

THE RESIDUAL PARAMAGNETISM IN COBALTIC COMPLEXES

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ABSTRACT

Temperature independent paramagnetism (χ_p) values of cobaltic complexes of the type $[\text{Co}(\text{R})_2\text{Cl}]\text{Cl}_2$, where 'R' is an amine have been calculated on the basis of Griffith and Orgel's theory. The calculated (χ_p) values were compared with those experimentally obtained from magnetic susceptibility measurements. The orbital reduction factor " κ " values in all the cases were obtained to examine bonding effects. A decreasing order of the calculated (χ_p) values in terms of the amine 'R' is established.

INTRODUCTION

DEVELOPMENT in the ligand field theory lead interest in the magnetic studies of cobaltic complexes. On the basis of ligand field theory Griffith and Orgel¹ calculated the amount of the second order paramagnetism (χ_p) for the octahedral complexes of trivalent cobalt. They showed that in the cobaltic complexes, since the ground state of the system is $t_2^6 \ ^1A_{1g}$, only the high frequency term representing the temperature independent paramagnetism (Van Vleck paramagnetism) contributes to the paramagnetic susceptibility. In the present investigation the authors have made use of Griffith and Orgel's theory and calculated the χ_p values of the cobaltic complexes.

EXPERIMENTAL

Magnetic susceptibilities and the (χ_p) values of the cobaltic complexes of the type $[\text{Co}(\text{R})_2\text{Cl}]\text{Cl}_2$ where 'R' is an amine have been reported by the authors². Absorption spectra of all these complexes in the visible region were recorded on the automatic Beckman DB-Spectrophotometer. It was possible to record directly a curve representing percentage transmittance against wavelength. The maximum absorption (λ_{max}) in these complexes was found to be in the region of wavelength 490 m μ and 540 m μ . By using the information obtained from these measurements (χ_p) values were calculated theoretically. Following Griffith and Orgel's relation was used for this purpose³.

$$\chi_p = \frac{2N\beta^2 \langle [t_2^5 e \ ^1T_{1g}^z | L_z | t_2^6 \ ^1A_{1g}]^2 \rangle}{K}, \text{ i.e.,}$$

$$\chi_p = \frac{4.085}{K} \quad \dots (1)$$

where T_1^z is the 'Z' component of T_1 , ' β ' is the Bohr magneton and K is expressed in cm⁻¹. K was obtained experimentally as $K = 1/\lambda_{\text{max}}$, values thus obtained alongwith experimentally observed values are reported in Table I.

DISCUSSION OF THE RESULTS

Cobaltic complexes are in general of low spin type, with $t_2^6 e^0$ configuration. All the cobaltic

complexes studied in the present investigation are diamagnetic². They are therefore of low spin type with ($t_2^6 \ ^1A_{1g}$) as ground state and ($t_2^5 e \ ^1T_{1g}$) as excited state. It is observed from the results in Table I that the agreement in calculated and observed values of χ_p is excellent for the complexes formed with ortho-chloroaniline, meta-anisidine, meta-phenetidine and benzedine. For the other complexes the calculated values of χ_p are much higher than the observed ones. According to Griffith and Orgel the estimated probable errors in their theoretical calculations is about 20%. In the data for para-anisidine-complex and *m*-chloroaniline complexes, the disagreement is much greater. The lack of good agreement between the observed and calculated χ_p values may partly be due to the uncertainties involved in use of the susceptibility data of the chloride ion reported by different workers is divergent. Further, the diamagnetic susceptibilities of the amines when complexed with Co (III) may not be the same as that of free amines. In aromatic amines the values of the diamagnetic anisotropy in the free amine and complexed amine are likely to be different. This may be the case with complexes with ortho-phenetidine, pyridine, and *m*-toluidine.

Orbital Reduction Factor:

It is significant to note that the observed values are always less than the theoretical estimates. The results probably reflect bonding effects which were not taken into consideration in Griffith and Orgel's theory. Their theory assumes that the ' t_2 ' orbitals approximate very closely to the ' d ' orbitals. This would however, not be the case in the presence of bonding which has been neglected in the theory. By introducing a factor ' κ ' on the r.h.s. of the expression (1) it is possible to make an allowance for the departure from pure ' d ' orbitals. This was done by Griffith¹. He suggested a modified expression for the χ_p term.

$$\chi_p = 2N\beta^2 \cdot \frac{24 \cdot \kappa^2}{K} \quad \dots (2)$$

where ' κ ' is the orbital reduction factor. For pure ' d ' orbitals ' κ ' is equal to 1 and low spin complexes ' κ ' will be close to unity. Thus, (1- κ)

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TABLE I
 Observed and calculated (χ_p) values of cobaltic complexes

Sl. No.	Formula of the complex (complexing ligand)	χ_p (obs.) in c.g.s. units	λ_{\max} in $m\mu$ from graphs	Energy of transition in cm^{-1} $K=1/\lambda_{\max}$	χ_p (calc.) $\chi_p=4.085/K$ in c.g.s. units	Orbital reduction factor "k"	Extinction coefficient "E"
1.	[Coen ₂ (C ₂ H ₄ N ₄) Cl] Cl ₂ (dicyandiamide)	131.73	495	20190	202.2	0.8071	197.8
2.	[Coen ₂ (C ₅ H ₅ N) Cl] Cl ₂ H ₂ O (pyridine)	153.24	510	19610	208.3	0.8576	223.9
3.	[Coen ₂ (C ₆ H ₄ · NH ₂ · OC ₂ H ₅) Cl] Cl ₂ (ortho-phenetidine)	153.70	510	19610	208.3	0.8590	406.5
4.	[Coen ₂ (C ₆ H ₄ · NH ₂ · CH ₃) Cl] Cl ₂ · H ₂ O (meta-toluidine)	166.14	520	19230	212.4	0.8844	98.0
5.	[Coen ₂ (C ₆ H ₄ · NH ₂ · Cl) Cl] Cl ₂ (meta-chloroaniline)	171.12	510	19610	208.3	0.9063	189.4
6.	[Coen ₂ (C ₆ H ₄ NH ₂ · OCH ₃) Cl] Cl ₂ · H ₂ O (para-anisidine)	186.40	510	19610	208.3	0.9459	249.4
7.	[Coen ₂ (C ₆ H ₄ · NH ₂ · Cl) Cl] Cl ₂ (ortho-chloro-aniline)	208.39	515	19420	210.4	0.9953	227.8
8.	[Coen ₂ (C ₆ H ₄ · NH ₂ · OCH ₃) Cl] Cl ₂ (meta-anisidine)	208.53	520	19230	212.4	0.9909	116.6
9.	[Coen ₂ (C ₆ H ₄ · NH ₂ · OC ₂ H ₅) Cl] Cl ₂ (meta-phenetidine)	211.48	520	19230	212.4	0.9979	219.3
10.	[Coen ₂ (C ₆ H ₅ · NH ₂ · C ₆ H ₅ NH ₂) Cl] Cl ₂ (benzedine)	214.91	540	18520	220.1	0.9880	133.8

* [Coen₂ (C₆H₄NH₂ · CH₃) Cl] Cl₂ · H₂O → $\kappa = 0.92$ (ortho-toluidine)

[Coen₂ (C₆H₄NH₂ · OCH₃) Cl] Cl₂ · H₂O → $\kappa = 0.82$ (ortho-anisidine)

[Coen₂ (C₆H₄NH₂ · CH₃) Cl] Cl₂ → $\kappa = 0.65$ (para-toluidine)

[Coen₂ (C₆H₄ · NH₂ · OC₂H₅) Cl] Cl₂ → $\kappa = 0.74$ (para-phenetidine)

[Coen₂ (C₆H₅NH₂) Cl] Cl₂ → $k = 0.51$. (Aniline).

is a measure of the deviation of actual orbitals from being pure 'd' orbitals. From the study of a large number of cobaltic complexes, Kanekar and Nipankar⁴, Assumssen and Ballhausen⁵ and Datar and Patankar⁶ calculated the values of orbital reduction factor 'κ' using the formula ' $\kappa = \sqrt{\chi_p(\text{obs.})/\chi_p(\text{calc.})}$ '. The authors in the present investigation calculated 'κ' values in the same manner which are reported in Table I.

The values of 'κ' reported fall within the range of 0.8 to 1.0. Findings of the other authors^{4,5,6} indicated that the values of 'κ' vary between 0.7 and 1.0 for ligands containing nitrogen and oxygen donors. The observations made by the authors in the present investigation are similar to the results of all these workers.

A careful scrutiny of 'κ' values shows that for the complexes with *o*-chloroaniline, *m*-anisidine, *m*-phenetidine and benzedine, the orbital reduction factor is unity whereas for the other complexes the magnitude varies between 0.8 and 1.0. It is therefore, apparent that the bonds formed between the metal atom and the ligands pyridine, *o*-phene-

tidine, *m*-toluidine, *m*-chloroaniline, *p*-anisidine and dicyandiamide are relatively stronger than those formed with the former ligands. Among the ligands forming a stronger bond, the one formed with dicyandiamide is the strongest and it is noteworthy that this is the only aliphatic amine used as the complexing ligand, the others being aromatic with the exception of pyridine. A comparison of 'κ' values for phenetidines and chloroanilines shows that the bonding effect in the case of meta-chloroaniline is much greater than that in ortho-chloroaniline whereas this order is exactly reverse in the case of ortho- and meta-phenetidines. The smaller bonding effect in the case of *o*-chloroaniline may be attributed to the steric factor. However, it is not clear why OC₂H₅ in *o*-phenetidine should not affect the 'κ' value in the same manner, since Cl and OC₂H₅ are known to be similar in their behaviour as regards their electro-negativity and size of the substituent. It is known that though Cl group is electron releasing, many times it acts as electron attracting group like NO₂ group. It is possible that in *o*-chloroaniline it withdraws electronic charge

from the nitrogen atom of NH_2 group thus decreasing its power for bond formation. This may account for the weak bonding of this ligand as compared with that of *o*-phenetidine.

Comparative study of 'κ' values for isomeric complexes :

An attempt has been made to examine the orbital reduction factors for the isomeric substituted ligands in these complexes with a view to study the effect of substituents on the bonding. The authors² have measured the magnetic susceptibility values of a few complexes with substituents like CH_3 , OCH_3 , OC_2H_5 and Cl groups. For a complete comparison it is necessary to have the data on all position isomers. Datar and Patankar⁶ have calculated the values of orbital reduction factor from the knowledge of the magnetic susceptibility of the cobaltic complexes of aliphatic and aromatic amines in this laboratory. His values have been taken for this comparison. The values taken from Datar and Patankar are reported at foot-note of Table I.

A glance at the values of 'κ' suggests that introduction of a substituent in aniline in various positions in benzene nucleus causes a decrease in the value of orbital reduction factor indicating that these substituents weaken the bond between metal and the ligand to a considerable extent. Among the isomeric compounds it is observed that in anisidines the lowering in 'κ' values is indicated by the order meta > para > ortho.

This order is slightly different for phenetidines, it being meta > ortho > para. In toluidines and chloro substituted anilines this order is found to be ortho > meta > para. It is therefore, concluded that in the former series, the strength of the bond is highest for meta compounds, the decrease in the trend of order being ortho > para > meta and para > ortho > meta respectively for anisidines and phenetidines. In the latter the same can be represented as para > meta > ortho. Since the substituents used in the present investigation are all ortho-para orienting, it is expected that for ortho-para isomeric compounds the electro-negativity of nitrogen in these compounds, should be greater than that in meta compounds. Accordingly, corresponding to higher electronegativity of nitrogen, one should expect a stronger bond between the metal and the ligand, and the order of the strength of the bond should be ortho > para > meta. This reasoning appears to be justified from 'κ' values for anisidines, and is in partial agreement for phenetidines. In both these series the ortho and para compounds form

the stronger bonds between the metal and nitrogen as compared to meta compounds. The slight difference in the order of 'κ' values between ortho and para compounds for anisidines and phenetidines may be attributed to the steric factor in the ease of *o*-phenetidine, the OC_2H_5 group being larger than OCH_3 group. The results of chloro and methyl substituted anilines are however, contrary to these expectations. It appears that in these compounds some other factor is more effective in non-release of electronic charge towards the nitrogen atom thus accounting for the weaker bonds in ortho substituted compounds.

Calculation of extinction coefficient

The extinction coefficient was calculated by using the expression based on Lambert Beer's law—

$$\log I/I_0 = ECL \text{ where } \log I/I_0 = \text{optical density at } \lambda_{\max}$$

C = Concentration of the solution

L = Length of the path which is 1 cm and

E = Extinction coefficient

Directly from the graph we get the percentage transmittance corresponding to λ_{\max} . The percentage transmittance was converted into optical density by the formula $\text{O.D.} = 2 - \log T$, where T = percentage transmittance at λ_{\max} .

It has been stated earlier that the octahedral cobaltic complexes show an absorption band in the visible region which can be assigned to the transition ${}^1A_{1g} \rightarrow {}^1T_{1g}$. The band observed in the region of 490 to 540 mμ in these complexes has been ascribed to *d-d* transition ${}^1A_{1g} - {}^1T_{1g}$. This is also observed from the experimentally observed values of extinction coefficients reported in Table I which are of the order of 100 as expected for *d-d* transitions.

The data indicate that the χ_p (calculated values decrease in the following order of 'R'. Benzidine > meta-phenetidine ~ meta-anisidine ~ meta-toluidine > ortho-chloro-aniline > para-anisidine ~ meta-chloroaniline > ortho-phenetidine > pyridine > dicyanidiamide.

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