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Spectral studies of platinum(II) complexes with 2,3-disubstituted quinazolin-(3H)-4-ones

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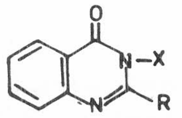
A number of platinum(II) complexes of 2,3-disubstituted quinazolin-(3H)-4-ones have been synthesized and characterized based on analytical, conductivity, magnetic, infrared, electronic and PMR data. The reactions between $PtCl_2$ and O-O donor ligands such as 2-(R)-3-(X) substituted quinazoline-(3H)-4-ones, where R = methyl/phenyl and X = hydroxyl (MHQ/PHQ), hydroxyethyl (MHEQ/PHEQ), *o*-hydroxyphenyl (MHPQ/PHPQ) and carboxymethyl (MCMQ/PCMQ), yield neutral complexes of the type $Pt(O\text{-}O)_2$. The O-N donor ligands like 2-(R)-3-(X) substituted quinazoline-(3H)-4-ones, where R = methyl/phenyl and X = amino (MAQ/PAQ), anilino (MANQ/PANQ), *o*-aminophenyl (MAPQ/PAPQ) and 2′-pyridyl (MPQ/PPQ), yield ionic complexes of the type $Pt(O\text{-}N)_2Cl_2$. The infrared and PMR spectral data of the metal complexes indicate that MHQ, PHQ, MHEQ, PHEQ, MHPQ, PHPQ, MCMQ and PCMQ act as mononegative bidentate ligands and MAQ, PAQ, MANQ, PANQ, MAPQ, PAPQ, MPQ and PPQ act as neutral bidentate. The complexes are assigned square-planar structures.

In continuation of our earlier work[1-3], we report here the synthesis of a series of platinum(II) complexes with various 2,3-disubstituted quinazolones (structure-I), where X is invariably a donor group and R a methyl or phenyl group. The complexes have been characterized based on analytical, conductivity, magnetic, infrared, electronic and PMR data.

Experimental

All the chemicals and solvents used were of AR grade. $PtCl_2$ was obtained from M/s Johnson-Matthey (England). All the ligands were prepared as reported in literature[4-11] and their purities were checked by TLC and melting point determinations.



(I)

R = CH_3	R = C_6H_5
X = OH (MHQ)	X = OH (PHQ)
= $-CH_2OH$ (MHEQ)	= $-CH_2OH$ (PHEQ)
= o-OHC_6H_5 (MHPQ)	= o-$OH C_6H_5$ (PHPQ)
= $-CH_2COOH$ (MCMQ)	= $-CH_2COOH$ (PCMQ)
= $-NH_2$ (MAQ)	= $-NH_2$ (PAQ)
= $-NH C_6H_5$ (MANQ)	= $-NH C_6H_5$ (PANQ)
= o-$NH_2 C_6H_5$ (MAPQ)	= o-$NH_2C_6H_5$ (PAPQ)
= 2′-NC_5H_5 (MPQ)	= 2′-NC_5H_5 (PAQ)

For the preparation of the complexes 1 g of platinum(II) chloride was dissolved in one ml of conc. hydrochloric acid and the contents were diluted to 100 ml to get a 0.1 *N* solution. A calculated amount of platinum(II) chloride solution was taken in a beaker and treated with equal volume of water. To this solution was added the ligand dissolved in methanol (30 ml) drop by drop with constant stirring. In all the cases the ligand was in slight excess over that required for 1:3 (metal to ligand) molar ratio. The reaction mixture was refluxed on a water bath for about 30-60 min. The complex separated out in the neutral medium on cooling. It was filtered through a sintered glass crucible and washed with hot water and methanol. The complexes were dried *in vacuo* over fused calcium chloride.

The analytical data (C,H,N) for the ligands and their metal complexes were obtained from the Microanalytical Laboratory, Calcutta University, Calcutta. Molar conductivities of the complexes in DMF were measured using a Digisun digital conductivity meter, model DI-909. Magnetic susceptibilities were measured at room temperature by Gouy method using $Hg[Co(NCS)_4]$ as the calibrant. Infrared spectra of the ligands and the complexes in the region 4000-200 cm^{-1} were recorded in KBr and nujol on a Perkin-Elmer infrared spectrophotometer model-283. Electronic spectra of the complexes were recorded in DMF on a Shimadzu multipurpose recording spectrophotometer model MPS-5000 and PMR spectra of the ligands and the complexes were obtained in d_6-DMSO on a Jeol 100 MHz spectrometer.

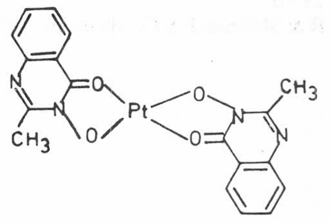
Table 1 — Analytical and Physical Data of Pt(II) Complexes

Complex	Colour	Found (Calc.), %			Molar conductance $(\mathrm{Ohm}^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1})$
$[Pt(MHQ)_2]$	Yellow	39.12 (39.65)	10.56 (10.27)	2.12 (2.57)	18
$[Pt(PHQ)_2]$	Yellow	50.86 (50.22)	8.96 (8.37)	2.82 (2.69)	20
$[Pt(MHEQ)_2]$	Orange Yellow	44.86 (43.92)	9.44 (9.32)	3.82 (3.67)	15
$[Pt(PHEQ)_2]$	Orange Yellow	53.12 (52.96)	7.82 (7.72)	4.16 (3.59)	20
$[Pt(MHPQ)_2]$	Red Brown	51.82 (51.64)	8.24 (8.03)	3.85 (3.16)	18
$[Pt(PHPQ)_2]$	Brown	58.52 (58.46)	6.82 (6.44)	3.27 (3.17)	20
$[Pt(MCMQ)_2]$	Yellow	41.86 (41.97)	8.96 (8.90)	2.96 (2.86)	12
$[Pt(PCMQ)_2]$	Yellow	51.22 (50.99)	7.56 (7.44)	2.56 (2.92)	14
$[Pt(MAQ)_2]Cl_2$	Brown	35.96 (35.06)	13.82 (13.63)	2.84 (2.92)	136
$[Pt(PAQ)_2]Cl_2$	Brown	45.95 (45.40)	12.12 (11.35)	3.23 (2.97)	142
$[Pt(MANQ)_2]Cl_2$	Green	47.22 (46.87)	11.56 (10.94)	3.72 (3.39)	130
$[Pt(PANQ)_2]Cl_2$	Green	53.12 (53.81)	10.12 (9.42)	3.56 (3.36)	132
$[Pt(MAPQ)_2]Cl_2$	Orange	46.82 (46.87)	10.73 (10.94)	3.76 (3.39)	145
$[Pt(PAPQ)_2]Cl_2$	Orange	54.26 (53.81)	9.56 (9.42)	3.72 (3.36)	147
$[Pt(MPQ)_2]Cl_2$	Brown	45.94 (45.40)	11.56 (11.35)	3.56 (2.97)	145
$[Pt(PPQ)_2]Cl_2$	Brown	52.71 (52.77)	9.12 (9.72)	3.56 (3.01)	140

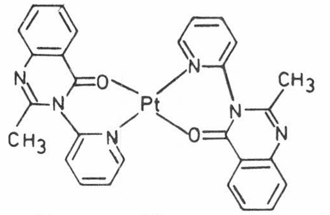
Results and discussion

All the complexes are stable at room temperature, are non-hygroscopic and soluble in acetone, DMF and DMSO. The analytical and physical data of the complexes are collected in Table 1. The analytical data of the complexes indicate that the metal to ligand molar ratio is 1:2 and that the complexes of MAQ, PAQ, MANQ, PANQ, MAPQ, MPQ and PPQ have two chloride ions each. The molar conductance values of complexes in dimethylformamide at 1×10^{-3} *M* concentration, suggest that the complexes are non-electrolytes except those of MAQ, PAQ, MANQ, PANQ, MAPQ, PAPQ, MPQ and PPQ which are 1:2 electrolytes[12]. All the complexes are found to be diamagnetic.

The most important bands occurring in the infrared spectra of free ligands and their metal complexes have been compared in order to ascertain the bonding sites in the ligands. The IR bands of the free ligands due to carbonyl (~ 1700 cm^{-1})[13], phenolic O-H (3600-3100 cm^{-1})[14] and carboxylic O-H (~ 2500 cm^{-1})[15] stretching modes are absent in the spectra of the complexes. The bands due to stretching modes of amino (3340-3360 cm^{-1})[16], imino (~ 3200 cm^{-1})[16] and C=N (~ 1610 cm^{-1})[17] groups in the ligands are lowered by 50 cm^{-1} in the spectra of complexes. These data suggest that the complexation is through oxygen (after deprotonation) or nitrogen. Two new bands appear in the far infrared region at 400 and 450 cm^{-1} due to the ν(M-N) and ν(M-O), respectively[18,19].



II (a) $[Pt(MHQ)_2]$



II (b) $[Pt(MAQ)_2]Cl_2$

Further evidence for the above mode of coordination comes from the PMR spectral data. The PMR peaks observed for the free ligands due to hydroxyl (9.6-10.5 δ) and carboxylic (10.8 δ) protons are absent in the spectra of the complexes. The signals recorded for NH_2 (6.2 δ) and —NH (6.5-6.6 δ) protons are shifted to down field by 2 ppm.

All the complexes show two electronic spectral bands around 20000 and 24000 cm^{-1} which may bes due to the transitions $^1B_{1g} \leftarrow {}^1A_{1g}$ and $^1E_g \leftarrow {}^1A_{1g}$, respectively, characteristic of square-planar geometry[20]. In addition to these bands, other bands are also observed in the higher energy side which may probably represent LMCT and MLCT type absorptions.

Based on the above spectral and physical data, a square planar geometry may be tentatively proposed for all the new complexes (structure II).

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