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Characterisation of Some Cobalt(II) Complexes Derived from Heterocyclic Ligands 3-Methyl-4-Nitro-1-(*Para*-Nitrophenyl)-5-Pyrazole and Imidazoles

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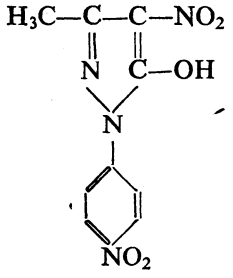
Some octahedral complexes of the 3-methyl-4-nitro-1-(para-nitrophenyl)-5-pyrazolonate, acetate and sulphates of cobalt(II) with imidazoles have been prepared and characterised. The general molecular formulae arrived on the basis of analytical data are $[Co(pyrazole)_2(imd)_4]$, $[Co(CH_3COO)_2(imd)_4]$, $[Co(H_2O)_4(imd)_2]SO_4$ and $[Co(imd)_6]SO_4$, where imd = imidazole, 2-methyl-imidazole or benzimidazole. The infrared, magnetic and electronic data of the complexes are discussed in the light of the structures assigned.

INTRODUCTION

The studies on pyrazole-5-one and imidazoles have attracted attention of chemists by virtue of their applicability as potential ligands for a large number of transition metals[1-4]. We have attempted a systematic study of the complexes derived from pyrazole-5-one and imidazoles. The structures of the complexes have been established using analytical, conductance, infrared, magnetic and electronic spectral data.

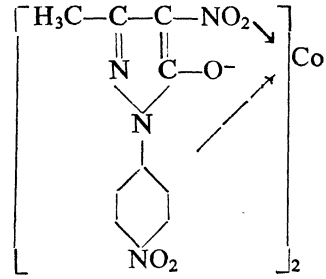
EXPERIMENTAL

The ligand 3-methyl-4-nitro-1-(*para*-nitrophenyl)-5-pyrazole has the structure.



Treatment of this compound with cobalt(II) sulphate gives yellow precipitate, which does not give the test for sulphate ion. It appears that the deprotonation of pyrazole-5-one has occurred. Thus the compound behaves as mononegative-5-pyrazolonate ion, two of which are added to

cobalt(II) as shown below.



The complexes have been prepared by the following method:

3 gm of di-3-methyl-4-nitro-1-(*para*-nitrophenyl)-5-pyrazolonatecobalt (II), cobalt(II) acetate or sulphate was suspended in 150 ml of ethanol (A). The calculated quantity of imidazoles dissolved in ethanol was then added to solution A. The reactants were refluxed for about 40 hrs till the coloured solution B was obtained. The solution B was concentrated and the complex crystallised at low temperature.

Conductivity of complexes was measured on a Philips PR 9500 instrument. The infrared spectra were recorded on a Perkin Elmer model 177 spectrophotometer. The magnetic measurements were done at room temperature using Gouy's method. The electronic spectra were recorded on a Unicam SP 8000 spectrophotometer.

RESULTS AND DISCUSSION

The molecular formulae have been obtained from the analytical data given in Table 1. The molar conductance values indicate that pyrazole-5-one and acetate complexes are non-electrolytes, while sulphate complexes are electrolytes. The coordination of ligands is obtained from infrared spectra.

(i) The cobalt(II) sulphate and 2-methylimidazole complex contains a broad band at 3380 cm^{-1} which is the coordinated OH stretching frequency[5].

(ii) In hexacoordinated cobalt(II)-5-pyrazolonate complexes, the Co stretching frequency occurs in free pyrazole-5-one at 1670 cm^{-1}; this band is absent in complexes indicating coordination through this group.[6]

(iii) The imidazoles contain both —N= and —NH groups. It is the iminic nitrogen which is utilised as donor atom. The NH stretching frequency in complexes is at slightly higher energy (near 3200 cm^{-1}) than in free ligand indicating that hydrogen bonding is somewhat reduced upon coordination. A strong band near 1500 cm^{-1} in imidazole, 1480 cm^{-1} in 2-methylimidazole and 1505 cm^{-1} in benzimidazole complexes has been assigned to $\rangle C{=}N-$ stretching frequency[7,8]. There is a

TABLE 1

ANALYTICAL DATA OF COBALT(II) COMPLEXES, FOUND (CALC.)

Complex	%M	%C	%H	%N	Molar conductance (mhos) water	Colour	μ_{eff} B.M.
$[Co(C_{10}H_7O_5N_4)_2]$	9.78 (10.07)	40.78 (41.04)	2.11 (2.41)	18.80 (19.14)	26.18	Yellow	5.68
$[Co(C_{10}H_7O_5N_4)_2(C_3H_4N_2)_4]$	5.88 (6.87)	44.99 (44.81)	3.22 (3.52)	25.78 (26.13)	5.39*	Orange-yellow	5.98
$[Co(C_{10}H_7O_5N_4)_2(C_4H_6N_2)_4]$	6.01 (6.44)	47.72 (47.32)	3.87 (4.18)	24.23 (25.41)	22.11	Violet	5.80
$[Co(C_{10}H_7O_5N_4)_2(C_7H_6N_2)_4]$	5.02 (5.27)	54.81 (54.50)	3.23 (3.62)	21.34 (21.19)	26.20	Brown	5.86
$[Co(CH_3COO)_2(C_3H_4N_2)_4]$	12.77 (13.11)	42.44 (42.26)	4.50 (4.93)	25.12 (24.93)	37.84	Purple	5.05
$[Co(CH_3COO)_2(C_4H_6N_2)_4]$	11.09 (11.66)	47.16 (47.53)	5.58 (5.97)	22.55 (22.16)	40.04	Light violet	5.31
$[Co(CH_3COO)_2(C_7H_6N_2)_4]$	8.77 (9.07)	59.34 (59.16)	4.22 (4.65)	17.45 (17.25)	34.32	Deep violet	5.82
$[Co(C_3H_4N_2)_6]SO_4$	10.01 (10.46)	38.76 (38.36)	3.89 (4.28)	29.68 (29.82)	Insoluble	Dark purple	5.34
$[Co(H_2O)_4(C_4H_6N_2)_2]SO_4$	12.70 (13.23)	21.21 (21.57)	5.46 (5.82)	12.67 (12.58)	41.14	Violet	5.02
$[Co(C_7H_6N_2)_6]SO_4$	6.38 (6.82)	58.70 (58.38)	3.79 (4.19)	19.21 (19.45)	Insoluble	Deep violet	5.82

*In ethanol.

very small decrease in this frequency when compared to free ligand and hence coordination is suggested to be through the iminic nitrogen. The lower coordination number of 2-methylimidazole complexes may be due to very high basicity of the ligand[9].

(iv) The bands near 1570 cm^{-1} (ν_{as}) and 1415 cm^{-1} (ν_s) have been assigned to a unidentate acetate group[10–12].

(v) Two strong bands appear in the range 1120–1100 cm^{-1} and 630–600 cm^{-1}. These are assigned to be ν_3 and ν_4 modes of uncoordinated sulphate ion[13,14].

On the basis of magnetic and electronic spectra, the complexes are assigned octahedral structure as discussed below.

The μ_{eff} values lie in the range 5.02–5.98 B.M. indicating the presence of three unpaired electrons. The high values of these complexes are mainly due to orbital contribution, which arises because of the greater quenching effect of the more unsymmetrical ligand field on the residual orbital moment.

The higher values may also be due to the higher ligand field strength of the ligands[15,16], the complexes are, therefore, assigned to have spin free outer orbital octahedral structure.

In the electronic spectra, three main bands centred between 25.25–17.05, 19.08–14.28 and 9.80–7.27 kK are seen. These corresponds to the three transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)\nu_1$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)\nu_2$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)\nu_3$. The ν_2 is weakest of all. The various ligand field parameters have been calculated which lie near Dq, 980 cm^{-1}; B, 1024 cm^{-1} and β, 0.85.

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