The Syntheses and Properties of Some 2,4-Dimethyl-1,5-benzodiazepinium Halogenometalates

Akira Ouchi, Toshio Takeuchi, Mitsuhisa Nakatani, and Yoshiaki Takahashi
Department of Chemistry, College of General Education, The University of Tokyo, Komaba, Meguro-ku, Tokyo

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When 2,4-dimethyl-1,5-benzodiazepinium halide was reacted with a metal halide in ethanolic media, crystalline products, $M(C_{11}H_{13}N_2)_xX_y$ (where X=Br, Cl; M=Co(II), Mn(II), Zn(II), Cd(II), Sb(III) (chloride), Cu(II) (chloride), and Cu(I) (bromide)), were obtained. They are all new compounds. Their electronic and infrared spectra resemble those of the sarting chloride or bromide. The infrared band at about 1639 cm^{-1} of the chloride shifts to the lower-wave-number side when it is turned into a halogenometalate. On the other hand, the characteristic ν(M–X) bands were found in the far-infrared spectra of the halogenometalates, These compounds are likely to be ionic compounds consisting of the halogenometalato anion and the 2,4-dimethyl-1,5-benzodiazepinium cation.

Although tropolone and its derivatives were used as the ligands of the metal chelates, comparatively little investigation has been made of the metal compounds containing seven-membered ring components. Diazepines are relatively easily synthesized by the condensation of diamine with diketones, as has been studied by Thiele[1)] and Lloyd,[2—6)] and these compounds have the seven-membered ring. From *o*-phenylenediamine and acetylacetone, for example, 2,4-dimethyl-3*H*-1,5-benzodiazepine is obtained. This compound forms a salt, deep violet in color, with hydrochloric acid. The salt is stable in the solid state, and it can be kept in the open air at room temperature without decomposition. There have been several discussions about the bonding structure of the salt,[4,7,8)] but at any rate it is clear that the salt contains the 2,4-dimethyl-1,5-benzodiazepinium cation and that, therefore, the seven-membered ring was kept and not destroyed. When the salt was mixed with the anhydrous metal halides in an ethanolic medium, crystalline precipitates were obtained. These products are as deeply colored as the original dimethyl-benzodiazepinium salt. Repeated syntheses and elemental analyses gave reproducible results. Therefore, these products seem to be a new species containing the seven-membered ring.

Experimental

Instruments. The infrared spectra were obtained by the Nujol or hexachloro-1,3-butadiene mull procedure, using a 403G-type infrared spectrophotometer of Japan Spectroscopic Co., Ltd. The electronic spectra were obtained with a Hitachi EPS-2-type automatic recording spectrophotometer. The magnetic moments were measured with a Gouy balance at room temperature.

The Syntheses of the Compounds: *The Synthesis of the 2,4-Dimethyl-1,5-benzodiazepinium Chloride Dihydrate*: This compound was synthesized from *o*-phenylenediamine and acetylacetone according to the Thiele or Lloyd method.[1,4)]

The bromide was obtained by almost the same method, but using hydrobromic acid in place of hydrochloric acid. The bromide obtained was the dihydrate as the chloride.

The Synthesis of 2,4-Dimethyl-1,5-benzodiazepinium Tetrachlorocobaltate(II) Monohydrate: Five-tenths of a gram (2.1 mmol) of cobalt(II) chloride hexahydrate was heated, and the crystalline water was removed. A 99% ethanolic solution of the blue anhydrous salt (about 5 m*l*) and a 99% ethanolic solution of the 2,4-dimethyl-1,5-benzodiazepinium chloride dihydrate (0.5 g (2.0 mmol) in 5 m*l* of the solvent) were mixed and stirred. A crystalline precipitate appeared. The product was filtered off after it had stayed one night in a refrigerator. It was washed with 99% ethyl alcohol and then with ethyl ether. The recrystallization of the products has not yet been successful.

The other compounds were synthesized by almost the same method from the 2,4-dimethyl-1,5-benzodiazepinium chloride or bromide and the metal halides of the same halogen element.

In the case of the copper salt, the product from the chloride is paramagnetic and divalent, but the product from the bromide is diamagnetic and probably univalent. The analytical results support the results.

Some metal salts, nickel(II) halides, for example, do not give the precipitate by this method. Probably this is because of the instability of the halogeno complexes of these metals.

Results and Discussion

The elemental analyses, the chemical formula, and the magnetic moments of the compounds thus obtained are shown in Table 1. As the table shows, these compounds have the formula of ML_xX_y (where L^+ is the 2,4-dimethyl-1,5-benzodiazepinium ion and where X is Cl or Br). The oxidation number of the L is always +1. Although these compounds are all synthesized in the 99% ethanol medium, some of them contain crystalline water.

From the magnetic moments of cobalt complexes, it is possible to infer how the central cobalt ion is surrounded by ligands—either octahedrally or tetrahedrally. Due to the spin-orbit interaction, the magnetic moments of the cobalt complexes are higher than the spin-only value; if the magnetic moment is 4.7—

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Table 1. The analyses and the magnetic moments of compounds
(Figures are given in % for analyses and B.M. for magnetic moments)

		Metal	Halogen	C	H	N	Magnetic moments
$LCl \cdot 2H_2O$	Calcd		14.49	53.99	7.00	11.45	
	Found		14.30	53.78	6.46	11.59	
$LBr \cdot 2H_2O$	Calcd		27.63	45.69	5.93	9.69	
	Found		28.50	45.58	6.17	9.68	
$CoL_2Cl_4 \cdot H_2O$	Calcd	10.43	25.09	46.75	4.99	9.91	
	Found	10.47	24.78	46.73	5.15	9.87	4.77
CoL_2Br_4	Calcd	8.13	44.08	36.45	3.62	7.73	
	Found	8.66	44.45	36.48	3.65	7.73	4.98
$CuL_2Cl_4 \cdot H_2O$	Calcd	11.15	24.88	46.37	4.95	9.83	
	Found	11.31	24.38	46.37	4.87	9.81	1.82
$CuLBr_2$	Calcd	16.02	40.30	33.31	3.30	7.06	
	Found	16.80	39.88	33.04	2.91	6.99	(dia)
ZnL_2Cl_4	Calcd	11.81	25.61	47.73	4.73	10.12	
	Found	11.52	25.80	47.35	4.72	9.94	(dia)
ZnL_2Br_4	Calcd	8.94	43.70	36.13	3.58	7.66	
	Found	8.99	44.10	36.29	3.39	7.65	(dia)
$CdLCl_3$	Calcd	28.67	27.13	33.70	3.34	7.15	
	Found	28.50	27.00	33.87	3.28	7.14	(dia)
CdL_2Br_4	Calcd	14.44	41.06	33.94	3.37	7.20	
	Found	14.60	41.00	34.10	3.46	7.20	(dia)
MnL_2Cl_4	Calcd	10.11	26.11	48.64	4.82	10.31	
	Found	10.41	26.45	48.37	4.63	10.26	6.11
MnL_2Br_4	Calcd	7.62	44.33	36.65	3.63	7.77	
	Found	7.21	45.30	36.61	3.73	7.78	6.10
$SbLCl_4$	Calcd	27.87	32.47	30.25	3.00	6.41	
	Found	27.50	32.27	30.22	2.60	6.43	(dia)

$L^+ = C_{11}H_{13}N_2^+$ (2,4-dimethyl-1,5-bezodiazepinium ion)

5.2 B.M., it is in the octahedral form, while if it is 4.4—4.8 B.M., it is in the tetrahedral form. The observed magnetic moments of the products are 4.77 B.M. and 4.98 B.M., as the table shows. The dithiolium halogenometalates which contain CoX_4^{2-} ions have magnetic moments of 4.6—4.8 B.M.,[9-11] this value is a little high, though it is expected, as in the tetrahedral configuration. Therefore, although the magnetic moments of these complexes are a little higher than that expected for the tetrahedral form, the central ion is probably surrounded tetrahedrally by four halogen atoms in these complexes. A deformed octahedral form, including additional coordination of the halogen atoms of other complex molecules or the halogen-bridging structure, is also probable. However, a strong coordination of the 2,4-dimethyl-1,5-benzodiazepinium cation to the central metal ion is less probable.

In the cases of copper compounds, only the Cu(I) compound was obtained from copper(II) bromide, while only the Cu(II) compound was obtained from copper(II) chloride. The stability of the copper(I)-compounds depends very strongly on the nature of the counter-anion or the ligand present, while the stabilities of Cu(I) halides are in the order of CuI>CuBr >CuCl; CuF is yet unknown. On the other hand, the dimethyl-benzodiazepinium salt seems to have a little reducing ability. Consequently, it reduced the copper(II) bromide to the stable copper(I) salt, while it is not a strong enough reagent as to produce the less stable copper(I) chloride.

The electronic absorption spectra of the ethanolic solution of these products were also examined. These metal compounds show spectra almost identical with those of the 2,4-dimethyl-1,5-benzodiazepinium halides. The main peaks (in kK) and their intensities (in log ε shown in parentheses) are as follows: 44.5 (4.1), 38.3 (4.4), 37.2 (4.4), ~30 (~3) 28.4 (3.0), 19.6 (2.9), 16.4 (2.5). As the absorption coefficients of the bands of the ion are too high, the peaks of the *d-d* bands of metals as well as the specific bands of the halogenometalates are not identified. Moreover, the halogenometalato ion may be decomposed into metal and halogen ions in such a dilute ethanolic solution.

The infrared spectra of these compounds were also examined. The general pattern of the spectra of the metal compounds resembles that of the 2,4-dimethyl-1,5-benzodiazepinium chloride in the finger-print region.

The exact assignments of the peaks are not easy, as the vibrations of the dimethylbenzodiazepinium ion

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conjugate with each other and they can be separated into group vibrations only with difficulty. However, bands in the region of 1350—1650 cm^{-1} are likely to consist of ν(C=N), ν(C=C) or a mixture of them; at least, the contribution of these vibrations to these bands is probably important.

In the far-infrared region, there are some bands which are characteristic of the metal compounds and which are not observed in the spectra of the chloride of the ligand. Although no exact assignments were easily obtained, their ν(M–X) bands were tentatively assigned. The maxima of these bands are shown in Table 2.

TABLE 2. THE WAVE NUMBERS OF SOME INFRARED SPECTRUM BANDS OF THE COMPOUNDS (cm^{-1})

	ν(C=N), ν(C=C) or the mixture of them		ν(M–X)
LCl·2H_2O	1639 s	1595 s	
LBr·2H_2O	1643 sh 1630 s	1594 s	
CoL_2Cl_4·H_2O	1625 m	1598 s	291 s
CoL_2Br_4	1621 s	1598 s	223 s
CuL_2Cl_4·H_2O	1622 m	1600 s	254 s
$CuLBr_2$	1630 s	1587 s	<200
ZnL_2Cl_4	1627 s	1595 s	297 s
ZnL_2Br_4	1622 s	1597 s	200 s
$CdLCl_3$	1627 s	1597 s	266 s
CdL_2Br_4	1621 s	1597 s	<200
MnL_2Cl_4	1629 s	1598 s	282 s
MnL_2Br_4	1622 s	1597 s	218 s
$SbLCl_4$	1618 s	1600 s	280 s

s: strong, sh: shoulder, m: medium.

The wave numbers of the ν(M–X) bands of these compounds are very similar to the values observed in the spectra of other halogenometallates.[12–14] The ν(M–X) bands of bromocuprate and bromocadmate compounds are not observed above 200 cm^{-1}. However, as the edge absorption appears near 200 cm^{-1}, they are expected to be found in the lower wave number region.

The band of the chloride at 1639 cm^{-1} shift to the lower wave number side, about 10—20 cm^{-1}, when the metal compounds are formed, as is shown in Table 2. This is probably caused by a slight change in the bonding states in the seven-membered-ring system of the cation—a prohibition of the tautomerism transition, for example. Thus, however, difficult as it is for a strong bond between the cation and metal ion to exist, some kind of interference between the cation and halogenometalato ion, such as was shown in the case of 3,5-dimethyl-1,2-dithiolium tetrachloroferrate(II), is to be expected in this case, too.[15]

Consequently, these metal compounds probably consist of the 2,4-dimethyl-1,5-benzodiazepinium cation and halogenometalato anion.

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