

NOTE

Synthesis and Characterization of Platinum(II) Complexes Derived from Maltol and Kojic Acid

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Two platinum(II) complexes are synthesized using K_2PtCl_4 and maltol or kojic acid as ligands and are characterized using elemental analysis, IR, UV and 1H NMR spectra. Based on the spectral data it is found the ligands coordinate to the metal through C(4)O and phenolic (OH) groups.

Key Words: Maltol, Kojic acid, Platinum, Infrared spectrum, Proton, Nuclear magnetic resonance.

Complexes of platinum group metals are being studied extensively because of their antitumour and antibacterial activity¹⁻⁵. Among them *cis-platin*^{1,2} is a potent drug for the treatment of a variety of human tumours. In this regard, attempts have been made to synthesize less toxic and more potent drugs. Several binary and ternary complexes of Pt(II) and Pd(II) were reported with nucleic acid constituents, amino acids and other nitrogen containing ligands⁶⁻¹⁴. Khan *et al.*^{15,16} have reported mixed ligand complexes of Pt(II) and Pd(II) with amino acids, methionine and ethionine and with purines, pyrimidines and nucleosides. Some of these complexes exhibited biological activity, very few complexes with substituted pyrimidines, however, have been reported^{12,17-20}. In view of the importance of these complexes as biologically active compounds, we report in this note the synthesis and characterization of binary complexes of Pt(II) with 3-hydroxy-2-methyl-4[H]-pyran-4-one (maltol) and 5-hydroxy-2(hydroxymethyl) 4[H]-pyran-4-one (kojic acid).

The ligands maltol and kojic acid were obtained from Lancaster. $[K_2PtCl_4]$ was purchased from S.D. Fine Chemicals. Two complexes were prepared by treating aqueous solutions of K_2PtCl_4 (0.8301 g, 2 mM) with kojic acid (0.2922 g, 2 mM) or maltol (0.2522 g, 2 mM) in a molar ratio of 1 : 1. The reaction mixture was stirred for 3 h, the solution was then reduced to a smaller volume on a water bath, cooled and treated with ice-cold acetone. The resulting yellow precipitate was filtered, recrystallized from aqueous ethanol and dried in a desiccator over fused $CaCl_2$.

The percentage elemental analysis of the maltol (MA) complex was found (calcd.) to be: Pt 47.03 (46.99); C 17.23 (17.35); H 1.16 (1.21); Cl 17.23 (17.11).

Similarly for kojic acid (KA) complex the percentage values were found to be: Pt 45.36 (45.01); C 16.63 (16.71); H 1.23 (1.16); Cl 16.64 (16.47). The close resemblance of experimental and calculated values suggests the general formula as $K[MA-PtCl_2]$ or $K [KA-PtCl_2]$.

The IR spectra of the complexes have been compared with the corresponding ligands (Table-1). The bands due to (C=C) which appear at 1630, 1556 cm^{-1} (maltol); 1660, 1579 cm^{-1} (kojic acid) in the free ligands have shifted to 1606, 1505 cm^{-1} (maltol complex), 1637, 1540 cm^{-1} (kojic acid complex) in the corresponding chelates. The (C=O) stretching bands at *ca.* 1630 cm^{-1} in free ligands have suffered a shift of *ca.* 24 cm^{-1} in the chelates. In addition to pronounced shifts in the (C=O) and (C=C) stretching frequencies in the complexes the bands at about 3200 cm^{-1} due to the phenolic OH in the free ligands are absent in the complexes indicating chelate formation. This suggests that the maltol is coordinated to the metal ion through both oxygen atoms of the carbonyl and hydroxyl groups and that the delocalization of the olefinic and carbonyl electrons of maltol takes place. The bands at 1290 cm^{-1} and 1229 cm^{-1} in the ligands and complexes are due to aromatic C—O—C stretching frequencies. The IR spectral ligands of maltol or kojic acid and their corresponding metal complexes are given in Table-1. The appearance of new bands in both complexes at 435, 437 in maltol complexes and at 434 in kojic acid complex is due to stretching frequency of (M—O) bonds. The (Pd—O) bond stretching frequency in maltol complex is reported at 410 cm^{-1} .

TABLE-1
CHARACTERISTIC IR BANDS (cm^{-1}) OF THE ISOLATED COMPLEXES
(IR SPECTRA TAKEN IN KBr PELLETS)

Ligand/Complex	$\nu(C=O)$	$\nu(C=C)$	$\nu(Pt-O)$	Others
Maltol (MA)	1630	1556, 1456	—	3271, 3059
$[MA-Pt-Cl_2]$	1606	1505, 1419	453, 437	3412
Kojic acid (KA)	1660, 1610	1579, 1471	—	3177, 2924, 2849
$[KA-Pt-Cl_2]$	1637	1540, 1458	434	

In the free ligand electronic spectra (maltol) the peaks are observed at 257.5, 306.5 and 445.5 nm respectively while in its complex (Pt-maltol complex) the peaks are observed at 258, 307 and 454 nm respectively. The peaks observed at 258, 307 nm are due to $\pi-\pi^*$ transition while the peak observed at 454 nm is due to *d-d* transition. Similarly in Pt-kojic acid complex a peak is observed at 261 nm which is assigned to $\pi-\pi^*$ transition and that observed at 460 nm is assigned to *d-d* transition.

In the NMR spectra of free ligand maltol peaks are observed at 7.92 ppm C(6)-H, and 2.35 ppm ($-CH_3$). In the Pt-maltol complex the peaks C(5)-H and C(6)-H are shifted downfield by 0.24 and 0.11 ppm respectively.

In the NMR spectra of free ligand kojic acid peaks are observed at 7.92 ppm

C(g)-H, 6.50 ppm C(3)-H, and 4.40 ppm C(2)-CH₂. In the Pt-kojic acid complex the peaks C(3)-H and C(6)-H are shifted downfield by 0.12 and 0.24 ppm respectively.

From the above spectral studies conducted on Pt complexes, it is concluded that the complexes are square-planar Pt(II) complexes of the form K[(L)PtCl₂] which acts as bidentate ligand coordinating through C(4)-O- and phenolic (—OH) groups.

ACKNOWLEDGEMENT

The financial assistance by UGC, New Delhi in the form of major research project is highly acknowledged.

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