Copper(II) complexes of tetraazamacrocycles derived from β-diketones and diaminoalkanes

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Copper(II) complexes of the type [Cu(L)][NO₃]₂ (where L = tetraazamacrocycle with 18 to 34-membered ring) have been synthesized by the template condensation of β-diketones such as 2,4-pentanedione, 1-phenyl-1,3-butanedione and 1,3-diphenyl-1,3-propanedione with various diaminoalkanes. These complexes have been characterized by elemental analyses, molar conductances, magnetic moments and IR and electronic spectra.

A large number of tetraazamacrocycles have been synthesized using metal ions as templates⁵. Several Cu(II) complexes of tetraazamacrocycles have been reported⁶. However, Cu(II) complexes of unsaturated tetraazamacrocycles derived from β-diketones and having larger rings have not been studied so far. Ni(II) and Zn(II) complexes with such macrocycles have been reported earlier from these laboratories⁷. In the present note, Cu(II) complexes of large ring tetraazamacrocycles derived from β-diketones such as 2,4-pentanedione, 1-phenyl-1,3-butanedione or 1,3-diphenyl-1,3-propanedione and diaminoalkanes H₂N(CH₂)ₙNH₂ (n = 4, 5, 6, 7, 8, 9, 12) are described.

Experimental

2,4-Pentanedione (BDH), 1,4-diaminobutane (Fluka), 1,5-diaminopentane (Aldrich) and 1,6-diaminohexane (Koch light) were purified by distillation before use. 1,7-Diaminohexane (Aldrich), 1,8-diaminoctane (Fluka), 1,9-diaminononane (Aldrich), 1,12-diaminododecane (Fluka), 1-phenyl-1,3-butanedione (Sisco Chem., India) and 1,3-diphenyl-1,3-propanedione (Sisco Chem., India) were used as supplied. Cu(NO₃)₂·3H₂O (Fluka) was of AR grade.

Copper was determined iodometrically. Iodine liberated was titrated against sodium thiosulphate solution by using starch as indicator. Nitrogen was determined by Kjeldahl's method. Molar conductances of the complexes were measured on a Systronics direct reading conductivity meter 304, using 10⁻³ M solutions in DMSO. Infrared spectra of the complexes were recorded as KBr pellets in the region 200-4000 cm⁻¹ on a Perkin-Elmer 577 Grating IR spectrophotometer. Electronic spectra were recorded in DMSO in the region 200-800 nm on Hitachi U-2000 spectrophotometer. Magnetic measurements were carried out on a Gouy balance at Banasthali Vidyapith, Banasthali, Rajasthan.

Synthesis of Cu(II) complexes of tetraazamacrocycles derived from 2,4-pentanedione and diaminoalkanes

Cu(NO₃)₂·3H₂O (4.2 mmol) was dissolved in 20 mL n-butanol and 2,4-pentanedione (8.4 mmol in 15 mL n-butanol) was added with constant stirring. It was followed by the addition of a solution of 1,4-diaminobutane (8.4 mmol in 15 mL n-butanol) drop-wise. A blue solid appeared during the addition of the diamine. It was stirred for ~ 6 h. The product was filtered, washed with n-butanol and dried in vacuo.

Similar method was adopted for the synthesis of Cu(II) complexes of macrocycles derived from 2,4-pentanedione and 1,5-diaminopentane, 1,6-diaminohexane, 1,7-diaminooctane, 1,8-diaminoctane, 1,9-diaminononane or 1,12-diaminododecane.

Synthesis of Cu(II) complexes of tetraazamacrocycles derived from 1-phenyl-1,3-butanedione and diaminoalkanes

To a solution of Cu(NO₃)₂·3H₂O (2.4 mmol in 15 mL n-butanol) a solution of 1-phenyl-1,3-butanedione (4.8 mmol in 15 mL n-butanol) was added with stirring. It was followed by addition of 1,4-diaminobutane (4.8 mmol in 15 mL n-butanol). Light green solid appeared. Contents were stirred for ~ 6 h. The product was filtered, washed with small aliquots of n-butanol and dried in vacuo.

Similarly, Cu(II) complexes of tetraazamacrocycles derived from 1-phenyl-1,3-butanedione and 1,5-diaminopentane, 1,6-diaminohexane, 1,7-diaminooctane, 1,8-diaminoctane, 1,9-diaminononane or 1,12-diaminododecane were synthesized.
Synthesis of Cu(II) complexes of tetraaza macrocycles derived from 1,3-diphenyl-1,3-propanedione and diaminoalkanes

Cu(NO$_3$)$_2$.3H$_2$O (0.92 mmol) was dissolved in 10 mL n-butanol at 50°C with stirring. To this, a mixture of 1,3-diphenyl-1,3-propanedione (1.84 mmol in 5 mL n-butanol) and 1,4-diaminobutane (1.84 mmol in 5 mL n-butanol) was added dropwise with continuous stirring at same temperature. A green solid appeared during the addition of the diamine. Stirring was continued for ~6 h. The product was filtered, washed with n-butanol and dried in vacuo.

Similar method was used for the synthesis of Cu(II) complex of the macrocycle derived from 1,3-diphenyl-1,3-propanedione and 1,6-diaminohexane.

Results and discussion

Cu(II) complexes (I) of tetraaza macrocycles have been obtained by 1:2:2 molar reactions of Cu(NO$_3$)$_2$.3H$_2$O with β-diketones such as 2,4-pentanediione, 1-phenyl-1,3-butanedione or 1,3-diphenyl-1,3-propanedione and different diaminoalkanes (Structure I).

![Diagram](image)

The resulting Cu(II) complexes of macrocycles are green, blue or greyish blue solids which decompose on heating. These are insoluble in most of the organic solvents such as carbon tetrachloride, chloroform, nitromethane and dimethylformamide but are readily soluble in DMSO. The analyses and the characteristics of the complexes are recorded in Table I.

The molar conductances of $10^{-3}$ M solutions in DMSO of Cu(II) tetraaza macrocyclic complexes are observed in the range 41-87 ohm$^{-1}$ cm$^2$ mol$^{-1}$ (Table I) corresponding to 2:1 electrolytes indicating that both the nitrate groups are ionic. Thus the complexes are square planar. Conductances in DMSO in the range 50-80 ohm$^{-1}$ cm$^2$ mol$^{-1}$ have been reported for Mn(II) and Cd(II) complexes of 2,9-dihydrazino derivative of 1,10-phenanthroline, which have been shown to be 2:1 electrolytes.

IR spectra of a few representative Cu(II) complexes have been recorded. No bands are observed at ~ 1700 cm$^{-1}$ which could be ascribed to unreacted C=O group. This suggests that cyclization has occurred. For Co(II), Ni(II) and Cu(II) complexes of a 16-membered N$_6$-tetradentate macrocycle absence of various vibrations of free or coordinated carbonyl group at ~ 1700 or ~ 1680 cm$^{-1}$ has been reported as an evidence for the formation of cyclic product. All the Cu(II) complexes show a medium to strong intensity band at ~ 1560 cm$^{-1}$ corresponding to azomethine C=N stretching frequency. Presence of this band along with the disappearance of usual C=O stretching mode indicates the formation of Schiff base macrocycle. Fujiwara et al. have assigned absorption band in the region 1560-1575 cm$^{-1}$ to νC=N in Cu(II) and Ni(II) complexes of the macrocycle 6,13-dinitro-5, 7, 12, 14-tetramethyl-1, 4, 8,11-tetraazacyclotetradeca-1,5,7,12-tetraene. In the complexes of macrocycles derived from 1-phenyl-1,3-butadiene or 1,3-diphenyl-1,3-propanedione a medium intensity absorption band in the region 1400-1500 cm$^{-1}$ can be assigned to phenyl ring absorptions. A medium intensity band in the region 3180-3210 cm$^{-1}$ in all the complexes may be attributed to ν=NH vibrations. A strong absorption band at 3200 cm$^{-1}$ due to the presence of –NH group has been reported for Ni(II), Co(II) and Cu(II) complexes of dibenzo(2,4,10,12-tetramethyl-1,5,9,13-tetraazaclorhexadeca-1, 3,9,11-tetraene). New bands at 1360 cm$^{-1}$ and 820 cm$^{-1}$ may be assigned to ionic nitrate. In the organotellurium(IV) tetraaza macrocyclic complexes bands at ~ 1351 and ~ 825 cm$^{-1}$ have been reported for ionic nitrate.

Electronic spectra of a few representative Cu(II) macrocyclic complexes have been recorded. Absorp-
tion bands at ~ 16050-17216 cm⁻¹ and 20618-20880 cm⁻¹ are assigned to ³B₁g → ³A₁g and ²B₁g → ²E₂ transitions respectively. These bands correspond to square planar geometry of the complexes. The spectra also exhibit absorption bands at ~ 30,000 cm⁻¹ or above which may be charge transfer bands. Bands at 16700 and 16130-16420 cm⁻¹ have been reported for ligand field transitions of square planar Cu(II) complexes of the macrocycle [Me₄[14]tetraeneN₄] and for Cu(II) complexes of β-substituted tetraazamacrocycles. Fujisawa and coworkers have reported higher energy bands at ~ 29000 cm⁻¹ or above as charge transfer type. A single broad band at 16.00 K and two weak shoulders at 22.00 K and 12.50 K have been attributed to ²B₁g → ²A₁g, ²B₁g → ²E₂ and ²B₁g → ²B₂ transitions respectively for the Cu(II) complexes of macrocycle, dibenzo(c,j)-1,6,9,14-tetraazacyclohexadeca-1,6,8,13-tetraene.

The magnetic moment of one representative complex [CuMe₄[18]tetraeneN₄](NO₃)₂ was found to be 2.27 BM which is usual for one unpaired electron. Slightly higher value of magnetic moment may be due to the orbital contribution. For square planar Cu(II) complexes of the macrocycle dibenzo(c,j)-1,6,9,14-tetraazacyclohexadeca-1,6,8,13-tetraene the μₑₑ values have been reported in the range 2.11-2.22 BM. Magnetic moments in the range 2.09-2.33 BM have been reported for Cu(II) complexes of a macrocycle derived from benzil and m-phenylenediamine. Cu(II) complexes of the macrocycle(b,i)dibeno (m-dinitrobenzo)-5,8-diaza-1,12-dioxocyclotetradeca-4,8-diene have been reported to possess magnetic moments in the range 2.05-2.15 BM.

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References