

Studies of mercury(II), mercury(I), zinc(II) and cadmium(II) complexes with pyrazoles

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A few Hg(II) and Hg(I) derivatives of the formula $XHgpz^*$ ($X = Cl, NO_3$) and $(NO_3)Hg_2pz^*$ respectively ($Hpz^* =$ pyrazole or 3,5-dimethylpyrazole) have been synthesized in alcoholic or aqueous medium. No ring C(4)-mercuration is observed. With Zn(II), polymeric products of the composition $Zn(pz^*)_2 \cdot H_2O$ have been obtained. Cd(II) gives a product of undefined composition. The complexes have been characterized by elemental analysis, infrared and mass spectra.

The chemistry of pyrazoles with non-transition metals is rather limited¹ and more so with group 12 metals, with the exception of some conflicting reports on the interaction of Hg(II) with pyrazoles²⁻⁴. Thus, our interest in the chemistry of pyrazole derivatives of boron⁵⁻⁸ has prompted us to investigate the interaction of pyrazole and its 3,5-dimethyl derivative (structure I) with the group 12 metals and the results of our investigations are reported here.

Experimental

IR spectra were recorded on a Perkin-Elmer FT-IR 1600 (4000-400 cm^{-1}) or on a Perkin-Elmer 883 or 597 spectrophotometer (4000-200 cm^{-1}) in KBr. Elemental analyses were performed on a Perkin-Elmer 240 C elemental analyser. Mass spectral data were obtained on an Electron Impact Mass Spectrometer Finnigan 4500 (70 eV).

Preparation of sodium pyrazolide and 3,5-dimethylpyrazolide

Sodium pyrazolide (Napz) and sodium 3,5-dimethylpyrazolide (Napz*) were prepared by adding equimolar quantities of freshly cut sodium in small pieces with stirring to solutions of pyrazole (Hpz) and 3,5-dimethylpyrazole (Hpz*) in benzene, followed by refluxing the mixture for 3 h. On cooling to room temperature, the precipitate was separated by filtration, washed with benzene and dried *in vacuo*. These were preserved in well-stoppered flasks.

Preparation of the metal complexes of pyrazoles Procedure for $C_3H_3N_2ClHg(ClHgpz)$ (1) and $C_5H_7N_2ClHg(ClHgpz^*)$ (2)

A solution of sodium pyrazolide (0.45 g, 5 mmol) in absolute ethanol (20 ml) was added dropwise with stirring to a solution of $HgCl_2$ (1.36 g, 5 mmol) in absolute ethanol (20 ml). Immediately a colourless solid precipitated. The resultant mixture was stirred for 3 h and then filtered. The crude solid product (essentially in quantitative yield) was washed successively with distilled water, ethanol, and acetone and finally dried *in vacuo*. Thus the reaction products, respectively, (1) and (2), were obtained. Two more sets of reactions were carried out with each of the two pyrazolides using metal and pyrazolide in 2:1 and 1:2 molar ratios. The products were identical with the products obtained from 1:1 molar ratio reactions. These two compounds are insoluble in all common organic solvents, such as ethanol, chloroform, benzene, acetone, DMSO and DMF.

Procedure for $C_3H_3N_3O_3Hg[(NO_3)Hgpz]$ (3), $C_5H_7N_3O_3Hg[(NO_3)Hgpz^*]$ (4), $C_3H_3N_3O_3Hg_2[(NO_3)Hg_2pz]$ (5) and $C_5H_7N_3O_3Hg_2[(NO_3)Hg_2pz^*]$ (6).

Pyrazole (0.34 g, 5 mmol) or 3,5-dimethylpyrazole (0.59 g, 5 mmol) was dissolved in water (50 ml) in a round bottomed flask equipped with a reflux condenser and a magnetic stirrer. An aqueous solution of $Hg(NO_3)_2$ (1.62 g, 5 mmol) or $Hg_2(NO_3)_2$ (2.62 g, 5 mmol) was added dropwise with stirring whereby a colourless solid precipitated. The mixture was stirred for 2 h at room temperature for complete precipitation, then filtered and the residue repeatedly washed with distilled water, ethanol, acetone and finally dried *in vacuo*. The reaction products were obtained in essentially quantitative yields (Table 1).

Two more sets of reactions were carried out using 2:1 and 1:2 metal to ligand ratios with each of the two ligands and the products (yields ca. 95%) were found to be the same as those obtained from the 1:1 molar ratios of the reactants.

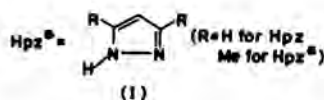


Table 1—Characterization data on the pyrazole derivatives of Group 12 metals

Compd. No.	Compound	Yield (%)	m.pt. (°C)	Found (Calcd), %		
				C	H	N
1	C ₃ H ₃ N ₂ ClHg	96	> 300	11.73 (11.89)	1.07 (0.99)	9.21 (9.23)
2	C ₃ H ₇ N ₂ ClHg	90	> 300	18.37 (18.13)	2.11 (2.11)	8.40 (8.45)
3	C ₃ H ₃ N ₃ O ₃ Hg	90	265 (d)	10.64 (10.93)	1.05 (0.91)	12.65 (12.74)
4	C ₃ H ₇ N ₃ O ₃ Hg	95	> 300	16.80 (16.79)	1.96 (1.95)	11.83 (11.74)
5	C ₃ H ₃ N ₃ O ₃ Hg ₂	98	> 300	6.17 (6.79)	0.76 (0.57)	7.64 (7.92)
6	C ₃ H ₇ N ₃ O ₃ Hg ₂	96	> 300	10.70 (10.76)	1.34 (1.25)	7.34 (7.53)
7	C ₆ H ₈ N ₄ OZn	96	295 (d)	33.23 (33.74)	3.80 (3.77)	26.71 (26.23)
8	C ₁₀ H ₁₆ N ₄ OZn	98	295 (d)	45.49 (43.89)	5.58 (5.89)	20.78 (20.47)

All the four compounds are insoluble in all common organic solvents such as chloroform, benzene, acetone, ethanol, DMSO and DMF.

Mass spectral data for C₃H₃N₃O₃Hg (3): m/z 270 (pzHg⁺ + 1, 40%), 202 (Hg⁺, 60%), 68 (pz⁺ + 1, 100%).

Procedure for C₆H₈N₄OZn(Znpyz₂·H₂O) (7) and C₁₀H₁₆N₄OZn(Znpyz₂·H₂O) (8)

A solution of sodium pyrazolide (0.9 g, 10 mmol) or 3,5-dimethylpyrazolide (1.18 g, 10 mmol) in absolute ethanol (30 ml) was added dropwise with stirring to a solution of ZnCl₂ (0.68 g, 5 mmol) in absolute ethanol (20 ml). Immediately a colourless solid precipitated. The resultant mixture was stirred for 3 h and then filtered. The crude solid product (essentially in quantitative yield) was washed with ethanol and acetone and finally dried *in vacuo*. The reaction products were (7) and (8) respectively. Two more sets of reactions were carried out with each pyrazolide using metal and pyrazolide in 1:1 and 2:1 molar ratios. The products (yields ca. 45%) were identical with the products obtained from 1:2 molar ratio reactions (yields 96% and 98% respectively) (Table 1).

Mass spectral data for C₆H₈N₄OZn (7): m/z 218 (M⁺ + 2, 13%), 200 (218-H₂O, 5%), 84 (218-2pz, 48%), 69 (pz⁺ + 2, 100%), 68 (pz⁺ + 1, 85%), 67 (pz⁺, 40%).

Mass spectral data for C₁₀H₁₆N₄OZn (8): m/z

548 [2(M⁺ + 2), 11.5%], 274 (M⁺ + 2, 21%), 244 (274-2Me, 43%), 177 (100%), 95 (pz⁺, 20%), 65 (95-2Me, 13%).

Reaction of cadmium chloride and sodium pyrazolide

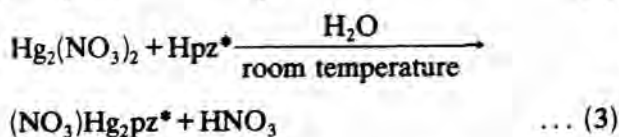
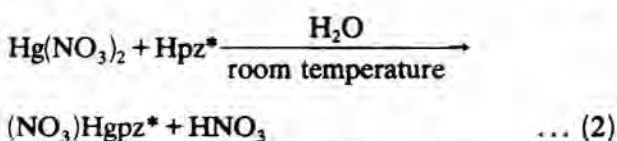
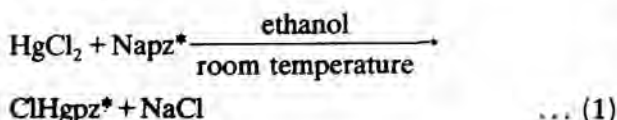
A solution of sodium pyrazolide (0.45 g, 5 mmol) in absolute ethanol (20 ml) was added dropwise with stirring to a solution of CdCl₂·2H₂O (1.1 g, 5 mmol) in absolute ethanol (20 ml). Immediately a colourless solid precipitated. The resultant mixture was stirred for 3 h and then filtered. The residue was washed successively with distilled water, ethanol and acetone, and finally dried *in vacuo*. Two more sets of reactions were carried out using metal and pyrazolide in 1:2 and 2:1 molar ratios. In all the cases, the products were same as evident from the IR spectra and analytical data which did not correspond to any rational formulation. A typical analysis of the product: [Found: C, 2.66, H, 0.62, N, 1.86, Calcd. for C₃H₃N₂ClCd. C, 14.35, H, 2.81, N, 11.16%]. IR (cm⁻¹, KBr) 3480 br ν(OH), 3105 w ν(C-H)(pz).

Results and discussion

The reactions between HgCl₂ and azoles, pyrazole and 3,5-dimethylpyrazole, in aqueous medium were reported to give N(1)-mercurated and both N(1)- and C(4)-mercurated products respectively², even when N(2) was free. There was also

a report³ on the isolation of adducts, $\text{MX}_2\text{L}_2\cdot n\text{H}_2\text{O}$ where $\text{M}=\text{Zn}, \text{Cd}, \text{Hg}$; $\text{X}=\text{Cl}, \text{NO}_3, \text{ClO}_4, \text{BF}_4, \text{SCN}, \text{CH}_3\text{COO}, 1/2(\text{SO}_4)$ and $\text{L}=3,5\text{-dimethylpyrazole}$. This claim for $\text{Hg}(\text{II})$ was later refuted by another group⁴. Since with the same ligand(s), different products were reported, we carried out the reactions of HgCl_2 with the anions of the ligands, viz., pyrazolide (pz^-) and 3,5-dimethylpyrazolide (pz^*) as their Na salts so that both N(1) and N(2) were free to make bonds as well as C(4). These reactions were carried out in three different molar ratios of metal to pyrazolide ions, viz., 1:1, 2:1 and 1:2. The reactions were carried out in absolute alcohol. However, with all the three molar ratios, the same compounds were obtained for both the ligands in ~95% yield. The compounds were precipitated from the solvent and are insoluble in all common organic solvents and do not melt below 300°C.

Although, the reaction between HgCl_2 and 3,5-dimethylpyrazole was reported to give both N- and C-mercurated products² or an adduct $\text{HgCl}_2(\text{Hpz}^*)_2\cdot 2\text{H}_2\text{O}$ (ref. 3), we found that the reactions between HgCl_2 and pyrazolide, and 3,5-dimethylpyrazolide (as their sodium salts) in absolute alcohol afforded only the N-mercurated products ClHgpz (1) and ClHgpz^* (2) respectively, presumably reacting through N(1) only. Similarly, reactions of $\text{Hg}(\text{NO}_3)_2$ with pyrazole and 3,5-dimethylpyrazole yielded the products of the compositions $(\text{NO}_3)\text{Hgpz}$ (3) and $(\text{NO}_3)\text{Hgpz}^*$ (4) respectively. With $\text{Hg}_2(\text{NO}_3)_2$ similar products, viz., $(\text{NO}_3)\text{Hg}_2\text{pz}$ (5) and $(\text{NO}_3)\text{Hg}_2\text{pz}^*$ (6) respectively were obtained. In the cases of $\text{Hg}(\text{I})$ and $\text{Hg}(\text{II})$ nitrates, the reactions were carried out in aqueous medium as mercury salts are not soluble in absolute alcohol. The reactions are shown in Eqs (1-3).

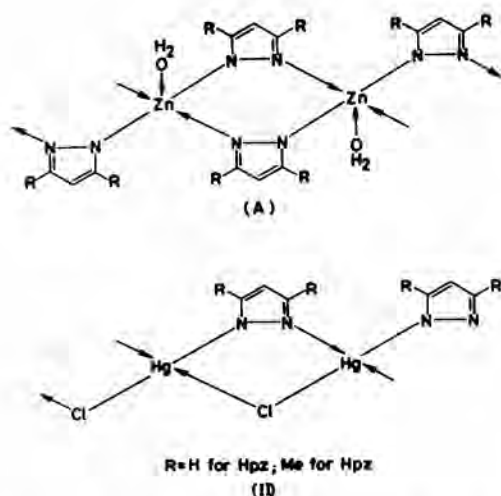


In all the above cases, the reactions were carried out in the metal to ligand ratios of 1:1, 1:2

and 2:1, so that at least in the latter cases there could be a possibility of insertion of a second metal in the pyrazole ring or the formation of metal bispyrazolides. As the $\text{Hg}(\text{I})$ and $\text{Hg}(\text{II})$ nitrates are insoluble in absolute alcohol, pyrazole and 3,5-dimethylpyrazole were taken instead of the corresponding sodium pyrazolides, because pyrazolides hydrolyse in water producing alkali. The latter reacts with the mercury salts precipitating basic mercuric salts along with the mercury pyrazolides. However, in all the above cases, whether the reactions were carried out in ethanol or water no insertion of a second metal in the pyrazole ring, either by C(4) and N(2)-mercuration (as $\text{pz}^* \rightarrow \text{Hg}$) took place.

In the cases of reactions of ZnCl_2 with pyrazoles, their sodium salts were used and ethanol was used as the solvent. Colourless solids were precipitated, which decompose at 295°C. The compounds analysed as $\text{Znpz}_2^*\cdot\text{H}_2\text{O}$ (where pz^* =pyrazolide and or 3,5-dimethylpyrazolide ions). The reactions were carried out in the metal:ligand ratio of 1:1, 1:2 and 2:1, but the same product was obtained in all the cases with each ligand, although in lesser yield when the ratio was 1:1. For cadmium the reactions were carried out both in water and ethanol taking $\text{CdCl}_2\cdot 2\text{H}_2\text{O}$ and either pyrazolide or pyrazole depending on the solvent. In both the cases, no pure products corresponding to any rational formulation could be isolated presumably due to hydrolysis of cadmium salts⁹ (vide supra). Thus the experiments with cadmium were not pursued further. The physical and analytical data of the compounds (1)-(8) are given in Table 1.

In the infrared spectra, zinc compounds show the presence of $\nu(\text{O}-\text{H})$ bands at 3440-3275 cm^{-1} owing to water. The $\nu(\text{C}-\text{H})$ (pz^*) bands arising from pyrazolyl and 3,5-dimethylpyrazolyl groups are found to occur at 3150-3040 cm^{-1} , while for 3,5-dimethylpyrazolyl ligand, additional $\nu(\text{C}-\text{H})$ stretching owing to CH_3 group occur at 2980-2840 cm^{-1} . The appearance of the 3120 cm^{-1} band in (2) indicates that C(4)-mercuration has not taken place. The $\text{Hg}-\text{Cl}$ stretchings in HgCl_2 itself occur at 405 and 348 cm^{-1} (ref. 10). The terminal $\text{Hg}-\text{Cl}$ stretchings in some organomercury compounds were observed at 334 and 325 cm^{-1} (ref. 11). Thus the absorption bands which occur at 303 and 304 cm^{-1} in (1) and (2) respectively may be assigned to $\nu(\text{Hg}-\text{Cl})$ (bridging). The presence of NO_3 group is indicated by the occurrence of absorption bands at 1430 and 1298 for (3), 1460 and 1285 for (4), 1422 and 1297 for (5), and



1530 and 1218 for (6) in consonance with the absorptions owing to monodentate NO_3 group found in the literature¹². In the zinc compounds no characteristic low energy bands are found excepting those arising from the ligands. The ^1H NMR spectra of the compounds could not be recorded as the compounds are insoluble in most common organic solvents including DMSO. Electron impact mass spectra of one mercury compound (3) and two zinc compounds (7) and (8) could be recorded. Mercury has seven isotopes and zinc has five. The molecular and other metal containing ions listed are based on ^{202}Hg and ^{64}Zn isotopes. Compound (3) which analysed as $(\text{NO}_3)\text{Hgpz}$ shows major peaks at 270 and 202 as clusters having the same isotope distribution pattern as that of mercury itself. The peaks correspond to $\text{pzHg}^+ + 1$ and Hg^+ respectively. The zinc compounds show the highest peaks at 218 for (7) and 548 for (8). While the former peaks corresponds to $\text{M}^+ + 2$ peak for $\text{Znpz}_2\cdot\text{H}_2\text{O}$, the latter corresponds to $2(\text{M}^+ + 2)$ peak for $(\text{Znpz}_2\cdot\text{H}_2\text{O})$. Thus the mass spectral data indicate that the compound (8) is polymeric in nature

through coordination of pyrazole nitrogens and one water molecule to zinc giving pentacoordinated structure, which is especially common with zinc(II)¹³, having a unit composition as $\text{Znpz}_2\cdot\text{H}_2\text{O}$ (A). Water bands are also found in the infrared spectra. Compound (7) appears to be monomeric from the mass spectral data but under the high temperature and high vacuum conditions, the polymer might have dissociated fully to monomeric $\text{Znpz}_2\cdot\text{H}_2\text{O}$. The polymeric nature is also suggested by the fact that they are insoluble in common organic solvents and are high melting. The Hg(II) chloro complexes may also be polymeric through both halogen and pyrazole ring bridging (structure II).

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