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Steric Effect in Ni(II) & Co(II) Complexes of Methyl Substituted N-Benzoyl-N-phenylhydroxylamines (N-phenylbenzohydroxamic Acids)

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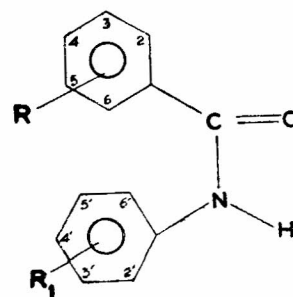
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Positions of the methyl substituents in some methyl substituted N-benzoyl-N-phenylhydroxylamines acids (N-phenylbenzohydroxamic acids) are found to exert a steric influence in the formation of their Ni(II) and Co(II) complexes. When the methyl group is present in 3-, 4-, 3'- or 4'-position, no steric hindrance is observed and the complexes obtained are highly polymeric and octahedral. However, methyl substitution in the 2- or 2'- or in both the positions exert large steric hindrance which results in a significant reduction in the degree of polymerization yielding trimeric octahedral Ni(II) complexes. The complexes have been characterized by cryoscopic, magnetic moment and absorption spectral studies. The tendency of polymerization is greater in the case of Co(II) complexes, but N-*o*-tolyl-2-methylbenzohydroxamic acid (ligand II) yields only a dimeric pentacoordinated Co(II) complex.

HYDROXAMIC acid derivatives ($R'CONR''OH$) are known to be excellent reagents for the spectrophotometric determination of vanadium^{1,2}. Majumdar and Das³ have earlier pointed out that the specificity of N-*o*-tolyl-benzohydroxamic acid (I, $R = H$; $R_1 = 2'-CH_3$) towards vanadium arises out of the steric influence of the *ortho*-substituted methyl group in the N-phenyl ring. Molecular models show that this steric effect is likely to be of importance in the formation of the 1:2 complexes of some bivalent metals which are very much prone to attain hexacoordination through polymerization of the 1:2 species. In order to test the validity of this idea, Ni(II) and Co(II) complexes of some hydroxamic acid derivatives have been isolated and characterized on the basis of analytical, electronic spectral, molecular weight and magnetic moment data.

N-(*o*-Tolyl)-2-methylbenzohydroxamic acid (II, $R = 2'-CH_3$; $R_1 = 2-CH_3$) was prepared according to the method of Pal and coworkers⁴. Other ligands, viz. N-phenyl-2-methylbenzo-(III, $R = 2-CH_3$; R_1



I, $R = H$; $R_1 = 2-CH_3$

II, $R = 2-CH_3$; $R_1 = 2-CH_3$

III, $R = 2-CH_3$; $R_1 = H$

IV, $R = H$; $R_1 = 3-CH_3$

V, $R = 3-CH_3$; $R_1 = H$

VI, $R = H$; $R_1 = 4-CH_3$

VII, $R = 4-CH_3$; $R_1 = H$

$=H$); N-(*m*-tolyl)-benzo-(IV, $R = H$; $R_1 = 3-CH_3$); N-phenyl-3-methylbenzo-(V, $R = 3'-CH_3$; $R_1 = H$); N-(*p*-tolyl)-benzo-(VI, $R = H$; $R_1 = 4'-CH_3$); and N-phenyl-4-methylbenzo-(VII, $R = 4-CH_3$; $R_1 = H$)-hydroxamic acids were prepared by the literature method¹.

Ni(II) complexes—A solution of $NiCl_2 \cdot 6H_2O$ (1 g) in ethanol (20 ml) was added to a hot solution of the ligand (2.21 g), also in ethanol (30 ml). A saturated aqueous solution of sodium acetate (2.25 g) was added to the above mixture. In the cases of ligands IV, V, VI and VII and the unsubstituted N-phenylbenzohydroxamic acid, immediate precipitation of the compounds occurred. The compounds were filtered, washed with ethanol and dried in air. With ligands I, II and III, however, the complexes were obtained by diluting the ethanol solution with water. These were then filtered, washed with hot water, dried in air and recrystallized from benzene-ligroin (60-80°) mixture.

Co(II) complexes—A solution of $CoCl_2 \cdot 6H_2O$ (1 g) in acetone (50 ml) was added to the ligand solution (2.21 g in about 20 ml of acetone). An aqueous solution of sodium hydroxide (1 M) was added dropwise with constant stirring till the deep-blue colour changed to wine-red. The solution was then diluted with water. In the case of ligands I and II, equal volume of and excess of water were added respectively to obtain the complexes. The separated crystals were filtered, washed with water and finally recrystallized from acetone (for ligand I) and benzene-ligroin (60-80°) (for ligand II).

The complex with ligand III changed into an insoluble form on precipitation from acetone solution by the addition of water. However, a complex soluble in benzene could be isolated by diluting the acetone solution with about 20 ml of benzene and then washing the solution 2-3 times with water. This benzene solution was dried with anhydrous sodium sulphate, diluted with ligroin (60-80°) and kept in a deep-freeze overnight. The precipitated complex was then filtered, washed with ligroin and dried in air. But this complex also slowly changed to the insoluble form in the solid state and as such

TABLE 1 — MELTING POINT, ELECTRONIC SPECTRAL, MOLECULAR WEIGHT AND MAGNETIC MOMENT DATA OF Ni(II) AND Co(II) COMPLEXES

Complex*	Decomposition point (°C)	Electronic spectra		Mol. weight	Magnetic moment (BM)
		Solvent	λ_{\max} (nm) (ϵ_{\max})		
Ni(III) ₂	170	Benzene	665 (7.8), 780 (sh), 1020-30 (6.2)	1466 (1532)†	3.13
		Pyridine	620-25 (12.8), 780 (3.2), 1000-10 (13.1)		
Ni(I) ₂	167	Benzene	665 (6.7), 800 (sh), 1020-30 (8.0)	1405 (1532)†	3.17
		Pyridine	625 (12.7), 780 (3.4), 1000-10 (11.7)		
Ni(II) ₂	178	Benzene	670-75 (7.0), 810 (sh), 1010 (8.2)	1695 (1616)†	3.48
		Pyridine	630 (12.8), 780 (3.3), 1000 (11.6)		
Ni(II) ₃ Py ₂	206				3.24
Co(III) ₂	191				4.40
Co(I) ₂	145				4.67
Co(II) ₂	154	Benzene	750 (sh), (8.3)	983 (1078)‡	4.41
		Pyridine	560 (43.3), 1000 (6.0)		

*I, II and III are the ligands as numbered in the text.

†Calculated for trimer.

‡Calculated for dimer.

molecular weight and spectra in benzene could not be taken.

Ni(II) complex of the ligand II yielded a pyridine adduct on dissolving the former in a minimum quantity of the latter and keeping the solution for 2 days after dilution with excess water. Light-blue crystals obtained were filtered, washed with water and dried in a desiccator over CaCl₂. The TG curve of this compound shows a single break at 143° which corresponds to the loss of two pyridine molecules simultaneously.

All the compounds were characterized by elemental analysis.

Magnetic measurements at room temperature were carried out using a Gouy balance calibrated with Hg[Co(NCS)₄]. Cryoscopic measurements were made in sodium-dried benzene. Hilger Uvispeck and Spectromom 201 spectrophotometers were used for the electronic spectral studies.

A Chevenard-Jounier thermobalance ADAMEL type CTTB No. 107 was used to record the change in weight of the substance as a function of temperature. The rate of heating was maintained at 5° per min.

Ni(II) complexes with ligands IV, V, VI and VII (class A complexes) are found to be highly insoluble in all common organic solvents including pyridine; their magnetic moments range from 3.12 to 3.42 B. M. But the Ni(II) complexes (class B complexes) with ligands containing the CH₃ group in 2 (ligand III) or 2' (ligand I) or in both the positions (ligand II) are highly soluble in polar and non-polar organic solvents. Analytical, cryoscopic, magnetic moment and electronic spectral data (Table 1) indicate that the class B complexes are trimeric octahedral compounds^{5,6} structurally resembling the trimeric bis(acetylacetonato) complex of nickel⁷. The band for the transition ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (*P*) is obscured by the strong charge-transfer band observed around 400 nm. The absorption spectra of the trimeric class B complexes in pyridine show two isosbestic points near 720 and 830 nm indicating the coordination of two molecules of pyridine to Ni(II) maintaining, however, their octahedral configuration.

Thus, it may be concluded that the phenylhydroxamic acid derivatives have the tendency to form polymeric Ni(II) complexes and the degree of polymerization depends on the position of methyl substituent. It is very high where the methyl substituent, in both the phenyl rings, is not suitably placed to exert any steric influence (ligands IV, V, VI and VII). Where the substituted methyl group is in a position to exert steric influence (ligands I, II and III), the degree of polymerization is largely reduced giving relatively weaker trimeric complexes which can be broken down by a strong coordinating solvent like pyridine.

The tendency of polymerization is observed to be much greater in the case of Co(II) complexes with the ligands I, II and III. The cryoscopic data (Table 1) of the Co(II) complex with ligand II in benzene suggest a dimeric structure for the complex unlike the corresponding Ni(II) complex. The nature of the visible absorption spectrum of this Co(II) complex in benzene is different from the corresponding Ni(II) complex and the magnetic moment value is slightly lower than that expected for an octahedral configuration⁵. This complex, thus, may be concluded to be five-coordinated. It may be pointed out that some dimeric five-coordinated bis-ligated Schiff base complexes of Co(II) have been reported⁸ to show slightly lower than normal magnetic moment values.

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