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A Nickel(II) Schiff Base Complex Linked to Viologen via Number Six of the Methylene Groups

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Abstract

A nickel(II) Schiff base complex linked to viologen via number six of the methylene groups was prepared and characterized. The characteristic absorption band of a methylviologen radical appeared with the reduction of the derivative by sodium dithionite in a DMF–H_2O solution, and then disappeared with aeration.

Bromoalkyl derivatives of the complex with a varying number ($n = 2$–5) of methylene groups were also prepared.

Introduction

Complexes such as $[Ru(bpy)_3]^{+2}$, metalloporphyrin, and metallophthalocyanine have been used as sensitizers for the photochemical decomposition of water to hydrogen [1–3]. The effect of spacer chain length on the photoinduced electron transfer reaction was also investigated in a porphyrin–viologen-linked system to elucidate the reaction mechanism [4].

Recently, we found that a ruthenium Schiff base complex can act as the photosensitizer in the electron transfer reaction from triethanolamine to dimethylviologen [5]. It should be interesting to control the distance between the photosensitizer and the electron acceptor in the viologen-linked ruthenium Schiff base derivatives.

To obtain preliminary information on the preparation of the ruthenium Schiff base complex linked by viologen, we prepared the nickel(II) Schiff base complex linked to viologen via number six of the methylene groups (Fig. 1).

Experimental

Syntheses

1-Methyl-4,4′-bipyridinium (MV) iodide was prepared according to the procedure described in ref. 6.

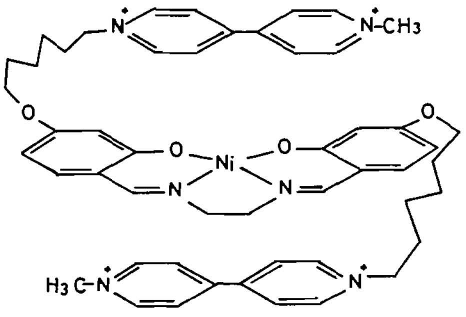

Fig. 1. Abbreviation of the nickel(II) Schiff base complex linked by methylviologen: complex 3.

[*N,N*′-Bis(4-hydroxysalicylidene)ethylenediaminato]nickel(II), complex 1, was prepared in a similar method described for the preparation of a Salen complex with nickel(II). By recrystallization from methanol, red needles were obtained and characterized by means of elemental analysis. *Anal.* Found: C, 52.06; H, 4.95; N, 7.28. Calc. for $C_{16}H_{14}N_2O_4Ni \cdot MeOH$: C, 52.48; H, 4.67; N, 7.20%.

NiL-$[O(CH_2)_6Br]_2$ (2)

A mixture of 0.5 g (1.3 mmol) of complex 1 and 3.9 g (16 mmol) of 1,6-dibromohexane was dissolved into a 100 ml solution of *N,N*-dimethylformamide (DMF) suspending 2.2 g (16 mmol) of potassium carbonate, and was left standing with stirring at room temperature for 3 days. After filtration of the solution, the filtrate was concentrated under a reduced pressure, and then an adequate amount of chloroform was added to the solution. After further filtration of undissolved materials, the filtrate was poured on to a silica gel column. Complex 2 was then obtained by the addition of an adequate amount of hexane to the red solution eluted with chloroform. Derivatives with a varying number ($n = 2$–5) of methylene groups were also prepared using a similar method to that described above.

NiL-$[O(CH_2)_6MV]_2Br_2I_2$ (3)

A mixture of 50 mg (0.073 mmol) of complex 2 and 70 mg (0.23 mmol) of MV iodide was dissolved into 100 ml of ethanol, and refluxed for 3 days. The

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TABLE 1. Results of Elemental Analyses and Yields

	Found (%)			Calculated (%)			Yields (%)
	C	H	N	C	H	N	
NiL–[O(CH$_2$)$_2$Br]$_2$	41.93	3.77	4.81	42.07	3.54	4.90	13
NiL–[O(CH$_2$)$_3$Br]$_2$	44.22	4.41	4.90	44.11	4.05	4.67	72
NiL–[O(CH$_2$)$_4$Br]$_2$	45.92	4.14	4.66	45.97	4.51	4.47	62
NiL–[O(CH$_2$)$_5$Br]$_2$	47.64	4.95	4.30	47.67	4.93	4.27	59
NiL–[O(CH$_2$)$_6$Br]$_2$	49.70	5.53	4.04	49.22	5.32	4.10	36
NiL–[O(CH$_2$)$_6$MV]$_2$ Br$_2$I$_2$·12H$_2$O	38.87	5.63	5.53	38.17	5.72	5.80	27

TABLE 2. ^{1}H NMR Signals of the Nickel(II) Complexes in DMSO-d$_6$ ^{a}

	δ_1 ^{b}	δ_2	δ_3	δ_4	δ_5	δ_6	δ (benzene + azomethine)		
NiL–[O(CH$_2$)$_2$Br]$_2$	4.27	3.78					6.17	7.18	7.74
	(t, 4H)	(t, 4H)					(t, 4H)	(d, 2H)	(s, 2H)
NiL–[O(CH$_2$)$_3$Br]$_2$	4.03	2.22	3.64				6.18	7.15	7.72
	(t, 4H)	(t, 4H)	(t, 4H)				(t, 4H)	(d, 2H)	(s, 2H)
NiL–[O(CH$_2$)$_4$Br]$_2$	3.96	1.94	1.83	3.60			6.17	7.13	7.71
	(t, 4H)	(t, 4H)	(t, 4H)	(t, 4H)			(t, 4H)	(d, 2H)	(s, 2H)
NiL–[O(CH$_2$)$_5$Br]$_2$	3.92	1.86	1.72	1.53	3.56		6.15	7.13	7.70
	(t, 4H)	(t, 4H)	(t, 4H)	(t, 4H)	(t, 4H)		(t, 4H)	(d, 2H)	(s, 2H)
NiL–[O(CH$_2$)$_6$Br]$_2$	3.91	1.80	1.69	1.44	1.44	3.54	6.15	7.13	7.70
	(t, 4H)	(br, 4H)	(br, 4H)	(br, 4H)	(br, 4H)	(br, 4H)	(m, 4H)	(d, 2H)	(s, 2H)
NiL–[O(CH$_2$)$_6$MV]$_2$ Br$_2$I$_2$ ^{c}	3.90	2.02	1.69	1.44	1.38	4.71	6.13	7.13	7.72
	(br, 4H)	(br, 4H)	(br, 4H)	(m, 4H)	(m, 4H)	(m, 4H)	(m, 4H)	(d, 2H)	(s, 2H)

[a] s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. [b] The subscript of δ is numbered from the position of the methyl group adjacent to the oxygen atom in the side chains. [c] The complex further shows the signals from the methyl and bipyridinium parts in the MV groups at 4.45 (s, 6H) and 9.29–9.40 ppm (m, 16H), respectively.

resulting precipitates were washed with small amounts of water and dried at *ca.* 100 °C for 3 h. The complex was strongly hygroscopic, and thus it was kept in a well-sealed tube.

Measurements

The electronic spectra in solution and the infrared spectra using KBr pellets were measured on a Hitachi 200-20 spectrophotometer and a Hitachi 260-50 spectrophotometer respectively. The FT-^{1}H NMR spectra were recorded with a JEOL-GX 270 spectrophotometer at 270 MHz. The chemical shifts were determined in ppm, using TMS as the internal standard.

Results and Discussion

The results of elemental analyses, yields and ^{1}H NMR spectra of the complexes obtained are shown in Tables 1 and 2.

The yield of the bromo derivative prepared from complex **1** with dibromoethane is less than those with the other dibromoalkanes, probably due to the steric hindrance of another neighboring bromine atom in dibromoethane when it reacts with complex **1**.

The complexes **1**–**3** show absorption bands around 530 nm in methanol arising from the d–d transition, which is characteristic of square planar nickel(II) complexes.

^{1}H NMR signals arising from the hydroxy groups of complex **1** (10–12 ppm) disappear in complexes **2** and **3**. The signals from the benzene rings of the Salen parts in complexes **1**–**3** appear at almost the same region (6–8 ppm). The proton signals from the methylene groups adjacent to the electronegative atoms are shifted to lower magnetic fields; the order of the shift is the pyridinium cation > oxygen > bromine. Complex **3** also shows the new signals from the methyl groups and pyridine rings in the methylviologen parts at 4.45 and 8.8–9.5 ppm, respectively.

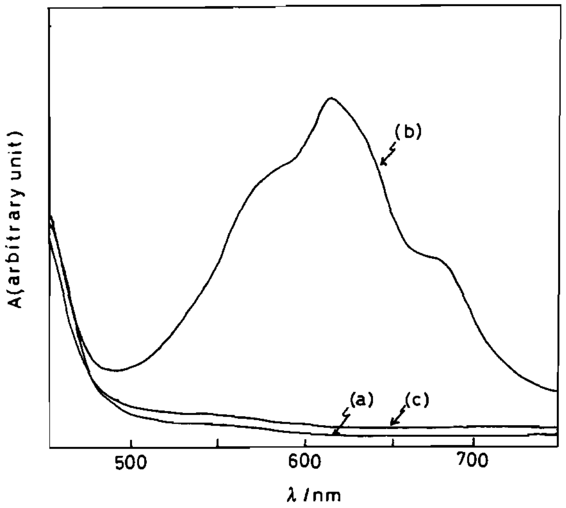

Fig. 2. UV spectra of complex 3 in the mixture solvent of H_2O–DMF: (a) the solution degassed, (b) after addition of sodium dithionite, (c) after aeration of (b).

The signals from the ethylene groups of the Salen parts were covered by the solvent signal of DMSO.

In the IR spectra, complex 2 shows a band at 2800–2900 cm^{-1} which is assigned to the C–H stretching of the methylene groups. Furthermore, complex 3 shows the band assignable to the C–H stretching of the methyl groups at 3050 cm^{-1}.

The characteristic absorption band of a methylviologen radical appeared with the addition of sodium dithionite into the degassed DMF–H_2O mixture solution of complex 3 (Fig. 2). The band immediately disappeared with aeration, and the original spectrum of complex 3 was recovered. These facts confirm that methylviologen is contained in complex 3.

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