Synthesis and characterization of the complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with phenylbutazone

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The hydroxo-bridged complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with 4-butyl-1,2-diphenylpyrazolidine-3,5-dione(phenylbutazone, PB) and chloro-bridged complex of Hg(II) with PB have been synthesized and characterized. The IR spectral studies indicate that except for Hg(II), the coordination is through nontautomeric carbonyl group. In the case of Hg(II) complex both tautomeric and nontautomeric carbonyl groups participate in bonding. This is supported by proton NMR spectral studies of the diamagnetic complexes.

The coordination chemistry of biologically active molecules has been of great interest since the complexation is found to alter the activity of the organic compounds considerably[1-4].

Phenylbutazone (4-butyl-1,2-diphenylpyrazolidine-3,5-dione, PB) is a nonsteroidal anti-inflammatory drug which exhibits analgesic, antipyretic and antirheumatic properties. It has been reported that, phenylbutazone exhibits keto-enol tautomerism[5] (Structure I). It exists in the keto form in solvents like acetone and chloroform, whereas in a basic solvent like pyridine it exists in enol form. In this note, we report the synthesis and spectral analyses of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes with phenylbutazone.

Keto form   Enol form
(I)
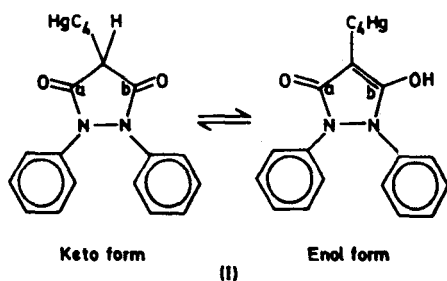
Experimental

Phenylbutazone was procured from Sigma Company and used as such. The metal salts used were of AR grade.

Preparation of the complexes

A solution of phenylbutazone (2 mmol) was prepared in NaOH (0.1 M) solution. A slight excess of the ligand was used to exclude 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) complex, (ii) aqueous solution of metal chloride (2 mmol) in the case of Cu(II), Zn(II), Cd(II) and Hg(II) complexes, (iii) aqueous solution of metal chloride (2 mmol) and the mixture was heated over water bath for 1 h for Co(II), Ni(II) and Mn(II) complexes, (iv) aqueous solution of $FeSO_4$ (1 mmol) followed by air oxidation in case of Fe(III) complex.

The solid complex separated in each case was filtered, washed with water and dried over P_4O_{10} in a desiccator. The complexes were obtained as micro crystalline powder in high yields (<90%). The metal estimation of the complexes was carried out using a Varian Techtron AA-60 atomic absorption spectrophotometer and ICP ARL 3410, after decomposing the complexes in con. HNO_3. The elemental analysis was carried out using Carlo Erba elemental analyser. The molar conductance values of the complexes were measured in nitrobenzene using Systronics direct reading type conductivity meter. Room temperature (28 ± 2°C) magnetic measurements were carried out using PAR Model 155 Vibrating Sample Magnetometer and also by Gouy method. The IR spectra of the ligand and the complexes were recorded on a Perkin-Elmer 397 IR spectrophotometer in the range 4000-400 cm^{-1} in KBr pellet as well as in nujol mull. The far IR spectrum of the Hg(II) complex was recorded on Polytech FIR-30 fourier far IR spectrometer. Thermogravimetric studies were carried out on Delta Series TGA7 (heating rate 10°C/min, in nitrogen atmosphere). The solid state electronic spectra were recorded on Shimadzu UV 200s using MgO as standard in the range 250-800 nm and on Varian CARY 2380 (UV-VIS-NIR) in nujol mull in the range 200-1500 nm. The proton NMR spectra of diamagnetic complexes in CDCl$_3$ were recorded on Varian EM 390, 90 MHz NMR spectrometer. The ESR spectrum of

Table 1—Analytical data of phenylbutazone and its complexes

Empirical formula colour	Found (Calc), %				Stability range from ambient temperature up to (K)	Final mass loss (%)	
	M	C	H	N		Found	Calc.
$C_{19}H_{20}N_2O_2$ White	—	74.40 (73.92)	6.34 (6.54)	9.74 (9.08)	—	—	—
$CrPB_2(OH)_3$ Pale green	7.20 (7.22)	65.45 (66.00)	6.25 (5.97)	8.12 (7.80)	445	89.77	89.45
$MnPB(OH)_2$ Cream	14.44 (13.82)	58.00 (57.38)	5.90 (5.54)	6.80 (7.04)	445	81.63	82.15
$FePB_2(OH)_3$ Light orange	7.50 (7.71)	63.82 (63.01)	5.50 (5.94)	8.32 (7.74)	427	89.58	89.00
$CoPB(OH)_2$ Brown	14.56 (14.70)	57.20 (56.80)	4.95 (5.48)	7.08 (5.90)	392	83.54	81.33
$NiPB(OH)_2$ Pale green	14.43 (14.64)	57.36 (56.84)	5.83 (5.48)	7.29 (6.98)	427	82.64	81.38
$CuPB(OH)_2$ Light green	15.50 (15.65)	56.79 (56.16)	5.20 (5.42)	7.20 (6.90)	401	71.76	72.58
$ZnPB(OH)_2$ White	16.82 (16.10)	56.25 (55.85)	5.80 (5.39)	6.19 (6.86)	409	81.72	80.05
$CdPB(OH)_2$ White	24.35 (24.64)	50.35 (50.17)	4.78 (4.84)	6.88 (6.16)	427	70.71	71.80
HgPBCl Light yellow	36.20 (36.83)	41.20 (41.86)	3.62 (3.67)	5.30 (5.10)	392	No residue	

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 indicate that the complexes can be represented as M PB$_2$ (OH)$_3$ [M − Cr(III) or Fe(III)] and M PB(OH)$_2$ (where M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II) or Cd(II)]. The Hg(II) complex has the formula, HgPBCl. The nitrobenzene solutions of the complexes exhibit negligible molar conductance values supporting their non-ionic nature. The bands in the ligand spectrum are well reproduced in the spectra of the complexes with only minor changes. The free ligand has two bands assignable to carbonyl groups. The sharp band at 1740 cm^{-1} is assigned to the $vC = O$ vibrations of the tautomeric carbonyl group (Structure I, b) whereas this band disappeared in the spectrum of the sodium salt of the ligand. The absorption at 1700 cm^{-1} assigned to the vibration of the nontautomeric carbonyl group (Structure I, a) is shifted to 1720 cm^{-1} in the spectrum of the sodium salt since the C = O group is released from hydrogen bonding. The IR spectrum of the ligand also shows absorption at 1940 cm^{-1} characteristic of hydrogen bonding. The disappearance of this band in the spectra of the complexes

shows that H-bonding is absent in the complexes. It is interesting to note that there is no apparent change in the carbonyl stretching frequency in the complexes except for the Hg(II) complex. This can be rationalized as follows. The band at 1740 cm^{-1} due to tautomeric carbonyl group which disappeared in the spectrum of the sodium salt reappears in the spectra of the complexes. The band at 1700 cm^{-1} of the ligand due to nontautomeric carbonyl group which appears at 1720 cm^{-1} is shifted to 1700 cm^{-1}. It shows monodenticity of the ligand and that the ligand interacts with the metal in the keto form with the nontautomeric carbonyl group coordinating to the metal ion. The IR spectra of the complexes also show a band ~ 1100 cm^{-1} and sharp band ~ 3400 cm^{-1}. These bands are attributed to the O − H bending of M − O − H moiety and O − H stretching of coordinated OH respectively[6]. The hydroxyl group most probably acts as a bridge between two metal atoms forming either dimeric or polymeric metal complexes (Structure II). The presence of M − OH − M band in the range 500-590 cm^{-1} for all complexes is in agreement with the earlier findings[7]. 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 1660 cm^{-1}. This indicates the participa-

tion of both the carbonyl groups in coordination for Hg(II) complex. The absence of a 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 ~ 320 cm^{-1}. This is in agreement with the linear polymer structure involving long chains of metal halogen units[8,9].

The observed magnetic moment values corrected for diamagnetism and temperature independent paramagnetism are less than the spin only value. Such deviations from the normal value due to metal-metal interactions[10] are not uncommon for dimeric or polymeric complexes[11] with bridged groups. The visible absorption spectrum of Cr(III) complex shows two broad bands at 29,410 and 20,000 cm^{-1} which correspond to the spin allowed transitions, $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ and $^4A_{2g} \rightarrow {}^4T_{2g}(F)$ (Oh symmetry). The transitions $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ may be overlapped with $^4A_{2g} \rightarrow {}^4T_{2g}(F)$. This complex has a magnetic moment value 3.37 BM at room temperature, which is lower than the theoretical spin only value of 3.87 BM. This may be explained in terms of coupling between the two paramagnetic $(S = 3/2)$ Cr(III) centres. The EPR spectrum of the powder sample at room temperature shows a single broad signal with $g$iso at 1.94 (ref. 12). A comparison of the room temperature ESR spectrum with the spectrum at liquid nitrogen temperature of this compound shows the same pattern of $g$iso value.
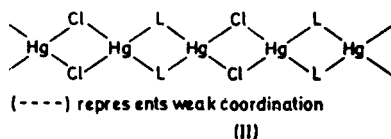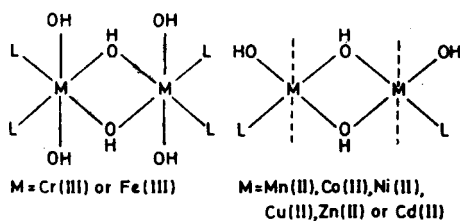
The high spin Mn(II) and Fe(III) complexes with d^5 configuration have the ground state $^6A_{1g}$ and all the $d-d$ transitions are spin and Laporte forbidden[13]. The Mn(II) and Fe(III) complex exhibit a weak and a broad band at 12,190 and 21,140 cm^{-1} respectively which could be attributed to $^6A_{1g} \rightarrow {}^?T_{1g}(^4G)$ transitions[14-18]. The Mn(II) and Fe(III) complexes show magnetic moment values of 5.46 and 5.01 BM which are lower than the spin only value of 5.93 BM. For Co(II) complexes with octahedral geometry, three transitions expected are $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$. The transition $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ is not generally observed[19]. In the present case, the band at 20,000 cm^{-1} may be tentatively attributed to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and a weak band at 8330 cm^{-1}, to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$. The magnetic moment value obtained for Co(II) complex is 3.57 BM. The transitions expected for octahedral Ni(II) complex are $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ref. 21). The band at 17,860 cm^{-1} in the present complex is assigned to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and the one at 27,780 cm^{-1} to $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions[22,23]. The magnetic moment value observed for Ni(II) complex is lower (1.28

BM) than the spin only value of 2.8 BM. The Cu(II) complex shows only one broad band at 19,230 cm^{-1} which is suggestive of distorted octahedral geometry[24]. It shows magnetic moment value of 1.39 BM.

The proton NMR spectral data for the ligand and a few complexes were recorded in CDCl$_3$. The phenyl protons and CH$_3$ protons in the ligand and complexes absorb at 7.3 and 0.9 δ ppm respectively and three CH$_2$ protons absorb at 1.4, 1.6 and 2.1 δ ppm. In the free ligand the ^{4}C − H proton exhibits a triplet signal at 3.4 δ due to splitting with the CH$_2$ protons. This signal is absent in Hg(II) complex and is retained in Zn(II) and Cd(II) complexes. 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 thermogravimetric analyses of the complexes were also carried out. The TG curves indicate the absence of water molecules. Infact, there is no detectable change in the TG curves up to 120°C. The thermal stability patterns of the complexes can be seen from Table 1. The complexes are stable from ambient temperature up to about 400K. The Cr(III) and Mn(II) complexes appear to be slightly more stable (up to 445K) than the others. The Cr(III), Hg(II) and Fe(III) complexes undergo single stage decomposition, whereas all the other complexes undergo a two-stage decomposition. The final mass loss was in agreement with the values calculated for their oxides.

The solid state electronic spectral data indicate an octahedral geometry around the metal ions in the case of Cr(III), Mn(II), Fe(III), Co(II) and Ni(II) complexes and distorted octahedral geometry in the case of Cu(II) complex. The magnetic moment data determined at room temperature suggest the presence of considerable metal-metal interactions in the complexes. From the above experimental data, di-

M = Cr(III) or Fe(III)   M=Mn(II),Co(III),Ni(II),
                              Cu(II),Zn(II) or Cd(II)

(----) represents weak coordination

(III)

meric or polymeric structures (Structure II) with bridging groups have been proposed for the complexes.

Acknowledgement

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