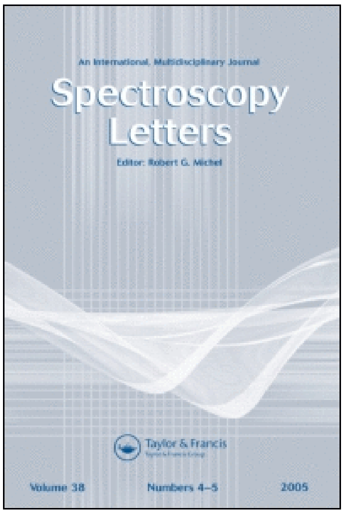

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Spectroscopic Study of Complexes between Cobalt(II) and Nickel(II) with Ethyl α-Ketocyclopentylcarboxylate

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SPECTROSCOPIC STUDY OF COMPLEXES BETWEEN COBALT(II) AND NICKEL(II) WITH ETHYL α-KETOCYCLOPENTYLCARBOXYLATE

Key words: Co(II) and Ni(II) complexes, UV-V spectra

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INTRODUCTION

As shown in a previous paper(1), the ethyl α-ketocyclopentylcarboxylate (hereafter HCBCP, according to its non-systematic name carbetoxycyclopentanone) easily undergoes a keto-enolic tautomerism, the enolic, de-protonized species thus forming coordination compounds with Mn(II), Fe(III), Co(II), Ni(II), and Cu(II). In addition to this bidentate ligand, the complexes usually contain coordinated water molecules, thus completing a distorted octahedral coordination around the metallic site. The immediate environment of the metal in these complexes is very similar to that existing in their acetylacetonate compounds, $M(acac)_n$ (n=2 or 3). These acac derivatives

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have been widely studied in the literature, and so, Co(II) is known to form a complex $[Co(acac)_2(H_2O)_2]^{(2)}$ with near-octahedral coordination and the water molecules in trans position$^{(3)}$ (D_{4h} symmetry). When dehydrated by heating at 331 K, the water-free derivative has a tetramer structure, $[Co(acac)_2]_4$, in the solid state$^{(4,5)}$, thus again attaining a distorted octahedral environment around the metallic site. Similar studies have been carried out with $[Ni(acac)_2]$ (6-8).

In this paper, the spectroscopic (V-UV) parameters of the complexes formed between Ni(II) and Co(II) with $CBCP^-$ are determined, and their behaviour in several solvents are studied. In spite of their similarity, the Cobalt complex is easily hydrolyzed in non-polar solvents by its own coordinating water molecules, while for the Nickel analogu. .his process does not seem to take place.

EXPERIMENTAL

The complexes have been synthetized according to$^{(1)}$. All chemicals were from Fluka or Merck (p.a.). The electronic spectra were recorded in a Shidmazu mod. UV-240 spectrophotometer with an integrating sphere accessory for solid samples using MgO as a reference, and coupled to a mod. PR-1 graphic printer. Magnetic susceptibilities were measured at room temperature using a Stanton MC-5 Gouy balance provided with a Newport C electromagnet.

RESULTS AND DISCUSSION

Figure 1 shows the V-UV spectra of $[Ni(CBCP)_2(H_2O)_2]$, both in the solid state and in CCl_4 solution. Two bands corresponding to d-d transitions are recorded at ca. 660-760 and 390 nm, that, taking into account the near-octahedral oxygen environment around the metallic ion, similar to that existing in the exa-aquo complex, can be ascribed to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) transitions, respectively, the first one splitted by spin-orbital coupling. In the UV region two bands at 290 nm (splitted in the solid state) and 230 nm are recorded, and are due to the ligand, as

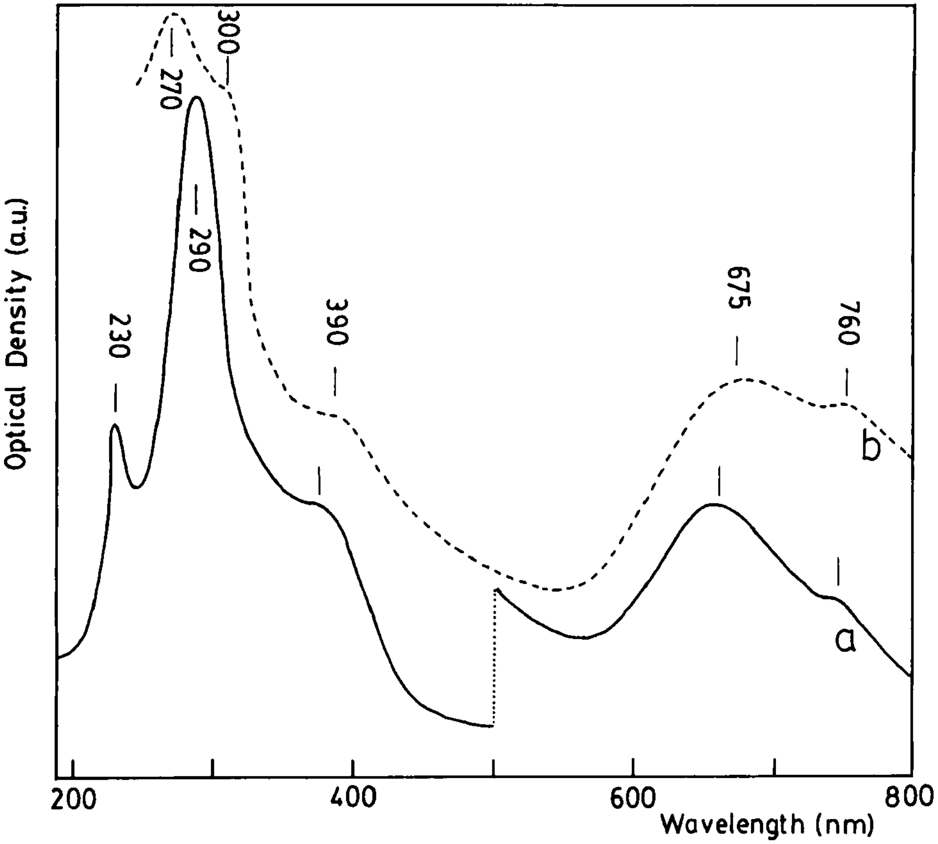

FIG. 1.- Electronic spectra of $[Ni(CBCP)_2(H_2O)_2]$. (a) in CCl_4 (b) in solid state.

the UV spectrum of NaCBCP shows these two same bands at 285 and 215 nm.

The band at 660-750 nm showing a so wide splitting, makes somewaht difficult to state unambiguously the position of its maximum in order to calculate 10Dq and B, and so, assuming a local octahedral symmetry around the metallic ion, the value of 10Dq has been determined from the magnetic properties of this compound. For octahedral complexes with ground state of symmetry A (d^8, Ni(II), among others) the effective magnetic moment, μ_{eff}, is given by$^{(9)}$:

$$\mu_{eff} = \mu_{s.o.} \left(1 - \frac{\alpha\,\lambda}{10Dq}\right)$$

where $\mu_{s.o.}$ is the magnetic moment due to spin only, λ is the spin-orbital coupling (-315 cm^{-1} for Ni(II)) and α=4$^{(9)}$. So, taking into account that for $[Ni(CBCP)_2(H_2O)_2]$ μ_{eff}=3.24 MB (2.83 MB for spin only), 10Dq results to be 8920 cm^{-1}.

According to Ballhausen$^{(10)}$, the energy of the first band for octahedral d^8 species coincides with 10Dq, and with the transition energy ratios tabulated by Lever$^{(11)}$, the energy of the second transition, from those of ν_1=8920 cm^{-1} and ν_3=25640 cm^{-1}(390 nm) results ν_2=14700 cm^{-1}, equivalent to 680 nm. Moreover, from expressions given by Ballhausen$^{(10)}$ for ν_1, ν_2, and ν_3 for octahedral d^8 species, the value of B is given by

$$B = \frac{2\nu_1^2 + \nu_3^2 - 3\nu_1\nu_3}{15\nu_3 - 27\nu_1}$$

and thus, B=908 cm^{-1} for $[Ni(CBCP)_2(H_2O)_2]$. Taking B_0=1030 cm^{-1} for the free Ni(II) ion$^{(12)}$, the nephelauxetic parameter β results 0.882. The Jørgensen parameter "f" for the environment around the Ni(II) cation can be obtained considering that 10Dq=fxg and that g(Ni^{2+}) = 8700 cm^{-1} $^{(13)}$, thus obtaining f=1.025, very close to those of water and oxalate.

The V-UV spectra of $[Co(CBCP)_2(H_2O)_2]$ are shown in Fig. 2. Only one band, multi-splitted and centered at ca. 500 nm, can be ascribed to a d-d transition. Taking into account that the effective magnetic moment for this compound is 5.05 MB (3.87 for $\mu_{s.o.}$ and 5.20 MB for $\mu_{orbital}$) the compound should exhibit the expected weak field configuration; in such a case, the observed band at ca. 500 nm should be ascribed to the third spin-allowed transition $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ for d^7 species in an octahedral environment. The band at 358 nm has been ascribed to a charge transfer process in CoO$^{(14)}$ (octahedral oxygen environment), while bands at lower wavelengths coincide with those reported for $[Ni(CBCP)_2(H_2O)_2]$ and NaCBCP.

For this complex the value of 10Dq cannot be obtained from the magnetic measurements as octahedral high spin d^7 species have a T

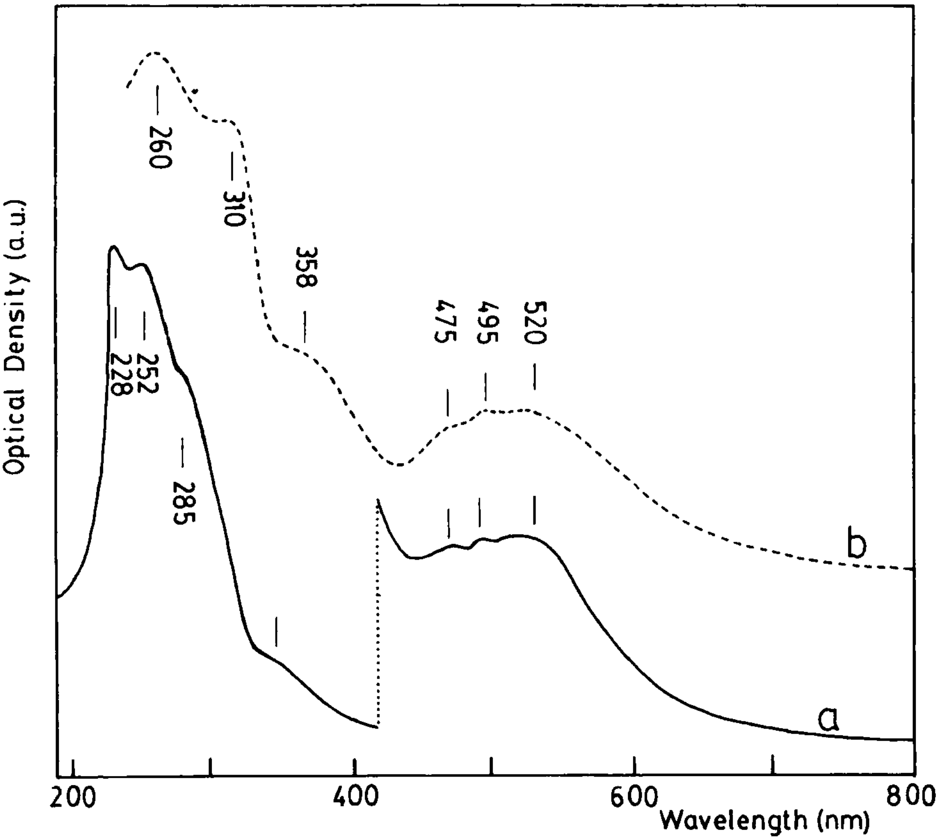

FIG. 2.- Electronic spectra of $[Co(CBCP)_2(H_2O)_2]$. (a) in CCl_4 (b) in solid state.

ground term and the magnetic moments are usually temperature dependent. On the other hand, it cannot either be obtained from the spectrum, as only one band is recorded. However, The spectroscopic parameters (10Dq and B) can be tentatively estimated from Jørgensen equation, 10Dq=fxg, taking f=1.025 (as deducted above) and $g(Co^{2+})$ = 9000 cm^{-1}(13). In such a case, 10Dq=9220 cm^{-1}. As, according to(10), $\nu_3=(225B^2 + 100Dq^2 + 180DqB)^{\frac{1}{2}}$ for high spin, octahedral d^7 species, B would then be 885 cm^{-1}, and taking B_0=971 cm^{-1} for the free Co(II) ion(12), β=0.911.

It should be stressed that the f values here used do not correspond to that of the pure $CBCP^-$ ligand, but to the $[(CBCP)_2(H_2O)_2]$ environment around the metallic ion as a whole, and assuming an octahedral geometry.

The two compounds here studied are not expected to polymerize in the solid state if their similarities with the corresponding acac derivatives of these same metals are considered. However, their behaviours in non-polar solvents are very different. While the spectrum of $[Ni(CBCP)_2(H_2O)_2]$ in CCl_4, benzene, toluene or CH_2Cl_2 remains unchanged with time, that of $[Co(CBCP)_2(H_2O)_2]$ changes from pink to brownish-green and finally a greenish precipitate is obtained. Fig. 3 shows the spectra recorded after different times; the band at ca. 500 nm is steadily missed, while a new band at ca. 600 nm develops. These changes slightly depend on the nature of the solvent and the complex concentration, but in all cases the keto- form of the free ligand (characterized by strong i.r. absorptions at 1725 and 1755 cm^{-1}) can be recovered from the solution, while the precipitate has been found to be (X-ray diffraction) a Cobalt(II) oxide. This same effect is observed if acetic acid is used as a solvent, but in this case the green solution (band at ca. 600 nm) appears immediately after solution of the complex, and then turns to a pink colour (probably Cobalt(II) acetate), the acidic properties of the solvent avoiding the precipitation of the oxide.

The kinetic analysis of the decomposition process has been carried out from the initial decomposition rates, r_0 (measured as the slopes at time=0 to the curves absorbance of the band at 600 nm vs. time) for different concentrations, as the process leading to an heterogeneous system makes meaningless studying changes in absorbance of bands originated by appearing or desappearing species.

Figure 4 shows the results of such an analysis for the process taking place in CCl_4. From data in this figure it can be concluded that the process follows a first order mechanism with a rate law

$$r = k\ [\text{complex}]$$

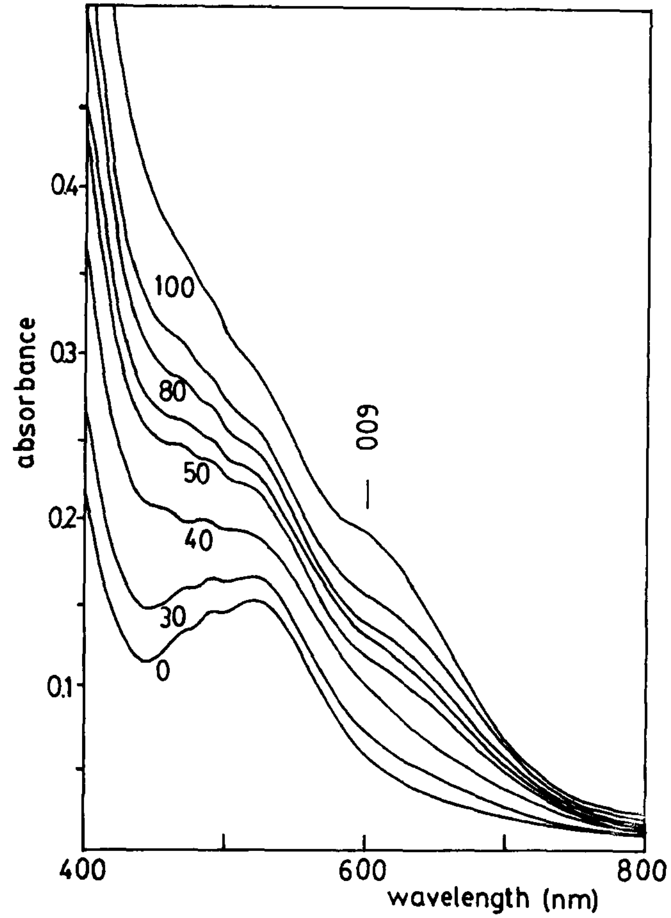

FIG. 3.- Spectra of $[Co(CBCP)_2(H_2O)_2]$ dissolved in $CCl_4(5x10^{-3}M)$ after different standing times indicated(min) on the curves.

The rate constant, as given by the slope of the straight line in Fig. 4, is $4x10^{-5}$ s^{-1}.

Taking into account that the reaction is first order, and the nature of the final products, the tentative mechanism depicted in Fig. 5 can be assumed. According to this mechanism, it seems plausible the migration of two protons from the coordinated water molecules to the $CBCP^-$ moieties, thus recovering the keto- form (more

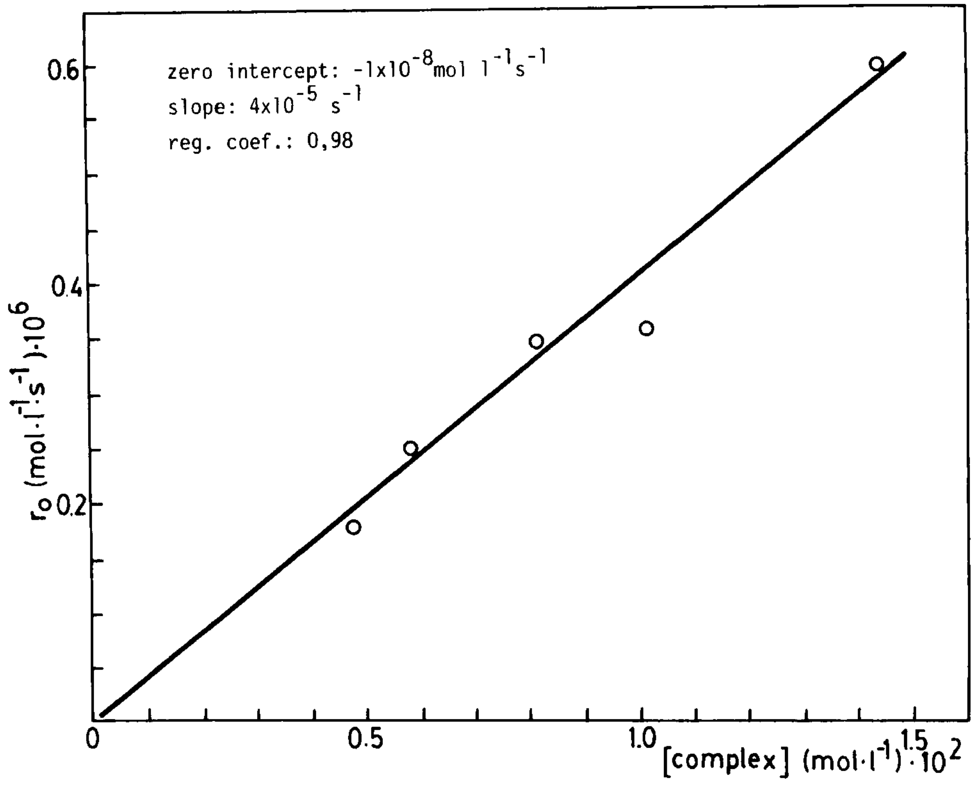

FIG. 4.- Kinetic analysis of self hydrolysis of $[Co(CBCP)_2(H_2O)_2]$.

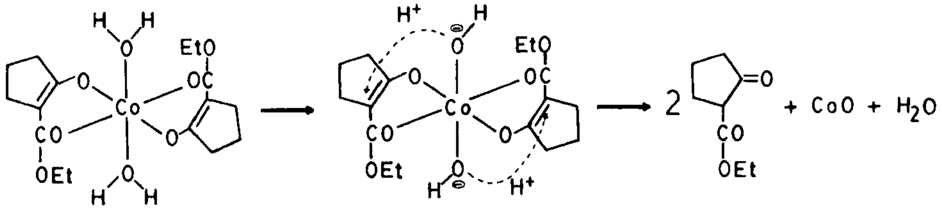

FIG. 5.- A possible mechanism for self hydrolysis of $[Co(CBCP)_2(H_2O)_2]$ in CCl_4.

stable in non-basic media that the enolic one if un-coordinated), and leading to the precipitation of hydrated Cobalt(II) oxide.

The reason why this process occurs for the cobalt complex, but not for the nickel analogue remains obscure. However, some insight can be obtained if the Crystal Field Stabilization Energies (CFSE's) for both complexes are considered. Both complexes being high spin, the CFSE will be $-8Dq_{Co}$ and $-12Dq_{Ni}$(15). Taking for Dq the values calculated above, the CFSE's would be 7380 and 19700 cm^{-1} for Co(II) and Ni(II), respectively, corresponding to 88 and 127 kJ mol^{-1}, i.e., the nickel complex would be more stable than the cobalt one because of its CFSE, so probably avoiding its self-hydrolysis.

REFERENCES

1. M.A. Bañares Muñoz, A. Angoso Catalina, S. Yañez Arias; An. Quim. 75, 795 (1979).
2. J.P. Fackler; Prog. Inorg. Chem.; 7, 361 (1966).
3. H. Montgomery, E.C. Lingafelter; Acta Cryst.; 17, 1481 (1964).
4. F.A. Cotton, R.C. Elder; J. Am. Chem. Soc.; 86, 2294 (1964).
5. F.A. Cotton, R.H. Soderberg; Inorg. Chem.; 3, 1 (1964).
6. F.A. Cotton, J.P. Fackler; J. Am. Chem. Soc.; 83, 2818 (1961).
7. Choplin-gast, R. Hugel; Bull. Soc. Chim. France; 4, 1244 (1970)
8. Choplin-gast, R. Hugel; J. Inorg. Nucl. Chem.; 34, 2595 (1972).
9. F.E. Mabbs and D.J. Machin; "Magnetism and Transition Metal Complexes", Chapman and Hall, London, 1973.
10. C.J. Ballhausen; Adv. Chem. Phys.; 5, 33 (1963).
11. A.B.P. Lever; J. Chem. Ed.; 45, 712 (1968).
12. D. Sutton; "Electronic Spectra of Transition Metal Complexes", McGraw-Hill Publ., Berkshire, England, 1975.
13. J.E. Huheey; "Inorganic Chemistry: Principles of Structure and Reactivity", 2nd ed., Harper International Ed., New York, 1978.
14. J.H. Ashley, P.C.H. Mitchell; J. Chem. Soc. (A); 2821 (1968)
15. B. Douglas, D.H. McDaniel, J.J. Alexander; "Concepts and Models of Inorganic Chemistry", 2nd ed., Wiley, New York, 1983.

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