

TABLE I

Compounds	%Metal Found (Reqd.)	%Nitrogen Found (Reqd.)	IR Bands in cm^{-1}						$\nu(\text{M}-\text{N})/\nu(\text{M}-\text{S})$
			$\nu(\text{NH}) + \nu(\text{OH})$	$\delta(\text{NH}_2)$	$\beta(\text{NH}_2)$	Thioamide Bands			
						I	II	III & IV $\nu(\text{C}=\text{S})$	
Pd(pth)	25.91 (26.05)	13.62 (13.71)	3060br (3220sbr)	1612s (1598s)	1490m (1476s)	1575m (1530s)	1390w (1375s)	722sh (1010sbr, 840s)	
Pd(ath) ₂	22.30 (22.72)	12.08 (11.95)	3188s, 3115s (3248br, 3185m)	1602s (1603vs)	1465m (1460m)	1570s (1530m)	1408m (1386s)	960s, 706m (940s, 840s)	422m, 345s
Pd(fth) ₂	27.19 (27.37)	14.81 (14.42)	3095m (3230m, 3170m, 3130m, 3105w)	1610m (1580s)	1470sh (1475s)	1560w (1540br)	1390s (1390s)	1010m, 708w (1005s, 820m)	456m, 336m
Pd(o-hth) ₂	24.00 (24.15)	12.62 (12.72)	3200s (3275sbr, 3235mbr)	1615m (1605s)	1480s (1465s)	1560s (1515br)	1375s (1365mbr)	700m (1000vs, 820vs)	
Pd(p-hth) ₂	22.49 (22.33)	11.88 (11.76)	3000br, 2400br (3030br, 2390br)	1580br (1575s)	1435br (1440mbr)	1530sh (1500br)	1370m (1375m)	715br (1012s, 830sbr)	403m, 335m

s=strong ; w=weak , m=medium ; br=broad and sh=shoulder.
The ir bands in paranthesis are those of the free ligands.

dsp² covalent bonding. The electronic absorption spectra of DMF solutions of the complexes do not display ligand field bands in visible region, they rather display strong absorption below 420 nm which probably envelopes the ligand field band expected for Pd(II) in square planar environment.

Free thiohydrazides display two to three distinct ir bands (Table I) in 3μ region due to $\nu(\text{NH})$, $\nu_s(\text{NH}_2)$ and $\nu_{as}(\text{NH})$ vibrations⁷. In complexes, the coordinated thiohydrazides display only a broad and medium band between 3100 and 3250 cm^{-1} . The $\delta(\text{NH}_2)$ vibration of thiohydrazides is not affected appreciably but the $\beta(\text{NH}_2)$ is shifted to higher wavenumber indicating the involvement of hydrazine part terminal nitrogen in bond formation^{8,9}. Free o-hthH and p-hthH display a broad and medium band near 2650-2350 cm^{-1} attributable to hydrogen bonded phenolic OH which are retained in their Pd(II) complexes indicating that phenolic group is not involved in coordination with Pd(II) ions. The ligands possess potential thioamide group and therefore display characteristic thioamide bands (I to IV) in the region 1550-770 cm^{-1} . The thioamide bands I and II are raised to higher frequencies while thioamide band IV mainly due to $\nu(\text{C}=\text{S})$ is shifted to lower frequencies indicating the bonding of thiocarbonyl sulphur by deprotonation of thiol tautomer of the ligands^{10,11}. In far infrared region, the complexes display two to three medium to weak bands assignable to Pd-N and Pd-S vibrations. The energy of these bands are well within the range expected for $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{S})$ vibrations^{12,13}.

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Studies on Rh(III) and Pt(IV) Complexes of Schiff Bases

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COMPLEXES of Rh(III) and Pt(IV) with the Schiff bases, N-4-methylphenacylidene anthranilic acid (MPAA) and N-4-methylphenacylidene-o-aminophenol(MPAP) have been isolated and assigned octahedral structures on the basis of analytical, magnetic, electronic and ir spectral data. Electronic spectral studies indicate that the ligand field bands observed for Rh(III) complexes are analogous to those observed in Pt(IV) complexes.

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TABLE 1—ANALYTICAL DATA*, PHYSICAL PROPERTIES OF THE COMPLEXES

Complexes and their colour	pH of isolation	Decomp. point °C	%Analysis : Found(Calcd.)				Mol. wt. Found (Calcd.)
			C	N	Cl	Metal	
[Rh(C ₁₅ H ₁₁ NO ₂) ₃].Cl Blackish brown	4.0	225	56.80 (57.22)	4.02 (4.17)	5.00 (5.29)	15.16 (15.64)	612 (671)
[Rh(C ₁₅ H ₁₁ NO ₂) ₃].Cl Violet	4.5	138	58.00 (58.86)	4.26 (4.54)	5.68 (5.79)	16.25 (16.74)	570 (615)
[Pt(C ₁₅ H ₁₁ NO ₂) ₃].Cl ₂ Red	3.5	221	48.00 (48.12)	3.92 (3.50)	8.70 (8.89)	24.03 (24.38)	752 (798)
[Pt(C ₁₅ H ₁₁ NO ₂) ₃].Cl ₂ Dark brown	3.8	143	48.88 (48.51)	3.69 (3.77)	9.24 (9.56)	25.89 (26.28)	715 (742)

* Satisfactory H analysis was obtained for all the complexes.

Experimental

The Schiff bases were prepared and characterised as reported earlier¹. Ethanolic solutions of the ligands were used throughout. Metal chlorides were A. R. grade (Johnson and Matthey). The organic solvents were of reagent quality and were dried just prior to use.

The complexes of Rh(III) and Pt(IV) were isolated by refluxing a stoichiometric mixture of the metal chloride and ligand in ethanol solution on waterbath for 3.0-4.5 hr. On refrigeration for a few days, reaction mixture yielded blackish brown, violet, red and dark brown crystals of complexes which were washed with water, ethanol and ether and dried in vacuum (yield 60-70%). Elemental analysis were made at C. D. R. I., Lucknow and metals were estimated by standard methods². Molecular weight of the complexes were determined cryoscopically in benzene. Melting and decomposition points were detected by using Toshniwal melting point apparatus. The results of analysis and physical properties are recorded in Table 1.

Magnetic studies of the complexes were made on Guoy balance and the electronic spectra were recorded in nujol-mull on a Cary-14 recording spectrophotometer. The ir spectra of the complexes were recorded on a model 577-Perkin-Elmer Infrared spectrophotometer in CSI medium. The ligand-metal ratio was determined by pH-metric titrations on Philips pH-meter PP9040 and showed 2:1 complexation.

Results and Discussion

The complexes of Rh(III) and Pt(IV) are diamagnetic as expected, the ground state suggesting spin paired octahedral stereochemistry. The ground state of Rh(III) and Pt(IV) which belongs to d⁶ system is ¹A_{1g}. Four bands can be expected corresponding to ¹A_{1g}→³T_{1g}, ¹A_{1g}→³T_{2g}, ¹A_{1g}→¹T_{1g} and ¹A_{1g}→¹T_{2g} transitions³.

The visible spectra of Rh(III) complexes in acetone showed absorptions at 15000 (14800) cm⁻¹, 19500 (19450) cm⁻¹, 25900 (26000) cm⁻¹ which are consistent with six-coordinated pseudooctahedral stereochemistry of these complexes⁴. The first two

appear to be the split components of transition ¹A_{1g}→¹T_{1g} expected in octahedral complexes⁴. The complexes also appear to have effective D_{4h} symmetry and hence the first two bands may be assigned to the transition ¹A_{1g}→¹E_g and ¹A_{1g}→¹A_{2g} in the increasing order of energy. The third band appearing at 25900 (26000) cm⁻¹ is assigned to transition ¹A_{1g}→¹T_{2g}. The values of different crystal field parameters such as 10D_q, B, C, β and ligand field stabilisation energy calculated are 21750(21775) cm⁻¹, 400(409), 2250(2325), 0.55(0.56) and 149.16 k.cal/mol respectively. In addition to the three d-d bands, the complexes show more bands around 32000, 39500 cm⁻¹ which have been attributed to Rh(III) complexes ligand→metal charge-transfer transitions.

An octahedral geometry for the platinum complexes is supported by electronic spectra. In case of Pt(IV) complexes, three bands are assigned to the transitions at 17200(18250) cm⁻¹ [¹A_{1g}→³T_{2g}], 23900 (24200) cm⁻¹ [¹A_{1g}→³T_{1g}] and 38300 (38600) cm⁻¹ [¹A_{1g}→¹T_{1g}]⁴. Since in Pt(IV) complexes the CT band in the visible region masks all the weak d-d transitions, no definite information regarding the structure could be obtained from the electronic spectra.

Infrared spectra studies: One strong band in the case of each ligand in the region 1600-1616 cm⁻¹ has been observed due to azomethine (-CH=N-) group. This is considerably lowered in the spectra of the complexes, showing thereby complex formation through this group which is further supported by the appearance of bands corresponding to M-N bands in the region 510-530 cm⁻¹.

The stretching deformation modes of the phenolic OH group disappear in the spectra of the MPAP complexes indicating the loss of phenolic proton on complexation and formation of M-O band in the region 425-475 cm⁻¹. However, an absorption band appearing at 2700 cm⁻¹ due to OH of carboxylic group⁵ in MPAA also disappear on complexation because of the formation of M-O band due to loss of proton.

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Far-Infrared Spectra of Copper(II) *n*-Alkanoates

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DESPITE the wealth of data¹⁻³ about copper(II) carboxylates, far-infrared studies of the metal ligand frequencies have, with the exception of some reports⁴⁻⁸, escaped attention. These workers assigned Cu-O stretching vibrations to copper(II) acetate complexes. Moreover, these studies lack a study of the copper-oxygen vibrations based on selection rules and a reasonable assignment could not be proposed. In the present communication, we have tried to include the selection rules to calculate the Cu-O (acetate) vibrations in different possible moieties, compared with the total number of vibrations actually observed and proposed a tentative assignment of Cu-O bands of some copper(II) *n*-alkanoates.

Experimental

Complexes were prepared by the literature routes⁹⁻¹². All the compounds were identified by elemental analysis as in Table 1.

Complexes	Cu%		O%		H%	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
Cu(CH ₃ COO) ₂ ·H ₂ O	27.65	27.5	25.53	25.6	4.25	4.3
Cu(CH ₃ COO) ₂ ·2H ₂ O	31.83	31.7	24.06	24.4	4.01	4.18
Cu(CH ₃ COO) ₂	34.98	34.9	26.44	26.4	3.81	3.27
Cu(C ₂ H ₅ COO) ₂	30.34	30.3	34.36	34.2	4.77	4.7
Cu(<i>n</i> -C ₃ H ₇ COO) ₂	26.73	26.8	40.42	39.8	5.89	5.8
Cu(C ₆ H ₅ CH ₂ COO) ₂	19.04	20.0	57.57	57.65	4.19	4.2
Cu(C ₁₀ H ₇ CH ₂ COO) ₂	14.64	14.6	66.43	66.5	4.15	4.2

Far-infrared spectra were obtained as Nujol mulls between 500-200 cm⁻¹ on a Perkin-Elmer 377 spectrophotometer.

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Results and Discussion

Magnetic susceptibility, uv and visible spectral studies^{13,14} of copper(II) acetate, propionate, *n*-butyrate, phenylacetate and α -naphthylacetate show a dimeric bridged cage type of structure for these complexes, similar to that of copper(II) acetate monohydrate¹⁵.

In the structure of copper(II) acetate monohydrate the moiety immediately around the copper atom is CuO₅ in which the Cu atom is slightly above the plane of four oxygen atoms at the corners of a square base and the fifth oxygen atom is coordinated to the copper atom at *trans* axial position. The fifth oxygen atom is in principle, of different nature as shown in Fig. 1. The Cu atom is also linked to other Cu atom by a very weak δ -bond.

O* = Hydroxyl Oxygen.

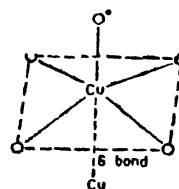


Fig. 1. Dimeric structure of copper(II) acetate monohydrate.

No Cu-Cu bond has, therefore, been considered. The CuO₅ moiety belongs to the point group C_{4v}. For other anhydrous *n*-alkanoates the moiety is CuO₄ which also belongs to the C_{4v} point group. For CuO₄ moiety 2A₁+2B₁+B₂+2E normal vibrations are allowed of which only 2A₁+2E vibrations are active in infrared, whereas for the CuO₅ moiety 3A₁+2B₁+B₂+3E vibrations are allowed by the selection rules of which only 3A₁+3E are active in infrared. The presence of 4 and 6 bands in CuO₄ and CuO₅ moieties respectively lead us to conclude that the symmetry is not lowered.

If the Cu atom lie in the plane of the four oxygen atoms, the moiety CuO₄ has D_{4h} symmetry and will have 1A_{2u}+2E_u infrared active band from A_{1g}+B_{1g}+B_{2g}+A_{2u}+B_{2u}+2E_u vibrations allowed by selection rules.

Observed Cu-O bands and molecular structure: The total number of Cu-O bands observed are mentioned in Table 3. All vibrations due to ligands were neglected by comparing the spectra of copper(II) complexes with that of sodium salts of corresponding ligand. Vibrations due to lattice and crystal symmetry are not considered because these are very weak and mostly lie below 200 cm⁻¹. It has also been assumed that bending vibrations might be mixed with ring deformation due to existence of the ring in the structures.

The square pyramidal structure for CuO₅ moiety in copper(II) acetate monohydrate is well established¹⁵. Therefore, the CuO₄ moieties of anhydrous copper(II) *n*-alkanoates can be presumed to have square pyramidal structure which is supported