

PREPARATION AND CHARACTERIZATION OF 2-(METHYLAMINO) PYRIDINE COMPLEX OF Cu(I)

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ABSTRACT : 2-(Methylamino) pyridine (HMAP) reacts with MeLi in THF and generates the lithium salt (LiMAP). Further reaction of $[Cu(TMEDA)_2][CuCl_2]$ (TMEDA = tetramethylethylenediamine) with one equivalent of this ligand in THF leads to the formation of a yellow dimeric Cu(I) complex, $[Cu(MAP)]_2$. Analytical data, molecular weight, and magnetic susceptibility measurements, confirm the formula $[Cu(MAP)]_2$.

KEY WORDS : Preparation, Characterization, Cu(I) Complex, 2-(Methylamino) pyridine.

INTRODUCTION :

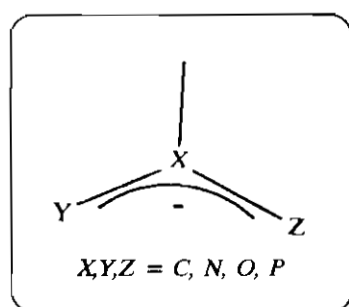
The coordination chemistry of copper(I) has been studied extensively in recent years and a multiplicity of stoichiometries has been observed. Copper(I) complexes show a variety of coordination environments ranging in coordination number from two to five in monomeric species [1-11]. Copper(I) stereochemistry is dictated by steric and electron effects of the ligand [1,12-14]. The use of the bulky ligands have permitted the isolation of a number of crystalline two-coordinate metal complexes [1, 13-16]. The number of ligands bound to the univalent metal such as Cu(I) seems to be

influenced greatly both by the chemical nature of the ligands and the geometry they impose. The three center anionic chelating ligands have a remarkable ability for enforcing dimeric, trimeric, tetrameric, and hexameric aggregation, and short metal-metal contacts in some cases [17-25]. Penta-, Octa- and dodecanuclear copper(I) complexes are unusual [26-28]. Several infinite- sheet,- chain, and - layer copper(I) complex polymers have been investigated by the X-ray and neutron diffraction methods [29-32]. Copper(I), but not copper(II), forms a variety of compounds with Cu-C bonds [6,7,19,22,24,25].

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Very short metal-metal bonds have also been found in the chemistry of divalent transition metals in the presence of two or more anionic bridging ligands which have the characteristic three-center chelating geometry and the four pi electron configuration of an allylic system (scheme 1) [33-35].



Scheme (1)

Copper(I) chloride is the best starting material for the preparation of the most Cu(I) complexes. In some cases such as Cu(I) amido complexes, CuCl disproportionates to Cu(0) and CuCl₂. Therefore, the best candidate for the preparation of these complexes is CuCl in the presence of N, N, N', N' - tetramethylethylenediamine[36]. Reaction of [Cu(TMEDA)₂][CuCl₂] or CuCl with a series of bidentate amides possessing a three center chelating geometry has resulted in the formation of dinuclear complexes [37,38]. In this research project, complex of MAP[MAP=2-(methylamino)pyridine] with [Cu(TMEDA)₂][CuCl₂] has been prepared and investigated.

EXPERIMENTAL :

All manipulations were carried out under a purified nitrogen atmosphere in a Schlenk apparatus. All solvents and N, N, N', N' - tetramethylethylenediamine, TMEDA, were dried and distilled by standard methods before using. Infrared spectra were recorded on a Perkin-Elmer 393 instrument from Nujol mull prepared in a dry-box. Elemental analyses were performed with an elemental analyzer CHN-O-RAPID, Heraeus and an atomic absorption, 2830, Perkin-Elmer. Samples for

magnetic susceptibility measurements were sealed in calibrated tube inside a dry-box. Measurements were carried out at room temperature using a Guoy balance (Johnson-Mathey). Magnetic moments were calculated by following standard methods [39], and corrections for underlying diamagnetism were applied to the data [40]. Molecular weight determined in benzene by cryoscopic molecular weight measurements.

Preparation of CuCl

Into a warm solution of copper sulfate, CuSO₄ · 5H₂O (25.00g, 0.10mol) and sodium chloride (12.00g., 0.20mol) in 70mL of water, contained in a flask, sulfur dioxide was passed, while the solution was stirred continually. The originally clear green solution immediately darkened and soon became opaque, while colorless crystals of cuprous chloride accumulated. After cooling to room temperature, the white crystals were filtered by isolation filter under nitrogen atmosphere, and washed by aqueous sulfur dioxide and then absolute ethanol. The solid was dried and stored under nitrogen in sealed ampoules (yield ≈75%).

Preparation of [Cu(TMEDA)₂][CuCl₂]

The complex was prepared by the reaction of tetramethylethylenediamine in THF with CuCl. A 0.10mole of CuCl was suspended in THF (100mL) containing 0.10mole TMEDA under nitrogen atmosphere. After a few minutes of stirring at boiling point of THF, a clear colorless solution was obtained. By cooling down the hot solution very slowly, large white crystals were formed which were suitable for X-ray crystallography. The product was then identified by single-crystal X-ray diffraction [36]. The complex was found to be diamagnetic, air and moisture sensitive, and white in color which is not surprising for Cu(I) complexes. Magnetic measurement: $\mu_{\text{eff}}=0$.

IR(Nujol mull, KBr, cm⁻¹):

[Nujol: 3000-2860(vs), 1455(s), 1375(s), 1345(w, sh)].

[Cu(TMEDA)₂][CuCl₂]: 1410(w), 1360(s), 1290(vs), 1255(s), 1195(m), 1170(s), 1135(s), 1105(m), 1070(m), 1055(w), 1035(s), 1015(s), 965(vs), 810(m), 800(vs), 780(s), 600(m), 480(m), 450(s), 410(s).

Preparation of [Cu(MAP)]₂

To a stirred 100mL THF solution of dry 2-(methylamino) pyridine (4.00g, 36.98mmol) was added an equivalent of MeLi (0.812g, 21.7mL, 1.7M, 36.96mmol, 50% in diethyl ether) at ≈40°C. The mixture was stirred and allowed to warm slowly to ambient temperature (1h). To this solution was added an equivalent of Cu(I) in the form of [Cu(TMEDA)₂][CuCl₂] [7.95g, 18.49mmol] producing a yellow microcrystalline compound. The solid was dried and stored under nitrogen in sealed ampoules (yield ≈55%). Elemental analysis, molecular weight, and magnetic susceptibility measurements confirm the formula [Cu(MAP)]₂.

Magnetic measurement: $\mu_{\text{eff}}=0$

IR(Nujol mull, KBr, cm⁻¹):

[Nujol: 3000-2860(vs), 1455(s), 1375(s), 1345(w, sh)].

[Cu(MAP)]₂: 1610(s), 1532(w), 1490(s), 1402(s), 1290(s), 1270(m), 1170(m), 1122(w), 1060(m), 1005(m), 840(vw), 815(w), 750(s, Cu-N stretch), 722(m), 653(vw), 638(vw).

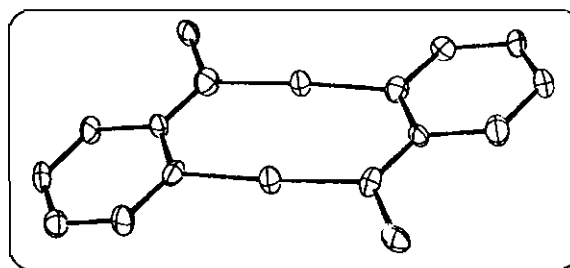
Anal. Calcd (found) for C₁₂H₁₄N₄Cu₂: C, 42.22 (42.28); H, 4.14(4.10); N, 16.42(16.32); Cu, 37.23 (37.35).

M.W. Calcd (found): 341.36 (336.9) [Cryoscopy in cyclohexane].

RESULTS AND DISCUSSION :

Copper(I) compounds are diamagnetic and colorless, except when the anion present is colored or when charge-transfer absorption takes place in the visible region of the spectrum. The Cu...Cu distances are 2.456(2)Å and 2.447(2)Å in [Cu(BAP)]₂·H₂O and [Cu(DPT)]₂ complexes respectively which are shorter than that of metallic copper (2.56Å). (HDPT= 1,3-Diphenyltriazene) [37,38]. 2-(methylamino) pyridine (HMAP) reacts with MeLi in THF and

generates lithium salt (LiMAP). Further reaction of [Cu(TMEDA)₂][CuCl₂] with an equivalent (Cu/ligand: 1eq/1eq) of LiMAP in THF leads to the formation of a yellow microcrystalline compound. Elemental analysis, molecular weight, and magnetic susceptibility measurements, confirm the dimer or dinuclear Cu(I) complex, [Cu(MAP)]₂. The complex is diamagnetic and geometry of each Cu atom probably is nearly linear (scheme II):



Scheme (II)

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