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A STUDY OF THE METAL COMPLEXES OF 2,1,3-BENZOSELENADIAZOLE, 2,1,3-BENZOTHIADIAZOLE AND THEIR DERIVATIVES - I

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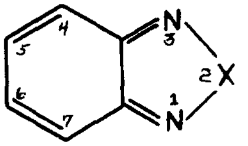
Introduction

The metal complexes of 2,1,3-benzoselenadiazole, (I), $C_6H_4N_2Se$, with Pd^{2+}, Cd^{2+}, Zn^{2+}, Hg^{2+}, Cu^{2+}, Mn^{2+}, Ag^{1+}, Ce^{4+}, and Ti^{4+} have been prepared.(1,2,3,4) These very insoluble complexes had either Cl^{1-}, Br^{1-}, I^{1-}, CNO^{1-}, $CNSe^{1-}$, N_3^{1-}, or NO_3^{1-}, as the anoin. This report is a more thorough characterization of some of these compounds. In addition, complexes with 2,1,3-benzothiadiazole, (II), $C_6H_4N_2S$, as the ligand were prepared and characterized. Substituents were placed at the 5-position of I and the resulting molecule studied as a ligand.



I X = Se
II X = S

Data collected in this study show significant differences in the thermal stabilities of complexes when the atom in the 2-position was changed. 5- substitution also affected the thermal stabilities of some of the complexes. The presence of bridging or terminal halides was shown by the positions of the metal halide infrared absorptions.

Experimental

2,1,3-benzoselenadiazole, 5-methyl-2,1,3-benzoselenadiazole, (III), 5-chloro-2,1,3-benzoselenadiazole, (IV), and 5,6-dimethyl-2,1,3-benzoselenadiazole, (V), were prepared from the corresponding ortho-phenylenediamine and selenous acid.(4) 2,1,3-benzothiadiazole was purchased from Aldrich Chemical Company. $CuCl_2$, $HgCl_2$, $CdCl_2$, $ZnCl_2$ and $AgNO_3$ were reagent grade and were not further purified.

Complexes of I with two molecules of ligand per one cation, 2:1 complexes, were prepared by mixing equal volumes of a 0.1 M solution of the ligand dissolved in ethanol-water with a 0.01 M solution of the salt dissolved in the same solvent. Complexes of I with one molecule of ligand per one cation, 1:1 complexes, formed when stoichiometric amounts of the reactants were mixed. 1:1 complexes with the other ligands formed under the same conditions that formed 2:1 complexes with I. The products precipitated immediately and were insoluble in all solvents. They were washed and dried in a vacuum at 60°.

The compositions of the complexes were determined in several ways. A solution of the salt was titrated conductometrically with a solution of the ligand. Thermogravimetric analysis (tga) was performed on the complexes as was carbon-hydrogen-nitrogen analysis. Infrared spectra of the complexes pressed in KBr pellets were recorded from 2.5 to 40 microns on a Perkin-Elmer 457. Differential thermal analysis (dta) and tga were done using a Fisher Model 260 Thermanalyzer under a nitrogen atmosphere. The rate of heating was 10° per minute. Tga was also performed by letting the sample sit 16 hours at a given temperature before the temperature was increased. This data gave the thermal stabilities of the complexes when they were maintained at elevated temperatures for prolonged periods of time.

Results

The results of the dta experiments are given in Table I. The temperature when the transition broke from the baseline was taken as the transition temperature. "Exo" refers to an exothermic process and "endo" refers to an endothermic process. The color of the complex is given following the formula.

The combined results of the tga and dta experiments indicated which transitions were accompanied by a weight loss. All of the $CdCl_2$ complexes lost one

TABLE I

DTA of the Complexes

Complex	Tranistion #1 (°C)	Transition #2 (°C)	Transition #3 (°C)	Transition #4 (°C)
$CdCl_2(I)_2$, (wh)	210 (endo)	225 (endo)	350 (endo)	380 (endo)
$CdCl_2(I)$, (y)	350 (endo)	380 (endo)		
$CuCl_2(I)_2$, (gr)	210 (endo)	240 (endo)	270 (endo)	322 (exo)
$CuCl_2(I)$, (br)	270 (endo)	322 (exo)		
$AgNO_3(I)$, (y)	240 (exo)			
$HgCl_2(I)_2$, (wh)	230 (endo)	265 (endo)		
$HgCl_2(I)$, (y)	265 (endo)			
$CdCl_2(II)$, (wh)	275 (endo)	310 (endo)		
$CuCl_2(II)$, (y-br)	260 (endo)			
$AgNO_3(II)$, (wh)	235 (exo)			
$HgCl_2(II)$, (wh)	185 (endo)			
$CdCl_2(III)$, (y)	330 (endo)	375 (endo)		
$CuCl_2(III)$, (y-br)	270 (endo)	290 (exo)		
$CdCl_2(IV)$, (br)	290 (endo)	340 (endo)		
$CuCl_2(IV)$, (gr)	260 (endo)	282 (endo)	292 (endo)	312 (exo)
$CdCl_2(V)$, (y)	370 (endo)	375 (endo)		
$CuCl_2(V)$, (y-br)	265 (endo)	282 (exo)		

molecule of ligand in a process that dta showed to have two endotherms. $CuCl_2(I)_2$ lost one molecule of I in a two-step endothermic process. Except for $CuCl_2(II)$, all of the other 1:1 $CuCl_2$ complexes decomposed by a process that began endothermally but then went exothermic. The last exotherm probably was a rearrangement of the product, $CuCl_2$. $CuCl_2(II)$ lost its one ligand in a single endotherm. The 1:1 $AgNO_3$ complexes lost their ligands in a single exothermic process that included the decomposition of the product, $AgNO_3$. The $HgCl_2$ complexes lost each ligand in a single endothermic process. $HgCl_2$, the final product, vaporized during the last endothermic decomposition.

The complexes with I were thermally more stable than the corresponding complexes with II. This result is consistent with other data concerning the basicity of the donor nitrogen atom as a function of the X atom in the 2-position.(5) The $CdCl_2$ complexes with I, III, IV, and V exhibited the trend in thermal stability predicted from the effect of 5-substitution on the donor properties of the nitrogen atom.(5) The complex with V was most stable because of the greater ability of V to stabilize a negative charge on the nitrogen atom. Likewise, $CdCl_2$(IV) was the least stable. The $CuCl_2$ complexes did not follow the expected trend.

Results of the prolonged thermal stabilities of the complexes show 1:1 complexes with I began to decompose above 180°. Complexes with V were stable up to 140°, and complexes with III and IV were stable up to 100°. The 2:1 complexes with I began to lose weight above 80°.

Infrared spectra of the complexes were recorded. Some identifying peaks for the complexes with I and II are included in Table II. Shifts in the fre-

TABLE II

Infrared Spectra of the Complexes

Compound	Frequencies of Absorption (cm^{-1})
I	350, 385, 560, 740, 758, 800, 852, 1140
$CdCl_2(I)_2$	350, 392, 559, 740, 765, 772, 1130
$CdCl_2(I)$	360, 382, 561, 744, 783, 1162
$CuCl_2(I)_2$	316, 354, 403, 563, 740, 761, 788, 819, 840, 1130, 1150
$CuCl_2(I)$	280, 306, 370, 395, 570, 740, 778, 805, 829, 1162
$HgCl_2(I)_2$	304, 326, 351, 390, 558, 720, 740, 768, 804, 840, 1148
$HgCl_2(I)$	305, 350, 380, 558, 716, 740, 766, 1150
II	390, 420, 532, 588, 740, 810, 844, 915
$CdCl_2(II)$	405, 412, 526, 592, 740, 842, 858, 920
$CuCl_2(II)$	318, 413, 529, 596, 740, 860, 880, 937
$HgCl_2(II)$	346, 398, 420, 530, 590, 750, 827, 838, 850, 860, 920

quencies of absorption of modes associated with I or II were observed when the ligands were complexed. In addition, some complexes had absorptions from M-Cl modes.

$CuCl_2(I)_2$, $CuCl_2(I)$, $CuCl_2(II)$, $CuCl_2(III)$, $CuCl_2(IV)$, and $CuCl_2(V)$ had Cu-Cl modes that absorbed at 316, 306, and 280, 318, 305, 290 and 275 and 304 cm^{-1}, respectively. These are all in the range expected from the bridging Cu-Cl mode.(6) The lack of a Cd-Cl absorptions above 250 cm^{-1} in $CdCl_2(I)_2$, $CdCl_2(I)$, and $CdCl_2(II)$ suggests bridging chlorides in these complexes.(7) To satisfy this requirement and the requirement of stoichiometry, the 2:1 complexes must have octahedral geometry with unidentate ligands, and the 1:1 com- must also have octahedral geometry but with bidentate ligands.

Cd-Cl modes in $CdCl_2(III)$, $CdCl_2(IV)$, and $CdCl_2(V)$ appeared at 270, 310, and 270 cm^{-1}, respectively. $HgCl_2(I)$ had a Hg-Cl absorption at 305 cm^{-1} and $HgCl_2(II)$ had one at 346 cm^{-1}. The positions of these peaks indicate the M-Cl modes are from terminal chlorides.(7-9) This requirement and the requirement of stoichiometry suggests 4-coordination with either bridging ligands and all terminal chlorides, or terminal ligands with some bridging and some terminal chlorides, the latter being most likely. Thus these complexes probably are dimeric tetrahedrals with unidentate ligands. The reason for these $CdCl_2$ complexes being different from those with I and II is not apparent. Quite possibly the identifying Cd-Cl mode with complexes of I and II could be found just below 250 cm^{-1}, the limit of our instrument. $HgCl_2(I)_2$ had terminal Hg-Cl absorptions at 304 and 326 cm^{-1}. Assuming the ligands in this complex also are not bridged, this complex would have to be monomeric and tetrahedral.

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