Anionic Trihalogenononoquinoline/isoquinoline-
cobalt(II) complexes

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Ethanolic suspensions of non-electrolytic Co(II) complexes
having the formula CoLX2 on halogenation with chlorine and
bromine yield 1:1 electrolytic complexes containing [CoLX]2+, 
[CoLY2]2+ and [CoLXY2]2+ moieties where L is
quinoline or isoquinoline, X = Cl and Y = Br. These compounds
have been characterised on the basis of analytical, conductance,
magnetic moment, infrared and electronic spectral data which
provide evidence for a distorted-tetrahedral structure around the
metal atom.

OXIDATION and reduction reactions of several
metal complexes have been studied earlier. Oxidations of d3 cobalt(II) to a d6 cobalt(III)
form was studied long back. In a similar effort, to oxidise the metal ion in complexes of the type
CoL2X2, Roy and Ramana Rao1 isolated compounds having the formula [LH]2 [CoX4]. They
worked in ethanolic medium where solvolysis took place. It was therefore thought worthwhile to carry
out the halogenation reactions in carbon disulphide medium or in a mixed solvent medium and study
the course of reactions. Even though oxidation could not be achieved, several interesting new complexes
have been obtained and these are reported in this note.

The Co(II) complexes, CoL2X2, were prepared
according to the method of King and coworkers3,4.
These were characterised on the basis of analysis, conductance,
magnetic susceptibility, IR and electronic spec-
tral data. Unicam SP-200 and SP-500 spectrophotometers were used for spectral measurements.

Bromination — To an ethanolic suspension of the
dichloro or dibromo complex, were added carbon
disulphide (10 ml) and the respective ligand (5 ml).
Liquid bromine (4 ml in 10 ml of carbon disulphide)
was then added dropwise to the above suspension
with vigorous shaking and the resulting mixture was heated under reflux for 15-30 min.
The deep-blue coloured suspension changed to light-
blue. It was filtered, washed and dried
in vacuo.

Chlorination — Pure and dry chlorine gas was
passed through an ethanolic suspension of dibromo
do dichloro complex containing 5 ml of the ligand
and 15 ml of carbon disulphide with vigorous shak-
ing the colour changed from deep-blue to either
light-blue or bluish-green. The resulting compounds
were allowed to stand for one hr and were filtered,
washed with ethanol followed by ether and dried
in vacuo.

The analyses, melting point, conductance, magnetic
moment and electronic spectral data of the complexes are recorded in Table 1.

When CoL2X2 is treated with chlorine or bromine
three possible reactions may take place: (i) oxidation of bivalent cobalt to a higher oxidation state, (ii)
substitution in the quinoline ring and (iii) solvoly-
lysis of the halogen and consequent addition of the
hydrogen halide to the ligand base forming quater-
nary halides.

Several Ni(II) and Co(II) complexes containing
ligands with N, P, As and S donor atoms have
been previously shown4,5 to undergo oxidation of
the metal on halogenation. Babaeva6 reported
the formation of the pyridinium tetrachloroco-
ابلت(II) from the reaction of chlorine with bis
(pyridine)cobalt dichloride in methanol solution,
whilst oxidation took place when CoPy2Br2 was
treated with bromine. Anionic mixed ligand com-
plexes of the type [NiLCl3Br]2- and [PyH] [HMn-
PyCl3] have also been reported8,9. Halogenation of
oxine complexes of Fe(III), Cr(III) and Al(III)
resulted10 in attack at 5-, 6- and 7-positions of
8-hydroxyquinoline producing halosubstituted
ligands in the complexes. Thus, one finds in the
literature instances of all the three possibilities envis-
aged above. The aim of the present investigation
was to oxidise cobalt(II) to higher oxidation states.
But, no oxidation took place in Cs2 medium. So
a mixed solvent medium of ethanol and carbon
disulphide was tried with an extra addition of the
ligand and consequent addition of the
hydrogen halide to the ligand base forming quater-
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hydrogen halide to the ligand base forming quater-
nary halides.
Hence, it is assumed that the halogen reacts with nitrogen donor ligands giving rise to tetra co-ordinated hydrogen halide which forms quaternary halides with hydrogen of ethanol forming the corresponding hydrochloroformate ester, recorded using hexachlorobutadiene as mulling agent and the 'IN - Hand 3N-H frequencies for tetrahedral cobalt(II) complexes in the literature.

Some intensity. Molar extinction coefficients (E) for tetrahedral complexes are high compared to octahedral complexes and the values of E for the complexes under report lie within the range reported for tetrahedral cobalt(II) complexes in the literature.

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**References**


### Synthesis, Magnetic & Spectral Studies On Some Adducts of Manganese(II) Acetylacetonate

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Adducts of manganese(II) acetylacetonate with sulphur and nitrogen containing ligands have been prepared. Their diffuse reflectance spectra, infrared spectra and magnetic properties have been investigated. Racah inter-electronic repulsion parameter B and C, Slater-Condon-Shortley parameter Fz and Fa, crystal field splitting energy (Dq), nephelauxetic ratio and ligand contribution to complex (la) have been calculated. It has been possible to distinguish between the sulphur and nitrogen coordination of thioureas on the basis of IR data.

†Physics Division, Defence Laboratory, Jodhpur.

<table>
<thead>
<tr>
<th>Compound</th>
<th>m.p. (°C)</th>
<th>Found (Calc.), %</th>
<th>( \mu_{eff} ) (B. M.)</th>
<th>( \nu_{max} (\text{e}) ) (cm(^{-1}))</th>
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<td>4.46</td>
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</tr>
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</table>

Notes

Only two halogen atoms instead of three shown in the present investigation, since the ring halogen can not be liberated by the treatment of dilute nitric acid and requires prior fusion. Moreover, the product would have been a non-electrolyte whereas all the compounds reported here are 1:1 electrolytes, \( \Delta_M \) being in the range of 90–150 mho cm\(^2\) mole\(^{-1}\). Hence, it is assumed that the halogen reacts with hydrogen of ethanol forming the corresponding hydrogen halide which forms quaternary halides with nitrogen donor ligands giving rise to tetra co-ordinated anionic complexes containing a ligand molecule bonded to metal ion.

The infrared spectra of these compounds were recorded using hexachlorobutadiene as mulling agent and the \( \nu \)N—H and \( \delta \)N-H frequencies were observed around 3000–3500 and \( \sim 1500 \text{ cm}^{-1} \) respectively. The presence of these N—H absorption bands is a definite indication of the presence of quinolinium and isoquinolinium cations in the complexes.

All the complexes exhibit intense bands in the region 14,880–16,580 cm\(^{-1}\) in their solution electronic spectra (Table 1) characteristic of cobalt(II) ion in a tetrahedral environment. The band near 16000 cm\(^{-1}\) is associated with the transition \( 4A_1(F) \rightarrow ^4T_1 (P) \) for a species of undistorted tetrahedral symmetry. The complexity of the bands in this region is attributed to spin-orbit coupling effect which splits the \(^4T_1 (P) \) state and allows the transition to the neighbouring doublet state to gain some intensity. Molar extinction coefficients (e) for tetrahedral complexes are high compared to octahedral complexes and the values of e for the complexes under report lie within the range reported for tetrahedral cobalt(II) complexes in the literature.