

In the ir spectra (KBr), a very strong ν_{C-N} band was observed at $2\ 020\text{ cm}^{-1}$ for $\text{Cs}_2[\text{Re}(\text{NCS})_6]$ and at $2\ 055\text{ cm}^{-1}$ for the two dinuclear complexes indicating that the complexes are most probably isothiocyanato ones^{1,2}. In ethanol medium, the cyanide band could be resolved in none of the complexes. This fact would favour the formulation $[(\text{SCN})_6\text{Re}-\text{Re}(\text{NCS})_6]^{4-}$ for the dinuclear complexes, since the presence of both bridging and terminal thiocyanate is likely to give more than one cyanide band.

The electronic spectra of $\text{Cs}_2[\text{Re}(\text{NCS})_6]$ in ethanol showed intense charge transfer bands at $38\ 600$ and $23\ 300\text{ cm}^{-1}$ which agree with the earlier observations^{1,2}. The spectra of $\text{Cs}_2[\text{Re}_2(\text{NCS})_{12}]$, however, gave intense bands at $29\ 400$ and $22\ 900\text{ cm}^{-1}$.

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Diacido Complexes of Palladium(II) with Morpholine

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MORPHOLINE ($\text{C}_4\text{H}_9\text{NO}$) is a potential nitrogen and oxygen donor ligand and its complexes with some transition metal ions are known¹⁻⁶. Zn^{2+} and Cd^{2+} complexes contain one and two ligand molecules³⁻⁶. In the bis-complexes, morpholine is bonded through N atom in chair form, while in mono complexes, it is a bridging ligand bonded to the metal atom through both nitrogen and oxygen atoms by retaining its chair conformation. The complexes of morpholine with platinum metals are not known in detail⁷. The platinum metal complexes are becoming important as anticancer agents⁸. The present paper describes the preparation and characterisation of palladium(II) complexes $[\text{Pd}(\text{L})_2(\text{X})_2]$, where L=morpholine; $\text{X}=\text{Cl}^-$, Br^- , I^- , NO_2^- and SCN^- .

Experimental

$[\text{PdL}_2\text{X}_2]$ ($\text{X}=\text{Br}^-$, I^- , SCN^- or NO_2^-): An aqueous solution of palladium(II) chloride (0.001 mol in 50 ml) was treated with an excess of potassium salt of the requisite anion (in about 1 : 4 molar ratio) and warmed to get a clear solution. To the resulting solution morpholine (0.002 mol)

was added dropwise with stirring, when a cream or orange-yellow precipitate was formed. The precipitate was digested on a steam-bath for 0.5 h, and filtered, washed with ethanol and dried over fused CaCl_2 , (90–95%).

$[\text{PdL}_2\text{Br}_2]$ (light green form): The cream yellow variety of the dibromo complex (~5 g) was suspended in ethanol (50 ml) and morpholine (2 ml) and refluxed on a steam-bath for 2 h when the yellow compound was completely transformed to a light green product. It was filtered, washed with ethanol and dried over fused CaCl_2 .

Chemical analysis (Table 1), electronic reflectance and ir spectra of the complexes were performed as reported earlier⁹.

TABLE 1—ANALYTICAL DATA OF $[\text{PdL}_2\text{X}_2]$ COMPLEXES

Compd.	Analysis %: Found/(Calcd.)	
	M	N
$[\text{PdL}_2\text{Br}_2]$	23.96 (24.00)	06.38 (06.36)
$[\text{PdL}_2\text{I}_2]$	19.98 (19.85)	05.38 (05.24)
$[\text{PdL}_2(\text{SCN})_2]$	26.99 (26.79)	14.72 (14.62)
$[\text{PdL}_2(\text{NO}_2)_2]$	27.35 (27.41)	15.12 (15.05)

Results and Discussion

The interaction of morpholine with palladium(II) gave only bis-complexes, $[\text{PdL}_2\text{X}_2]$ ($\text{X}=\text{Cl}^-$, Br^- , I^- , NO_2^- or SCN^-). The dihalo complexes dissolve in excess of morpholine in aqueous solution but attempts to get solid complexes were unsuccessful. The cream-yellow dibromo, $[\text{PdL}_2\text{Br}_2]$ complex on prolonged refluxing in ethanol with excess of morpholine changed to a light green isomeric product. However, the isomeric products could not be isolated with other diacido complexes. The diacido complexes are insoluble in water, methanol and ethanol but dissolved in dimethylformamide and pyridine. The complexes were diamagnetic. The solid state reflectance spectra of the complexes displayed a medium band or shoulder in the region 390–430 nm. The green dibromo complex displayed this band at 420 nm while λ_{max} of the yellow product was at 400 nm. The absorption bands were assigned to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transition, usually observed in the square-planar palladium(II) complexes¹⁰.

The ν_{N-H} of the free ligand ($3\ 300\text{ cm}^{-1}$) shifted to lower frequency by $130 \pm 10\text{ cm}^{-1}$ and δ_{NH} of ligand ($1\ 455\text{ cm}^{-1}$) by $5-10\text{ cm}^{-1}$ in almost all the complexes, indicating the bonding of morpholine through nitrogen atom¹¹. The sharp ν_{C-O-O} bands

of chair form in the ligand were located at 1 075 and 1 135 cm^{-1} and these remained unaltered in complexes, indicating the coordination of complexes in the chair form. The dithiocyanato complex displayed $\nu_{\text{C}=\text{N}}$ at 2 100 cm^{-1} as sharp and strong band, while $\nu_{\text{C}-\text{S}}$ at 710 cm^{-1} and δ_{NCS} at 490 cm^{-1} fall in the range of S bonded thiocyanate group^{12, 13}. The splitting of $\nu_{\text{C}=\text{N}}$ band could not be observed in $[\text{PdL}_2(\text{SCN})_2]$ suggesting *trans*-bonding of SCN groups. The dinitro complex $[\text{PdL}_2(\text{NO}_2)_2]$ displays $\nu_{\text{as}}(\text{NO}_2)$ at 1 430 cm^{-1} as well as $\nu_{\text{s}}(\text{NO}_2)$ at 1 375 cm^{-1} as strong and broad bands and δ_{ONO} at 820 cm^{-1} . The ir frequencies of NO_2 group were observed in the range of N-bonded nitro groups^{13, 14}. The absence of splitting of δ_{ONO} and $\nu_{\text{as}}(\text{NO}_2)$ vibrations also suggested *trans*-bonding of nitro group in $[\text{PdL}_2(\text{NO}_2)_2]$. The ir bands of the cream yellow and greenish yellow $[\text{PdL}_2\text{Br}_2]$ complexes differed appreciably in the far-ir region. The greenish yellow variety displayed six bands in the far-ir regions at 485s, 455s, 360s, 310w, 265s and 240s cm^{-1} while the cream-yellow variety displayed only four bands at 480m, 360s, 265w and 240w cm^{-1} . The occurrence of more bands in greenish complex indicated *cis*-arrangement of the ligand molecules around palladium(II)¹⁵. The new ir bands in the region 500–240 cm^{-1} of the complexes were presumably due to $\nu_{\text{M}-\text{N}}$, $\nu_{\text{M}-\text{X}}$ and $\nu_{\text{M}-\text{S}}$ vibrations¹⁶.

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Heterogeneous Coated Wire Copper(II) and Cobalt(II) Ion Selective Electrodes based on Solid Ion-Exchange Resin

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THE present paper describes the use of a coated wire electrode in which a liquid ion-exchanger has been replaced by a solid ion-exchange resin. Cu^{2+} and Co^{2+} ion-sensitive electrode were prepared using the metal form of a solid cation-exchange resin as the electroactive material and silicone rubber as the inert binder. Nernstian response, response time, effect of pH, working range, and selectivity coefficient have been evaluated.

Experimental

All the chemicals were of AnalaR grade and all the solutions prepared in double-distilled water. Solid cation-exchange resin (Dowex 50W-4) was treated with saturated solutions of metal chlorides through the column to obtain its metal forms. One part of the metal form of the cation-exchange resin was mixed with four parts of silicone rubber (Sylartivi-11, Metroark) to make a homogeneous paste and a few drops of catalyst which was supplied by the manufacturer (Metroark) along with the silicone rubber, were added to it. A small portion of the paste thus formed was coated on one end of the copper wire attached to central conductor of coaxial cable; care was taken to form a small bead at the tip of the wire. It was dried in air and treated with 0.1 M metal(II) solution.

A Philips PR 9405 M pH meter was used for the potential measurements with a saturated calomel electrode as reference electrode. The electrodes were pretreated with solutions of metal(II) ions before measurements.

Results and Discussion

The parameters, like Nernstian response, response time, pH dependence, working range, selectivity coefficient and life time have been evaluated¹ for both Cu^{2+} and Co^{2+} sensitive coated wire electrodes. The results are summarised in Table I.