BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2942—2943 (1972)

The Syntheses and Properties of Some 2-Methyl-4-phenyl-1,5-benzodiazepinium Chlorometalates

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(Received March 22, 1972)

In a previous paper,[1] the present authors reported on the syntheses of 2,4-dimethyl-1,5-benzodiazepinium halogenometalates. However, similar compounds with different substituent on the 2 and/or the 4 position of the 1,5-benzodiazepinium ring have not yet been studied. It seemed that it would be of interst to study the influence of the substituents on the stability of the complex. In this way, some new compounds, 2-methyl-4-phenyl-1,5-benzodiazepinium chlorometalates, were obtained by the same synthetic technique as was used for the 2,4-dimethyl derivatives.

Experimental

The Syntheses of the 2-Methyl-4-phenyl-1,5-benzodiazepinium Chlorometalates. The chloride was synthesized from *o*-phenylenediamine and benzoylacetone by Thiele's method.[2] The chloride and the anhydrous metal chloride were separately dissolved in ethyl alcohol and then mixed. The mixture was kept in a refrigerator overnight, thus yielding crystalline products.

Instruments. The IR spectra were obtained by means of a JASCO model IR-G IR as well as model 403G spectrophotometer. The electronic spectra were obtained with a Hitachi EPS-3T-type automatic recording spectrophotometer.

Results and Discussion

The analytical results of the 2-methyl-4-phenyl-1,5-benzodiazepinium salts are shown in Table 1.

The magnetic moment of the tetrachlorocobaltate(II), as measured by a Gouy balance at room temperature, was 4.44 B.M (per mole of cobalt(II)); this fact shows the cobalt(II) ion is coordinated and is in the tetrahedral configuration.[3]

In the far IR region, the spectra of all of these chlorometalates have the characteristic bands, as is shown in Table 2; these bands are not observed in the spectrum of the simple chloride. They were identified as ν(M–Cl) bands by reference to Nakamoto's[4] and Ferraro's[5] data. This proves the existence of the tetrahedral chlorometalate ion in these compounds. As the wave numbers of the bands of 2-methyl-4-phenyl derivatives are lower than those of the corresponding 2,4-dimethyl-1,5-benzodiazepinium salts, the chlorometalate ions of the former compounds can be said to be less stable.

Table 1. Elemental analyses (%)

		C	H	N	Cl	M
$[C_{16}H_{15}N_2]_2[CoCl_4]\cdot H_2O$	C	55.73	4.64	8.13	20.61	8.56
	F	55.91	4.65	8.20	21.10	8.60
$[C_{16}H_{15}N_2]_2[ZnCl_4]$	C	56.72	4.43	8.27	20.98	9.60
	F	56.55	4.31	8.21	21.59	9.65
$[C_{16}H_{15}N_2]_2[CdCl_4]$	C	53.04	4.15	7.73	19.61	15.47
	F	53.00	4.08	7.68	20.67	15.42
$[C_{16}H_{15}N_2]_2[HgCl_4]$	C	47.23	3.69	6.89	17.47	24.72
	F	47.20	3.66	6.78	17.39	a)

a) The usual EDTA titration gave always a little too low analysis (about 23%), due to the interference of the coexistent components.

Table 2. ν (M-Cl) band of the chlorometalates (cm^{-1})

$[C_{16}H_{15}N_2]_2[CoCl_4]\cdot H_2O$	275
$[C_{16}H_{15}N_2]_2[ZnCl_4]$	255
$[C_{16}H_{15}N_2]_2[CdCl_4]$	245
$[C_{16}H_{15}N_2]_2[HgCl_4]$	280
$[C_{16}H_{13}N_2]_2[CoCl_4]\cdot H_2O$	291
$[C_{11}H_{13}N_2]_2[ZnCl_4]$	297
$[C_{11}H_{13}N_2]_2[CdCl_4]$	266

The IR spectra in the 400—4000 cm^{-1} region of these chlorometalates and of the simple chloride with the same 1,5-benzodiazepinium ion were almost identical. Consequently, in these compounds the 2,4-disubstituted 1,5-benzodiazepinium ion does not seem to coordinate to the metal ion, but seems to work as a counter cation, although some kind of interaction between the cation and the anion may exist as in the case of dithiolium halogenometalates.[6,7]

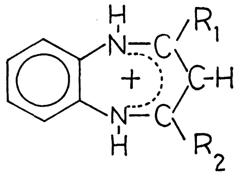

Fig. 1. The 2,4-disubstituted 1,5-benzodiazepinium ion.
1 $R_1=R_2=CH_3$: 2,4-dimethyl-1,5-benzodiazepinium ion $C_{11}H_{13}N_2$
2 $R_1=CH_3$, $R_2=C_6H_5$: 2-methyl-4-phenyl-1,5-benzodiazepinium ion $C_{16}H_{15}N_2$

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Table 3. Some infrared absorption bands of the salts of 1,5-benzodiazepinium derivatives

	$[C_{11}H_{13}N_2]Cl \cdot 2H_2O$	$[C_{11}H_{13}N_2][CoCl_4] \cdot H_2O$	$[C_{16}H_{15}N_2]Cl \cdot 3H_2O$	$[C_{16}H_{15}N_2][CoCl_4] \cdot H_2O$
ν(N–H)	3275(m)	3275(m)	3250(m)	3270(m)
	3200(m)	3200(m)	3175(m)	3200(m)
ν(C=C), ν(C=N) or the mixture of them	1639(s)	1625(m)	1610(s)	1615(s)
	1595(s)	1598(s)	1590(s)	1590(s)
δ(C–H) of benzene ring	760(s)	760(s)	760(s)	760(s)

It is of interest to compare some wave numbers of the infrared absorption bands of the 2-methyl-4-phenyl-1,5-benzodiazepinium salts with those of 2,4-dimethyl derivatives. The results are shown in Table 3. The assignments of the band were obtained by reference to those of 2,4-dimethyl derivatives presented in the previous paper1) as well as in Bellamy's books.8,9)

The bands caused by the benzene ring of the cation are almost identical in the two types of salts, as in the case of the δ(C–H) (760 cm^{-1}) of the benzene ring shown in the table.

The ν(C=C), ν(C=N), or mixed bands appear in the 1400—1600 cm^{-1} region of both derivatives are not very different from each other. In the spectra of both derivatives, two ν(N–H) bands at about 3200—3270 cm^{-1} were observed, on the other hand, no characteristic bands appeared in the 2550—2800 cm^{-1} region (ν(N–H) of $-NH_3^+$).

From these results, the seven-membered rings of both ions seem to have pseudo aromaticity and to be stabilized. The ring of the 2-methyl-4-phenyl derivative is, however, likely to be less stable; consequently, the cation cannot stabilize the tetrabromometalate anion and solid tetrabromometalates were not obtained, although those of the 1,4-dimethyl derivatives had already been synthesized.1)

Table 4. Electronic spectra of the 1,5-benzodiazepinium salts in ethyl alcohol solution

Figures are given in kK and logε (calculated about the cation) in parentheses

$[C_{11}H_{13}N_2]_2[CoCl_4] \cdot H_2O$	$[C_{16}H_{15}N_2]_2[CoCl_4] \cdot H_2O$
44.5 (4.09)	44.1 (4.10)
38.2 (4.35)	37.6 (3.80)
37.2 (3.32)	36.6 (4.40)
30.1 (2.90)	29.7 (3.20)
28.4 (3.00)	
19.6 (2.90)	19.4 (3.01)

These 2-methyl-4-phenyl-1,5-benzodiazepinium chlorometalates as well as the chloride are all deep violet in color, and the electronic absorption spectra of their ethyl alcohol solutions are almost identical. The data of the main peaks of the chlorometalates, together with those of the 2,4-dimethyl derivative, are shown in Table 4. The *d-d* band was covered by stronger bands and was not identified. The patterns of the spectra of the salts containing the same cation are almost the same; moreover, the spectra of the 2,4-dimethyl and 2-methyl-4-phenyl derivatives resemble each other. These spectral patterns and their intensities seem to be characteristic of the 1,5-benzodiazepinium seven-membered ring of the cation; therefore, both the rings seem to have a considerable pseudo-aromatic character.

The chlorides of the 2,4-dimethyl-, 2-methyl-4-trifluoromethyl-, and 2,4-bis(trifluoromethyl)-1,5-benzodiazepinium were synthesized by almost the same method, but they were much less stable than those of the 2,4-dimethyl or the 2-methyl-4-phenyl derivatives. The solid chlorides obtained were pale in color and were crystallized out only from concentrated hydrochloric acid media. They were easily decomposed even by a dilute acid solution or when kept in the open air for several days. Their solid halogenometalates were not separated when the metal chloride was added to a concentrated hydrochloric acid solution of the chloride.

A ν(N–H) band of these chlorides appeared at 2550 cm^{-1}, as in usual amine hydrochlorides. Consequently, it may be concluded that the seven-membered ring cation with delocalized π-electrons is stabilized by the electron-donating property of the methyl groups on the 2 and/or 4 position of the ring; on the other hand, if such an electron-withdrawing group as a phenyl or trifluoromethyl group is bonded to the position, the ring is destabilized. The halogenometalate anion seems to be stabilized by such a stable, large-size cation. Therefore, if the cation is not stable, the halogenometalate anion is not stabilized and the salts are not obtained in the solid state.

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