

# MAGNETIC SUSCEPTIBILITY OF COBALTIC COMPLEXES

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## ABSTRACT

Cobaltic complexes of the type  $[\text{Coen}_2(\text{R})\text{Cl}]\text{Cl}_2$  where 'R' is an aliphatic or aromatic amine were prepared in a chemically pure state and their magnetic susceptibilities were measured by Guoy method. All complexes were found to be diamagnetic. The susceptibility values were compared with their experimentally computed values assuming strict additivity. The deviations from additivity have been explained on the basis of Van-Vleck's equation.

## EXPERIMENTAL

**C**OBALTIC complexes of the type  $[\text{Coen}_2(\text{R})\text{Cl}]\text{Cl}_2$  where 'R' is an aliphatic or aromatic amine were prepared in a pure state by following the method suggested by John C. Bailar Jr. and L. B. Clapp<sup>1</sup>. The starting material namely trans-dichloro-diethylenediamine-cobaltic chloride was also prepared in the laboratory as described by Furness<sup>2</sup>. Cobalt chloride was of B.D.H. 'Analar' grade. The organic bases were of A.R. quality and they were further purified by conventional methods. Their purity was checked by their physical constants.

The purity of the complexes was ascertained by analysing them for nitrogen and chloride contents. Magnetic susceptibilities of these complexes and their components were measured on a modified form of Guoy<sup>3</sup> balance described by Prasad and co-workers<sup>4</sup>. All the complexes were found to be diamagnetic. The results of these measurements are given in Table I in which  $\chi$  and  $\chi_m$  denote respectively the specific and molar susceptibilities expressed in  $-1 \times 10^{-6}$  c.g.s. units.

Assuming strict additivity the molar magnetic susceptibilities of these complexes were computed

TABLE I

Sr. No.	Complexing ligand	Formula of the complex	Colour of the complex (Time of reaction)	Elemental Analysis		Molecular weight of the complex	$\chi$	$\chi_m$	$\Sigma\chi_d$ (Computed)	$\chi_p = \Sigma\chi_d - \chi_m$
				Nitrogen Calc. (Found)	Chloride Calc. (Found)					
1.	Dicyan-diamide	$[\text{Coen}_2(\text{C}_2\text{H}_4\text{N}_4)\text{Cl}]\text{Cl}_2$	Bright-red (2 hr)	—	28.81 (29.05)	369.72	0.234	86.32	218.05	131.73
2.	Pyridine	$[\text{Coen}_2(\text{C}_5\text{H}_5\text{N})\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$	Bright crimson red (0.5 hr)	—	27.84 (27.31)	382.74	0.184	70.50	223.74	153.24
3.	Ortho-phenetidine	$[\text{Coen}_2(\text{C}_6\text{H}_4\text{NH}_2\text{OC}_2\text{H}_5)\text{Cl}]\text{Cl}_2$	Pale-red (24 hr)	16.57 (15.90)	25.21 (24.80)	422.40	0.269	113.4	267.10	153.70
4.	Meta-toluidine	$[\text{Coen}_2(\text{C}_6\text{H}_3\text{NH}_2\text{CH}_3)\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$	Pale-crimson (0.5 hr)	17.05 (16.70)	27.14 (27.50)	392.40	0.212	82.99	249.13	166.14
5.	Meta-chloro-aniline	$[\text{Coen}_2(\text{C}_6\text{H}_4\text{NH}_2\text{Cl})\text{Cl}]\text{Cl}_2$	Crimson red (24 hr)	16.80 (15.90)	34.37 (34.43)	413.21	0.196	81.00	252.12	171.12
6.	Paraanisidine	$[\text{Coen}_2(\text{C}_6\text{H}_4\text{NH}_2\text{OCH}_3)\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$	Dirty pink (0.5 hr)	16.41 (15.90)	24.94 (24.30)	426.40	0.161	68.77	255.17	186.40
7.	Ortho-chloro-aniline	$[\text{Coen}_2(\text{C}_6\text{H}_3\text{NH}_2\text{Cl})\text{Cl}]\text{Cl}_2$	Purple (24 hr)	16.80 (16.50)	34.37 (34.50)	413.21	0.108	44.63	253.02	208.39
8.	Meta-anisidine	$[\text{Coen}_2(\text{C}_6\text{H}_3\text{NH}_2\text{OCH}_3)\text{Cl}]\text{Cl}_2$	Pink red (0.25 hr)	16.41 (15.80)	24.94 (24.85)	426.40	0.108	46.03	254.56	208.53
9.	Meta-Phenetidine	$[\text{Coen}_2(\text{C}_6\text{H}_3\text{NH}_2\text{OC}_2\text{H}_5)\text{Cl}]\text{Cl}_2$	Pink red (24 hr)	16.57 (16.00)	25.21 (25.50)	422.40	0.130	54.94	266.42	211.48
10.	Benzidine	$[\text{Coen}_2(\text{C}_6\text{H}_4\text{NH}_2)_2]\text{Cl}_2$	Dirty violet (0.25 hr)	11.92 (12.00)	22.67 (21.91)	469.87	0.160	75.21	290.12	214.91

\*Molecular weights of the complex were determined ebullioscopically.

( $\Sigma\chi_d$ ) by adding experimentally observed values of the susceptibilities of their components. The deviations in the observed and the computed values are shown in the last column of the same table.

#### DISCUSSION OF THE RESULTS

It is evident from the results that the molar magnetic susceptibilities of the complexes are all diamagnetic. It is, therefore, concluded that all of them are spin paired complexes of trivalent cobalt. Further it is seen that the observed values of molar susceptibilities of these complexes are much lower in magnitude than their computed values. Guoy method gives results up to 1% accuracy. These deviations are therefore outside the limits of experimental error and are, therefore, significant.

According to Van-Vleck<sup>5</sup>, the molar susceptibility of a polyatomic molecule in  $\Sigma$  state may be written as  $\chi_m = \chi_d + \chi_p$ , where  $\chi_d$  represents the diamagnetic term which is a function of all the electronic orbits in the molecule and  $\chi_p$  represents second order paramagnetic term independent of temperature which arises on account of mixing of the ground and excited states of electrons in the molecule. Since the nature of the various ligands complexing with the cobalt ion do not differ much, the contribution of  $\chi_d$  term to the  $\chi_m$  value of

the complex is not likely to be affected considerably. Therefore it may be concluded that there is a substantial contribution of the temperature independent paramagnetism due to cobalt atom in all these complexes. The difference [ $(\Sigma\chi_d - \chi_m) = \chi_p$ ] thus gives the residual paramagnetism. The  $\chi_p$  values thus calculated are given in the last column of Table I. Since all the complexes studied in this investigation are of the type  $[\text{Coen}_2(\text{R})\text{Cl}]\text{Cl}_2$ , where 'R' is an aliphatic or aromatic amine, comparison of these  $\chi_p$  values would be possible. Examination of these results show that these values vary with the nature of the ligand 'R'. The data indicate that  $\chi_p$  values decrease in the following order of 'R':

Benzidine > *m*-phenetidine > *m*-anisidine > *o*-chloroaniline > *p*-anisidine > *m*-chloroaniline > *m*-toluidine > *o*-phenetidine > pyridine > di-cyandiamide.

1. John, C. Bailer Jr. and Clapp, L. B., *J. Am. Chem. Soc.*, 67, p. 171.
2. Furnellus, *Inorganic Synthesis*, Vol. II.
3. Guoy, *Compt. Rend.*, 1889, 109, 936.
4. Prasad and co-workers, *Proc. Ind. Acad. Sci.*, 1944, 20 A, 224.
5. Van-Vleck, *Theory of Electric and Magnetic Susceptibilities*, Oxford University Press, 1932.

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