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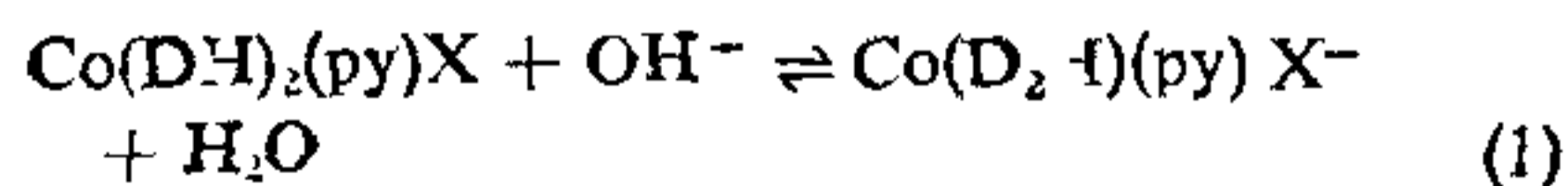
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DEPROTONATION CONSTANTS OF SOME TRANS-ACIDOPYRIDINEBIS(DIMETHYL- GLYOXIMATO)COBALT(III) COMPLEXES

It has been observed that the addition of alkali to solutions of *trans*-bis(dimethylglyoximate)cobalt(III) complexes results in a rapid and reversible change in the visible and near uv-region, attributable to the reversible loss of a bridging proton by the dimethylglyoxime ligands¹⁻⁴. The effect of various groups on the ease of dissociation of this proton can be measured in terms of the proton dissociation constant, thus providing a direct measure of the electronic transmission in these complexes. In this note, we report the results of our studies on the deprotonation equilibrium constants of the following complexes; *trans*-Co(DH)₂(py)I, *trans*-Co(DH)₂(py)NCS, and *trans*-Co(DH)₂(py)NO₂. Also, we reinvestigated the complexes, *trans*-Co(DH)₂(py)Br, *trans*-Co(DH)₂(py)Cl and *trans*-Co(DH)₂(py)N₃ (where DH⁻ = dimethylglyoximate anion) under the present experimental conditions.

All the complexes were prepared as reported in the literature^{5,6}.

The equilibrium may be represented as



where the deprotonation constant K is given by

$$K = \frac{[\text{Co(D}_2\text{H)}(\text{py})\text{X}^-]}{[\text{Co(DH)}_2(\text{py})\text{X}]_{\text{eq}} [\text{OH}^-]_{\text{eq}}} \quad (2)$$

Values of K were determined spectrophotometrically at 370 nm for Co(DH)₂(py)I and at 400 nm for all

the other complexes in aqueous dimethylsulphoxide (10% v/v) and at an ionic strength 1.0 M (NaNO₃). The values are shown in Table I. These constants are a useful measure of the acidity of the hydrogen bonded proton and the trend in their values may be explained on the basis of the electronic transmission in these systems. The following is the order of increasing K values I⁻ ~ Br⁻ < Cl⁻ ~ N₃⁻ < NCS⁻ < NO₂⁻

TABLE I

Deprotonation constants of some *trans*-acidopyridinebis(dimethylglyoximate)cobalt(III) complexes

Temp. = 27.0° C, Solvent = aq. DMSO (10% v/v);
I = 1.0 M (NaNO₃)

Complex	K (M ⁻¹)
Co(DH) ₂ (py)I	1023 ± 40
Co(DH) ₂ (py)Br	1098 ± 85
Co(DH) ₂ (py)Cl	1664 ± 590
Co(DH) ₂ (py)N ₃	1970 ± 319
Co(DH) ₂ (py)NCS	3198 ± 876
Co(DH) ₂ (py)NO ₂	6033 ± 1678

The greater acid-strengthening effect of the unsaturated ligands N₃⁻, NCS⁻ and NO₂⁻ can be explained on the basis of their electron withdrawal nature via the π-system of electrons from the ligand bound to the metal. Metal-ligand π-charge transfer from the filled d_{xy} or d_{yz} metal orbitals to the lowest unoccupied π* orbital on these ligands would reduce the electron density on the metal. This would enhance the Co-N bond strength because of a higher demand of the metal for the lone pair of the equatorial nitrogen resulting in turn in a stronger N-O bond and a weaker O-H bond, leading to greater acidity.

The coordinated halide ions increase the electron-density on the cobalt by inductive effects through the sigma bond systems, thereby decreasing the demand of the metal for the lone pair of the equatorial nitrogen of DH resulting in a weaker N-O bond, and stronger O-H bond, decreasing the acidity. From the results, it is seen that the deprotonation constants are not very sensitive to variation of halogens.

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HETEROTIC EFFECT OF CHEMICAL MUTAGENS IN *SOLANUM MELONGENA* L.

ALTHOUGH the importance of mutation breeding is well known, the use of chemical mutagens is of recent origin and they have been used extensively only during the last decade after the introduction of EMS (Ethyl methane sulphonate) by Heslot¹, Swaminathan^{3,4} and Majid². *Solanum melongena* (Brinjal) is a popular crop grown widely in many parts of the world. During the investigation on hybridization and mutation breeding with this crop, some noteworthy results have been obtained and described here briefly.

The cultivated varieties used in the present investigation were grown in the field for 2-3 generations before giving the treatment of different chemical mutagens, in order to get genetically pure seeds for the experiment.

Seeds of Pusa Purple Long (PPL), Green Long (GL), Round Black (RB), Giant of Banaras (GB) and Nurki Baigan (NB) were treated with EMS, DES (diethyl sulphate), caffeine, *m*-nitrophenol and a few other chemical mutagens. Seeds were soaked in solution of different concentrations (0.4%, 0.6% and 0.8%) of the mutagens for varying periods (18 and 24 hours) in petri dishes. In the case of EMS, solutions were prepared without buffer. Seeds of the control were soaked in distilled water. Seeds were sown in pots and 35 days old seedlings were transplanted to experimental plots at a distance of 90 cm between the plant and without any manure. *m*-Nitrophenol 0.4, 0.6 and 0.8% is lethal to all the varieties studied.

DES treatment resulted in an increase in the number of fruits per plant and in size and weight of the fruit

in several varieties. In Pusa Purple Long, the number of fruits per plant increased from 13 to 24 in M_1 generation and to 30-39 in M_2 generation. In Long Black, the increase was from 3 to 16 in M_1 as well as in M_2 generations (Fig. 1). Similar results were obtained in Round Black in M_1 and M_2 generations. Increase in the size of fruit was observed, in Pusa Purple Long in M_1 , in Long Black in M_1 (Fig. 2) and



FIG. 1. Long Black. A plant, showing increase in the number and size of the fruit of M_2 generation with 0.6% DES treatment.



FIG. 2. Fruits of *S. melongena* var. Long Black. Left pair, control; right pair, M_1 fruits from treatment with DES 0.6% showing enhanced vigour.