

## INFRARED ABSORPTION SPECTRAL STUDY OF MANGANESE(II), MANGANESE(III) AND COBALT(III)-8-QUINOLINATES

ARVIND T RANE

*Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba,  
Bombay-400 005, INDIA*

*(Received 17 May 1984)*

The i.r. absorption spectra of 8-quinolates of Mn(II), its dihydrate, Mn(III) and Co(III) have been studied in the near i.r. region. The spectrum of Co(III)-8-quinolate is compared with that of self-adduct,  $\text{CoQ}_2\cdot\text{HQ}$  and interpreted in terms of bonding.

**Key Words :** Cobalt(II); Cobalt(III); Manganese(II); Manganese(III); Self-Adduct; and 8-Quinolol

### INTRODUCTION

As a part of the research programme dealing with certain metal chelates of 8-quinolol, infrared absorption spectra of dihydrates and self-adducts of cobalt(II) and nickel(II) chelates of 8-quinolol were reported earlier.<sup>1</sup> Absorption spectra of the adducts of thorium and uranium<sup>2,3</sup> and nickel-8-quinolates<sup>4</sup> in the visible region were reported. Bullwinkel and Noble<sup>3</sup> defined adducts as the acid form of the chelates bonding through hydrogen atoms forming long chains. In the adduct formation of cobalt(II), in particular, it became necessary to check whether cobalt(II) chelate was really forming an adduct with one molecule of 8-quinolol as acid chelate through hydrogen atom as reported earlier<sup>3</sup> or forming a simple chelate  $\text{CoQ}_3$  by protonation, undergoing oxidation during the course of reaction. This doubt could be cleared by taking the actual i.r. spectrum of  $\text{CoQ}_3$  and comparing it with that of  $\text{CoQ}_2\cdot\text{HQ}$  obtained earlier<sup>1</sup>. Unlike cobalt(II), manganese(II) chelate does not form an adduct with 8-quinolol<sup>5</sup> but forms  $\text{MnQ}_3$  on oxidation. The infrared absorption spectra of the chelates of Mn(II), its dihydrate and Mn(III) are also given here for comparison.

### EXPERIMENTAL

#### *Preparation of Chelates*

The dihydrate of manganese(II)-8-quinolate was prepared like cobalt(II) chelate as described earlier.<sup>1</sup> Part of the chelate was dehydrated by keeping it in the oven at 160 °C for several hours.

Both the manganese and cobalt chloride solutions were oxidized with few drops of hydrogen peroxide and the chelates were precipitated as earlier. The chelates were dried in the oven at 160 °C to remove moisture and subjected to elemental analysis and their compositions were checked. The i.r. spectra were

taken on a Perkin-Elmer model 137B recording spectrophotometer in potassium bromide. The i.r. spectra of Mn(II), Mn(III) and Co(III) oxinates along with that of the adduct of Co(II), for comparison, are given in Fig. 1. The differential thermal analysis of the chelates were performed on DTA-02-Universal VEB, Laborektronik Halle, GDR.

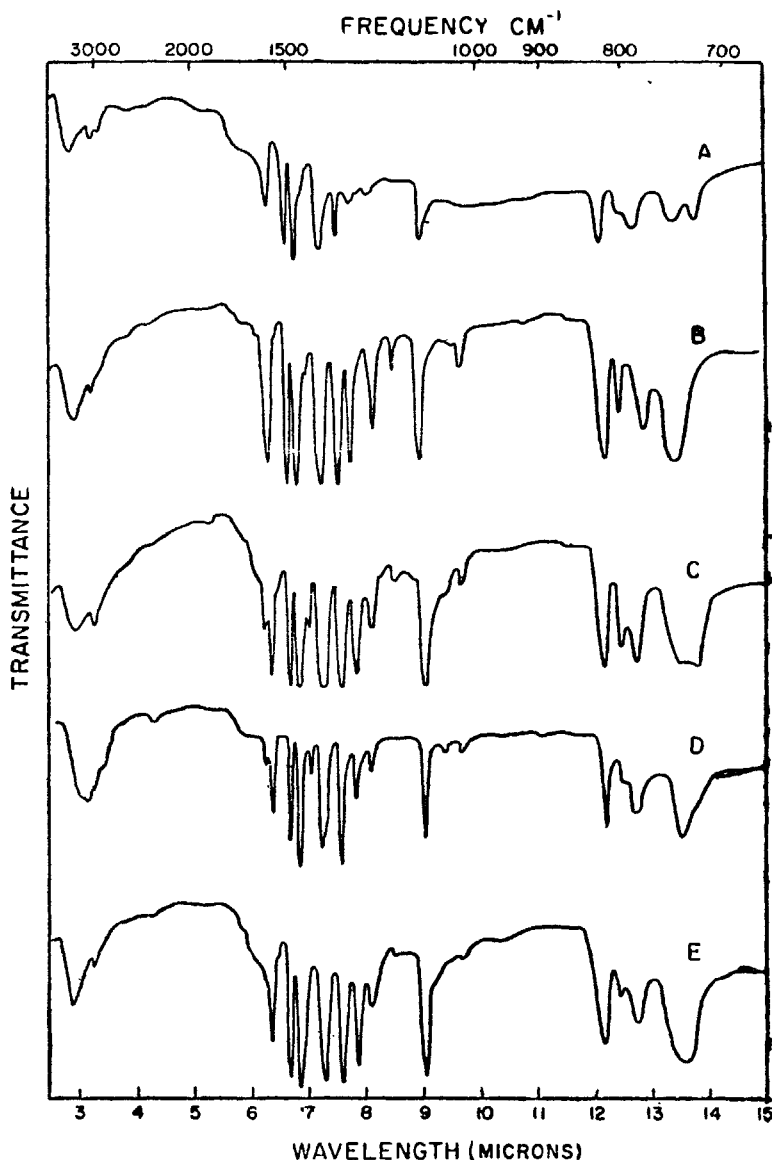


FIG. 1. Infrared absorption spectra of 8-quinolinates of Mn(II), its dihydrate,  $\text{MnQ}_3 \cdot 2\text{H}_2\text{O}$ , Mn(III), Co(III) and self-adduct  $\text{CoQ}_3 \cdot \text{HQ}$ .

A,  $\text{CoQ}_3 \cdot \text{HQ}$ ; B,  $\text{CoQ}_3$ ; C,  $\text{MnQ}_3$ ; D,  $\text{MnQ}_3 \cdot 2\text{H}_2\text{O}$ ; E,  $\text{MnQ}_3$ .

## RESULTS AND DISCUSSION

The elemental analysis of the chelates of Co(III) and Mn(III) confirmed that the chelates were anhydrous. In the differential thermal analysis, exothermic peaks were observed between 375–480 °C and 300–440 °C for Co(III) and Mn(III) respectively. In the case of  $\text{MnQ}_2 \cdot 2\text{H}_2\text{O}$ , however, a depression at 140 °C, due to endothermic reaction caused by the presence of water molecules, was seen. The endothermic reaction due to the presence of water molecules was further confirmed by taking DTA of anhydrous  $\text{MnQ}_2$  which showed a single exothermic peak between 300–410 °C. Similar endothermic reactions were observed in the DTA of  $\text{CoQ}_2 \cdot 2\text{H}_2\text{O}$  (148–180 °C) and  $\text{NiQ}_2 \cdot 2\text{H}_2\text{O}$  (130–198 °C).<sup>1</sup>

There is no remarkable difference between the i.r. spectra of  $\text{CoQ}_2$  and  $\text{CoQ}_3$  excepting in the peak at 13.4  $\mu\text{m}$ , which is sharper in the case of  $\text{CoQ}_3$ . Similar sharp peak is observed in the spectrum of  $\text{MnQ}_3$ .

The peaks at 2.9 and 3.25  $\mu\text{m}$  (3500, 3076  $\text{cm}^{-1}$ ) are present in  $\text{CoQ}_3$ ,  $\text{MnQ}_2$  and  $\text{MnQ}_3$  only, whereas a broad composite peak around 3  $\mu\text{m}$  is observed in the spectrum of  $\text{MnQ}_2 \cdot 2\text{H}_2\text{O}$ . Similar observation was reported<sup>1</sup> in the spectra of hydrated chelates of Ni(II) and Co(II). This is not unexpected as this peak is the characteristic of the bonded O-H stretching in Oxines<sup>6</sup> which gets nicely resolved into two peaks at 2.9 and 3.25  $\mu\text{m}$  (3500 and 3076  $\text{cm}^{-1}$ ) on the removal of water molecules.

The peaks at 7, 9.3 and 9.6  $\mu\text{m}$  reported earlier<sup>1</sup> in the hydrated chelates of Ni(II) and Co(II) are also present in  $\text{MnQ}_2 \cdot 2\text{H}_2\text{O}$  but totally absent in the spectra of  $\text{CoQ}_3$  and  $\text{MnQ}_3$ . This confirms the earlier views that these peaks are responsible for the presence of water molecules and could serve as the identification peaks for  $\text{H}_2\text{O}$ .

As in the previous spectra<sup>1</sup> a very strong peak appear at 9  $\mu\text{m}$  in the i.r. spectra of the chelates of Co(III), Mn(III) and Mn(II). This peak is present in all the metal-8-quinolinates, in the wavelength region assigned to the C-O vibration<sup>7</sup>. The 9  $\mu\text{m}$  peak can serve as a characteristic peak for the identification of the bond between the metal ion and the 8-quinolinate anion through oxygen. This peak appears in all the metal-8-quinolinates spectra reported by the previous workers, the appearance of which is due to diatomic vibrations, such that associated with the C-O group, rather than to more complex vibrations.<sup>7</sup> The position of the 9  $\mu\text{m}$  peak is found to vary slightly in  $\text{CoQ}_2$  and  $\text{MnQ}_2$  i.e. from 1111  $\text{cm}^{-1}$  to 1120  $\text{cm}^{-1}$ . Charles *et al.*<sup>7</sup> have found a linear relationship between the position of the 9  $\mu\text{m}$  peak and the atomic weight of metal for divalent metal chelates of 8-quinolinol. The position of the peak remains unaffected even after change in the valence state, in both the metals, cobalt and manganese.

In general the spectrum of  $\text{CoQ}_2$  appears to be more or less identical with that of  $\text{CoQ}_3$  but differs with the one obtained from the adduct,  $\text{CoQ}_2 \cdot \text{HQ}$ . Instead of two peaks at 13.35  $\mu\text{m}$  and 13.75  $\mu\text{m}$  (749.06 and 729.27  $\text{cm}^{-1}$ ) only one peak at 13.4  $\mu\text{m}$  is present in  $\text{CoQ}_3$ . This peak also appears in the spectrum of  $\text{MnQ}_2$ .

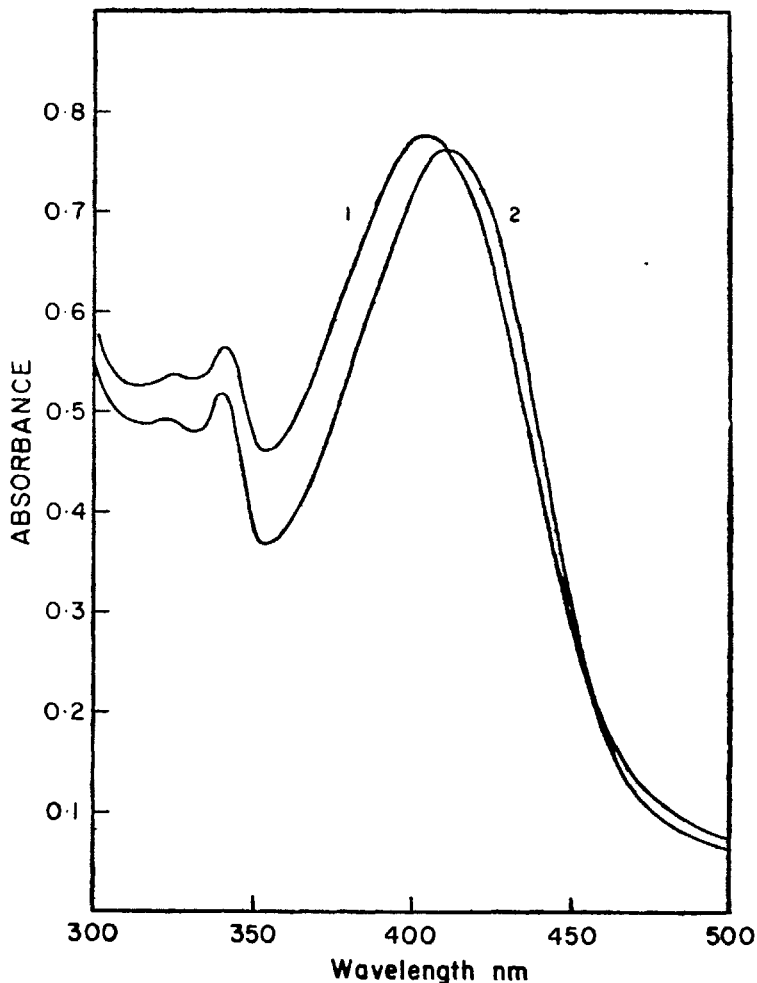


Fig. 2. Absorption spectra of Co(II)-8-quinolate and Co(III)-8-quinolate in the visible region.

1 — CoQ<sub>2</sub>

2 — CoQ<sub>3</sub>

The fact that the chelate CoQ<sub>3</sub> is formed by the oxidation of Co(II) to Co(III) was also confirmed by spectrum taken in the visible region. Bathochromic shift was observed in the absorption spectrum of CoQ<sub>2</sub> when it was oxygenated. On oxidation, the maxima shifted from 403nm to 410nm and the spectrum was identical to the one obtained from CoQ<sub>3</sub> in the present case (Fig. 2). No such shift in the wavelength but an increase in the absorbance was observed in the spectrum, in visible region, of the adduct, CoQ<sub>2</sub>·HQ.

On the basis of these findings, it is concluded that the adduct formation reported in the case of Co(II) is through H atom, the structure of which is described elsewhere.

## REFERENCES

1. A T Rane and V V Ravi, *Spectrochim. Acta* **38A** (1982) 937
2. T Moeller and M V Ramaniah, *J. Am. chem. Soc.* **75** (1953) 3946; *ibid* **76** (1954) 2022; *ibid* **76** (1954) 5251
3. E P Bulliwinkel and P Noble (Jr.), *J. Am. chem. Soc.* **80** (1958) 2955
4. K S Bhatki and A T Rane, *Indian J. Chem.* **18A** (1979) 92; *Proc. Indian Acad. Sci.* **88A** (1979) 313
5. A T Rane, *J. inorg. nucl. Chem.* **42** (1980) 1520
6. A D Cross and R A Jones, *An Introduction to Practical Infrared Spectroscopy*, 3rd Ed., Plenum Press, New York, (1969) p 91
7. R G Charles, H Freiser, R Fridel, L E Hilliard and W D Johnston, *Spectrochim. Acta* **8** (1956) 1