

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

5.1. Conclusions

Copper(II) alkylcarboxylates, $[\text{Cu}_2(\text{C}_n\text{H}_{2n+1}\text{COO})_4]$ ($n = 6, 7, 9, 11, 13, 15$) and $[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_7\text{CH}((\text{CH}_2)_5\text{CH}_3)\text{COO})_4]$, reacted with cyclam to give ionic mononuclear complexes in good yields (53 – 81%). The chemical formulas of these complexes are shown in **Table 5.1**.

Table 5.1 Chemical formula of copper(II) alkylcarboxylate-cyclam complex

Complex	Chemical Formula
1	$[\text{Cu}(\text{C}_{10}\text{H}_{24}\text{N}_4)(\text{H}_2\text{O})_2](\text{CH}_3(\text{CH}_2)_5\text{COO})_2 \cdot 2\text{H}_2\text{O}$
2	$[\text{Cu}(\text{C}_{10}\text{H}_{24}\text{N}_4)(\text{H}_2\text{O})_2](\text{CH}_3(\text{CH}_2)_6\text{COO})_2 \cdot 7\text{H}_2\text{O}$
3	$[\text{Cu}(\text{C}_{10}\text{H}_{24}\text{N}_4)(\text{H}_2\text{O})_2](\text{CH}_3(\text{CH}_2)_8\text{COO})_2 \cdot 2\text{H}_2\text{O}$
4	$[\text{Cu}(\text{C}_{10}\text{H}_{24}\text{N}_4)(\text{H}_2\text{O})_2](\text{CH}_3(\text{CH}_2)_{10}\text{COO})_2 \cdot 2\text{H}_2\text{O}$
5	$[\text{Cu}(\text{C}_{10}\text{H}_{24}\text{N}_4)(\text{H}_2\text{O})_2](\text{CH}_3(\text{CH}_2)_{12}\text{COO})_2 \cdot 2\text{H}_2\text{O}$
6	$[\text{Cu}(\text{C}_{10}\text{H}_{24}\text{N}_4)(\text{H}_2\text{O})_2](\text{CH}_3(\text{CH}_2)_{14}\text{COO})_2 \cdot 2\text{H}_2\text{O}$
7	$[\text{Cu}(\text{C}_{10}\text{H}_{24}\text{N}_4)(\text{H}_2\text{O})_2](\text{CH}_3(\text{CH}_2)_7\text{CH}((\text{CH}_2)_5\text{CH}_3)\text{COO})_2 \cdot 5\text{C}_2\text{H}_5\text{OH}$

All of the above complexes, except **1**, crystallized in the triclinic lattice in *P*-1 space group. Complex **1** was spatially arrayed in monoclinic polymorph in *P*2₁/*c* space group.

Comparative studies on complexes **1** and **6** (representing the other copper(II) alkylcarboxylate-cyclam complexes) revealed that **1** showed an antiferromagnetic interaction between the Cu(II) centres ($\mu_{\text{eff}} = 1.43$ BM), was thermally stable ($T_{\text{dec}} = 229.8$ °C), but did not have mesogenic properties.

In contrast, **6** did not show any magnetic interaction between the Cu(II) centres ($\mu_{\text{eff}} = 1.79$ BM), has a higher thermal stability ($T_{\text{dec}} = 264.6$ °C), and has mesogenic properties.

Copper(II) arylcarboxylates, $[\text{Cu}_2(p\text{-XC}_6\text{H}_4\text{COO})_4]$ ($X = \text{NH}_2, \text{OH}, \text{OCH}_3, \text{CH}_3, \text{C}\equiv\text{N}, \text{H}$) and $[\text{Cu}_2(\text{C}_6\text{F}_5\text{COO})_4]$, reacted with cyclam to give either covalent or ionic mononuclear complexes in fairly good yields (24 – 67%). The chemical formulas of these complexes are shown in **Table 5.2**.

Table 5.2 Chemical formula of copper(II) arylcarboxylate-cyclam complex

Complex	Chemical Formula
8	$[\text{Cu}(p\text{-H}_2\text{NC}_6\text{H}_4\text{COO})_2(\text{C}_{10}\text{H}_{24}\text{N}_4)].2\text{H}_2\text{O}$
9	$[\text{Cu}(p\text{-HOC}_6\text{H}_4\text{COO})_2(\text{C}_{10}\text{H}_{24}\text{N}_4)]$
10	$[\text{Cu}(\text{C}_{10}\text{H}_{24}\text{N}_4)(\text{H}_2\text{O})_2](p\text{-CH}_3\text{OC}_6\text{H}_4\text{COO})_2.2\text{H}_2\text{O}$
11	$[\text{Cu}(\text{C}_{10}\text{H}_{24}\text{N}_4)(\text{H}_2\text{O})_2](p\text{-CH}_3\text{C}_6\text{H}_4\text{COO})_2.\text{H}_2\text{O}$
12	$[\text{Cu}(p\text{-N}\equiv\text{CC}_6\text{H}_4\text{COO})(\text{C}_{10}\text{H}_{24}\text{N}_4)(\text{H}_2\text{O})](p\text{-N}\equiv\text{CC}_6\text{H}_4\text{COO}).3\text{H}_2\text{O}$
13	$[\text{Cu}(\text{C}_{10}\text{H}_{24}\text{N}_4)(\text{H}_2\text{O})_2](\text{C}_6\text{H}_5\text{COO})_2.2\text{H}_2\text{O}$
14	$[\text{Cu}(\text{C}_{10}\text{H}_{24}\text{N}_4)(\text{H}_2\text{O})_2](\text{C}_6\text{F}_5\text{COO})_2.2\text{H}_2\text{O}$

Comparative studies on **9** (representing covalent complexes), **10** (representing ionic complexes) and **12** (showing both covalent and ionic coordination modes) revealed that their magnetic properties (μ_{eff} values ~ 1.73 BM; absence of magnetic communication between the Cu(II) centres) and thermal stabilities ($T_{\text{dec}} \sim 196 - 270$ °C) were independent of the binding mode of the carboxylate group.

Molecular modelling was performed on complexes **1**, **8**, **9** and **10**, giving optimized structure, minimum energy, FTIR intensities and molecular electrostatic potential map. All theoretical calculations were in good agreement with the experimental data. The binding energies (BE) calculated for the ionic complexes (**1** and

10) were significantly more exothermic than their simulated covalent state. The BE values calculated for the covalent complexes (**8** and **9**) were also in favour to the actual covalent state.

5.2. Suggestions for future work

The crystal structures of all ionic complexes showed that the Cu(II) axial positions were weakly coordinated by H₂O molecules. Hence, it was of interest to attempt to link the magnetic centres to form equally spaced magnetic chain compounds as molecular magnetic materials. A suitable linker is 4,4'-bipyridine as Cu(II) has shown a strong preference for N-donor ligands.

Also, the ionic copper(II) arylcarboxylate-cyclam complexes may be reacted with a suitable N-donor neutral ligand carrying a long alkyl/alkyloxy chain, and the mesogenic properties investigated.

The reaction may be extended to [Cu₂(C_nH_{2n+1}COO)₄] (*n* = even numbers) and [Cu₂(*p*-XC₆H₄COO)₄] (*X* = halogen) in order to investigate the effect of odd-numbered carbon chains and electronic effect of the halogens on the structure and other properties, respectively.

Similar studies may be done by replacing Cu(II) with other first row transition metal(II) ions, especially Co(II) and Fe(II), to form spin-crossover complexes. Spin-crossover complexes are being studied for applications as molecular switches, thermal sensors and in information storage devices [1,2].

The molecular modelling calculation could also be improvised using a higher order computational method such as DFT-B3LYP.

References

- [1] Krivokapic, I., Zerara, M., Daku, M. L., Vargas, A., Enachescu, C., Ambrus, C., Tregenna-Piggot, P., Amstutz, N., Krausz, E., Hauser, A. *Coord. Chem. Rev.* (2007) 251, 364-378.
- [2] Olguin, J., Brooker, S. *Coord. Chem. Rev.* (2011) 255, 203-240.