Synthesis and structural studies of first row transition metal complexes of a new bi-ambidentate heterocyclic ligand

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Chromium(III), manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) complexes of 3-(3,5-dimethyl pyrazole-1-yl) quinoxaline-2-one have been prepared and characterised on the basis of analytical, electrical conductance, IR, electronic spectral and magnetic susceptibility studies.

Transition metal complexes derived from neutral heterocyclic ligands have received relatively less attention. Quinoxaline and pyrazoles form an important class of nitrogen heterocyclics which have been reported for a wide range of applicabilities. They possess potential metal binding nitrogen centers in the form of ring azomethine functions. A unique combination of two types of nitrogen heterocyclics namely quinoxalines and pyrazoles has been investigated for the formation of transition metal complexes. The present note deals with the synthesis and characterisation of chromium(III), manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) complexes of 3-(3,5-dimethyl pyrazole-1-yl) quinoxaline-2-one.

Experimental

All the chemicals used were either of AR or chemically pure grade. Metal percentage was estimated by decomposing the complexes through evaporation of perchloric acid solutions first and then dissolving the resultant salts in doubly distilled water to make the solutions of known concentrations. The metal contents were estimated from these solutions on an atomic absorption spectrometer Perkin Elmer-2380. Analysis of C, H, and N were done at the Central Instrumentation Laboratory, University of Hyderabad. Chlorine contents were estimated after igniting a definite weight of the complex in oxygen in the presence of KOH and H₂O₂ (ref. 5). IR spectra (KBr discs) were recorded in the 4000-400 cm⁻¹ region on a Schimadzu IR-435 and in nujol medium in the 4000-200 cm⁻¹ on a Perkin-Elmer 288-13. The electronic spectra were recorded in solid state on a Cary-2390 instrument. Magnetic susceptibilities of the complexes at room temperature were measured on a Faraday balance CAHN-7550-03 USA using HgCo(NCS)₄ as calibrant. Diamagnetic corrections using Pascal constants and temperature independent paramagnetic corrections were computed. The electrical conductance measurements were recorded using 10⁻³ M solution in DMSO with an Elico conducting bridge (Model CH-180) and a dip type cell calibrated with KCl solutions.

Synthesis of quinoxaline-2,3-dione

Orthophenylene diamine (5.5 g), oxalic acid dihydrate (6.5 g) and 4 N HCl (30 cc) were heated to boiling for 15 min. A crystalline solid appeared which was cooled, collected, washed with water and dried. The compound was dissolved in alkali and then acidified with HCl, so that, the pure quinoxaline-2,3-dione was obtained as white needles. Yield: 3 g, m.p. >350°C.

Synthesis of 3-hydrazino quinoxaline-2-one

To a mixture of quinoxaline-2,3-dione (10 g) and hydrazine hydrate (50 ml), water (50 ml) was added and heated under reflux for 2 h and cooled. The precipitate of 3-hydrazino quinoxaline-2-one was filtered off, washed with water and crystallised from butan-1-ol to give yellow needles. Yield: 9.4 g; m.p.>360°C.
Synthesis of 3-(3,5-dimethyl pyrazole-1-yl) quinoxaline-2-one

A mixture of 3-hydrazino quinoxaline-2-one (8.8 g) and acetyl acetone (20 ml) was refluxed for 2 h. The colourless product that separated out was filtered and recrystallised from benzene. Yield: 6.5 g; m.p. >168°C.

[Found: C, 64.48; H, 5.10; N, 23.31; C₁₂H₁₂N₂O
Calc.: C, 65.00; H, 5.00; N, 23.33%]. m/z 240.

1H NMR (DMSO-d₆): δ 2.3, δ 2.2 {methyl protons (6)}, δ 6.1 {−CH-proton (1)}, δ 7.3-7.9 (NH and phenol protons confirmed by D₂O exchange (5)). UV-Vis (νₘₓ in cm⁻¹): 43478 (ring π−π* transition) and 31746, 28169 (π−π* and n−π* transition) and 31746, 28169 (π−π* and n−π* transition). The data are consistent with the expected structure (Structure I).

Preparation of complexes

The ligand (1.20 g, 0.005 mol) was dissolved in methanol (25 ml) and to this solution, methanolic solution (25 ml) of divalent/trivalent metal chloride (0.0025 mol) was added. The pH of the mixture was adjusted to 7 with 1% alcoholic ammonia and the reaction mixture was refluxed for 3-4 h. The coloured product thus obtained was filtered in hot condition, washed successively with methanol and petroleum ether and dried in vacuo. The purity of the complexes was checked by TLC using methanol and solvent mixtures.

Results and discussion

Analytical data of C, H, N, Cl and metal are in good agreement with 1:2 metal-ligand stoichiometry for all the complexes except for Cu(II) complex where it is 1:1 (Table 1).

All the complexes neither melt nor decompose upto 300°C. Except chromium(III) and iron(III), all complexes show negligible conductivity thus proving that they are non-electrolytes. Chromium(III) and iron(III) complexes show conductance values of 74 mhos and 67 mhos respectively indicating to be 1:1 electrolytes. The analytical and conductivity data shows that one chloride is in the ionization sphere, while the other two chloride ions are in coordination.
sphere for chromium(III), and iron(III) complexes. In case of manganese(II), cobalt(II), nickel(II) and copper(II) complexes, the two chloride ions are in the coordination sphere.

In the IR spectrum the free ligand shows vNH at 2900 cm\(^{-1}\), vC=O at 1670 cm\(^{-1}\) and two azomethine groups show sharp peaks at 1574 and 1556 cm\(^{-1}\). Comparison of the infrared spectrum of free ligand with that of each metal complex suggests two possible modes of chelation. Manganese(II), cobalt(II) and nickel(II) complexes belong to the first category in which the infrared spectrum show notable downward shift\(^{11}\) in vC=O by about 40 cm\(^{-1}\), indicating that the exocyclic, lactam carbonyl oxygen is the binding site in these complexes. Further, there is a downward shift in vC=N (non-quinoxaline ring) to the extent of 10-15 cm\(^{-1}\) in these complexes suggesting coordination through the corresponding nitrogen\(^{12}\).

Chromium(III), iron(III) and copper(II) complexes belong to the second category in which the infrared spectra show no change in vC=O. Instead, the azomethine stretching frequencies show notable downward shifts\(^{12}\). These changes suggest the non-participation of carbonyl oxygen and participation of only the azomethine nitrogens in metal binding process. Weak non-ligand peaks observed in the range 494-510 cm\(^{-1}\) are due to vM-O, vM-N and vM-Cl vibrations\(^{13,14}\) in the corresponding complexes.

The magnetic susceptibility measurements and the calculated magnetic moments show that all the complexes are paramagnetic with high spin configurations\(^{15,15}\) of the central metal ions (Table 1).

The electronic spectra assignments are based on high-spin octahedral geometry for all the complexes except the copper(II) complex in which the three component band structure characteristic of square planer geometry is seen\(^{16}\). The inter electron repulsion parameter and nephelauxetic parameter have been evaluated for chromium(III) and nickel(II) complexes [for chromium(III) B=831 and \(\beta=0.806\); for nickel(II) B=883 and \(\beta=0.818\)]\(^{17}\). The transition patterns and \(v_{2}/v_{1}\) ratio (2.19) are both supportive of octahedral geometry in the case of cobalt(II) complex\(^{18}\).

The ESR spectrum of copper(II) complex shows that the g parameter is highly anisotropic and exhibits three components. The values are \(g_{x}=2.6521\), \(g_{y}=2.1295\), \(g_{z}=2.0088\). Copper(II) ion in this complex seems to be totally free from the influence of the nearest neighbouring copper ions of the adjacent complex molecules which coexist in the solid state the possible explanation for this could be the presence of bulky tricyclic ligand molecules in the coordination sphere due to which the interaction between consecutive copper ions of different complex molecules is initiated and such systems wherein metal-metal interaction is almost totally inhibited are referred as magnetically dilute systems. Further, the high \(\Delta g_{zz}\) value can be explained on the basis of large energy separation between \(d_{x^2-y^2}\) and \(d_{z^2}\) orbitals.

The biambidenticity of the ligand is a notable feature. It acts as NN donor in chromium(III), iron(III) and copper(II) complexes and as ON donor in manganese(II), cobalt(II) and nickel(II) complexes.

On the basis of elemental, conductance, magnetic and spectral data, octahedral geometries have been proposed for all the complexes except for copper(II) complex to which square plane geometry is proposed (Structures II-IV).

References