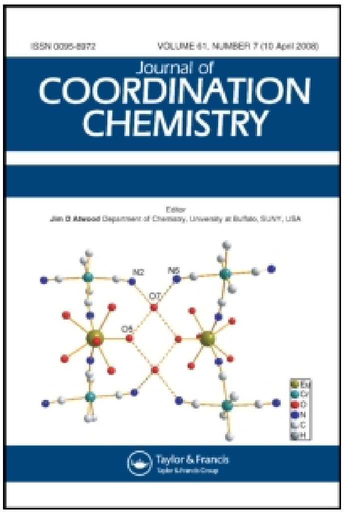

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Cu(II) AND Cu(I) COMPLEXES OF A MACROCYCLIC TETRATHIOETHER-INFLUENCE OF THE ANION ON STRUCTURE

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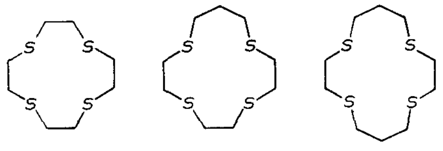
The macrocycle S_4-propano [16] (1,3,5,9-13-tetrathiacyclohexadecane) acts as a tetradentate ligand with copper(I) and copper(II) tetrafluoroborate but as two bidentate ligands in the presence of chloride.

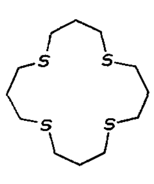
INTRODUCTION

Recently, several studies of tetradentate, macrocyclic, sulfur ligands including 1,4,7,10-tetrathiacyclododecane, TTC(I); 1,4,7,10-tetrathiacyclotridecane, TTE(II); and 1,4,8,11-tetrathiatetradecane, TTP(III), having 12, 13, and 14-membered rings, respectively, and their complexes with Ni(II), Fe(II), Co(III) and Rh(III) have been reported.[2,3,4,5,6] However, since copper complexes of these ligands had not been reported, we synthesized the macrocycle 1,5,9,13-tetrathiacyclohexadecane, to be referred to by the trivial name S_4-propano [16] [7], (IV) and examined the complexes which it forms with copper(II) salts.



I II III

FIGURE 1



IV

FIGURE 2

EXPERIMENTAL

Preparation of S_4-propano [16] (IV)

A solution of sodium ethoxide was prepared by dissolving 12.0 g (0.522 g-atom) of sodium in 750 ml ethanol. To this solution, separate solutions of 25.1 ml (0.250 mol) of 1,3-propanedithiol in 24.9 ml ethanol and 25.3 ml (0.250 mol) of 1,3-dibromopropane in 24.7 ml ethanol were added simultaneously *via* a syringe pump at 0.15 ml/min. After the addition of 5 ml of each solution, the addition rate was changed to 0.092 ml/min. After 6.5 hours, the addition was complete and the solution was refluxed for 30 minutes and allowed to stand under nitrogen at room temperature overnight. The reaction flask was fitted with a distillation head and the solvent was distilled off under reduced pressure until 125 ml remained. An equal volume of ether was added and the suspension filtered through a bed of Celite covered with a layer of activated charcoal. The filtrate was concentrated to a volume of about 50 ml, placed on a 50 x 3 cm silica gel column and eluted with 30–60° petroleum ether, 1:1 ether–petroleum ether, then ether. Distillation of the combined petroleum ether fractions, keeping the pot temperature below 90°C, yielded 13.6 g (0.092 mmol) 1,5-dithiacyclooctane, or S_2-propano [8], (V) (27.1%) b.p. 53–59°C at 0.025–0.070 torr[8]. The residue from the distillation was crystallized from ether–petroleum ether and was combined with the 1:1 ether–petroleum ether fractions from the chromatography for a total yield of 1.61 g (0.544 mmol) S_4-propano [16], (4.4%) m.p. 55–56°C (lit[7] 57.5–59°C); ir (KBr) 2840 cm^{-1}; 1420 cm^{-1} ($S-CH_2$), 730 cm^{-1} (C–S); nmr ($CDCl_3$) τ 7.12 (triplet, 16 protons, $S-CH_2$);

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τ 7.95 (heptet, 8 protons, C–CH_2–C), J = 7.0 Hz; mass spectrum m/e 296, 181, 147, 119, 115, 106.

Preparation of μ-(S_4-propano [16])-bis(dichlorocopper II)

A 296 mg (1.00 mmol) portion of S_4-propano [16] was added to a solution of 135 mg (1.01 mmol) of anhydrous copper(II) chloride in 75 ml of absolute ethanol, and the solution was allowed to stir overnight. Filtration of the solution yielded a dark blue-green precipitate. Concentration of the solution to a small volume produced a second crop. The combined precipitates were crystallized from ethanol yielding 246 mg (0.832 mmol) of μ-(S_4-propano [16])-*bis*(dichlorocopper II), (83.2%); m.p. 149–151°C (dec.), vis (ethanol) λ_{max}45 7 nm (ϵ = 2,000).

Anal: Calc. for $Cu_2(C_{12}H_{24}S_4)Cl_4$: %C, 26.50; %H, 4.25; Found: %C, 26.45; %H, 4.50.

Preparation of S_4-propano [16] copper(II) tetrafluoroborate

A solution of 253 mg (1.07 mmol) of copper(II) tetrafluoroborate in 5 ml of ethanol was added to a suspension of 275 mg (0.929 mmol) of S_4-propano [16] in 20 ml of ethanol, and the black solution was shaken for five minutes, cooled quickly in an ice bath and filtered immediately. The precipitate was taken up in 250 ml of dichloromethane, shaken at room temperature for five minutes and filtered. The filtrate was concentrated to 10 ml at reduced pressure at room temperature, and the black-red precipitate was collected and dried in *vacuo* yielding 299 mg (0.507 mmol) of S_4-propano [16] copper(II) tetrafluoroborate (54.6%).

Anal: Calc. for $Cu(C_{12}H_{24}S_4)(BF_4)_2 \cdot C_2H_5OH$; %C, 28.50; %H, 5.09; Found: %C, 28.36; %H, 4.99.

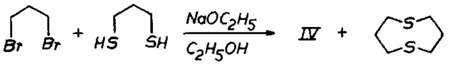
Preparation of S_4-propano [16] copper(I) tetrafluoroborate

A 60.2 mg (0.102 mmol) portion of the copper (II) tetrafluoroborate complex was dissolved in 20 ml of 1:1 ethanol-isopropanol, and the dark green solution boiled down to a few ml of bright yellow solution. Upon cooling, light yellow crystals precipitated S_4-propano [16] copper(I) tetrafluoroborate (66.3%), m.p. 253–254°C (dec.);

Anal: Calc. for $Cu(C_{12}H_{24}S_4)BF_4$; %C, 32.23; %H, 5.37; Found: %C, 32.10; %H, 5.32.

RESULTS AND DISCUSSION

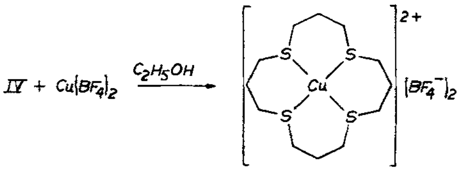
Complexes of macrocyclic tetrathioethers with several metal ions have been reported but few copper complexes have been prepared. As part of a study of metal complexes of mesocyclic dithioethers[9], we obtained an appreciable yield of the sixteen membered ring tetrathioether ligand during the synthesis of the eight membered ring dithioether(V).



V

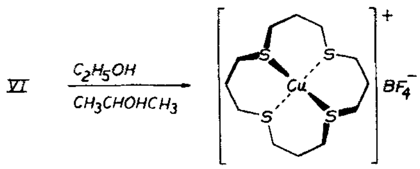
FIGURE 3

We have observed that reaction of S_4-propano [16] with copper(II) gives rise to two different products depending on the counterion. With non-coordinating anions such as ClO_4^- and BF_4^- the macrocycle functions as a tetradentate ligand and gives square planar copper(II) complexes. A similar planar structure has recently been reported for S_4-ethano-propano [14] with $Cu(ClO_4)_2$.[10] However, in the presence of coordinating ligands such as chloride, a binuclear complex is formed with the macrocycle probably functioning as two bidentate ligands by bridging two coppers rather than as a tetradentate ligand chelating one copper. Although the stoichiometry would be the same as for $Cu(S_4\text{-propano [16]})^{2+}$ and $CuCl_4^{2-}$, the complex cannot have this structure since the spectrum does not correspond to a super position of Cu(S_4-propano [16]$^{2+}$ and $CuCl_4^{2-}$ chromophores. In addition, Cu(S_4-propano [16])$^{2+}$ is unstable in the presence of moisture and protic solvents and is rapidly reduced to the Cu(I) complex.



VI

FIGURE 4



VII

FIGURE 5

In contrast, Cu_2Cl_4(S_4-propano [16]) is perfectly stable under these conditions and has properties similar to the 2,5-dithiahexane complex of $CuCl_2$.[11] Although it has not been clearly stated in the literature, it is not unusual for a polydentate ligand to function as a bridging ligand rather than a chelating ligand in the presence of certain anions. We reported that S_2-propano [8] (V) functions as a bridging ligand in Ni(dtco)$_2$Cl$_2$ but as a chelate in Ni(dtco)$_2$(BF$_4$)$_2$,[9] and Rosen and Busch have observed a bridging macrocycle in Ni_2(TTE)$_3$(BF$_4$)$_4$.[4] Thus, the "inside-out" complex formed by S_4-ethanol-propano [14] with $NbCl_5$ simply is another example of this behaviour.[10]

REFERENCES

1. Present Address: Department of Chemistry, Texas A&M University, College Station, Texas 77843.
2. W. Rosen and D. H. Busch, *Chem. Commun.*, **1969**, 148.
3. W. Rosen and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 4694 (1969).
4. W. Rosen and D. H. Busch, *Inorg. Chem.*, **9**, 262 (1970).
5. J. C. Dabrowiak, P. H. Merrell, J. A. Stone, D. H. Busch, *J. Amer. Chem. Soc.*, **95**, 6613 (1973).
6. K. Travis and D. H. Busch, *Inorg. Chem.*, **13**, 2591 (1974).
7. L. A. Ochrymowycz, C-P. Mak, and J. D. Michna, *J. Org. Chem.*, **39**, 2079 (1974).
8. J. R. Meadow and E. E. Reid, *J. Amer. Chem. Soc.*, **56**, 2177 (1944).
9. W. K. Musker and N. L. Hill, *Inorg. Chem.*, **11**, 710 (1972).
10. R. E. DiSimone and M. D. Glick, *J. Amer. Chem. Soc.*, **97**, 942 (1975).
11. C. D. Flint and M. Goodgame, *J. Chem. Soc.*, *A*, **1968**, 2178.