TABLE 1

Elemental analysis of metal complexes of DHAED

Complex	Metal %	Carbon %	Hydrogen %
$Cu(C_{18}H_{18}N_2O_4) \cdot 2H_2O$	14·79 (14·91)	50·84 (50·76)	5·73 (5·45)
$Ni(C_{18}H_{18}N_2O_4) \cdot 2H_2O$	13·68 (13·94)	51·54 (51·35)	5·56 (5·51)

Values in parenthesis are the calculated ones.

285 nm in Cu(II) complex and at 305 nm and 265 nm in Ni(II) complex may be charge-transfer bands.

The weak infrared absorption bands at 2896 cm^{-1} and at 2840 cm^{-1} in the reagent are assumed to be due to intermolecularly and intramolecularly hydrogen bonded OH groups respectively. The Cu(II) and Ni(II) complexes have somewhat broad bands at 3452 cm^{-1} and at 3320 cm^{-1} respectively and these are attributed to the ν OH frequencies of water molecules. The bands in the region 3160–3020 cm^{-1} in Cu(II) complex and at 2950 cm^{-1} in Ni(II) complex may be due to intermolecular hydrogen bonding persisting in the complexes. The C=N stretching frequency which appears as a shoulder at 1625 cm^{-1} in the reagent is shifted to 1595 cm^{-1} in both the complexes indicating coordination through nitrogens of the azomethine groups. The ν C–O band that appears at 1160 cm^{-1} in the reagent is shifted to higher frequencies as 1185 cm^{-1} and 1175 cm^{-1} in Cu(II) and Ni(II) complexes. This gives evidence that the coordination is also through oxygens of O-hydroxy groups. In the reagent and the complexes two more bands at 1230 cm^{-1} and around 995 cm^{-1} due to C–N and C–C stretchings have also been observed[1]. The bands at 500 cm^{-1} and at 470 cm^{-1} in the complexes represent M–N and M–O vibrations respectively[2].

The thermograms of Cu(II) and Ni(II) complexes show initial weight loss curves in the temperature range 200°–260° C and 200°–240° C respectively. These curves, in each case, correspond to the weight loss of two water molecules. The loss of water molecules at these high temperatures indicates that they are coordinated. Since the Ni(II) complex has been found to be diamagnetic, it may be described as a tetragonal diamagnetic one[3,4] with the water molecules in the axial position. The sharp decomposition associated with the loss of ligand starts at 310° C in both the complexes. The final products of decomposition of the complexes above 500° C correspond, in each case, to metallic oxide.

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1. Hazzard, B. J., *Organicum*, 1st Edition, Pergamon Press, 1973, p. 102.
2. Patel, M. N. and Patel, R. P., *J. Indian Chem. Soc.*, 1975, 52, 1046.
3. Nyholm, R. S., *J. Chem. Soc.*, 1950, p. 2061.
4. Burstall, F. H. and Nyholm, R. S., *Ibid.*, 1952, p. 3570.

COMPARATIVE STUDY OF RELATIVE ORDER OF LIGAND FIELD STRENGTH IN ISOMERIC SUBSTITUTED COBALTIC COMPLEXES

MAGNETIC susceptibility and temperature independent paramagnetism (T.I.P.) "χ_p" of the cobaltic complexes of the type [Co en$_2$ (R) Cl] Cl$_2$ where 'R' is an amine have been reported[1], "χ_p" values have been theoretically calculated using Griffith and Orgels[2,3] formula. Assuming "χ_p" as a measure of ligand field strength[2], a comparative study[4] has been made. In the present investigation a similar study is undertaken for cobaltic complexes with different substituted amines.

Results and Discussion

Griffith and Orgels[2] theory suggests that "χ_p" term should decrease as the ligand field strength increases. Hence aniline should have the highest ligand field strength and the substitution at different positions of aniline should result in a decrease in the ligand field strength. It would be interesting to compare "χ_p" values of isomeric substituted amines.

The order of "χ_p" values for toluidines is ortho > meta > para and for chloroanilines also it is ortho > meta. The order for the calculated "χ_p" with respect to toluidines and chloroanilines also follows the same trend as can be seen from the last column of Table I. Hence the agreement is good for toluidines and chloroanilines.

This order is different in anisidines where meta > para > ortho and in phenetidines when meta > ortho > para. Since the substituents used in this investigation are all ortho-para oriented, it could be expected that for ortho-para isomeric compounds the electronegativity of nitrogen should be greater than that in

TABLE I

" χ_p " values of isomeric substituted cobaltic complexes

Formula of the complex (complexing ligand)	" χ_p " (obs.)	" χ_p " (calc.)
1. [Coen$_2$(C$_6$H$_5$NH$_2$)Cl]Cl$_2$ (aniline)*	61·50	208·30
2. [Coen$_2$(C$_6$H$_4$NH$_2$Cl)Cl]Cl$_2$ (o-chloroaniline)	208·39	210·40
3. [Coen$_2$(C$_6$H$_4$NH$_2$Cl)Cl]Cl$_2$ (m-chloroaniline)	171·12	208·30
4. [Coen$_2$(C$_6$H$_4$NH$_2$CH$_3$)Cl]Cl$_2$ (o-toluidine)*	187·50	220·10
5. [Coen$_2$(C$_6$H$_4$NH$_2$CH$_3$)Cl]Cl$_2$·H$_2$O (m-toludine)	166·14	212·40
6. [Coen$_2$(C$_8$H$_4$NH$_2$CH$_3$)Cl]Cl$_2$ (p-toluidine)*	85·10	208·30
7. [Coen$_2$(C$_6$H$_4$NH$_2$OCH$_3$)Cl]Cl$_2$ (o-anisidine)*	142·30	212·40
8. [Coen$_2$(C$_6$H$_4$NH$_2$OCH$_3$)Cl]Cl$_2$·H$_2$O (m-anisidine)	208·53	212·40
9. [Coen$_2$(C$_6$H$_4$NH$_2$OCH$_3$)Cl]Cl$_2$ (p-anisidine)	186·40	208·30
10. [Coen$_2$(C$_6$H$_4$NH$_2$OC$_2$H$_5$)Cl]Cl$_2$ (o-phenetidine)	153·70	208·30
11. [Coen$_2$(C$_6$H$_4$NH$_2$OC$_2$H$_5$)Cl]Cl$_2$ (m-phenetidine)	211·48	212·40
12. [Coen$_2$(C$_6$H$_4$NH$_2$OC$_2$H$_5$)Cl]Cl$_2$ (p-phenetidine)*	117·70	214·20

* Values taken from Patankar and Datar[5].

meta compounds. This reasoning appears to be justified for anisidines and partially justified for phenetidines. From Langevin's theory[6] of diamagnetism, the susceptibility of meta compounds is expected to be higher than the other two isomers. In our investigation, " χ_p " values should be lowest for meta compounds and hence the ligand field strength highest for these compounds. The Langevin theory supports our findings for anisidines and phenetidines.

The slight change in the order for phenetidines may be attributed to the size of the substituents. The large substituents may, by steric effects, be restricting the delocalization of the electrons, thus reducing the value of $\sum\limits_{n} r^{-2}$ and hence lowering the susceptibility value. Hence, besides electronegativity, the electron density at various positions in benzene ring is also affected by steric effect and other factors. Datar *et al.*[7,8] have reported similar findings.

The order of the calculated " χ_p " values does not follow the same trend with respect to anisidines and phenetidines, probably due to the insensitivity of the method of calculation of " χ_p ". Thus the absorption bands for complexes of aniline, m-chloroaniline, p-toluidine, p-anisidine and ortho-phenetidine are all at 510 mμ and the " χ_p " for all these is 208·30.

Hence an exact correlation in the orders of " χ_p " is not possible. A somewhat partial agreement however can be expressed as follows:

(1) o-chloroaniline > m-chloroaniline > aniline.

(2) o-toluidine > m-toluidine > p-toluidine > aniline.

(3) m-anisidine > p-anisidine > o-anisidine > aniline.

(4) m-phenetidine > o-phenetidine > p-phenetidine > aniline.

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1. Dodwad, S. S. and Datar, M. G., *Curr. Sci.*, 1977, 46, 7.

2. Griffith, J. S. and Orgel, L. E., *Trans. Farad. Soc.*, 1957, 53, 601.

3. Dodwad, S. S. and Datar, M. G., *Curr. Sci.*, 1977, 46, 505.

4. — and —, *Ibid.*, 1977, 46, 757.

5. Datar, M. G. and Patankar, V. P. *J. Univ. Bombay*, 45 (72), 43.

6. Langevin, P., *J. Phys. Paris*, 1905, 4, 678.

7. Datar, M. G. and Bendigeri, A. B., *Curr. Sci.*, 1962, 31, 15.

8. — and Kenkre, D. S., *Ibid.*, 1963, 32, 161.