Table I. Selected Bond Lengths in $(C_4H_4N_2)Ru_3(CO)_{10}$[a]

Ru1-Ru2	2.743 (4)	Ru2-C8	2.16 (3)
Ru2-Ru3	2.859 (4)	Ru2-C9	2.06 (3)
Ru1-Ru3	2.857 (4)	Ru3-C9	2.15 (3)
Ru-C (av)	1.88[b]	Ru1-C10	2.07 (3)
Ru1-C8	2.08 (3)	Ru3-C10	2.20 (3)

[a] Bond lengths in Å. [b] Terminal carbonyls.

groups trans to the N atoms are not parallel and the bridging CO group, C8O8, is tilted out of the Ru_3 plane. Also Ru1-Ru2 is ~0.12 Å shorter than the other two Ru-Ru distances, which differ negligibly from those[11] in $Ru_3(CO)_{12}$ itself (2.849, 2.859, 2.837, each ±0.006). The expected mirror plane through Ru3 and perpendicularly bisecting the Ru1-Ru2 bond is violated by asymmetry in the bridging CO groups, for each of which the Ru-C distances differ by an average of 0.10 Å. The pattern of these deviations (both bonds to Ru1 are short, both to Ru3 are long) is inconsistent with the potential mirror symmetry nor does it seem to have any rationale in terms of electronic factors, as does the occurrence of unsymmetrical bridges in certain other cases.[1] Tentatively, we regard the asymmetry of the bridges as being at least partly a result of packing forces. It is possible that in the ideal structure (i.e., the one determined only by internal factors) the two Ru3-Ru1 and Ru3-Ru2 bridges might have the intrinsic asymmetry observed due to the different electron densities and different steric factors at Ru1 and Ru2 as compared to Ru3. However, the asymmetry of the bridge across Ru1 and Ru2 would then have to be attributed to extrinsic factors such as intermolecular contacts. One must, then, also recognize that if one such distortion could be of extrinsic origin, then so might all three. The molecule appears to retain its basic structure, perhaps undistorted, in solution since the infrared spectrum in THF shows at least five terminal bands (2083, 2035, 2003, 1998, and 1964 cm^{-1}) and a broad band at 1820 cm^{-1} with intensity ratios consistent with terminal and bridging groups in a 7:3 ratio. Further studies, especially by NMR are being conducted.[19]

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(13) This kind of situation has previously been considered for $Rh_4(CO)_{12}$ and $Co_4(CO)_{12}$, where a structure with four bridges and D_{2d} symmetry[14] may be (and, we believe, is) thermally accessible, but has not been positively observed spectroscopically, and need not necessarily be postulated to explain the observed CO scrambling.[15,16]
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(17) This structure is different from one with three edge bridges and C_{3v} symmetry previously proposed by Wei and Dahl[9] as "the instantaneous structure of the $(Fe_3(CO)_{12})$ molecule in solution." For reasons detailed elsewhere,[3] we do not agree that this proposal satisfactorily explains the ir spectra of solutions and we have proposed a quite different concept (that of fictile character) which, in our opinion, does account for all the experimental data.[3]
(18) The compound crystallizes in space group $P\bar{1}$ with the following unit cell dimensions: $a = 9.272$ (2) Å, $b = 13.727$ (2) Å, $c = 8.973$ (1) Å; $\alpha = 103.44$ (1)°, $\beta = 120.53$ (1)°, $\gamma = 90.01$ (1)°; $Z = 2$; 2304 reflections, Mo radiation, having $2\theta < 45°$ and $I_0 > 3\sigma(I_0)$; $R_1 = 0.061$, $R_2 = 0.091$.

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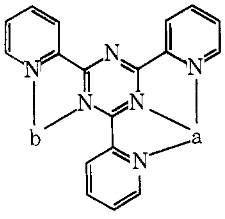
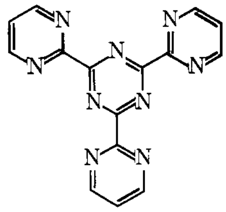
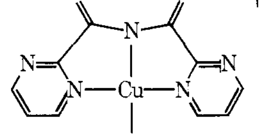
2,4,6-Tris(2-pyrimidyl)- and 2,4,6-Tris(2-pyridyl)-1,3,5-triazines Hydrolyze in the Presence of Copper(II) to Form a Novel Bis(aryl)carboximidato Chelate Complex

Sir:

The ligand 2,4,6-tris(2-pyridyl)-1,3,5-triazine, TPyT, has been used analytically in the spectrophotometric determination of iron,[1] ruthenium,[2] and cobalt.[3] Several transition metal and lanthanide complexes of this ligand have been studied,[4-15] the possibility of coordinating metals in both the (a) terpyridine- and (b) bipyridine-like sites being of particular interest.[11-15] The ligand 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine, TPymT, has the potential to coordinate three metal ions in terpyridine-like sites, but has not been extensively studied because of its unavailability.[16,17] In the present report we describe an improved synthesis of TPymT and its reaction with copper(II). Copper promotes hydrolysis of the ligand and forms a novel bis(2-pyrimidyl)carboximidato chelate complex, shown below. This chemistry is also found to occur with TPyT and with other metal ions, knowledge of which is important in conjunction with studies of the coordination properies and with analytical applications of these triazine ligands.







2-Cyanopyrimidine was synthesized by literature methods[18,19] (mp 40-41.5°, lit.[17] 41-42°). This pyrimidine (5.5 g, 0.052 mol) was heated with stirring in a stoppered flask at 150° for 48 h. The solidified product was then pulverized and washed with ether to remove any unreacted starting material. The yield of crude TPymT was 4.6 g (83.6%). Purification was achieved by dissolving 8.0 g of crude product in 150 ml of 6 N HCl, decolorizing with activated charcoal, precipitating the hy-

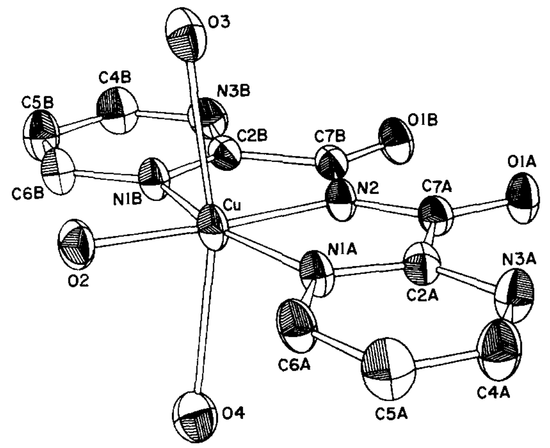


Figure 1. Structure of the bis(2-pyrimidyl)carboximidatotriaquocopper(II) complex showing the 50% probability thermal ellipsoids. Selected bond distances (in Å): Cu-N1A, 2.016 (3); Cu-N1B, 2.002 (3); Cu-N2, 1.938 (3); Cu-O2, 1.973 (3); Cu-O3, 2.522 (2); Cu-O4, 2.487 (2); interbond angles (in degrees): N1A-Cu-N2, 82.1 (1); N1B-Cu-N2, 81.5 (1); O2-Cu-N2, 173.7 (1); O2-Cu-O3, 80.2 (1); O2-Cu-O4, 85.5 (1); O3-Cu-O4, 165.7 (1). Hydrogen atoms are not shown.

drochloride salt with acetone, and freeing the triazine by dissolution of the salt in 50 ml of concentrated NH_4OH from which the product precipitated in 65% yield (5.2 g). The structure and purity were established by the mass spectrum (parent ion, 315), proton NMR spectrum (doublet, 9.57 ppm, 2 H; triplet, 8.39 ppm, 1 H; from internal DSS in an approximately 3 M DCl solution), and infrared spectrum (pyrimidine modes, no N-H or carbonyl bands).

The coordination chemistry of the TPymT ligand is currently under investigation. Preliminary results indicate that it is possible, in certain cases, for the ligand to bind more than one metal, for example, two lead atoms.[20] An interesting reaction was observed with divalent copper. When TPymT (0.105 g, 0.33 mmol) was shaken with a 15-ml aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.242 g, 1 mmol), a green colored solution formed (copper(II) terpyridine complexes are green[21]) that turned blue-green within several hours and finally became blue overnight. Slow evaporation of solvent yielded blue, needle-like crystals, the infrared spectrum of which showed a carbonyl band at 1726 cm^{-1}. Analytical[22] and x-ray crystallographic data established the compound to be bis(2-pyrimidyl)carboximidatotriaquocopper(II) nitrate dihydrate, $\{[(C_4H_3N_2CO)_2N]Cu(OH_2)_3\}(NO_3) \cdot 2H_2O$.

The complex crystallizes in the triclinic system, space group $P\bar{1}$, with two formulas in the reduced unit cell having the following dimensions: $a = 13.626$ (3), $b = 6.512$ (1), $c = 10.497$ (2) Å; $\alpha = 101.48$ (1), $\beta = 109.32$ (1), $\gamma = 94.83$ (1)°; $\rho_{\text{calcd}} = 1.734$, $\rho_{\text{obsd}} = 1.732$ (7) g/cm^3. The structure, shown in Figure 1, was determined by the heavy atom method using 3385 independent reflections ($2\theta < 55°$, $F_o^2 > 3\sigma(F_o^2)$) collected on a four-circle automated diffractometer at 24° using monochromatized Mo Kα radiation. Refinement by full-matrix least-squares methods is currently at a value of 0.043 for the conventional agreement factor $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. Details will be reported elsewhere.

The copper promoted hydrolysis of TPymT to form the bis(2-pyrimidyl)carboximidatotriaquocopper(II) chelate complex (Figure 1) also occurs with the pyridine analogue, TPyT. When 0.312 g (1 mmol) of TPyT was shaken with 0.724 g (3 mmol) of $Cu(NO_3)_2 \cdot 3H_2O$ in 20 ml of water, a green solution formed that turned blue overnight. Evaporation of solvent produced blue needles having a 1710-cm^{-1} infrared band of an imide group. Chemical analysis of a sample dried to constant weight showed the compound to be bis(2-pyridyl)carboximidatocopper(II) nitrate.[23] To our knowledge, neither of these bis(aryl)carboximidato ligands, alternatively named as bis(arylcarbonyl)aminato derivatives, has been previously prepared. The hydrolytic reaction of the corresponding triazine in the presence of copper(II) affords a good method of obtaining them.

Alkyl and aryl substituted triazines are known to hydrolyze,[24] but these reactions generally require vigorous conditions.[25] This report shows that cupric ion promotes the hydrolysis, and preliminary infrared spectral evidence indicates that other metal ions do the same. The TPyT molecule is hydrolyzed by stirring it with cobalt(II) in cold water for a period of 24 h (ir band at 1735 cm^{-1}, ν_{CO}), boiling it for 30 min in water with $PdCl_2$ (ν_{CO}, 1725 cm^{-1}), or refluxing it for several hours with K_2PtCl_4 in water (ν_{CO} 1730 cm^{-1}). These hydrolytic reactions most likely resemble those of the unmetalated triazines, since the other product isolated from the reaction of copper(II) with TPyT was the expected picolinamide (mass spectrum parent ion, 122).[26]

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(23) Calcd for $C_{12}H_8N_4O_5Cu$: C, 40.97; H, 2.29; N, 15.93. Found: C, 41.00; H, 2.29; N, 16.27. From the weight lost upon drying it appears that there were 4.5 H_2O molecules per copper atom in the crystal: calcd wt loss, 18.73%; found: 18.73%

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