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The Preparation and some Properties of Copper(II) and Nickel(II) Schiff Base Complexes having Various Peripheral Substituent Groups

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The hydrogen atom on methine carbon of N,N'-bis(acetylacetone)ethylenediaminatocopper(II) or -nickel(II) was found to be replaced by a chlorine, bromine or iodine atom. Further conversion of the halogen atom of the complex occurred with a sodium salt of phenol, benzenethiol or succinimide. The UV data of substituted compounds give some information on substituents.

Introduction

Schiff base complexes have received considerable attention as biomimic model compounds [1–5]. The first report of a synthetic reversible cobalt(II)–oxygen carrier was made by Tsumaki in 1938 [6]. He showed that N,N'-bis(salicylidene)ethylenediaminatocobalt(II), Co(SALEN), absorbs molecular oxygen reversibly in the solid state. Recently, Fe(SALEN) has become attractive as the model compound of natural iron protein, hemerythrin, which binds molecular oxygen reversibly [7]. Cu(SALEN) is also a potential model compound of hemocyanin. N,N'-bis(acetylacetone)ethylenediaminatocobalt(II), Co(ACACEN) has been reported to bind molecular oxygen reversibly in N,N-dimethylformamide at 0 °C [8, 9]. The study of substituent effects (*e.g. cis* effect) of Schiff base complexes will be useful to sort out the electronic parameters governing biological oxygen transport and redox process [10]. Therefore, the synthesis of the Schiff base complexes containing various peripheral groups in their ligand parts must improve the study of biomimic model systems. The present report deals with the electrophilic and nucleophilic substitutions on the methine carbon atoms of Cu(ACACEN) and Ni(ACACEN) (Fig. 1).

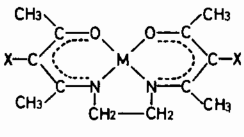

Fig. 1. Cu(X_2ACACEN) and Ni(X_2ACACEN); M = copper(II) and nickel(II); X = H, Cl, I, phenoxy, phenylthio, and succinimido groups.

Experimental

Cu(ACACEN) and Ni(ACACEN) were prepared according to the procedure of Martell *et al.* [11].

Electrophilic Substitutions

N-bromosuccinimide (1.78 g, 0.01 mol) was added to 1.52 g (0.005 mol) of Cu(ACACEN) in 50 ml of dichloromethane, after which the mixture was left standing with stirring for 20 minutes at 0 °C. The solution [solution A] was concentrated under a reduced pressure. The resulting solid was recrystallized from dichloromethane–methanol, yielding a bromo derivative, Cu(Br_2ACACEN). Ni(Br_2ACACEN) was obtained in a similar manner as above. Chloro and iodo derivatives were synthesized from N-chlorosuccinimide and N-iodosuccinimide respectively in a similar manner as that of the bromo compounds. An iodo derivative of copper(II) was not obtained because of the decomposition of Cu(ACACEN) during the reaction.

Nucleophilic Substitutions

Phenoxy derivatives

Sodium phenoxide (2.9 g, 0.025 mol) was added to the solution A and was left to stand for 3 days at room temperature with stirring, after which the precipitates were filtered off. The filtrate was concentrated under a reduced pressure and the resulting solid was recrystallized from dichloromethane–methanol, yielding a phenoxy derivative, Cu[$(PhO)_2$-ACACEN]. A phenoxy derivative of nickel(II) was not obtained in the way used for the copper(II) derivative.

Phenylthio derivatives

A phenylthio derivative of copper(II), Cu[$(PhS)_2$-ACACEN] was obtained by adding sodium benzenethiolate to the solution A in a similar manner described above. A phenylthio derivative of nickel(II) was also synthesized by using N-iodosuccinimide instead of N-bromosuccinimide in the way used for the copper(II) derivative. Furthermore, a white crystal of $(PhS)_2$ACACEN containing no metal was obtained by adding benzenethiol to the solution A.

TABLE I. Analytical, Yields, and IR Data.

Compound	Calculated %			Found %			Yield %[a]	IR cm^{-1} [b]
	C	H	N	C	H	N		
$Cu(X_2ACACEN)$								
Cl	40.63	4.54	7.90	40.80	4.44	7.43	62.0	1563
Br	32.49	3.64	6.32	32.14	3.45	5.89	41.9	1551
PhO	61.33	5.58	5.96	61.81	5.54	5.69	21.1	1580, 1592
PhS	57.41	5.22	5.58	57.96	5.11	5.65	22.4	1542, 1580
succinimido	50.05	5.04	11.67	49.98	5.29	11.66	14.3	1582, 1702
$Ni(X_2ACACEN)$								
Cl	41.19	4.61	8.01	41.04	4.51	7.44	66.8	1562
Br	32.49	3.64	6.32	32.66	3.48	5.72	55.2	1545
I	27.05	3.03	5.26	26.62	3.18	5.73	38.6	1542
PhS	57.96	5.27	5.63	58.46	5.25	5.15	17.4	1530, 1580
$(PhS)_2ACACEN$								
	65.72	5.98	6.39	66.03	6.28	5.61	10.0	1570

[a] Based on M(ACACEN). [b] The characteristic bands appearing in the 1500–1700 cm^{-1} region.

TABLE II. PMR Spectra.[a]

Compound	δ values (ppm) in $CDCl_3$				
	CH_3	CH_2	CH	C_6H_5	OH
$Ni(X_2ACACEN)$					
H	1.88 (d, 12H)	3.08 (s, 4H)	4.92 (s, 2H)		
Cl	2.12 (d, 12H)	3.15 (s, 4H)			
Br	2.19 (d, 12H)	3.14 (s, 4H)			
I	2.37 (s, 12H)	3.17 (s, 4H)			
PhS	2.23 (s, 12H)	3.19 (s, 4H)		6.96–7.32 (m, 10H)	
$(PhS)_2ACACEN$					
	2.28 (s, 12H)	3.58–3.64 (m, 4H)		7.01–7.21 (m, 10H)	10.60 (s, 2H)

[a] Key: s = singlet, d = doublet, t = triplet, m = multiplet.

Succinimido derivatives

A mixture of succinimide (1.0 g, 0.01 mol) and sodium hydroxide (0.4 g, 0.01 mol) in methanol was heated on a water bath and the solution was concentrated until tarry precipitates were formed. Then, the solution A was added to the 3 ml methanol solution containing tarry sodium succinimide. In a similar treatment described above, a succinimido derivative of copper(II) was obtained. On the other hand, a succinimido derivative of nickel(II) was not obtained in the way used for the copper(II) derivative.

Measurements

The electronic spectra in solution and the infrared spectra using KBr pellets were measured on a Hitachi 124-type spectrophotometer and a Hitachi 215-type spectrophotometer respectively. The PMR spectra were recorded with a JEOL-MH 100 spectrophotometer at a frequency of 100 MHz. The chemical shifts were determined in ppm, using TMS as the internal standard. The elemental analyses were carried out by means of a Yanagimoto MT 2 CHN Corder.

Results and Discussion

The results of elemental analyses, yields, IR, and PMR spectra of the substituted compounds are shown in Tables I and II.

TABLE III. Electronic Spectra of the Schiff Base Metal (II) Complexes.*

Compound	λ max (nm) in dichloromethane					
	π–π*			Charge transfer		d–d
$Cu(X_2ACACEN)$						
H		277	311	340 sh		544
		(275)	(306)	(335 sh)		(540)
Cl		277	326	350 sh		544
Br		278	326	350 sh		543
PhS	252[a]	275 sh	313	335 sh		545
PhO	274[b]	280	327	350 sh		545
succinimido		279	308	335 sh		545
$Ni(X_2ACACEN)$						
H		270		353	358	565
		(268)		(352)	(357)	(562)
Cl		288		365	384	578
Br		287		365	385	574
I		293		365	384	570
PhS	250[a]	265sh		355	372	548

*The data in parentheses are quoted from Ref. 12 (measured in methanol). [a]Band arising from the phenylthio group. [b]Band arising from the phenoxy group. sh = shoulder.

IR and PMR

In IR spectra, the phenoxy and phenylthio derivatives show the band characteristic of a benzene ring at 1580–1590 cm^{-1}, and the succinimido derivative shows the band of carbonyl groups vicinal to the imide nitrogen at 1702 cm^{-1}. The PMR signal of methine protons in Ni(ACACEN) disappears in its substituted compounds. The phenylthio derivative of nickel(II) also shows the PMR signal of its benzene ring protons at 6.76–7.32 ppm. The PMR signal of methyl groups of the halogen derivatives of nickel(II) are shifted to lower magnetic fields in the order of Cl, Br, and I substituted compounds. This tendency is attributed to the magnetic anisotropic effect of halogen atoms rather than to their inductive effect. The PMR signal of methyl groups of phenylthio derivative of nickel(II) is shifted to a lower magnetic field, compared with its parent compound, Ni(ACACEN). This may result from the effect of the ring current of benzene.

Electronic Spectra

From the electronic spectra given in Table III, we can see that the phenylthio and succinimido derivatives show the absorption band due to a π–π* transition at the same wavelengths as those of their parent compounds, Cu(ACACEN) and Ni(ACACEN), while the absorption bands of the π–π* transition of the chloro, bromo, iodo, and phenoxy derivatives are shifted to longer wavelengths, compared with those of their parent compounds.

The tendency seems to depend on the extention of a π system of the Schiff base ligand with participation of lone-pair electrons of the substituents, as is seen in the case of acetylacetonato metal(II, III) derivatives [13]. That is, the oxygen atom of the phenoxy group has sp or sp^2 hybridized orbitals and the electrons of the nonhybridized p orbital must participate in the π system of the Schiff base ligand. Therefore, the absorption band of the phenoxy derivative shifts to longer wavelengths. The sulfur atom of the phenylthio group may have hybridized sp^3 orbitals and have no electrons which take part in the π system of the Schiff base ligand; thus, the absorption bands of the phenylthio derivatives show no shift to longer wavelengths. The succinimido group of the copper(II) is perpendicular to the Schiff base ligand because of the steric hindrance between the carbonyl group of the imide and the methyl groups of the Schiff base. Therefore, the absorption band arising from the π–π* transition is not shifted. Furthermore, the absorption bands arising from d–d transitions of the nickel(II) derivatives are shifted to longer wavelengths in the order of H, I, Br, and Cl substituted compounds, while those of copper(II) derivatives do not show significant shifts (Table III). The absorption band of the d–d transition of the phenylthio derivative of nickel(II) is largely shifted to shorter wavelengths in both dichloromethane and pyridine solvents, compared with the other derivatives. This large shift may be attributed to the distortion of the square planar configuration of the complex. Further studies (cyclic voltammetry, dc polarography, and differential-pulse polarography) on a series of substituted Schiff base complexes are expected to elucidate the *cis* effect in the biomimic model system.

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