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 $[\text{Co}(\text{kozate})_2]$ 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 magne-

tic 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 ago¹. 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.

Anal. $[\text{Cu}(\text{C}_6\text{H}_5\text{O}_4)_2]$

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 (10 ml. each). 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.

Anal. $[\text{Co}(\text{C}_6\text{H}_5\text{O}_4)_2] \cdot 0.5 \text{ H}_2\text{O}$

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.

Anal. $[\text{Ni}(\text{C}_6\text{H}_5\text{O}_4)_2] \cdot 0.5 \text{ H}_2\text{O}$

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^{4a}. Carbon and hydrogen were analysed microanalytically. Magnetic susceptibility measurements were taken at room temperature (298 °K) in a Gouy Balance using G. R. copper(II) sulphate pentahydrate as the calibrant and applying a field strength of 8000 gauss. The electronic spectra of nujol mulled solids were recorded with the help of a Cary 14 recording spectrophotometer by following the method described in the literature^{4b}. I.R. spectra were determined from KBr pellets using a Beckman IR 10 spectrophotometer.

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

² R. L. DUTTA and A. SYAMAL, J. Indian chem. Soc. **44**, 381 [1967].

³ A. SYAMAL, *ibid.* **44**, 806 [1967] ; **45**, 755 [1968].

⁴ a) A. SYAMAL, *ibid.* **44**, 793 [1967] ; **45**, 374 [1968] ; b) J. R. WASSON, Chemist-Analyst **56**, 36 [1967].

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 value⁵. 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^{6,7}. 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 asymmetric d-d band at 13,420 cm⁻¹. This frequency is much lower than an expected band in a square planar or octahedral complex and this suggests a pseudo-tetrahedral structure for the complex⁶. 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 ⁴F ground state of cobalt(II) is split into ⁴A₂, ⁴T₂ and ⁴T₁(F) and three spin-allowed transitions ⁴T₂ ← ⁴A₂(ν₁), ⁴T₁(F) ← ⁴A₂(ν₂) and ⁴T₁(P) ← ⁴A₂(ν₃) are expected^{8,9}. The mull spectra of [Co(kozate)₂] exhibit three bands at 19,600 (sh), 18,180 (sh), and 7140 cm⁻¹. Since ν₁ band is not usually observed due to the weak character of ⁴T₂ ← 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) complexes¹⁰ 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 band¹¹.

COTTON and GOODGAME¹² have made approximate calculations of crystal field parameters for tetrahedral cobalt(II) complexes utilising the following relations¹³:

$$\begin{aligned}\nu_1 &= \Delta \\ \nu_2 &= 1.5 \Delta - 7.5 B' - Q \\ \nu_3 &= 1.5 \Delta - 7.5 B' - Q \\ Q &= \frac{1}{2} [0.6 \Delta - 15 B']^2 - 0.64 \Delta^2]^{\frac{1}{2}}\end{aligned}$$

where B' = effective value of Racah interionic repulsion integral and Δ = 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 Δ and β and the values are listed in Table I.

Δ, cm ⁻¹	4100
ν ₂ , cm ⁻¹	7140
ν ₃ , cm ⁻¹	18,890
B', cm ⁻¹	915 *
β = $\frac{B'}{B}$	0.94
μ _{eff.} , B.M.	4.50
λ', cm ⁻¹	160 **

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 μ_{eff.} and Δ one can obtain the effective value for the spin orbit coupling constant, λ' from the following relations¹⁵:

$$\mu_{\text{obs.}} = \mu_{\text{s.o.}} - \frac{15.56 \lambda'}{\Delta} = 3.89 - \frac{15.56 \lambda'}{\Delta}.$$

The value of λ' is included in Table I. Generally the reduction of B' and λ' 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) complex¹⁶.

⁵ F. A. COTTON and G. WILKINSON, *Advanced Inorganic Chemistry*, Interscience, New York 1966, p. 901.

⁶ D. FORSTER and D. M. L. GOODGAME, *J. chem. Soc.* **1964**, 2790.

⁷ R. L. DUTTA, D. DE, and A. SYAMAL, *J. Indian chem. Soc.* **45**, 663 [1968].

⁸ C. J. BALLHAUSEN, *Introduction to Ligand Field Theory*, McGraw Hill Book Co., New York 1962, p. 258.

⁹ J. A. COSTAMAGNA and R. LEVITUS, *J. inorg. nuclear Chem.* **28**, 2685 [1966].

¹⁰ a) J. T. DONOGHUE and R. S. DRAGO, *Inorg. Chem.* **1**, 866 [1962]; b) R. H. HOLM, A. CHAKRAVORTY, and L. J. THERIOT, *ibid.* **5**, 625 [1966] and references therein.

¹¹ R. S. DRAGO, *Physical Methods in Inorganic Chemistry*, Reinhold Publishing Corporation, New York 1965, p. 412.

¹² F. A. COTTON and M. GOODGAME, *J. Amer. chem. Soc.* **83**, 1777 [1961].

¹³ Y. TANABE and S. SUGANO, *J. physic. Soc. Japan* **9**, 753 [1954].

¹⁴ Ref. 8, p. 130.

¹⁵ F. A. COTTON and R. H. HOLM, *J. chem. Physics* **31**, 188 [1959]; **32**, 1168 [1960].

¹⁶ D. R. EATON and E. A. LALANCETTE, *ibid.* **41**, 3534 [1964].

Nickel(II) complex: The observed magnetic moment ($\mu_{\text{eff.}} = 3.50 \text{ B.M.}$) of green $[\text{Ni}(\text{kozate})_2]$ indicates that the structure of the complex is tetrahedral¹⁷. The mull spectra of $[\text{Ni}(\text{kozate})_2]$ exhibit two bands at $15,625 - 15,035 \text{ cm}^{-1}$ and 6895 cm^{-1} . The spectrum of a T_d Ni(II) complex is expected to contain three bands around $3000 - 5000 \text{ cm}^{-1}$, $6500 - 10,000 \text{ cm}^{-1}$, and $12,000 - 17,000 \text{ cm}^{-1}$ due to the transitions ${}^3T_2 \leftarrow {}^3T_1(F) (\nu_1)$, ${}^3A_2 \leftarrow {}^3T_1(F) (\nu_2)$ and ${}^3T_1(P) \leftarrow {}^3T_1(F) (\nu_3)$ respectively^{10a, 18}. Since the ν_1 band is not usually observed in T_d nickel(II) complexes and is often masked by the organic part of the molecule, the bands at 6895 cm^{-1} and $15,625 - 15,035 \text{ cm}^{-1}$ are assigned to ν_2 and ν_3 respectively^{10b, 18}. 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 $400 - 4000 \text{ cm}^{-1}$ 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 band¹⁹. The infra-red spectra of $[\text{Cu}(\text{kozate})_2]$, $[\text{Co}(\text{kozate})_2]$, and $[\text{Ni}(\text{kozate})_2]$ 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 ($\sim 50 \text{ cm}^{-1}$) on coordination with the metal ions. In the corresponding vanadyl and uranyl complexes also shifting of $\nu(\text{C}=\text{O})$ band of the ligand to lower frequency of about 45 cm^{-1} was observed. The infra-red spectra of the ligand is transparent in $400 - 500 \text{ cm}^{-1}$ region. In the copper(II), cobalt(II), and nickel(II) complexes, however, a medium intense band is observed in the $445 - 450 \text{ cm}^{-1}$ region. The origin of this band may safely be attributed to the MO stretching mode²⁰.

¹⁷ J. R. MILLER, in: *Advances in Inorganic and Radiochemistry* (edited by H. J. EMELEUS and A. G. SHARPE), Academic Press, New York 1962, p. 147.

¹⁸ Ref. 11, p. 179.

¹⁹ F. A. COTTON, in: *Modern Coordination Chemistry* (edited by J. LEWIS and R. G. WILKINS), Interscience, New York 1960, p. 301.

²⁰ M. MIKAMI, I. NAKAGAWA, and T. SHIMANOCHI, *Spectrochim. Acta* [London], Sec. A **23**, 1037 [1967]; K. NAKAMOTO, *Infra-red Spectra of Inorganic and Coordination Compounds*, Wiley, New York 1963, p. 224, 225.