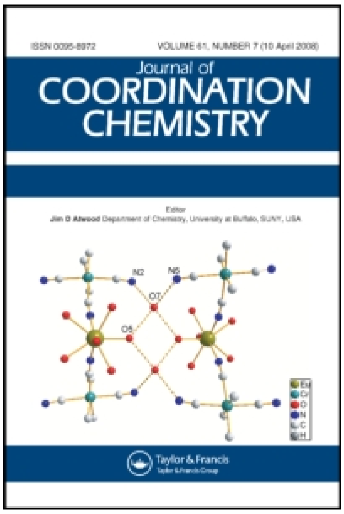

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Preparation, Spectroscopic Properties and Characterization of Oxovanadium(IV), Isothiocyanatomanganese(III), Cyanocobalt(III) and Cobalt(II) Complexes with a Bis-Crown Ether Tetraaza[14]Annulene

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To cite this Article Sakata, Kazunori , Miyamoto, Yasushi , Hashimoto, Mamoru and Tsuge, Akihiko(2002) 'Preparation, Spectroscopic Properties and Characterization of Oxovanadium(IV), Isothiocyanatomanganese(III), Cyanocobalt(III) and Cobalt(II) Complexes with a Bis-Crown Ether Tetraaza[14]Annulene', Journal of Coordination Chemistry, 55: 11, 1283 — 1291

To link to this Article: DOI: 10.1080/0095897021000041194

URL: http://dx.doi.org/10.1080/0095897021000041194

J. Coord. Chem., 2002, Vol. 55(11), pp. 1283–1291

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PREPARATION, SPECTROSCOPIC PROPERTIES AND CHARACTERIZATION OF OXOVANADIUM(IV), ISOTHIOCYANATO-MANGANESE(III), CYANOCOBALT(III) AND COBALT(II) COMPLEXES WITH A BIS-CROWN ETHER TETRAAZA[14]ANNULENE

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(Received 21 September 2001)

Oxovanadium(IV), isothiocyanatomanganese(III), cyanocobalt(III) and cobalt(II) complexes of tetraaza[14]annulene appended with two crown ethers at 2,3- and 11,12-positions have been prepared. Cation complexation behavior of these cavity-bearing tetraaza[14]annulene complexes has been investigated by optical absorption methods. The cation K^+, which necessitates two crown ether cavities for complexation, induces dimerization of the tetraaza[14]annulene complexes, whereas the Na^+ does not. Formation of the sandwich complexes due to dimerization is hindered by the steric interactions involving the axial ligand as judged by the blue shift of the intense band around 385–425 nm. Judging from its ESR spectrum, the cobalt(II) complex becomes a monomeric dioxygen complex of a 1 : 1 molar ratio in the presence of O_2 and pyridine at 77 K.

Keywords: Macrocyclic complexes; Crown ethers; Cations; Dimerization; Axial ligands; Dioxygen cobalt(II)

INTRODUCTION

Tetraaza[14]annulenes substituted with crown ether rings are currently receiving great interest [1–4]. Recently, we reported that these compounds and their nickel(II) and copper(II) complexes can be aggregated by addition of potassium and ammonium salts, which become complexed to the crown ether rings [2,4]. Central to aggregation, the dimerization process is widespread among tetraaza[14]annulenes and their metal complexes in solution. In order to study the effect of steric influence at the axial position which is essential to the understanding of the dimerization process, we utilized optical spectra of the oxovanadium(IV), isothiocyanatomanganese(III) and cyanocobalt(III) complexes that form five-coordinate square-pyramidal species.

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ISSN 0095-8972 print: ISSN 1029-0389 online © 2002 Taylor & Francis Ltd
DOI: 10.1080/0095897021000041194

In the present case we report the syntheses of oxovanadium(IV), isothiocyanatomanganese(III), cyanocobalt(III) and cobalt(II) complexes with bis-crown ether tetraaza[14]annulene, namely 2,3,11,12-bis(1′,4′,7′,10′,13′-pentaoxatridecamethylene)-5, 14-dihydro-7, 16-diethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine. Various cations were employed for the complexation study. The dimerization was followed by optical absorption methods. The oxovanadium(IV), isothiocyanatomanganese(III) and cyanocobalt(III) complexes delineate the effect of steric influences at the axial positions on the energetics of the dimerization process.

EXPERIMENTAL

Physical Measurements

Melting points were measured on a Yanaco MP-500D micro melting point apparatus. Elemental analyses were determined with a Yanaco CHN MT3 instrument. FAB mass spectra were measured with a JEOL JMS-SX102A gas chromatograph–mass spectrometer in glycerin matrix. IR spectra in the 400–4000 cm^{-1} region were recorded on a Hitachi 260-30 spectrophotometer at room temperature with KBr disks. Ultraviolet and visible spectra covering the 15 000–32 000 cm^{-1} range were obtained using a Shimadzu UV 200S double beam spectrophotometer with chloroform and chloroform–methanol (5 : 1 v/v) solutions at room temperature. ^{1}H NMR spectra were recorded on a JEOL JNM-A500 spectrometer in trifluoroacetic acid-*d* and chloroform-*d*-methanol-d_4 (5 : 1 v/v). Chemical shifts are given in ppm relative to tetramethylsilane (TMS) as internal reference. ESR spectra were measured on a JEOL JES-RE2X X-band spectrometer equipped with a 100 kHz field modulation unit. The spectrum of the cobalt(II) complex was run in *N*,*N*-dimethylformamide at 77 K in the presence of pyridine and O_2, the sample concentration being *ca.* 10^{-3} mol dm^{-3}. Manganese ion in magnesium oxide was used as the standard reference.

Synthesis of 2,3,11,12-Bis(1′,4′,7′,10′,13′-pentaoxatridecamethylene)-5,14-dihydro-7,16-diethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecine ***(H_2L)*** *and (2,3,11,12-bis(1′,4′, 7′,10′,13′-pentaoxatridecamethylene)-7,16-diethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato) nickel(II)* ***(NiL)*** The preparation procedures of **H_2L** and **NiL** have been reported previously [2].

Preparation of (2,3,11,12-Bis(1′,4′,7′,10′,13′-pentaoxatridecamethylene)-7,16-diethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)oxovanadium(IV) (***VOL***) A mixture of **H_2L** (0.072 g, 0.099 mmol), bis(2,4-pentanedionato)oxovanadium(IV) (0.050 g, 0.19 mmol) [5] and benzyl alcohol (20 cm^3) was heated at 200°C for 1 h with stirring. After the reaction mixture cooled to room temperature, solvent was evaporated to dryness *in vacuo*. The resulting solid was recrystallized from toluene to give fine brown crystals. The yield was 0.025 g (32%), mp > 300°C. IR (KBr): 2940, 2860 (C–H), 1520, 1450 (C=C, C=N), 960 (V=O) cm^{-1}. EIMS: *m*/*z* 789 (M^+, ^{51}V), 789.71 (calc. for molecular weight). *Anal.* Found: C, 57.56; H, 6.31; N, 6.98%. Calc. for $C_{38}H_{50}N_4O_{11}V$: C, 57.79; H, 6.38; N, 7.09%.

Preparation of (2,3,11,12-Bis(1′,4′,7′,10′,13′-pentaoxatridecamethylene)-7, 16-diethyldibenzo[b,i] [1,4,8,11]tetraazacyclotetradecinato)isothiocyanatomanganese(III) ***(Mn(NCS)L)*** A mixture of **H_2L** (0.050 g, 0.069 mmol), bis(2,4-pentanedionato)isothiocyanatomanganese(III) (0.030 g, 0.096 mmol) [6,7] and acetone (10 cm^3) was heated under reflux for 1 h with stirring, and then allowed to cool to room temperature. The crystalline product was recovered by filtration and washed three times with methanol and diethylether, respectively, to obtain fine dark green crystals. The yield was 0.026 g (45%), mp > 300°C. IR (KBr): 2940, 2860 (C–H), 2060 (N≡C–S), 1518, 1430 (C=C, C=N) cm^{-1}. FABMS: *m/z* 835 (M^+), 835.79 (calc. for molecular weight). *Anal.* Found: C, 55.81; H, 6.26; N, 8.06%. Calc. for $C_{39}H_{50}N_5O_{10}SMn$: C, 56.04; H, 6.03; N, 8.38%.

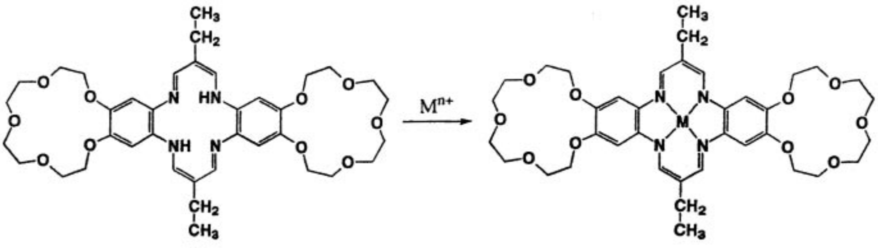
Preparation of (2,3,11,12-Bis(1′,4′,7′,10′,13′-pentaoxatridecamethylene)-7,16-diethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)cobalt(II) ***(CoL)*** A mixture of **H_2L** (0.095 g, 0.13 mmol) and *N*,*N*-dimethylformamide (5 cm^3) was heated at 150°C, and then cobalt(II) acetate tetrahydrate (0.050 g, 0.20 mmol) was added to it. The reaction mixture was held under reflux for 5 min in a nitrogen atmosphere. The product was separated by filtration and washed twice in cold diethylether to give violet needles. **CoL** is gradually oxidized by atmospheric oxygen. The yield was 0.062 g (61%), mp > 300°C. IR (KBr): 2930, 2870 (C–H), 1520, 1427 (C=C, C=N) cm^{-1}. FABMS: *m/z* 781 (M^+), 781.70 (calc. for molecular weight).

Preparation of (2,3,11,12-Bis(1′,4′,7′,10′,13′-pentaoxatridecamethylene)-7, 16-diethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)cyanocobalt(III) ***(Co(CN)L)*** A mixture of **CoL** (0.050 g, 0.064 mmol), sodium cyanide (0.025 g, 0.51 mmol) and acetone (20 cm^3) was heated under reflux while air was continuously bubbled through it. The mixture was allowed to stand at room temperature, then the crystalline solid that formed was isolated by filtration and washed thoroughly with methanol to obtain fine green crystals. The yield was 0.033 g (64%), mp (dec.) 294–297°C. IR (KBr): 2950, 2870 (C–H), 2120 (C≡N), 1520, 1440 (C=C, C=N) cm^{-1}. FABMS: *m/z* 807 (M^+), 807.22 (calc. for molecular weight). *Anal.* Found: C, 57.70; H, 6.04; N, 8.38%. Calc. for $C_{39}H_{50}N_5O_{10}Co$: C, 57.99; H, 6.24; N, 8.67%.

RESULTS AND DISCUSSION

Preparation of the Metal Complexes

The reaction of **H_2L** with cobalt(II) acetate in boiling *N*,*N*-dimethylformamide yielded the corresponding cobalt(II) complex under a nitrogen atmosphere. On the other hand, the oxovanadium(IV) and the isothiocyanatomanganese(III) complexes were not prepared from **H_2L** and each salt. The oxovanadium(IV) complex is obtained by the ligand exchange reaction of bis(2,4-pentanedionato)oxovanadium(IV) with **H_2L** in boiling benzyl alcohol. The isothiocyanatomanganese(III) complex is also prepared by the ligand exchange reaction of bis(2,4-pentanedionato)isothiocyanatomanganese(III) with **H_2L** in boiling acetone. The cyanocobalt(III) complex is obtained by the oxidative reaction of **CoL** with oxygen in the presence of sodium cyanide.



H_2L ML

M = VO(IV), MnNCS(III), Ni(II), Co(II), CoCN(III)

Infrared Spectra

Characteristic IR bands are summarized in the experimental section. After formation of the complexes, IR bands due to the C=N and C=C stretching modes shift to lower frequency. The behavior is analogous to that of tetraaza[14]annulene complexes with no crown ether group [8]. The medium intensity band at 960 cm^{-1} for **VOL** is associated with the V=O stretching mode by reference to porphyrin and related oxovanadium(IV) complexes [9,10]. **Mn(NCS)L** shows a medium band at 2060 cm^{-1} which is correlated with the C≡N stretch of a coordinated NCS group. This band is comparable to that of Fe(OEP)NCS (OEP octaethylporphyrin) and of the tetraaza[14]annulene isothiocynatomanganese(III) complex with no crown ether; these are *N*-bonded complexes [7,11]. Hence, **Mn(NCS)L** is also *N*-bonded. **Co(CN)L** reveals a medium band at 2120 cm^{-1}, which is attributed to the C≡N stretch by reference to known cyano complexes [12].

Ultraviolet and Visible Spectra

The general spectroscopic features and the positions of absorption for **VOL**, **Mn(NCS)L** and **Co(CN)L** are very similar to those for tetraaza[14]annulene complexes with no crown ether substituent [8,13–15]. It suggested that these remain unaffected by electronic and steric effects of the substituted crown ether groups. Since **CoL** is not stable in solutions, electronic spectra and the molar extinction coefficients were not obtained exactly. The relevant $\pi \rightarrow \pi^*$ and CT transition bands are summarized in Table I.

NMR Spectra

In accord with a diamagnetic nature of the present nickel(II) and the cyanocobalt(III) complexes, **NiL** and **Co(CN)L** gave well resolved ^{1}H NMR spectra. The chemical shift

TABLE I Characteristic absorption bands in the electronic spectra of crown tetraaza[14]annulene complexes[a]

Complex	*Transition energy in* cm^{-1} (ε) $\pi \rightarrow \pi^*$/CT
VOL	19600sh(21000), 23600(55100), 27000(32900)
Mn(NCS)L	16600(10900), 17900sh(7530), 25800(35200)
Co(CN)L	18300(12700), 22900sh(22800), 25500(35200)

[a] Measured in chloroform at room temperature.

TABLE II ^{1}H NMR data for crown tetraaza[14]annulene nickel(II) and cyanocobalt(III) complexes[a]

Complex	*Ethyl* *–CH$_3$*	*–CH$_2$–*	*Crown* *–O–CH$_2$–*	*Aromatic*	*Methine* *–N=CH–*
NiL	1.69(t) (J = 7.5 Hz)	3.59(q) (J = 7.5 Hz)	4.12(m) 4.18(m) 4.39(m) 4.86(m)	8.39(s)	9.78(s)
Co(CN)L	1.77(t) (J = 7.6 Hz)	3.70(q) (J = 7.6 Hz)	4.14(m) 4.22(m) 4.43(m) 4.94(m)	8.57(s)	10.63(m)

[a] Chemical shifts in ppm for internal TMS. Measured in trifluoroacetic acid-*d*. Multiplicity of the proton signal is given in parentheses after the δ value: s = singlet; t = triplet; q = quartet; m = multiplet.

assignments were performed on the basis of comparison with the nickel(II) and the cyanocobalt(III) complexes with no crown ether substituents [8,15]. ^{1}H NMR data and their assignments for **NiL** and **Co(CN)L** are listed in Table II. The ethyl and methylene resonances in the crown ether groups and the aromatic and methine signals are shifted downfield on formation of the complexes. The downfield shift for **Co(CN)L** is much larger in magnitude than that observed for **NiL**. This can be attributed to the deshielding effect due to the positive charge offered by the metal ion in the complexes. Since the oxidation number of cobalt is greater than that of nickel, the deshielding effect of **Co(CN)L** is much greater than that of **NiL**. Consequently, the larger downfield shift of **Co(CN)L** is interpreted on the basis of the above deshielding effect. The magnitude of the downfield shifts of the ethyl, methylene and aromatic protons is much smaller than that of the methine protons. This may be attributable to the fact that the ethyl, methylene and aromatic proton groups are placed further from the positive charge of the metal ions.

ESR Spectra

The ESR spectrum of **CoL** is shown in Fig. 1 in the presence of pyridine and O_2 in *N*,*N*-dimethylformamide at 77 K. A set of eight hyperfine lines based on the cobalt nucleus ($I = 7/2$) was observed for the parallel component of g-tensor at lower field and for the perpendicular component of the g-tensor at higher field, respectively. The feature is similar to that of other common dioxygen cobalt(II) complexes [16]. Spin Hamiltonian parameters are comparable to those of Co(acacen)PyO$_2$ acacen: *N*,*N′*-bis(1-methyl-3-oxobutylene)ethylenediamine) [17]. Consequently, we attribute the spectrum to a monomeric dioxygen cobalt(II) complex of 1 : 1 stoichiometry.

Aggregation

^{1}H NMR spectra of **H$_2$L** in the mixed solvent chloroform-*d*-methanol-*d*$_4$ (5 : 1 v/v) are shown in Fig. 2. The spectrum is obviously broad (Fig. 2A). On the other hand, in dimethyl sulfoxide-*d*$_6$ the spectrum changes and very sharp NMR signals appear. Crown porphyrin compounds exhibit similar solvent-dependent ^{1}H NMR spectra which result from self aggregation of porphyrins [18,19]. Consequently, we attribute the spectrum to aggregated tetraaza[14]annulenes. Since tetraaza[14]annulene with no

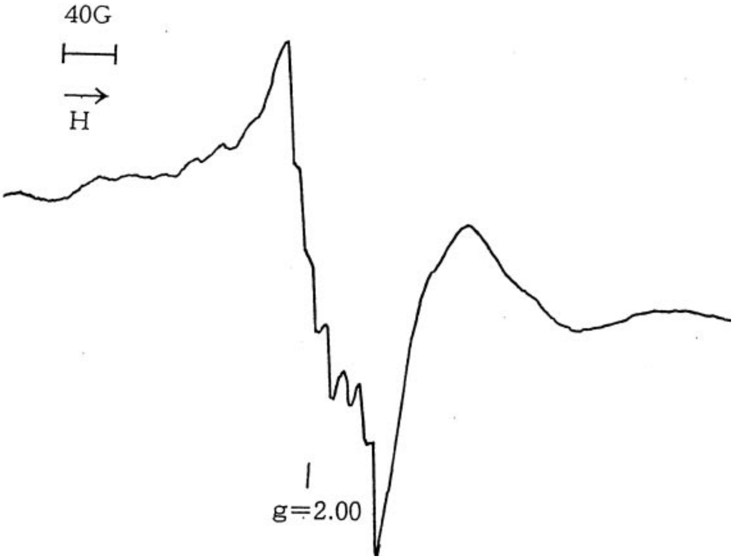


FIGURE 1 ESR Spectrum of **CoL** in *N*,*N*-dimethylformamide containing pyridine and O_2 at 77 K ($g_{\parallel} = 2.083$, $g_{\perp} = 1.997$, $A_{\parallel}^{\mathrm{Co}} \times 10^4 = 20.2\,\mathrm{cm}^{-1}$, $A_{\perp}^{\mathrm{Co}} \times 10^4 = 13.9\,\mathrm{cm}^{-1}$).

crown ether group does not aggregate, it is thought that the driving force for aggregation is concerned with the crown substituent groups.

The effect of the addition of Na^+ ions to the mixed solvent containing **H_2L** is shown in Fig. 2, where spectra A, B, C and D correspond to ratios of **H_2L**: Na^+ of 1 : 0, 1 : 0.25, 1 : 0.5 and 1 : 2, respectively. In the addition of Na^+ ions, the spectra change (Fig. 2 (A–D)) and well resolved NMR signals appear. This spectrum is assigned to a monomeric compound. This seems to indicate that the introduction of the Na^+ ions into the crown ether cavities prevents any aggregation of the compounds because of the strong repulsion induced by two Na^+ ions in each compound. In addition, the downfield shift of the methylene signals in the crown ether is extremely small on the formation of the sodium complexes because of the weakness of the deshielding effect. A similar phenomenon is observed on **NiL**.

Cation Complexation Leading to Dimer Formation

We studied the stoichiometry of complexation of various alkali salts with **H_2L**, **VOL**, **Mn(NCS)L**, **Co(CN)L** and **NiL** in chloroform–methanol (5 : 1 v/v) by electronic spectroscopy. **H_2L**, **VOL**, **Mn(NCS)L**, **Co(CN)L** and **NiL** were dissolved in chloroform–methanol and the alkali salts, dissolved in methanol, were added in limited amounts. Addition of K^+ and NH_4^+ to **H_2L**, **VOL**, **Mn(NCS)L**, **Co(CN)L** and **NiL** affects the $\pi \rightarrow \pi^*$/CT transition bands of the tetraaza[14]annulene compounds by a reduction in peak intensity around 380–550 nm, an increase in peak intensity and a blue shift (5–16 nm) of the intense band around 380–450 nm, and some broadening. Such changes are most obvious for K^+ with respect to the amount needed to effect them. Figure 3 shows an example of the results. After each addition, changes in the absorption maximum were determined and plotted against the molar ratio of

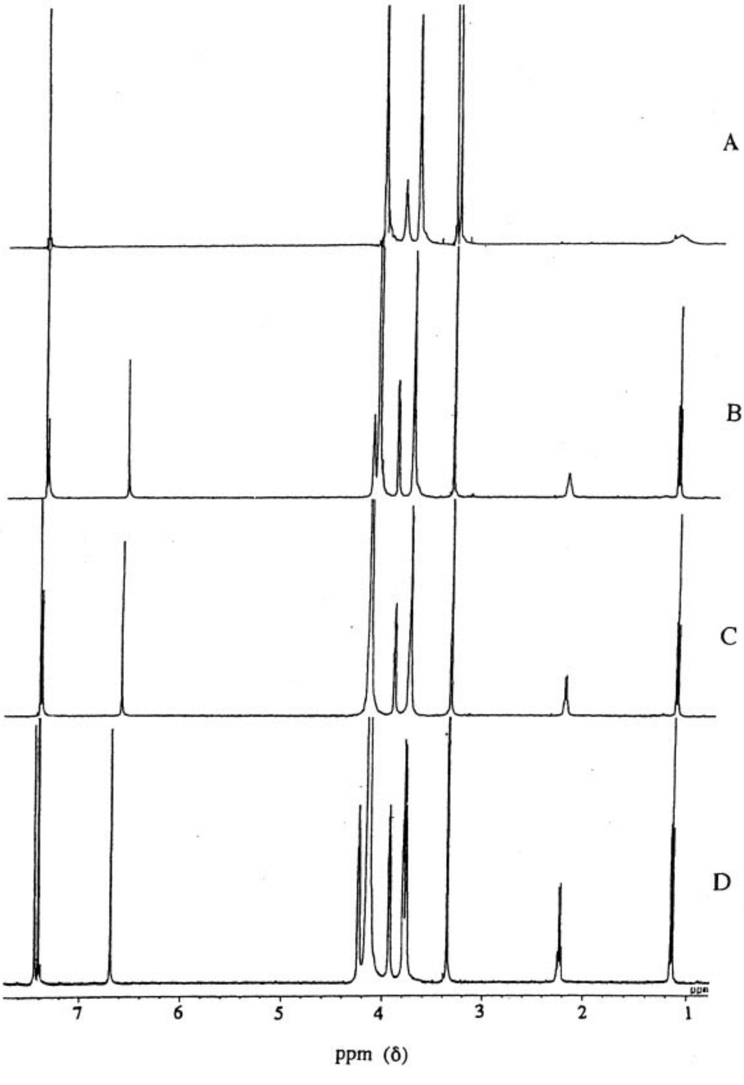


FIGURE 2 ^{1}H NMR spectra of $\mathbf{H_2L}$ at room temperature in chloroform-*d*–methanol-d_4 (5 : 1 v/v) after addition of Na^+ ions; TMS as internal reference: A, $\mathbf{H_2L}:Na^+ = 1:0$; B, $\mathbf{H_2L}:Na^+ = 1:0.25$; C, $\mathbf{H_2L}:Na^+ = 1:0.5$; D, $\mathbf{H_2L}:Na^+ = 1:2$.

the guest (K^+, NH_4^+, etc.) to host (**H_2L, VOL**, etc.). Figure 4 is an example of the result. These well-defined changes show that **H_2L, VOL, Mn(NCS)L**, **Co(CN)L** and **NiL** form 2 : 2 (crown/cation) complexes with K^+ and NH_4^+. On the other hand, Na^+ did not cause any appreciable change in visible absorption. This seems to indicate that the potassium ion is sandwiched between two crown ether units and the sodium ion resides within the ether ring. This behavior is similar to that observed for dimerization of crown porphyrin and crown phthalocyanine systems [20,21]. Accordingly, the addition of K^+ and NH_4^+ causes dimerization of these compounds, whereas the addition of Na^+ gives rise to a monomeric system because of strong electrostatic repulsion. We suggest that under our conditions with sodium and potassium salts the

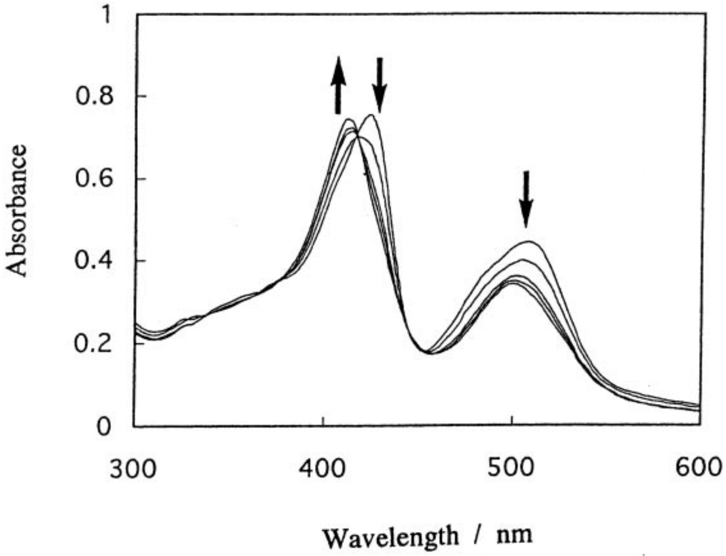


FIGURE 3 Changes in absorption spectra of **VOL** caused by the addition of CH_3COOK in chloroform–methanol (5 : 1 v/v) at room temperature. The arrows show the directions of the spectroscopic changes.

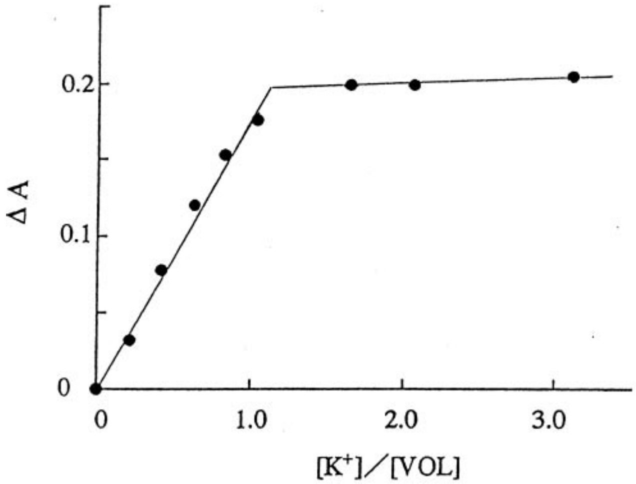


FIGURE 4 Absorbance increase at 413 nm plotted against the ratio of K^+ to **VOL** in chloroform–methanol (5 : 1 v/v) at room temperature.

aggregation is mainly determined by the cations. To this point no effect of the axial ligand in the compounds has been observed. Here the effect of the axial ligand is appreciable. We explain this in the following way. In order to study the effect of the steric effects of the axial ligand in the complexes we can compare the blue shift of **H_2L** and **NiL** (square-planar geometry) with that of **VOL**, **Mn(NCS)L** and **Co(CN)L** (square-pyramidal geometry). The order increases in the series **Mn(NCS)L** (5 nm) < **Co(CN)L** (6 nm) < **VOL** (9 nm) < **NiL** (14 nm) < **H_2L** (16 nm). When the sandwich complexes are formed in solution, the superposition is hindered by steric requirements of the axial ligand.

Acknowledgments

The authors are grateful to the Center for Instrumental Analysis, Kyushu Institute of Technology for elemental analyses, mass spectra, ESR spectra and NMR spectra.

References

[1] R. Kruse and E. Breitmaier (1981). *Chem. Ber.*, **114**, 832.
[2] K. Sakata and T. Annoura (1990). *Inorg. Chim. Acta*, **176**, 123.
[3] K. Sakata, T. Kawano and T. Annoura (1994). *Synth. React. Inorg. Met.-Org. Chem.*, **24**, 905.
[4] K. Sakata, M. Shimoda and M. Hashimoto (1996). *J. Heterocyclic Chem.*, **33**, 1593.
[5] R.A. Rowe and M.M. Jones (1957). *Inorg. Synth.*, **5**, 114.
[6] B.R. Stults, R.S. Barianelli and V.W. Day (1975). *Inorg. Chem.*, **14**, 772.
[7] K. Sakata, Z. Wang, M. Hashimoto, A. Tsuge and Y. Tanoue (1999). *Synth. React. Inorg. Met.-Org. Chem.*, **29**, 265.
[8] K. Sakata, M. Hashimoto, N. Tagami and Y. Murakami (1980). *Bull. Chem. Soc. Jpn.*, **53**, 2262.
[9] J.G. Erdman, V.G. Ramsey, N.W. Kalenda and W.H. Hanson (1956). *J. Am. Chem. Soc.*, **78**, 5844.
[10] J.M. Assour, J. Goldmacher and S.E. Harrison (1965). *J. Chem. Phys.*, **43**, 159.
[11] H. Ogoshi, E. Watanabe, Z. Yoshida, J. Kincaid and K. Nakamoto (1973). *J. Am. Chem. Soc.*, **95**, 2845.
[12] K. Nakamoto (1997). *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Part B, 5th Edn., p. 105. Wiley, New York.
[13] K. Sakata, H. Nakamura and M. Hashimoto (1984). *Inorg. Chim. Acta*, **83**, L67.
[14] K. Sakata, M. Hashimoto and H. Yoshino (1985). *Inorg. Chim. Acta*, **99**, 231.
[15] K. Sakata, T. Annoura and M. Hashimoto (1988). *Inorg. Chim. Acta*, **150**, 153.
[16] R.D. Jones, D.A. Summerville and F. Basolo (1979). *Chem. Rev.*, **79**, 139.
[17] B.M. Hoffman, D.L. Diemente and F. Basolo (1970). *J. Am. Chem. Soc.*, **92**, 61.
[18] K.M. Smith (1975). *Porphyrins and Metalloporphyrins*. Elsevier, Amsterdam.
[19] D. Dolphin (1979). *The Porphyrins*, Vol. IV. Academic Press, New York.
[20] O.E. Sielcken, M.M. van Tilborg, M.F.M. Roks, R. Hendriks, W. Drenth and R.J.M. Nolte (1987). *J. Am. Chem. Soc.*, **109**, 4261.
[21] N. Kobayashi and A.B.P. Lever (1987). *J. Am. Chem. Soc.*, **109**, 7433.