

Copper (I) and (II) complexes of melamine

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Abstract

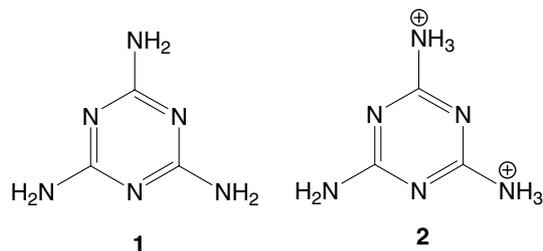
Coordination of copper (I) and (II) salts to melamine (Mel) produces [CuX(Mel)] [X = Cl (**5a**), Br (**5b**), I (**5c**), NO₃ (**5d**)], [CuX₂(Mel)₂] · S [X = Cl, S = H₂O (**6a**); X = Cl, S = 2 MeOH (**6b**); X = Br, S = 1/2H₂O (**6c**); X = OAc, S = none (**6d**)], and [Cu(OAc)₂(Mel)] (**7**). The chemical identity of the complexes has been confirmed by elemental analysis, X-ray powder diffraction, thermogravimetry, and infrared analysis.

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Keywords: Copper; Complex; Infrared; Melamine; Thermogravimetry; X-ray

1. Introduction

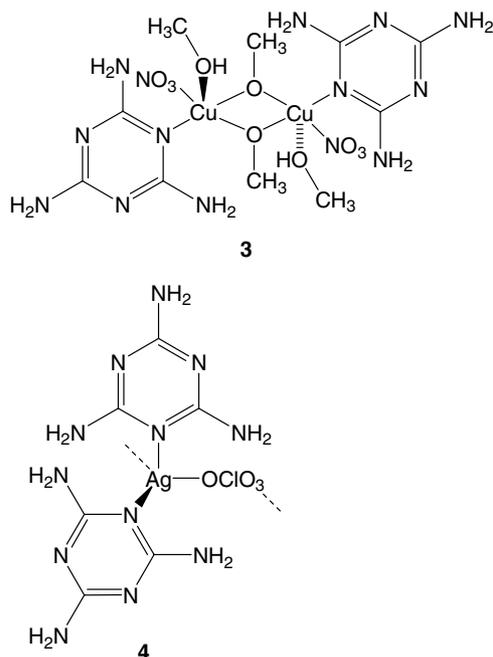
Melamine (2,4,6-triamino-*s*-triazine, **1**) has long been known as a monomer for melamine formaldehyde resins, but it is also an important fire retardant additive for polymers [1]. As part of our ongoing studies of copper complexes as fire retardant/smoke suppression additives for chlorinated polymers [2], we decided to undertake an investigation of the coordination chemistry of copper salts with melamine (Mel). Despite its apparent promise as a ligand, investigations into the coordination chemistry of melamine in the literature are remarkably few (see below). This fact probably owes much to the insolubility of melamine in all common solvents, except hot water. Nevertheless, our studies have also shown that melamine is a surprisingly poor ligand, especially in aqueous medium. The likely reason for the foregoing observations is the extensive hydrogen bonding that causes melamine to form a robust network structure [3].



The metal compounds of melamine that have been reported to date are almost exclusively limited to group 11 metals and largely fall into one of three categories: melaminium dication (**2**) salts associated with coordination anions [4], inorganic salts cocrystallized with melamine (showing hydrogen bonding but not coordination between the two networks) [5], and a few serendipitously formed coordination complexes [6]. Two of the latter complexes have been structurally characterized. Reaction of diacetyl-melamine with Cu(NO₃)₂ in methanol provided melamine complex **3**, and AgClO₄ reacted with melamine in water/methanol produced **4**. The dimer units that comprise the Cu(II) complex **3** contain internal hydrogen bonds between methanol or methoxide oxygen atoms and melamine

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hydrogen atoms. In addition, the intermolecular hydrogen bonds knit the dimer units into sheets, similar to those found for melamine itself [3]. The structure of the Ag(I) cation **4** is simpler, consisting of $[\text{Ag}(\text{Mel})_2]^+$ units linked into chains through weakly bridging perchlorate–silver interactions and additionally by hydrogen bonds between the perchlorate oxygen atoms and melamine hydrogen atoms. The coordination of melamine in both of these complexes occurs through one aromatic nitrogen atom, with no evidence of chelation to the amine nitrogen atoms.



There has been a report of Cu(II) salt reactions with melamine [7]. The reported complexes $[\text{CuCl}_2(\text{Mel})_2]$ and $[\text{CuX}_2(\text{Mel})]$ ($\text{X} = \text{Cl}, \text{Br}, \text{OAc}$) were formed by heating butanol or methanol solutions of Cu(II) salt with melamine. No crystal structures were reported in this study. Herein we report the synthesis and characterization of a series of Cu(I) and Cu(II) melamine complexes.

2. Experimental

2.1. General

All compounds were reagent grade and were used as received, except for CuCl and CuBr, which were freshly recrystallized from HCl and HBr, respectively. $[\text{Cu}(\text{NC-Me})_4]\text{BF}_4$ was prepared according to a literature method [8]. All copper-containing products were analyzed for copper content by atomic absorption as previously described [9]. Analyses for C, H, and N were carried out by Atlantic Microlabs, Norcross, GA. Thermogravimetric analyses (TGA) were run using a TA Instruments Q500 instrument in high resolution mode (heating rate dependent upon mass loss activity) under 60 mL/min N_2 flow. X-ray powder

diffraction analyses were carried out on a Scintag XDS 2000 diffractometer (Cu $\text{K}\alpha$, 3–60°, 0.05° step, 1.0 s/step) and manipulated using the JADE software package [10]. Infrared (IR) spectra were collected from KBr pellets on a Digilab FTS 7000 FTIR spectrophotometer.

2.2. Preparation of $[\text{CuBr}(\text{Mel})]$ (**5b**)

Copper (I) bromide (217 mg, 1.51 mmol) was dissolved in 30 mL Ar-degassed MeCN. The solution was filtered through Celite. Melamine (126 mg, 1.00 mmol) was added. The suspension was sealed in a thick-walled glass tube and heated to 100 °C with stirring in an oil bath. After 20 h, the MeCN had lost the pale green color associated with the solution of CuBr. The suspended solid was collected by means of filtration, washed with fresh MeCN and diethyl ether, and then dried under vacuum (white solid, 235 mg, 0.872 mmol, 87.4%). *Anal. Calc.* for **5b**: Cu, 26.73; C, 16.67; H, 2.80; N, 38.35. *Found*: Cu, 26.67; C, 16.63; H, 2.79; N, 38.84%. *Selected IR data* (cm^{-1}): 3459, 3425, 3352, 3195, 3140, 1659, 1600, 1575, 1541, 1477, 1448, 1028, 798.

2.3. Preparation of $[\text{CuCl}(\text{Mel})_{1.1}]$ (**5a**)

Synthesized as for **5b** but CuCl was added. Mint solid, yield 87.5%. *Anal. Calc.* for **5a**: Cu, 26.73; C, 16.67; H, 2.80; N, 38.35. *Found*: Cu, 26.67; C, 16.63; H, 2.79; N, 38.84%. *Selected IR data* (cm^{-1}): 3454, 3426, 3348, 3199, 3137, 1664, 1601, 1577, 1540, 1467, 1447, 1031, 797.

2.4. Preparation of $[\text{CuI}(\text{Mel})]$ (**5c**)

Synthesized as for **5b** but CuI was added. White solid, yield 91.6%. *Anal. Calc.* for **5c**: Cu, 20.07; C, 11.38; H, 1.91; N, 26.55. *Found*: Cu, 20.03; C, 11.54; H, 1.84; N, 26.31%. *Selected IR data* (cm^{-1}): 3469, 3408, 3326, 3145, 1703, 1688, 1653, 1623, 1566, 1530, 1498, 1020, 816.

2.5. Preparation of $[\text{CuNO}_3(\text{Mel})]$ (**5d**)

Synthesized as for **5b** except “CuNO₃” was first prepared in MeCN solution through comproportionation of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ with Cu wool until the solution was colorless. Excess copper wool was then removed, melamine was added, and the procedure for **5b** was followed. White solid, yield 93.5%. *Anal. Calc.* for **5d**: Cu, 25.25; C, 14.32; H, 2.40; N, 38.96. *Found*: Cu, 24.57; C, 14.53; H, 2.37; N, 38.68%. *Selected IR data* (cm^{-1}): 3459, 3426, 3337, 3195, 3143, 1672, 1660, 1618, 1571, 1541, 1466, 1450, 1026, 790.

2.6. Preparation of $[\text{CuCl}_2(\text{Mel})_2] \cdot 2\text{MeOH}$ (**6b**)

Copper (II) chloride dihydrate (171 mg, 1.00 mmol) was dissolved in 30 mL Ar-degassed MeOH. Melamine (252 mg, 2.00 mmol) was added. The mixture was sealed

in a thick-walled glass tube and heated to 100 °C with stirring in an oil bath. After 14 h, the lime green MeOH had bleached to a very pale green color and the white solid had become yellow-green. The solid was collected by means of filtration, washed with fresh MeOH and diethyl ether and then dried under vacuum. (white solid, 347 mg, 0.770 mmol, 77.0%). *Anal.* Calc. for **6b**: Cu, 14.10; C, 21.32; H, 4.47; N, 37.29. Found: Cu, 14.64; C, 20.60; H, 4.37; N, 37.95%. Selected IR data (cm⁻¹): 3331, 3157, 1651, 1540, 1474, 1017, 801, 783.

2.7. Preparation of [CuCl₂(Mel)₂] · H₂O (**6a**)

Synthesized as for **6b** except the solvent used was BuOH. Yellow solid, yield 92.5%. *Anal.* Calc. for **6a**: Cu, 15.70; C, 17.81; H, 3.49; N, 41.53. Found: Cu, 15.77; C, 17.67; H, 3.44; N, 40.65%. Selected IR data (cm⁻¹): 3425, 3410, 3373, 3312, 3177, 1702, 1680, 1652, 1622, 1561, 1535, 1475, 1023, 804, 782.

2.8. Preparation of [CuBr₂(Mel)₂] · 1/2H₂O (**6c**)

Synthesized as for **6b** except CuBr₂ was added and the solvent used was MeCN. Pea green solid, yield 99.6%. *Anal.* Calc. for **6c**: Cu, 13.11; C, 14.87; H, 2.70; N, 34.68. Found: Cu, 13.19; C, 15.06; H, 2.94; N, 34.50%. Selected IR data (cm⁻¹): 3425, 3410, 3373, 3312, 3214, 3171, 1702, 1680, 1652, 1622, 1535, 1475, 1020, 804, 781.

2.9. Preparation of [Cu(OAc)₂(Mel)₂] · H₂O (**6d**)

Synthesized as for **6b** except Cu(OAc)₂ · H₂O was added and the solvent used was MeCN. Aqua solid, yield 85.5%. *Anal.* Calc. for **6d**: Cu, 14.00; C, 27.68; H, 4.18; N, 38.74. Found: Cu, 14.06; C, 27.61; H, 4.09; N, 38.63%. Selected IR data (cm⁻¹): 3470, 3410, 3337, 3249, 3191, 3133, 1653, 1627, 1553, 1468, 1437, 1028, 814.

2.10. Preparation of [Cu(OAc)₂(Mel)] (**7**)

Synthesized as for **6b** except Cu(OAc)₂ · H₂O and melamine were reacted in equimolar proportions in MeCN. Aqua solid, yield 91.5%. *Anal.* Calc. for **7**: Cu, 20.65; C, 27.32; H, 3.93; N, 27.31. Found: Cu, 20.43; C, 27.00; H, 3.96; N, 28.18%. Selected IR data (cm⁻¹): 3470, 3420, 3353, 3244, 3137, 1651, 1626, 1553, 1467, 1437, 1031, 813.

3. Results and discussion

3.1. Synthesis

Initial attempts to form Cu(I)–melamine complexes in our lab focused on the use of aqueous ammoniacal solutions of copper (I) ion, which are produced via hydroxylamine reduction of CuSO₄ · 5H₂O [11]. Melamine (Mel) was dissolved in warm degassed water and was added via syringe to a nitrogen-purged colorless solution of “Cu₂SO₄”

prepared as previously described [11]. Encouragingly, the solution remained colorless, showing no sign of copper oxidation. Slow cooling of the solution to 5 °C, resulted in the formation of colorless crystals. However, these crystals contained no copper and were shown by melting point analysis to be merely recrystallized melamine. Thus, under these experimental conditions (0.20 M Cu₂SO₄, 0.60 M melamine 3.0 M NH₃), ammonia coordination proved to be favored over that of melamine.

A non-aqueous approach was pursued next. The use of organic solvents necessitated working with melamine as a suspended solid in copper-containing solutions. Acetonitrile was the solvent of choice for most of the reactions, however, methanol and *n*-butanol were also effective for several of the copper (II) salt reactions. The reaction mixtures containing the dissolved copper salt and solid melamine were heated overnight in sealed, thick-wall reaction tubes. Typically, the solution color lessened during the reaction, indicating the transfer of copper to the suspended melamine. The products were filtered and subjected to chemical analysis.

The favored products of CuX (X = Cl, Br, I, NO₃) with melamine conformed to the formula [CuX(Mel)] (**5**). The only problematic results came from the CuCl reaction, which reproducibly formed **5a** as [CuCl(Mel)]_{1,1–1,3}. A replicate CuCl reaction was carried out in the presence of copper wool to help prevent possible formation of Cu(II). Although the product of this reaction was whiter in color, chemical analysis still revealed excess melamine. The use of large excesses (about 10-fold) of copper salt resulted in the materials roughly conforming to [(CuX)₂(Mel)] for X = Cl, Br. However, elemental analyses for these products were not of high quality. Although X-ray powder diffraction and thermogravimetry results suggested that [(CuX)₂(Mel)] might be an independent phase (see below), a mixture of **5** and CuX could not be ruled out. Nevertheless, no evidence was found for the formation of [(CuX)₂(Mel)] products for X = I, NO₃; instead the isolated solids invariably analyzed as **5c** and **5d**. Attempts to dissolve away any adsorbed (rather than bonded) copper salt were carried out by heating the various Cu(I)–melamine complexes in fresh acetonitrile at 100 °C over several days. These experiments produced no changes in sample composition. Products of reactions involving the use of excess melamine yielded irreproducible chemical analyses. Subsequent X-ray analysis of these powders clearly revealed the presence of both **5** and free melamine. Hence, copper-poor phases with melamine do not appear to exist.

When [Cu(NCMe)₄]BF₄ was dissolved in MeCN and heated with melamine, the solid recovered proved to be unreacted melamine. What makes this result particularly surprising is the demonstrated reaction of the nitrate salt with melamine. Conproportionation of Cu(NO₃)₂ · 2.5H₂O with Cu in acetonitrile produces “CuNO₃”, which almost certainly exists in solution as [Cu(NCMe)₄]NO₃. The formation of [CuNO₃(Mel)] (**5d**) but not of [CuBF₄(Mel)] under essentially identical conditions points to the possible

necessity of anion coordination since NO_3^- is a superior ligand to BF_4^- .

All of the Cu(I)–melamine products were white or nearly white in color. This absence of color suggests that copper coordination is occurring through the amine nitrogen atoms, rather than those of triazine. The known Cu(I) complexes of diazine and triazine ligands invariably show significant color due to metal to ligand charge transfer absorptions in the visible spectrum [9,12].

In contrast to the results obtained with Cu(I), the Cu(II) salts generally formed products analyzing as $[\text{CuX}_2(\text{Mel})_2]$ (6). Water or alcohol solvent was retained in several cases, presumably as an additional ligand for copper. The only 1:1 Cu(II):Mel product realized was $[\text{Cu}(\text{OAc})_2(\text{Mel})]$ (7). The lack of isolated 1:1 complexes for CuCl_2 and CuBr_2 with melamine in the current study stands in contrast to the results reported previously [7].

3.2. X-ray powder diffraction

X-ray powder diffraction analysis was used to help characterize the new products. Sharp line diffractograms were obtained in all cases, indicating good sample crystallinity. Comparison of diffraction patterns was used to help confirm that the products were single-phase materials. Thus for example, the powder diffraction pattern of **5a** was compared to those of CuCl and melamine, see Fig. 1. The diffraction pattern of **5a** revealed no evidence of CuCl or melamine peaks. The diffractogram from the material provisionally identified as $[(\text{CuCl})_2(\text{Mel})]$ also appeared to be distinct from those of CuCl, melamine and **5a** (Fig. 1). Within the sensitivity constraints of X-ray powder diffraction, neither melamine nor copper salts were observed as contaminant phases in any of the copper–melamine products. Although the X-ray data were not of sufficient quality to allow for cell indexing, the occurrence of similar powder

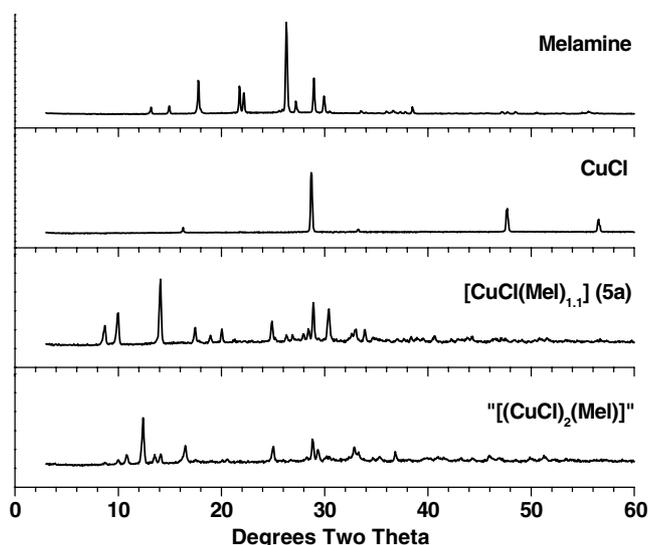


Fig. 1. X-ray powder diffraction traces for CuCl–melamine compounds.

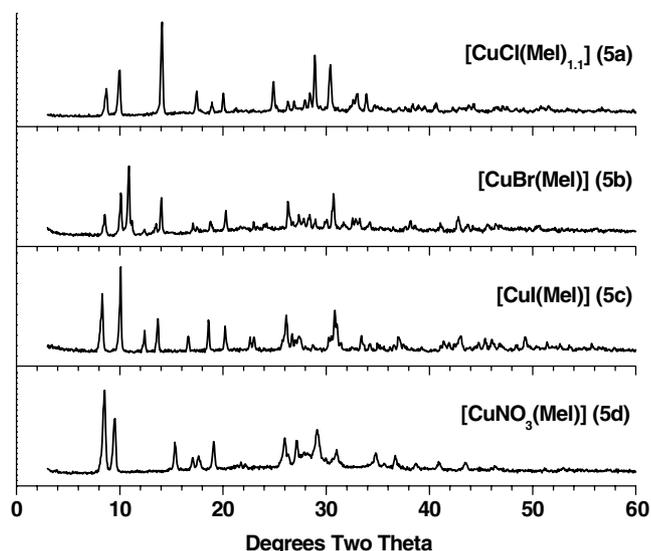
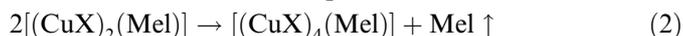
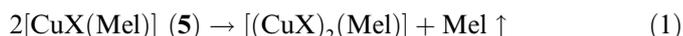


Fig. 2. X-ray powder diffraction traces for the Cu(I)–melamine compounds (5).

patterns for the **5** products shown in Fig. 2 suggests possible crystallographic isomorphism between these apparently low symmetry phases.

3.3. Thermogravimetric analysis

All of the melamine complexes were examined using TGA. The results and interpretations are collected in Table 1. Melamine itself sublimates between about 210 and 260 °C under the TGA conditions used. The TGA results for compounds **5** are shown in Fig. 3. Thermal analysis results for **5a** show four closely spaced mass losses occurring above 300 °C and separated from one another by shallow plateaus. The first three steps appear to represent the stepwise loss of melamine illustrated in the following equations:



The mass percent represented in the first plateau corresponds well to $[(\text{CuCl})_2(\text{Mel})]$. Also suggestive is the fact that, after the initial mass loss from **5a**, the subsequent mass loss profiles for the **5a** residue and that of the material provisionally identified as $[(\text{CuCl})_2(\text{Mel})]$ were identical. The plateau at about 380–390 °C may represent $[(\text{CuCl})_4(\text{Mel})]$, a phase that has not been synthesized. Volatilization of the remainder of the melamine leaves CuCl. The decomposition temperature of the residual CuCl from the melamine complexes corresponds to that of free CuCl. However, while authentic CuCl largely sublimates, leaving only a few percent residual mass, the decomposition of CuCl from the melamine complexes leaves significant residual mass, nearing that of the initial copper content. Hence, in addition to CuCl sublimation, reductive elimination, reaction (4) is also occurring, as has previously been observed [12].

Table 1
Thermogravimetric analysis results

Complex	Temp. (°C)	Possible product	wt% (theory)	wt% (expt)
5a	205–340	(CuCl) ₂ (Mel)	68	66
	340–390	(CuCl) ₄ (Mel)	55	51
	390–425	CuCl	42	37
	425–510	Cu	27	24
5b	235–335	(CuBr) ₂ (Mel)	77	75
	335–380	CuBr	53	60
	380–620	Cu/sublimation		9
5c	215–330	CuI	60	58
	500–580	Cu	24	21
5d	220–410	CuNO ₃	50	57
	410–435	Cu	25	29
6a	190–350	CuCl ₂	33	33
	350–590	Cu	16	14
6b	45–240	CuCl ₂ (Mel) ₂	86	91
	240–335	CuCl ₂	30	35
	335–590	Cu	14	15
6c	200–350	(CuBr ₂) ₂ (Mel)	59	58
	350–480	CuBr ₂	46	47
	350–675	Cu	13	14
6d	195–215	Cu(OAc) ₂ (Mel)	71	76
	215–290	CuOAc	28	30
	300–630	Cu	15	16
7	185–210	Cu(OAc) ₂	59	64
	210–270	CuOAc	40	45
	315–470	Cu	21	26

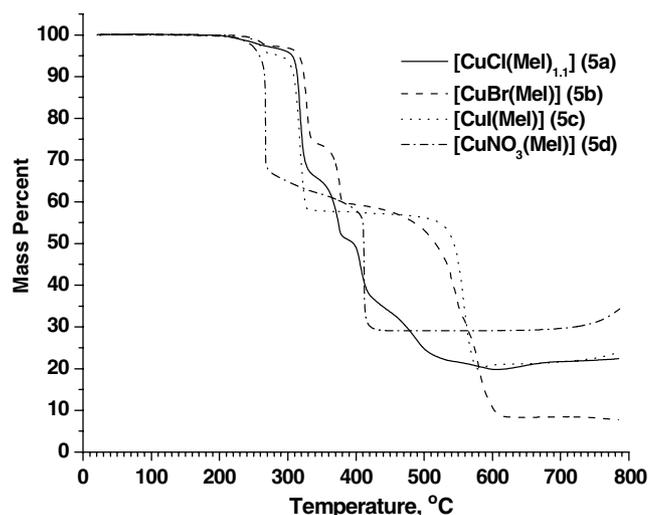


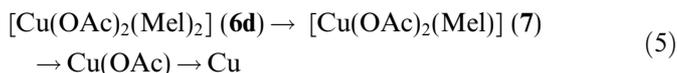
Fig. 3. TGA traces for the Cu(I)-melamine compounds (5).



The behavior of the copper (I) bromide sample **5b** was similar to that of the **5a**, with the notable exception that there is no evidence of a [(CuBr)₄(Mel)] phase. In addition, the residual CuBr undergoes sublimation to a greater extent, leaving little final residue at high temperature. Nevertheless, the onset of decomposition for the analogous CuCl- and CuBr-derived materials is similar. In contrast

to the behavior of the chloride and bromide complexes, **5c** and **5d** fail to show evidence of any more copper-rich phases, see Fig. 3. Consistent with this observation is the fact that no copper-rich CuI or CuNO₃ materials could be synthesized. Reductive elimination (Eq. (4)) is favored for the iodide and nitrate, the residual mass corresponding closely to the original copper content of the samples.

The copper (II) complexes exhibited somewhat more complicated decomposition behavior (see Fig. 4). The [CuCl₂(Mel)₂] complexes (**6a** and **6b**) underwent the loss of solvent and melamine to give CuCl₂, which then reduced to copper in a complicated series of steps. The TGA traces showed only slight inflections during the loss of melamine. In contrast to this behavior, the bromide **6c** trace presented several possible intermediates during the loss of melamine. The most significant plateau corresponded to a possible formula [(CuBr₂)₂(Mel)]. Following this possible intermediate, an inflection corresponding to CuBr₂ was noted, followed by a series of steps ending with copper metal. The two Cu(OAc)₂-melamine complexes appear to undergo a series of decomposition steps that are summed up in the following equation:



3.4. Infrared analysis

The IR spectrum of melamine has long been known and has been reinterpreted fairly recently [13,14]. The IR spectrum of melamine consists of three principal absorption regions. The 2800–3500 cm⁻¹ region encompasses the N–H stretching modes, the sharp higher frequency bands corresponding to non-hydrogen bonded N–H and the broad lower frequency bands representing hydrogen bonded N–H. The 1440–1650 cm⁻¹ region contains ring distortion, N–H bending, and two complex

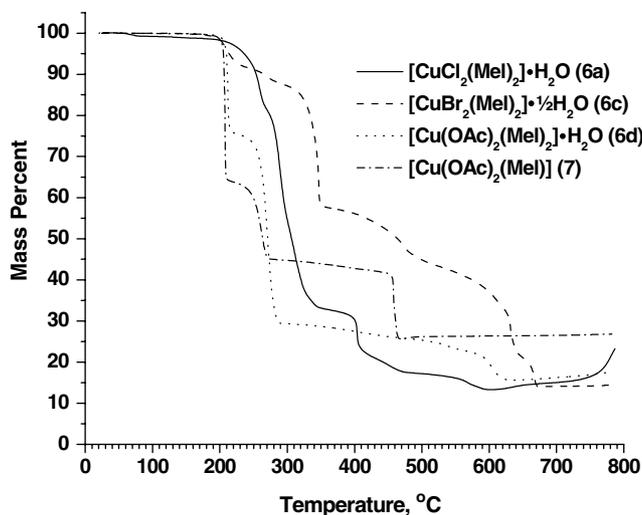


Fig. 4. TGA traces for the Cu(II)-melamine compounds (6 and 7).

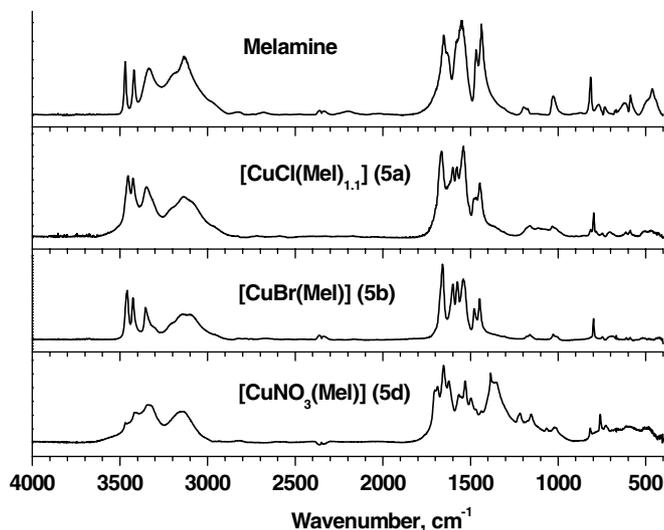


Fig. 5. IR spectra for Cu(I)-melamine compounds (5).

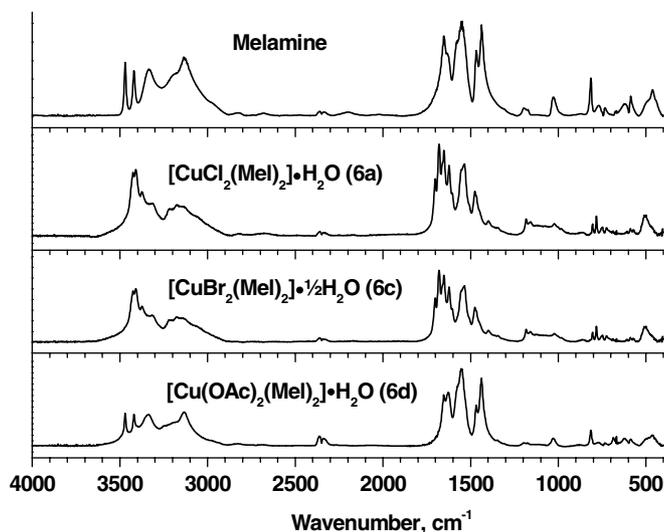


Fig. 6. IR spectra for Cu(II)-melamine compounds (6 and 7).

molecular modes. The 800–1050 cm^{-1} region contains two additional complex molecular modes. The spectrum of melamine is compared with those of the copper-melamine

complexes in Figs. 5 and 6 and in Table 2. The band identities are adapted from the literature [14] and are interpreted under D_{3h} symmetry.

Several trends can be noted from examination of the data. All of the copper complexes retain both free and hydrogen bonded N–H stretching bands. Relative to melamine, the Cu(I)-melamine complexes' two free amine bands tend to move closer to one another in frequency, while the hydrogen bonded amine bands shift to higher frequencies. The Cu(II) complexes show a primarily downward shift in N–H stretching frequency. The fact that all of the copper-melamine products, with the exception of the acetate complexes (see below), show changes in the N–H stretching region is consistent with the lack of color in these complexes in suggesting amine, rather than triazine, coordination.

In the N–H stretching region, and throughout the IR spectrum, the $\text{Cu}(\text{OAc})_2$ -melamine complexes **6d** and **7** show almost no differences from melamine itself. This result possibly indicates little or no melamine coordination with copper, possibly due to the presence of the chelating acetate anion. Two hydrogen bonded hybrid networks between melamine and $\text{Cu}(\text{PyHy})_2$ and $\text{Cu}(\text{H}_2\text{NTA})\text{Cl}$ [PyHy = 5-(2-pyridylmethylene)hydantoin and H_2NTA = dihydrogen nitrilotriacetate] have been characterized previously [5], representing precedent for non-coordinating metal-melamine network formation.

The E' ring distortion IR band is blue shifted for all of the Cu complexes except **5c**, **6b** and the aforementioned acetate complexes. This shift suggests an increase in ring rigidity, perhaps due to increased network interaction. Removal of E' band degeneracy is evident in many of the Cu compound spectra. This removal of degeneracy is even more evident in the N–H bending bands. Once again, it is noteworthy that the acetate complexes show neither splitting nor shifting of these bending bands. Upon coordination there is a consistent red shift of the A'_1 symmetrical bending mode (1626 cm^{-1} for melamine). The four low frequency bands (1468, 1436, 1027, and 814 cm^{-1} for melamine) show fairly consistent trends in their coordination shifts: the 1468 cm^{-1} band shows blue shifts, 1436 cm^{-1}

Table 2
IR data for melamine and copper-melamine complexes^{a,b}

Compound	Free N–H	Hydrogen bonded N–H	E' ring distortion	A'_1 and E' N–H bending	E' and A'_1 modes	E' mode	A''_2 mode	
Melamine	3470, 3420	3334, 3187, 3137	1651	1626 1553	1468 1436	1027	814	
5a	3454, 3426	3348, 3199, 3137	1664	1601 1577, 1540	1467 1447	1031	797	
5b	3459, 3425	3352, 3195, 3140	1659	1600 1575, 1541	1477 1448	1028	798	
5c	3462, 3424	3355, 3195, 3134	1651	1604 1570, 1540	1472 1449	1018	799	
5d	3469, 3408	3326, 3145	1703, 1688, 1653	1623 1566, 1530	1498	Obscured	1020	816
6a	3425, 3410, 3373	3312, 3177	1702, 1680, 1652	1622 1561, 1535	1475	1023	804, 782	
6b	Obscured	3331, 3157	1651	1540	1474	1017	801, 783	
6c	3425, 3410, 3373	3312, 3214, 3171	1702, 1680, 1652	1622 1535	1475	1020	804, 781	
6d	3470, 3410	3337, 3249, 3191, 3133	1653	1627 1553	1468 1437	1028	814	
7	3470, 3420	3353, 3244, 3137	1651	1626 1553	1467 1437	1031	813	

^a All data in cm^{-1} .

^b See [13] for more detailed melamine band assignments.

shows blue shifts for Cu(I) products, and 1027 and 814 cm^{-1} bands show red shifts. No splitting of these bands is evident. Given the vibrational complexity of the underlying modes, the trends for these low frequency bands are difficult to interpret.

4. Conclusion

Melamine has been shown to act as a ligand for both Cu(I) and Cu(II) salts. The resulting insoluble networks reveal 1:1 metal salt:melamine stoichiometry for Cu(I), with the exception of CuCl, which forms $[\text{CuCl}(\text{Mel})_{1.1-1.3}]$. In addition 2:1 complexes were realized for CuCl and CuBr. For Cu(II) salts 1:2 stoichiometry was favored. Only $\text{Cu}(\text{OAc})_2$ produced a 1:1 compound. Thermogravimetric analysis results suggested step-wise removal of melamine for the CuCl and CuBr complexes. Infrared analysis reveals modest shifts and symmetry removal in the complexes, with the possible exception of the $\text{Cu}(\text{OAc})_2$ products. It is possible that the latter materials are composed of separate $\text{Cu}(\text{OAc})_2$ and melamine networks, probably associated through hydrogen bonds. Lack of Cu(I) charge transfer color and analysis of IR data suggest melamine coordination occurs through amine groups.

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