Transition Metal Chemistry **29**: 916–920, 2004.

Interaction of manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) with acetylhydrazine, formed *in situ*; first crystal structure of tris(acetylhydrazine) nickel(II) perchlorate

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Received 17 June 2004; accepted 28 June 2004

Abstract

A series of transition metal complexes of the type $[M(ah)_3](ClO_4)_2$ *(1–6)* [$M = Mn^{II}$, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}, ah = acetylhydrazine] have been prepared by the reaction of $M(ClO_4)_2 \cdot 6H_2O$ with acetylhydrazine formed *in situ* by the reaction of hydrazine hydrate and acetylsalicylic acid methyl ester. The chelating behaviour of acetylhydrazine and overall geometry of these complexes have been spectroscopically investigated by means of FT-IR, ^{1}H-n.m.r. and electronic spectral techniques, as well as by elemental analysis data, molar conductance values and magnetic susceptibility measurements. Single X-ray structure determination of complex *(4)* revealed three acetylhydrazine ligands coordinated to nickel ion in a bidentate manner maintaining an octahedral environment. In all other complexes too, an octahedral geometry has been proposed on the basis of results obtained by various physico-chemical studies.

Introduction

Studies on the reactivity of functionally substituted hydrazines have immense value since they have long been proposed to exhibit a plethora of biological activities [1–6]. The coordination chemistry of hydrazine and substituted hydrazines [7–9] presents some aspects of interest, including the influence that the ancillary ligands and central metal may have in determining the different coordination modes *i.e.* η^1, η^2, μ *etc.* of the hydrazine ligand and understanding of the properties that coordination to a metal fragment may induce on an NH_2NH_2 or $RNHNH_2$ molecule towards reduction, oxidation and deprotonation reactions.

Interest in the mode of action of certain *N*-acylhydrazines as antitubercular drugs, particularly *N*-isonicotinoylhydrazine (inh) [2, 10, 11], has prompted investigations on the complexing ability of these compounds [11–13]. However, the study of inh complexes is complicated by the presence of a third potential coordination site where, the heterocyclic nitrogen atom may lead to the formation of polymeric complex [12].

In view of the fact that there has been no evidence of tuberculostatic activity of acetylhydrazine, attempts were directed to study the pharmacological and antimicrobial activities in some derivatives of acetylhydrazine *viz*; the hydrazone of [(2-benzothiazolylthio)acetyl]hydrazine possesses antimicrobial activity [14], *N*,*N*′-diphenyl-*N*,*N*′-bis[(acetylthioacetyl)]hydrazine acts as an anticataract agent and shows antioxidant and sulphide-reducing effects [15] and N-1-8 (4-bromo-3-methylphenyl)-2-[2-(5-(2,3-dichlorophenyl)-2H-1,2,3,4-tetraazol-2yl)acetyl]hydrazine-1-carbothioamide and analogs bind with CD4 which have been reported [16] to inhibit HIV infection. The chelating behaviour of acetylhydrazine has been studied by several groups of workers and some complexes of acetylhydrazine with transition metals and/or rare earth metals have been reported [17–28] describing their basic synthetic details and analysis of i.r. and u.v.-vis spectra.

Recently, scientists have begun exploring the use of nickel(II) complexes with amide ligands [29] in view of the fact that nickel(II) complexes with several oligopeptide ligands cause DNA cleavage in the presence of oxidants [30–33], in some instances with sequence selectivity [31, 33]. Thus the design of biologically active coordination compounds needs knowledge about the complexing behaviour of the ligand system. The development of acetylhydrazine chemistry is of particular significance because the ligand bears some structural resemblance to amino acids.

All the above facts encouraged us to synthesize transition metal complexes of acetylhydrazine, anticipating their expected interesting biological activities. The ligand, acetylhydrazine, formed ‘*in situ*’ by reacting hydrazine hydrate and acetylsalicylic acid methyl ester, selectively chelates first row transition metal ions. The present communication gives the synthesis and physicochemical studies of the complexes of the type $[M(ah)_3](ClO_4)_2$ [M = Mn , Fe , Co, Ni, Cu and Zn; ah = acetylhydrazine] and the first X-ray crystal structure of, $[Ni(ah)_3](ClO_4)_2$.

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Experimental

Materials and methods

The metal salts $M(ClO_4)_2 \cdot 6H_2O$ (all Aldrich) were commercially pure samples. Acetylhydrazine was synthesized by the stoichiometric reaction between hydrazine hydrate (Sigma) and acetylsalicylic acid methyl ester (TCI, Tokyo). The solvent MeOH (AR grade) was used without further purification.

Synthesis of Mononuclear $[M(ah)_3](ClO_4)_2$ (1–6) Complexes

Caution: Perchlorate salts of metal complexes are potentially explosive and should be handled in small quantities. However, we worked with these perchlorate salts without any incident.

A MeOH solution (10 cm^3) of hydrazine hydrate (0.3 mmol) was mixed with 0.3 mmol of acetylsalicylic acid methyl ester in MeOH (10 cm^3) and stirred for *ca.* 1 h at room temperature, followed by the addition of 0.1 mmol of $M(ClO_4)_2 \cdot 6H_2O$ [M = Mn^{II} , Fe^{II} , Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}] dissolved in MeOH (5 cm^3). The reaction mixture was refluxed and stirred for *ca.* 6 h. The resulting solution was allowed to stand at room temperature for about a week, leading to the isolation of microcrystalline solids for manganese(II), iron(II), cobalt(II), copper(II) and zinc(II). However good quality single crystals were obtained only for nickel(II).

The elemental analyses were obtained from the microanalytical laboratory of CDRI, Lucknow, India. The FT-IR spectra (4000–200 cm^{-1}) were recorded as CsCl discs on a Perkin-Elmer 2400 spectrophotometer. The ^{1}H-n.m.r. spectra were recorded on a Jeol Eclipse 400 NMR spectrometer in DMSO-d_6. Metals and chlorides were determined volumetrically [34] and gravimetrically [35], respectively. The electronic spectra of the complexes in DMSO were recorded on a Pye-Unicam 8800 spectrophotometer at room temperature. Magnetic susceptibility measurements were carried out using a Faraday balance at 25 °C. The electrical conductivities of 10^{-3} M solutions in DMSO were obtained on a digital APX 185 conductivity bridge equilibrated at 25 ± 0.01 °C.

Crystals of the complex *(4)* were obtained from MeOH solution. A blue prismatic crystal having approximate dimensions $0.20 \times 0.20 \times 0.20$ mm was mounted on a glass fibre. All measurements were made on a Rigaku AF C7R diffractometer with graphite monochromated radiation. The structure was solved by heavy atom Patterson methods, expanded using Fourier techniques, and refined on *F* by full matrix least square. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. Intensity data were corrected for Lorenz and polarization.

Results and discussion

A series of mononuclear complexes of the type, $[M(ah)_3](ClO_4)_2$ [M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, ah = acetylhydrazine] have been prepared by the reaction of $M(ClO_4)_2 \cdot 6H_2O$ with acetylhydrazine formed '*in situ*'.

It is well known that the acetylation of hydrazine leads to the formation of acid hydrazide [1, 24, 36, 37] as shown below:

$$RCOOR + NH_2{-}NH_2 \longrightarrow RCONH \cdot NH_2 + ROH$$

Therefore, it is apparent that possibly the following reaction takes place while reacting acetylsalicylic acid methyl ester and hydrazine hydrate

$$(Me)OCOC_6H_4CO(OMe) + N_2H_4 \cdot H_2O \longrightarrow (HO)C_6H_4CO(OMe) + NH_2NH \cdot COMe$$

The acetylhydrazine thus formed selectively chelates with first row transition metal ions resulting in the formation of complexes having the proposed composition $[M(ah)_3](ClO_4)_2$. It may be visualised from this type of reaction the possibility of having different derivatives or even it may give a method for synthesis of salicylic acid itself.

The analytical data of all the complexes (Table 1) agree well with the proposed composition. The molar conductance values (Table 1) measured in DMSO (10^{-3} M) are indicative [38] of the 1:2 electrolyte nature of the complexes. All the complexes are stable in the atmosphere and do not decompose until their melting point. They are soluble in DMSO, H_2O, MeOH, and MeCN.

I.r. spectra

The major i.r. spectral features of the complexes *(1–6)* are listed in Table 2. I.r. spectra show bands characteristic of $[\upsilon(N{-}H)]$ and $[\delta(NH_2)]$ of the $NHNH_2$ group of acetylhydrazine moiety (Table 2) whose position correspond to that reported earlier [7] suggesting coordination of the NH_2 group. The lowering in the position of these bands may possibly be due to intramolecular hydrogen bonding ($N_{22b} \ldots O_{11}, N_{12b} \ldots \ldots O_{22}$). A sharp band appearing at *ca.* 398–415 cm^{-1} corresponds to $\nu(M{-}N)$ vibration [39]. A drop in the $\nu(CO)$ carbonyl stretching frequency (1630–1655 cm^{-1}) shows the carbonyl oxygen to be the donor site in these complexes [7]. The presence of a distinct $\nu(M{-}O)$ band (510–528 cm^{-1}) gives additional support [40] to the above conclusion. Strong intensity bands appearing at *ca.* 985–1004 cm^{-1} may be ascribed to the $\nu(N{-}N)$ vibration [40]. The absorption bands appearing in the 2921–2950 cm^{-1} region correspond to $\nu(C{-}H)$ stretching modes of acetyl $-CH_3$ group [6]. All the complexes show medium intensity bands in the 1085–1112 and 932–948 cm^{-1} regions which may reasonably be assigned to perchlorate $(ClO_4)^{-2}$ vibration modes [41].

Table 1. Yield (%), colour, molar conductance and analytical data for the compounds

Complex	Yield (%)	Color	Found (calcd.)%					Molar conductivity
			M	Cl	C	H	N	(Ω^{-1} cm^{-2} mol^{-1})
$[Mn(ah)_3]$ $(ClO_4)_2$ *(1)*	35	pale pink	11.5	14.9	15.1	3.8	17.6	96
			(11.5)	(14.9)	(15.1)	(3.8)	(17.65)	
$[Fe(ah)_3]$ $(ClO_4)_2$ *(2)*	51	brown	11.7	14.8	15.1	3.8	17.6	118
			(11.7)	(14.9)	(15.1)	(3.8)	(17.6)	
$[Co(ah)_3]$ $(ClO_4)_2$ *(3)*	43	pink	12.3	14.75	15.0	3.75	17.5	116
			(12.3)	(14.8)	(15.0)	(3.8)	(17.5)	
$[Ni(ah)_3]$ $(ClO_4)_2$ *(4)*	41.2	blue	12.2	14.75	15.0	3.8	17.5	108
			(12.2)	(14.8)	(15.0)	(3.8)	(17.5)	
$[Cu(ah)_3]$ $(ClO_4)_2$ *(5)*	38	green	13.1	14.6	14.85	3.7	17.3	103
			(13.1)	(14.6)	(14.9)	(3.7)	(17.3)	
$[Zn(ah)_3]$ $(ClO_4)_2$ *(6)*	53	colourless	13.4	14.55	14.8	3.7	17.25	112
			(13.4)	(14.6)	(14.8)	(3.7)	(17.3)	

^{1}H-n.m.r spectra

The ^{1}H-n.m.r. spectrum of the Zn complex *(6)* shows a triplet at 6.18 p.p.m. (3H, NH) and a doublet at 6.58 p.p.m. (6H, NH_2) corresponding [7] to the $NHNH_2$ group of the acetylhydrazine ligand. However, the NH_2 signal is downfield shifted possibly due to the involvement of two of the NH_2 groups in intramolecular hydrogen bonding (N_{22b} …… O_{11}, N_{12b}……O_{22}). The presence of a singlet at 1.98 p.p.m. may be attributed [6, 42] to the methyl protons (9H, $\text{—}CH_3CO$) of the acetyl group.

Electronic spectra

Further confirmation regarding the overall geometry of these complexes has been obtained from magnetic susceptibility measurements and electronic spectral studies (Table 3).

The observed magnetic moment 5.88 B.M. for manganese(II) corresponds to a high spin octahedral d^5 system. The observed ligand field transitions at 22,738 and 18,679, designated for $^6A_{1g} \rightarrow {}^4T_{2g}$ and $^6A_{1g} \rightarrow {}^4T_{1g}$ transitions, further support the octahedral geometry of $[Mn(ah)_3](ClO_4)_2$ [43].

A weak intensity band in the electronic spectrum of iron(II) at 11,659 cm^{-1} assigned to $^5T_{2g} \rightarrow {}^5E_g$ and the observed magnetic moment (Table 3) corresponds to high spin d^6 octahedral environment around iron(II) [43].

However the electronic spectrum of the cobalt(II) complex gave three bands at 21,000, 14,695 and 8100 which may be ascribed to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transitions respectively, consistent with an octahedral geometry around the cobalt(II) ion [43]. The magnetic moment of 5.20 B.M. complements the electronic spectral findings of $[Co(ah)_3](ClO_4)_2$.

The observed magnetic moment and bands observed in the spectrum for $[Ni(ah)_3](ClO_4)_2$ (Table 3) correspond to an octahedral environment around nickel(II) [43].

The electronic spectrum of the copper(II) complex exhibits a broad band centered at 19,462 cm^{-1} with a shoulder at 16,389 cm^{-1} which may be assigned to $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions, respectively consistent [43] with distorted octahedral environment around metal ion. The magnetic moment value of 1.77 B.M further corroborates the electronic spectral findings.

Single crystal structure of $[Ni\ (ah)_3](ClO_4)_2$ (4)

The X-ray analysis of the complex $[Ni(ah)_3](ClO_4)_2$ was undertaken to ascertain the mode of coordination of acetylhydrazine. The crystal structure revealed (Figure 1) that three acetylhydrazine ligands coordinates to the nickel(II) ion *via* their carbonyl oxygen and terminal amine nitrogen atoms forming five membered chelate rings.

Table 2. I.r. vibrational frequencies (cm^{-1}) of the complexes

Complex	ν(N—H)	δ(NH2)	ν(M—N)	ν(CO)	ν(M—O)	ν(N—N)	ν(CH)	Perchlorate $(ClO_4)_2^{2-}$ bands
$[Mn(ah)_3]$ $(ClO_4)_2$ *(1)*	3248, 3198	1575	398	1635	510	985	2921	1090, 932
$[Fe(ah)_3]$ $(ClO_4)_2$ *(2)*	3250, 3195	1578	412	1650	515	995	2945	1085, 937
$[Co(ah)_3]$ $(ClO_4)_2$ *(3)*	3255, 3210	1590	410	1655	525	1000	2940	1110, 940
$[Ni(ah)_3]$ $(ClO_4)_2$ *(4)*	3265, 3194	1580	415	1630	520	1004	2936	1112, 941
$[Cu(ah)_3]$ $(ClO_4)_2$ *(5)*	3260, 3208	1582	400	1648	528	998	2950	1089, 935
$[Zn(ah)_3]$ $(ClO_4)_2$ *(6)*	3253, 3200	1592	405	1645	518	989	2948	1095, 948

Table 3. Magnetic moments, electronic spectral data and assignments

Complex	μ_{eff} (B.M)	Band position (cm^{-1})	Assignments
[Mn(ah)$_3$] (ClO$_4$)$_2$ *(1)*	5.88	22,738	$^6A_{1g} \rightarrow {}^4T_{2g}$
		18,679	$^6A_{1g} \rightarrow {}^4T_{1g}$
[Fe(ah)$_3$] (ClO$_4$)$_2$ *(2)*	5.46	11,659	$^5T_{2g} \rightarrow {}^5E_g$
		21,000	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
		14,695	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
[Co(ah)$_3$] (ClO$_4$)$_2$ *(3)*	5.20	8,100	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
[Ni(ah)$_3$] (ClO$_4$)$_2$ *(4)*	3.02	27,338	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
		20,218	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
		11,220	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
[Cu(ah)$_3$] (ClO$_4$)$_2$ *(5)*	1.77	19,462	$^2B_{1g} \rightarrow {}^2E_g$
		16,389	$^2B_{1g} \rightarrow {}^2B_{2g}$

The triclinic unit cell consists of discrete cation $[Ni(ah)_3]^{2+}$ and $(ClO_4)_2^{2-}$ anions which reinforce packing through intramolecular hydrogen bonding. The N…O contacts extends between the two acetylhydrazine ligands and $(ClO_4)_2^{2-}$ anions *i.e.* O_{11}…N_{22b} and N_{12b}…O_{22}.

As shown in the Figure 1 the complex cation exhibits an octahedral environment with nickel(II) ion coordinated to three nitrogen atoms (N_{22b}, N_{12b}, N_{32b}) and three oxygen atoms (O_{22a}, O_{12a}, O_{32a}) of acetylhydrazine ligands.

Crystal data for [Ni(ah)$_3$](ClO$_4$)$_2$

Formula weight = 479.83, space group $= P1^{-}$, a (Å) = 10.480(3), b (Å) = 10.505(4), c (Å) = 9.750 (2), $\alpha(^\circ) = 105.16(3)$, $\beta(^\circ) = 106.72(2)$, $\gamma(^\circ) = 111.40(3)$, V (Å^3) = 872.5(6), $Z = 2$, F (000) = 492, $D_{\text{calcd.}} = 1.827$, T(K) = 293, μ(Mo$K\alpha$) (cm^{-1}) = 1.486, Scan rate (° min^{-1} in ω) = 16, 2θ range (°) = 3.0–55.0, number of reflections measured = 4317, number of unique reflections used ($I_0 > 2\sigma$ (I_c) (M) = 3558, variables (N) = 235, S = 1.055, max./min residual (e Å^{-3}) 0.697 /–0.673.

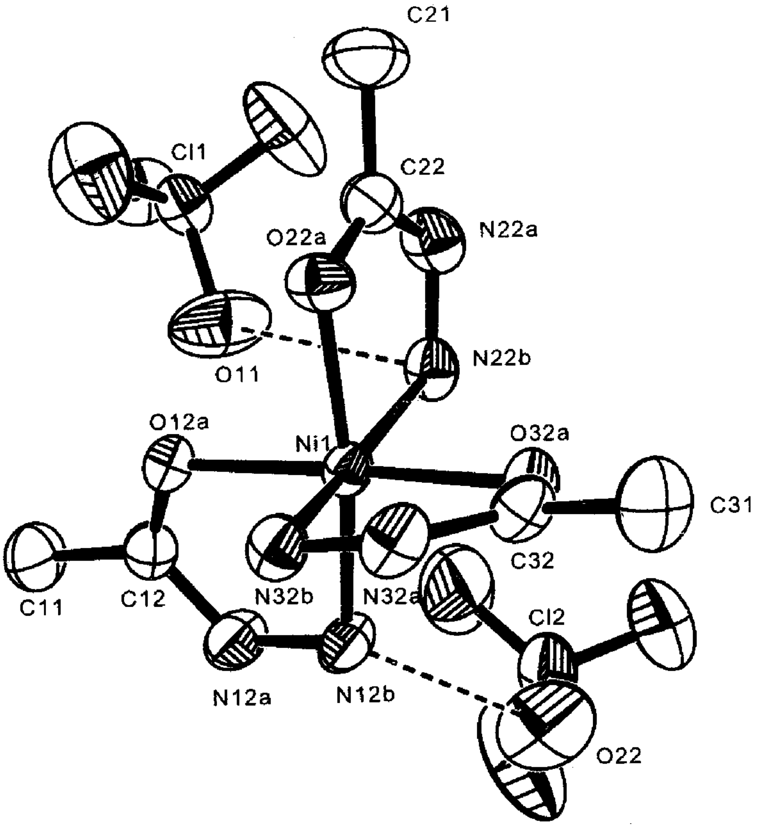

Fig. 1. An ORTEP drawing of [Ni(ah)$_3$](ClO$_4$)$_2$ with the numbering scheme.

Refinement based on $|F|$, converged at a final R value of 0.046 ($wR_2 = 0.137$) defined by $R = \Sigma\ (|F_0|-|F_c|)/\Sigma|F_0|$ and $wR_2 = [\Sigma w\ (|F_0|-|F_c|)^2/\Sigma w|F_0|^2]^{1/2}$.

Supplementary material

Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 IEZ, UK, quoting the deposition number 231108.

Acknowledgements

The chairman, Department of Chemistry, AMU is acknowledged for providing necessary facilities. The author, Prof. M. Shakir thanks the Daiko foundation, Japan for financial support.

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