Synthesis and characterization of chromium(III), manganese(II), iron(III), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II) and mercury(II) complexes of oxyphenbutazone

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Metal complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with 4-butyl -1- (4-hydroxyphenyl) -2- phenyl-3; 5-pyrazolidinedione (oxyphenbutazone, OPB) have been synthesized and characterised. The IR spectral studies show that except for Hg(II), the ligand coordinates to the metal ion through the nontautomeric carbonyl group. In the case of Hg(II) complex, both tautomeric and nontautomeric carbonyl groups coordinate to the two Hg atoms. This is supported by the NMR spectrum of the complex.

In a previous communication[1], we reported the synthesis and characterisation of some metal complexes of phenylbutazone (4-butyl-1, 2-diphenyl-3, 5-pyrazolidinedione, PB). Oxyphenbutazone (4-butyl -1- (4-hydroxyphenyl) -2-phenyl-3, 5-pyrazolidinedione, OPB) is a non-narcotic, analgesic and anti-inflammatory pyrazolidinedione derivative. It is one of the metabolites of phenylbutazone and is better tolerated[2,3]. It exhibits keto-enol tautomerism (structure I). In this note, we report the synthesis and spectral analysis of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with oxyphenbutazone.

Ketoform   Enolform

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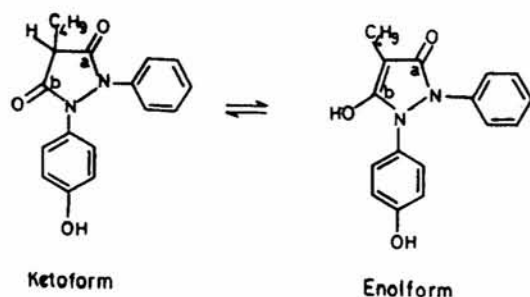
Experimental

Oxyphenbutazone monohydrate (m.pt.-124-5°C) procured from Sigma Company (USA) was used as such. The metal salts used were of AR grade.

Preparation of the complexes

A solution of oxyphenbutazone (3 mmol) was prepared in NaOH solution (0.1 M). A slight excess of the ligand was used to avoid excess alkali. The resulting suspension was filtered and the filtrate added slowly with stirring to the following metal salts.

(i) An aqueous solution of metal chloride (1 mmol) in the case of Cr(III) and Mn(II) complexes, (ii) aqueous solution of metal chloride (3 mmol) in the case of Cu(II) complex, (iii) aqueous solution of metal chloride (1.5 mmol) and the resulting mixture was heated for 1 h in the case of Co(II) and Ni(II) complexes and (iv) aqueous solution of $FeSO_4 7H_2O$ (1.5 mmol) followed by air oxidation in the case of Fe(III) complex.

The solid complexes separated were filtered, washed with water and dried over P_4O_{10} in a desiccator. The complexes were obtained as microcrystalline powder in high yields (> 90%).

The metals were analysed using standard procedures[4]. The elemental analysis was carried out using Heraus-CHN-O-rapid analyser. The molar conductance measurements of the complexes in acetonitrile were made using Elico CM 82T conductivity bridge. The room temperature $(28 \pm 2°C)$ magnetic data were obtained on a PAR model 155 vibrating sample magnetometer. The IR spectra of the ligand and the complexes were recorded on Perkin-Elmer 397 IR spectrophotometer in the range 4000-400 cm^{-1} in KBr pellet. The TG studies of some of the complexes were carried out on a Delta Series TGA 7 (heating rate $-20°C$/min in nitrogen atmosphere). The solid state electronic spectra were recorded on Varian CARY 2380 UV-VIS-NIR spectrophotometer in nujol mull in the range 200-1500 nm. The proton NMR spectra of the ligand and Hg(II) complex were recorded on Varian EM 390, 90 MHz NMR spectrometer. The ESR spectrum of the Cr(III) complex was recorded on Varian E-112 X-Q band spectrometer.

Results and discussion

The analytical data of the complexes are presented

in Table 1. The data show that the Cr(III), Mn(II) and Fe(III) complexes have the formulae $Cr(OPB)_3(OH)_3$, $Mn(OPB)_3(OH)_2$ and $Fe(OPB)_2(OH)_3 \cdot H_2O$ whereas Co(II), Ni(II) and Zn(II) complexes have the general formula $M(OPB)_2(OH)_2$ and Cu(II) and Cd(II) complexes are of the composition $M(OPB)(OH)_2$. The Hg(II) complex has the formula Hg(OPB)Cl. The complexes are either insoluble or sparingly soluble in most of the organic solvents. The molar conductance values of the complexes in acetonitrile suggest that they are non-electrolytic in nature.

The IR spectrum of the free ligand has two bands assignable to carbonyl groups. A sharp band observed at $1720\ cm^{-1}$ is attributed to the $\nu C=O$ vibration of the tautomeric carbonyl group. This assignment is based on the observation that the spectrum of the sodium salt of the ligand does not show the band at $1720\ cm^{-1}$. The absorption at $1680\ cm^{-1}$ can be assigned to the $\nu C=O$ of the non-tautomeric carbonyl group. This band is shifted to $1700\ cm^{-1}$ in the spectrum of the sodium salt. This blue shift can be due to the release of this $C=O$ group from hydrogen bonding present in the parent compound on salt formation. The absorption frequencies of carbonyl groups in the ligand are at a low frequency compared to that of phenylbutazone (1740 and $1700\ cm^{-1}$) (Ref. 1) due to intermolecular hydrogen bonds. It has been reported that the crystal structure of OPB (two OPB molecules and two water molecules/unit cell) is stabilised by van der Waals' interactions and OH...O hydrogen bonds[5]. It is interesting to note that there is no apparent change in the non-tautomeric $C=O$ stretching frequencies in the complexes. The band due to non-tautomeric carbonyl group observed at $1680\ cm^{-1}$ in the spectrum of oxyphenbutazone and at $1700\ cm^{-1}$ in the spectrum of the sodium salt, occurs at $1680\ cm^{-1}$ in the complexes. The band of oxyphenbutazone at $1720\ cm^{-1}$ due to tautomeric carbonyl group which is absent in the spectrum of the sodium salt appears in the spectrum of the complexes with a slight blue shift of the order of $10\text{-}20\ cm^{-1}$. This is due to breakage of intermolecular hydrogen bonds with water molecules. These observations clearly show that OPB coordinates with the metal ion in the keto form through the nontautomeric carbonyl group. The strong broad band at $\sim 3200\ cm^{-1}$ in the free ligand is assigned to the phenolic OH stretch. This band is shifted to $3300\ cm^{-1}$ in the complexes after release from H-bonding[6]. The free ligand also shows two strong bands at 3500 and $3450\ cm^{-1}$ assignable to the asymmetric and symmetric $O-H$ stretch of associated water molecule[7]. These bands are retained and the band at $3200\ cm^{-1}$ undergoes no shift in the case of Fe(III) complex. This may be due to the presence of coordinated water molecule in the case of Fe(III) complex which may be hydrogen bonded with phenolic OH. The other complexes do not show bands characteristic of coordinated water molecules. However, the band observed at $3400\ cm^{-1}$ in the case of Cu(II) complex may be due to $O-H$ stretch of coordinated hydroxyl group[8]. The IR spectra of the complexes also show bands at 550-580 and at ~ 1120 cm^{-1} which are assigned to $M-OH-M$ bond

Table 1—Analytical data of oxyphenbutazone and its complexes

Empirical formula	Found (Calc.), %				
	M	C	H	N	Cl
Cr (OPB)₃ (OH)₃	4.13	63.64	6.24	8.48	—
(Pale green)	(4.83)	(63.56)	(5.85)	(7.81)	
Mn(OPB)₃(OH)₂	4.87	65.42	5.79	7.91	—
(Cream)	(5.17)	(64.39)	(5.84)	(7.78)	
Fe(OPB)₂(OH)₃H₂O	4.80	58.37	5.71	7.46	—
(Light brown)	(7.22)	(58.94)	(5.82)	(7.24)	
Co(OPB)₂(OH)₂	8.88	61.94	5.68	6.69	
(Light brown)	(7.94)	(61.48)	(5.66)	(7.55)	
Ni(OPB)₂(OH)₂	6.40	58.94	5.58	7.23	—
(Pale green)	(7.90)	(61.50)	(5.66)	(7.55)	
Cu(OPB)(OH)₂	16.50	53.75	4.55	6.28	
(Light green)	(15.06)	(54.04)	(5.22)	(6.64)	
Zn(OPB)₂(OH)₂	8.00	59.30	6.23	7.18	—
(White)	(8.70)	(60.39)	(5.61)	(7.48)	
Cd(OPB)(OH)₂	23.70	48.39	4.93	5.29	—
(White)	(23.81)	(48.47)	(4.68)	(5.96)	
Hg(OPB)Cl	36.10	41.50	4.06	5.01	6.5
(Light yellow)	(35.79)	(40.68)	(3.57)	(5.00)	(6.3)

frequency and O−H bending of the M−O−H moiety[9−12]. In the case of Hg(II) complex, the band due to tautomeric carbonyl group is absent and the band due to non-tautomeric carbonyl group is shifted to 1650 cm^{-1}. This suggests the participation of both tautomeric and non-tautomeric carbonyl groups in bonding. The absence of the band due to tautomeric carbonyl group indicates the complexation of this group in the enol form. This is supported by the NMR spectral studies. The Hg-Cl stretching coupled with the ligand vibration occurs as a broad band at 320 cm^{-1} (ref. 12). This is in agreement with the linear polymer structure involving long chains of metal halogen units. The M−O stretching frequencies observed for the complexes indicate that the M−O bond strength is in the order Cr(III)(460) > Fe(III)(450) and Mn(II)(410) < Co(II)(430) < Ni(II)(450) < Cu(II)460, and almost follows the Irwing-Williams order of stability[13].

The observed magnetic moments are slightly less than the spin only value except for the Cr(III) complex. The Cr(OPB)$_3$(OH)$_3$, has a magnetic moment value of 4.567 BM at room temperature. This is higher than the spin only value of 3.87. This deviation may be caused by ferromagnetic interaction between chromium atoms. But to ascertain the nature of magnetic behaviours, it is worthwhile to carry out the magnetic measurements at different temperatures. Such an investigation could not be carried out due to lack of facilities. The μ_{eff} values for Mn(II), Co(II), Ni(II), and Cu(II) are 5.71, 3.19, 2.74 and 1.57 B.M. respectively. In the case of Fe(III) complex, the μ_{eff} value obtained is 3.38 B.M. The lower value observed for Fe(III) complex suggests the presence of considerable antiferromagnetic interaction in the complex[14]. The other complexes where hydroxyl group act as a bridging group, metal-metal interaction may be present and hence the observed magnetic moment values are lower than the spin only values[15].

The visible absorption spectrum of Cr(III) complex shows absorption maximum at ∼ 16,950 and 24,100 cm^{-1}, which are assigned to $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4T_{2g} \rightarrow T_{1g}(F)$ transitions respectively[16]. The $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ transition is probably obscured by high energy transitions. The electronic spectrum of Mn(II) complex shows a band with a maximum at 27,780 cm^{-1} which is assigned to charge transfer. The Fe(III) complex shows two bands with maxima at 25,000 and 20,410 cm^{-1} which are assigned to charge transfer and $^6A_{1g} \rightarrow {}^4T_{1g}$ transitions[17]. The spectrum of Co(II) complex shows only one d-d absorption maximum at 20,000 cm^{-1} which corresponds to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition[18]. A band is observed at 27,030 cm^{-1} which can be attributed to charge transfer. The electronic spectrum of Ni(II) complex shows two bands one with a maximum at 21,740 cm^{-1} and the other at 15,390 cm^{-1}. These bands are assigned to $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ respectively[19]. The electronic spectrum of Cu(II) complex shows a broad comparatively low intensity band with a maximum at 14,290 cm^{-1}. The position band shape and intensity indicate that the Cu(II) ion is in a distorted octahedral environment[20]. A broad band with a maximum at 25,000 cm^{-1} may be assigned to charge transfer.

The ESR spectrum of Cr(III) complex in the polycrystalline state shows a broad signal with g_{iso} = 1.978 (ref. 21).

The proton NMR spectral data of the ligand and Hg(OPB)Cl were recorded in CDCl$_3$ and deuterated acetone respectively. The NMR spectrum of Cd(OPB)(OH)$_2$ and Zn(OPB)$_2$(OH)$_2$ could not be recorded as they were insoluble in common organic solvents. The phenyl protons and CH$_3$ protons in the ligand and complex absorb at 6.6-7.3 and 0.9 δ ppm respectively and three CH$_2$ protons absorb at 1.3, 1.4 and 2.1 δ ppm. The ^{4}C-H proton in the free ligand exhibits a triplet signal at 3.4 due to splitting with the CH$_2$ protons. This signal is absent in the complex. This conclusively proves that the enol form is coordinating in the case of Hg(II) complex. The structure of the complex is likely to be polymeric with chlorobridges. The carbonyl oxygen and the enolic oxygen of the ligand are coordinated to two Hg atoms to form a polymeric structure. The signals corresponding to the phenolic O-H and water molecules of the free ligand could not be located in the NMR spectrum.

The thermogravimetric analyses of some of the complexes were also carried out. The TG curves show the absence of any coordinated water molecule in the complexes except for the Fe(III) complex. In the case of Fe(III) complex, the first stage of decomposition corresponds to the elimination of one molecule of water. The percentage of water lost as indicated by TG curve agrees well with the calculated value of 2.2. The thermal stability of the complexes is in the order Cr(III) = Mn(II) > Ni(II) > Cu(II) > Co(II) > Fe(III). The Cr(III) and Ni(II) complexes undergo single stage decomposition. All the other complexes undergo decomposition in two or more stages. The final mass loss observed was in agreement with the values calculated for their respective oxides.

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