

SHORT COMMUNICATIONS

SYNTHESIS OF NOVEL OXAZOLE AND ISOXAZOLE DERIVATIVES OF CHROMIUM(III)

Albert Chukwuemeka Ukwueze
Department of Chemistry, University of Lagos, Lagos, Nigeria

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ABSTRACT. The synthesis and characterization of new complexes of general formula CrX_3L_3 ($X = Cl, Br, I$; $L = 2,4$ -dimethyloxazole, 3,5-dimethylisoxazole, 3-methyl-5-nitroisoxazole, 2-methyl-5-nitrooxazole) have been reported. All the complexes are studied by chemical analysis, infrared, ultra-violet and proton resonance spectroscopy in order to provide information about the donor atom competition of the ligands and elucidate the coordination and structure of the complexes. Evidences indicate monodentate coordination through nitrogen atom, and distorted octahedral structures for all the complexes prepared.

INTRODUCTION

A considerable number of transition metal complexes with heterocyclic ligands in which the latter behave as monodentate N-bonded and sometimes bridging N-ring or O-ring-bonded have been investigated [1-5]. Such ligands include the following; 3-amino-5-methylisoxazole, 5-amino-3,4-dimethylisoxazole and 2,5-diphenyloxazole. In these investigations much attention was focused on establishing the stoichiometries of the complexes and the atom to atom connectivity of each complex. As far as reports indicate the effect which the substituents on the ligand have on the overall coordination chemistry of these complexes has not been explored. We have therefore undertaken this investigation in an attempt to verify the competition of the donor atoms, namely: N and O in the oxazole and isoxazole rings especially when electron-donating and electron-withdrawing substituents are present. The following ligands were used in forming complexes with chromium(III) halides: 2,4-dimethyloxazole (2,4-DMO), 3,5-dimethylisoxazole (3,5-DMI), 2-methyl-5-nitrooxazole (2,5-MNO) and 3-methyl-5-nitroisoxazole (3,5-MNI).

EXPERIMENTAL

Physical methods. The infrared spectra in the $4000 - 600 \text{ cm}^{-1}$ range were recorded on a Perkin-Elmer 257 spectrometer. The proton NMR were recorded on a Varian T60 spectrophotometer using TMS as external standard and $CDCl_3$ as solvent. The elemental analysis was carried out on a Perkin Elmer 240 microanalyzer.

Starting materials. The chromium(III) halides purchased from BDH chemicals were of analytical grade and were used without further purification. The ligands; 2,4-dimethyl-

oxazole (2,4-DMO), 3,5-dimethylisoxazole (3,5-DMI), 2-methyl-5-nitrooxazole (2,5-MNO), and 3-methyl-5-nitro-isoxazole (3,5-MNI) were also commercially available and used without further purification.

Complexes. Chromium(III) chloride was allowed to react with the corresponding ligand in 1:3 molar ratio using ethanol as solvent and under reflux for about 4 h. In most cases crystallization was not immediate and was induced by concentrating the reaction mixture. Other chromium(III) complexes were also prepared in a similar way. Results of elemental analysis were in satisfactory agreement with calculated values.

RESULTS AND DISCUSSION

The results of the analyses indicate that each of the 2,4-dimethyloxazole and 3,5-dimethylisoxazole chromium(III) complexes has two molecules of water of crystallization per mole while each of the 3-methyl-5-nitrooxazole and 3-methyl-5-nitroisoxazole has three molecules of water of crystallization per mole.

Table 1. Infrared spectral data of the chromium(III) complexes (cm^{-1}).

Complexes	$\nu_{\text{O-H}}$	$\nu_{\text{H-O-H}}$	$\nu_{\text{C-O-C}}$	$\nu_{\text{C=N}}$	$\nu_{\text{N=O}}$
$\text{CrCl}_3 \cdot (2,4\text{-DMO})_3 \cdot 2\text{H}_2\text{O}$	3420	1640	1082.815	1680	-
$\text{CrBr}_3 \cdot (2,4\text{-DMO})_3 \cdot 2\text{H}_2\text{O}$	3410	1635	1085.813	1680	-
$\text{CrCl}_3 \cdot (2,4\text{-DMO})_3 \cdot 2\text{H}_2\text{O}$	3400	1640	1083.815	1675	-
$\text{CrCl}_3 \cdot (3,5\text{-DMI})_3 \cdot 2\text{H}_2\text{O}$	3340	1620	1085.815	1680	-
$\text{CrBr}_3 \cdot (3,5\text{-DMI})_3 \cdot 2\text{H}_2\text{O}$	3340	1625	1085.812	1680	-
$\text{CrCl}_3 \cdot (3,5\text{-DMI})_3 \cdot 2\text{H}_2\text{O}$	3350	1620	1080.815	1670	-
$\text{CrCl}_3 \cdot (2,5\text{-MNO})_3 \cdot 3\text{H}_2\text{O}$	3230	1650	1083.813	1680	1560
$\text{CrBr}_3 \cdot (2,5\text{-MNO})_3 \cdot 3\text{H}_2\text{O}$	3250	1640	1082.815	1675	1555
$\text{CrCl}_3 \cdot (2,5\text{-MNO})_3 \cdot 3\text{H}_2\text{O}$	3240	1640	1085.815	1675	1560
$\text{CrCl}_3 \cdot (3,5\text{-MNI})_3 \cdot 3\text{H}_2\text{O}$	3360	1625	1083.812	1680	1550
$\text{CrBr}_3 \cdot (3,5\text{-MNI})_3 \cdot 3\text{H}_2\text{O}$	3350	1630	1085.810	1680	1560
$\text{CrCl}_3 \cdot (3,5\text{-MNI})_3 \cdot 3\text{H}_2\text{O}$	3350	1630	1085.812	1675	1560
2,4-DMO			1085.815	1660	-
3,5-DMI			-	1660	-
2,5-MNO			1085.815	1660	1560
3,5-MNI			-	1660	1560

Infrared evidence. All the complexes contain water of crystallization and this is shown by the absorption vibrational modes for $\nu_{\text{(OH)}}$ at 3420 cm^{-1} and $\nu_{\text{(H-O-H)}}$ at $1650 - 1620 \text{ cm}^{-1}$ regions. The $\nu_{\text{(C-O-C)}}$ in the free ligands, i.e. 2-methyl-5-nitrooxazole and 3-methyl-5-nitroisoxazole occur at 1085 cm^{-1} and 815 cm^{-1} for the asymmetric and symmetric vibrations, respectively. In the chromium(III) complexes with these ligands there is no appreciable shift in the $\nu_{\text{(C-O-C)}}$ absorption frequencies. This indicates that the C-O-C groups in these free ligands are the same as in the complexes, implying that the oxygen atom is not coordinated to chromium(III). As Table 2 indicates, blue shifts of $ca 20 \text{ cm}^{-1}$ are

apparent in the infrared spectra of the complexes for the $\nu_{(C=N)}$ absorptions. This is as a result of the drift of electrons from the ligands through the nitrogen atom to chromium(III). A comparison of the infrared spectra of chromium(III) complexes with those of 2-methyl-5-nitrooxazole and 3-methyl-5-nitroisoxazole shows that the $\nu_{(O-N=O)}$ stretching vibrations remain insignificantly unchanged at the 1650 cm^{-1} and 1620 cm^{-1} regions indicating that the nitro group is not involved in bonding with chromium(III) in the complexes. From these results and the spectroscopic and analytical data, reactions 1-4 are presumed to have occurred.

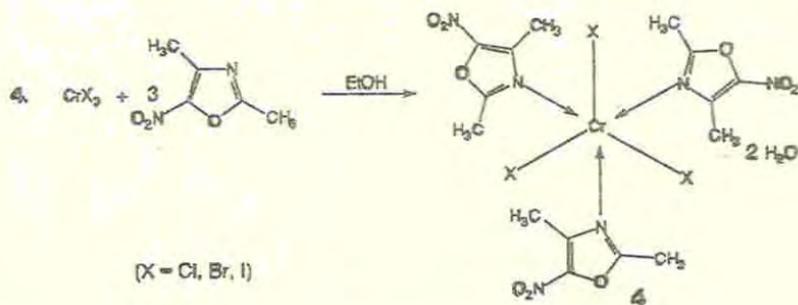
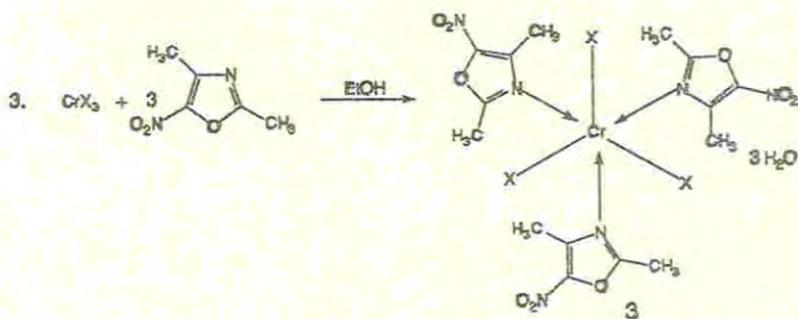
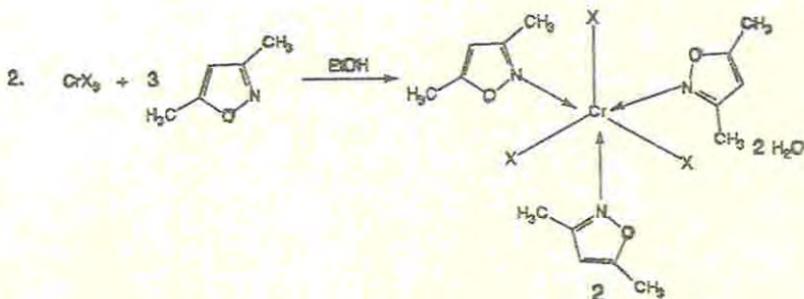
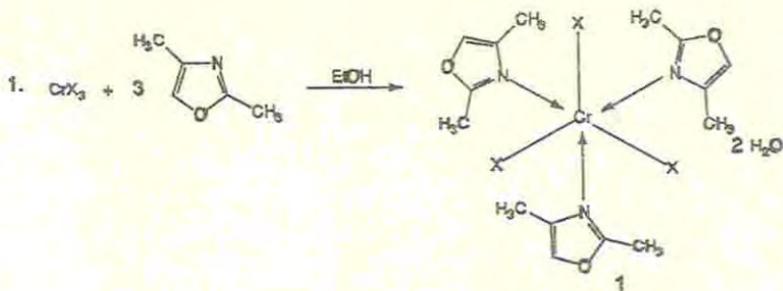
Proton NMR evidence. The proton resonance spectra of 2,4-dimethyloxazole and 3,5-dimethylisoxazole are characterized by signals corresponding to C-H, and CH_3 protons observed at δ 7.5 and 3.6, 3.5, respectively. In the chromium(III) complexes of these ligands the signals are observed down field (Table 2). This is attributed to the deshielding effect of the protons caused by electron delocalization as a result of the drift of electrons from the ligands to chromium(III) through nitrogen atom.

The proton resonance spectra of 2-methyl-5-nitrooxazole and 3-methyl-5-nitroisoxazole are also characterised by signals corresponding to C-H and CH_3 protons, but in this case, they are observed at δ 7.8, 3.8 and 3.9. Similar down-field observations occur in the resonance signals of these protons in chromium(III) complexes with these ligands. The presence of the electron withdrawing group (NO_2) has a deshielding effect on these protons and so their resonance signals are observed at lower field than the ligands having electron donating group (CH_3) as shown in Table 2. These observations are in agreement with our previous reports [6-9].

Table 2. Proton resonance spectral data of the complexes.

Complexes	$^1\text{C-H}$	$^1\text{CH}_3$
$\text{CrCl}_3 \cdot (2,4\text{-DMO})_3 \cdot 2\text{H}_2\text{O}$	7.9	3.80, 3.90
$\text{CrBr}_3 \cdot (2,4\text{-DMO})_3 \cdot 2\text{H}_2\text{O}$	8.0	3.80, 3.85
$\text{CrCl}_3 \cdot (2,4\text{-DMO})_3 \cdot 2\text{H}_2\text{O}$	8.1	3.85, 3.90
$\text{CrCl}_3 \cdot (3,5\text{-DMI})_3 \cdot 2\text{H}_2\text{O}$	8.0	3.80, 3.90
$\text{CrBr}_3 \cdot (3,5\text{-DMI})_3 \cdot 2\text{H}_2\text{O}$	8.1	3.85, 3.90
$\text{CrCl}_3 \cdot (3,5\text{-DMI})_3 \cdot 2\text{H}_2\text{O}$	8.0	3.80, 3.85
$\text{CrCl}_3 \cdot (2,5\text{-MNO})_3 \cdot 3\text{H}_2\text{O}$	8.4	4.30, 4.40
$\text{CrBr}_3 \cdot (2,5\text{-MNO})_3 \cdot 3\text{H}_2\text{O}$	8.4	4.35, 4.50
$\text{CrCl}_3 \cdot (2,5\text{-MNO})_3 \cdot 3\text{H}_2\text{O}$	8.4	4.20, 4.40
$\text{CrCl}_3 \cdot (3,5\text{-MNI})_3 \cdot 3\text{H}_2\text{O}$	8.5	4.30, 4.50
$\text{CrBr}_3 \cdot (3,5\text{-MNI})_3 \cdot 3\text{H}_2\text{O}$	8.5	4.35, 4.50
$\text{CrCl}_3 \cdot (3,5\text{-MNI})_3 \cdot 3\text{H}_2\text{O}$	8.4	4.30, 4.40
2,4-DMO	7.5	3.50, 3.60
3,5-DMI	7.5	3.50, 3.60
2,5-MNO	7.8	3.80, 3.90
3,5-MNI	7.8	3.80, 3.96

Ultraviolet spectral evidence. An analysis of the d-orbital splitting pattern of chromium(III) ion shows that all complexes with this metal ion must have three unpaired electrons



irrespective of the strength of the ligand field [9,10]. In chromium(III) complexes with the title ligands the UV spectra, (Table 3), indicate that the spin-allowed transitions from the ground state (${}^4A_{2g}$) to the first and second states (${}^4T_{2g}$ and ${}^4T_{1g}$) are observed. Results indicate that chromium(III) is under considerable compression. This observation is realized from the values of the crystal field splitting for chromium(III) under a less compressed chemical environment, for example the hexa-aquo chromium(III) ion, $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ has the bands at 17,400, 24,700 and 37,000 cm^{-1} [10-12]. The corresponding bands in the complexes feature at higher energies as Table 3 indicates. The net effect of these ligands on chromium(III) ion is a distortion of the symmetry.

Table 3. UV spectral data of the complexes.

Chromium(III) complexes	$\nu_1(\text{cm}^{-1})$	$\nu_2(\text{cm}^{-1})$	$\nu_3(\text{cm}^{-1})$
$\text{CrCl}_3 \cdot (2,4\text{-DMO})_3 \cdot 2\text{H}_2\text{O}$	18,200	25,600	38,000
$\text{CrBr}_3 \cdot (2,4\text{-DMO})_3 \cdot 2\text{H}_2\text{O}$	18,100	25,710	38,000
$\text{CrCl}_3 \cdot (2,4\text{-DMO})_3 \cdot 2\text{H}_2\text{O}$	18,250	25,630	38,100
$\text{CrCl}_3 \cdot (3,5\text{-DMI})_3 \cdot 2\text{H}_2\text{O}$	18,250	25,600	37,900
$\text{CrBr}_3 \cdot (3,5\text{-DMI})_3 \cdot 2\text{H}_2\text{O}$	18,150	25,500	38,100
$\text{CrCl}_3 \cdot (3,5\text{-DMI})_3 \cdot 2\text{H}_2\text{O}$	18,200	25,600	37,950
$\text{CrCl}_3 \cdot (2,5\text{-MNO})_3 \cdot 3\text{H}_2\text{O}$	18,350	25,850	39,100
$\text{CrBr}_3 \cdot (2,5\text{-MNO})_3 \cdot 3\text{H}_2\text{O}$	18,340	25,900	39,000
$\text{CrCl}_3 \cdot (2,5\text{-MNO})_3 \cdot 3\text{H}_2\text{O}$	18,400	25,850	39,150
$\text{CrCl}_3 \cdot (3,5\text{-MNI})_3 \cdot 3\text{H}_2\text{O}$	18,410	25,800	39,140
$\text{CrBr}_3 \cdot (3,5\text{-MNI})_3 \cdot 3\text{H}_2\text{O}$	18,350	25,820	39,100
$\text{CrBr}_3 \cdot (3,5\text{-MNI})_3 \cdot 3\text{H}_2\text{O}$	18,350	25,800	39,100
$\text{Cr}(\text{H}_2\text{O})_6^{3+}$	17,400	24,700	37,000

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