

the base adducts have absorption bands in the U.V. region around 220, 270 and 310 nm indicating E<sub>1</sub>, E<sub>2</sub> (and the ester) and B bands respectively of the nitrogen base.

Copper complexes show one broad absorption band in the 650–675 nm region. It has been observed that greenish colours and absorptions in the vicinity of 700 nm are indicative of penta or hexa coordinated Cu(II). Recent studies<sup>9</sup> on electronic spectra of Cu(II) indicate that the three transitions  $2B_1 \rightarrow 2A_1$  ( $\nu_1$ ),  $2B_1 \rightarrow 2B_2$  ( $\nu_2$ ),  $2B_1 \rightarrow 2E$  ( $\nu_3$ ) are close in energy and often give rise to a single broad band envelope. So the present complexes probably have a distorted octahedral configuration. This is in conformity with some earlier observations by Graddon<sup>10</sup> *et al.*

Cobalt(II) complexes have two absorption bands around 520 and 500 nm which may be assigned as the  $4T_{1g}(F) \rightarrow 4T_{1g}(P)$  transition. The splitting might be due to tetragonal distortion or spin-orbit coupling effect. Actually three spin allowed d-d transitions are expected for octahedral cobalt(II) complexes. The  $4T_{1g}(F) \rightarrow 4T_{2g}$  transition which occurs around 1200 nm could not be recorded as it was beyond the range of instrument used. The other transition i.e.,  $4T_{1g}(F) \rightarrow 4A_{2g}$  is usually weak since it involves a two electron process. Weakness combined with closeness of this transition to  $4T_{1g}(F) \rightarrow 4T_{1g}(P)$ , renders it unobserved. The cobalt(II) complexes presumably have a highspin octahedral configuration as reported for adducts of Co(II) acetylacetonates by Fackler and co-workers<sup>11</sup> and Horrocks<sup>12</sup> *et al.*

Three absorption bands are noticed for nickel(II) complexes around 950, 630, 400 nm. Octahedral nickel(II) ion has three distinct spin-allowed transitions. The above three absorption bands may be assigned to the three transitions i.e.,  $3A_{2g} \rightarrow 3T_{2g}$  ( $\nu_1$ ),  $3A_{2g} \rightarrow 3T_{1g}(F)$  ( $\nu_2$ ) and  $3A_{2g} \rightarrow 3T_{1g}(P)$  ( $\nu_3$ ), respectively. Hence the nickel(II) complexes reported in the present investigation are highspin octahedral complexes similar to compounds reported earlier<sup>13</sup>. Complexes of zinc are six coordinated octahedral similar to the base adducts of acetylacetonates by Graddon<sup>14</sup> *et al.*

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## Synthesis of some Derivatives of Pyrazolo [3, 4-d]-pyrimidin-4, 6-diones\*

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A number of quinazoline-4-ones and quinazoline-4,6-diones were earlier synthesised in our laboratories and some of them showed very interesting pharmacological properties. In continuation of our work in this field, some pyrazolo [3,4-d]-pyrimidin-4,6-diones were synthesised in order to find out what effect replacement of a benzo group by a pyrazolo group will have upon the pharmacological activity.

Ethyl ethoxymethylenecyanoacetate<sup>1</sup> was treated with phenylhydrazine to give 1-aryl-5-aminopyrazolo-4-carboxylate (I). Treatment of I with aryl or alkylisocyanate gave the urea derivative (II), which was cyclised with sodium ethoxide in ethanol to give the pyrazolo-[3,4-d]-pyrimidin-4,6-dione. Substituted phenylhydrazines were prepared by reported methods<sup>2</sup>. The table gives the list of compounds which were prepared.

These compounds were screened for CNS depression properties and anti-inflammatory activity. None of the compounds showed any significant CNS depression properties. Quite a few of them showed anti-inflammatory properties. Compounds VIII and XII have shown anti-inflammatory properties equivalent to Aspirin in rats at 200 mg/kg dose level.

## Experimental

### 1-phenyl-5-aminopyrazole-4-carboxylate (I) :

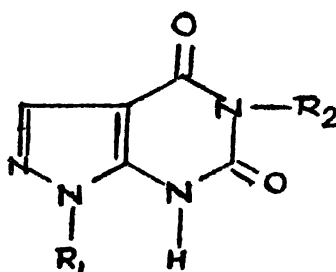
A mixture of ethyl ethoxymethylenecyanoacetate (16.9 g; 0.1 mole) and phenylhydrazine (10.8 g; 0.1 mole) in ethanol (100 ml) was refluxed for 2 hr. Ethanol was distilled off under reduced pressure and the solid obtained was crystallised from benzene-petroleum ether mixture; m.p. 96–98° (reported<sup>3</sup> 99–101°); yield = 15.6 g.

### 1-phenyl-5-phenylureidopyrazole-4-carboxylate (II) :

A mixture of I (4.6 g; 0.02 mole) and phenylisocyanate (2.4 g; 0.02 mole) in dry pyridine (10 ml.) was

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TABLE



No.	R <sub>1</sub>	R <sub>2</sub>	m.p. °C	% Nitrogen	
				Calculated	Found
I	Phenyl	Phenyl	259-62	18.4	18.5
II	Phenyl	<i>o</i> -Tolyl	234-36	17.7	17.7
III	Phenyl	<i>p</i> -Tolyl	277-78	17.7	17.6
IV	Phenyl	<i>o</i> -Anisyl	294-96	16.7	16.4
V	Phenyl	<i>o</i> -Chlorophenyl	245-47	16.6	16.4
VI	<i>p</i> -Tolyl	Phenyl	311-13	17.7	17.6
VII	<i>p</i> -Tolyl	<i>o</i> -Tolyl	246-47	16.8	17.2
VIII	<i>p</i> -Tolyl	<i>m</i> -Tolyl	185-87	16.8	17.1
IX	<i>p</i> -Tolyl	<i>p</i> -Tolyl	260-63	16.8	16.8
X	<i>p</i> -Chlorophenyl	Phenyl	303-05	16.6	16.2
XI	<i>p</i> -Chlorophenyl	<i>o</i> -Tolyl	163-64	15.9	16.2
XII	<i>p</i> -Chlorophenyl	<i>m</i> -Chlorophenyl	252-55	15.0	15.4
XIII	<i>p</i> -Anisyl	Phenyl	184-85	16.8	17.0
XIV	<i>p</i> -Anisyl	<i>o</i> -Tolyl	180-82	16.1	16.3
XV	<i>p</i> -Anisyl	<i>m</i> -Chlorophenyl	186-87	15.2	15.6

kept at 110° for 2 hr, cooled and poured into ice-cold 2*N* aqueous hydrochloric acid (100 ml.). The separated solid was crystallised from benzene-petroleum ether mixture; m.p. 143-45°; yield = 5.5 g.

#### 1,5-diphenylpyrazolo [3,4-d]-pyrimidine-4,6-dione :

II (3.5 g; 0.01 mole) in absolute alcohol (40 ml.) containing 0.25 g of sodium, was kept under reflux for 2 hr. Alcohol was distilled off under reduced pressure and to the residue was added 100 ml. of water. The insoluble part was filtered off and the clear aqueous solution was acidified with dilute hydrochloric acid. The separated solid was crystallised from aqueous alcohol; m.p. 259-61°; yield = 2.1 g. Found : N, 18.51; C<sub>17</sub>H<sub>12</sub>N<sub>4</sub>O<sub>2</sub> requires : N, 18.42%.

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#### Nitrogen Transport during Non-Faradaic Electrolysis

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PALIT has demonstrated<sup>1,2</sup> that electrolysis of dilute solutions at low current density gives results apparently incompatible with Faraday's law. He calls it non-Faradaic electrolysis, the following three anomalies being its main features<sup>1,2</sup>: (i) Volume deficit, (ii) Ratio anomaly and (iii) Co-liberation (i.e., liberation of H<sub>2</sub> and O<sub>2</sub> together on the same electrode). Some independent confirmations of these anomalies are now forthcoming<sup>4,5</sup>.

However under the same conditions if the electrolysis is done in an open-to-air type cell as shown in Figure 1 both the electrode gases contain a considerable proportion of nitrogen<sup>3</sup>. Furthermore, Palit has reported<sup>3</sup> that if in the intermediate portion of a cell which is evidently quite away from the electrodes are kept enclosed some electroneutral gases such as nitrogen or argon, the latter get transported out of this