Short Communication

Synthesis and characterization of gallium (III) derivatives of sterically hindered heterocyclic β-diketone

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Abstract

Some new organic derivatives of heterocyclic β-diketone [4-chlorobenzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (CMPPOH)] of the type $Ga(OPr^i)_{3-n}(CMPPO)_n$ (where n=1,2and 3) have been synthesized by the reactions of $Ga(OPr^i)_3$ and heterocyclic β-diketone in different molar ratios. These derivatives were characterized by elemental analyses, mol. wt. measurements and their probable structures have been proposed on the basis of IR and ^{1}H NMR spectral studies.

Keywords- Elemental analyses, spectral studies, sterically hindered heterocyclic β-diketones

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INTRODUCTION

4-Acyl-3-methyl-1-phenyl-2-pyrazolin-5-ones constitute an interesting class of ligands because of their pharmacological[1] and potential biological activities, such as, anti-inflammatory[2], antitumor[3], anticonvulsant[4], antimicrobial[5], antiviral[6], antihistaminic[7] fungicidal activities[8] and anti-HIV-1 activity.[9-11] Acyl pyrazolones are good chelating ligands.[12-13] In this paper we have report the synthesis of $Ga(OPr^i)_{3-n}(OPPMC)_n$ (n=1,2and 3) compounds. These compounds have been characterized by elemental analysis molecular weight measurements and their probable structures have been proposed on the basis of IR, and ^{1}H NMR spectral data.

MATERIALS AND METHODS

All the reactions were carried out under anhydrous conditions and the solvents were dried by standard procedure.[14] Heterocyclic β-diketone ligands have been synthesized by literature method.[15] Gallium isopropoxide has been prepared by literature method.[16] Gallium was estimated as oxinate.[17] Isopropyl alcohol in the azeotrope was estimated by oxidimetric method.[18] ^{1}HNMR spectra have been recorded on a JEOL 400 MHz spectrophotometer. ^{1}H NMR has been recorded in $CDCl_3$ using TMS as internal reference. IR spectra have been recorded on 8400 SHIMADZU FT-IR spectrophotometer as nujol mull on KBr cell in the range 4000-400 cm^{-1}.Carbon and hydrogen were analysed by a coleman-33 carbon hydrogen analyser. Molecular weights were determined ebulioscopically using Beckmann thermometer. Since similar methods have been used to synthesize these compounds, the preparative detail of one representative compound is given in detail. Synthetic and analytical data of the other analogous compounds are summarized in Table-1.

Synthesis of $Ga(OPr^i)_2$ (OPPMC)

CMPPOH (0.75 g; 8.27 m mol) was added to toluene solution (~50ml) of $Ga(OPr^i)_3$ (0.59m; 8.46 mol) and the solution was refluxed on a fractionating column for about 3 hours. The isopropanol in the reaction was fractionated out azeotropically with toluene. The product was soluble in toluene. After stripping off the solvent under reduced pressure, a light brown coloured solid was obtained in good yield which was purified by recrystallization from a mixture of toluene and hexane

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RESULT AND DISCUSSION

The reactions of $Ga(OPr^i)_3$ with (4-chlorobenzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one(CMPPOH) ligand was carried out in 1:1, 1:2 and 1:3 molar ratios in refluxing toluene.

$$Ga(OPr^i)_3 + n\ CMPPOH \longrightarrow Ga(OPr^i)_{3-n}(OPPMC)_n + n\ Pr^iOH$$

(Where n=1,2and 3)

The isopropanol liberated during the reaction was fractionated out azeotropically with toluene.. After the completion of the reaction the removal of solvent under reduced pressure yield coloured solid compounds. These derivatives are soluble in common organic solvents like chloroform, methanol, THF etc. and are purified by toluene and n-hexane mixture.

All these derivatives are light brown (1) or yellow (2-3) colored solids. The molecular weight determinations indicate that the compounds $Ga(OPr^i)(OPPMC)_2$ and $(OPr^i)Ga(CMPPO)_2$ are of dimeric nature whereas the compound $Ga(CMPPO)_3$ is monomeric.

I. R. Spectra

The appearance of a new band at 440, 610 and 700 cm^{-1} (Table-2) due to ν Ga-O indicates, the deprotonation of OH group and the formation of gallium- oxygen bond The stretching bands due to C–O of the isopropoxy groups appears at 1180-1130 and 930 cm^{-1}. Another band due to ν C=O in the region 1490-1510 cm^{-1} is shifted during complexation. The medium intense absorption bands observed in the spectra of the free ligand in the region 1570 and 1590 cm^{-1} due to C=C and phenyl group remain unchanged in the spectra of gallium complex. This indicates that nitrogen atom of the heterocyclic ring does not take part in the complexation.

^{1}H NMR Spectra

The signal due to enolic proton of the free CMPPOH ligand at 12.3 ppm is absent in all these complexes indicating the deprotonation of this group and formation of Ga-O bond (Table-2). The signals due to ClC_6H_4 group protons attached with C = O group in ligand shows an upfield shift in the specra of complexes due to the involvement of ClC_6H_4 -C=O group in the bonding. A doublet appears at 1.20 ppm and a broad signal at 3.4-4.0 ppm in the spectrum of the derivative $Ga(OPr^i)(OPPMC)_2$ have been assigned to gem dimethyl and –CH protons respectively. Presence of one set of signals in this range in the compound $Ga(OPr^i)(OPPMC)_2$ for isopropoxy group indicates the presence of only bridging isopropoxy groups. Two sets of signals for the methyl (doublet) and methine (septet) signals for isopropoxy groups in the spectra of these derivatives $Ga(OPr^i)_2(OPPMC)$ appear in the range of 0.9 - 1.30 ppm and 3.6-4.3ppm respectively. Presence of two sets of signals in the spectra of this compound indicates the presence of terminal and bridging isopropoxy groups. Other proton signals are observed at their expected positions.

CONCLUSION

In view of the monomeric nature of tris derivative; $Ga(CMPPO)_3$ and monofunctional bidentate nature of ligand, the following structure (Fig-1) has been proposed-

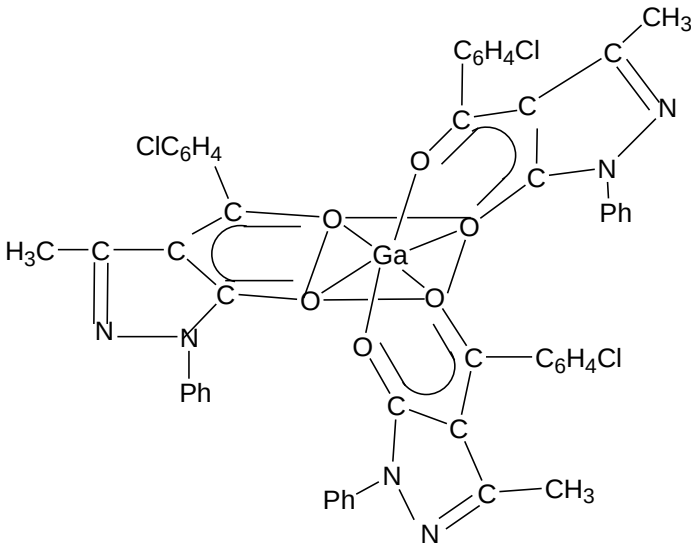

Figure 1

In view of dimeric nature, presence of only one set of signal for isopropoxy group (bridging) in ^{1}HNMR spectra of compound (OPr^i)Ga(CMPPO) and monofunctional bidentate nature of ligand, the following structure (Fig-2) has been proposed-

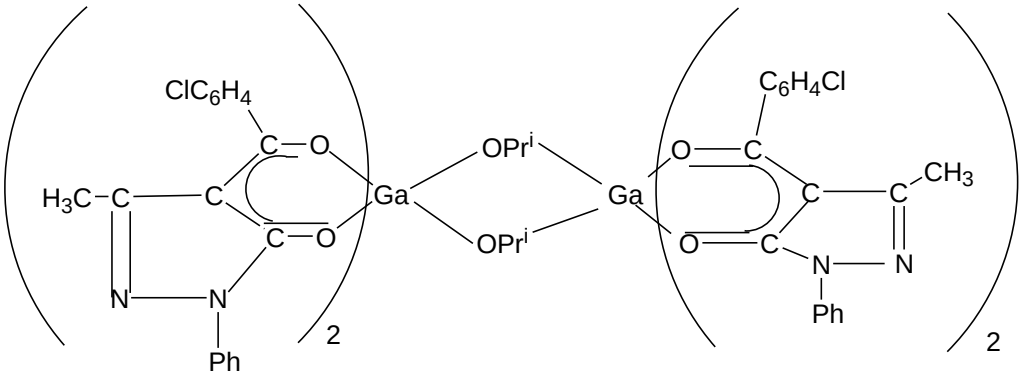

Figure 2

In view of dimeric nature, presence of two set of signals (bridging and terminal) of isopropoxy groupand monofunctional bidentate nature of ligand, the following structure (Fig-3) has been proposed for the derivatives (OPr^i)$_2$ Ga(CMPPO)-

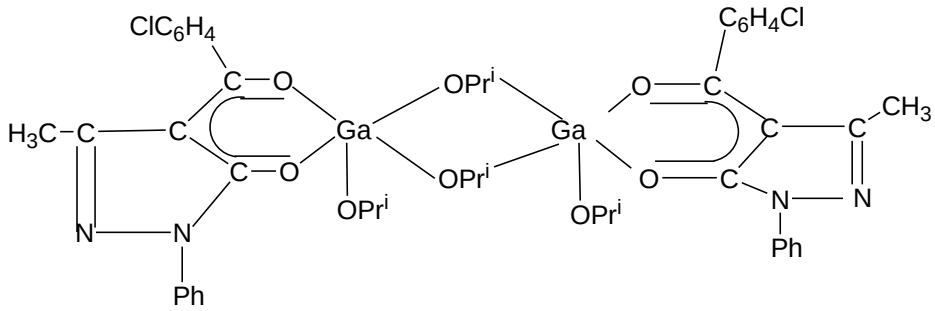

Figure 3

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Conflict of Interest: None Declared

Table 1: Synthetic and analytical data of $Ga(OPr^i)_{3-n}$ $(OPPMC)_n$ complexes

S.No	Compound (Yield %)	Colour/ Physical State (mp °C)	Reactants g(mmol)			%Analysis found (Calcd.)				Molecular weight found (calcd)
			$Ga(OPr^i)_3$	LH	Molar ratio	C	H	N	Ga	
1	$Ga(OPr^i)_2[OC(ClC_6H_4)C:CON(Ph)N:CCH_3]$ (90)	Light brown / solid (135)	0.59 (8.46)	0.75 (8.27)	1:1	26.92 (27.08)	30.90 (30.86)	2.60 (2.74)	13.82 (13.92)	1020 (499.2)
2.	$Ga(OPr^i)[OC(ClC_6H_4)C:CON(Ph)N:CCH_3]_2$ (88)	Light yellow / solid (165)	0.62 (8.89)	1.57 (7.05)	1:2	28.98 (29.16)	2.08 (2.05)	1.70 (1.83)	9.08 (9.27)	1524 (751.7)
3.	$Ga[OC(ClC_6H_4)C:CON(Ph)N:CCH_3]_3$ (89)	Light yellow / solid (189)	0.52 (7..45)	1.98 (6.52) p-C_6H_4Cl	1:3	57.60 (57.78)	3.48 (3.42)	2.40 (2.64)	6.86 (6.94)	1060 (1004.2)

Table 2: I. R and ^{1}HNMR data of complexes $Ga(OPr^i)_{3-n}$ $(OPPMC)_n$

S.No	Compound	I. R. (cm^{-1})					^{1}HNMR (ppm)		
		ν C⋯O	ν C—O Terminal	ν C—O bridging	ν Ga—O	CH_3 (Ligand)	Phenyl protons	Gem dimethyl (isopropoxy)	-CH (isopropoxy)
1	$Ga(OPr^i)_2[OC(ClC_6H_4)C:CON(Ph)N:CCH_3]$	1500m	1180m 1130m	980w	440m, 660m, 710m	1.8s	7.2-7.9m	1.3, 0.9d	3.6-4.2b
2.	$Ga(OPr^i)[OC(ClC_6H_4)C:CON(Ph)N:CCH_3]_2$	1505m	1180m 1130m	980w	440m, 670m, 700m	1.8s	7.2-7.9m	1.2d	3.4-4.0b
3.	$Ga[OC(ClC_6H_4)C:CON(Ph)N:CCH_3]_3$	1490m	-	-	445m, 670m, 710m	1.8s	7.2-7.9m	-	-