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CHEMICAL AND INFRA-RED SPECTROSCOPIC STUDIES OF METAL(II) HALIDE COMPLEXES OF PYRAZINE

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Abstract—The preparation and characterization of complexes of pyrazine with zinc, cadmium and mercury halides exclusive of fluoride is reported. The preparation of pyrazine-d_4 is described. Infra-red data for pyrazine-d_4 complexed with $HgCl_2$ satisfy Teller-Redlich product rule ratios constructed for the isolated pyrazine molecule. The spectra are discussed, and a polymeric crystalline structure is proposed for the 1 : 1 complexes.

In common with many other nitrogen-containing heterocyclic aromatic and non-aromatic ring structures, pyrazine has for many years been known to form addition compounds with metal halides. Stoehr(1) reported the formation of 1:1 adducts of pyrazine with $ZnCl_2$, $AgNO_3$, $CuSO_4$, $HgCl_2$ and $AuCl_3$. More recently, Lever *et al.*(2) reported studies of complexes of pyrazine with Co(II), Ni(II), and Cu(I). Diprotonated pyrazine ion(3) has $pK_1 = -5·78$ and $pK_2 = +0·65$ which may be taken to show that pyrazine acts as a weak base towards the proton. On this basis, it would be expected that pyrazine should form only weak complexes generally involving bonding between only one of the ring nitrogen atoms and the metal atom. However, magnetic and spectroscopic evidence has been interpreted(2) as indicating that both ring nitrogens are often involved in forming pyrazine-bridged polymeric species. X-ray investigations of dibromo-2,5-dimethylpyrazine nickel(II)(4) and pyrazine-silver nitrate,(5) though of a preliminary nature, seem compatible with this interpretation. The investigations reported in the present work support and extend these considerations.

EXPERIMENTAL

Pyrazine-d_4 was prepared by vapour-phase exchange of pyrazine with deuterium oxide over a palladium-on-asbestos catalyst maintained near 230°C during the exchange. The catalyst was occasionally activated by absorption of deuterium gas at temperatures near 275°. The apparatus used was similar to that described by Perkampus and Baumgarten.(6) The spectra of our incompletely exchanged samples agreed with spectra published by these authors. Their spectra and concomitant analyses indicated our most completely exchanged sample contained 96–97 atom per cent deuterium.

Infra-red spectra of the complexes were obtained as Nujol mulls with a Perkin-Elmer Model 21 infra-red spectrophotometer equipped with a NaCl or CsBr prism. Spectra obtained with KBr pellets indicated that significant halogen exchange occurred between the pellet matrix and the complex. When KCl was used with metal chloride complexes to obviate this difficulty, the refractive

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(1) C. Stoehr, *J. Prakt. Chem.* **47**, 439 (1893); **48**, 18 (1893); **51**, 449 (1895).

(2) A. B. P. Lever, J. Lewis and R. S. Nyholm, (a) Nature Lond. **189**, 58 (1961); (b) *J. Chem. Soc.* 1235 (1962); (c) 3156 (1963); (d) 5042 (1963).

(3) A. S. Chia and R. F. Trimble, Jr., *J. Phys. Chem.* **65**, 863 (1961).

(4) F. D. Ayres, P. Pauling and G. B. Robertson, *Inorg. Chem.* **3**, 1303 (1964).

(5) R. G. Vranka and E. L. Amma, Presented at 145th National Meeting of the American Chemical Society, New York (1963).

(6) H. H. Perkampus and E. Baumgarten, *Spectrochim. Acta* **19**, 1473 (1963).

index match was so poor that useful spectra did not result. In the CsBr region, pellets pressed from pure CsI powder were used as windows. Nujol mulls were sandwiched between two of these. Spectra of good quality resulted, in part because large amounts of Nujol may be tolerated in the CsBr region, and in part because the long wavelengths encountered there are not sensitive to particle sizes that would lead to partial opacity in the shorter wavelength region. No appreciable halogen exchange of mulled compounds with the CsI windows was noted, though some were slightly discoloured when used with mercury compounds due to formation of HgI_2 on the pellet surface. HgI_2 is transparent in the CsBr region, and since the reaction occurred only at the surface, the resulting spectra were inappreciably distorted from this source.

All pyrazine complexes were prepared by the addition of about 25 millimoles of pyrazine to 10 mmoles of metal halide, both dissolved in the same solvent. As long as adequate pyrazine was present, the quantity of excess pyrazine was not found to be significant. The pyrazine-$d_4 \cdot HgCl_2$ adduct was prepared by precipitation from exhausted exchange water by the addition of excess saturated aqueous $HgCl_2$ solution. The complexes were recovered by filtration, washed with solvent and dried in vacuo over $CaCl_2$. Except for the complicated HgI_2 adduct, which could be recrystallized from boiling ethyl acetate, the complexes were inappreciably soluble in a variety of common solvents. This obviated the determination of molecular weights. The $HgCl_2$ complex was also precipitated under microscope observation and photomicrographs were made. Both dendritic growth and rectangular platelet formation were observed, the former corresponding to rapid, the latter to slow precipitation.

Complex compositions were determined by elemental analysis. In the cases of the $HgCl_2$, $CdCl_2$, $CdBr_2$ and CdI_2 complexes, compositions were checked by conductometric titration. Since the results of the two methods agreed, only the elemental analyses are reported here. All of the complexes except the HgI_2 and $ZnBr_2$ materials are 1:1 adducts.

Dichloropyrazinemercury(II). This adduct was prepared from aqueous solution. (Found: C, 14·2; H, 1·1; N, 7·7. Calc. for $C_4H_4N_2Cl_2Hg$: C, 13·7; H, 1·1; N, 8·0%)

Dibromopyrazinemercury(II). This compound was prepared from ethyl acetate solution. (Found: C, 11·1: H, 1·0; N, 6·3. Calc. for $C_4H_4N_2Br_2Hg$: C, 10·9; H, 1·0; N, 6·4%).

The compound between mercuric iodide and pyrazine was prepared from ethyl acetate solution. The complex was very unstable and lost pyrazine rapidly. The freshly precipitated material was a white solid which turned yellow and finally red as pyrazine was released. Analysis of the complex indicated that most of the initially bound pyrazine had been evolved.

Dichloropyrazinecadmium(II). This compound was precipitated from aqueous solution. (Found: C, 18·3; H, 1·7; N, 10·8. Calc. for $C_4H_4N_2Cl_2Cd$: C, 18·2; H, 1·5; N, 10·6%).

Dibromopyrazinecadmium(II). This compound was prepared in aqueous solution. (Found: C, 14·0; H, 1·2; N, 8·0. Calc. for $C_4H_4N_2Br_2Cd$: C, 13·6; H, 1·1; N, 8·0%)

Diiodopyrazinecadmium(II). This compound was prepared in aqueous solution. (Found: C, 11·0; H, 1·1; N, 6·3. Calc. for $C_4H_4N_2I_2Cd$: C, 10·8; H, 0·9; N, 6·3%).

Dichloropyrazinezinc(II). Identical samples of this complex and the other zinc adducts could be prepared from either acetone or ethyl acetate. Analytical preparations were from acetone as the solvent. (Found: C, 22·4; H, 2·2; N, 13·2. Calc. for $C_4H_4N_2Cl_2Zn$: C, 22·2; H, 1·8; N, 13·0%).

Zinc bromide and pyrazine gave a complex which had an approximate stoichiometry of one and one-half moles pyrazine per mole of zinc bromide. It is possible that the compound initially formed is the bis-pyrazine complex. As is seen in Table 1, the complex evolved pyrazine rather easily, but no 1:1 adduct could be prepared by removal of the additional pyrazine. (Found: C, 20·1; H, 1·8; N, 11·2. Calc. for $C_6H_6N_3Br_2Zn$: C, 20·9; H, 1·7; N, 12·2%).

Diiodopyrazinezinc(II). This complex was prepared for analysis from acetone. (Found: C, 12·2; H, 1·2; N, 7·1. Calc. for $C_4H_4N_2I_2Zn$: C, 12·0; H, 1·0; N, 7·0%).

The thermal stabilities of the complexes were investigated by heating approximately one-gramme samples of the materials in a sublimation apparatus in which the pressure was reduced to 5 mm. The cold finger was cooled with solid carbon dioxide. The temperature of the solid sample was raised at a rate of 20°C per hr until evidence of change in the solid was noted. The results are summarized in Table 1.

The principal bands in the infra-red spectra of these materials are listed in Table 2. Bands in the NaCl region are probably accurate within 5 cm^{-1}, while those in the CsBr region are reproducible to within 1 cm^{-1}. The pyrazine complexes of silver nitrate and cuprous iodide are included because

TABLE 1.—THERMAL STABILITIES OF PYRAZINE COMPLEXES

Complex	T_{max}, (°C)	Time at T_{max}, (hr)	Comments
$ZnCl_2 \cdot C_4H_4N_2$	220	4	No change.
$ZnBr_2 \cdot 1 \cdot 5C_4H_4N_2$	120	2	Slow evolution of pyrazine.
$ZnI_2 \cdot C_4H_4N_2$	220	4	No sublimate. Complex darkens slightly.
$CdCl_2 \cdot C_4H_4N_2$	220	4	No change.
$CdBr_2 \cdot C_4H_4N_2$	220	4	Trace pyrazine evolved.
$CdI_2 \cdot C_4H_4N_2$	220	6	Trace pyrazine evolved.
$HgCl_2 \cdot C_4H_4N_2$	90	6	Complex sublimed unchanged.
$HgBr_2 \cdot C_4H_4N_2$	90	6	Complex sublimed unchanged.
$HgI_2 \cdot (C_4H_4N_2)_x$	60	1	Rapid evolution of pyrazine.

TABLE 2.—SOME INFRA-RED BANDS OF PYRAZINE COMPLEXES

All absorb at 1420 ± 8 *vs*, 1162 ± 3*s*, 1120 ± 5*s*, 1080 ± 10 *w*. Additional bands occur at

$ZnCl_2 \cdot C_4H_4N_2$	1482 *s*, 1053 *s*, 790 *s*, 468 *s*.
$ZnBr_2 \cdot C_4H_4N_2$	1068 *vs*, 1062 *vs*, 816 *vs*, 804 *vs*, 468 *vs**, 446 *vs**.
$ZnI_2 \cdot C_4H_4N_2$	1065 *vs*, 1060 *vs*, 814 *vs*, 802 *vs*, 468 *vs**, 444 *vs**.
$CdCl_2 \cdot C_4H_4N_2$	1490 *m*, 1082 *m*, 1048 *vs*, 802 *vs*, 447 *s**.
$CdBr_2 \cdot C_4H_4N_2$	1046 *vs*, 790 *vs*, 449 *s**.
$CdI_2 \cdot C_4H_4N_2$	1481 *m*, 1040 *vs*, 786 *vs*, 450 *s**.
$HgCl_2 \cdot C_4H_4N_2$	1032 *vs*, 802 *vs*, 433 *s**.
$HgBr_2 \cdot C_4H_4N_2$	1380 *s*, 1032 *vs*, 792 *s*, 432 *s**.
$AgNO_3 \cdot C_4H_4N_2$	1365 *s*†, 1320 *s*, 1080 *vs*, 1050 *vs*†, 1040 *m*†, 990 *m*, 815 *vs*†, 805 *s*.
$Cu_2I_2 \cdot C_4H_4N_2$	1047 *s*, 800 *s*, 743 *w*, 720 *w*.

* Average of two determinations.

† Attributed to NO_3^-.

of their known structures.[4,5] Infra-red spectra of $HgCl_2$, pyrazine and $HgCl_2$, pyrazine-d_4 are separately presented in Table 3.

DISCUSSION

LEVER *et al.*[2] concluded that in complexes in which pyrazine is bonded through only one of its nitrogen atoms, the low local symmetry experienced by the pyrazine moiety allows a band to appear in the 950–1000 cm^{-1} region. It would then be expected that the band should be absent in pyrazine bridge polymers of long chain length, and weak in others of shorter chain length. The band should then arise in terminal pyrazine moieties, thus leading to the possibility of using the band intensity as a measure of polymer chain length in these cases. Reference to Table 3 shows that the band occurs weakly in the mercuric chloride complex. Examination of the original spectra shows that it occurs weakly in the cadmium chloride complex and is present as a low intensity doublet in the zinc bromide and zinc iodide complexes, though it is apparently absent in the other adducts. Since these observations should indicate more extensive polymer formation as the band intensity decreases, it might be expected that compounds exhibiting the band would be relatively more soluble in common organic solvents and perhaps might be more nearly sublimable without change. However, as was indicated earlier, none of the complexes are appreciably soluble in any common solvent and molecular weights could not be obtained.

Reference to Table 1 shows that it is difficult to establish a direct correlation

Table 3.—Infra-red spectra of $HgCl_2$·pyrazine and $HgCl_2$·pyrazine-d_4 in cm^{-1}

$HgCl_2$-pyrazine	$HgCl_2$·pyrazine-d_4
433 *vvs*	412 *vs*
793 *s**	597 *w*†
802 *vs*	616 *m*
981 *vvw*	823 *w*†
1032 *vvs*	836 *w*†
1074 *w*	845 *w*
1120 *vs*	865 *vvs*
1162 *s*	878 *m*†
1180 *vw*	918 *vvw*
1260 *vw*	941 *vvw*
1342 *vw*	958 *w*†
1383 *vw*	1031 *m*
1412 *vvs*	1120 *w*
1454 *vw*	1158 *vw*
1479 *vw*	1176 *s*
2564 *w*	1272 *vvs*
2580 *w*	1309 *m*†
3000 *w*	1345 *m*†‡
3065 *m*	1403 *w*
	2280 *w*
	2300 *w*
	3065 *vw*†

* Due to HgBrCl·pyrazine
† Due to isotopic contaminant
‡ v_{14} accidentally coincident with band due to isotopic contaminant?

between the 950 cm^{-1} band system and the observed thermal stabilities. Thus, $HgCl_2$·pyrazine should have shorter chain lengths than the mercuric bromide complex, but both adducts sublime unchanged. The cadmium chloride complex should have a shorter chain length than either the cadmium bromide or iodide complexes, yet of the three the chloride is the most stable thermally. The differences in behavior in the cadmium systems are, however, very small. Only the zinc chloride complex accords completely with prediction, exhibiting great stability and no band in the 950 cm^{-1} region.

The doublet structure found in many bands in spectra of the zinc bromide complex, the zinc iodide complex, and one form of the mercuric iodide complex presumably arises from crystal field interaction, and indicates a crystal structure grossly different from those of the other compounds investigated. The zinc complexes are more easily ground than the other compounds and exhibit the greatest intensity of the 950 cm^{-1} band system, and thus probably have the shortest chain length.

Califano and co-workers(7) disagreed in some details with the earlier assignment of Lord *et al.*(8) and have recently reassigned the infra-red active fundamentals in pyrazine. Even more recently, Simmons *et al.*(9) reassigned both infra-red and Raman active fundamentals in pyrazine. They suggested two assignments for the infra-red active fundamentals, each of which differed from that of Califano *et al.* as well as

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(7) S. Califano, G. Adembri and G. Sbrana, *Spectrochim. Acta* **20**, 385 (1964).

(8) R. C. Lord, A. L. Marston and F. A. Miller, *Spectrochim. Acta* **9**, 113 (1957).

(9) J. D. Simmons, K. K. Innes and G. M. Begun, *J. Mol. Spectrosc.* **14**, 190 (1964).

from that of LORD *et al.* Evidently the problem of the assignments in pyrazine cannot be considered as closed at this time. Fortunately, neither the assignment for the out-of-plane hydrogen bending mode (ν_{11}) nor that for the out-of-plane ring bend (ν_{16b}) is controversial. All authors agree that ν_{11} occurs at 785 cm^{-1} in the vapour and 804 cm^{-1} in the liquid, while ν_{16b} occurs at 418 cm^{-1} in the vapour and 417 cm^{-1} in the liquid. The bands observed in all complexes in these regions are apparently to be associated with similar motions in the pyrazine moiety of the complexes.

The occurrence of these bands in the 800 and 450 cm^{-1} regions of the spectra of all complexes investigated, although occasionally split by crystal field forces, may be taken as evidence establishing the ability of the pyrazine ring to maintain its essential molecular integrity in the complexes. Further evidence supporting this thesis is provided by the deuterium compound. If the Teller-Redlich product rule ratio is constructed for the isolated pyrazine molecule and the frequencies observed for the mercuric chloride complex substituted therein, the following agreement is found for the B_{2u} pyrazine frequencies:

$$1{\cdot}37 = \frac{802 \times 433}{616 \times 412} = \frac{(\nu_{11}\nu_{16b})^{\mathrm{H}}}{(\nu_{11}\nu_{16b})^{\mathrm{D}}} = \left(\frac{m_{\mathrm{D}}}{m_{\mathrm{H}}} \times \frac{M_{\mathrm{H}}}{M_{\mathrm{D}}}\right)^{\frac{1}{2}} = 1{\cdot}38$$

where m_{H}, m_{D}, M_{H} and M_{D} are respectively the masses of a hydrogen atom, a deuterium atom, pyrazine and pyrazine-d_4. Superscripts H and D refer to pyrazine and pyrazine-d_4 complex frequencies respectively.

Unfortunately, in species B_{1u} and B_{3u} the situation is not clear-cut. One assignment given by CALIFANO *et al.* suggests the assignment given in column I of Table 4. The two assignments given by SIMMONS *et al.* suggests the assignments given in columns II and III of Table 4. The final assignment must make use of the 1120 cm^{-1} band in mercuric chloride-pyrazine and of the 1176 cm^{-1} band in mercuric chloride-pyrazine-d_4, since both of these bands are quite strong, and since the 1120 cm^{-1} band has been observed in the spectrum of every pyrazine complex investigated to date. However, since product rule agreement may be obtained in a number of distinct ways in these symmetry species, further work must be done on the pyrazine assignments before assignments in the complexes can be made with assurance.

TABLE 4.—ALTERNATE SUGGESTED ASSIGNMENTS OF PYRAZINE·$HgCl_2$ AND PYRAZINE-d_4·$HgCl_2$ FUNDAMENTALS. THE THEORETICAL TELLER-REDLICH PRODUCT RULE RATIO, τ, IS 1·95 FOR BOTH SYMMETRY SPECIES

	CAS(7)		SIB(9)I		SIB(9)II	
	pyz	pyz-d_4	pyz	pyz-d_4	pyz	pyz-d_4
	3065	2280	3065	2280	3065	2280
B_{1u}	1479	1403	1479	1403	1412	1176
	1162	1031	1074	1031	1074	1031
	1032	865	1032	865	1032	865
τ	1·91		1·76		2·01	
	3065	2280	3065	2280	3065	2280
	1412	1272	1412	1345	1479	1403
B_{3u}	1342	1345	1342	1272	1162	1120
	1074	845	1120	845	1120	845
τ	1·90		1·97		1·95	

Though sought, neither a metal–nitrogen nor a metal–halogen stretch was found.

In spectra of thick samples of $HgCl_2$,pyrazine and $HgCl_2$,pyrazine-d_4, the beginning of a broad weak band was observed. Its absorption maximum is apparently beyond the useful range of the CsBr prism. This band was not observed in the mercuric bromide complex, indicating that it probably originates in the asymmetric $HgCl_2$ stretch in the complex. In pure $HgCl_2$, the asymmetric stretch occurs near 376 cm^{-1}.(10,11) In other cases of interest here, the metal–halogen stretch lies lower, occurring for example at 271 cm^{-1} in pure $HgBr_2$ and at 335 cm^{-1} in pure HgBrCl.(10)

If the structures of the polymeric complexes were analogous to the structure reported for dibromo-2,5-dimethylpyrazinenickel(II),(4) the metal–halogen bonds would be nearly perpendicular to the plane containing the pyrazine rings and the metal–nitrogen bonds. Several consequences would ensue. First, the symmetric and asymmetric $HgCl_2$ stretching vibrations should mix to some extent with the out-of-plane vibrations of the rings. The product rule agreement exhibited above for these vibrations indicates that such mixing must be minimal. Second, the drastic decrease in $HgCl_2$ asymmetric stretching frequency on complex formation may now be rationalized as follows: the metal-halogen bonding orbitals are aligned nearly parallel with the π-orbitals of the pyrazine ring. Each ring orbital contributes but one electron to the π-structure, while each metal–halogen bonding orbital may contribute two electrons. Since the lowest unoccupied orbital in pyrazine occurs at a considerably lower energy than the corresponding orbital in benzene (owing to the presence of the nitrogen atoms in the pyrazine ring), electron delocalization from the filled metal–halogen bonding orbital into the ring vacancies could occur. This would produce a lower electron density in the metal–hydrogen bond, leading to a smaller force constant and lower stretching frequency, as observed. Interactions of this type could explain the apparent increased stability of the pyrazine–metal halide complexes over that which one might expect from the basicity of pyrazine towards the proton. In the proton case, of course, only simple sigma type bonds may be formed between the donor and acceptor atoms.

A secondary consequence of such delocalization should be to increase the extent of double bond character in the metal-nitrogen and ring carbon–carbon bonds, thus producing a series of 1,4-cyclohexadienelike structures. By analogy with cyclohexadinene,(12) in which the out-of-plane ring bending frequency ν_{16b} is so low it is not observable with prism instrumentation, the increase in double bond character in the carbon–carbon bonds should lead to a decrease in the out-of-plane ring bending frequency in the complexes. Reference to Table 2 shows that the greatest extent of double bond character and electron delocalization should be found with the mercury compounds and the least with the zinc compounds. Indeed, in the zinc case, it appears that only the chloride complex is stable as a high polymer.

If the explanation offered here is correct, the effect should be general. Lower-lying uncomplexed metal–halogen stretches should be shifted to even lower frequencies on complex polymer formation, and thus be generally unobservable with the available equipment.

The failure to observe a metal–nitrogen stretch is easily explained on the assumption of polymer formation. When complexing occurs at both nitrogens, the resulting

(10) G. J. JANZ and D. W. JAMES, *J. Chem. Phys.* **38**, 905 (1963).

(11) F. A. MILLER, G. L. CARLSON, F. F. BENTLEY and W. H. JONES, *Spectrochim. Acta* **16**, 135 (1960).

(12) H. D. STIDHAM, *Spectrochim. Acta* **21**, 23 (1964).

polymer chain may be regarded as being composed alternately of heavy metal atoms and light stiff aromatic rings with long but random chain length. Under these conditions, there is no single metal–nitrogen stretch, just as in polyethylene there is no single carbon–carbon stretch. Rather, there are a large number of such stretching frequencies situated at a very large number of different places in the specturm. None of these stretching frequencies occurs with great intensity since no two frequencies occur at the same place due to the random chain length. The failure to reinforce leads to disappearance into the background, thus accounting for the lack of a metal–nitrogen stretch.

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