

MIXED-LIGAND COMPLEXES OF TITANIUM (III), RHODIUM (III) AND PLATINUM (IV) WITH DIPHENIC ACID AND HETEROCYCLIC BASES

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Fifteen new mixed-ligand complexes of titanium (III), rhodium (III) and platinum (IV) with diphenic acid (DAH_2) and nitrogen-containing heterocyclic bases have been prepared. The complexes have the composition $\text{K}[\text{M}(\text{DA})_2\text{L}]$, $\text{K}_2[\text{M}(\text{DA})_2(\text{OL})]$, $[\text{Pt}(\text{DA})_2\text{L}]$ and $\text{K}[\text{Pt}(\text{DA})_2(\text{OL})]$, where $\text{M} = \text{Ti}(\text{III})$ or $\text{Rh}(\text{III})$; $\text{DA} =$ dianion of diphenic acid; $\text{L} =$ 2-aminopyridine (Apy), 2,2'-bipyridine (Bipy), 2,2'-biquinoline (Biq) or 1,10-phenanthroline (Phen); $\text{OL} =$ anion of 2-pyridinol. The complexes were characterised on the basis of elemental analyses, conductivity measurements, magnetic measurements, infra-red and electronic spectral studies. All the complexes were found to be octahedral.

Key words: Mixed-ligand complexes, Diphenic acid, Heterocyclic bases.

Introduction

Diphenic acid has been used as an analytical reagent [1,2] and as a bidentate ligand in the formation of complexes with metal ions [3]. Heterocyclic bases are well known therapeutic agents [4-6] and their activity is generally enhanced when they are allowed to form complexes with metal ions [7]. Many complexes of platinum and rhodium act as active catalysts in reactions of industrial importance [8-10]. Some complexes of platinum exhibit potent antitumor activity [11]. The preparation and characterisation of mixed-ligand complexes of some metal ions with diphenic acid as primary and heterocyclic bases as secondary ligands have been reported [12-15]. Keeping these facts in view, we report herein the syntheses and characterisation of the mixed-ligand complexes of Ti(III), Rh(III) and Pt(IV) with diphenic acid and bidentate nitrogen-containing heterocyclic bases. The present paper deals with the synthetic aspects of the complexes and the subsequent papers will deal with the uses of these complexes in various fields.

Experimental

Physical measurements. IR spectra (KBr discs or Nujol mulls) were recorded with a Pye-Unicam SP3-300 IR spectrophotometer. Electronic spectra in $\text{N,N}'$ -dimethylformamide (DMF) were recorded on a Ultrospec K-4053 spectrophotometer. Magnetic measurements were carried out on a Johnson-Matthey magnetic susceptibility balance. Conductivities of $5 \times 10^{-4}\text{M}$ solutions of the complexes in DMF were measured at 26° using a WPA CM35 conductivity meter and dip-type cell with platinized electrodes. Melting points of the complexes were recorded with an electrothermal melting point apparatus.

Reagents and chemicals: All chemicals used were of reagent grade. Diphenic acid, rhodium (III) chloride and platinum (IV) chloride were obtained from Fluka Chemika

(Switzerland), Titanium (III) chloride was obtained from BDH and all other chemicals were used as supplied by E. Merck.

Preparation of the complexes. The general method for the preparation of the complexes was the following. Diphenic acid (0.002 mole) was dissolved in ethanol to which a solution of KOH (0.004 mole) in distilled water was added. This mixture was then added to a solution of metal chloride (0.001 mole) in distilled water followed by the addition of a solution of L or 2-pyridinol (0.001 mole) in ethanol (Biquinoline was dissolved in acetone. The solution of 2-pyridinol was prepared in one molar equivalent of aqueous KOH) with continuous stirring. The resulting mixture was heated at 70° for 1 hr. and then cooled. The precipitate formed was filtered, washed several times successively with distilled water and ethanol and dried under vacuum over silica gel.

Results and Discussion

Elemental analysis and conductivity. The analytical data and other physical properties of the complexes are given in Tables 1 and 2 respectively. All the complexes are insoluble in water but soluble in DMF. The molar conductance values (Table 2) indicate that the complexes 1-4, 6-9 and 15 are 1:1 electrolytes [16], complexes 5 and 10 are 1:2 electrolytes [16] and complexes 11-14 are non-electrolytes in DMF revealing that the anions are covalently bonded in all the cases. The analytical data and molar conductance values are consistent with six-fold coordination of Ti(III), Rh(III) and Pt(IV) complexes.

IR studies. Salient features of the IR spectra of the complexes are shown in Table 3. Free diphenic acid (DAH_2) shows a broad band at $3400\text{-}3600\text{ cm}^{-1}$, a very strong band at 1700 cm^{-1} and a strong band at 1450 cm^{-1} due to $\nu(\text{O-H})$, $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$, respectively. The complexes display $\nu(\text{C=O})$ bands at $1600\text{-}1630\text{ cm}^{-1}$ and $\nu(\text{C-O})$ bands at $1390\text{-}1430$

cm^{-1} , significantly lower than the free ligand value which indicates the coordination of diphenic acid through its carboxylate anions. The $\nu(\text{O-H})$ observed for the free diphenic acid disappears upon coordination revealing that diphenic acid is a bidentate, dinegative ligand coordinating through both carboxylate anions. The expected $\nu(\text{O-H})$ band due to 2-pyridinol (HOL) was also absent in the spectra of complexes 5, 10 and 15 revealing that 2-pyridinol is a uninegative, bidentate ligand coordinating through oxygen and nitrogen as well. Further support for the presence of M-O bonding is evident from the appearance of $\nu(\text{M-O})$ modes at $390\text{-}430\text{ cm}^{-1}$ in the spectra of these complexes [17].

The characteristic ring vibrations of the heterocyclic bases in the range $1400\text{-}1600\text{ cm}^{-1}$ generally show significant

TABLE 1. ANALYTICAL DATA AND YIELDS OF THE COMPLEXES
(CALCULATED VALUES ARE GIVEN IN PARENTHESES).

Compound	No.	Yield (%)	Metal (%)	C (%)	H (%)	N (%)
K[Ti(DA) ₂ (Apy)]	1	72	7.05 (7.24)	59.66 (59.89)	3.48 (3.32)	4.15 (4.23)
K[Ti(DA) ₂ (Bipy)]	2	67	6.35 (6.62)	62.70 (63.05)	3.40 (3.31)	3.71 (3.87)
K[Ti(DA) ₂ (Biq)]	3	60	5.60 (5.81)	66.57 (67.04)	3.35 (3.40)	3.26 (3.40)
K[Ti(DA) ₂ (Phen)]	4	80	6.48 (6.41)	64.30 (64.23)	3.26 (3.21)	3.70 (3.74)
K ₂ [Ti(DA) ₂ (OL)]	5	82	6.90 (6.83)	56.63 (56.47)	2.90 (2.85)	2.10 (1.99)
K[Rh(DA) ₂ (Apy)]	6	64	14.09 (14.36)	54.95 (55.29)	3.00 (3.07)	3.78 (3.90)
K[Rh(DA) ₂ (Bipy)]	7	70	12.85 (13.22)	58.30 (58.59)	3.13 (3.08)	3.45 (3.59)
K[Rh(DA) ₂ (Biq)]	8	68	11.76 (11.71)	62.61 (62.84)	3.24 (3.18)	3.07 (3.18)
K[Rh(DA) ₂ (Phen)]	9	75	12.70 (12.82)	59.58 (59.83)	2.90 (2.99)	3.40 (3.49)
K ₂ [Rh(DA) ₂ (OL)]	10	66	13.38 (13.60)	51.90 (52.36)	2.55 (2.64)	1.72 (1.85)
[Pt(DA) ₂ (Apy)]	11	71	24.92 (25.36)	51.24 (51.48)	2.95 (2.86)	3.45 (3.64)
[Pt(DA) ₂ (Bipy)]	12	60	23.15 (23.46)	54.37 (54.85)	2.72 (2.88)	3.23 (3.36)
[Pt(DA) ₂ (Biq)]	13	65	20.70 (20.94)	58.91 (59.26)	2.93 (3.00)	2.88 (3.00)
[Pt(DA) ₂ (Phen)]	14	75	22.92 (22.80)	55.86 (56.12)	2.88 (2.80)	3.20 (3.27)
K[Pt(DA) ₂ (OL)]	15	63	23.74 (24.10)	48.52 (48.93)	2.35 (2.47)	1.54 (1.72)

DA = dianion of diphenic acid ($\text{C}_{14}\text{H}_8\text{O}_4$); Apy = 2-aminopyridine ($\text{C}_5\text{H}_6\text{N}_2$); Bipy = 2,2'-bipyridine ($\text{C}_{10}\text{H}_8\text{N}_2$); Biq = 2,2'-biquinoline ($\text{C}_{18}\text{H}_{12}\text{N}_2$); Phen = 1,10-phenanthroline ($\text{C}_{12}\text{H}_8\text{N}_2$); OL = anion of 2-pyridinol ($\text{C}_5\text{H}_4\text{NO}$).

changes on complexation [18], but in our present complexes these bands could not be distinguished because of overlapping with $\nu(\text{C=O})$ and $\nu(\text{C-O})$ bands. The in-plane and out-of-plane ring deformation modes of the heterocyclic bases observed at 610 cm^{-1} and $\sim 420\text{ cm}^{-1}$ respectively, undergo shifts to higher frequencies in the present complexes confirming their coordination through nitrogen [19]. The presence of M-N bonding in the complexes is evident from the appearance of $\nu(\text{M-N})$ modes at $315\text{-}360\text{ cm}^{-1}$ in the spectra of the complexes [20].

TABLE 2. PHYSICAL PROPERTIES OF THE COMPLEXES
(D = DECOMPOSE).

Com-* pound	Colour	Melting point ($\pm 0.5^\circ$)	Molar conduc- tance ($\text{Ohm}^{-1}\text{cm}^2\text{mole}^{-1}$)	Magnetic moment (B.M.)
1	Cream	334	78.27	1.81
2	Cream	310	85.40	1.74
3	Yellow	328	81.47	1.68
4	Yellow	337	76.15	1.84
5	Cream	>360	160.28	1.77
6	Reddish black	356	82.00	0.00
7	Reddish black	325	80.07	0.00
8	Reddish black	338	89.34	0.35
9	Black	314	84.13	0.16
10	Black	>360	153.36	0.00
11	Red	300	3.19	0.32
12	Cream	285(d)	4.26	0.27
13	Reddish brown	306	12.14	0.46
14	Yellowish brown	294	7.45	0.00
15	Chocolate	345	71.50	0.20

* See Table 1.

TABLE 3. IR SPECTRAL DATA FOR THE COMPLEXES (BAND
MAXIMA IN CM^{-1}).

Compound*	$\nu(\text{C=O})$	$\nu(\text{C-O})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
1	1620s	1400s	420m	360m
2	1610s	1400s	425m	340w
3	1630vs	1390s	410w	335m
4	1600s	1390m	410m	350m
5	1620vs	1395s	430m	340w
6	1600m	1410m	390w	350m
7	1615m	1420m	430w	360w
8	1630s	1400m	415m	320m
9	1610s	1410m	390w	330w
10	1625m	1410m	420m	325w
11	1620s	1425s	400w	340m
12	1600s	1430m	415w	320w
13	1625s	1420m	420w	315w
14	1610s	1425m	410w	330m
15	1630s	1425m	425m	325w

*Relative band intensities are denoted by vs, s, m and w, meaning very strong, strong, medium and weak, respectively. *See Table 1.

Magnetic moments. The observed values of effective magnetic moment of the complexes at room temperature are given in Table 2. The magnetic moment values of Ti(III) complexes (1.68-1.84 B.M.) indicate that the complexes 1-5 are paramagnetic with one unpaired electron [21]. The magnetic moment values of Rh(III) and Pt(IV) complexes (0.00-0.46 B.M.) indicate that the complexes 6-15 are diamagnetic in nature [22,23] and this revealed that there was no change in the oxidation state of the metal ions on complex formation.

Electronic spectra. The electronic spectral data of Ti(III) complexes are given in Table 4 and that of Rh(III) and Pt(IV) complexes are given in Table 5. The Ti(III) complexes produced one band in the region 19723-20661 cm^{-1} . The band is obviously derived from the transition ${}^2T_{2g} \rightarrow {}^2E_g$ for octahedral Ti(III) complexes [24, 25]. The absorption spectra of diamagnetic octahedrally coordinated d^6 metal ion complexes give rise to two spin-allowed ${}^1T_{1g}$ and ${}^1T_{2g}$ and two spin-forbidden ${}^3T_{1g}$ and ${}^3T_{2g}$ excited states. But three d-d transitions have been observed in the spectra of the present Rh(III) and Pt(IV) complexes. Two of these are spin-allowed bands involving transitions ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ and one is spin-

forbidden band involving transition ${}^1A_{1g} \rightarrow {}^3T_{1g}$. Rh(III) complexes gave three bands in the regions 14947- 15432 cm^{-1} , 19530-20283 cm^{-1} and 25974-27173 cm^{-1} corresponding to the transition ${}^1A_{1g} \rightarrow {}^3T_{1g}$, ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$, respectively. Similarly, Pt(IV) complexes gave three bands at 18903-19305 cm^{-1} , 28571-29069 cm^{-1} and 34965-35587 cm^{-1} corresponding to the transitions ${}^1A_{1g} \rightarrow {}^3T_{1g}$, ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$, respectively. In addition to these d-d transitions Rh(III) and Pt(IV) complexes gave one metal to ligand charge transfer band in the region 37174-38314 cm^{-1} and 38461- 39215 cm^{-1} , respectively. All these bands are consistent with octahedral Rh(III) and Pt(IV) complexes [22,26-28].

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TABLE 4. ELECTRONIC SPECTRAL DATA OF Ti(III) COMPLEXES.

Compound*	Spectral band maxima (cm^{-1}) with assignment	
	${}^2T_{2g}$	$\rightarrow {}^2E_g$
1		20449
2		19723
3		20325
4		20661
5		19960

*See Table 1.

TABLE 5. ELECTRONIC SPECTRAL DATA OF Rh(III) AND Pt(IV) COMPLEXES.

Compound*	Spectral band maxima (cm^{-1}) with assignment			Charge transfer
	${}^1A_{1g} \rightarrow {}^3T_{1g}$	${}^1A_{1g} \rightarrow {}^1T_{1g}$	${}^1A_{1g} \rightarrow {}^1T_{2g}$	
6	15060	19723	27173	37453
7	15128	19530	26881	38314
8	14947	20120	25974	38167
9	15267	20283	26315	37878
10	15432	19960	26954	37174
11	18903	29069	35087	38461
12	19047	28571	34965	38910
13	19305	28901	35335	39215
14	19157	28818	35460	39062
15	19267	28818	35587	38610

*See Table 1.

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