BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Série des sciences chimiques
Volume XVII, No. 10, 1969

ORGANIC CHEMISTRY

Infrared Spectroscopic Investigation of Metal Complexes of 1-Hydroxyanthraquinone

by

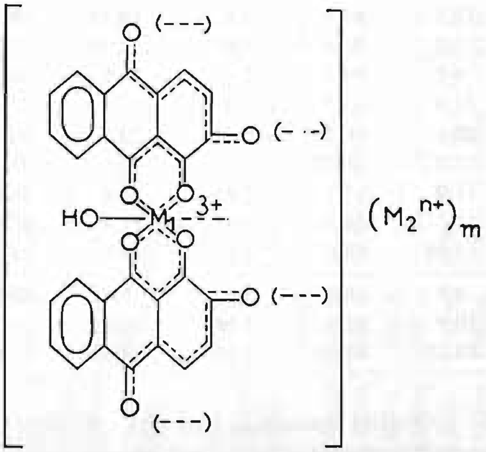
Z. JAWORSKA and T. URBAŃSKI

Presented by T. URBAŃSKI on July 2, 1969

The structure of some metal complexes of alizarine, such as the calcium-aluminium lake (Turkey Red) have called attention of chemists primarily for their practical importance. Since the classic work of Graebe and Liebermann in 1868 [1], and Liebermann and Kostanecki [2], a number of authors studied the structure of metal complexes of alizarine. Among more recent views on the problem, the most important were those expressed by Pfeiffer [3], Hoffmann [4], and Rutishauser [5].

However, only a series of quite recent papers by Kiel and Heertjes [6] describe the use of a modern spectroscopic and X-ray technique to elucidate the structure of several metal complexes of alizarine and its derivatives.

They came to the conclusion that the structure of lakes can be expressed by the schematic formula



in which M_1^{3+} is a tervalent metal (Al, Fe, or Cr) and M_2 is hydrogen or univalent (Na, K), divalent (Ca, Ba) or quadrivalent (Sn) metal. This formula corresponds basically to the classical presentation of the structure of alizarine complexes given as early as 1908 by Werner [7] and 1913 by Pfeiffer [3].

In the present paper (which is the first in the series), we tried to elucidate the structure of simpler metal complexes composed of 1-hydroxyanthraquinone and one of the metals: Cu, Mg, Ca, Zn, Cd, Pb, Mn, Co, Ni. So far only Geyer and Smith [9] tried to establish the structure of metal complexes of 1-hydroxyanthraquinone by examining their electronic spectra.

Also the potassium salt of 1-hydroxyanthraquinone was examined.

Experimental

1-Hydroxyanthraquinone was prepared according to Roemer [10]. It was purified by dissolving in aqueous sodium hydroxide, precipitating with hydrochloric acid, washing with water, and crystallizing from ethanol; m.p. 200—201°. The purity was verified with paper chromatography.

Complexes of metals and 1-hydroxyanthraquinone were obtained as a rule by acting with one equivalent of a metal acetate on two moles of 1-hydroxyanthraquinone.

Complexes of Mg, Ca, Zn, Cd, Pb, Mn, Co, Ni. 1-Hydroxyanthraquinone (2.2 g., 0.01 mole) was dissolved in hot methanol (600 ml.) cooled to 50° and the metal acetate (0.005 equivalent) solution in methanol was added.

In the preparation of the complexes of Mg, Ca, Zn, Cd, and Pb, 12 per cent aqueous ammonia (3 ml.) was added dropwise to the solution. Complexes of Ni and Co formed precipitates without addition of ammonia.

The collected precipitates were washed with methanol and extracted with the same solvent in a Soxhlet extractor.

TABLE I

Analysis

Complex of	$C_{28}H_{14}O_6M$ and $C_{28}H_{14}O_6M\cdot 2H_2O$					
	Calculated			Found		
	Metal	C	H	Metal	C	H
Cu	12.5	65.9	2.8	12.15	66.2	2.8
Mg	5.2	71.4	3.0	5.35	70.9	3.2
Ca	8.2	69.1	2.9	8.6	68.9	3.05
Zn	12.8	65.7	2.8	13.1	65.4	2.85
Cd	20.1	60.2	2.5	20.2	59.5	2.55
Pb	31.7	51.45	2.1	31.6	51.1	2.2
Mn	11.0	67.1	2.8	10.6	66.9	2.95
Co	11.7	66.55	2.8	11.4	65.9	2.9
Ni	11.65	66.6	2.8	11.5	66.3	2.9
$Mg\cdot 2H_2O$	4.8	66.4	3.6	5.05	66.8	3.6
$Co\cdot 2H_2O$	10.9	62.1	3.35	10.6	62.2	3.35
$Ni\cdot 2H_2O$	10.85	62.15	3.35	10.55	61.6	3.4

Complexes of Cu, hydrated complexes of Mg, Ni, Co. 1-Hydroxyanthraquinone (2.2 g., 0.01 mole) was dissolved in ethanol as before, and aqueous solution of a metal acetate (0.005 equivalent) was added. In the preparation of hydrated Mg complexes, aqueous 12 per cent ammonia (3 ml.) was added.

The collected precipitates were washed with water, ethanol, and dried at 100°. They were extracted with ethanol in a Soxhlet extractor during several hours. They were dried at 100° (when dried at 150° they lost water).

TABLE II

1-hydroxy-antraquinone	Cu	Mg	Ca	Zn	Cd	Pb	Mn	Co	Ni	K	Mg 2H$_2$O	Co 2H$_2$O	Ni 2H$_2$O	Assignment
	Complexes									Salt	Hydrates			
											3542 vs	3540 vs	3552 vs	O—H stretching
											3358 w	3340 w	3373 w	
	3092 vw	3066 vw	3047 vw		3090 vw	3076 vw	3071 vw	3080 vw	3054 vw	3064 vw	3120 s	3142 s	3130 s	C—H aromatic
1666 s	1673 s	1670 s	1665 s	1673 s	1673 s	1665 s	1673 s	1670 s	1667 vs	1651 vs	1650 s	1651 vs	1651 vs	C=O free
1632 vs	1613 vs	1627 vs	1639 vs	1625 vs	1623 vs	1623 vs	1625 vs	1618 vs	1616 vs	1625 vs	1627 vs	1618 vs	1618 vs	C=O ¹)
1590 vs	1590 vs	1590 vs	1590 vs	1590 vs	1590 vs	1590 vs	1590 vs	1590 vs	1588 vs	1588 vs	1590 vs	1590 vs	1590 vs	C=C aromatic
1576 sh	1566 vs		1585 vs	1576 s	1576 vs	1576 vs	1576 vs	1576 sh	1568 sh					
1535 w	1519 vs	1524 vs	1528 s	1526 vs	1531 s	1533 s	1528 s	1524 s	1519 vs	1516 vs	1519 vs	1519 vs	1519 vs	C=C chelate ring
1465 s		1455 s		1445 w	1455 m	1445 sh	1453 sh	1453 m	1453 m	1453 vs	1445 s	1445 m	1458 m	C=O (free and bonded reduced intensity when bonded)
1450 s	1445 m	1448 s	1448 s	1441 m	1444 s	1444 s	1443 m	1441 m	1439 s		1448 sh	1446 s	1443 s	
	1422 s	1420 vs	1422 s	1422 s	1420 s	1418 s	1422 s	1420 s	1417 vs	1410 vs	1420 vs	1422 vs	1417 vs	chelate ring
	1394 vs													
1363 vs	1373 s	1377 vs	1363 vs	1376 vs	1363 vs	1356 vs	1363 vs	1375 vs	1377 vs	1388 vs	1380 vs	1377 vs	1380 vs	
		1340 s			1338 s		1340 s			1354 vs				
1326 m	1316 sh	1316 sh		1326 s		1330 vs		1328 s	1316 s		1330 m		1316 sh	
1297 vs	1302 vs	1302 vs	1302 vs	1302 vs	1302 vs	1297 vs	1302 vs	1302 vs	1302 vs	1307 vs	1302 vs	1302 vs	1302 vs	C=O and aromatic ring
1274 s	1274 s	1264 sh									1264 vs	1264 vs	1264 vs	
1262 s	1259 vs	1257 vs	1257 vs	1257 vs	1257 vs	1252 vs	1257 vs	1257 vs	1257 vs	1252 vs	1257 vs	1257 vs	1257 vs	
1231 s	1236 s	1231 vs	1229 s	1236 s	1229 s	1224 s	1231 s	1231 s	1229 s	1215 vs	1231 vs	1231 vs	1229 vs	C—O phenolic deformation
	1189 m	1186 m	1186 w	1189 w	1191 m	1186 w	1189 w	1186 m	1189 m	1189 m	1189 m	1189 m	1189 m	
1165 m	1167 s	1160 sh	1160 s	1170 s	1165 s	1167 s	1172 w	1165 s	1160 s	1153 s			1165 sh	
1158 m		1151 s	1146 s	1158 s	1151 s	1153 vs	1151 s	1156 s	1151 s	1146 s	1153 s	1153 s	1153 s	
				1151 s										
1099 vw	1102 vw	1099 vw	1099 vw	1099 vw	1099 vw	1099 vw	1099 vw	1099 vw	1099 vw	1099 vw	1099 vw	1099 vw	1099 vw	
1068 w	1071 w	1071 w	1068 m	1071 w	1071 w	1071 w	1068 w	1073 m	1071 m	1071 s	1073 w	1073 s	1073 s	
1042 w	1042 w	1042 m	1042 m	1042 w	1042 m	1042 w	1042 w	1045 m	1045 m	1045 m	1045 w	1045 m	1045 m	
1021 m	1024 m	1024 s	1021 m	1024m	102 4 m	1024 s	1024 m	1024 m	1024 s	1024 s	1024 m	1024 s	1024 s	

s — strong, w — weak, m — middle, vw — very weak; ¹) bonded with OH group

Potassium salt of 1-hydroxyanthraquinone. 1-Hydroxyanthraquinone (1.1 g., 0.005 mole) was dissolved in acetone (200 ml.), and potassium acetate (0.49 g., 0.005 mole) dissolved in anhydrous ethanol was added. The salt precipitated was collected, dried at 100°, and washed with acetone to remove the unreacted 1-hydroxyanthraquinone and dried again. For $C_{14}H_7O_3K$ calcd.: 64.1 C, 2.75 H, 14.9%K; found: 63.3 C, 2.9 H, 13.9% K.

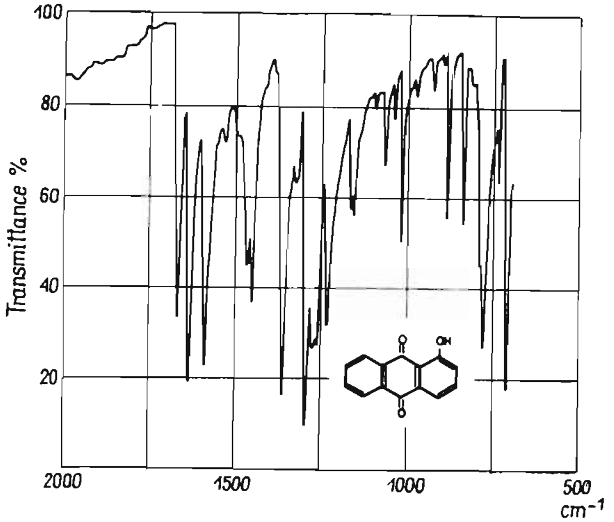


Fig. 1

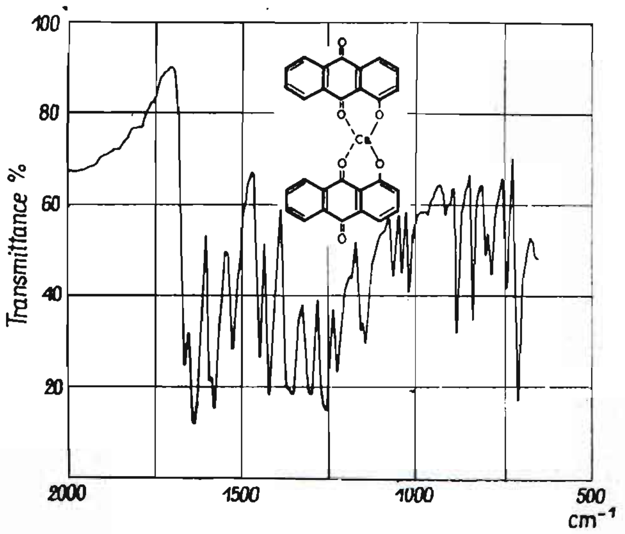


Fig. 2

The infrared absorption spectra were measured on a Hilger H-800 double-beam spectrophotometer with sodium chloride optics. The substances studied were pressed in pellets with potassium bromide.

The main bands of the spectra are collected in Table II and typical recordings are given in Figs. 1—4.

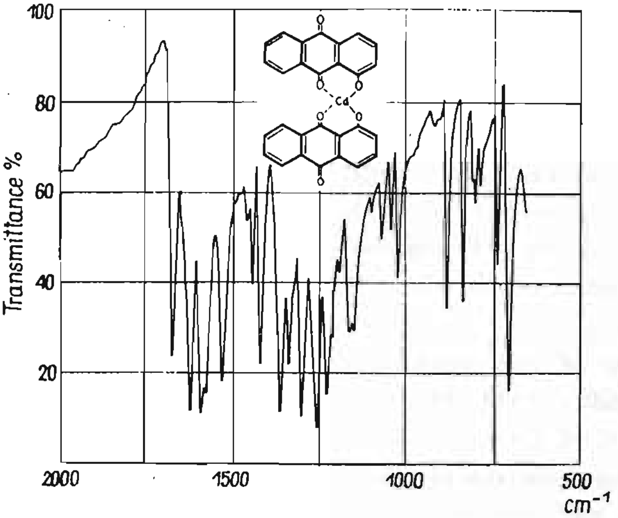


Fig. 3

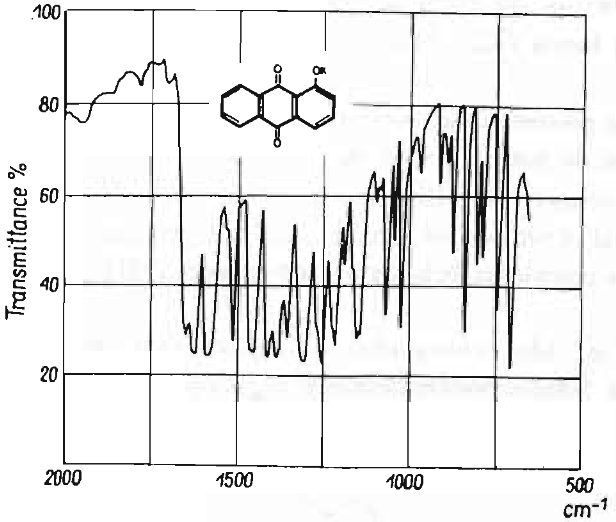


Fig. 4

Discussion

O—H stretching vibrations. There is no band of OH group in the spectrum of 1-hydroxyanthraquinone, most likely due to the hydrogen bond between OH and one of the C=O groups. A few bands of the wave numbers higher than 3000 cm.$^{-1}$. appear only in the complexes which form hydrates (complexes of Co, Ni, and Mg).

C—H stretching aromatic vibrations. These are very week and have not been registered in all compounds examined.

C=O stretching vibrations. Two strong bands are present in all compounds examined. One of them of a higher frequency (1673—1651 cm.$^{-1}$) should be assigned to "free" carbonylic group and the other one of lower frequency (1639—1613 cm.$^{-1}$) — to the carbonyl bonded by intra — and inter-molecular hydrogen bond with OH group in 1-hydroxyanthraquinone or by chelation in the complexes of the carbonylic group with metal replacing hydrogen of the OH group.

Aromatic skeletal vibrations. Two bands should be assigned to these vibrations: one of them is a very strong band of a remarkably firm position at 1590 cm.$^{-1}$; the second one in the spectrum of 1-hydroxyanthraquinone is a shoulder, at 1576 cm.$^{-1}$, which separates as a very strong peak of the same wave number in the complexes.

Vibrations of the chelate ring (1533—1519 and 1422—1410 cm.$^{-1}$). Very strong bands at 1533—1519 cm.$^{-1}$ present in the spectra of complexes should be assigned to C$\overset{-}{-}$C for the chelate ring formed when the hydrogen atom of the phenolic group is replaced with metal [8]. In 1-hydroxyanthraquinone the hydrogen atom is not strongly bonded to the oxygen atoms of both phenolic and carbonyl groups and hence the band is relatively weak.

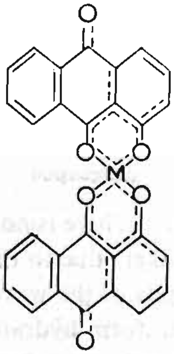
The frequency of the band depends on the metal forming the complex.

Very strong bands 1422—1410 cm.$^{-1}$ should probably be also assigned to the chelate rings.

They are not present in the spectrum of 1-hydroxyanthraquinone. Their positions in the spectrum do not vary with the metal that forms the complexes.

C—O deformation vibrations. Strong bands of C—O deformation vibrations typical of phenols lie between 1236 and 1224 cm.$^{-1}$ for 1-hydroxyanthraquinone and the complexes. It has a lower frequency (1215 cm.$^{-1}$) in the potassium salt.

Structure of the complexes. It appears that the chelate structure of complexes of a 1-hydroxyanthraquinone suggested by Geyer and Smith [9] (as below)



is in agreement with the results of our examination of their IR spectra. Also the existence of the hydrogen bond between OH and one C=O group in 1-hydroxyanthraquinone should be considered as being confirmed.

The authors are much indebted to Dr. U. Dąbrowska and Mr. W. Sokół for carrying out spectroscopic measurements.

DEPARTMENT OF ORGANIC TECHNOLOGY, TECHNICAL UNIVERSITY, WARSAW
(KATEDRA TECHNOLOGII ORGANICZNEJ, POLITECHNIKA, WARSZAWA)

REFERENCES

[1] G. Graebe, A. Liebermann, Z. Chem., **11** (1868), 279.
[2] A. Liebermann, S. Kostanecki, Ber., **18** (1885), 2142.
[3] P. Pfeiffer, Ann., **398** (1913), 159.
[4] E. Hoffmann, Thesis, Dresden, 1937; quoted by E. G. Kiel and P. M. Heertjes [6].
[5] H. E. Fierz-David, M. Rutishauser, Helv. Chim. Acta, **23** (1940), 1529.
[6] E. G. Kiel, P. M. Heertjes, J. Soc. Dyers and Colourists, **79** (1963), 21, 61, 186, 363.
[7] A. Werner, Ber., **41** (1908), 1062.
[8] R. P. Dryden, A. Winston, J. Phys. Chem., 62 (1959), 635.
[9] B. P. Geyer, G. M. P. Smith, J. Am. Chem. Soc., **64** (1942), 1649.
[10] H. Roemer, Ber., **15** (1882), 1793.