottky electrode barrier (ϕ_S), jump distance (d) and dielectric constant (ε) have been determined. The aim of this study is also to understand the mechanism of conduction of this zinc(II) complex.

1. Introduction

The electrical conductivities of quinoline compounds and also aromatic polymers have received considerable attention [1–3]. Because of its physiological activity, analytical and industrial applications, the chemistry of quinoline and its metal complexes have attracted the attention of many researchers [4, 5]. A common feature of the two groups of 7-formyl-8-hydroxyquinoline as ligand is that the oxygen atom takes part in coordination, while the nitrogen atom of the pyridine group remains uncoordinated. It has been found that organic compounds containing the O–N and/or S–N linkage are of interest due to their superior electrical conduction [2]. In the present study, we have prepared and studied the d.c. conduction mechanism of a novel bis(7-formyl-8-hydroxyquinoline)zinc complex.

2. Experimental procedure

7-formyl-8-hydroxyquinoline (HL) was prepared according to El-Sonbati [6–10]. $ZnL_2 \cdot 2H_2O$ was prepared by direct reaction of a hot solution of anhydrous zinc chloride (0.01 mol) in EtOH (30 ml) with a solution of the required amount of ligand (0.02 mol) in EtOH (30 ml). The reaction mixture was stirred at room temperature on a water bath for 0.5–1 h. The precipitate was collected by filtration, washed with EtOH followed by Et_2O, and dried *in vacuo* with P_2O_5. The yield was 65% and the melting point 300 °C. Analysis gave the following results. Found: Zn, 14.8; C, 54.0; H, 4.5; N, 6.5%. $ZnC_{20}H_{20}N_2O_4$ calculated: Zn, 15.6; C, 53.9; H, 4.5; N, 6.3%.

Analysis of the metal was carried out by standard methods [7, 8]. C, H and N contents were obtained by the Microanalytical Unit of Cairo University. The other measurements were carried out as reported earlier [6–10].

The conductivity measurements were carried out using a current meter with an accuracy of 2–4%. Current–voltage characteristics were measured with a d.c. step voltage applied to the specimens at a certain temperature. The dielectric constant was measured using a Leibold amplifier.

3. Theoretical considerations

The behaviour of current in the high temperature range with applied field is analysed with respect to the following three conduction mechanisms [11]: Schottky emission, ionic conductivity and Poole–Frenkel effect.

Schottky emission is essentially thermoinoic emission from a metal electrode into the conduction band of a dielectric over the potential barrier at the metal–dielectric interface, with image force correction taken into account. The current density J_{Sch} in this

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mechanism is given by

$$J_{\mathrm{Sch}} = AT^2 \exp\left(\frac{\beta_S E^{1/2} - \phi_S}{kT}\right) \qquad (1)$$

where A is the familiar Richardson–Dushman constant ($\simeq 120\ \mathrm{A\,cm^{-2}\,K^{-2}}$), ϕ_S the Schottky electrode barrier, E the field and

$$\beta_S = \left(\frac{e^3}{4\pi\varepsilon_0\varepsilon_r}\right)^{1/2} \qquad (2)$$

where other symbols have their usual meanings.

For ionic conduction, Mott and Gurney [12] derived the following expression for the current (I) in low fields, based on a model of diffusion of lattice defects of ions and a carrier hopping process:

$$I = I_0 \exp\left(\frac{-\phi_i}{kT}\right) \sinh\left(\frac{edE}{2kT}\right) \qquad (3)$$

where e is the electronic charge, d the jump distance, I_0 a constant, ϕ_i the activation energy and other symbols have their usual meanings. Equation 3 is reduced to

$$I = I_0 \exp\left(\frac{-\phi_i}{kT}\right) \exp\left(\frac{edE}{2kT}\right) \qquad (4)$$

which is very similar to an expression derived by Lawson [13] for the high-field dependence of current.

On the other hand, the Poole–Frenkel effect is a bulk effect, caused by the field-lowering of the coulombic barrier surrounding charge donor sites. The usual conductivity equation for this model [5] is

$$\sigma = \sigma_0 \exp\left(\frac{\beta_{\mathrm{pf}} E^{1/2} - \phi_p}{2kT}\right) \qquad (5)$$

where σ is the conductivity, ϕ_p the thermoinoic work-function of a trap site, and

$$\beta_{\mathrm{pf}} = \left(\frac{e^3}{\pi\varepsilon_0\varepsilon_r}\right)^{1/2} \qquad (6)$$

The relation between the Schottky and Poole–Frenkel coefficients [14] is

$$\beta_S = \frac{1}{2}\beta_{\mathrm{pf}} \qquad (7)$$

4. Results and discussion

4.1. Characterization of ligand and metal chelate

The ^{1}H nuclear magnetic resonance (NMR) spectra of the ligand and the complex of Zn(II) were recorded in DMSO-d_6. The aromatic protons in the ligand appear in the region 7.1–8.9 p.p.m. The signal at 10.1 p.p.m. indicates that the hydroxyl proton is hydrogen-bonded. The disappearance of this signal in the complex confirms that the complex formation is by deprotonation [6].

The most characteristic bands of the i.r. spectrum of the ligand were assigned on the basis of a careful comparison of the latter with that of 8-hydroxyquinoline. The spectrum of $ZnL_2 \cdot 2H_2O$ displays a strong band at 1582 cm^{-1}, assigned to C = N, aromatic. This band is not altered greatly compared with ν (C = O) of the aldehyde group which is shifted to a lower frequency upon complexation, indicating participation of its oxygen in bonding. Furthermore, the band at 3390 cm^{-1} due to the phenolic OH disappears from the spectrum of the complex with the appearance of a C–O band at lower frequency (ca. 1160 cm^{-1}), indicating deprotonation with involvement of the oxygen atom in bonding. The new band appearing at ca. 400 cm^{-1} is assigned to the ν (M–O) [4, 6] vibration; the carbonyl band experiences a lower shift (ca. 30 cm^{-1}), lending support to the participation of the carbonyl oxygen in bonding. The water molecules are eliminated at 110 °C. The spectrum also shows a band in the 3550–3340 cm^{-1} region, indicating the presence of water molecules; the absence of 940 and 730 cm^{-1} bands indicates that the water is not coordinated.

On the basis of the above discussion, it is clear that the ligand is attached to the zinc (II) ion, forming a six-membered ring, as a monobasic bidentate. Tetrahedral geometry is the most preferred one for the tetracoordinated Zn(II) complex.

4.2. Electrical conductivity

The current–voltage (I–V) characteristics of $ZnL_2 \cdot 2H_2O$ complex on a logarithmic scale at different temperatures are shown in Fig. 1. It can be seen

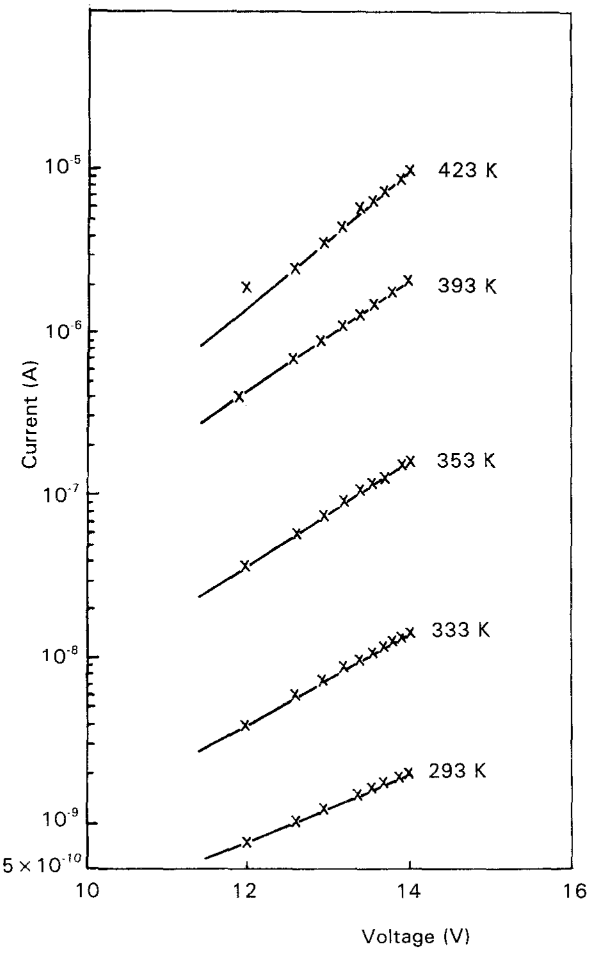

Figure 1 I–V characteristics on a logarithmic scale at various temperatures (thickness = 0.16 cm).

that the current increases linearly with increasing voltage. This ohmic behaviour indicates that the current density is controlled by the thermal bulk generation of charge carriers [15].

The specific electrical conductivity of the solid ($\Omega^{-1}\ \mathrm{cm}^{-1}$) was evaluated from $\sigma = Id/AV$, where d (cm) is the film thickness, $A\,(\mathrm{cm}^2)$ its area, V (V) the potential across the film and I (A) the current flowing through the film. Fig. 2 shows the electrical conductivity of samples of the complex, as-prepared and annealed at different temperatures (323, 373 and 423 K) for a fixed time (1 h) as a function of temperature. The figure shows that the conductivity can obey the equation

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \tag{8}$$

It is clear that the conductivity of the samples depends on temperature as well as on the annealing temperature. The conductivity of the annealed samples is less than that of the as-prepared one. This decrease may be due to the rearrangement of atoms inside the molecules. The observed inflection in the curves may be attributed to a change in conduction mechanism.

The activation energy (E_a) of unannealed (as-prepared) sample was calculated by the least-squares method and had the value of 0.68 eV. This value is similar to those reported for narrow-band semiconductors [16]. The activation energy of the annealed samples is listed in Table I. From this table it is clear that E_a decreases with increasing temperature of annealing.

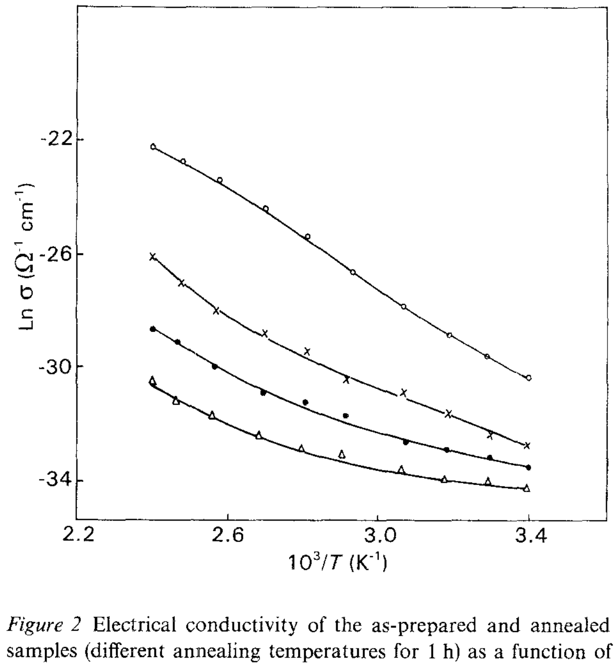

Figure 2 Electrical conductivity of the as-prepared and annealed samples (different annealing temperatures for 1 h) as a function of $1/T$: (○) as prepared, (×) 323 K, (●) 373 K, (△) 423 K.

TABLE I Dependence of activation energy (E_a) values on annealing temperature

Annealing temperature (K)	E_a (eV)
As-prepared	0.68
323	0.61
373	0.44
423	0.36

4.3. Conduction mechanism

To establish the conduction mechanism in the Zn(II) complex, the data of Fig. 1 were replotted in the form of log I versus $E^{1/2}$ (Schottky emission), log I versus E (ionic conduction) and ln σ versus $E^{1/2}$ (Poole–Frenkel effect).

Fig. 3 shows the Schottky plots (log I against $E^{1/2}$) in the temperature range 293–423 K. The experimental values of β_S and ε are listed in Table II. From this table the value of β_S increases with increasing temperature. The Schottky barrier potential ϕ_S was obtained from the slopes of the plots of $\log(I_0/T^2)$ against $1/T$ (Fig. 4), where I_0 is the extrapolated value of I at $E = 0$ (Fig. 3). A value of ϕ_S of 0.717 eV is obtained.

Fig. 5 shows the difference between the experimental and theoretical values of dielectric constant.

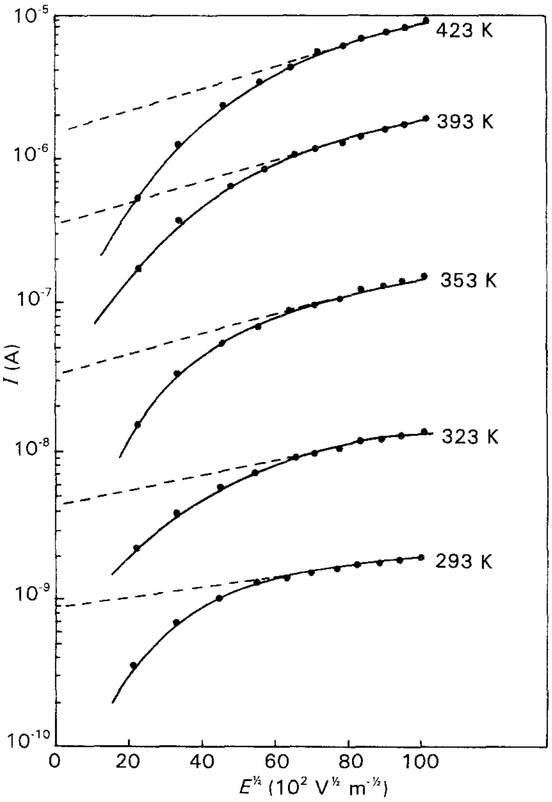

Figure 3 Schottky conduction plot for 0.16 cm thickness of sample with silver paste electrode.

TABLE II Dependence of Schottky coefficient (β_S) and ε on temperature

Temperature (K)	β_S ($\mathrm{C\ cm^{-1/2}\ V^{-1/2}}$)	ε
293	4.9×10^{-23}	1.53
323	6.4×10^{-23}	0.89
353	7.5×10^{-23}	0.65
393	7.7×10^{-23}	0.62
423	7.9×10^{-23}	0.59

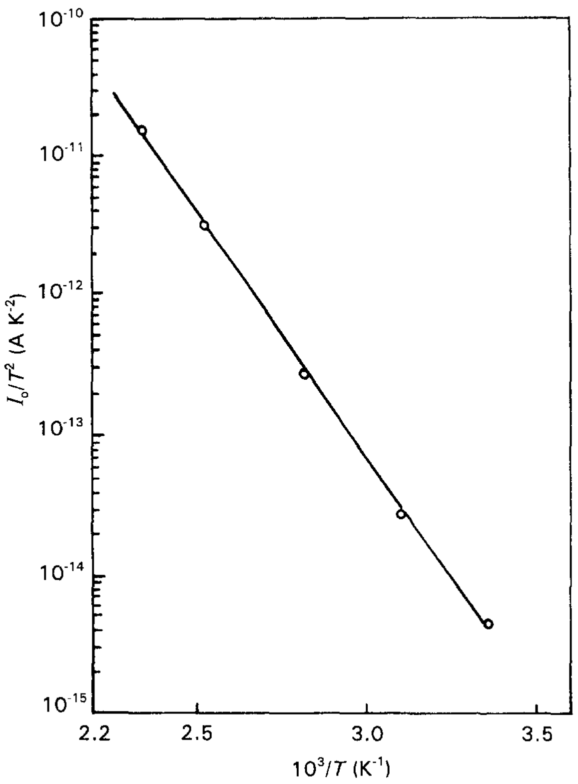

Figure 4 Log(I_0/T^2) versus $1/T$ for $ZnL_2 \cdot 2H_2O$ complex.

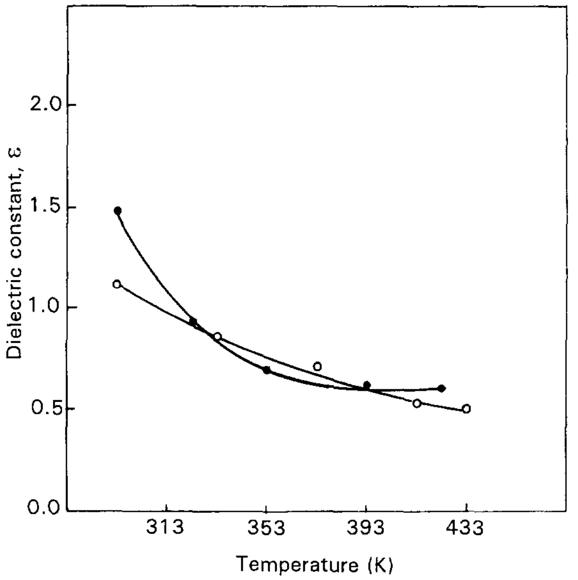

Figure 5 Dielectric constant versus temperature for $ZnL_2 \cdot 2H_2O$ complex: (●) theoretical, (○) experimental.

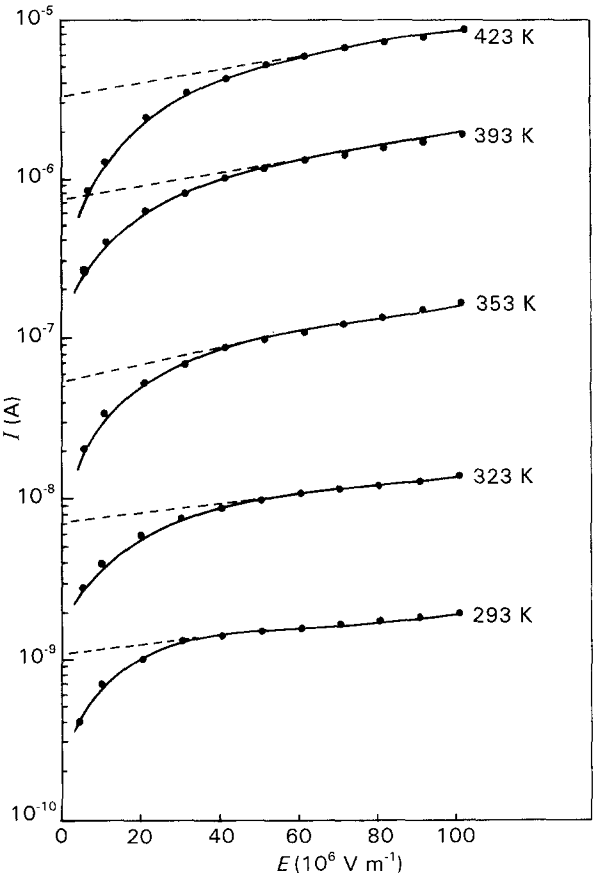

Figure 6 Ionic conduction plot for $ZnL_2 \cdot 2H_2O$ complex.

TABLE III Dependence of jump distance (d) on temperature

Temperature (K)	d (nm)
293	0.302
323	0.378
353	0.586
393	0.664
423	0.709

The theoretical values were calculated from Equation 2. The figure shows a decrease of ε with temperature increase. This decrease can be ascribed to the effect of temperature on the material density. The increase in temperature induces an expansion of molecules, (thus lowering the number of molecules per unit volume of insulator material. This causes some decrease in electronic polarization and hence a decrease of the dielectric constant of the material [17].

For ionic conduction, plots of log I against E for the specimens are given in Fig. 6. The slopes of the straight lines at high fields are equal to $(ed/2kT)$, where d is the jump distance which is evaluated as a function of temperature and given in Table III. The plots were extrapolated to obtain I_{0s} (i.e. I at $E = 0$) and the activation energy ϕ_i was estimated from a plot of log I_{0s} against $1/T$ (Fig. 7). The value of the activation energy is 0.71 eV.

On the other hand, the Poole–Frenkel effect is a bulk effect, caused by the field-lowering of the coulombic barrier surrounding charge donor sites. As shown in Fig. 8, the relation between ln σ and $E^{1/2}$ is a straight line at a constant temperature. This suggests that the Poole–Frenkel mechanism does not operate in the present material. Poole–Frenkel coefficients are tabulated in Table IV.

5. Conclusion

The electrical conductivity of a novel bis(7-formyl-8-hydroxyquinoline)zinc(II) complex has been mea-

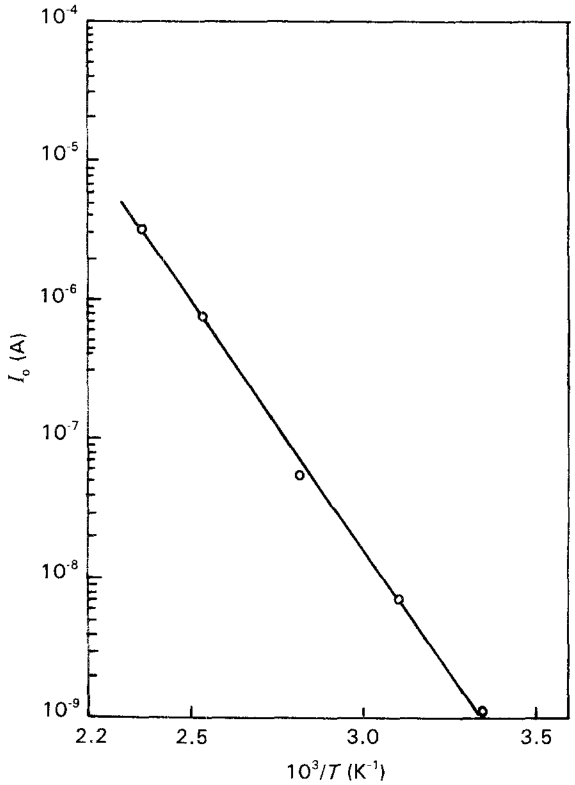

Figure 7 Log$I$ versus $1/T$ for $ZnL_2 \cdot 2H_2O$ complex.

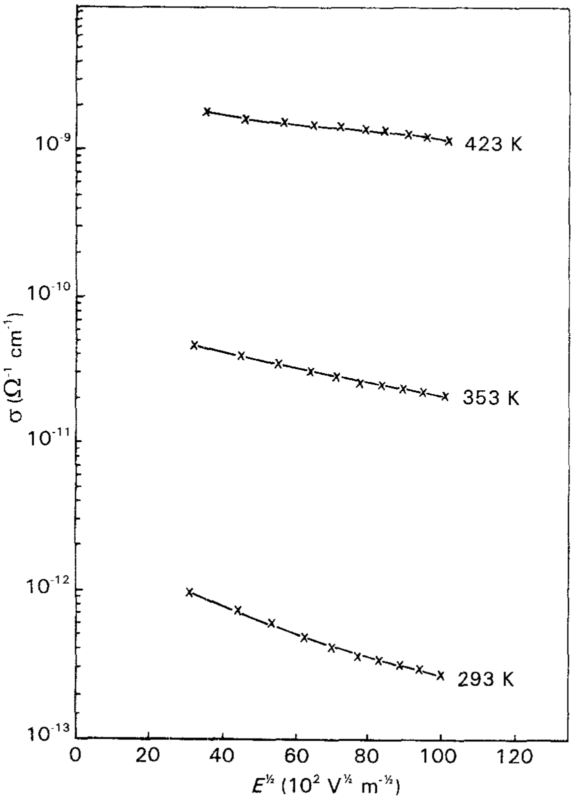

Figure 8 Poole–Frenkel conduction for $ZnL_2 \cdot 2H_2O$ complex.

TABLE IV Dependence of Poole–Frenkel coefficient (β_{pf}) on temperature

Temperature (K)	β_{pf} (C $cm^{-1/2}$ $V^{-1/2}$)
293	9.8×10^{-23}
323	12.8×10^{-23}
353	15.0×10^{-23}
393	15.4×10^{-23}

sured at various temperatures of annealing for one hour. A complete set of conduction parameters has been calculated. Both Schottky and ionic mechanisms operate during the transport process, i.e. there is a mixed electrode–bulk mechanism.

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Received 11 August 1993
and accepted 16 June 1994