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Nature of metal complexes of 1-hydroxyanthraquinone*†

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Abstract—An analysis has been made of i.r. absorption spectra of chelates of 1-hydroxyanthraquinone and transition metals in the region between 1000 and 300 cm^{-1}, together with earlier data for the regions 3600–1000 cm^{-1}. It is suggested that water molecules in dihydrates are bonded with carbonyl groups and are not coordinated to the metal ions. Also, the values of the chelate ring vibrations and comparisons with the analogous 5-hydroxy 1,4 naphthaquinone ligand suggest an unsymmetrical electron distribution in the chelate rings of 1-hydroxyanthraquinone metal chelates, and their resulting weaker nature.

INTRODUCTION

EXTENSIVE investigations on the structure of β-diketone metal chelates by crystallographic [1], vibrational [2, 3] and nuclear magnetic resonance [4] spectroscopic methods have shown that there is a symmetrical electron distribution in the chelate ring resulting in approximately equal carbon—carbon, carbon—oxygen and metal—oxygen bonds. However chelates from closely similar ligands like 1-hydroxyanthraquinone, where substitution on carbon atoms which form part of the chelate brought about bond fixation, have received very little attention. Since certain preliminary investigations by two of us [5], there has been a recent report on such chelates [6] of various divalent cations of alkaline earth and transition metals, which were prepared by using the sodium salt instead of the usual acetate method. A brief discussion of their i.r. spectra has also been given. Metal chelates of 8-hydroxy 1,4 naphthaquinone have been recently investigated [7] by the i.r. spectroscopic method.

To gain more insight into the nature of 1-hydroxy-anthraquinone metal chelates we have extended our i.r. studies to the low frequency region (till 300 cm^{-1}) and analysed the various bands so as to assign vibration frequencies pertaining to the chelate ring.

EXPERIMENTAL

The preparation of the complexes have already been reported [5]. The spectra were recorded on Perkin–Elmer 221 i.r. spectrophotometer equipped with sodium

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[1] E. C. LINGAFELTER and R. L. BRAUN, *J. Am. Chem. Soc.* **88,** 2951 (1966).
[2] H. F. HOLTZCLAW and J. P. COLLMAN, *J. Am. Chem. Soc.* **79,** 3318 (1957).
[3] K. NAKAMOTO and A. E. MARTELL, *J. Chem. Phys.* **32,** 588 (1960); K. NAKAMOTO, P. J. MCCARTHY, A. RUBY and A. E. MARTELL, *J. Am. Chem. Soc.* **83,** 1066, 1272 (1961).
[4] J. P. FACKLER, *Progr. Inorg. Chem.* **7,** 374 (1966).
[5] Z. JAWORSKA and T. URBANSKI, *Bull. Acad. Pol. Sci.* **17,** 579 (1969).
[6] R. A. WALKER, *Spectrochim. Acta* **27A,** 1785 (1971).
[7] R. S. BOTTEI and C. P. MCEACHERN, *J. Inorg. Nucl. Chem.* **32,** 2653 (1970).

Table 1. Characteristic i.r. absorption bands of 1-hydroxyanthraquinone metal chelates

1-Hydroxy anthra-quinone	Cu	Mg	Zn	Cd	Mn	Co	Ni	K	Mg.2H_2O	Co.2H_2O	Ni.2H_2O	Assignment
1672 s	1670 s	1674 m	1672 m	1670 s	1676 m	1672 m	1673 m	1652 m	1650 s	1655 s	1650 s	Non-coordinated C=O stretching
1638 vs	1610 s	1620 vs	1625 s	1615 s	1625 s	1620 s	1620 s	1624 vs	1628 vs	1618 vs	1620 vs	Coordinated C=O stretching
1530 m	1515 vs	1520 m	1525 m	1525 s	1530 s	1535 m	1528 vs	1510 m	1515 s	1518 m	1518 s	$\text{C}\overset{\cdots}{-}\text{C}$ stretching (chelate)
1445 m	1412 s	1410 m	1415 m	1412 s	1412 m	1412 m	1415 s	1405 s	1412 s	1412 m	1409 m	C—O stretching (chelate)
1270 sm	1265 s	1267 s	1255 m	1250 s	1252 s	1250 s	1265 sh	1260 sh	1267 vs	1267 s	1265 vs	$\text{C}\overset{\cdots}{-}\text{C}$ stretching (chelate)
1266 s	1250 s	1252 s					1255 s	1250 s	1254 s	1265 sh	1257 s	
424 *w*	468 s	437 s	443 s	420 s	429 s	443 s	450 s		448 s	445 s	450 s	Metal oxygen stretching
	377 m	365 m	365 m	357 m	356 m	370 m	369 m		370 m	368 m	372 m	Metal oxygen stretching

chloride prism grating and caesium bromide prism interchanges. They were calibrated with carbon dioxide and water vapour bands and checked with polystyrene and 1, 2, 4 trichlorobenzene.

RESULTS AND DISCUSSION

The bands characteristic of the metal chelate ring are tabulated in Table 1 and the spectra of the ligand and some typical chelates in the region 14–35 μm are shown in Figs. 1 and 2.

Hydrated chelates

All the chelates which were obtained as dihydrates gave rise to two broad bands in the hydroxy stretching region at 3510 and 3100–3140 cm^{-1} along with a lowering in the free carbonyl absorption by about 20 cm^{-1} (1650 cm^{-1}) as compared with non-hydrates. The hydroxy deformation mode expected at 1590–1650 cm^{-1} could not be discerned through overlapping carbonyl absorption. NAKAGAWA and SHIMANOUCHI [8] observed two additional bands in the region 900–450 cm^{-1} ascribed to OH_2 rocking and wagging modes respectively in coordinated aquo complexes.

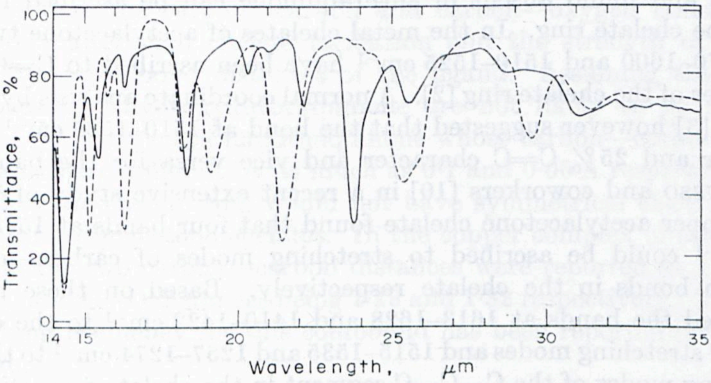

Fig. 1. Spectra of 1-hydroxyanthraquinone (——), copper chelate (– – –).

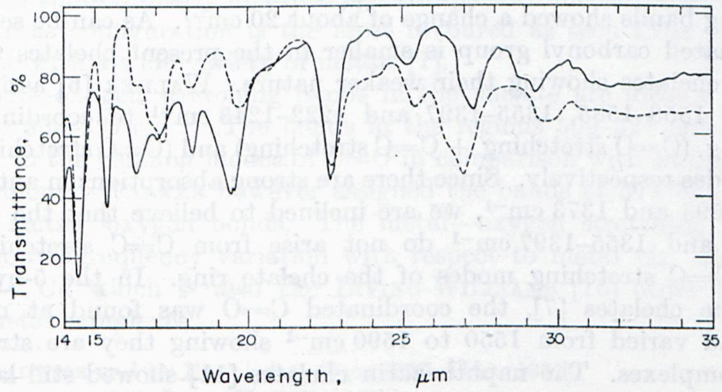

Fig. 2. Spectra of cobalt chelate dihydrate (——), cobalt chelate anhydrous (– – –).

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[8] I. NAKAGAWA and T. SHIMANOUCHI, *Spectrochim. Acta* **20**, 429 (1964).

A comparison of the hydrated and anhydrous spectra of cobalt and nickel complexes showed no prominent bands in the above region ascribable to these modes. In fact two bands at 1300–1360 cm^{-1} found in the anhydrous compounds were absent in the hydrates. These features suggested that the water molecules in these dihydrates are not coordinated to the metal ions, and they are held by hydrogen bonds with non-coordinated carbonyl groups in such a way as to increase the symmetry of the coordinated ligand.

Chelate ring vibrations

In the double bond region, the non-coordinated carbonyl groups were found at 1666–1676 cm^{-1} (except in hydrates as mentioned above) which is very close to the value found for 1-hydroxyanthraquinone. The coordinated carbonyl was found in the region 1613–1628 cm^{-1} compared to the hydrogen bonded C═O at 1632 cm^{-1} in the ligand. The next two bands at 1575–1590 and 1560–1575 cm^{-1} are similar to those found in anthraquinone [9] (1574 and 1593 cm^{-1}) and are ascribed to aromatic ring stretching modes. A band lying in the region 1515–1535 cm^{-1} in the chelates and found absent in anthraquinone can be ascribed to the C—C stretching of the chelate ring. In the metal chelates of acetylacetone two bands in the regions 1570–1600 and 1510–1525 cm^{-1} have been ascribed to C═O and C═C stretching modes of the chelate ring [2]. A normal coordinate analysis by NAKAMOTO and coworkers [3] however suggested that the bond at 1510–1525 cm^{-1} has ~75% C═O character and 25% C═C character and vice versa for the band at 1570–1600 cm^{-1}. MUSSO and coworkers [10] in a recent extensive study of ^{2}H, ^{13}C and ^{18}O labelled copper acetylacetone chelate found that four bands at 1575, 1397 and 1527, 1281 cm^{-1} could be ascribed to stretching modes of carbon—oxygen and carbon—carbon bonds in the chelate respectively. Based on these assignments we have ascribed the bands at 1613–1628 and 1410–1422 cm^{-1} to the coordinated C═O and C—O stretching modes and 1515–1535 and 1257–1274 cm^{-1} to the carbon—carbon stretching modes of the C—C—C segment in the chelate respectively.

While the coordinated carbonyl and C—O groups showed a variation of about 15 cm^{-1} in its stretching modes depending on the metal ions, the corresponding C—C stretching bands showed a change of about 20 cm^{-1}. As can be seen the shift in the coordinated carbonyl group is smaller in the present chelates than in the acetylacetone chelates showing their weaker nature. WALKER [6] assigned bands at 1610–1634, 1558–1585, 1355–1397 and 1222–1248 cm^{-1} to coordinated C═O, C═C stretching, (C═O stretching + C═C stretching) and (C═C stretching + C═O stretching) modes respectively. Since there are strong absorptions in anthraquinone [9] at 1574, 1593 and 1373 cm^{-1}, we are inclined to believe that the absorptions at 1558–1585 and 1355–1397 cm^{-1} do not arise from C═C stretching + C═O stretching + C═C stretching modes of the chelate ring. In the 5-hydroxy 1, 4 naphthaquinone chelates [7], the coordinated C═O was found at much lower frequencies and varied from 1550 to 1590 cm^{-1} showing they are stronger than the present complexes. The naphthazarin chelates [11] showed still larger shifts.

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[9] C. PECILE and B. LUNELLI, *J. Chem. Phys.* **46,** 2109 (1967).

[10] B. BOCK, K. FLATAU, H. JUNGE, M. KUHR and H. MUSSO, *Angew. Chem.* **10,** 225 (1971).

[11] R. S. BOTTEI and P. L. GERACE, *J. Inorg. Nucl. Chem.* **23,** 245 (1961).

In order to evaluate the bond character of 1-hydroxyanthraquinone chelates, it is important to consider the bond distances in the chelate ring. In the absence of crystallographic data on the molecular structures of the ligand and the chelates in the literature, the bond distances in the closely similar ligand 5-hydroxy 1, 4 naphthaquinone for which crystallographic data have been recently reported [12], were considered. In this, the two 4, 10 and 5, 10 carbon—carbon bond distances were 1·51 and 1·40 Å while the C=O and C—O bond distances were 1·26 and 1·33 Å respectively. The coordinated C=O frequencies in the chelates [7] as mentioned above varied from 1550 to 1590 cm^{-1} involving a larger shift than observed in the present compounds. In the β-diketone type ligand 1, 3 phenyl 1, 3 propanedione [13] the 1, 2 and 1, 3 carbon—carbon distances were much closer to one another (1·413 and 1·385 Å) and C=O and C—O distances were 1·292 and 1·317 Å respectively. Since the bond distances in the metal chelates of the above ligand were not available, the chelates of the analogous 2, 4 pentanediones were considered. The two carbon—carbon and carbon—oxygen distances were approximately equal (1·39 and 1·27 Å respectively).

It is clear that the carbon—carbon and carbon—oxygen bond distances are not appreciably altered in chelate formation and the strength of the chelate is related to favourable bond distances of the ligand. Assuming that the relevant bond distances in 1-hydroxyanthraquinone are not likely to be much different from those of 5-hydroxy 1, 4 naphthaquinone whose carbon—carbon and carbon—oxygen distances are different by as much as 0·1 and 0·06 Å respectively, it may be concluded that the chelate ring would not have symmetrical electron distribution as in the metal acetylacetone chelates. In the copper complex of ethylacetoacetate [14], the relevant two carbon—carbon distances were reported at 1·31 and 1·39 Å and the C=O and C—O distances being 1·28 and 1·32 respectively. The coordinated C=O stretching frequency for this compound has been reported [15] at 1591 cm^{-1} in chloroform.

As regards the symmetry of these chelates, they most probably have a *trans* configuration. This conclusion is based on the fact the spectra of the different metal chelates showed nearly identical spectral pattern for the chelate ring absorptions, and trans configuration is the most favoured as seen from the chelates of acetylacetone with a wide variety of metals [1].

The metal—oxygen stretching bands in the chelate are located in the region 420–468 and 356–377 cm^{-1}. The bands in the regions 500–524 and 392–402 cm^{-1} are ascribed to the bending modes of C=O in comparison with similar assignments in anthraquinone. WALKER however assigned the bands at 573–671, 494–532 and 408–481 to metal—oxygen bonds. The metal—oxygen stretching band at 420–468 cm^{-1} showed frequency variation with respect to metal viz. Cd $<$ Mn $<$ Zn $<$ Co $<$ Ni $<$ Cu which is also the IRVING-WILLIAMS [16] order of stability of transition metal complexes.

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[12] P. D. CHADWICK and D. HALL, *Acta Cryst.* **B27**, 1468 (1971).

[13] D. E. WILLIAMS, *Acta Cryst.* **21**, 340 (1966).

[14] G. A. BARCLAY and A. COOPER, *J. Chem. Soc.* 3746 (1965).

[15] R. P. DRYDEN and A. WINSTON, *J. Phys. Chem.* **62**, 635 (1958).

[16] H. IRVING and R. J. P. WILLIAMS, *Nature, Lond.* **162**, 746 (1948); *J. Chem. Soc.* 3192 (1953).