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Adducts of Some Methyl substituted N-phenylbenzohydroxamates of Cobalt(II) with Different Nitrogen Bases

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Preparation and characterisation of adducts of N-phenylbenzohydroxamates of Co(II) with different nitrogen bases are reported. Two kinds of adducts, $\text{Co}(\text{R})_2\text{B}_2$ and $\text{Co}(\text{R})_2\text{B}$ (where R is a N-arylbenzohydroxamic acid and B is a base molecule) have been isolated and characterised on the basis of elemental analyses, magnetic moment measurements and cryoscopic determination of molecular weights. The bases capable of causing steric hindrance furnish monomeric mono-adducts only.

IN a previous communication¹, investigations on the bis- and mono-base adducts of some trimeric octahedral methyl-substituted N-phenylbenzohydroxamates of nickel (II) were reported. Both the mono- and the bis-adducts were found to be octahedral, the mono-adducts attaining the octahedral stereochemistry through dimerisation. The difference between the stereochemistry of the parent Ni(II) and Co(II) hydroxamates² has prompted us to ascertain whether the base adducts of the

cobalt hydroxamates also differ from those of their nickel analogues. The results of the investigation are reported here.

Cobalt(II) hydroxamates—The three hydroxamates of cobalt(II), abbreviated as $\text{Co}(\text{R}_1)_2$, $\text{Co}(\text{R}_2)_2$ and $\text{Co}(\text{R}_5)_2$, where R_1H , R_2H and R_5H are N-o-tolylbenzohydroxamic acid, N-o-tolyl-o-toluohydroxamic acid and N-phenyl-o-toluohydroxamic acid, respectively, were employed in the study. These were prepared as reported earlier². Different bases and solvents utilised were the same as reported earlier¹.

A known amount of each of the three parent complexes was dissolved in a specified quantity of the base (pyridine, α -, β - or γ -picoline, piperidine, 2,4-lutidine, quinoline and 2,4,6-collidine) so that the resulting concentration of each solution was between 2.50 and $3.50 \times 10^{-2} M$ with respect to the metal ion. Solution was made, specially in case of $\text{Co}(\text{R}_5)_2$, by warming whenever required. Absorption spectrum of each solution was recorded in the range 450-1300 nm by a Spectromom 204 spectrophotometer.

Isolation of the base adducts—About 2.0 g of cobalt hydroxamate was dissolved in the minimum quantity of the base by warming on a water-bath, if necessary. An excess of ligroin (40°-60°) (preceded by the addition of about 5 ml of dry benzene) was added when either crystals or oily mass separated. In case an oily mass separated, it was kept at room temperature for 1-2 hr. The supernatant ligroin fraction was decanted off and the oily product was kept *in vacuo* for about 2 hr. It was then repeatedly titrated with fresh portions of ligroin till a solid mass was obtained. The solid mass was kept under ligroin for 1 hr, filtered, washed with ligroin and dried *in vacuo* over fused calcium chloride. When crystals were obtained, they were separated from the mother liquor by filtration, washed and dried as above. Physical characteristics and analytical data of the isolated complexes with $\text{Co}(\text{R}_1)_2$ and $\text{Co}(\text{R}_2)_2$ only are given in Table 1. Complexes with $\text{Co}(\text{R}_5)_2$ were unstable and polymerised slowly to insoluble products. Magnetic measurements and molecular weight determination (in dry benzene) were done as detailed earlier².

Two types of absorption spectra are exhibited by cobalt(II) complexes in different bases. In one type of spectra (Fig. 1, curve A), obtained when pyridine, β - or γ -picoline is used as solvent, two absorption maxima appear around 550 and 1000 nm. In the second type of spectra (Fig. 1, curve B) obtained using α -picoline, quinoline, lutidines, aniline or 2,6-dimethylaniline as solvent, the absorption maximum near 1000 nm disappears. But an absorption peak or a hump appears near 800 nm and the absorbance is found to increase slowly in the range 1100-1300 nm without showing any additional absorption maximum. With 2,6-lutidine, however, the λ_{max} appears near 700 nm but the nature of the curves is otherwise unaltered.

The spectrum of the adduct with 2,4,6-collidine (Fig. 1, curve C) resembles those of cobalt hydroxamates dissolved in pyridine, β -picoline or γ -pico-

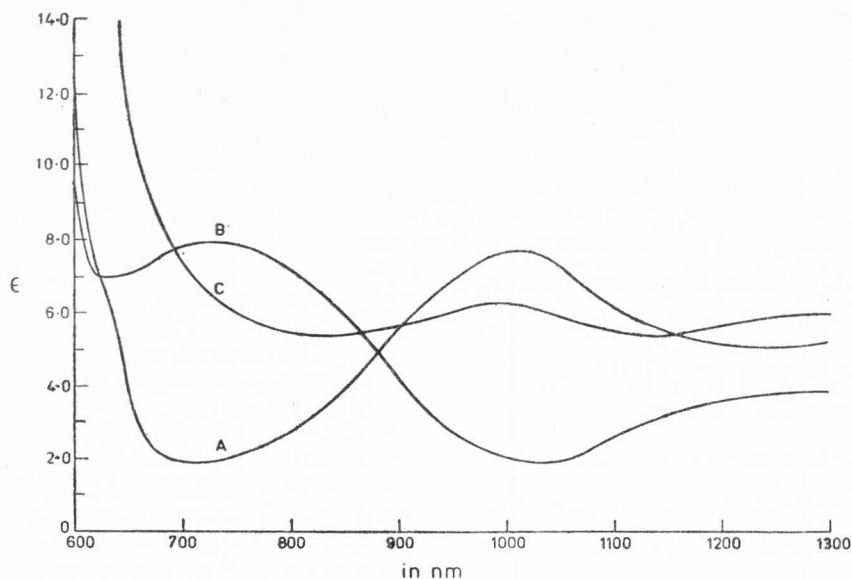


Fig. 1 — Absorption spectra of cobalt hydroxamates in nitrogen donor bases [A, $\text{Co}(\text{R}_1)_2$ in pyridine; B, $\text{Co}(\text{R}_1)_2$ in 2,6-lutidine; C, $\text{Co}(\text{R}_2)_2$ in 2,4,6-collidine].

TABLE 1 — CHARACTERISATION DATA OF BASE ADDUCTS OF COBALT HYDROXAMATES

Complex	Colour	Decomp. point (°C)	Found (Calc.), %		μ_{eff} (B. M.)	Molec. wt found (Calc. for monomer)
			Metal	N		
$\text{Co}(\text{R}_1)_2(\text{Py})_2$	Pink	130	8.60 (8.81)	8.09 (8.37)	4.91	689 (669)
$\text{Co}(\text{R}_1)_2(\beta\text{-Pic})_2$	Pink	108	8.50 (8.46)	7.49 (8.04)	4.88	—
$\text{Co}(\text{R}_1)_2(\text{Pip})_2$	Light brown	163	8.52 (8.65)	7.87 (8.22)	4.71	560 (596)
$\text{Co}(\text{R}_1)_2(\alpha\text{-Pic})$	Pink	114	9.83 (9.76)	6.10 (6.95)	4.76	675 (604)
$\text{Co}(\text{R}_1)_2(2,4\text{-L})$	Yellow	145	9.40 (9.54)	6.87 (6.80)	4.39	—
$\text{Co}(\text{R}_1)_2\text{Q}$	Yellow	82	9.45 (9.21)	6.62 (6.56)	4.67	—
$\text{Co}(\text{R}_1)_2\text{Colli}$	Pink	122	9.53 (9.35)	6.22 (6.67)	4.86	743 (630)
$\text{Co}(\text{R}_2)_2(\text{Py})_2$	Yellow	160	8.35 (8.46)	8.05 (8.03)	4.60	566 (697)
$\text{Co}(\text{R}_2)_2(\beta\text{ Pic})_2$	Pink	164	8.23 (8.13)	7.63 (7.73)	5.10	633 (725)
$\text{Co}(\text{R}_2)_2(\gamma\text{-Pic})_2$	Pink	164	8.32 (8.13)	7.50 (7.73)	4.75	602 (725)
$\text{Co}(\text{R}_2)_2(\text{Pip})_2$	Pink	158	8.25 (8.31)	7.63 (7.90)	4.91	619 (624)
$\text{Co}(\text{R}_2)_2(\alpha\text{-Pic})$	Pink	105	9.13 (9.32)	6.80 (6.64)	4.61	657 (632)
$\text{Co}(\text{R}_2)_2(2,4\text{-L})$	Pink	106	9.08 (9.12)	6.73 (6.50)	4.24	574 (646)
$\text{Co}(\text{R}_2)_2\text{Q}$	Yellow	173	8.90 (8.82)	6.07 (6.29)	4.40	681 (668)
$\text{Co}(\text{R}_2)_2(\text{Colli})$	Pink	168	8.63 (8.96)	6.27 (6.38)	4.69	720 (658)

Py = Pyridine; Pic = Picoline; Pip = Piperidine; 2,4-L = 2,4-Lutidine; Q = Quinoline; Colli = 2,4,6-Collidine.

line but the absorption maxima obtained with 2,4,6-collidine are not so prominent as obtained with other bases mentioned above.

It is apparent from the spectral data that with the bases like pyridine, β - and γ -picoline, the cobalt hydroxamates form octahedral³ adducts as found in the case of nickel hydroxamates earlier¹. But the cobalt hydroxamates unlike their nickel analogues¹ do not form octahedral adducts with the bases like α -picoline, 2,4- and 2,6-lutidines, quinoline, aniline and 2,6-dimethylaniline. The electronic spectra⁴ do not indicate any tendency on the part of cobalt hydroxamates to add up two molecules of these bases to furnish octahedral complexes. On the other hand, attainment of the octahedral stereochemistry by the mono-adducts of the cobalt hydroxamates with the said bases by polymerisation, as observed in the case of nickel(II) complexes, $[\text{Ni}(\text{R})_2\text{B}]_2$, may be ruled out. This is because, if such dimerisation occurs, one would expect an absorption maximum between 1100 and 1150 nm.

The formulae of the isolated products, their elemental analyses, colour, decomposition point, magnetic moment and molecular weight data are shown in Table 1. Mono-adducts result with bases capable of imparting steric hindrance while the other bases furnish bis-adducts. No definite compound could, however, be isolated from 2,6-lutidine. Magnetic moments of the bis-adducts are normal⁵ for any octahedral cobalt(II) complex but the mono-adducts have slightly lower values (Table 1) which are consistent with the penta-coordination⁴ of the central atom. The experimentally determined molecular weights of these adducts reveal the monomeric structure in all the cases except for $\text{Co}(\text{R}_1)_2\text{Colli}$ and $\text{Co}(\text{R}_2)_2\text{Colli}$ where the experimental molecular weights in benzene are much higher than the values calculated for monomers. It seems that these are octahedral unlike other 1 : 1 base adducts of cobalt hydroxamates. In solution, however, it seems that these compounds exhibit an equilibrium between the monomeric five-coordinated species and the dimeric octahedral species. Therefore, the other mono-adducts are definitely five-coordinated species and do not dimerise to attain the octahedral stereochemistry as observed in the case of the corresponding nickel(II) complexes¹. Cryoscopic data point out that there is a slight dissociation of the base adducts in benzene solution.

In all the adducts, the $\nu\text{C}=\text{O}$ (carbonyl) remains almost at the same position as observed in the parent metal hydroxamates suggesting that the five-membered chelate rings do not open up after the addition of the base molecules. Infrared spectral studies further reveal that both the bases are coordinated to the central atom since in case of bis-adducts there is a single $\nu\text{N}-\text{H}$ band for the piperidine adducts and a single $\nu\text{C}=\text{N}$ band for the other base adducts.

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Complexes of Cobalt(II) with Schiff Bases Derived from Salicylaldehyde & Some Amino Acids

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Complexes of cobalt(II) with schiff bases derived from salicylaldehyde and the amino acids, DL-2-aminobutyric acid, L-valine, β -alanine, 3-aminobutyric acid, 4-aminobutyric acid and L-methionine have been synthesised and characterised. Magnetic and spectral data indicate the complexes to be octahedral.

THOUGH schiff base complexes of cobalt(II) have been widely investigated with regard to their ability to function as oxygen carriers¹⁻⁴, there is no report of such studies with complexes of schiff bases derived from amino acids. Most of the oxygen active complexes are square-planar and in the presence of monodentate ligands acquire square-pyramidal configuration. In view of this a study of the stereochemical aspects of the schiff base complexes of cobalt(II) involving bidentate and tridentate amino acids is considered worthwhile. The amino acids employed were DL-2-aminobutyric acid, L-valine, β -alanine, 3- and 4-aminobutyric acids and L-methionine.

The schiff base complexes were prepared by reacting cobalt(II) acetate with the preformed schiff base. A mixture of the appropriate amino acid (0.01 mol) dissolved in the minimum amount of water and an aq. alcoholic solution of salicylaldehyde (0.01 mol) was heated to $\sim 50^\circ$ over a water-bath. An aq. solution of cobalt (II) acetate (0.01 mol) was added dropwise to the schiff base under nitrogen atmosphere and the solid product which separated out in about 15 min collected, washed successively with water, ethyl alcohol and ether and dried over anhydrous calcium chloride *in vacuo*.

The schiff base complexes involving bidentate amino acids have been prepared both under nitrogen atmosphere as well as under atmospheric conditions and under both the conditions the same products have been isolated. However, schiff base complexes of cobalt (II) involving tridentate amino acids could not be prepared under atmospheric conditions. Though several tridentate amino acids like serine, asparagine, aspartic acid, histidine, glutamine, glutamic acid and methionine were used in the preparation of schiff base complexes, only those involving methionine, asparagine