BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (12), 3753—3754 (1979)

Complexes of Zinc-group Metals with 8-Amino-2-methylquinoline

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(Received May 12, 1979)

Synopsis. Some complexes of zinc-group metals with 8-amino-2-methylquinoline have been synthesized. They are seemed to have a monomeric tetrahedral form except for the mercury(I) complex containing a perchlorate ion as a counter anion.

8-Amino-2-methylquinoline (amq) is obtained by the reduction of 8-nitro-2-methylquinoline.[1-2] Although it is expected that the quinoline is able to coordinate to metal ions, in analogy with 8-aminoquinoline, which has essentially the same structure as the amq some differences might exist for the methyl group on the 2-position. The present authors, therefore, synthesized zinc-group metal complexes of amq and studied their properties by electronic, IR and/or far IR spectra, and molar conductances. The experimental results show the metal complexes to have a tetrahedral form, different from the zinc complex synthesized by Litzow and his coworkers.[3-7]

Experimental

Physical Measurements. The IR spectra in the NaCl region were measured with a JASCO IRA-1 type spectrophotometer as a nujol mull or a KBr disk. The far-IR spectra were obtained by means of a nujol mull using a JASCO DS 403G IR spectrophotometer. The reflectance spectra were obtained with a Shimadzu Double-beam UV-200 spectrophotometer. The electronic conductivities were measured using a Toa Conduct Model CM-1DB and a cell with a cell constant of 0.9845 cm^{-1}. The measurements were made at 25 °C by employing a 10^{-3} mol/dm^3 *N,N*-dimethylformamide solution.

Materials. Metal perchlorate and halide of a GR-grade reagent of the Wako Chemical Co., Ltd., were used as starting materials without any further purification. 8-Amino-2-methylquinoline of the Tokyo Kasei Co., Ltd., was used after recrystallization with ligroin.

Syntheses. The metal complexes were prepared the following manner. To an ethanol solution containing 0.0025 mol of metal salt, about 0.0065 mol of a ligand in ethanol was added, after which the mixture was allowed to stand for several hours. The precipitate thus formed was filtered off. After washing with ethanol, it was dried in a vacuum desiccator over anhydrous calcium chloride.

Results and Discussion

The color and elemental analyses of the metal complexes are given in Table 1, together with the yields based on the starting materials.

As is shown in Table 2, the molar conductances may be classified into two values. The values of the type of $M(amq)_2(ClO_4)_2$ and $Hg_2(amq)_2(ClO_4)_2$ lie in the 130—170 S cm^2 mol^{-1} range. The values are representative for 1:2 electrolytes in *N,N*-dimethylformamide.[8] On the other hand, the conductances of $M(amq)X_2$ are all under 30 S cm^2 mol^{-1} except $Zn(amq)I_2$. Consequently, these complexes seem to be essentially non-electrolyte, and they seem to be interact with solvent molecules. In the case of $Zn(amq)I_2$, it

TABLE 1. ELEMENTAL ANALYSES (Figures are given in wt%)

Compound	Color	Calcd (Found), %				Yield %
		C	H	N	M	
$Zn(amq)Cl_2$	Brown	40.79 (40.79	3.41 3.41	9.51 9.52	22.20 22.31)	75
$Zn(amq)Br_2$	Yellow-brown	31.33 (31.62	2.63 2.65	7.51 7.38	17.05 17.10)	85
$Zn(amq)I_2$	Dark-pink	25.16 (25.39	2.11 2.34	5.87 5.91	13.69 13.33)	79
$Zn(amq)_2(ClO_4)_2$	Brown	41.37 (41.52	3.47 3.54	9.65 9.59	11.26 11.19)	76
$Cd(amq)Cl_2$	Yellow-green	35.14 (35.29	2.95 3.07	8.20 8.32	32.91 32.98)	69
$Cd(amq)Br_2$	Green-yellow	27.91 (28.12	2.34 2.36	6.51 6.52	26.11 26.26)	81
$Cd(amq)I_2$	Yellow-green	22.90 (23.12	1.92 2.30	5.34 5.33	21.43 21.57)	72
$Cd(amq)_2(ClO_4)_2$	Yellow-green	38.27 (38.12	3.21 3.21	8.93 8.81	17.91 17.80)	58
$Hg(amq)Cl_2$	Brown	27.93 (28.23	2.35 2.46	6.52 6.53	46.68 47.09)	78
$Hg_2(amq)_2(ClO_4)_2$	Pink	26.21 (26.45	2.20 2.23	6.11 6.06	43.77 43.97)	31

amq: 8-amino-2-methylquinoline.

Table 2. Molar conductances (0.001 mol/dm³ in DMF)

Compound	in S cm² mol⁻¹
$Zn(amq)Cl_2$	3.1
$Zn(amq)Br_2$	10.4
$Zn(amq)I_2$	102.4
$Zn(amq)_2(ClO_4)_2$	163.2
$Cd(amq)Cl_2$	16.7
$Cd(amq)Br_2$	21.9
$Cd(amq)I_2$	25.5
$Cd(amq)_2(ClO_4)_2$	156.4
$Hg(amq)Cl_2$	4.3
$Hg_2(amq)_2(ClO_4)_2$	168.8

amq: 8-amino-2-methylquinoline.

appears that the complex undergoes considerable solvolysis in the solution the following manner,

$$Zn(amq)I_2 \overset{DMF}{\rightleftharpoons} [Zn(amq)I(DMF)]^+ + I^- \quad (1)$$

$$[Zn(amq)I(DMF)]^+ \overset{DMF}{\rightleftharpoons} [Zn(amq)(2DMF)]^{2+} + I^- \quad (2)$$

The IR spectra of free amq show two peaks, at 3440 and 3320 cm^{-1}, of ν_{NH_2}, The peaks shift to the 3120—3280 cm^{-1} range in the metal complexes. A peak about 1340 cm^{-1} in the free ligand also shifts to the lower-wave-number side in 15—20 cm^{-1}. In these metal complexes, therefore, the quinoline seems to bond to the metal ion, with its two nitrogen atoms as a bidentate ligand.[9] The strong bands in the range 950—1140 and about 620 cm^{-1} in the complexes containing a perchlorate group are regarded as simple perchlorate ions.[6-7,10-11] In general, terminal M-X stretching bands of metal complexes with a metal-halogen bond appear in the regions of 200—400 cm^{-1} for MCl, 200—300 cm^{-1} for MBr, and 100—200 cm^{-1} for MI.[12] The wave number observed in the 150—600 cm^{-1} region can be assigned to that of the terminal M-X bands.

The reflectance spectral data in the visible region are shown in Table 3. The bands are all regarded as CT bands. The absorption peaks of the bands change in accordance with the bathochromic effect in the $M(amq)X_2$ type of complexes.[13]

From the experimental results presented above, it is presumed that the metal complexes obtained are in a tetrahedral configuration, since the four coordinated zinc-group metal ions are usually in the tetrahedral form.[14]

In the case of $Hg_2(amq)_2(ClO_4)_2$, the mercury is +1 of the oxidation state. It is qualitatively confirmed in the usual manner that Hg(1) forms a black color when reacted with an alkali solution. Therefore, the complex appears to be dimeric with the $(Hg-Hg)^{2+}$ ion, and the dimers appear to interact with each other in the solid state with mercury, but the structure has not been revealed.

The authors would like to thank Dr. Henry Freiser of the University of Arizona, who gave them a chance to do this work. The authors also wish to express their gratitude to Dr. Yukichi Yoshino of Tokyo University for his continuing encouragement. The authors thank Drs. Kan Kimura and Yoshimitsu Hirao of Aoyama-Gakuin University for their useful discussions.

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Table 3. Reflectance spectral data (Figures are given in cm^{-1})

Compound						
amq	24150,	23700,	19920(sh),			
$Zn(amq)Cl_2$	23530,	23360,	19920(sh),		16890	
$Zn(amq)Br_2$	23700,	22990,	19800(sh),		16670	
$Zn(amq)I_2$	23810,	22720,	19760(sh),		16530	
$Zn(amq)_2(ClO_4)_2$	23530,	22830,		18520(sh),	16390,	14180(sh)
$Cd(amq)Cl_2$	23360,	22930,	19880(sh),		16390	
$Cd(amq)Br_2$	23620,	22900,	19800(sh),		15870	
$Cd(amq)I_2$	23700,	22830,	19760(sh),		15500	
$Cd(amq)_2(ClO_4)_2$	23700,	22990,	19720(sh),	18520(sh),	16390,	13793(sh)
$Hg(amq)Cl_2$	23700,	22990,	19800(sh),		16260	
$Hg_2(amq)_2(ClO_4)_2$	23700,	22990,	19420(sh),	18520(sh),	16390,	13920(sh)

amq: 8-amino-2-methylquinoline, sh: shoulder.