A perusal of Table 2 reveals that the value of $k_{OA}^0$ decreases on increasing the concentration of Triton X-100. From this it follows that irreversible electrode processes tend to become more so when Triton X-100 is added in increasing amounts.

The observations on the variation of $\alpha$ with increasing concentrations of Triton X-100 are in conformity with the views of Mites$^{22}$. According to him the most common effect of non-ionic maximum suppressors (such as Triton X-100) is to decrease the rate constant $k_{OA}^0$, and the value of $\alpha$ is also decreased.

Triton X-100 with well known surface active properties is likely to be adsorbed on the mercury surface. This is further confirmed by the decrease of the interfacial tension, measured by the drop time method$^{23}$, on the solution-mercury interface. The adsorbed molecules displace ions from the Helmholtz layer, thereby altering the charge distribution in the double layer and they may also displace the reaction surface away from the electrode. Both these effects alter the potential at the reaction surface. Thus a bridge that may serve to effect the electron transfer from the electrode to an ion at the reaction surface when the maximum suppressor is absent may become impossible to be constructed when it is present.

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**References**


**Dimeric Halo Complexes of Cr(IV)**


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Stable dimeric complexes of Cr(IV) of the type [Cr(OH)$_2$X$_2$Py]$_2$ (X = Cl, Br, I) have been prepared by the alcoholic reduction of halochromate(VI) in the presence of pyridinium hydrohalide in pyridine medium. The complexes have been characterized on the basis of reflectance, IR and magnetic moment data.

**Table 1** — Reflectance and IR Spectral Data of the Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$A_{\text{max}}$ (nm)</th>
<th>Important IR bands (cm$^{-1}$)$^\dagger$</th>
<th>$A_{\text{max}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(OH)$_2$Cl$_2$Py$_2$</td>
<td>262, 293, 403, 500, 660</td>
<td>3410(s, br), 905(s), 800(s)</td>
<td>262, 293, 403, 500, 660</td>
</tr>
<tr>
<td>Cr(OH)$_2$Br$_2$Py$_2$</td>
<td>256, 285, 397, 500, 665</td>
<td>3400(s, br), 920(s), 830(s)</td>
<td>256, 285, 397, 500, 665</td>
</tr>
<tr>
<td>Cr(OH)$_2$I$_2$Py$_2$</td>
<td>256, 295, 394, 575, 778</td>
<td>3390(s, br), 917(s), 815(s)</td>
<td>256, 295, 394, 575, 778</td>
</tr>
<tr>
<td>K[Cr(OH)$_2$ClPyO$_2$]$^\ast$</td>
<td>262, 388, 488, 690$^\ast$</td>
<td>3420(s, br), 912(s), 825(s), 770(m)</td>
<td>262, 388, 488, 690$^\ast$</td>
</tr>
</tbody>
</table>

$^\dagger$Reflectance spectrum taken in water.

$^\ast$Coordination pyridine bands are excluded.
The authors wish to thank Dr. P. K. Singh, Principal, for laboratory facilities, Prof. R. P. Rastogi of Gorakhpur University for encouragement and to the UP State Council of Science and Technology for financial assistance.

References


Reactions of Bis(diethyl dithiocarbamato)nickel(II) with 4-Methyl- & 4-Vinyl-pyridines

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Bis(diethyl dithiocarbamato)nickel(II) when reacted separately with 4-methylpyridine and 4-vinylpyridine (L) in ethanolic medium forms compounds having the composition [Ni(dtc)2-L]. They are diamagnetic and non-electrolytes. Infrared spectra indicate the presence of bonded ligands. The complexes are pentacoordinated as revealed by their electronic absorption spectra with nickel atom surrounded by four sulphur and one nitrogen donor atoms.

In Ni(II) complexes tetra- and hexa-coordination is a common feature and penta-coordination is rare. The preferred coordination number depends upon the polarizability of the ligands reacting with the metal ion. It is therefore, worthwhile to see whether this less common penta-coordination can be stabilized by providing a hetero-donor atom environment round the nickel ion. With this in view the reaction of bis(diethyl dithiocarbamato)nickel(II) with 4-methyl- and 4-vinylpyridines has been studied and the complexes formed isolated and characterized. Ethanolic solution of nickel chloride was reacted with ethanolic solution of sodium diethyl dithiocarbamate (Na-dtc) in the ratio 1:2. The precipitated light green compound was suction-filtered, washed with ethanol and dried in vacuo. The composition of this compound was established to be Ni(dtc)2 by elemental analysis and infrared spectral study. This freshly prepared complex was reacted with 4-methylpyridine and 4-vinylpyridine separately in ethanolic medium in the stoichiometric ratios of 1:1 and 1:2. The reaction mixture was refluxed for 6 hr and the resulting products were suction-filtered, washed with ethanol followed by ether and then dried in vacuo. (i) Ni(dtc)2-4-me-py (Found: Ni, 13.6; S, 29.0; Calc.: Ni, 13.4; S, 28.6%), m.p. >300; \( \Lambda_M \) 0.5 mhos. Ni(dtc)2-4-vi-py (Found: Ni, 12.8; S, 28.2%, m.p. >300; \( \Lambda_M \) 0.6 mhos.

51 (1974), 710.

McCormick and Roy* have reported that Ni(II) forms planar, diamagnetic and tetra-coordinated compounds [Ni(dtc)2] with a series of dithiocarbamates. Nickel(II) 5-diketonates on reaction with nitrogen and sulphur donor ligands were found by us to give hexacoordinated compounds, Ni(II)-[dik]3L. Bis(diethyl dithiocarbamato)zinc(II) was reacted with some substituted pyridines and several penta-coordinated compounds having the composition Zn(dtc)2 were obtained. Dithiocarbamate is a uni-negative, bidentate ligand and so neutral ligands cannot replace it; they can be simply added on if the requirements are satisfied. Neutral bidentate nitrogen donor ligands like o,a-dipipyridyl and o-phenanthroline were reacted with Ni(dtc)2 but with no consequence. So, it is clear that the coordination number cannot be increased to six. In the present investigation when several neutral unidentate nitrogen donor ligands were tried, reaction took place only with 4-methylpyridine and 4-vinylpyridine resulting in the addition of only one mole of the ligand. Even when excess of ligand in the ratio 1:2 was taken, only one mole of the ligand was added. This explains why there was no reaction when a bidentate ligand was used. Very low values of molar conductance, \( \Lambda_M \) (0.5 mhos) in nitrobenzene (10-2M solution), indicate the non-electrolytic nature. The compounds are diamagnetic as expected for a penta-coordinated nickel(II) compound involving 3d54s2 hybrid orbitals.

In diethyl dithiocarbamate, \( \nu(C-S) \) was reported at 1480-1550 and \( \nu(C-S) \) at 989-1006 cm\(^{-1}\). The sample of Ni(dtc)2, prepared by us exhibits bands at 1525 and 985 cm\(^{-1}\) corresponding to \( \nu(C-S) \) and \( \nu(C-S) \) respectively. In the 4-methylpyridine and 4-vinylpyridine adducts, the \( \nu(C-N) \) and \( \nu(C-S) \) frequencies are observed at 1520, 1518 and 980, 995 cm\(^{-1}\) respectively. It is, therefore, clear that dithiocarbamate ligands in the complex remain undisturbed. In addition to the absorption bands due to diethyl dithiocarbamate, characteristic bands due to 4-methylpyridine and 4-vinylpyridine are also observed in the complexes Ni(dtc)2. There is no evidence, either analytical or spectral, for the presence of a coordinated water molecule. Hence the complexes under report are definite examples of penta-coordination of nickel(II) being surrounded by four sulphur atoms and one nitrogen atom. Pentacoordination of nickel(II) gains further support from electronic spectral data. Sacconi had shown that in penta-coordinated configuration, the ground state term of the nickel(II) ion splits into a relatively large number of terms on lowering the symmetry as compared to that of tetrahedral or octahedral configuration. Bertini reported absorption bands at 8000, 10000, 13000 and 16000 cm\(^{-1}\) and postulated the existence of five-co-ordinate high spin nickel(II) complexes with mixed salicylaldimine ligands. It was also suggested that four-coordinated planar complexes of nickel(II) do not show appreciable absorption below 18000-20000 cm\(^{-1}\).

In the present investigation, the electronic spectrum of Ni(dtc)2-4-vi-py in CHCl\(_3\) exhibited maxima (4) at 11420 (57), 12500 (51), 16600 (150), 17540 (142) and 2125 (340) cm\(^{-1}\) while Ni(dtc)2-4-me-py

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References

3. *Department of Chemistry, Gorakhpur University, Gorakhpur.

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