Manganese(II), Cobalt(II), Nickel(II), Copper(II) and Zinc(II) Complexes of N-(*o*-Hydroxy Methyl Substituted Benzyl) Glycines

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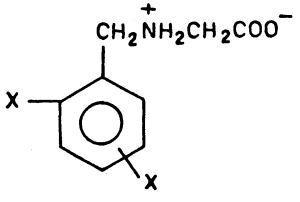
1 : 1 Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of N-(*o*-hydroxy methyl substituted benzyl) glycines have been isolated from 50% (v/v) aqueous dimethylsulphoxide medium and characterized by elemental analysis and spectral measurements.

INTRODUCTION

Isolation and characterization of uranyl(II) and thorium(IV) complexes of N-[*o*-hydroxy methyl substituted (of H) benzyl] glycines/alanines have earlier been reported from these laboratries[1]. The work described here relates to the preparation of 1 : 1 complexes of several 3*d*-block metal ions, *viz.*, Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with N-(*o*-hydroxy methyl substituted benzyl) glycines [Structure (I)], *viz.*, (i) N-(2-hydroxy-3-methyl benzyl) glycine (H_2hmbg-3), (ii) N-(2-hydroxy-6-methyl benzyl) glycine (H_2hmbg-6) and (iii) N-(2-hydroxy-5-methyl benzyl) glycine (H_2hmbg-5) which were obtained as coloured solids. These complexes were characterized by elemental analysis, as well as by IR and PMR spectral measurements.



(Where X=-H or $-CH_3$)

(I)

EXPERIMENTAL

All the reagents used were of analytical grade. The various ligands undertaken in the present work were prepared by methods reported earlier[2]. The metal contents in the complexes were determined by EDTA titrations, after their decomposition. The details of the various instruments used were identical to those described before[1].

Preparation of 1 : 1 Mn(II) H_2hmbg-3 Complex

A solution of H_2hmbg-3 (1.4641 g; 7.4995 mmole in 5 mL of DMSO + 5 mL water) was added dropwise to a solution of manganese acetate (1.8382 g; 7.5 mmole in 5 mL DMSO + 5 mL water). The reaction mixture was then refluxed on a water bath. After *ca.* 8 h of reflux, the product isolated as a dark brown solid

which was filtered under suction and washed with 50% (v/v) aqueous DMSO 2–3 times and then air dried. The product was found to be sparingly soluble in dimethylsulphoxide but insoluble in other common organic solvents.

TABLE-1
ANALYTICAL DETAILS OF N-(*o*-HYDROXY METHYL SUBSTITUTED BENZYL) GLYCINES AND THEIR 1 : 1 METAL COMPLEXES

Compound (colour)	m.p. (°C)	% Analysis, Found (Calcd.)			
		C	H	N	M
H_2hmbg-3 (off white)	190	61.48 (61.52)	6.70 (6.71)	7.15 (7.18)	—
H_2hmbg-6 (off white)	88	61.40 (61.52)	6.68 (6.71)	7.16 (7.18)	—
H_2hmbg-5 (off white)	148	61.42 (61.52)	6.68 (6.71)	7.15 (7.18)	—
Mn(hmbg-3)·3H_2O (dark brown)	220	39.25 (39.47)	5.67 (5.67)	4.62 (4.63)	18.09 (18.18)
Mn(hmbg-6)·3H_2O (dark brown)	240(d)	39.28 (39.47)	5.67 (5.67)	4.64 (4.63)	18.08 (18.18)
Mn(hmbg-5)·3H_2O (dark brown)	225	39.27 (39.47)	5.66 (5.67)	4.64 (4.63)	18.25 (18.18)
Co(hmbg-3)·3H_2O (light pink)	205	39.14 (39.25)	5.58 (5.59)	4.57 (4.57)	19.16 (19.25)
Co(hmbg-6)·3H_2O (light pink)	215	39.15 (39.25)	5.59 (5.59)	4.56 (4.57)	19.17 (19.25)
Co(hmbg-5)·3H_2O (pink)	210	39.15 (39.25)	5.58 (5.59)	4.56 (4.57)	19.20 (19.25)
Ni(hmbg-3)·3H_2O (light blue)	290	39.40 (39.33)	5.60 (5.61)	4.59 (4.59)	19.14 (1922)
Ni(hmbg-6)·3H_2O (classic)	270	39.13 (39.33)	5.61 (5.61)	4.59 (4.59)	19.14 (19.22)
Ni(hmbg-5)·3H_2O (ocean spray)	260	39.45 (39.33)	5.60 (5.61)	4.58 (4.59)	19.16 (19.22)
Cu(hmbg-3)·3H_2O (olive green)	310	38.56 (38.64)	5.50 (5.51)	4.49 (4.50)	20.28 (20.44)
Cu(hmbg-6)·3H_2O (dark green)	300(d)	38.61 (38.64)	5.49 (5.51)	4.48 (4.50)	20.30 (20.44)
Cu(hmbg-5)·3H_2O (dark green)	290	38.50 (38.64)	5.48 (5.51)	4.48 (4.50)	20.46 (20.44)
Zn(hmbg-3)·3H_2O (pink)	180	38.29 (38.41)	5.46 (5.48)	4.46 (4.48)	20.98 (20.91)
Zn(hmbg-6)·3H_2O (dirty white)	170	38.32 (38.41)	5.46 (5.48)	4.47 (4.48)	20.83 (20.91)
Zn(hmbg-5)·3H_2O (light yellow)	120(d)	38.25 (38.41)	5.46 (5.48)	4.48 (4.48)	20.85 (20.91)

Abbreviations: H_2hmbg-3 (or -6 or -5) = $HOC_6H_3(CH_3)\overset{+}{N}H_2CH_2COO^-$

TABLE-2

CHARACTERISTIC INFRARED FREQUENCIES (cm^{-1}) of N-(*o*-HYDROXY METHYL SUBSTITUTED BENZYL) GLYCINES AND THEIR METAL COMPLEXES

Compound	ν(OH) and aromatic ν(C—H)	ν(H_2O)	ν(N—H) and aromatic ν(C—H)	ν(C—H) of —CH_2— and —CH_3 group	ν(NH) of $>\overset{+}{N}H_2$ group	δ(H_2O)	ν_{asym}(COO)	ν_{sym}(COO)	Δν(COO)	ν(C—N)	ν(M—O)	ν(M—N)
H_2hmbg-3	3600–3000 vb	—	—	2950 vb 2855 wb	2390 wb	—	1635 vsb	1400 m	—	1230 s	—	—
H_2hmbg-6	3500–3000 vb	—	—	2910 mb 2860 wb	2375 wb	—	1640 vsb	1405 m	—	1230 m	—	—
H_2hmbg-5	3500–3000 vb	—	—	2910 mb 2870 w	2380 w	—	1635 vsb	1400 s	—	1225 m	—	—
Mn(hmbg-3)·3H_2O	—	3400 mb	3250–3000 wb	2950 w 2850 w	—	1630 sb	1610 vsb	1380 m	230	1255 s	605 m	450 m
Mn(hmbg-6)·3H_2O	—	3390 mb	3200–3000 b	2910 w 2855 s	—	1635 s	1610 vsb	1380 s	230	1260 m	610 w	460 w
Mn(hmbg-5)·3H_2O	—	3390 mb	3200–3000 wb	2920 vs 2855 w	—	1630 s	1610 vsb	1380 s	230	1260 s	600 m	450 w
Co(hmbg-3)·3H_2O	—	3400 mb	3250–3000 b	2920 m 2860 w	—	1685 s	1610 vsb	1390 s	220	1255 m	530 w	450 w
Co(hmbg-6)·3H_2O	—	3390 mb	3200–3000 wb	2910 mb 2855 w	—	1680– 1645 mb	1615 vsb	1380 m	235	1260 m	520 w	480 w
Co(hmbg-5)·3H_2O	—	3400 mb	3200–3000 b	2910 w 2870 w	—	1685 s	1615 vsb	1390 m	225	1260 s	615 w	480 w

Compound	ν(OH) and aromatic ν(C—H)	ν(H_2O)	ν(N—H) and aromatic ν(C—H)	ν(C—H) of —CH_2— and —CH_3 group	ν(NH) of >$\overset{+}{N}H_2$ group	δ(H_2O)	ν_{asym}(COO)	ν_{sym}(COO)	Δν(COO)	ν(C—N)	ν(M—O)	ν(M—N)
Ni(hmbg-3)·3H_2O	—	3350 vb	3250–3000 b	2925 s 2855 w	—	1680 s	1615 vsb	1390 m	225	1255 s	600 w 530 w	460 w
Ni(hmbg-6)·3H_2O	—	3390 mb	3250–3000 wb	2910 w 2860 w	—	1685 s	1620 vsb	1390 m	230	1260 m	615 w	460 w
Ni(hmbg-5)·3H_2O	—	3400 mb	3250–3000 wb	2915 s 2860 w	—	1685 s	1620 vsb	1380 m	240	1260 m	615 w	460 w 440 s
Cu(hmbg-3)·3H_2O	—	3400 mb	3250–3000 b	2950 w 2855 w	—	1680 s	1610 vsb	1385 m	225	1255 s	615 w	480 w
Cu(hmbg-6)·3H_2O	—	3405 mb	3250–3000 wb	2920 w 2860 w	—	1660 vs	1620 vs	1370 s	250	1265 s	610 w	495 w
Cu(hmbg-5)·3H_2O	—	3400 mb	3200–3000 b	2910 w 2870 w	—	1685 s	1640 vsb	1370 s	270	1255 s	620 w	460 s
Zn(hmbg-3)·3H_2O	—	3390 mb	3250–3000 b	2920 m 2860 w	—	1685 m	1620 vsb	1390 m	230	1265 m	600 s	480 w 430 w
Zn(hmbg-6)·3H_2O	—	3390 mb	3250–3000 wb	2910 w 2855 w	—	1685 s	1620 vsb	1390 m	230	1265 m	615 m	480 w
Zn(hmbg-5)·3H_2O	—	3390 mb	3200–3000 b	2910 s 2870 w	—	1675 s	1630 vsb	1390 m	240	1255 w	620 s 520 w	460 w

Abbreviations: s = strong, m = medium, w = weak, mb = medium broad, b = broad, wb = weak broad, sb = strong broad, vb = very broad, vsb = very strong broad.

TABLE-3
PROTON MAGNETIC RESONANCE SPECTRAL DATA (δ VALUES) OF N-(*o*-HYDROXY METHYL SUBSTITUTED BENZYL) GLYCINES AND THEIR METAL COMPLEXES

Compound	Aromatic ring	Phenolic OH	H_2O	$>\overset{+}{N}H_2$	>NH	—CH_2—attached with		—CH_3 attached with benzene ring
						Benzene ring	Glycine part	
H_2hmbg-3	6.50–7.10 t	4.50–5.70 h	—	3.55 s	—	3.15 s	2.50 s	2.15 s
H_2hmbg-6	6.40–7.10 t	4.40–5.60 h	—	3.65 s	—	3.20 s	2.45 s	2.15 s
H_2hmbg-5	6.50–7.00 t	4.50–5.50 h	—	3.70 s	—	3.25 s	2.45 s	2.15 s
Mn(hmbg-5)·3H_2O	6.50–7.00 m	—	3.40 s	—	3.10 s	3.25 s	2.45 s	2.15 s
Co(hmbg-3)·3H_2O	6.50–7.10 m	—	3.35 s	—	3.00 s	3.15 s	2.50 s	2.15 s
Ni(hmbg-3)·3H_2O	6.50–7.25 m	—	3.45 s	—	3.15 s	3.25 s	2.50 s	2.15 s
Cu(hmbg-6)·3H_2O	6.45–7.10 m	—	3.40 s	—	3.05 s	3.20 s	2.45 s	2.15 s

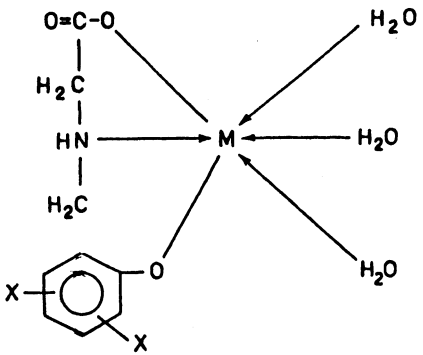
Abbreviations: s = singlet, t = triplet, m = multiplet, h = hump

Similar procedure was adopted for the preparation and purification of other 1 : 1 complexes.

Table-1 records the details of the various complexes, while Tables-2 and 3. provide respectively the IR and PMR spectral data.

RESULTS AND DISCUSSION

On the basis of analytical data, characteristic IR frequencies and PMR data, the modes of bonding[3–7] in the various metal complexes prepared in general are shown in structure (II).



(Where M=Mn (II), Co (II), Ni (II), Cu (II) or Zn (II), X= -H or $-CH_3$)

(II)

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