

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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Received 2 August 1980; revised and accepted 22 November 1980

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

and glutamine could be isolated under nitrogen atmosphere. In the other cases addition of cobalt(II) acetate to the preformed schiff base resulted in a dark brown solution and no solid could be isolated. The dark brown complexes of asparagine and glutamine schiff bases obtained under nitrogen atmosphere were insoluble in water and common organic solvents. These could not be fully characterised as the analytical data are found to be inconsistent. It is possible that partial or total oxidation of cobalt(II) had occurred.

Schiff base complexes of cobalt (II) derived from bidentate amino acids are brown in colour and are insoluble in water and common organic solvents like alcohol, acetone, benzene and chloroform. They are partly soluble in coordinating solvents like dimethylformamide, dimethyl sulphoxide and pyridine. The N-salicylidene-4-aminobutyrate complexes are totally insoluble in any of the solvents.

The analytical data on the complexes of bidentate amino acid schiff bases and L-methionine schiff base correspond to a stoichiometric composition of $\text{Co}(\text{SB}) \cdot 2\text{H}_2\text{O}$ (Table 1). The infrared spectra of these complexes show the following characteristic bands: 3250 which may be assigned to the presence of water molecules, 1650 ($\nu_{\text{C}=\text{N}}$) and 1600 ($\nu_{\text{as}} \text{COO}^-$) superimposed on the phenyl ring absorption and $\sim 1400 \text{ cm}^{-1}$ ($\nu_{\text{s}} \text{COO}^-$).

Thermogravimetric analyses of the complexes indicate the presence of two water molecules per cobalt atom, which are lost around 180°C showing clearly that they are coordinated to the metal.

Conductance measurements ($3\text{--}5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) in methanol of the schiff base complexes derived from bidentate α -amino acids and the tridentate L-methionine indicate that they are non-electrolytes, in accord with the expectation of a neutral complex formed by dianionic ligands with a dipositive metal ion.

The electronic spectra of α -amino acids and L-methionine schiff base complexes in dimethyl

sulphoxide show three absorption bands similar to octahedral complexes of cobalt (II). The low energy absorption band around 9500 cm^{-1} has been assigned to the transition ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, a shoulder at 15500 to ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transition and the band in the region 19000-19500 cm^{-1} to the transition ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$.

Diffuse reflectance spectra of the solid complexes also show bands similar to those observed in solution, except the weak intensity band at 15500 cm^{-1} . This indicates that the metal atom retains the octahedral geometry in both the phases. The diffuse reflectance spectra of cobalt(II) schiff base complexes derived from β - and γ -amino acids are similar to those of N-salicylidene- α -amino acid complexes indicating the similarity in geometries. In the case of L-methionine schiff base complex of $\text{Co}(\text{II})$, apparently the thioether group is not involved in coordination.

Magnetic susceptibility measurements indicate the schiff base complexes derived from α -, β - and γ -amino acids to be paramagnetic with moments ranging from 4.85 to 4.95 B. M., and these are in agreement with the predicted values for octahedral complexes involving three unpaired electrons.

An octahedral configuration around the central metal ion is indicated from spectral and magnetic data. Since only five coordination sites are filled, three by the schiff base and two by water molecules, the plausible explanation is that the complexes are at least dimeric if not polymeric. It is also observed that even a strong coordinating solvent like DMSO (solvent used for recording electronic spectra) is unable to coordinate with the metal atom increasing the coordination number to six in a mononuclear set up.

Molecular weight measurements could not be undertaken because of the insolubility of the complexes in suitable solvents. This insolubility also indicates polymeric nature of the species. However, the dimeric structure proposed by Theriot *et al.*⁵

TABLE 1—ANALYTICAL DATA ON COBALT (II)-SCHIFF BASE COMPLEXES

Cobalt Complex	% Metal		% Carbon		% Hydrogen		% Nitrogen		Decomposition temp.* °C
	Calc.	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.	Exptl.	
Salicylidene-2-aminobutyrate-2H ₂ O	19.50	19.20	43.68	43.20	5.62	5.40	4.63	4.70	310
Salicylidene-valinate-2H ₂ O	18.64	18.50	45.54	44.3	5.37	5.10	4.43	4.25	285
Salicylidene- β -alaninate-2H ₂ O	20.45	20.50	41.64	42.5	4.81	5.20	4.85	4.80	295
Salicylidene-3-aminobutyrate-2H ₂ O	19.50	19.30	43.68	44.00	5.62	5.10	4.63	4.40	295
Salicylidene-4-aminobutyrate-2H ₂ O	19.50	19.30	43.68	43.10	5.62	5.50	4.63	4.80	275
Salicylidene-methioninate-2H ₂ O	16.92	17.10	41.35	40.6	4.90	5.10	4.02	3.80	280

*From TGA studies.

for N-salicylidene- α -amino acid complexes of cobalt(II) appears to be applicable in the case of the present complexes involving schiff bases derived from α -, β - and γ -amino acids. The experimental data are also in agreement with a dimeric structure.

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Mixed Chelate Complexes of Manganese(III)

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Received 14 August 1980; revised and accepted 16 December 1980

Five mixed chelate complexes of manganese(III), viz. $Mn(tsc)_2(acac)$, $Mn(tsc)_2(pyca)$, $Mn(tsc)_2(et_2dte)$, $Mn(acac)_2(pyca)$ and $Mn(acac)(pyca)_2$, where $tscH$ = thiosemicarbazide, $acacH$ = acetylacetone, $pycaH$ = picolinic acid, et_2dte = diethyldithiocarbamate, have been isolated. The thiosemicarbazido complexes have been obtained on oxidation of manganese(II) by air in alkaline medium whereas the other two mixed chelates have been obtained from manganese(III) compounds by substitution reactions. The compounds have been characterized on the basis of their elemental analyses, molecular weight, molar conductance, magnetic susceptibility, infrared and electronic spectral data.

THE 3+ oxidation state of manganese has been well-characterized by the preparation of a number of anionic, cationic and neutral complexes and a good number of mixed chelate and mixed ligand complexes¹⁻⁶. The complexes were generally obtained starting from the manganese(III) compounds. In the present investigation besides the usual method for isolating Mn(III) complexes, a method involving

oxidation of divalent to trivalent manganese in the presence of ligands has been used.

(i) *Preparation of $Mn(tsc)_2(acac)$, $Mn(tsc)_2(pyca)$ and $Mn(tsc)_2(et_2dte)$* —Ethanol solutions of manganese(II) chloride, acetylacetone/picolinic acid/sodium salt of diethyldithiocarbamic acid and thiosemicarbazide in 1 : 1 : 2 molar ratio were reacted. Ethanol sodium hydroxide solution was added to it till faintly alkaline and then air was bubbled through the resulting solution for one hour when the colourless solution darkened and the compounds separated out. These were filtered, washed with ethanol, ether and dried *in vacuo*.

(ii) *Preparation of $Mn(acac)_2(pyca)$* —Tris (acetylacetonato)manganese(III), $Mn(acac)_3$, in chloroform and picolinic acid in ethanol were refluxed in 1 : 1 molar ratio for one hour. The volume was reduced to one-third by suction and the contents kept overnight when the compound separated out. It was filtered, washed with ethanol, ether and dried *in vacuo*.

(iii) *Preparation of $Mn(acac)(pyca)_2$* —Tris (acetylacetonato)manganese(III), $Mn(acac)_3$, in chloroform and picolinic acid in ethanol were mixed in 1 : 2 molar ratio and refluxed for 15 min when the compound separated out. It was filtered, washed with ethanol, ether and dried *in vacuo*.

Elemental analyses (Table 1) carried out by standard methods were consistent with the formulations of the compounds. The molar conductances for $\sim 10^{-3}$ M solutions of the complexes in nitrobenzene medium range between 2.1 and 2.9 mho cm^2 mole⁻¹ indicating the non-electrolytic nature of the compounds.

The magnetic moment values (determined using Gouy method) of 4.92-5.08 B.M. (Table 1) indicate the presence of four unpaired electrons corresponding to high-spin manganese(III) state with ⁵E_g ground term. The molecular weight measurements (Rast method using camphor) indicate that the compounds are monomeric.

Thiosemicarbazide exists in the tautomeric forms (I) and (II) and can act as a neutral or charged chelating group⁷.

Haines and Sun⁸ have reported that in thiosemicarbazido complex, the band at 1049 cm^{-1} for free thiosemicarbazide becomes very weak and a new strong band appears at 960 cm^{-1} . Such features can

TABLE 1 — ANALYSES, COLOUR, MELTING POINTS, MAGNETIC SUSCEPTIBILITY AND MOLECULAR WEIGHTS DATA OF MIXED CHELATE MANGANESE(III) COMPLEXES

Compound	Colour	m.p. (°C)	Found (Calc.) %		μ_{eff} (B.M.)	Mol. wt found (calc.)
			Mn	S		
$Mn(tsc)_2(acac)$	Chocolate	>300	16.04 (16.44)	18.70 (19.19)	5.05	356.2 (335.9)
$Mn(tsc)_2(pyca)$	Grey	>300	15.11 (15.38)	17.43 (17.95)	5.0 ^d	338.1 (357.2)
$Mn(tsc)_2(et_2dte)$	Greyish-brown	>300	14.43 (14.32)	33.01 (33.43)	4.93	369.8 (357.2)
$Mn(acac)_2(pyca)$	Grey	150	14.43 (14.63)	—	4.92	349.0 (375.2)
$Mn(acac)(pyca)_2$	Pink	160	13.74 (13.79)	—	5.08	437.1 (398.2)