

TABLE II
Infrared spectra (KBr) pellets) in cm^{-1} of complexes

Compound	N-H stretch	N-H bend and thioamide CN	C-S stretch	Ring C-N-C	Ring C-O-C
MTA ligand	3140m 3080m	1580m 1520s	700s	1150m	1110s
$\text{TeCl}_4 \cdot 2\text{MTA}$	3450m 3160m	1575m 1535m	690s	1145m	1100s
$\text{TeBr}_4 \cdot 2\text{MTA}$	3420m 3150m	1570m 1535m	690s	1145m	1110s
$\text{TeI}_2 \cdot 2\text{MTA}$	3450br 3160m	1580m 1530m	690s	1150m	1095s

dichloromethane) indicated molecular weights of 700 and 885 respectively for the two complexes. This showed that the complexes were monomeric in solution (expected; 714 and 892 respectively). No suitable solvent was available for $\text{TeI}_2 \cdot 2\text{MTA}$.

The infrared characteristics of the complexes are indicated in Table II.

In view of the poor ligation characteristics of the ethereal O and the thiureide N and the acknowledged soft basicity of thiureide S and the soft acidity of Te(II) and to a less extent of Te(IV), coordination of MTA to Te only through S is expected in the complexes although MTA has four possible coordination sites. In conformity with this expectation, the C-S stretch of the ligand does show a significant lowering in the complexes though not to an appreciable extent. Far i.r. results were collected but it was difficult to pick out the Te-S absorptions from the large number of bands observed in this region.

The electronic spectra of the complexes in dichloromethane ($2-4 \times 10^{-5}$ M solutions) revealed mostly intraligand transitions at ν 44 kK ($\phi \epsilon = 2.4 - 9.7 \times 10^4$ in $\text{mol}^{-1} \text{cm}^2$), 38 kK ($2.9 - 6.4 \times 10^4$) and 35 kK ($1.6 - 3.6 \times 10^4$). In addition the chloro complex showed charge transfer absorption at 23.53 kK (1.03×10^3) and the bromo complex at 24.39 kK (6.18×10^3) and 23.26 kK (1.8×10^3).

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GRAVIMETRIC ESTIMATION OF Pd(II) WITH *o*-(2-PYRROLIDENEIMINO) BENZOIC ACID

SEVERAL gravimetric reagents^{1,2} have been suggested for the estimation of Pd(II). The present note deals with the use of *o*-(2-pyrrolideneimino) benzoic acid (H_2PB) as a gravimetric reagent for Pd(II) since the synthesis of the reagent is simple and the reagent highly specific. The Pd(II)-complex is insoluble in water and can thus form the basis of a quantitative separation procedure.

H_2PB was prepared from pyrrole-2-carboxaldehyde and *o*-aminobenzoic acid by the method reported earlier³, m.p. 180°. It gives a lemon-yellow precipitate with Pd(II) in the pH range 0.7-3.2.

A stock solution of Pd(II) (0.6 g/l) in 0.1M HCl was standardised gravimetrically by the dimethyl glyoxime method⁴.

Determination of Pd(II): An aliquot of the metal ion solution was diluted to about 150 ml, its pH was adjusted between 0.7-3.2 with HCl (1.0 N) and

heated between 50–60°. Then it is treated with an excess of 1% solution of H₂PB in 10% ethanol till no further precipitation took place. It was heated on a water-bath for half an hour, filtered hot through a sintered glass crucible (porosity 4), washed with water-alcohol mixture (containing 1% EtOH) until free from the reagent, dried at 100–110° and weighed as Pd (C₁₂H₈N₂O₂) (H₂O). The results obtained are given in Table I.

TABLE I

Results of gravimetric estimation of Palladium(II)

Weight of complex mg	Palladium, mg		
	Found	Calcd.	Error %
297.30	97.52	97.74	0.22
272.15	88.32	88.55	0.26
240.65	78.09	78.29	0.25
190.12	61.64	61.86	0.35
160.45	52.04	52.19	0.28

Effect of foreign ions: In order to assess possible analytical applications of the reagent, the effect of some ions which often accompanied palladium was studied. Alkali metal salts were used for the solutions of anions and nitrates, chlorides and sulphates for the solution of cations. For 0.1 gm of the Pd(II) solution, the tolerance limit is 10 mg for Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II), 5 mg for UO₉⁺² and VO⁺², 100 mg for Pt(IV) and 2 mg for Rh(III).

Structure: The molecular weight of Pd(II)-complex in benzene was found by ebulliometry to be 327 ± 12. The elemental analysis and molecular weight data suggest 1:1 (metal-ligand) stoichiometry besides the presence of one water molecule. The magnetic susceptibility measurement indicates the complex to be diamagnetic. The electronic absorption spectra of the complex in benzene consist of three bands with their peaks at 22400, 26800 and 30500 cm⁻¹ assignable respectively to the transitions ¹A_{1g} → ¹B_{1g}; ¹A_{1g} → ¹E_g and ¹A_{1g} → ¹A_{2u} which suggest its square-planar stereochemistry⁵.

The i.r. spectra of H₂PB show bands at 3190, 2750, 1690 and 1600 cm⁻¹ assignable to bonded νNH, νCOOH, νC=O and νC=N, respectively. In the spectra of the Pd(II)-complex, the bands at 3190 cm⁻¹ and 2570 cm⁻¹ have disappeared indicating the complexation through imine nitrogen and carboxylate oxygen, respectively. The appearance of three new bands, at 1590, 530 and 565 cm⁻¹ can be assigned to the

presence of νC=N, νPd-O and νPd-N, respectively. The band observed at 3400 cm⁻¹ may be due to the presence of νOH of water molecule.

The very small value (1.5 ohm⁻¹ cm² mole⁻¹) of molar conductance of 10⁻³ M solution of complex in dioxane indicates its non-electrolytic nature.

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COLORIMETRIC METHOD FOR ESTIMATION OF OXYMETAZOLINE HYDROCHLORIDE

THE application of acid-dye¹ method has been extended for colorimetric estimation of oxymetazoline hydrochloride. Bromo cresol green and bromo phenol blue have been applied as reagents. The pH for bromo cresol green is 3.4 and for bromo phenol blue is 2.5. For both reagents λ-maximum is 420 nm, colour stability is one hour. In the case of bromo phenol blue, Beer's law is obeyed between 4 to 16 μg/ml and in the case of bromo cresol green the Beer's law is obeyed between 3 to 15 μg/ml. The results obtained were compared with the N.F.² method.

The review article¹ on acid-dye method reveals that acid-dye method is not used for oxymetazoline hydrochloride. National Formulary (N.F.)² describes u.v. and non-aqueous titration methods. The Drugs Standards Laboratory, American Pharmaceutical Association³ has reported qualitative and quantitative tests for oxymetazoline hydrochloride. The quantitative methods are same as N.F.². In qualitative tests one lengthy colour reaction with sodium nitropruside has been reported but it is not extended for assay procedure. The proposed acid-dye method is the first colorimetric method for estimation of oxymetazoline hydrochloride.

Experimental

Standard solution of oxymetazoline was prepared in water to give a concentration of 20 μg/ml. Similarly sample solution of nasal drop was diluted to give concentration of 20 μg/ml. Bromo cresol green and bromo phenol blue solutions were prepared by dissolving 40 mg of each to 100 ml distilled water.