Synthesis and Spectral Studies of Some Magnesium Complexes of Aromatic Hydrazones

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Abstract. Six esters were synthesized from their parent acids, while their corresponding hydrazides were subsequently synthesized from these esters. The hydrazides, on reaction with benzaldehyde, produced their respective hydrazones, namely, benzoic hydrazone (***BH***), *m*-nitrobenzoic hydrazone (***m*-NBH**), *p*-nitrobenzoic hydrazone (***p*-NBH**), 3,5-dinitrobenzoic hydrazone (**3,5-DNBH**), *m*-aminobenzoic hydrazone (***m*-ABH**), and *p*-aminobenzoic hydrazone (***p*-ABH**). These hydrazones, on interaction with magnesium chloride yielded their corresponding magnesium complexes. These complexes were off-white, grey or brownish in colour. These complexes were characterized on the basis of spectral data and metal analysis. Metal to ligand stoichiometry of 1 : 3/2 and 1 : 5/2 has been proposed for the complexes. The relevant infrared bands in the ligands and complexes were used to assign the probable point(s) of coordination.

Keywords: aromatic hydrazones, magnesium complexes, benzoic hydrazones, magnesium hydrazones, magnesium-hydrazone complex

Introduction

The magnesium ion is an essential component of all living systems. It plays a structural role in bones and teeth. More importantly, magnesium ion is involved in a variety of cellular biochemical processes (Skauge *et al.*, 2002; Lee, 1996; Cotton and Wilkinson, 1989). The properties of hydrazones have attracted considerable interest owing to their biological activity and application as analytical reagents (Baldini *et al.*, 2004; Chohan *et al.*, 2004; Kasuga *et al.*, 2003; Khan *et al.*, 2002; Rashid and Khan, 2002; Bacchi *et al.*, 1998; RuWen *et al.*, 1992; Pandey, 1986).

Studies have shown that the incorporation of different metals into the hydrazone moiety enhances their biological activities and or industrial applications (Padhye *et al.*, 2005; Nomiya *et al.*, 2004; Gokhale *et al.*, 2003; Li *et al.*, 2000; RuWen *et al.*, 1992; Fazlic *et al.*, 1991; Obadovic *et al.*, 1990).

No work has yet been reported on magnesium hydrazone complexes, which formed the basis of the present study. The synthesis and spectral studies of magnesium complexes of some new hydrazones is reported in this communication.

Materials and Methods

Chemicals and reagents. Analytical grade reagents and solvents were used (Aldrich and Fluka Chemicals).

Synthesis of ligands. The esters were first synthesized from their parent acids, while the hydrazides were subsequently synthesized from the respective esters following the methods reported earlier (Bacchi *et al.*, 1998; Adeniyi and Patel, 1993; RuWen *et al.*, 1992; Bontchev *et al.*, 1981; Vogel, 1978; Yale *et al.*, 1953).

Hydrazones. Equimolar mixtures (0.05 moles) of benzaldehyde and the respective previously synthesized hydrazides, with few drops of concentrated hydrochloric acid in 25 ml ethanol, were heated under reflux for 2 h. After cooling, water was added to the reaction mixture, filtered and dried to yield the corresponding hydrazones (Rashid and Khan, 2002; Turan-Zitouni *et al.*, 1997; Kamitori *et al.*, 1988; Pandey, 1986). The reactions are summarized by the following general equation:

$$Ph\text{-}CHO + Ph'CONHNH_2 \rightarrow PhCH=NHCOPh' + H_2O$$
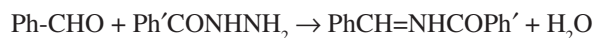
where:

Ph = C_6H_5; Ph′ = C_6H_5 (benzoic hydrazone; **BH**)

Ph = C_6H_5; Ph′ = *m*-$NO_2C_6H_4$ (*m*-nitrobenzoic hydrazone; ***m*-NBH**)

Ph = C_6H_5; Ph′ = *p*-$NO_2C_6H_4$ (*p*-nitrobenzoic hydrazone; ***p*-NBH**)

Ph = C_6H_5; Ph′ = 3,5-($NO_2)_2C_6H_3$ (3,5-dinitrobenzoic hydrazone; **3,5-DNBH**)

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Ph = C_6H_5; Ph′ = m-$NH_2C_6H_4$ (m-aminobenzoic hydrazone; **m-ABH**)

Ph = C_6H_5 ; Ph′ = p-$NH_2C_6H_4$ (p-aminobenzoic hydrazone; **p-ABH**)

Preparation of complexes. *Complex [Mg(BH)$_{3/2}$]Cl$_2$.5H$_2$O.*
Magnesium complex of benzoic hydrazone was prepared by stirring 0.5 g (2.3 mmol) benzoic hydrazone with 0.454 g (2.3 mmol) $MgCl_2.6H_2O$ in 40 ml methanol for 16 h on Griffin Minimag magnetic stirrer. The mixture was then refluxed for 2 h. An off-white precipitate was formed on cooling, which was filtered, washed thoroughly with methanol and dried in vacuum over silica gel (Adeniyi and Patel, 1999; 1993).

Complex [Mg(m-NBH$_{5/2}$]Cl$_2$.H$_2$O. Magnesium complex of *meta*-nitrobenzoic hydrazone was prepared by stirring 0.5 g (1.9 mmol) m-nitrobenzoic hydrazone with 0.4 g (1.9 mmol) $MgCl_2.6H_2O$ in 40 ml methanol for 5 h on a magnetic stirrer. After this period, the mixture was refluxed for 2 h and a grey precipitate was formed on cooling. The solid was washed with methanol and dried over silica gel in a desiccator (Turan-Zitouni *et al*., 1997; Obadovic *et al*., 1990).

Complex [Mg(p-NBH)$_{5/2}$]Cl$_2$.H$_2$O. Magnesium complex of p-nitrobenzoic hydrazone was prepared by the same method as adopted for *[Mg(m-NBH)$_{05/2}$]Cl$_2$.H$_2$O*, but instead of m-, p-nitrobenzoic hydrazone was used. The resultant mixture was then refluxed for 2 h and a light brown precipitate appeared on cooling. The precipitate was washed and dried as before (Pandey, 1986).

Complex [Mg(3,5-DNBH)$_{3/2}$]Cl$_2$.4H$_2$O. This complex was prepared by stirring 0.5 g (1.6 mmol) 3,5- dinitrobenzoic hydrazone with 0.32 g (1.6 mmol) $MgCl_2.6H_2O$ in 40 ml of methanol for 5 h. The mixture was then refluxed for 2 h. A dark brown precipitate was formed on cooling. The precipitate was washed several times with methanol and dried over silica gel (Nawar and Hosny, 1999; Adeniyi and Patel, 1993; Pandey, 1986).

Complex [Mg(m-ABH)$_{3/2}$]Cl$_2$.H$_2$O. For the synthesis of this complex, 0.45 g (1.87 mmol) m-aminobenzoic hydrazone was stirred with 0.4 g (1.87 mmol) $MgCl_2.6H_2O$ in 40 ml methanol for 5 h. At the end of this period, the mixture was refluxed for 2 h. A brown precipitate formed on cooling. This precipitate was washed with methanol and dried as before (Kasuga *et al*., 2003; Adeniyi and Patel, 1999).

Complex [Mg(p-ABH)$_{3/2}$]Cl$_2$.H$_2$O. Magnesium complex of p-aminobenzoic hydrazone was prepared by stirring 0.023 g (0.1 mmol) p-aminobenzoic hydrazone with 0.019 g (0.1 mmol) $MgCl_2.6H_20$ in 40 ml methanol for 5 h, and refluxed for 2 h. This was allowed to stand for 3 months, after which

period brown precipitate was formed. The precipitate was filtered, washed with methanol, and dried in vacuum over silica gel (Adeniyi and Patel, 1993).

Physicochemical measurements. The melting/decomposing temperatures of the ligands and complexes were determined using a calibrated Griffin melting point apparatus. The results are shown in Tables 1 and 2.

Magnesium was determined by EDTA titrations, after digesting with concentrated nitric acid. Eriochrome black T was used as the indicator (Vogel and Basset, 1980).

The solubilities of the ligands and complexes were carried out in water, *n*-hexane, ethanol, methanol, acetone, petroleum ether and trichloromethane.

The infrared spectra of the ligands and complexes were obtained using KBr pellets in the range 4000-500 cm^{-1} on a Buck Scientific M 500 infrared spectrometer. The relevant spectral data are listed in Table 3.

Results and Discussion

The melting/decomposition temperatures and colour of the hydrazones are presented in Table 1. The melting points ranged between 98-206 °C. The compounds were mostly whitish, yellowish or brown in colour. These observations are in good agreement with the properties of similar hydrazones reported earlier (RuWen *et al*., 1992; Pandey, 1986). The ligands were insoluble in water and generally found to have poor solubilities in the organic solvents used. However, **m-NBH**, **p-NBH**, **p-ABH** and **m-ABH** were soluble in ethanol, whereas **3,5-DNBH**, **m-ABH** and **p-ABH** were soluble in methanol, while **3,5-DNBH** and **p-ABH** were also soluble in acetone.

The complexes were mostly brown (Table 2), however, [Mg(BH)$_{3/2}$]Cl$_2$.5H$_2$O was off-white and [Mg(m-NBH)$_{5/2}$]

Table 1. Physical data of the ligands

Ligand	Formula	m.p. (°C)	Colour
BH	$C_{14}H_{12}N_2O$	198-200	white
***m*-NBH**	$C_{14}H_{11}N_3O_3$	180-182	off-white
***p*-NBH**	$C_{14}H_{11}N_3O_3$	210-212	light yellow
3,5-DNBH	$C_{14}H_{10}N_4O_5$	200-202	deep yellow
***m*-ABH**	$C_{14}H_{13}N_3O$	98-100	light brown
***p*-ABH**	$C_{14}H_{13}N_3O$	204-206	light yellow

m.p. = melting point; **BH** = benzoic hydrazone; ***m*-NBH** = *m*-nitrobenzoic hydrazone; ***p*-NBH** = *p*-nitrobenzoic hydrazone; **3,5-DNBH** = 3,5-dinitrobenzoic hydrazone; ***m*-ABH** = *m*-aminobenzoic hydrazone; ***p*-ABH** = *p*-aminobenzoic hydrazone

$Cl_2.H_2O$ was grey. The formation of coloured complexes by magnesium, a non-transition element (Cotton and Wilkinson, 1989), has been reported for magnesium hydrazide complexes (Adeniyi and Patel, 1999). The complexes had sharp melting points between 130 °C and 300 °C.

The complexes were insoluble in water and showed poor solubilities in organic solvents except [Mg(**m-ABH**)$_{3/2}$] $Cl_2.H_2O$ and [Mg(**p-ABH**)$_{3/2}$]$Cl_2.H_2O$, which were soluble in ethanol, methanol and acetone. Poor solubilities have been reported for magnesium hydrazide complexes (Adeniyi and Patel, 1999), and may be taken as an indication of polymerization (Nomiya *et al*., 2004; Kasuga *et al.,* 2003; Fazlic *et al*., 1991).

As shown in Table 2, reactions involving 1:1 metal to ligand ratios gave complexes having 1:3/2 and 1:5/2 metal to ligand stoichiometries. Similar metal to ligand stoichiometries have been earlier reported for cadmium and magnesium dihydrazide complexes (Adeniyi and Patel, 1999; 1993). These metal to ligand stoichiometries further amplify the proposed polymeric nature of these complexes.

The infrared spectra of the complexes, as compared to those of the free ligands (Table 3) revealed strong and weak absorption peaks in the range 3441-3697 cm^{-1}, which have been attributed to ν OH vibrations (Li *et al*., 2000).

The bands around 1652-1697 cm^{-1} were assigned to ν C=O in the complexes and ligands. In [Mg (**BH**)$_{3/2}$]$Cl_2.5H_2O$, there was a shift to lower frequency from 1697 cm^{-1} in the ligand (**BH**) to 1652 cm^{-1} in the complex (Table 3). This shift to lower frequency suggests that the carbonyl group was involved in the bonding (Adeniyi and Patel, 1999; Nawar *et al*., 1999). However, the C=O band shifted to higher frequencies in [Mg (**m-NBH**)$_{5/2}$]$Cl_2.H_2O$, [Mg(**3,5-DNBH**)$_{3/2}$]$Cl_2.4H_2O$, [Mg(**p-ABH**)$_{3/2}$]$Cl_2.2H_2O$, and [Mg(**m-ABH**)$_{3/2}$]$Cl_2.H_2O$, whereas the frequency of the complex [Mg(**p-NBH**)$_{5/2}$]$Cl_2.H_2O$ remained

Table 2. Physical data of the magnesium complexes of aromatic hydrazones

Complex*	Formula	Mg** (%)	m.p. (°C)	Colour
[Mg(**BH**)$_{3/2}$]$Cl_2.5H_2O$	$MgC_{21}H_{20}N_3O_{6.5}Cl_2$	4.60 (4.73)	202-204	off- white
[Mg(**m-NBH**)$_{5/2}$]$Cl_2.H_2O$	$MgC_{35}H_{29.5}N_{7.5}O_{8.5}Cl_2$	3.10 (3.09)	320-322	grey
[Mg(**p-NBH**)$_{5/2}$]$Cl_2.H_2O$	$MgC_{35}H_{29.5}N_{7.5}O_{8.5}Cl_2$	3.08 (3.09)	298-300	light brown
[Mg(**3,5-DNBH**)$_{3/2}$]$Cl_2.4H_2O$	$MgC_{21}H_{23}N_6O_{11.5}Cl_2$	3.83 (3.81)	178-180	dark brown
[Mg(**p-ABH**)$_{3/2}$]$Cl_2.2H_2O$	$MgC_{21}H_{23.5}N_{4.5}O_{3.5}Cl_2$	4.95 (4.96)	130-132	brown
[Mg(**m-ABH**)$_{3/2}$]$Cl_2.H_2O$	$MgC_{21}H_{21.5}N_{4.5}O_{2.5}Cl_2$	5.26 (5.15)	188-190	brown

* = refer Table 1 for nomenclature of the ligands; ** = figures in parentheses are the calculated values; m.p. = melting point

Table 3. Relevant IR data (cm^{-1}) of the ligands and magnesium complexes of aromatic hydrazones

Ligands/complexes*	ν OH	ν C=O	ν CN	ν C=N	δ NH
BH	3667 s	1697 s	1646 s	1554 s	1530 m
[Mg(**BH**)$_{3/2}$]$Cl_2.5H_2O$	3667 s	1652 s	1636 s	1549 s	1530 m
m-NBH	3621 w	1675 s	1621 s	1576 s	1534 s
[Mg(**m-NBH**)$_{5/2}$]$Cl_2.H_2O$	3530 w	1697 s	1621m	1561 s	1534 s
p-NBH	2667 w	1697 s	1614 s	1598 s	1524 w
[Mg(**p-NBH**)$_{5/2}$]$Cl_2.H_2O$	3516 s	1697 m	1656 m	1559 s	1524 w
3,5-DNBH	3682 s	1682 m	1621 m	1591 w	1534 m
[Mg(**3,5-DNBH**)]$Cl_2.4H_2O$	3697 s	1697 s	1606 w	1584 s	1546 m
m-ABH	3616 w	1691 s	1602 m	1559 s	1515 m
[Mg(**m-ABH**)]$Cl_2.H_2O$	3667 w	1697 s	1652 m	1546 s	1515 m
p-ABH	3441 w	1695 s	1617 m	1583 m	1514 m
[Mg(**p-ABH**)$_{3/2}$]$Cl_2.2H_2O$	3667 w	1697 s	1656 m	1546 s	1560 m

* = refer Table 1 for nomenclature of the ligands; s, m, w = respectively, strong, medium, weak

unchanged as compared to the frequency of the ligand (**p-NBH**) (Table 3). These observations suggest that the carbonyl oxygen was not involved in coordination in these complexes (Chohan *et al.*, 2004; Li *et al.,* 2000; Adeniyi and Patel, 1993).

It may be noted from Table 3 that the bands between 1602-1646 cm^{-1} in the ligands due to ν CN shifted to lower frequencies in [Mg(**BH**)$_{3/2}$] Cl$_2$.H$_2$O and [Mg(**3,5-DNBH**)$_{3/2}$]Cl$_2$.4H$_2$O indicating CN coordination, but remained unchanged in the complex [Mg(**m-NBH**)$_{5/2}$]Cl$_2$.H$_2$O, and shifted to higher frequencies in the remaining complexes. This shows that the C-N nitrogen was not involved in binding to magnesium (Chohan *et al.*, 2004; Turan-Zitouni *et al.*, 1997; Obadovic *et al.*, 1990).

In the IR spectra of the ligands and their complexes, the strong absorption bands ranging from 1554-1598 cm^{-1}, assigned to ν C=N (Chohan *et al.*, 2004; Li *et al.*, 2000), shifted to lower frequencies by 5-39 cm^{-1}. This shows that in the C=N bond, nitrogen atom binds to the metal ion (Mg).

The bands in the ligands between 1514-1534 cm^{-1}, due to the deformation NH, remained either unchanged or shifted to higher frequencies in the complexes suggesting that the NH group was not involved in bonding in the complexes (Nomiya *et al.*, 2004; Kasuga *et al.*, 2003; Turan-Zitouni *et al.*, 1997; Fazlic *et al.*, 1991).

The structural deductions for the complexes (Table 2) are tentative pending future X-ray structural studies.

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