CHEMISTRY LETTERS, pp. 689-692, 1979. Published by the Chemical Society of Japan

SYNTHESIS AND LUMINESCENCE SPECTRA OF THE COBALT(II) COMPLEX WITH KOJATE[1)]

Masayuki MUTO, Satoru YOKOTA,* Yusuke YAMAMOTO,**
Masayoshi NAKAHARA,** and Wasuke MORI***
Department of Chemistry, Faculty of Education, Wakayama University,
Masago-cho, Wakayama 640
*Department of Applied Microbiological Technology, Kumamoto Technical College,
Ikeda-machi, Kumamoto 860
**Department of Chemistry, Faculty of Science, Rikkyo University,
Nishi-Ikebukuro, Toshima-ku, Tokyo 171
***Institute of Chemistry, College of General Education, Osaka University,
Toyonaka, Osaka 560

A new complex, $Co(koj)_2 \cdot H_2O$ (Hkoj: kojic acid), was synthesized, and its IR spectrum indicated that kojates in it are coordinated to cobalt as bidentate ligands. When the complex was excited with ultraviolet light, it exhibited luminescence spectra having maxima at about 20000 cm^{-1} in aqueous and acidic solutions, and even in the solid state.

A new complex, $Co(koj)_2 \cdot H_2O$ (Hkoj: abbreviation for kojic acid), has been synthesized, and some peculiarities about it noted. First of all, it seemed somewhat strange that the color of the complex was brilliant yellow, on the other hand, the known cobalt(II) kojate complex, $Co(koj)_2 \cdot 1/2H_2O$,2) is pale orange, while the kojate ions are coordinated to cobalt(II) as bidentate ligands in both complexes. It was curious, too, that in spite of its paramagnetism, one could measure the pmr spectra without broadening of signals in acidic solutions. The most striking aspect of the complex, however, was that it exhibited light green luminescence in aqueous and acidic solutions and even in the solid state when exposed to ultraviolet light. Concerning luminescence spectra of cobalt complexes, no study has been hitherto reported, except that of a few cobalt(III) cyano complexes.3)

Synthesis: A slurry of $Co(OH)_3$ was added to a kojic acid suspension with stirring, whereupon the expected product was formed as a yellow precipitate. Found: H, 3.24; C, 40.39; Co, *ca.*16%. Calcd. for $Co(C_6H_5O_4)_2 \cdot H_2O$: H, 3.37; C, 40.13; Co, 16.40%.

Magnetic measurments: The complex gives paramagnetic susceptibity, $\mu = 4.82$ B.M.. Fig. 1 shows the magnetic susceptibity *vs.* temperature plot of the new complex with that of the known complex, $Co(koj)_2 \cdot 1/2H_2O$. Both curves are similar, indicating that the new complex is monomer, as in the case of the known complex.

IR spectra: The IR spectrum of the new complex is shown in Fig. 2 with that of free kojic acid. Two new absorption bands regarded as Co – O stretching appear at about 460 and 435 cm^{-1}, which can never be found in the spectrum of free kojic acid, while in the spectrum of $K_3[Co(ox)_3]$ (H_2ox: abbreviation for oxalic acid) only one band attributable to Co – O stretching by ring deformation appears in the range of 446 cm^{-1}.4) With regard to the fact that there is a clear difference between the IR spectra of the kojato and oxalato complex, it can be said that in the oxalato complex the chelate ring is symmetrical, whereas in the case of kojato complex it is unsymmetrical. Therefore, it is probable that the band obserbed in the spectrum of the oxalato complex at about 450 cm^{-1} splits into two bands in that of the kojato complex. Strangely enough, in spite of the difference in color (see above), the IR spectrum of the new complex is almost similar in pattern and peak positions to that of the known complex (1/2 hydrate); *i.e.*, it is obvious that the central cobalt atom is surrounded with four anionic oxygen atoms in both complexes.

Luminescence spectra: The luminescence spectra of a powdered sample and an aqueous solution, excited with 365 nm Hg line at room temperature, are shown in Fig. 3, and those of acidic solution, 6N $HClO_4$ and 6N H_2SO_4, are shown in Fig. 4, together with their absorption spectra. The maximum of the former samples were at about 20000 cm^{-1}, and those of the latter at about 19000 cm^{-1}. the light green luminescence from the aqueous and acidic solutions is directly visible even when the solutions were exposed to the daylight. In the solution, the luminescence intensities decreased gradually with time without any significant change in the spectral pattern. This indicates that luminescent species photodecomposes into non- luminescent products under the exposure to ultraviolet light. In the solid state, the luminescence intensity did not decrease, but it was very weak compared with that of the aqueous and acidic solutions. When the temperature was lowered to 20 °K in the

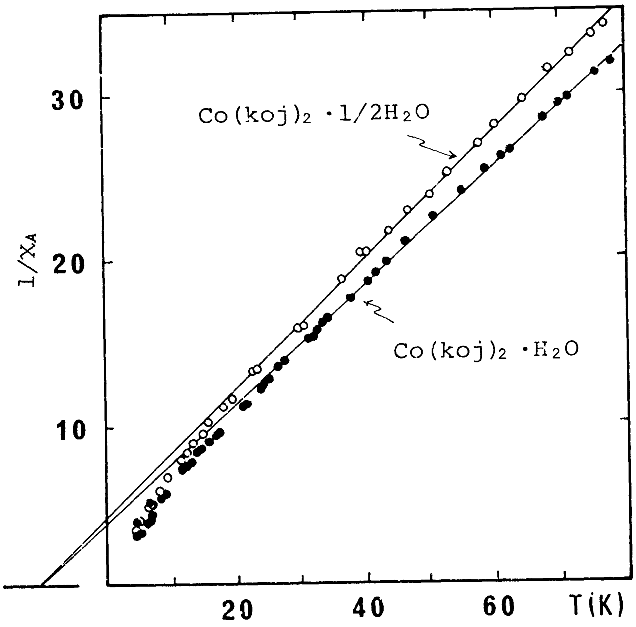

Fig. 1. Magnetic susceptibity *vs.* temperature for $Co(koj)_2 \cdot H_2O$ and $Co(koj)_2 \cdot 1/2H_2O$.

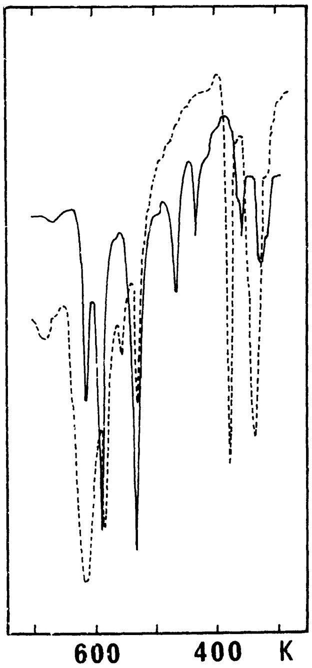

Fig. 2. IR spectra of $Co(koj)_2 \cdot H_2O$ (———) and kojic acid (-------).

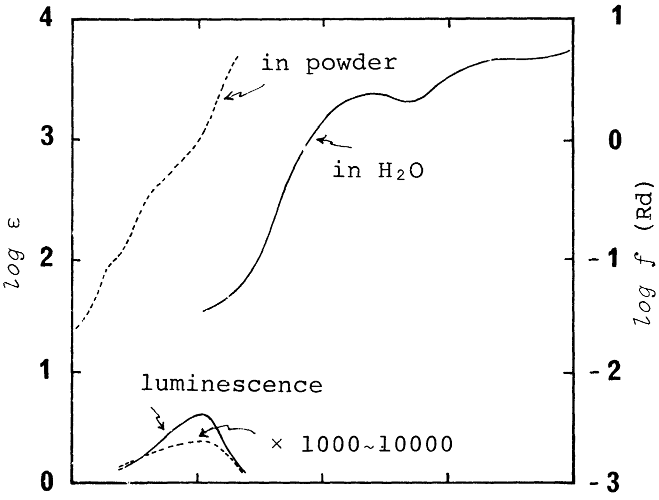

Fig. 3. Absorption, diffuse reflectance and luminescence spectra of $Co(koj)_2 \cdot H_2O$.

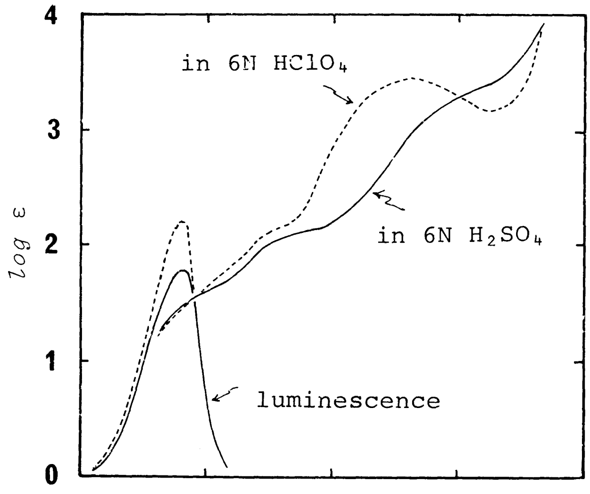

Fig. 4. Absorption and luminescence spectra of $Co(koj)_2 \cdot H_2O$ in acidic solutions.

solid state, no increase in luminescence intensity nor any change in the spectrum could be observed. This suggests that (i) $Co(koj)_2$ itself is not luminescent, but its protonated species, or some photoproduced species derived from it are probably luminescent, and (ii) weak luminescence from the powdered sample is probably due to the interaction of $Co(koj)_2$ with crystal water. On the basis of the luminescence band position and intensity, it can be definitely said that the luminescent level is not the d－d excited one, which is nearly equal to the luminescent level in other luminescent cobalt complexes.3)

We are now going on to ask whether this light green luminescence can be observed in other cobalt(II) 3-hydroxy-4-pyronato complexes, or other metal kojato or 3-hydroxy-4-pyronato complexes.5)

References and Notes

1) Presented at the 27th Symposium of Coordination Chemistry held at Shinshu University, Matsumoto, September, 27, 1977; and at the 28th Symposium of Coordination Chemistry held at Ehime University, Matsuyama, October, 11, 1978.

2) J. W. Wiley, G. N. Tyson, Jr. and J. S. Steller, *J. Am. Chem. Soc.*, 64, 963 (1962).

3) For example, a) G. B. Porter and M. Mingardi, *J. Chem. Phys.*, 49, 4354(1966); b) G. A. Crosby, *J. Chem. Phys.*, 64, 160(1967); c) F. Zuloaga and M. Kasha, *Photochem. Photobiol.*, 7, 549(1968); d) H. Kataoka, Y. Yamamoto, M. Nakahara and Y. Kondo, *Nippon Kagaku Zasshi*, 92, 274(1971); e) H. Kataoka, *Bull. Chem. Soc. Jpn.*, 46, 2078(1973); f) K. W. Hipps and G. A. Crosby, *Inorg. Chem.*, 13, 1543(1974).

4) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", John Wiley and sons, Inc., New York(1963), p. 245.

5) At present it has become apparent that the known complex (1/2 hydrate) gives luminescence spectrum in an acidic solution (H_2SO_4) having maxima at about 19000 and 22500 cm^{-1}, which is distinct from that of the new complex. Thus, we have to study luminescence spectra concerning two varieties of metal kojato complexes, prepared by conventional method and by our method.

(Received March 2, 1979)