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ELECTRICAL PROPERTIES OF Co(II) AND Ni(II) POLYCHELATES OF 1,4-DIHYDROXYANTHRAQUINONE

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LIGANDS possessing at least two sets of bidentate groups may result in the formation of polymeric metal chelates, also called polychelates. Several polychelates of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) with *o*-hydroxythiosemicarbazones¹, terephthalaldehyde bis-(4-phenylthiosemicarbazone)², and Schiff bases of terephthalaldehyde and hydrazides³ have recently synthesized. This communication deals with the synthesis of Co(II) and Ni(II) polychelates of 1,4-dihydroxyanthraquinone and with the study of their electrical properties (d.c and a.c. conductivity and relative dielectric constant). Since any two successive metal atoms are in conjugation with each other, such polymers may exhibit unusual electrical properties as this type of alternate single-double bond system provides a suitable channel for the electrons. However, the ease of electron flow, to a large extent, depends upon the oxidation state of the metal atom as well as on the surroundings/substituents.

Preparation of the polychelate

Polychelates have been prepared by reacting equimolar aqueous ethanolic solution of metal salts and 1,4-dihydroxyanthraquinone; pH of the reaction mixture was adjusted between 7.5–8.5 by using sodium acetate. The mixture was refluxed for 3–4 hr on a water bath. It was then concentrated to get a viscous mass, which was washed several times with hot water and alcohol to remove excess of the reactants. The complex so obtained was dried in vacuum over P₄O₁₀. The amorphous dark coloured solid so obtained was analysed and found (approximately) to be 1:1 metal:ligand complex as expected for linear chain polymer.

Found:

Co(II)–C = 50.45%; H = 3.00%; M = 18.71%

Ni(II)–C = 50.49%; H = 3.05%; M = 17.04%

Calc.

Co(II)–C = 46.90%; H = 3.40%; M = 19.65%

Ni(II)–C = 48.62%; H = 3.50%; M = 18.21%

The infrared spectra of the complexes taken in CsI showed the characteristic bands due to ν_{OH} of coordinated water molecule, $\nu_{C=O}$, δ_{OH} and ν_{M-O} at (cm⁻¹) 3050–3400, 1600–1605, 1310 and 390 and 370 respectively.

The magnetic moment at room temperature (30°C) of Co(II) and Ni(II) polychelates as determined by Gouy's method taking mercury tetrathiocyanato chelate(II) as reference has been found to be 4.8 and 2.2 B.M. respectively. The lower experimental value of the magnetic moment suggests a polymeric nature of the polychelates under study⁴.

The complexes do not melt up to 360°C and are insoluble in most common organic solvents. However, these are sparingly soluble in DMSO. The poor solubility behaviour of the complexes is also suggestive of their polymeric nature. The possible structure of the polychelate has been shown in figure 1.

Measurement of conductivity and dielectric constant

The direct current and alternating current electrical conductivity (d.c. and a.c.) and dielectric constant (ϵ') of

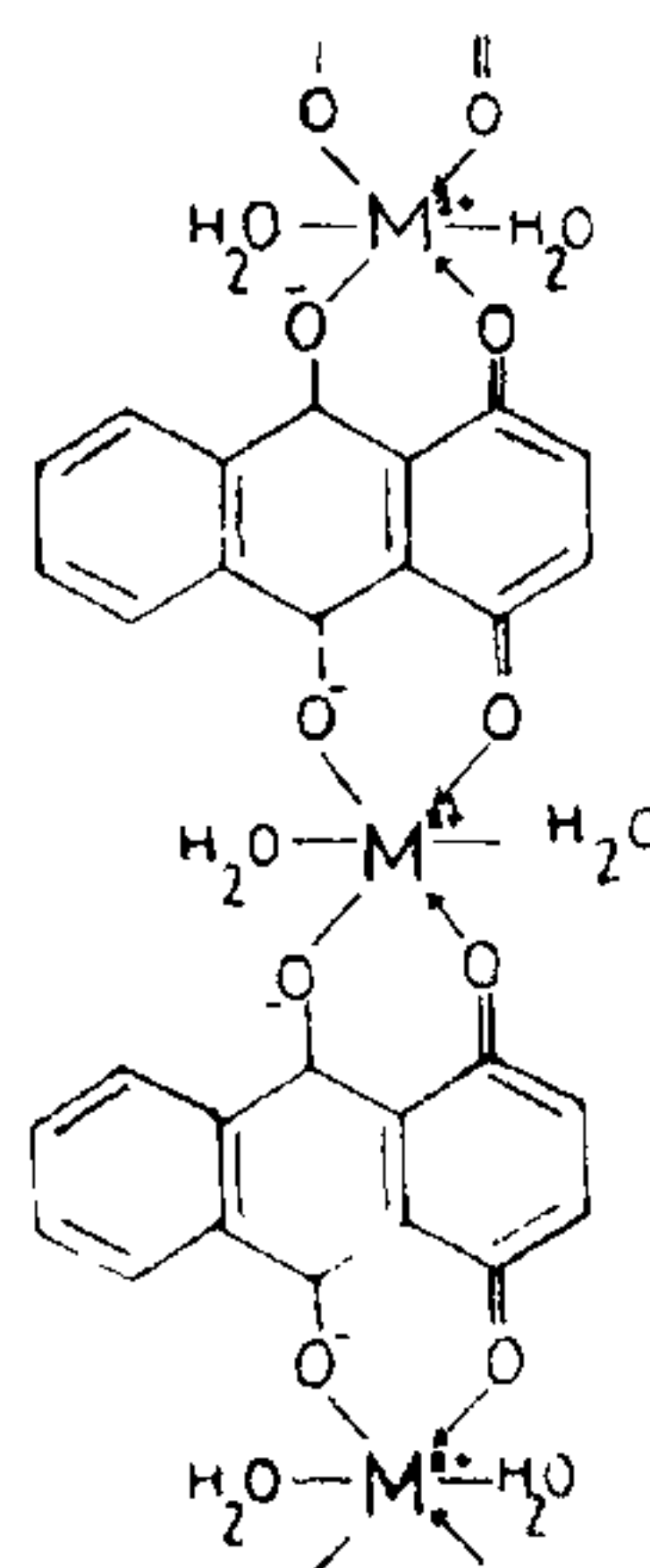


Figure 1.

the pellets prepared from finely-powdered polymer sample at a pressure of $7.03 \times 10^6 \text{ kg/m}^2$, were measured at 30°C at a frequency of 1 MHz.

The d.c. and a.c. conductivity of the parent ligand, 1,4-dihydroxyanthraquinone is $7.23 \times 10^{-13} \Omega^{-1} \text{ cm}^{-1}$ and $8.06 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}$ respectively but this value has been found to increase dramatically in the case of polychelates of Co(II) and Ni(II) to $6.60 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$ and $2.20 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$ ($\sigma_{\text{d.c.}}$) and $1.26 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$ and $5.14 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ ($\sigma_{\text{a.c.}}$) respectively. Further, the dielectric constant of Co(II) and Ni(II) polychelates is 112 and 21 respectively against 2.29 of 1,4-dihydroxyanthraquinone. The a.c. conductivity at 1 MHz is higher than d.c. conductivity in case of 1,4-dihydroxyanthraquinone and its Co(II) and Ni(II) complexes.

This suggests that the mechanism of conduction is "hopping" though a metal is also present in the latter cases. The short range motion of electron under applied a.c. field seems to give rise to a higher a.c. conductivity. This has also been observed in many low mobility amorphous and crystalline materials⁵.

The dielectric constant of Co(II) and Ni(II)-polychelate is higher than that of 1,4-dihydroxyanthraquinone. The increase in dielectric constant in polychelates can be attributed to the increase in the percentage ionic character of the bond as a result of coordination. The relative motion of the ions in applied a.c. field gives rise to a larger ionic polarization which accounts for an increase in the dielectric constant. However, a dielectric constant of 21 and 112 appears to be too high to arise from ionic polarization alone. Since both the metal ions belong to 3d series these might be existing in more than one valency state in the polychelates under study. Hopping of the electrons from one valency state to the other will effectively provide a bipotential model and dipolar polarization. This explains the observed higher dielectric constant of the metal chelates under study.

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ROLE OF AZOTOBACTER IN NITROGEN FIXATION IN THE PRESENCE OF OIL CAKES AND DICALCIUM PHOSPHATE

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THE presence of *Azotobacter* in soils and its participation in symbiotic nitrogen fixation are highly relevant to nitrogen fixation in soils¹. The present report relates to the effect of ground nut oil cake (GOC) and mustard oil cake (MOC) alone and also in combination with a phosphorus fertilizer, dicalcium phosphate (DCP), and KCl on nitrogen fixation and the growth of *Azotobacter* in the medium black soil.

These soils amended with cakes (GOC or MOC) and also with cakes and DCP and cakes, DCP and KCl were regularly exposed to sunlight for 8 hr every day for 180 days. Similar sets were kept in the dark for the same period to study the effect of light on nitrogen fixation and the growth of *Azotobacter*. The soil samples were analyzed at intervals of 90 days for total carbon² and total nitrogen³. The *Azotobacter* population in soil was determined by serial dilution technique⁴ on nitrogen-free medium. The data obtained on *Azotobacter* count were subjected to 'Q test'⁵ to reject any statistically suspect value. Standard deviations were also calculated to indicate the precision.

It was observed that the *Azotobacter* count and nitrogen fixation increased in the presence of oil cakes. The increase was enhanced further when DCP and DCP and KCl were also present along with GOC or MOC. The results are presented in figure 1 which show significant enhancement in the amount of nitrogen fixed in 180 days with an increase in the *Azotobacter* population. The *Azotobacter* count was somewhat larger in the dark than in light, but nitrogen fixation was always more in light than in dark. These results find support from a recent study on the role of *Azotobacter* in nitrogen fixation⁶.