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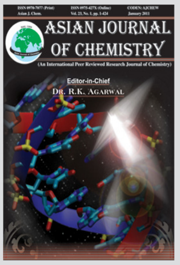

Synthesis Characterization and Antifungal Activity of Trivalent and Tetravalent Metal/Non-metal Derivatives of N-(2-Methyl)phenylglycine

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The trivalent (boron, aluminium, iron, arsenic and antimony) and tetravalent (silicon, titanium and selenium) metal/non-metal derivatives of N-(2-methyl)phenylglycine have been prepared by the interaction of their corresponding isopropoxide with the N-(2-methyl)phenylglycine in 1:1, 1:2, 1:3 and 1:4 molar ratios in benzene medium. The course of reaction was monitored by estimating the amount of isopropanol liberated in benzene-isopropanol azeotrope in each case. The compounds thus prepared were generally obtained as coloured solids and amongst them those containing isopropoxy group(s) was found to be hygroscopic. All these compounds were characterized by azeotrope and elemental analysis, as well as by spectral measurements. They were tested *in vitro* for their antifungal activity against *Aternaria alternate* and *Fusarium oxyporum*.

Key Words: Synthesis, B, Al, Fe, As, Sb, Si, Ti, Se, Derivatives, N-(2-Methyl)phenylglycine.

INTRODUCTION

Considerable interest is now being evinced towards synthesis of newer phenylglycine {N-(2-methyl)phenylglycine (LH_2)} derivatives with trivalent (boron, aluminium, iron, arsenic and antimony) and tetravalent (silicon, titanium and selenium) metal/non-metal because of their potential uses as pharmaceuticals[1] and herbicides[2], besides their utility as precursors in the preparation of agrofungicides[3], β-lactum antibiotics[4] and antitubercular agents[5]. Srivastava and Mehrotra[6] reported synthesis of N-(2-methyl-4-substituted phenylazo)phenylglycine dyes derived from N-(2-methyl)-phenylglycine, while Chandra *et al.*[7] examined the chelating tendencies of these azo dyes in solution. However, no systematic work appears to be on record towards examining the ligating properties of N-(2-methyl)phenylglycine either in solution or in solid state. This ligating tendency of N-(2-methyl) phenylglycine indicates its coordination to metal/non-metal and derived derivatives widely used as agro fungicides. The effect of substituent such ethoxy[8], methoxy[9,10], methyl[11], *etc*. present in the phenyl ring on of fungitoxicity of benzal derivatives has been studies. But so far no attampent has been made to investigate the N-(2-methyl)phenylglycine derivatives which display a vital role in fungitoxcity.

These prepared trivalent and tetravalent derivatives of N-(2-methyl) phenylglycine by alcoholysis reactions involving the interaction of the corresponding metal/non-metal isopropoxide with the latter in 1:1, 1:2, 1:3 and 1:4 (1:1 and 1:2 were reported earlier[12]) molar ratios in benzene, as a reaction medium. The course of reactions was monitored by estimating the amount of isopropanol liberated in benzene-isopropanol azeotrope[13,14].

The various compounds thus prepared have been characterized by elemental analysis, as well as by IR, ^{1}H NMR and mass spectral measurements. It may be mentioned here that while the IR and ^{1}H NMR spectra were recorded for all the compounds prepared and mass spectra were taken only in the several representative cases. Nevertheless, the conclusion drawn from the ^{1}H NMR data were found to be in conformity to those inferred from the IR spectral measurements.

EXPERIMENTAL

The alcoholysis reactions were performed in a fractionating column (30 cm long) packed with Rachig rings and fitted to a total condensation variable take-off still head. Special weighting tubes and measuring pipettes with standard joints were used for the analytical sampling of the compounds. For filtration purpose, a specially designed G_4 sintered glass filtration funnel, fitted with a guard tube at the upper end and filled with fused calcium chloride was used.

Benzene (Qualigens; AR), isopropanol (Qualigens; AR) and diethyl ether (Qualigens; AR) were dried by standard procedures[15]. Boric acid (S.Merck; GR) was dried under vaccum, aluminium foil (E.Merck; AR) was dried in an atmosphere of chlorine. The arsenic trichloride (Riedel) and antimony trichloride (E.Merck; AR) were purified by distillation at 130 and 233 ºC, respectively. Titanium tetraisopropoxide (Fluka), silicon tetrachloride (E.Merck) and selenium tetrachloride (E.Merck) were used, as such. The various metal/non-metal isopropoxides were prepared by already reported methods[16].

Boron was estimated by Thomas method[17], while aluminium as aluminium oxinate[18]. Iron was estimated as ferric oxide[18]. Arsenic(III) and antimony(IV) were first oxidized to arsenic(V) and antimony(V), respectively and then estimated iodometrically[19]. All the analytical samples were first digested with conc. nitric acid followed by conc. sulphuric acid, before estimating the metal/non-metal contents by the above procedures.

For the estimation of silicon, the analytical sample was digested with conc. sulphuric acid, followed by conc. nitric acid and then ignited and weighed as silicon dioxide[19-21]. The analytical sample of titanium was digested with conc. nitric acid followed by conc. sulphuric acid and then from the cooled acidic solution, titanium was precipitated as its cupferron complex which was ignited and weighed as titanium dioxide[19]. Selenium was estimated in the elementary form by digesting the analytical sample with fuming nitric acid followed by passage of SO_2 in the presence of HCl, which resulted in the precipitation of selenium quantitatively[19].

Melting points were recorded an electrothermal digital m.p. apparatus and are uncorrected. The ^{1}H NMR spectra were recorded on a Brucker IFS 66v FT-IR spectrometer in the 4000-400 cm^{-1} region, while the ^{1}H NMR spectra were taken in DMSO-d_6 solution and recorded on a 400 MHz JEOL GSX 400 NB FT-NMR spectrometer, using tetramethylsilane as an internal standard. The electrospray mass spectra were recorded on a Micormass Quattro II triple quandrupole mass spectrometer. The samples were introduced into the ESI source through a syringe pump at 0.4 mL/h. The ESI capillary was 3.5 kV^2 and the cone voltage was 25-50 V.

Preparation of N-(2-methyl)phenyglyine: N-(2-Methyl)-phenylglycine was prepared, adopting procedure almost identical to that described by Srivastava and Mehrotra[6].

Preparation of metal/non-metal derivatives of LH_2: General procedure: A mixture of isopropoxide of the metal/non-metal and LH_2 in appropriate stoichiometry in dry benzene taken in a round bottom flask, was refluxed on a wax bath (90-100 ºC), using a fractionating column. After several hours (Table-1) of reflux the isopropanol-benzene azeotrope was fractionated out and the amount of isopropanol liberated was estimated by an oxidimetric method[19,20, 22,23] [liberated isopropanol was first oxidized to acetone, by a known volume of $K_2Cr_2O_7$ (N) solution in 12.5 % H_2SO_4 which was then estimated iodometrically by titrating against standard sodium thiosulphate (N/5) solution] to monitor the completion of the reaction. After the completion of the reaction, the excess of the solvent from the reaction mixture was removed *in vacuo*, when the product isolated as a coloured solid which was washed with dry benzene (3-4 times) followed by dry ether (2-3 times) and finally dried under suction.

RESULTS AND DISCUSSION

The relevant analytical details of the various compounds prepared are summarized in Table-1. The molecular weights (Table-1) obtained from the mass spectral measurements in several representative cases are good in agreement with the corresponding calculated values.

Since, LH_2 exists in zwitter ionic form (structure **I**) as evident from IR and ^{1}H NMR spectral measurements, the alcoholysis reactions resulted in the replacement of isopropoxy groups from the metal/non-metal isopropoxide by one or both the hydrogens from the $>\overset{+}{N}H_2$ group of LH_2 with the liberation of isopropanol and formation of a new class of organo derivatives of trivalent and tetravalent metals/non-metals. The reaction between metal/non-metal isopropoxide and LH_2 may be illustrated as follows:

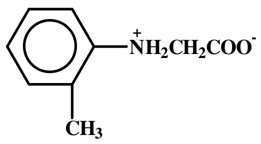
$$M(OPr^i)_3 + 3LH_2 \longrightarrow M(LH)_3 + 3Pr^iOH$$

(where, M = B, Al, Fe, As, Sb)

$$M(OPr^i)_4 + 3LH_2 \longrightarrow M(LH)_3\ (OPr^i) + 3Pr^iOH$$

$$M(OPr^i)_4 + 4LH_2 \longrightarrow M(LH)_4 + 4Pr^iOH$$

(where, M = Si, Ti, Se).



Structure **I**

The characteristic IR frequencies as identified are in case of LH_2 and its metal/non-metal derivatives and their ^{1}H NMR data are summarized in Tables 2 and 3, respectively.

IR spectrum of LH_2: The existence of LH_2 in zwitter ionic form[24] is positively indicated by the appearance of ν(N-H) of the $>\overset{+}{N}H_2$ group in form of a medium band at 2570 cm^{-1}. A strong absorption at 1600 cm^{-1} corresponds to the overlapping of ν_{as}(COO) and aromatic ν(C=C)[24,25], while an other strong absorption at 1400 cm^{-1} occurs due to ν_s(COO)[25].

IR spectra of metal/non-metal derivatives: The mode of bonding of the metal/non-metal atom with LH_2 in these derivatives has been examined on the basis of the following observations.

Metal(III)/non-metal(III) derivatives

1:3 Derivatives: (i) The band due to ν(N-H) of the zwitter ionic $>\overset{+}{N}H_2$ group as observed in LH_2 at 2570 cm^{-1} is found to disappear here with the appearance of a new ν(N-H) band in the region 3400-3100 cm^{-1} indicating deprotonation of the $>\overset{+}{N}H_2$ group to > N-H (which is also supported by liberation of only one proton in the azeotrope analysis) as a result of bonding of the imino nitrogen to the metal/ non-metal atom. (ii) The strong board bands in the region 1630-1620 cm^{-1} display N-H deformation. (iii) A shift of 10-20 cm^{-1} in ν_s(COO) as compared LH_2 suggests possible bonding of the carboxylate

TABLE-1
ANALYTICAL DETAILS OF THE VARIOUS METAL(III, IV)/NON-METAL(III, IV) DERIVATIVES OF N-(2-METHYL)PHENYLGLYCINE

Derivatives (molar ratio) (colour)	Reflux time (h)	m.p. (ºC)	Azeotrope analysis Pr^iOH (g): Found (calcd.)	Elemental analysis (%): Found (calcd.)				m.w.*
				C	H	N	M	
$B(LH)_3$ (1:3) (brown)	22	200	0.67 (0.67)	64.30 (64.42)	6.00 (6.01)	8.00 (8.35)	2.10 (2.15)	503.4 (503.4)
$Al(LH)_3$ (1:3) (cream white)	12	188	0.98 (0.98)	62.15 (62.42)	5.80 (5.82)	8.07 (8.09)	5.17 (5.19)	519.5 (519.5)
$Fe(LH)_3$ (1:3) (brown)	18	240	0.50 (0.50)	59.01 (59.13)	5.49 (5.51)	7.64 (7.66)	10.14 (10.18)	548.4 (548.4)
$As(LH)_3$ (1:3) (dark brown)	12	205	0.71 (0.72)	57.12 (57.15)	5.31 (5.33)	7.39 (7.41)	13.15 (13.20)	567.5 (567.5)
$Sb(LH)_3$ (1:3) (light brown)	10	230	1.07 (1.08)	52.58 (52.79)	4.90 (4.92)	6.82 (6.84)	19.80 (19.82)	614.3 (614.3)
$Si(LH)_3 (OPr^i)$ (1:3) (light brown)	25	>300	1.62 (1.63)	62.01 (62.15)	6.41 (6.43)	7.21 (7.25)	4.84 (4.85)	579.4 (579.4)
$Si(LH)_4$ (1:4) (dark brown)	20	>300	0.98 (0.99)	63.01 (63.14)	5.87 (5.89)	8.16 (8.18)	4.09 (4.10)	–
$Ti(LH)_3 (OPr^i)$ (1:3)(reddishbrown)	10	220	1.00 (1.01)	59.92 (60.10)	6.20 (6.22)	7.00 (7.01)	7.97 (7.99)	599.6 (599.6)
$Ti(LH)_4$ (1:4)(reddishbrown)	12	>300	0.81 (0.82)	61.05 (61.36)	5.70 (5.72)	7.75 (7.95)	6.78 (6.80)	–
$Se(LH)_3 (OPr^i)$ (1:3) (light brown)	10	300	0.58 (0.59)	57.05 (57.14)	5.90 (5.91)	6.65 (6.66)	12.50 (12.52)	–
$Se(LH)_4$ (1:4) (light brown)	12	240	0.73 (0.74)	58.55 (58.77)	5.47 (5.48)	7.60 (7.62)	10.70 (10.73)	735.7 (735.7)

$OPr^i = OC_3H_7$, $LH_2 = CH_3C_6H_4\overset{+}{N}H_2CH_2COO^-$; *Obtained by mass spectral measurements.

TABLE-2
CHARACTERISTIC INFRARED FREQUENCIES (cm^{-1}) OF N-(2-METHYL)PHENYLGLYCINE AND ITS METAL(III, IV)/NON-METAL(III, IV) DERIVATIVES

Ligand (LH_2)	M(III) $(LH)_3$	Derivatives M(IV) $(LH)_3 (OPr^1)$	M(IV) $(LH)_4$	Assignments
3070 (wb)	3400-3100 (w, mb, sb)	3300-3100 (wb, sb)	3400-3100 (mb, sb)	Overlapping of ν(N-H) and aromatic ν(C-H)
2900-2705 (w)	2990-2910 (w)	2995-2860 (w)	2980-2860 (w)	ν(C-H) of the $-CH_2-$ and $-CH_3$ groups
2570 (m)				$\nu(N-H)$ of the $\overset{+}{N}H_2$ group
1600 (s)			1650-1640 (m, s, sb)	Overlapping of $\nu_{as}(COO^-)$ and aromatic ν(C=C)
	1620-1615 (mb, sb)	1635-1620 (s, sb)		Overlapping of $\nu_{as}(COO^-)$, aromatic ν(C=C) and N-H deformation
1515-1435 (s)	1585-1405 (w, m, s)	1545-1515 (w, wb, m)	1550-1430 (w, mb)	Overlapping of the aromatic skeletal vibration and C-H bending modes of the $-CH_2-$ and $-CH_3$ groups
1400 (s)	1390-1385 (w, m, s)		1390-1385 (m, s)	$\nu_s(COO^-)$
		1395-1380 (w, m,)		Overlapping of $\nu_{s(}COO^-)$ and C-H bending modes of *gem*-dimethyl structure of the isopropoxy groups
	235-225	245-225	265-235	$\Delta\nu$ COO^- [$\nu_{as}(COO^-$ - $\nu_s(COO^-)$
		1195-1120 (w)		ν(C-O) of the isopropoxy group
	1390 (wb)			ν(B-O)
	1515 (s)			ν(B-N)
	625-540 (w, mb, sb)	770-565 (w)	705-545 (w)	ν(M-O)
	510-530 (w)	590-435 (w)	585-435 (w)	ν(M-N)
1155-920 (s, m, w)	1095-1025 (s, m)	1095-1055 (w)	1095-1025 (m, w)	C-H in-plane bending modes
850-680 (s, m)	870-700 (s, m)	880-805 (m, w)	805-705 (w, m)	C-H out-of-plane bending modes

oxygen to the mental/non-metal atom. (iv) The separation value, $\Delta\nu$ COO [ν_{as}(COO – ν_s(COO)] between 250-230 cm^{-1} indicates unidentate bonding of the carboxylate group to the metal/non-metal atom[26]. (v) The absorptions in the region 625-540 cm^{-1} may be assigned to ν(M-O), while those in the region 490-435 cm^{-1} correspond to ν(M-N).

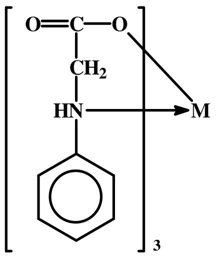
It is suggested that B, Al, Fe, As or Sb atom in $M(III)(LH)_3$ exhibits hexa-coordination in each case as a result of bonding with one of the oxygen from the three carboxylate group, as well as the nitrogen from each of the three imino groups (obtained by the deprotonation of the $> \overset{+}{N}H_2$ group) available from three moles of LH_2 (structure **II**).

Metal(IV)/non-metal(IV) derivatives

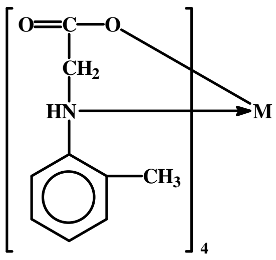
1:3 Derivatives: In these derivatives, the mode bonding is similar to those of the 1:3 derivatives except the bands in the region 1390-1380 cm^{-1} occur due to the overlapping of

TABLE-3
^{1}H NMR SPECTRAL DATA (δ VALUE) OF N-(2-METHYL)PHENYLGLYCINE AND ITS METAL(III, IV)/NON-METAL(III, IV) DERIVATIVES

Ligand (LH_2)	M (III) (LH_3)	δ values (in ppm) derivatives M(IV) $(LH)_3(OPr^i)$	M(IV)$(LH)_4$	Assignments
6.50-7.35 (m)	6.70-7.45 (m)	6.30-7.30 (m)	6.30-7.35 (m)	Aromatic ring protons
2.45 (s)	2.65-2.75 (s)	2.65-2.75 (s)	2.65-2.75 (s)	$-CH_2-$ protons (of glycine part)
3.90 (s)	3.55-3.70 (s)	3.50-3.60 (s)	3.60-3.70 (s)	>N–H proton of the $>\overset{+}{N}H_2$ group
2.20 (s)	2.00-2.15 (d)	2.10-2.11 (d)	2.05-2.10 (d)	$-CH_3$ protons (attached with the benzene ring)
		1.10-1.15 (d)		$-CH_3$ Protons of the isopropoxy group
		4.10-420 (m)		-CH protons of the isopropoxy group.



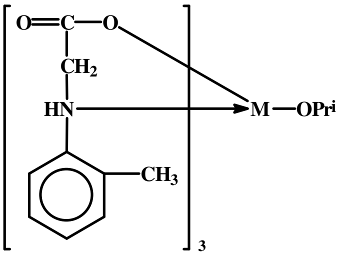
Structure **II** (where M = B, Al, Fe, As and Sb)



Structure **IV** (where M = Si, Ti and Se)

ν_{as}(COO) and C-H bending modes of *gem*-dimethyl structure of the isopropoxy group suggesting the attachment of the isopropoxy group to the metal/non-metal atom. Further ν(C-O) of the isopropoxy group[27] is identified by the absorption in the region 1195-1150 cm^{-1}. The weak bands in the region 690-490 cm^{-1} occur due to ν(M-O), while the others in the region 500-410 cm^{-1} correspond to ν(M-N).

Thus, Si, Ti or Se atom in $M(LH)_3(Opr^i)$ exhibits hepta-coordination as a consequence of bonding with one of the oxygen from each of the three carboxylate groups, as well as the nitrogen from each of the three imino groups (obtained by the deprotonation of the $>\overset{+}{N}H_2$ group) available from three moles of LH_2, along with an isopropoxy group (structure **III**).



Structure **III** (where M = Si, Ti and Se)

1:4 Derivatives: In these derivatives, the mode of bonding is similar to those of the 1:3 metal(III)/non-metal(III) derivatives.

Thus, Si, Ti or Se atom in $M(LH)_4$ exhibits octa-coordination as a result of bonding with one of the oxygen from each of the four carboxylate groups, as well as the nitrogen from each of the four imino groups (obtained by the deprotonation of the $>\overset{+}{N}H_2$ group) available from moles of LH_2 (structure **IV**).

^{1}H NMR spectrum of LH_2: The existence of LH_2 in Zwitter ionic form is further supported by ^{1}H NMR measurements by the appearance of a singlet at δ 3.90 corresponding to the $>\overset{+}{N}H_2$ group protons[25]. The absence of any signal between 7.50-13.00 indicates the absence of the carboxylic acid group[25].

^{1}H NMR spectra of metal(III)/non-netal(III) derivatives: A New signal (singlet) in the region δ 3.50-3.65 in case of $M(III)(LH)_3$ shows coordination of the imino nitrogen (obtained by deprotonation of the $>NH_2$ group) to boron, aluminum, iron, arsenic and antimony.

^{1}H NMR spectra of metal(IV)/non-metal(IV) derivatives: The occurrence of a new signal (singlet) in the region δ 3.50-3.65 suggests coordination of the imino nitrogen (obtained by deprotonation of the $>\overset{+}{N}H_2$ group) to silicon, titanium and selenium in case of $M(IV)(LH)_3(OPr^i)$ and $M(IV)(LH)_4$, respectively, On the other hand, the occurrence of a doublet between δ 1.20-1.55 and a multiplet between δ 4.20-4.25 occur, respectively due to the $-CH_3$ and =CH protons of the isopropoxy group[28] in case of $M(IV)(LH)_3(OPr^i)$.

From the foregoing observation, it is evident that the mode of bonding of LH_2 to the metal/non-metal atom is in conformity with the conclusions drawn from the IR measurements earlier in the corresponding cases.

Antifungal activity: The antifungal activity of N-(2-methy1)phenylglycine and its derivatives has been evaluate by radial growth method[29] using Czapek's agar medium having the composition, glucose 20 g, agar-agra 20 g and distilled water 1000 mL. The principle involved in this technique is to poision the nutrient medium a fungitoxicant and then allowing a test fungus to grown on such a medium.

The test compounds is incorporated in the potato-dextrose agar medium in requisite amount to give a certain concentration (50, 100 and 200 ppm) and thoroughly mixed by constant stirring. The medium is then poured into the Petri plates and stored in a refrigerator. A disk of 7 mm of fungal culture of a specific age growing on the solid medium is then cut with a sterile cork borer. The plates are incubated at specific temperature, favourable for the growth of test fungus. Suitable checks kept where the culture discs are gown under the same condition on the agar medium without any fungicide. Three replicates were used in each case. The colony diameter after 4 days is measured to evaluate the fungitoxicity. The percent inhibition was calculated as: % Inhibition = (C-T) × 100/C where C and T are the diameters of the fungus colony in control and test discs, respectively.

The pathogenic fungi used for this investigation are *Aternaria althernate* and *Fusarium oxyporum*. The structure activity relationship shows that the presence of isopropoxy group in pheny1 ring showed strong activity against all test fungi (Table-4). The chelation theory[30] account for the metal complexes. The chelation reduces the polarity of the metal atom mainly because of partial sharing of its positive charge with the donor groups and possible *p* electron delocalization within the whole chelating ring. The chelation increases the lipophilic nature of the central atom, which subsequently favours its permeation through the lipid layer of the cell membrane.

TABLE-4
FUNGICIDAL SCREENING DATA OF N-(2-METHYL) PHENYLGLYCINE AND ITS DERIVATIVES, AVERAGE PER CENT GROWTH INHIBITION AFTER 6 DAYS AT 30 ± 2 ºC

Compound	*Aternaria alternata*			*Fusarium oxyporum*		
	50	100	200	50	100	200
Fe(III) (L) (OPr^1)	23	48	50	20	50	53
Fe(III) $(LH)_2$ (OPr^1)	20	44	53	31	53	72
Fe(III) $(LH)_3$	28	55	48	40	63	78
Ti(IV) (L) $(OPr^1)_2$	20	45	60	38	55	68
Ti(IV) $(L)_2$	23	31	56	29	36	57
Ti(IV) $(LH)_3$ (OPr^1)	35	49	66	51	58	62
Ti(IV) $(LH)_4$	30	56	60	44	53	62
LH_2	40	68	70	42	50	65

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