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THERMAL DECOMPOSITION OF COPPER–AZOLE COMPLEXES

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The thermal decomposition of complexes of the formulae $Cu(IMDAH)_xCl_2$, $Cu(BIMDAH)_xCl_2$ ($x = 2$ or 4), $Cu(BTAH)_2Cl_2$, $Cu(5MBTAH)_2Cl_2$, $Cu(BIMDA)_2$, $Cu(PDZ)Cl_2$, and $Cu(PYM)Cl_2$ (IMDAH = imidazole, BIMDAH = benzimidazole; BTAH = benzotriazole; 5MBTAH = 5-methyl-benzotriazole; PDZ = pyridazine; PYM = pyrimidine) has been studied in an oxidizing environment using thermogravimetric (TG) analysis. The TG profiles of all the complexes indicate degradation of the azole ligands and conversion to copper oxides. The Cu-azole complexes retain much higher fractions of the Cu in the degradation residue than the $Cu(PDZ)Cl_2$ and $Cu(PYM)Cl_2$ complexes which volatilize most of the Cu on thermal decomposition. These differences are interpreted on the basis of metal-ligand bonding and the participation of redox reactions in the thermal decomposition mechanism.

Azole ligands are used extensively as corrosion inhibitors in the antique [1] and printed circuit board industries [2]. The coordination nature of the metal-azole bonding as well as the molecular bond strength are important factors in determining the effectiveness of the corrosion inhibition process [3, 4]. To investigate the metal-azole chemistry and their thermal properties, several model complexes have been prepared by directly reacting the free ligand with a metal compound. Previously, we and others have used X-ray photoelectron spectroscopy (XPS) [3, 5], Fourier transform infrared spectroscopy (FTIR) [5], and X-ray diffraction [6] to study the coordination chemistry of these materials. In the current work we employ thermogravimetric (TG) analysis to investigate their thermal decomposition mechanisms [4].

Several authors have studied the effect of coordination chemistry and lattice distortion on the thermal stability of metal complexes [7–9]. The interpretation of the thermal degradation profile is complicated especially for copper complexes. This paper reports on the synthesis of several copper-azole complexes involving $CuCl_2$ and imidazole (IMDAH), benzimidazole (BIMDAH), benzotriazole

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(BTAH), 5-methyl-benzotriazole (5MBTAH), pyrimidine (PYM) or pyridazine (PDZ) ligands. The thermal stability and decomposition mechanism of these complexes in air will be discussed here.

Experimental

All CuL_xCl_2 (L = IMDAH, BIMDAH, BTAH, 5MBTAH, PDZ, PYM; $x = 2$ and 4) complexes were prepared by reacting the appropriate ratio of cupric chloride with ligand in dry ethanolic solution at ambient temperature, according to a previously described procedure [5]. The $Cu(BIMDA)_2$ complex (BIMDA = deprotonated form of BIMDAH) was prepared in 0.1 M NaOH solution as noted previously [5].

Elemental analysis for C, H, and N was performed at Desert Analytics, Tucson, Arizona using combustion techniques. Cu analysis was performed using iodometric determination. Table 1 summarizes these results in the form of weight percent values for Cu and the coordinated heterocyclic ligands.

A DuPont model 951 Thermal Gravimetric Analyzer coupled to a Model 9900 data station was used to obtain degradation profiles of these complexes. For all experiments the temperature was increased at a rate of 20 deg/min and a constant flow of air 250 cm^3/min was admitted to the sample chamber. Changing the heating rate was observed to affect the degradation temperatures but it did not appear to influence the overall shape of the TG profile. Nevertheless, our interest

Table 1 Weight percent values of copper(II) complexes obtained from elemental analysis[a] and molecular formulae

Complex	Cu wt.%		Ligand wt.%	
	obsd.	theory	obsd.	theory
$Cu(IMDAH)_2Cl_2$	23.4	23.5	50.1	50.3
$Cu(IMDAH)_4Cl_2$	16.1	15.6	63.8	67.0
$Cu(BIMDAH)_2Cl_2$[b]	17.3	17.1	64.5	63.7
$Cu(BIMDAH)_4Cl_2$[b]	10.0	10.5	76.7	77.9
$Cu(BTAH)_2Cl_2$	17.5	17.1	61.2	63.9
$Cu(5MBTAH)_2Cl_2$	15.9	15.9	65.3	66.5
$Cu(BIMDAH)_2$	21.0	21.3	79.0	78.7
$Cu(PDZ)Cl_2$	29.3	29.6	36.5	37.3
$Cu(PYM)Cl_2$	28.8	29.6	37.6	37.3

[a] Experimental reproducibility is ±0.6%.

[b] The anhydrous forms were analyzed.

here was to provide a comparative study among the different complexes and thus the heating rate does not influence our overall conclusions. The sample size was approximately 5.0 mg for all experiments.

Results and discussion

Figure 1 shows the degradation profiles for the free azole ligands. Initially, the degradation plot exhibits a slow rate followed by a rapid weight loss indicating the volatilization of the azoles. The free ligands are completely volatilized at temperatures above 210° for IMDAH, 275° for BIMDAH and 267° for BTAH. The initial slow rate in weight loss could be attributed to the loss of adsorbed water. Degradation profiles for the PYM and PDZ ligands were not obtained because these ligands are highly volatile liquids at room temperature. The TG profile for $CuCl_2 \cdot 2H_2O$ shown in Fig. 2 indicates that the water molecules dissociate at 90–180° and that $CuCl_2$ decomposes to form CuCl between 400 and 600°. This result is in agreement with a previous report [10]. A final weight percent of 7% was achieved at temperatures above 720°, indicating that almost all of the Cu has been lost from the sample. This residual material was analyzed with X-ray photoelectron spectroscopy and was found to contain a mixture of both Cu_2O and CuO. A similar Cu_xO mixture was also determined for all the residues from the Cu complexes.

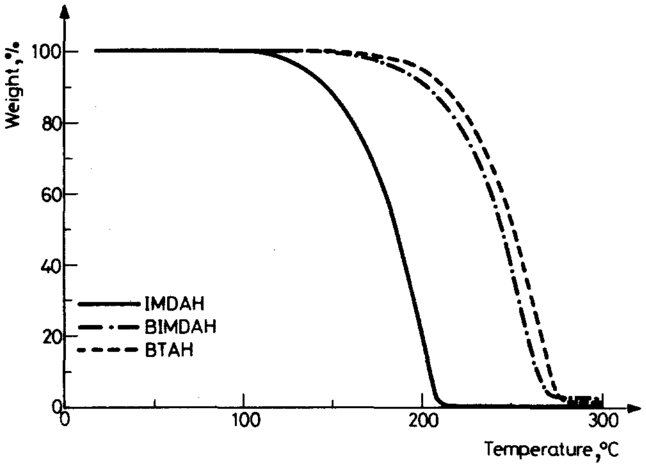

Fig. 1 TG profiles of the various azole ligands in this study

Figure 3 shows the degradation profiles for the two Cu-IMDAH complexes. The degradation mechanism for both complexes is similar, but, it is different than

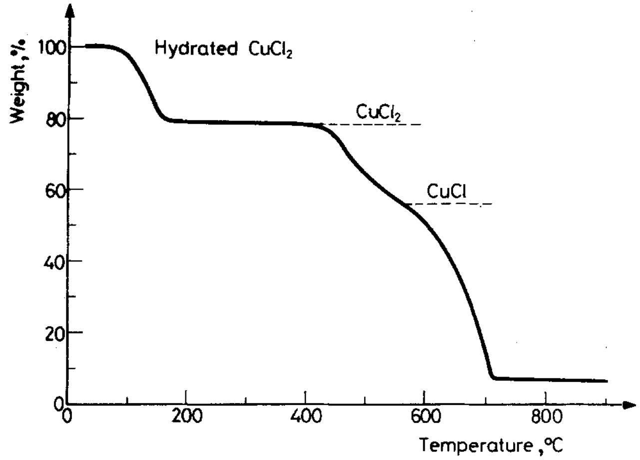

Fig. 2 TG profile of $CuCl_2 \cdot 2H_2O$ compound

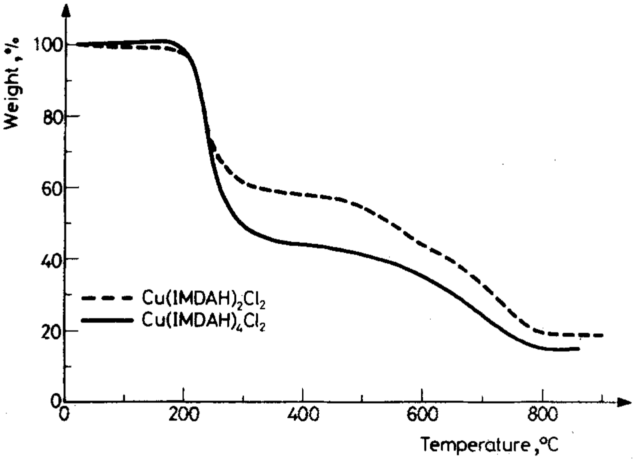

Fig. 3 TG profiles of Cu–IMDAH complexes

the one reported to occur in a nonoxidizing condition [7]. The weight loss observed at 190–260° in each compound corresponds to the loss of the IMDAH ligands. It is noted that the onset of the weight loss occurs at higher temperatures in these complexes than found for the free IMDAH ligand, consistent with the stabilization of the ligand on complexation [7, 8]. The residual weight percent at 450° does not indicate a complete loss of the azole ligands as has been observed for Pd–IMDAH complexes [4]. At temperatures above 800° the final weight percent for $Cu(IMDAH)_4Cl_2$ is 18%, suggesting conversion to Cu_2O. In the case of

$Cu(IMDAH)_2Cl_2$ the final weight percent is 21%, which is below the anticipated value of 26% for complete Cu_2O formation; this illustrates that some of the Cu metal has been removed, presumably by the vaporization of the CuCl and $CuCl_2$ species. Thus, it is interesting to note that most of the Cu in $CuCl_2$ is volatilized, whereas most of the Cu in the IMDAH complexes is converted to Cu_xO. This may be due to redox reactions taking place between the metal cation and the ligands during the thermal decomposition mechanism, an effect characterized previously for copper(II) chloride-amine systems [11].

Figure 4 shows the degradation profiles for the two Cu–BIMDAH complexes. The complexes are apparently each hydrated with one water molecule which dissociates at 130–150°. The TG profiles for the $Cu(BIMDAH)_2Cl_2 \cdot H_2O$ and $Cu(BIMDAH)_4Cl_2 \cdot H_2O$ complexes above 150° are more complicated than the IMDAH complexes and they suggest a stepwise loss of the BIMDAH ligands between 150° and 400°. As in the case of the IMDAH complexes, some of the decomposed BIMDAH ligand seems to remain in the residue at temperatures above 400°. However, the final residues at >800° for both $Cu(BIMDAH)_2Cl_2$ and $Cu(BIMDAH)_4Cl_2$ are 18% and 12%, respectively, in agreement with that expected for complete conversion to Cu_2O.

Figure 5 shows the degradation profiles for the Cu–BTAH and Cu–5MBTAH complexes. It is noted that the ligand decomposes at a lower temperature in the Cu–5MBTAH complex as compared to the Cu–BTAH complex. The complete decomposition occurs at 560° for Cu–5MBTAH while it occurs at 770° for Cu–BTAH. The complicated degradation profile of the $Cu(5MBTAH)_2Cl_2$ complex suggests that the ligands are lost in a stepwise manner. Again, the final

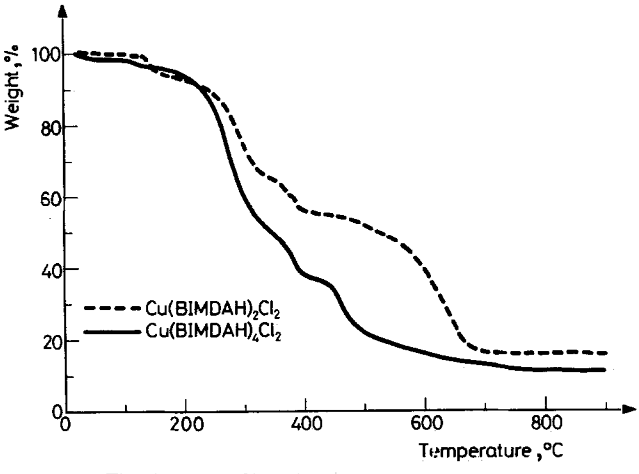

Fig. 4 TG profiles of Cu–BIMDAH complexes

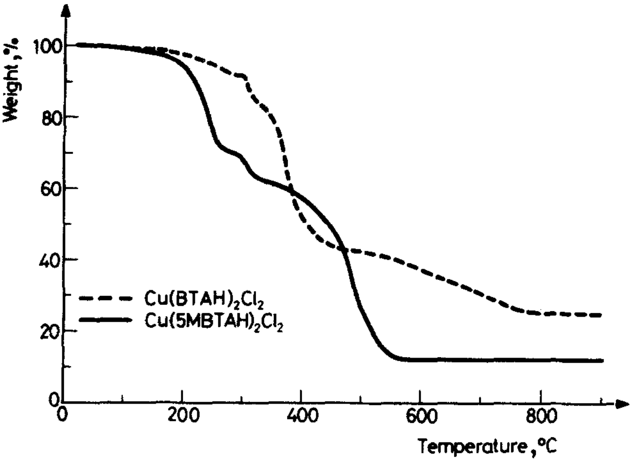

Fig. 5 TG profiles of Cu–BTAH and Cu-5MBTAH complexes

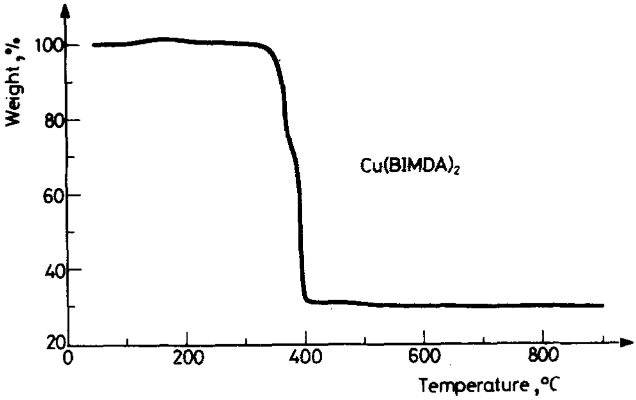

Fig. 6 TG profile of Cu(BIMDA)$_2$ complex

residue is predominantly a mixture of copper oxides (Cu$_x$O). The experimental determination of final weight percent is 14%, which compares with an expected value of 18% based on the formation of Cu$_2$O; this illustrates some loss of Cu through volatilization of CuCl$_x$. Similarly, in the case of Cu(BTAH)$_2$Cl$_2$ the ligands appear to be removed first, but the residual weight of 27% is much higher than those anticipated for Cu$_2$O (19%) and CuO (21%), indicating that the final residue is not simple oxide. XPS results could not conclusively determine the nature of the residual compound. The differences in the thermal mechanisms of these two closely related complexes are not readily apparent—these may indicate the influence of ligand substituent in the decomposition process.

Figure 6 shows the TG degradation profile for the Cu(BIMDA)$_2$ complex. This profile illustrates that the decomposition mechanism for this complex is relatively simple and it involves the loss of the BIMDA ligands at 320–400° and the formation of copper oxides. The expected weight percentages for Cu_2O (24%) and CuO (27%) are somewhat lower than the experimental residue of 30% and, thus, some ligand decomposition product apparently remains in the final copper oxide residue.

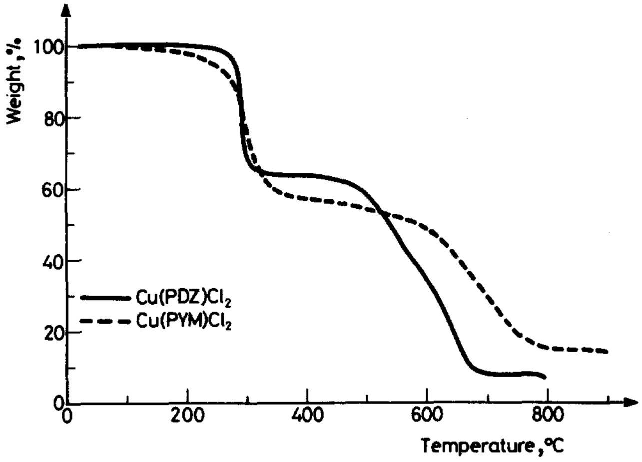

Fig. 7 TG profiles of Cu–PDZ and Cu–PYM complexes

Figure 7 shows the degradation profiles for the Cu(PDZ)Cl$_2$ and Cu(PYM)Cl$_2$ complexes. The TG profile for the Cu(PDZ)Cl$_2$ complex shows a very rapid weight loss at 260–310°. The results illustrate that each complex loses the ligand to form $CuCl_2$ (expected value 63%) with little interference from ligand char or oxide formation. The $CuCl_2$ residue in the Cu(PDZ)Cl$_2$ profile subsequently decomposes in a very similar fashion identical to that observed from $CuCl_2$ (see Fig. 2), whereas it occurs at higher temperatures for the Cu(PYM)Cl$_2$ complex. The final weight percentages observed for Cu(PDZ)Cl$_2$ and Cu(PYM)Cl$_2$ are 8% and 14%, respectively, illustrating that some residual Cu_xO remains at the end of the experiment.

Table 2 summarizes the experimentally determined residual weight percent of the copper(II) complexes studied. Also included are the expected values based on complete conversion of Cu to Cu_2O and CuO. This table provides a comparison of the decomposition mechanisms for all the compounds studied. It is noted that in $CuCl_2 \cdot 2H_2O$ almost all the Cu metal is volatilized from the sample and in the Cu(PDZ)Cl$_2$ and Cu(PYM)Cl$_2$ complexes substantial Cu metal is lost. In contrast, the Cu-azole compounds retain much higher amounts of Cu_xO in the degraded

Table 2 Experimentally determined wt.% from TG analysis of copper(II) complexes and the theoretical values based on complete conversion to copper oxides[a]

Complex	Experimental residue wt.%	Theory wt.%	
		Cu_2O	CuO
$CuCl_2 \cdot 2H_2O$	7	42	47
$Cu(IMDAH)_2Cl_2$	21	26	29
$Cu(IMDAH)_4Cl_2$	18	18	20
$Cu(BIMDAH)_2Cl_2 \cdot H_2O$	18	18	21
$Cu(BIMDAH)_4Cl_2 \cdot H_2O$	12	12	13
$Cu(BTAH)_2Cl_2$	27	19	21
$Cu(5MBTAH)_2Cl_2$	14	18	20
$Cu(BIMDAH)_2$	30	24	27
$Cu(PDZ)Cl_2$	8	33	37
$Cu(PYM)Cl_2$	14	33	37

[a] Experimental reproducibility is ±2%.

residue and in some cases the decomposed ligand adds to the weight. These differences are attributed to strong interactions between the azole ligands and the copper center (the azole ligands are significantly stronger bases than the diazine molecules [12]) and to the participation of redox reactions in the thermal decomposition mechanism.

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Zusammenfassung — Mittels thermogravimetrischer (TG) Analyse in oxydierender Umgebung wurde die thermische Zersetzung von Komplexen der Formel $Cu(IMDAH)_xCl_2$, $Cu(BIMDAH)_xCl_2$ mit $x = 2$ oder 4 sowie $Cu(BTAH)_2Cl_2$, $Cu(5MBTAH)_2Cl_2$, $Cu(BIMDA)_2$, $Cu(PDZ)Cl_2$ und $Cu(PYM)Cl_2$ (IMDAH = Imidazol, BIMDAH = Benzimidazol, BTAH = Benzotriazol, 5MBTAH = 5-Methyl-benzotriazol, PDZ = Pyridazin, PYM = Pyrimidin), untersucht. Die TG-Profile aller Komplexe zeigen einen Abbau der Azolliganden und eine Umformung zu Kupferoxiden. Bei den Cu-Azol-Komplexen bleibt während der thermischen Zersetzung ein weitaus größerer Teil des Kupfers im Rückstand enthalten, wohingegen bei den $Cu(PDZ)Cl_2$ und $Cu(PYM)Cl_2$ Komplexen das meiste Cu verdampft. Diese Unterschiede werden auf der Basis der Metall-Ligand-Bindung und mit der Beteiligung von Redoxreaktionen am thermischen Zersetzungsmechanismus erklärt.

Резюме — Методом ТГ в окислительной атмосфере изучено термическое разложение комплексов общей формулы $Cu(IMDAH)_xCl_2$, $Cu(BIMDAH)_xCl_2$ ($x = 2$ или 4), $Cu(BTAH)_2Cl_2$, $Cu(5MBTAH)_2Cl_2$, $Cu(BIMDA)_2$, $Cu(PDZ)Cl_2$ и $Cu(PYM)Cl_2$, где IMDAH = имидазол, BIMDAH = бензимидазол, BTAH = бензтриазол, 5MBTAH = 5-метилбензтриазол, PDZ = пиридазин, PYM = пиримидин. Профиль кривых ТГ для всех комплексов показал распад азоловых лигандов и образование оксидов меди. Остатки термического разложения комплексов медь — азолы содержат намного больше меди, чем таковые для комплексов $Cu(PDZ)Cl_2$ и $Cu(PYM)Cl_2$, при термическом разложении которых большинство меди улетучивается. Эти различия интерпретированы на основе связей металл-лиганд и участия в процессе термического разложения окислительно-восстановительных реакций.