Inorganica Chimica Acta, 204 (1993) 267–269

Short Communication

Selective synthesis of a novel non-symmetrical bimacrocyclic ligand and its dinickel(II) complex

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(Received June 6, 1992; revised October 12, 1992)

Abstract

A selective synthesis of non-symmetrical bimacrocyclic ligand by using the 'lariat' Ni(II) complex is reported. The bimacrocyclic ligand in which only one of the macrocycles has cyanoethyl groups has been synthesized and characterized by ^{13}C NMR and FAB mass spectroscopy. The dinickel(II) complex with the ligand has been isolated as the salt with one chloride and three perchlorates. The visible absorption spectrum of the dinickel(II) complex indicates that one of the Ni(II) ions has a square planar configuration and the other is five-coordinate.

Bimacrocyclic complexes where two macrocycles are linked by a C—C bond or a methylene chain have served as good models for the study of metal–metal interactions and the effects of accumulated metal ions [1]. A number of metal complexes with bimacrocyclic ligands having two of the same tetraazamacrocycles have been synthesized [1], though the ligands in which the two different tetraazamacrocycles are linked, i.e. non-symmetrical bimacrocyclic ligands, have not been reported to the best of our knowledge except for the bimacrocycle consisting of 13-membered and 14-membered rings [2].

For the syntheses of such complexes, the use of a 'lariat' complex in which one of the macrocycles does not contain metal ions affords one convenient method (Scheme 1). The vacant macrocycle of the 'lariat' Ni(II) complex enables the selective introduction of functional groups to only one of the two macrocycles in the bimacrocyclic ligand. Thereby, novel non-symmetrical bimacrocyclic ligands and their metal complexes having two coordination environments, functionalities and/or properties should be synthesized.

Recently, we reported a 'lariat' Ni(II) complex, the mononuclear Ni(II) complex with a bimacrocyclic ligand, L^1 [3]. In the present study, by using the 'lariat' Ni(II) complex, we have synthesized a new non-symmetrical bimacrocyclic ligand in which only one of the macrocycles has cyanoethyl groups along with its dinickel(II) complex.

The 'lariat' Ni(II) complex was prepared by our previously reported method [3]. To the complex, cyanoethyl groups were easily introduced by the Michael addition between acrylonitrile and the secondary amines of the vacant macrocycle in the 'lariat' complex in a methanol–water (1:1 vol./vol.) solution. After the Michael addition, the products were changed to dinickel(II) complexes, which were purified by column chromatography using a SP-Sephadex C-25 cation exchange resin with 0.4 mol dm^{-3} NaCl as an eluent. The desired product was isolated from the main band and recrystallized from acetonitrile–ethanol to give green crystals; the elemental analysis showed a satisfactory result for the dinickel(II) complex containing one chloride and three perchlorate anions. *Anal.* Calc. for $[Ni_2ClL^2](ClO_4)_3 \cdot 2H_2O$, $C_{35}H_{54}N_{10}Ni_2Cl_4O_{12} \cdot 2H_2O$: C, 38.15; H, 5.30; N, 12.71. Found: C, 38.23; H, 4.99; N, 12.54%. The free ligand, L^1, was easily cyanoethylated on the secondary amines to produce the fully substituted one with four cyanoethyl groups, L^3. On the other hand, the dinickel(II) complex with L^1 could not be cyanoethylated by this method; the coordinated secondary amines do not have free lone pairs to drastically decrease their reactivities. The non-symmetrical ligand, L^2, and its dinickel(II) complex were characterized as follows.

The IR spectrum of the dinickel(II) complex produced by the cyanoethylation showed a distinct peak at 2250 cm^{-1} which was assignable to ν(CN).

The FAB mass spectrum of the ligand liberated from the dinickel(II) complex showed a peak at m/z 615 $[M+1]$ for the ligand, L^2, which confirmed that two cyanoethyl groups were attached to the ligand, L^1, (m/z 509 $[M+1]$); the four-substituted ligand, L^3, showed a peak at m/z 721 $[M+1]$.

Furthermore, ^{13}C NMR spectra confirmed that the obtained bimacrocyclic ligand has both an unsubstituted macrocycle and a macrocycle bearing two cyanoethyl

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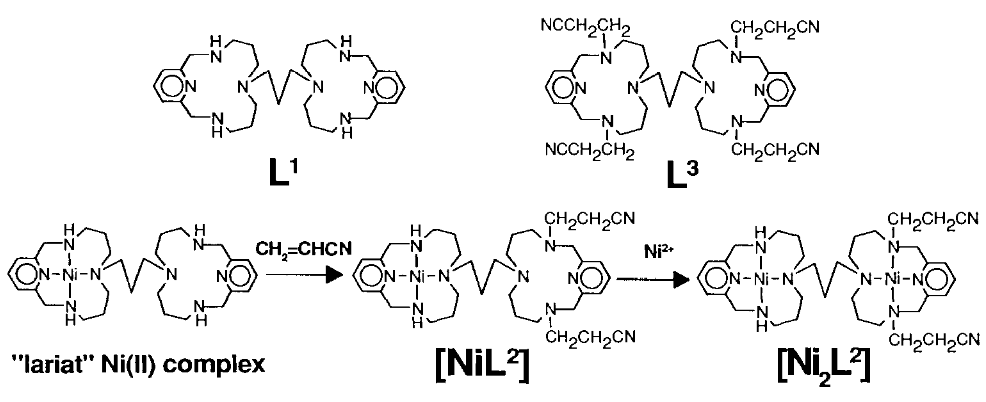

Scheme 1.

groups. Figure 1 shows the ^{13}C NMR spectra of the free ligand, L^2, as well as the ligands, L^1 and L^3. The ^{13}C NMR spectrum of L^2 was simply the sum of those for L^1 and L^3. Thus, the desired non-symmetrical bimacrocyclic ligand, L^2, and its dinickel(II) complex were obtained.

The dinickel(II) complex isolated in this study included one chloride and three perchlorates as counter anions. This was confirmed by the elemental analysis data as well as the FAB-mass spectrum which showed several groups of peaks due to the fragments formed by the stepwise liberations of chloride and three perchlorates from the dinickel(II) complex (*m/z* 965 [$M-ClO_4-Cl$], 865 [$M-2ClO_4-Cl$]. Each Ni(II) ion in the complex should be present in a different coordination mode which was investigated by measurement of visible absorption spectra. Figure 2 shows the visible absorption spectra of $[Ni_2L^1](ClO_4)_4$, $[Ni_2ClL^2](ClO_4)_3$ and $[Ni_2Cl_2L^3]Cl_2$ in a non-coordinating solvent, nitromethane. The absorption spectrum of $[Ni_2L^1](ClO_4)_4$ is a typical one observed for the square planar Ni(II) ion, showing an absorption band maximum at 465 nm. In the case of the fully substituted complex chloride, $[Ni_2Cl_2L^3]Cl_2$, the absorption spectrum showed absorption bands at 405 and 650 nm, due to the five-coordinate Ni(II) ion [4]. The chloride should coordinate to the Ni(II) ion as the result of a decrease in the in-plane ligand field splitting by the introduction of cyanoethyl groups to the secondary amines. The nitrogen donors of CH_2CH_2CN introduced on the Ni(II) complex are considered not to relate with the coordination [4], because the molecular model suggests that CH_2CH_2CN cannot take a configuration so as to coordinate to the closest Ni(II) ion. The absorption spectrum of $[Ni_2ClL^2](ClO_4)_3$ shows three absorption bands at 405, 465 and 650 nm, which are simply the sum of those observed for $[Ni_2L^1](ClO_4)_4$ and $[Ni_2Cl_2L^3]Cl_2$. These results indicate that one of the Ni(II) ions in $[Ni_2ClL^2](ClO_4)_3$ has a square planar configuration and the other is five-coordinate. Thus, the non-symmetrical bimacrocyclic ligand, L^2, serves two different coordination environments in one molecule to produce a homobinuclear metal complex in which properties of the metal ions are different. Further studies for introduction of other functional groups and a mononuclear Ni(II) complex with L^2 are now in progress.

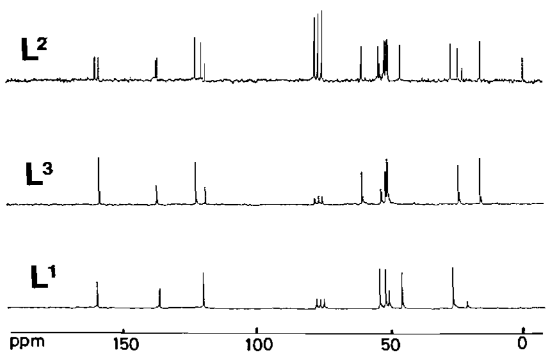

Fig. 1. ^{13}C NMR spectra of the free ligands.

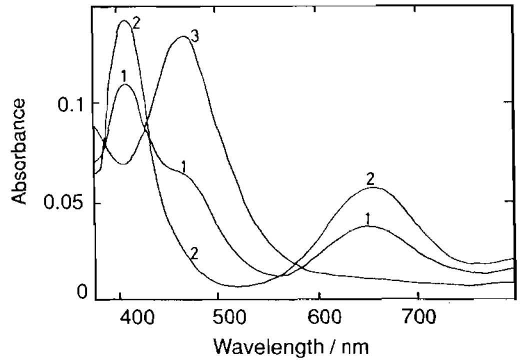

Fig. 2. Absorption spectra of 5×10^{-4} mol dm^{-3} $[Ni_2L^2Cl](ClO_4)_3$ (1), $[Ni_2L^3Cl_2]Cl_2$ (2) and $[Ni_2L^1](ClO_4)_4$ (3) in nitromethane.

Acknowledgement

The present work was partially supported by a Grant in Support of the Promotion of Research at Yokohama City University.

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