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Bis(isocyclam)dicopper(II) Complexes with a Linear Methylene Chain Bridge

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Abstract

New binucleating ligands, bis(isocyclam) with a linear methylene chain bridge, n-bicy (n = 2, 3, 4) and their copper(II) complexes, $Cu_2(n\text{-bicy})(ClO_4)_4 \cdot xH_2O$ and $Cu_2(n\text{-bicy})(NCS)_4 \cdot yH_2O$ have been synthesized. The magnetic moments of these complexes were normal, but the presence of magnetic coupling between copper(II) ions were clearly demonstrated by the hyperfine structure in the ESR spectra.

Introduction

During the last decade the importance of binuclear complexes has been increasingly recognized in the field of bioinorganic chemistry, since metal ions reside in proximate positions in some biological systems and are functioning cooperatively in enzymatic reactions, showing specific redox properties and oxygen carrying abilities [1]. In many such systems metal ions are not likely to be linked with rigid bridges such as those of conventional synthetic binuclear complexes, but rather linked with more flexible chains. Thus, the studies of binuclear complexes with a flexible bridge have become an attractive subject in coordination chemistry [2]. Recently, we have reported a series of dicopper(II) and dinickel(II) complexes containing two N_4-macrocycles connected with a methylene chain as shown in Fig. 1 [3, 4]. Some of these copper complexes showed a seven-lined hyperfine structure with an *A* value half of that of mononuclear complexes in the ESR spectra of frozen solution. This indicates the presence of magnetic interaction between the copper(II) centers.

In this paper we report the preparation and characterization of a series of dicopper(II) complexes containing two isocyclam rings connected with a methylene chain. Although bis(cyclam) complexes in which the two rings are directly linked to each other at the 2-carbon of the rings have been reported [5], the present complexes are the first example of a bis(saturated tetraazamacrocycle) complex with a flexible linear chain bridge. In the previous dap and dfp complexes the conjugated π-system of the rings might contribute to the stacking of the rings, giving rise to a weak magnetic interaction. Thus it is interesting to see if the present complexes exhibit a hyperfine structure demonstrating the magnetic interaction in ESR spectra as observed for the previous complexes.

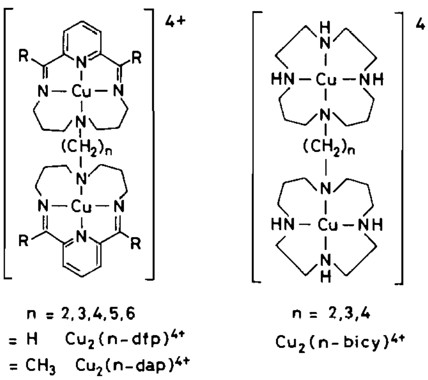

Fig. 1. dfp and bicy complexes.

Experimental

Synthesis of the Ligand

The ligand octahydrobromides, n-bicy 8HBr (n = 2 3 4), were synthesized according to scheme 1.

The procedures from the next step are described in the following for the case of n = 2.

N,N,N′,N′-tetrakis(p-tosylaminopropyl)ethylenediamine·2HCl·2H₂O (2)

The hexaamine hexahydrochloride (1) (9.2 g, 18 mmol) was added to an aqueous solution (60 ml) of sodium hydroxide (8 g, 200 mmol). To this mixture was added dropwise p-toluenesulphonyl chloride

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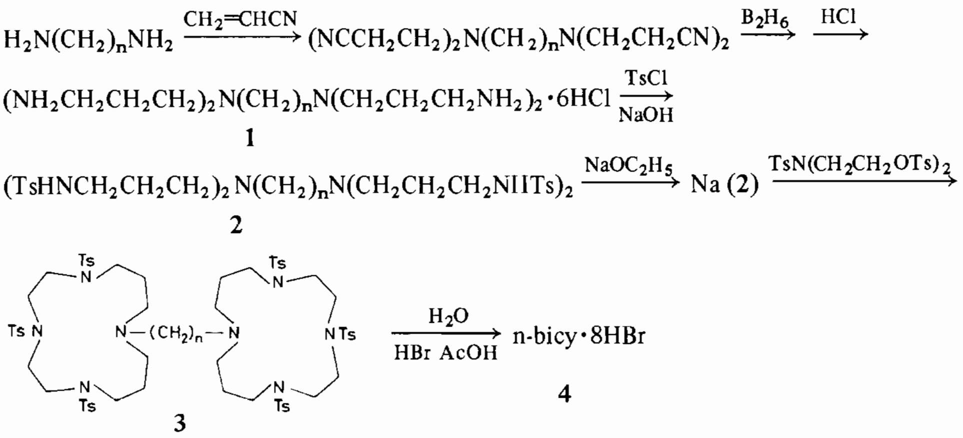

Scheme 1.

(15.4 g, 80 mmol) dissolved in 80 ml ether, with vigorous stirring during 1.5 h at room temperature. The mixture was further stirred for 2 h, and allowed to stand overnight. A white gummy solid separated and was washed with water four times, and dissolved in 100 ml of hot ethanol. The solution was filtered and acidified to pH 1 by adding concentrated hydrochloric acid to obtain white fine crystals, which were collected by filtration, washed with ethanol, and desiccated over P_2O_5. Yield 10 g (55%). The product thus obtained was used for the next step without further purification. For the purification the crude product was recrystallized from acetic acid. *Anal.* Found: C, 49.91; H, 6.53; N, 8.20%. Calcd. for $C_{42}H_{66}N_6S_4O_{10}Cl_2$: C, 49.73; H, 6.57, N, 8.29%.

1,1′-Ethylenebis(5,8,11-tri-p-tosyl-1.5,8,11-tetraazacyclotetradecane) (3)

Metallic sodium (0.75 g, 39 mmol) was dissolved in 100 ml of absolute ethanol, to which was added 5 g (5 mmol) of (2), and the mixture was stirred at 40–50 °C for 1 h, and filtered after standing for 1 h at room temperature. The resulting solid (NaCl) was washed with ethanol. The filtrate and the washings were combined and evaporated to complete dryness under reduced pressure to obtain a white gummy product (Na-2). This was dissolved in 50 ml anhydrous DMF, and heated at 110 °C. To this solution was added dropwise 5.75 g (10 mmol) of N,O,O′-tritosyl-bis(2-hydroxyethyl)amine with stirring in 3 h. Temperature of the reaction mixture was further kept at 110 °C for 2 h, and allowed to stand at room temperature for 1 h. During the all above procedures caution should be paid to exclude moisture. When DMF was removed by evaporation under reduced pressure, a reddish brown solid was obtained. This was dissolved in 200 ml of hot water, and extracted with benzene (300 ml in total) several times. The extracts were combined, dried with anhydrous sodium sulfate overnight, and filtered. When the filtrate was evaporated under reduced pressure, a reddish brown gummy solid (3) was obtained. This was used for the next step without further purification.

1,1′-Ethylenebis(1,5,8,11-tetraazacyclotetradecane)-octahydrobromide (4)

The crude product (3) was refluxed with a mixture of 100 ml of acetic acid and 100 ml of 47% HBr for 60 h. The reaction mixture was treated with active charcoal, and filtered while it was hot. The filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in water and evaporated to dryness again. A small amount of ethanol (~10 ml) was added to the residue and evaporated to dryness. This procedure was repeated. All those procedures were carried out in order to remove the excess hydrogen bromide completely. The pale brown product was dissolved in a small amount of hot water, and filtered. When ethanol was added to the filtrate and allowed to stand at room temperature, a pale brown solid precipitated. This was collected by filtration, washed with ethanol, and desiccated over P_2O_5 under vacuum. Yield, 2.4 g (36%). For the purification the product was recrystallized from water-methanol. *Anal.* Found: C, 24.73; H, 5.60; N, 10.45. Calcd. for $C_{22}H_{58}N_8Br_8$: C, 24.60; H, 5.45; N, 10.43%.

In the case of n-bicy·8HBr (n = 3 and 4), the final product was obtained as a pale yellow sticky mass, and was used for the synthesis of metal complexes.

Synthesis of Metal Complexes

$Cu_2(2\text{-bicy})(ClO_4)_4 \cdot H_2O$

The ligand octahydrobromide (322 mg, 0.3 mmol) and copper(II) chloride dihydrate (102 mg, 0.6 mmol) were dissolved in water (5 ml). An aqueous solution of silver perchlorate was added dropwise to this solution until silver holide no longer precipitated. The mixture was filtered, and the filtrate was brought to pH 9 by adding triethylamine. To this solution was added an excess of sodium perchlorate, and the mixture was evaporated by heating on a water bath until the surface became turbid. When the solution was cooled at room temperature, fine purple crystals were separated. The crystals were washed with methanol and then ether, recrystallized from water-methanol, and desiccated over P_2O_5. *Anal.* Found: C, 27.35; H, 5.26; N, 11.56; Cu, 13.1%. Calcd. for $C_{22}H_{52}N_8Cl_4O_{17}Cu_2$: C, 27.25; H, 5.41; N, 11.56; Cu, 13.1%.

$Cu_2(3\text{-bicy})(ClO_4)_4\cdot 3H_2O$

The crude ligand octahydrobromide (1.09 g) and copper(II) chloride dihydrate (0.5 g) were dissolved in water (10 ml). The solution was adjusted at *ca.* pH 9 by adding triethylamine, heated on a water bath for 10 min, and filtered after cooling to room temperature to remove excess copper as hydroxide. The blue filtrate was poured onto a short column of Sp-Sephadex C-25 (Na form), and eluted with a sodium chloride solution (0.5 mol dm^{-3}). Two separate bands, the earlier narrow and violet and the later broad and blue, were eluted. The earlier band portion was collected and evaporated to dryness under reduced pressure. To this residue was added 20 ml of ethanol to extract the complex, which was filtered. An ethanol solution of silver perchlorate was added dropwise to the filtrate until silver chloride no longer precipitated. The mixture was filtered, and the filtrate was evaporated to obtain fine violet crystals, which were collected by filtration, washed with ethanol and ether, recrystallized from water–methanol, and desiccated over P_2O_5. *Anal.* Found: C, 27.13; H, 5.64; N, 10.85; Cu, 12.3%. Calcd. for $C_{23}H_{58}N_8Cl_4O_{19}Cu_2$: C, 27.09; H, 5.73; N, 10.99; Cu, 12.46%.

$Cu_2(4\text{-bicy})(ClO_4)_4$

This was obtained by a procedure similar to that for the 3-bicy analog. *Anal.* Found: C, 29.35; H, 5.56; N, 11.19; Cu 12.9%. Calcd. for $C_{24}H_{54}N_8Cl_4O_{16}Cu_2$: C, 29.43; H, 5.56; N, 11.44; Cu, 12.97%.

$Cu_2(n\text{-bicy})(NCS)_4\cdot xH_2O$ $(n = 2, 3, 4)$

The perchlorate complex was dissolved in a small amount of hot water, and to this solution was added an excess of solid sodium thiocyanate. The mixture was heated on a water bath for 15 min. When the blue solution was allowed to stand at room temperature, blue fine crystals were formed which were collected by filtration, washed with methanol and ether, recrystallized from water–methanol, and desiccated over P_2O_5. *Anal.* Found: C, 38.00; H, 6.56; N, 20.35%. Calcd. for $C_{26}H_{54}N_{12}S_4O_2Cu_2$ ($n = 2$, $x = 2$): C, 37.98; H, 6.62; N, 20.44. Found: C, 39.12; H, 6.47; N, 20.07%. Calcd. for $C_{27}H_{55}N_{12}S_4Cu_2O_{1.5}$ ($n = 3$, $x = 1.5$): C, 40.53; H, 6.55; N, 21.01%. Found: C, 40.07; H, 6.70; N, 20.06%. Calcd. for $C_{28}H_{56}N_{12}S_4Cu_2O$ ($n = 4$, $x = 1$): C, 40.41; H, 6.78; N, 20.20%.

Elemental Analysis

The C, H, N elemental analyses were carried out at the Service Center of Elemental Analysis, Kyushu University. The copper contents were determined by use of a Shimazu Atomic Absorption Flame Spectrophotometer Model AA-610.

Measurements

Infrared spectra were measured with a Hitachi Infrared Spectrophotometer Model 215 on a KBr pellet. Electronic spectra were measured with a Shimazu Multipurpose Spectrophotometer Model MSP-5000. Magnetic susceptibilities were determined by the Faraday method, the apparatus being calibrated using $HgCo(NCS)_4$. Diamagnetic corrections were made using Pascal's constants.

ESR spectra were measured with a JES-FE3X ESR apparatus at the liquid nitrogen temperature using X-band.

Results and Discussion

The IR spectra of the bicy complexes are similar in a gross pattern to those of the corresponding mononuclear isocyclam complexes. More detailed observations, however, have revealed small but significant differences from-complex-to-complex in the fingerprint region, indicating the conformation differences in the ring and bridging chains. In the spectra of the perchlorates the absorption due to perchlorate ion was observed at about 1100 cm^{-1} with little splitting, suggesting very weak axial coordination as was demonstrated by X-ray for $Cu(cyclam)(ClO_4)_2$ [6]. The thiocyanate complexes showed the $\nu(CN)$ band at 2050–2060 cm^{-1}. The small shift of the band from that of the free ion shows the absence of strong coordination of thiocyanate ion [7].

The nujol mull spectra of the perchlorates and thiocyanates showed a d–d band at $18.3\text{–}18.8 \times 10^3$ cm^{-1} and $17.1\text{–}17.5 \times 10^3$ cm^{-1}, respectively. These results are consistent with the very weak axial coordination of the perchlorate and thiocyanate ions, as deduced from IR spectra. The aqueous solutions of all the n-bicy copper complexes showed similar spectra with two bands at 18×10^3 cm^{-1} and 36×10^3 cm^{-1} irrespective of anions. The identity of the spectra of the perchlorate and thiocyanate complexes suggests the dissociation of all the anions in aqueous solution. These spectra are also similar to that of isocyclam copper(II) perchlorate in gross pattern, but the ultraviolet band was red-shifted by ca. 2×10^3 cm^{-1} as shown in Table I. Such a band shift may be attributed to an interaction between the two chromophores or a change in aquation of isocyclam ring effected by the presence of another isocyclam ring in proximity.

TABLE I. Absorption Maxima of Electronic Spectra $\tilde{\nu}_{max}$ 10^3 cm^{-1} and ϵ/[Cu] cm^{-1}

Complexes	Solid (nujol mull)	Aqueous solution
Cu(icy)$(ClO_4)_2$[a]	18.3	17.9(176), 38.2(7540)
Cu(icy)$(NCS)_2$[a]	17.5	b
Cu_2(2-bicy)$(ClO_4)_4$	18.5	17.8(191), 36.1(6540)
Cu_2(2-bicy)$(NCS)_4$	17.3	b
Cu_2(3-bicy)$(ClO_4)_4$	18.7	18.2(199), 36.7(7540)
Cu_2(3-bicy)$(NCS)_4$	17.2	b
Cu_2(4-bicy)$(ClO_4)_4$	18.8	18.3(212), 36.5(8600)
Cu_2(4-bicy)$(NCS)_4$	17.1	b

[a] icy represents isocyclam. [b] In aqueous solution the perchlorate and thiocyanate complexes show the same spectra, and the anions of the complexes seem to dissociate completely.

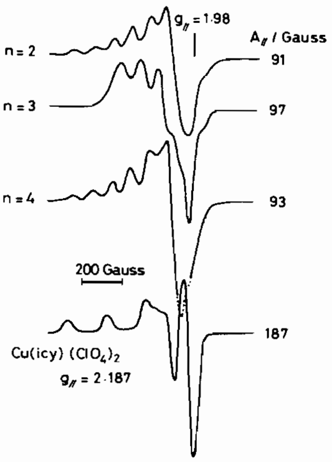

Fig. 2. ESR spectra of Cu_2(n-bicy)$(ClO_4)_4$ and Cu(icy)$(ClO_4)_2$ in DMF glass at liquid nitrogen temperature.

The X-band ESR spectra of the complexes in frozen DMF solution are shown in Fig. 2. The spectra of the perchlorate and thiocyanate n-bicy complexes are virtually the same. The fact that six or four hyperfine peaks were observed with an A value half of that of the mononuclear isocyclam complex is the clear indication of the coupling between the copper centers, though the magnetic moments (1.77–1.85 BM/Cu) are higher than the spin-only value. Thus, the present result is similar to that of the dap and afp complexes [4]. The only difference is that there is no apparent trend in the methylene chain length in the present case, whereas the decrease of the coupling was observed with elongating the methylene chain in the case of the dap and dfp complexes.

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