Kozic Acid Complexes of Copper(II), Cobalt(II) and Nickel(II)

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Kozic acid complexes of copper(II), cobalt(II), and nickel(II) are described. Kozic acid behaves as a bidentate ligand coordinating through oxygens. A tetrahedral structure is assigned to the complexes on the basis of magnetic and electronic spectral data. Approximate values of ligand field and electronic parameters are given for \([\text{Co(kozate)}]_2\) compound. Infra-red spectra of the complexes are discussed in the carbonyl and MO stretching region.

Kozic acid forms five-membered stable chelate ring with metal ion. WILEY et al. \(^1\) isolated the bis(kozato) copper(II) and on the basis of magnetic moment only, predicted its structure to be “planar or tetrahedral”. They also assigned a tetrahedral structure to cobalt(II) and nickel(II) kozates on the basis of magnetic data. In course of our investigations on the synthesis and characterisation of metal complexes of kozic acid \(^2\), \(^3\) we considered it worthwhile to study these complexes in detail in order to investigate their structure.

Experimental

The copper(II), cobalt(II) and nickel(II) complexes of kozic acid were prepared many years ago \(^4\). Since in this study the complexes were prepared by utilising modified methods, we like to describe details of their synthesis.

**Bis(kozato)-copper(II):** Copper(II) chloride dihydrate (0.51 g, 3 mmoles) was dissolved in 10 ml. of water and to this was added few ml. of dilute sodium acetate solution. The copper solution was added to an aqueous solution of kozic acid (0.85 g, 6 mmoles) with stirring. The green precipitate formed were suction filtered, washed with water followed by warm ethanol. The complex was dried at 130 °C.

**Analysis:** [Cu(C₆H₅O₄)₂] \(\cdot\) 0.5 H₂O

Calculated Cu 18.37 C 41.64 H 2.89

Found  Cu 18.14 C 41.40 H 2.95

Yield: 99.9 per cent.

**Bis(kozato)-cobalt(II):** Cobalt(II) chloride hexahydrate (0.68 g, 3 mmoles) and kozic acid (0.85 g, 6 mmoles) were dissolved separately in water to form a 1:1 solution. These two solutions were mixed and the pH of the mixture was adjusted to 6.0 with dilute ammonium hydroxide and allowed to stand at room temperature. Yellow microcrystals formed slowly. These were filtered, washed thoroughly with hot water and warm ethanol, and dried in air.

**Analysis:** [Co(C₆H₅O₄)₂] \(\cdot\) 0.5 H₂O

Calculated Co 16.82 C 41.42 H 3.14

Found  Co 16.70 C 41.31 H 3.28

Yield: 70 per cent.

**Bis(kozato)-nickel(II):** This was prepared as green microcrystals by following a similar procedure as described for the corresponding cobalt(II) compound.

**Analysis:** [Ni(C₆H₅O₄)₂] \(\cdot\) 0.5 H₂O

Calculated Ni 16.77 C 41.15 H 3.14

Found  Ni 16.91 C 41.29 H 3.36

Yield: 70 per cent.

The complexes are all insoluble in water and common organic solvents.

**Materials and methods:** Copper(II) chloride dihydrate, cobalt(II) chloride hexahydrate, nickel(II) chloride hexahydrate and kozic acid were all of Merck analytical grade reagents. Metals were determined as described previously \(^4\). Carbon and hydrogen were analysed microanalytically. Magnetic susceptibility measurements were taken at room temperature \((298 \text{ K})\) in a Gouy Balance using G. R. copper(II) sulphate as the calibrant and applying a field strength of 8000 gauss. The electronic spectra of nujol mullcd solids were recorded with the help of a Cary 14 recording spectrophotometer by following the method described in the literature \(^4\). I.R. spectra were determined from KBr pellets using a Beckman IR 10 spectrophotometer.

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\(^1\) J. W. WILEY, G. N. TYSON, and J. S. STELLER, J. Amer. chem. Soc. 64, 963 [1942].


\(^3\) A. SYMAL, ibid. 44, 806 [1967]; 45, 755 [1968].

Results and Discussion

Copper(II) complex: Magnetic moment of all copper(II) complexes are in the range 1.7 – 2.2 B.M. with the exception of subnormal values noted for Cu-Cu interaction. Tetrahedral copper(II) complexes generally exhibit some higher magnetic moment than those of planar or octahedral copper(II) complexes due to the addition of orbital contribution to the spin-only value. Copper(II) bis(kozate) records a magnetic moment of 1.95 B.M. which indicates a pseudo-tetrahedral configuration rather than a planar structure. Generally octahedral and planar copper(II) complexes exhibit bands around 15,000 – 18,000, and 19,000 cm⁻¹ respectively. Any d-d band due to a pseudo-tetrahedral structure occurs at much lower energy. The [Cu(kozate)₂] being insoluble in water and all common organic solvents, we recorded its mull spectra. The electronic spectra of bis(kozato)-copper(II) provide an evidence of a pseudo-tetrahedral structure for the complex. A single crystal X-ray study will determine the actual structure of the complex. But we are not yet able to prepare a single crystal of the compound.

Cobalt(II) complex: In a field of tetrahedral symmetry the 1F ground state of cobalt(II) is split into 4A₂, 4T₂ and 4T₁(F) and three spin-allowed transitions T₂ ← 4A₂ (ν₁), 4T₁(F) ← 4A₂ (ν₂) and 4T₁(P) ← 4A₂ (ν₃) are expected. The Mull spectra of [Co(kozate)₂] exhibit three bands at 19,600 (sh), 18,180 (sh), and 7140 cm⁻¹. Sinceν₂ band is not usually observed due to the weak character of T₂ ← 4A₂ transition, the observed bands should be assigned among ν₂ and ν₃, one having probably a double peak. In conformity with other tetrahedral cobalt(II) complexes the near infra-red band is assigned to the ν₂ transition. The doublet in the visible region with maxima at 19,600 and 18,180 cm⁻¹ should then be assigned to ν₃ band.

Cotton and Goodgame have made approximate calculations of crystal field parameters for tetrahedral cobalt(II) complexes utilising the following relations:

\[ \nu_1 = A \]
\[ \nu_2 = 1.5 \Delta - 7.5 B' - Q \]
\[ \nu_3 = 1.5 \Delta - 7.5 B' - Q \]
\[ Q = 1/4 \left( 0.6 \Delta - 15 B' \right)^2 - 0.64 \Delta^2 \]

where \( B' \) = effective value of Racah interionic repulsion integral and \( \Delta \) = ligand field strength modulus. The energy of 4A₂ to 4T₁(P) (i.e., ν₃) is obtained by averaging the two peaks to produce 18,890 cm⁻¹. The series of above equations are solved to produce \( \Delta \) and \( \beta \) and the values are listed in Table I.

<table>
<thead>
<tr>
<th>( \Delta ), cm⁻¹</th>
<th>( \nu_2 ), cm⁻¹</th>
<th>( \nu_3 ), cm⁻¹</th>
<th>( B' ), cm⁻¹</th>
<th>( \beta = B' )</th>
<th>( \mu_{eff} ), B.M.</th>
<th>( \lambda' ), cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>4100</td>
<td>7140</td>
<td>18,890</td>
<td>915 *</td>
<td>0.94</td>
<td>4.50</td>
<td>160 **</td>
</tr>
</tbody>
</table>

Table I. Magnetic, Spectral and Electronic Parameters for [Co(kozate)₂]. * Free ion value = 967 cm⁻¹ (ref. 10 a).
** Free ion value = 180 cm⁻¹ (ref. 14).

From \( \mu_{eff} \) and \( \Delta \) one can obtain the effective value for the spin orbit coupling constant, \( \lambda' \) from the following relations:

\[ \mu_{obs} = \mu_{e.o.} - \frac{15.56 \lambda'}{\Delta} = 3.89 - \frac{15.56 \lambda'}{\Delta} \]

The value of \( \lambda' \) is included in Table I. Generally the reduction of \( B' \) and \( \lambda' \) from the free ion values is taken as evidence of covalence in the metal ligand bond. The recorded magnetic moment (4.50 B.M.) of the complex is very close to that of a tetrahedral bis(pyrromethane)-cobalt(II) complex.

\[ \text{References:} \]

3 R. L. Dutta, D. De, and A. Syamal, J. Indian chem. Soc. 45, 663 [1968].
5 J. A. Costamagna and R. Levitt, J. inorg. nuclear Chem. 28, 2685 [1966].
Nickel(II) complex: The observed magnetic moment (μ_{eff} = 3.50 B.M.) of green [Ni(kozate)₂] indicates that the structure of the complex is tetrahedral. The mull spectra of [Ni(kozate)₂] exhibit two bands at 15,625 – 15,035 cm⁻¹ and 6895 cm⁻¹. The spectrum of a T₄ Ni(II) complex is expected to contain three bands around 3000 – 5000 cm⁻¹, 6500 – 10,000 cm⁻¹, and 12,000 – 17,000 cm⁻¹ due to the transitions ³T₂ ← ³T₁(F) (ν₁), ³A₂ ← ³T₁(F) (ν₂) and ³T₁(P) ← ³T₁(F) (ν₃) respectively. Since the ³T₂ band is not usually observed in T₄ nickel(II) complexes and is often masked by the organic part of the molecule, the bands at 6895 cm⁻¹ and 15,625 – 15,035 cm⁻¹ are assigned to ν₂ and ν₃ respectively. The splitting of the visible peak was not observed in this complex.

Infra-red spectra of the complexes: Infra-red measurements on the ligand kozic acid and its copper(II), cobalt(II), and nickel(II) complexes were examined in the range 400 – 4000 cm⁻¹ in KBr disks. Our aim was not to interpret the complete spectrum in the range studied but to determine the frequency of the carbonyl group since it is extremely sensitive to changes on coordination. In the spectra of the ligand, a strong band at 1650 cm⁻¹ can be assigned to carbonyl band. The infra-red spectra of [Cu(kozate)₂], [Co(kozate)₂], and [Ni(kozate)₂] were characterised by the presence of chelated carbonyl absorption at 1600 cm⁻¹ for all these three complexes. Thus the carbonyl frequency of the ligand is strongly shifted to lower frequency (∼50 cm⁻¹) on coordination with the metal ions. In the corresponding vanadyl and uranyl complexes also shifting of ν(C=O) band of the ligand to lower frequency of about 45 cm⁻¹ was observed. The infra-red spectra of the ligand is transparent in 400 – 500 cm⁻¹ region. In the copper(II), cobalt(II), and nickel(II) complexes, however, a medium intense band is observed in the 445 – 450 cm⁻¹ region. The origin of this band may safely be attributed to the MO stretching mode.

18 Ref. 11, p. 179.