Studies of 8-Mercaptoquinoline as Chelating Agents. I. Sodium Salt of 8-Mercaptoquinoline

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The infrared spectra of the sodium salt of 8-mercaptoquinoline and its related compounds have been measured in the region between 4000 and 400 cm^{-1}. Some substituent-sensitive bands have been investigated in order to find a clue to further infrared studies of its metal chelates. The thermal stabilities of the sodium salt have been examined by thermal gravimetric analysis and by differential thermal analysis. It has been shown that the sodium salt can be dried at temperatures between 100° and 200°C without any thermal change, and that, at *ca.* 210°C in air, the abrupt increase in weight of the sodium salt may be due to the absorption of oxygen. The effect of hydration on the sodium salt is discussed on the basis of results with regard to X-ray diffraction patterns, infrared spectra, and weights. The sodium salt is proposed to crystallize with two moles of water and to combine inequivalently with two waters of crystallization.

8-Hydroxyquinoline(oxine=HQ) is a convenient analytical reagent which reacts with various metal ions to form its metal chelates; the characteristics of the reagent and its metal chelates have been studied extensively.[1)]

Recently special attention has been paid to the 8-mercaptoquinoline(thiooxine=MQ) in which hydroxyl group of HQ is replaced by the thiol group and to the 8-selenoquinoline(selenooxine=SeQ) replaced by the selenol group.[2,3)] It may be of particular interest to compare the relationships between their dissociation constants and the stability constants of their metal chelates. Studies of MQ have been reported in the fields of analytical applications,[4–8)] absorption spectra,[4,9–11)] stability constants of metal complexes,[4,11)] and substituted compounds.[4,12–14)]

The central problem of this paper is to investigate the infrared spectra of the sodium salt of MQ for the purpose of finding a clue to further infrared studies of its metal chelates. Our interest lies particularly in the effect of the water of crystallization upon the infrared spectra because of its acceleration effect on the oxidation of the salt.

Experimental

Reagents. MQ, its disulfide, and its sodium salt were prepared and purified by the methods described in the literature.[8,11,15)] Hydrochloride of MQ was obtained from the Dojindo Pharmaceutical Co., Ltd. All the reagents were confirmed by a study of the absorption spectra.

Apparatus for Measurements. Thermal gravimetric analysis (TGA), differential thermal analysis (DTA), and studies by both X-ray diffractions and infrared spectra were carried out with a Chyo Thermobalance, a Rigaku-Denki Differential Thermal Analyser, a Rigaku-Denki Geigerflex D-3F X-Ray Analyser (Cu$K\alpha$ radiation) and a Hitachi EPI-2G Infrared Grating Spectrophotometer respectively. The weights of the salt were measured with a Mettler H-6 dig. Balance.

Results and Discussion

Infrared Spectra of MQ. The infrared spectra of MQ and its derivatives were obtained as Nujol and H.C.B. mulls. The infrared frequencies are summarized in Table 1. The spectra of MQ are essentially similar to those of HQ. In general, it has been suggested that a few bands in the 1600—1500 cm^{-1} region in quinoline derivatives are due to C=C and C=N vibrations.[16)] Furthermore, the bands in the 1200—1000 cm^{-1} region and those around 800 cm^{-1} are attributable to ring vibrations and C–H deformations influenced by chelation with a metal or by hydration respectively.[16)]

For the anhydride of MQ, which exists in a deep blue liquid, the effect of the substitution on the quinoline ring causes strong new bands at 2510, 990, and 654 cm^{-1}. The band at 2510 cm^{-1} is easily assigned to ν(SH), and the investigation of this vibration in a chloroform solution shows neither any possibility of hydrogen bonding nor any existence of the zwitter ionic from. The 990 cm^{-1} and the 654 cm^{-1} band rank as the highest and the second highest respectively of the substituent-sensitive bands affected

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1) An example is; R. G. W. Hollingshead, "Oxine and its Derivatives," Butterworths Scientific Publications, London (1954).

2) E. Sekido, Q. Fernando, and H. Freiser, *Anal. Chem.*, **36**, 1768 (1964); **37**, 1556 (1965).

3) N. Nakamura and E. Sekido, *Talanta*, **17**, 515 (1970).

4) There are a number of publications which systematically studied by Bankovsky's group. For example some of the titles of them are "Study of 8-Mercaptoquinoline and its Derivatives," and "Analytical Application of 8-Mercaptoquinoline and its Derivatives."

5) V. I. Kuznetsov, Yu. A. Bankovsky, and A. F. Iyevinsh, *Zh. Anal. Khim.*, **13**, 267 (1958).

6) Yu. A. Bankovsky and A. F. Iyevinsh, *Zh. Anal. Khim.*, **13**, 507 (1958).

7) Yu. A. Bankovsky, J. Cirule, and A. Ievins, *Zh. Anal. Khim.*, **16**, 562 (1961); *Chem. Abstr.*, **56**, 7988i (1962).

8) J. A. W. Dalziel and D. Kealey, *Analyst*, **89**, 411 (1964).

9) Yu. A. Bankovsky, L. M. Chera, and A. F. Iyevinsh, *Zh. Anal. Khim.*, **18**, 688 (1963).

10) P. D. Anderson and D. M. Hercules, *Anal. Chem.*, **38**, 1702 (1966).

11) A. Corsini, Q. Fernando, and H. Freiser, *Anal. Chem.*, **35**, 1424 (1963).

12) G. Buehmann and R. Schmuek, *J. Prakt. Chem.*, **17**, 414 (1962).

13) D. Kealey and H. Freiser, *Anal. Chem.*, **38**, 1577 (1966).

14) A. Kawase and H. Freiser, *ibid.*, **39**, 22 (1967).

15) A. Edinger, *Ber.*, **41**, 937 (1908).

16) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York (1958), p. 278.

Table 1. Observed frequencies (in cm^{-1}) of the 8-mercaptoquinolines and its disulfide

Sodium salt		Hydrochloride	8-Mercaptoquinoline	Disulfide
Salt	*Dry salt*			
3300 sb		3350 sb		
3055 m	3055 m		3050 m	3040 m
3015 m	3015 m		3015 m	3015 m
		2525 sb	2510 m	
1596 w	1598 w	1614 s	1600 s	1600 s
1583 w	1580 w	1592 s	1589 s	1588 s
1550 m	1550 m	1544 vs	1533 m	1552 w
1489 vs	1487 vs		1485 vs	1486 s
1446 s	1442 s	1440 w	1450 s	1448 s
1409 m	1406 m	1397 m	1412 m	1410 w
1366 w	1372 w	1378 m	1377 s 1364 s	1380 s 1368 s
1354 s	1356 s	1346 w	1352 s	1352 s
1294 s	1292 s	1280 s	1301 vs	1302 s
1231 w		1240 m		1238 w
1209 s	1212 s	1208 s	1216 m	1207 w
		1150 w	1144 w	1146 w
1189 w	1199 w	1141 w	1129 m	
		1129 w	1088 w	1130 w
1071 m	1067 m	1063 w	1064 m	1060 m
		1040 w	1028 w	1029 w
990 vs	990 vs	960 w	990 vs	974 s
835 w	837 w		(880 m)	833 w
817 s	808 m	820 vs	814 vs	819 s
800 w	800 w	800 w	798 vw	
785 s	772 s	768 s	782 vs	782 s
753 749 m	730 s	750 s	752 s	766 sh 760 m
690 b				755 sh
660 s	661 m	659 m	654 s	655 s
629 w	627 w	610 w	626 s	634 w 626 w
553 m	545 m	537 m	540 m	553 w
530 b				536 w
524 m	527 m	520 w	520 w	529 w
		460 w	460 w	
436 m	437 m	423 w	429 s	437 m

by the mass of the substituent atom directly bonded to the ring (HQ; 1093[17] and 781 cm^{-1},[18]), SeQ; 959 and 640 cm^{-1},[19])). Although a band near 9 μ assigned to the C–O vibration of metal oxinates[17] is clearly metal-sensitive, the 990 cm^{-1} and the 654 cm^{-1} bands also exhibit a similar character, as will be described in the succeeding paper.[20]

For the disulfide of MQ, the bands appear at 974 and 655 cm^{-1}. This is very important in the case of chelation between MQ and a metal because the oxidation of MQ can be checked by the presence of these bands.

The above facts suggest that these two bands with strong intensities usually have a considerable contribution by C–S bonding, though the lower band is more effective. Our consideration is supported also by the infrared studies of halogenobenzene[21] and benzenesulphonyl compounds.[22] Moreover, studies of this lower band of various metal chelates may be directly related to the analytical applications.[20]

For the sodium salt of MQ, a very strong and broad band around 3300 cm^{-1} assigned to bonded ν(OH) appears. On the other hand, with an increase in the degree of dryness, the sodium salt of MQ changes from light yellow to bright yellow (*dry salt*), and the physical state of the salt changes from rigid to bulky.

The thermal analysis and the X-ray diffraction measurement of the salt were carried out in order to confirm whether or not these phenomena resulted from the hydration on the salt.

Thermal Analysis of the Sodium Salt of MQ. Both TGA and DTA curves obtained in air and in nitrogen gas are shown in Fig. 1, where the scale of DTA is arbitrary. The dotted line and the solid line correspond to the curve of the sodium salt of MQ dried at room temperature (called *salt* hereinafter) and to that of the salt completely dried in a vacuum and at 150°C (called *dry salt*) respectively.

The weight loss of *salt* in the 100—200°C region is about 16% of the initial weight corresponding to *salt*

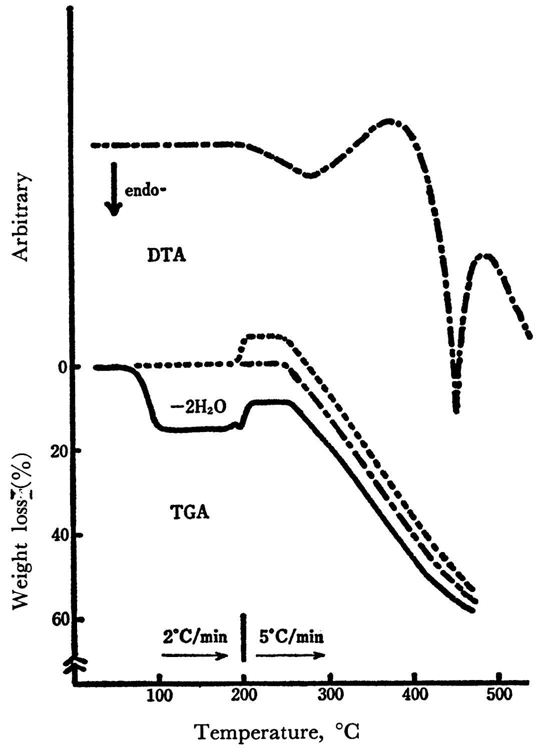

Fig. 1. DTA and TGA curves.
——: *salt* in air
----: *dry salt* in air
–·–: *dry salt* under nitrogen

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[17] R. G. Carles, H. Freiser, R. Freidel, L. E. Hilliard, and W. D. Johnston, *Spectrochim. Acta*, **8**, 1 (1956).

[18] R. J. Magee and L. Gordon, *Talanta* **10**, 851 (1963).

[19] Y. Mido, I. Fujiwara, and E. Sekido, to be published.

[20] Y. Mido and E. Sekido, This Bulletin, **44** 2130 (1971).

[21] D. H. Whiffen, *J. Chem. Soc.*, **1956**, 1350.

[22] T. Uno, K. Machida, and K. Hanai, *Spectrochim. Acta*, **24A**, 1705 (1968).

with two moles of water of crystallization. At *ca.* 210°C, an abrupt increase in weight (about 7.5%) takes place in both *salt* and *dry salt*, and both salts turn brownish. There is a constant part of the weight in the 210—250°C region, and a weight loss due to decomposition occurs at higher temperatures.

The DTA curve of *dry salt* in nitrogen gas shows no thermal change[23,24] until 258°C, where thermal decomposition sets in.

The abrupt increase in weight in TGA may be attributable to the absorption of oxygen, as in suggested by the following facts: (1) The DTA curve of *dry salt* in nitrogen gas (the dot-dash line in Fig. 1) or in carbon dioxide did not show an abrupt increase. (2) The infrared spectra of the sample dried at 210°C in air exhibited a new strong band near 1100 cm^{-1} referrable to some rearrangement of atoms, though those of the sample dried at the same temperature in a vacuum did not show such a band. From the fact that the compounds containing sulfur tend to be oxidized in the process of thermal reaction, it may be concluded that the strong band is connected with a S–O vibration. (3) The DTA curve of *dry salt* in nitrogen gas showed no thermal change around 210°C.

X-Ray Diffraction Measurements. The X-ray diffraction patterns for *salt* and *dry salt* are shown in Fig. 2. These patterns indicate that the crystal structure of *dry salt* is different from that of *salt*. The X-ray pattern for a salt, containing *ca.* 10% of water,[25] seems to be made up of the superposition of the patterns of both *salt* and *dry salt*. The X-ray pattern for the other salt, containing more than 16% of water,[25] is obscure and weak.

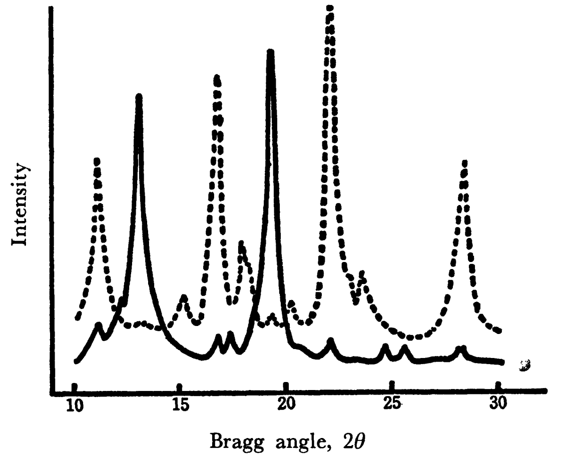

Fig. 2. X-Ray diffraction patterns of sodium salt of MQ.
——: *dry salt*, ----: *salt*

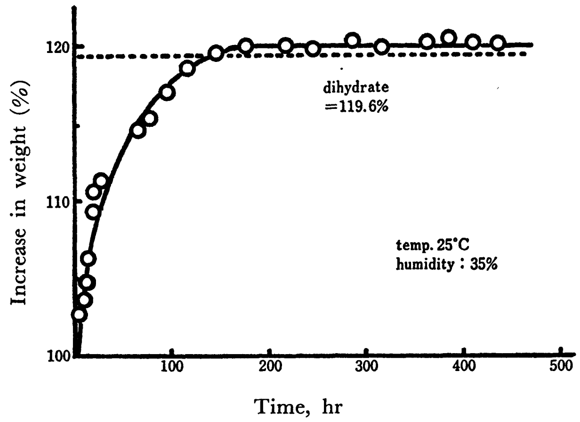

Fig. 3. Increase in weight due to the absorbing water on *dry salt* of MQ.

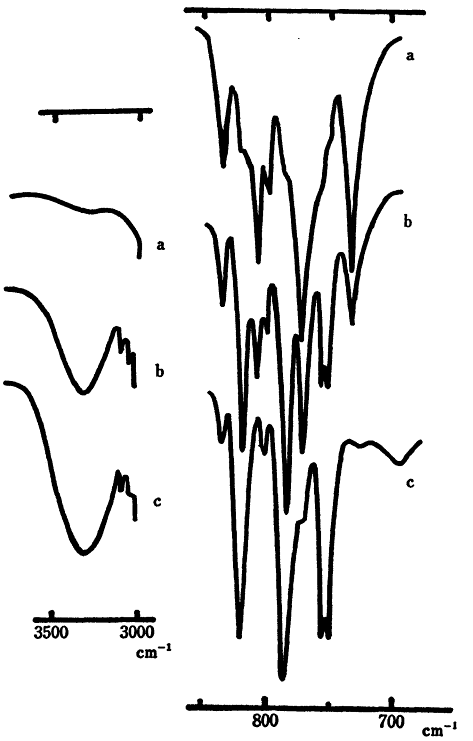

Fig. 4. O-H Stretching and C-H out-of-plane vibrations.
a) start, b) one day, c) one week

Effect of Hydration on the Infrared Spectra. It should be noted that the sodium salt of MQ is strongly hygroscopic and that this property is closely connected with the oxidation of the salt. An increase in weight due to the absorbing water on *dry salt* was examined as a function of time at 25°C and at a relative humidity of 35% (Fig. 3). The result obtained from the increase in weight was in agreement with one of the results from TGA—the finding that the salt crystallizes with two moles of water.

At the same time, the changes in the infrared spectra for the sodium salt of MQ were observed under the conditions specified above. The band at about 3300 cm^{-1} and the bands in the 850—700 cm^{-1} region exhibit remarkable changes in intensity and in frequency as is shown in Fig. 4. As the intensity of the 3300 cm^{-1} band(ν OH) becomes stronger and, simultaneously, those of these bands at 808, 772, and 730 cm^{-1} of *dry salt* diminish, two bands, at 817 and 785 cm^{-1}, and a doublet, at 753 and 749 cm^{-1}, appear and

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23) W. W. Wendlandt and G. R. Horton, *Anal. Chem. Acta*, **23**, 332 (1960).

24) W. W. Wendlandt and G. R. Horton, *Anal. Chem.*, **34**, 1098 (1962).

25) This quantity of water determined by the weight loss of a salt.

gradually become stronger in their intensities.[26] This doublet is not observed in *dry salt*. Moreover, in *salt* there are two broader bands, at 690 and 530 cm^{-1}, which probably correspond to the librational modes of the water of crystallization (Table 1).[27] On the substitution of heavy water on *salt*, the 3300 cm^{-1} band shifted and split into two bands, at 2450 and 2370 cm^{-1}, the 690 cm^{-1} band was replaced by a band at 505 cm^{-1}, and the 530 cm^{-1} band was expected to shift to the region below 400 cm^{-1}. These results may provide strong evidence for the existence of an inequivalent bonding between two waters of crystallization and sodium salt, but it does not sufficiently account for the absence of a water molecule cyclically bound through a hydrogen bonding as proposed by Bankovsky.[9]

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26) In the preliminary study for sodium salt of HQ and SeQ the same inclinations were also observed.

27) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Willey & Sons, Inc., New York London (1963), p. 156.