Complexes of Pyrrole-1,2-dithiodicarboximide with Fe(II), Co(I), Ni(0), Cu(I), Ag(I), Ru(II), Rh(I), Pd(0) & Pt(0)

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Complexes of pyrrole-1, 2-dithiodicarboximide (PDD) with Fe(II), Co(I), Ni(O), Cu(I), Ag(I), Ru(II), Rh(I), Pd(0) and Pt(0) have been isolated in the solid state. Their stoichiometries and structures have tentatively been assigned on the basis of analytical, magnetic and spectroscopic (IR, UV and visible) studies. The ligand functions as bidentate in all the complexes, except in [Ag(PDD) (PPh3)3]NO3 and [Rh(PDD) (CO)Cl(PPh3)3] where it behaves as monodentate.

The remarkable antitumor activity of cis-dichloro-diammineplatinum(II) and related species has stimulated much interest in the design and synthesis of a large number of model metal complexes, which could mimic the metal ions in the biological systems. In view of the potential interest in the complexing properties of sulphur and nitrogen containing ligands, the syntheses and characterisation of a few transition metal complexes of pyrrole derivatives were reported from our laboratory.

In continuation of our efforts in this area, this paper reports the syntheses and spectroscopic identification of the reaction products of pyrrole-1, 2-dithiodicarboximide(I) with various metal complexes.

Preparation of metal complexes: (i) Dichloro(PDD) bistriphenylphosphine)iron(II)
To a solution of [Fe(PPh3)2Cl2] (0.6 g, ~1 mmol) in benzene (15 ml) was slowly added a solution of POD (0.4 g, ~2 mmol) in benzene (10 ml). The red solution was refluxed for 1 hr, whereby the colour of the solution was changed to green in the first ten minutes. The clear solution was concentrated to half its original volume under reduced pressure. The greenish brown complex was precipitated by the addition of 10 ml pet ether, filtered, washed successively with water, ethanol and ether, dried in vacuo, and recrystallised twice from benzene-pet ether; m.p. 208; yield ~40%.

(ii) Dichloro(PDD)bistriphenylarsine) ruthenium(II)
A solution of PDD (0.3 g, 1.5 mmol) in benzene (10 ml) was added with stirring to a solution of [RuCl3(PPh3)3] (0.5 g, 0.5 mmol) in chloroform (15 ml). The resulting deep blue solution was centrifuged after 1 hr and the volume of the supernatant reduced to 10 ml under reduced pressure. The blue complex that precipitated out by the addition of 15 ml of pet ether (60-80), was filtered, washed with ethanol and ether, dried in vacuo and recrystallised from chloroform-pet ether, m.p. 208-19; yield ~48%.

(iii) Dichloro(PDD)bistriphenylarsine) ruthenium(II)
The procedure (ii) described above was used, taking RuCl3(AsPh3)2 MeOH in place of [RuCl3(PPh3)3]. The blue complex was recrystallised from chloroform-pentane; m.p. 230-32; yield ~55%.

(iv) Hydrido(PDD)bistriphenylphosphite) cobalt(I)
To a solution of [CoH(P(OPh3)3)] (0.6 g) in dichloromethane (20 ml), PDD (0.3 g, 2 mmol) in benzene (8 ml) was added with stirring. After stirring

Materials and Methods
All the chemicals used were either chemically pure or of analar grade. The solvents were dried and freshly distilled before use. All operations were carried out under pure and dry nitrogen atmosphere. Pyrrole-1, 2-dithiodicarboximide, hereafter referred as PDD; and the starting complexes, dichlorobis(triphenylphosphine) iron(II), dichlorotris(triphenylphosphine) ruthenium(II), trichlorobis(triphenylarsine) methanol-ruthenium(III), hydridotetrakis(triphenylphosphite) cobalt(I), chlorotris(triphenylphosphine) rhodium(I), chlorocarbonylbis(triphenylphosphine) rhodium(I), tetrakis(triphenylphosphite) nickel (0), tetrakis(triphenylphosphine) palladium(0), tetrakis(triphenylphosphine) platinum(0), chlorotris(triphenylphosphine) copper(I) and tetrakis(triphenylphosphine) silver(I) nitrate were prepared according to the methods described in the literature.

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\[
\begin{align*}
\text{N} & \quad \text{S} \\
\text{S} & \quad \text{NH}
\end{align*}
\]
for 2 hr, 10 ml of pet ether (60-80°) were added to the reduced bulk (10 ml) to get a dark brown complex, which were centrifuged, washed with pet ether and dried in vacuo; m.p. 168-70°; yield ~30%.

(v) Chloro(PDD)(triphenylphosphine)rhodium(I)
A solution of RhCl(PPh₃)₃ (0.3 g; ~0.3 mmol) in benzene (10 ml) was mixed with a solution of PDD (0.2 g, 1 mmol) in benzene (10 ml). The mixture was refluxed for 1 hr, cooled to room temperature, and 10 ml of pet ether (60-80°) were added to get a dark brown complex, which was centrifuged, washed with ethanol and ether, dried in vacuo and recrystallised from benzene-pet ether; m.p. 300°; yield ~60%.

(vi) Monocarbonylmonochloromono(PDD)bis(triphenylphosphine)rhodium(I)
The method as given in (ii) was adopted, taking [Rh(CO)Cl(PPh₃)₂] in place of [RuCl₂(PPh₃)₃]. The yellowish brown precipitate that settled down was centrifuged, washed with ethanol and ether, dried in vacuo and recrystallised from benzene-pet ether; m.p. 300°; yield ~60%.

(vii) Mono(PDD)bis(triphenylphosphite)nickel(I)
The above method (vi) was adopted, taking [Ni(P(OPh)₃)₄] in place of [Rh(CO)Cl(PPh₃)₂], to give a brown complex; m.p. 169-70°; yield ~30%.

(viii) Mono(PDD)bis(triphenylphosphine)palladium(0)
[Pd(PPh₃)₄] (0.6 g; ~0.5 mmol) in benzene (10 ml) was stirred with a solution of PDD (0.3 g; ~1.5 mmol) in benzene (10 ml). After 15 ml of pet ether (60-80°) were added after 1 hr to the resulting brown solution whereby a red-brown complex appeared which was centrifuged, washed with ethanol, ether, dried in vacuo, recrystallised from benzene-pet ether and stored in vacuo; m.p. 176-77°; yield ~65%.

(ix) Mono(PDD)bis(triphenylphosphine)platinum(0)
The procedure as described in (viii) was followed, taking [Pt(PPh₃)₄] in place of [Pd(PPh₃)₄]. A yellowish brown compound was obtained; m.p. 198-200°; yield ~60%.

(x) Monochloro(PDD)(triphenylphosphine)copper(I)
A solution of [CuCl(PPh₃)₂] (0.44 g; ~0.5 mmol) in benzene (15 ml) was stirred with a solution of PDD (0.3 g, 1.5 mmol) in benzene (7 ml) for 1 hr. The complex was precipitated by the addition of about 10 ml pet ether (60-80°) to the reduced bulk (10 ml). The white complex was recrystallised twice from benzene-pet ether, washed with n-pentane and dried in vacuo; m.p. 193-95°; yield ~42%.

(xi) Mono(PDD)(triphenylphosphine)silver(I)nitrate
A solution of [Ag(PPh₃)₄][NO₃] (0.6 g; ~0.5 mmol) in acetonitrile (15 ml) was stirred for 1 hr with a solution of PDD (0.3 g; ~1.5 mmol) in benzene (10 ml). The resulting red-brown solution was concentrated to 10 ml and to this was added dry-ether when a pale brown compound precipitated out. The precipitate was filtered off, successively washed with ethanol and ether, dried in vacuo and recrystallised twice from acetonitrile-ether; m.p. 300°; yield ~30%.

Physical measurements
Infrared spectra were recorded in KBr on a Perkin-Elmer 580 diffraction grating spectrophotometer in the range 4000-250 cm⁻¹. The electronic absorption spectra were recorded in chloroform on a Cary model 17-D spectrophotometer in the region 300-950 nm. Magnetic susceptibilities of the complexes were determined with the help of a Gouy balance at room temperature (25 ± 3°C), using mercury tetraethiocyanato(II) as the calibrant; diamagnetic corrections were made as outlined by Figgis and Lewis.¹⁷

Melting points of the complexes reported are uncorrected and were observed on a Fisher-Johns melting point apparatus.

Conductivities of millimolar solutions of the complexes in nitrobenzene were measured on an Elico conductivity meter type CM-80.

Results and Discussion
All the complexes are found to be non-ionic. Assuming that the metal ions adopt normally preferred geometries in their complexes, the analytical data (Table 1) are suggestive of the bidentate nature of PDD in all the complexes except silver and [Rh(PDD)(CO)Cl(PPh₃)₃] complexes, where the data are suggestive of monodentate nature of PDD. Irrespective of the fact that the ligand acts as a bidentate or a monodentate, it can coordinate with metal ions through any two or one of the three potential donor sites, viz. the imido-N and the two thiocarbonylsulphur atoms. The possible modes of coordination of PDD to metal ions have been arrived at on the basis of the comparative IR spectral studies of a number of related compounds.

Modes of bonding of PDD: IR spectral studies
The characteristic IR bands of pyrrole moiety (2910, 1550, 1470, 1450, 1140, 1040, 995, 750, 520 and 440...
Table 1—Characterisation Data of the Complexes and Their Possible Geometries

<table>
<thead>
<tr>
<th>Complex</th>
<th>Found (Calc) (%)</th>
<th>Possible geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Fe(PDD)Cl(PPh3)2</td>
<td>61.0</td>
<td>3.8</td>
</tr>
<tr>
<td>Ru(PDD)Cl(PPh3)2</td>
<td>58.1</td>
<td>3.5</td>
</tr>
<tr>
<td>Ru(PDD)Cl(AsPh3)2</td>
<td>52.8</td>
<td>3.4</td>
</tr>
<tr>
<td>Co(PDD)H(P(0 Phh)]</td>
<td>52.8</td>
<td>3.4</td>
</tr>
<tr>
<td>Rh(PDD)Cl(PPh3)]</td>
<td>50.4</td>
<td>3.1</td>
</tr>
<tr>
<td>Rh(PDD)(CO)Cl(PPh3)]</td>
<td>59.9</td>
<td>3.8</td>
</tr>
<tr>
<td>Ni(PDD)(P(OPh)3)]</td>
<td>59.3</td>
<td>3.7</td>
</tr>
<tr>
<td>Pd(PDD)(PPh3)]</td>
<td>62.9</td>
<td>4.0</td>
</tr>
<tr>
<td>Pt(PDD)(PPh3)]</td>
<td>56.7</td>
<td>3.5</td>
</tr>
<tr>
<td>Cu(PDD)(PPh3)]</td>
<td>54.5</td>
<td>3.4</td>
</tr>
<tr>
<td>Ag(PDD)(PPh3)](NO3)</td>
<td>48.2</td>
<td>3.2</td>
</tr>
</tbody>
</table>

18 cm\(^{-1}\) of the ligand do not undergo any shift in the spectra of the complexes (maximum shift ± 5 cm\(^{-1}\)) indicating, as expected, non-involvement of pyrrole ring nitrogen in bond formation. In case of bonding through \(-C(S)NHC(S)-\) moiety of the ligand, shifts in the positions of the thioimide bands are expected. The major shifts in the band positions arising due to this moiety are discussed below:

(a) The broadness of \(\nu\)NH of the free ligand at 3150 cm\(^{-1}\) (half-width = 100 cm\(^{-1}\)) was suggestive of hydrogen-bonding in the solid state. In the spectra of the complexes, this band shifted towards lower wavenumber and appeared around 3060 cm\(^{-1}\), suggesting increased electronegativity of the ring and the absence of deprotonation in the complexes.

(b) The spectra of the ligand as well as those of the complexes did not exhibit any band in the 2600-2000 cm\(^{-1}\) region, indicating that the ligand was present in the thione form.

(c) The four ligand bands in the region 1600-1300 cm\(^{-1}\) (1460, 1410, 1370 and 1350 cm\(^{-1}\)), have been assigned to the thioamide bands I and II, arising due to the coupled vibrations of \(\delta\)(NH), \(\nu\)(C = N) and \(\nu\)(C = S). In the spectra of the complexes, these bands shifted towards higher wavenumbers (1470 ± 5, 1435 ± 5, 1395 ± 5 and 1375 ± 5 cm\(^{-1}\), respectively). The shift of 1460 cm\(^{-1}\) band of the ligand, however, was relatively less in the complexes (≈ 10 cm\(^{-1}\)) than those of the other bands (≈ 25 cm\(^{-1}\)). These shifts suggested the interaction of the thioamide groups with metal ions, because of which, in the complexed state, the percentage contributions of the various internal coordinates [\(\delta\)(NH), \(\nu\)(C = N), \(\nu\)(C = C)] to the normal coordinates which gave rise to these bands were changed as compared to those in the free ligand. Since NH of the pyrrole ring group was involved in bond formation, the shift in the band position arising due to normal coordinate having major contribution from \(\delta\)(NH), should be relatively small (1460 cm\(^{-1}\) band). It was, therefore, assumed that 1460 cm\(^{-1}\) band could be assigned to \(\delta\)(NH) with minor contributions from \(\nu\)(C = N) and \(\nu\)(C = C). Furthermore, the blue shifts in the four band positions suggested the bonding of the metal ions through thiocarbonyl sulphur atom, resulting in the higher bond order of the CN group after complexation.

(d) Two broad bands at 1040 and 820 cm\(^{-1}\) of the free ligand shifted towards lower wavenumbers (≈ 20 cm\(^{-1}\)) in the spectra of the complexes. However, in the spectra of the [Rh(PDD)(CO)Cl(PPh3)]\(_2\) and in silver complexes, besides the band around 800 cm\(^{-1}\), another new band appeared around 850 cm\(^{-1}\). These bands have been assigned to thioamide bands III (having major contributions from \(\nu\)(C = C), \(\nu\)(C = N) and \(\nu\)(C = S) in the normal coordinate) and thioamide band IV (primarily due to \(\nu\)(C = S), respectively. The shifts in the positions of these bands towards lower wavenumbers...
in the complexes further confirmed the bonding of metal ion through thiocarbonyl sulphur.

It appears that the bonding of the metal ions through thiocarbonyl sulphur rendered the two thiocarbonyl groups non-equivalent in the complexes of rhodium and silver leading to two bands in their IR spectra. The bonded thiocarbonyl group is expected to absorb at a relatively lower wavenumber compared to the uncomplexed one. Therefore, the new band at 850 cm\(^{-1}\) in rhodium and silver complexes has been assigned to v(C=S) (uncomplexed).

(e) In the spectra of the complexes, the position of the ligand band at 490 cm\(^{-1}\) assigned to δ(C=S), shifted towards lower wavenumbers (~20 cm\(^{-1}\)).

(f) One or two new bands which appeared around 300 cm\(^{-1}\) in the spectra of all the complexes have been assigned to the coupled vibrations of v(M-S).

(g) The characteristic bands of triphenylphosphine or triphenylarsine were present in the spectra of all the complexes having PPh\(_3\) or AsPh\(_3\) as coligands.

(h) In the spectrum of silver complex, all the characteristic bands due to NO\(^{-}\) were present. It is, therefore, concluded, though tentatively, that the metal ions in all the complexes are bonded to sulphur atoms of the two thiocarbonyl groups.

Though from the IR spectra alone it is difficult to distinguish between monomeric and the polymeric nature of the complexes, the solubility of the complexes in non-aqueous solvents like dichloromethane, etc. indicates that the degree of polymerisation of the complexes is not of high order.

Room temperature magnetic moments: Geometry of the complexes

All the complexes, except that of Fe(II), are diamagnetic at room temperature. The diamagnetic nature of Ru(PDD)Cl\(_2\)(PPh\(_3\))\(_2\) and Ru(PDD)Cl\(_2\)(AsPh\(_3\))\(_2\) suggests that ruthenium(II) belongs to low spin d\(^6\)-system. Since all the known octahedral complexes of ruthenium(II) have been found to be low spin, it is assumed that the complexes, Ru(PDD)Cl\(_2\)(PPh\(_3\))\(_2\) and Ru(PDD)Cl\(_2\)(AsPh\(_3\))\(_2\) have octahedral geometries around ruthenium(II) ions.

The diamagnetic behaviour of [Rh(PDD)Cl(PPh\(_3\))]\(_2\), [Co(PDD)H\(_2\)(P(OPh))\(_3\)] is due to square planar geometry. The second diamagnetic complex, [Rh(PDD)(CO)Cl(PPh\(_3\))\(_2\)] could be assigned a square pyramidal geometry.

The complexes of Ni(II), Pd(II), Pt(II), Cu(I) and Ag(I), which were found to be diamagnetic, belong to d\(^{10}\)-system. Since d\(^{10}\) Ni(II), Pt(II) and Cu(I) complexes are diamagnetic and generally form tetrahedral complexes, it is assumed that the geometry for all the complexes under discussion is tetrahedral. Diamagnetic silver complex has been assigned a trigonal or linear geometry.

The iron complex has been found to be paramagnetic (5.0 B.M.), corresponding to four unpaired electrons. The value of magnetic moment of this complex is only slightly higher than the spin only value. [Generally, high spin iron(II) complexes exhibit a value of magnetic moment larger than 5.2 B.M.]. The slightly lower value observed may possibly be due to either distortion from the octahedral geometry or due to solid state effects.

Electronic spectral data

The UV spectrum of the ligand exhibited four absorption bands at 25640 (shoulder), 26667, 39216 and 42553 cm\(^{-1}\). The bands at 25640 and 26667 cm\(^{-1}\) have been assigned to n→π* and π→n* transitions, respectively. The bands at 39216 and 42553 cm\(^{-1}\) whose positions did not shift on complexation were characteristic of substituted pyrrole ring (π→π* transitions), suggesting that the metal ions did not interact with the π-system of the pyrrole ring, consistent with the IR spectral data. The free ligand band at 26667 cm\(^{-1}\) shifted towards higher wavenumbers, while that at 25640 cm\(^{-1}\), towards lower wavenumbers in the complexes. In practice, bonding between the thiocarbonyl sulphur and the metal centre ought to stabilise those orbitals having non-bonding electrons, while the π-levels should be destabilised. This effect will show up in the shifts in the band positions due to n→π* and π→π* transitions. The shifts in the positions of 25640 cm\(^{-1}\) towards lower wavenumbers and of 26667 cm\(^{-1}\) band towards higher wavenumbers, indirectly suggested that: (i) 25640 and 26667 cm\(^{-1}\) bands arose due to n→π* and π→π* transitions, respectively; and (ii) the thiocarbonyl groups of the ligand were interacting with the metal ions in the complexes.

In the spectra of all the complexes having PPh\(_3\), P(OPh)\(_3\) or AsPh\(_3\) the characteristic bands due to π→π* transitions of the phenyl group have also been observed.

The UV spectra of ruthenium(II) complexes exhibited two weak bands around 16000 and 19000 cm\(^{-1}\). One should expect in the spectra of low spin ruthenium(II) complexes (ground state \(^1\)A\(_{1g}\)) four bands arising due to \(^1\)A\(_{1g}\)→\(^3\)T\(_{1g}\), \(^1\)A\(_{1g}\)→\(^3\)T\(_{2g}\), \(^1\)T\(_{1g}\)→\(^3\)T\(_{1g}\) and \(^1\)T\(_{2g}\) transitions. Since the transitions due to \(^1\)A\(_{1g}\)→\(^3\)T\(_{1g}\) and \(^1\)T\(_{2g}\) will be spin-forbidden, the intensities of the bands arising due to these transitions should be very weak (ε<10). The bands around 16000 and 19000 cm\(^{-1}\) have, therefore, been assigned to \(^1\)A\(_{1g}\)→\(^1\)T\(_{1g}\) and \(^1\)T\(_{2g}\) transitions, respectively. Such bands have also been observed in the spectra of the analogous complexes of ruthenium(II).
In the spectra of rhodium(I) complexes (ground state $^{1}A_{1g}$), three spin-allowed and three spin-forbidden bands are expected. However, only one very weak band around 13333 cm$^{-1}$ was observed owing to the presence of an intense charge transfer band in the visible region. This band has been assigned to singlet-singlet transition$^{20-22}$.

As expected, the spectra of Ni(0), Pd(0), Pt(0), Cu(I) and Ag(I) complexes did not exhibit any band in the visible region (these metal ions belong to $d^{10}$-system). However, in the spectra of a few complexes a weak band was observed around 500 nm, which may be either due to charge transfer (M→L or L→M) or an intraligand band.

References
1 Rosenberg B, Plat Met Rei', 15 (1971) 42.