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Synthesis and properties of binuclear M(II)–Sn(IV)$(CH_3)_2$ (M = Cu, Co) complexes of *N,N′*-bis(3-carboxysalicylidene)ethylenediamine

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Abstract

The binucleating ligand *N,N′*-bis-(3-carboxysalicylidene)ethylenediamine (H_4fsaen) formed copper(II)–dimethyltin(IV) and cobalt(II)–dimethyltin(IV) complexes [MSn$(CH_3)_2$(fsaen)] (M = Cu, Co) where the copper(II) or cobalt(II) ion is bound at the N_2O_2 site and the tin(IV) ion at the O_4 site with two methyl groups at the axial positions. Both complexes are fairly stable towards atmospheric moisture in the solid state but decomposed into a mononuclear complex [M(H_2fsaen)] by a trace amount of water when dissolved in solution. Spectroscopic investigations on the Cu–Sn complex in pyridine revealed that the coordination of pyridine to the copper(II) is sterically hindered by the methyl groups attached to the neighbouring tin(IV). In the case of the Co–Sn complex such a steric effect of the methyl groups is not pronounced enough to hinder the coordination of pyridine to the axial site of the cobalt(II). ESR spectra at liquid nitrogen temperature revealed that the cobalt(II) ion adopts a pentacoordinate structure at room temperature and a hexacoordinate structure near liquid nitrogen temperature with pyridine molecule(s) at the axial site(s).

Introduction

The coordination chemistry of heteronuclear complexes comprised of dissimilar transition metal ions has been the subject of numerous studies in recent years because of much interest in elucidating the spin exchange mechanism between paramagnetic metal ions [1] and in mimicking the active sites of some metalloenzymes [2]. Another interest in heteronuclear complexes is to find new reactivities or functions associated with such heteronuclear centers where distinct features of the constituting metal ions are accumulated or amplified to give rise to unprecedented cooperative effects [3]. Because of this interest our studies are now extending to heterobinuclear complexes that contain a transition metal ion and a lanthanoid or non-transition metal ion in close proximity [4]. These complexes may be referred to as d–f and d–p complexes, respectively.

N,N′-Bis(3-carboxysalicylidene)ethylenediamine (abbreviated as H_4fsaen, see Fig. 1) is a potent binucleating ligand with two dissimilar coordination sites, N_2O_2 and O_4 sites, and affords heterobinuclear complexes of various combinations of metal ions [5, 6]. In this study we have synthesized copper(II)–dimethyltin(IV) and cobalt(II)–dimethyltin(IV) complexes of fsaen^{4-}. Such complexes are unique in that Werner-type and organometallic-type metal centers are held in close proximity. Our interest in this study is to examine if the mononuclear complexes [M(H_2fsaen)] can incorporate the dimethyltin(IV) ion at the O_4 site to afford M(II)–Sn(IV)$(CH_3)_2$ (M = Cu, Co) complexes, how reactive the methyl groups attached to the tin(IV) are, and what effects the methyl groups exert upon the neighbouring transition metal center.

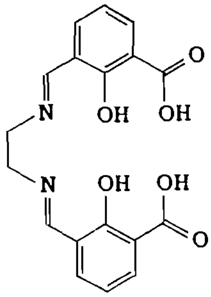

Fig. 1. Chemical structure of H_4fsaen.

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Experimental

Materials

3-Formylsalicylic acid was prepared by the literature method [7]. Dichlorodimethyltin(IV) and n-butyl lithium were purchased commercially. All the solvents (tetrahydrofurane, pyridine, ether) were thoroughly dehydrated in the usual ways and degassed before use.

Preparations

N,N′-Bis(3-carboxysalicylidene)ethylenediamine (H_4fsaen) and its mononuclear copper(II) and cobalt(II) complexes ([Cu(H_2fsaen)] [5a] and [Co(H_2fsaen)] [8]) were prepared following literature methods.

[CuSn(CH$_3$)$_2$(fsaen)]

To a suspension of [Cu(H_2fsaen)] (200 mg) in dry tetrahydrofurane (30 cm^3) was added butyl lithium (50 mg) and the mixture was stirred under gentle reflux for 1 h to yield a reddish di-lithium salt of the mononuclear complex. Then a tetrahydrofurane solution (5 cm^3) of dimethyldichlorotin(IV) (110 mg) was added and the mixture was refluxed with stirring for 2 h. The resulted violet microcrystals were separated by filter suction, washed with tetrahydrofurane, and dried *in vacuo*. The yield was 86%.

The same complex was obtained when lithium hydroxide (25 mg) was used as the base instead of butyl lithium.

Anal. Found: C, 42.62; H, 3.56; N, 4.72; Cu, 11.64. Calc. for $C_{20}H_{18}N_2O_6CuSn$: C, 42.54; H, 3.22; N, 4.96; Cu, 11.26%.

[CoSn(CH$_3$)$_2$(fsaen)]

All the operations shown below were carried out in an atmosphere of argon by the use of Schlenk apparatus. To a suspension of [Co(H_2fsaen)] (200 mg) in dry tetrahydrofurane (30 cm^3) was added butyl lithium (50 mg), and the mixture was refluxed for 1 h. Then a tetrahydrofurane solution of dimethyldichlorotin(IV) (110 mg) was added and the mixture was refluxed with stirring for 2 h to give orange microcrystals. They were collected by filter suction, washed with absolute ethanol, and dried *in vacuo*. The yield was 72%.

Anal. Found: C, 42.83; H, 3.14; N, 5.02; Co, 10.36. Calc. for $C_{20}H_{18}N_2O_6CoSn$: C, 42.90; H, 3.24; N, 5.00; Co, 10.52%.

Measurements

Elemental analyses of carbon, hydrogen and nitrogen were obtained at The Elemental Analysis Service Center of Kyushu University. Analyses for copper and cobalt were made on a Shimadzu atomic absorption flame emission spectrophotometer model AA-610. Infrared (IR) spectra were recorded on a JASCO IR-810 spectrometer on KBr disks or nujoll mulls. Electronic spectra in the visible and near ultraviolet regions were measured on a Shimadzu UV-240 spectrometer at room temperature. Spectra in the near IR region were measured on a Shimadzu MPS-5000 spectrometer. Pyridine (py) and *N,N*-dimethylformamide (dmf) used as solvents for spectral measurements were dehydrated in the usual ways and degassed before use. Magnetic susceptibilities were measured with a Faraday balance designed in our laboratory. The apparatus was calibrated with $[Ni(en)_3]S_2O_3$ [9]. Electron spin resonance (ESR) spectra were obtained in frozen solution at liquid nitrogen temperature on a JES-FE3X spectrometer.

Results and discussion

Synthesis and general characterization

The synthesis of the complexes was carried out by the stepwise incorporation of two metal ions into the ligand. The mononuclear copper(II) and cobalt(II) complexes [M(H_2fsaen)] were converted into the di-lithium salts by the reaction with either lithium hydroxide or n-butyl lithium and then the di-lithium salts were reacted with dichlorodimethyltin(IV) to give M(II)–Sn(IV)$(CH_3)_2$ (M = Cu, Co) complexes in good yields. The elemental analytical results suggested the formulation of MSn(fsaen)$(CH_3)_2$ (M = Cu, Co). In spite of our many efforts we have not succeeded in obtaining large single crystals suitable for X-ray structural analysis. Thus, the characterization of the complexes was made based on conventional physicochemical techniques.

The magnetic moments for the Cu–Sn and Co–Sn complexes (per molecule) are 1.83 and 2.27 μ_B, respectively. Evidently, the cobalt(II) ion is low-spin. In the IR spectra of the complexes the C=O vibration of the carboxylate group appears at ~1550 cm^{-1}, indicating that the carboxylate group coordinates to the tin(IV) ion [5]. The C–H vibrations appearing in the region 2900–2800 cm^{-1} are much more intense compared with the corresponding bands for the precursor complexes [M(H_2fsaen)]. This is an indication that the methyl groups are bound to the tin(IV) ion. The crystal structures of Cu(II)–Co(II) [5h], Cu(II)–Ni(II) [10], Cu(II)–Fe(III) [11], and Cu(II)–Mg(II) [12] of fsaen^{2-} have been determined, where the second metal ion at the O_4 site takes a distorted-octahedral or a square-pyramidal structure with the O_4 donor sets in the equatorial plane and water molecule or chloride ion at the axial sites.

The ionic radii (Shannon–Prewitt radii [13]) of those metal ions bound at the O_4 site of the dinucleating ligand fall in the range 0.79–0.86 Å. Tin(IV) ion is comparable to those metal ions in the ionic radius (0.83 Å). Hence we presume that the tin(IV) ion resides on the O_4 site and two methyl groups are bonded to the axial sites *trans* to each other.

The Co–Sn complex is air-sensitive and decomposed in open atmosphere into uncharacterized species. In the solid state both complexes were significantly stable towards atmospheric moisture. Further, the methyl–tin bond was intact even when the complexes were treated in anhydrous boiling alcohols. In solutions, however, the complexes were readily decomposed by a trace amount of contaminated water to give the monomeric complexes [M(H_2fsaen)] (M = Cu, Co).

Electronic spectra

From the above discussion it is shown that the methyl groups are strongly bonded to the axial sites of the tin(IV) ion. It seems interesting to examine the steric effect of the methyl groups upon the coordination of solvents or bases at the axial site of the neighbouring transition metal ion. Unfortunately the Cu–Sn complex is hardly soluble in most solvents except for pyridine. The Co–Sn complex is soluble in pyridine and dmf but sparingly soluble in other solvents. Therefore, our spectral investigations are limited to pyridine solutions for the Cu–Sn complex and to pyridine and dmf solutions for the Co–Sn complex. The electronic spectra of the Cu–Sn and Co–Sn complexes have been compared with the spectra of related, well-characterized *N*,*N*′-disalicylideneethylenediaminatocopper(II) [Cu(salen)] and *N*,*N*′-disalicylideneethylenediaminatocobalt(II) [Co(salen)], respectively. Our spectral comparisons are restricted to the region up to 25000 cm^{-1}, because the ligands fsaen^{4-} and salen^{2-} differ significantly from each other in the electronic structure so that the electronic spectra of their complexes are ligand-dependent in the region higher than 25000 cm^{-1}.

The electronic spectrum of the Cu–Sn complex in pyridine is shown by trace 1 in Fig. 2. Electronic spectra of [Cu(salen)] in chloroform and in pyridine are given by traces 2 and 3, respectively. [Cu(salen)] adopts a planar configuration in chloroform and assumes a purple color. Its spectrum shows a d–d band maximum at 18500 cm^{-1} [14–16]. A pyridine solution of [Cu(salen)] is deep blue and shows a d–d band maximum at 16500 cm^{-1} and a discernible shoulder near 14000 cm^{-1}. This spectral feature is characteristic of pentacoordinated copper(II) with a pyridine molecule at the axial site [17]. The spectrum of the Cu–Sn complex resembles on the whole that of [Cu(salen)] in chloroform (trace 2) except for the slightly weakened intensity of the d–d band. The result clearly demonstrates that the Cu–Sn complex retains a planar configuration around the copper(II) ion even in pyridine.

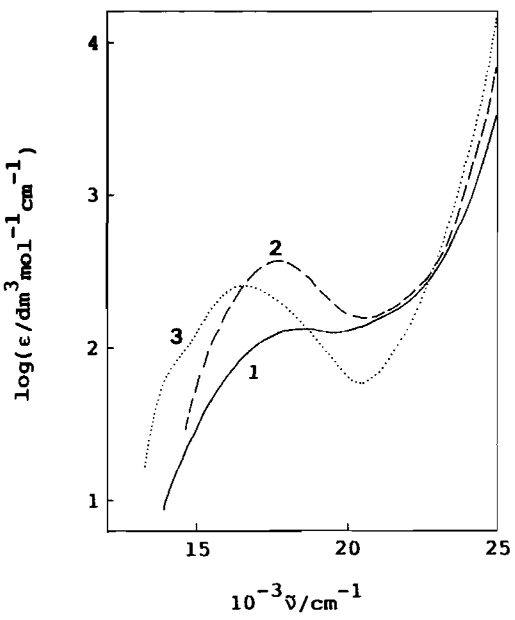

Fig. 2. Electronic spectra of the Cu–Sn complex in pyridine (trace 1), [Cu(salen)] in chloroform (trace 2), and [Cu(salen)] in pyridine (trace 3).

The X-ray structural analyses for the Cu(II)–Co(II) [5h], Cu(II)–Ni(II) [10] and Cu(II)–Mg(II) [12] complexes of fsaen^{4-} have revealed that the intermetal distance falls in the range 2.975–3.025 Å. If a pyridine molecule is coordinated to the axial site of the copper(II) ion, the pyridine ring and the methyl carbon are held in a close distance (*c*. 3.0 Å) which is significantly shorter than the sum of the van der Waal's radii of the aromatic ring and methyl group (*c*. 4.0 Å). Thus, it appears that the coordination of pyridine to the axial site of the copper(II) ion is sterically hindered by the methyl groups attached to the tin(IV) ion.

Electronic spectra of the Co–Sn complex in pyridine and dmf are shown in Fig. 3. In dmf solution the complex shows a weak near IR band at 7200 cm^{-1} and a visible band at 18000 cm^{-1}. Such a spectral feature is very similar to that of [Co(salen)] in chloroform [17]. The near IR band is known to be characteristic of planar cobalt(II) of salen-like Schiff bases and assigned to a d–d component [18, 19]. Thus, it is evident that the Co–Sn complex adopts a planar configuration around the cobalt(II) ion. Non-coordination of dmf molecules to the cobalt(II) ion might be ascribed to the steric effect by the methyl groups attached to the neighbouring tin(IV),

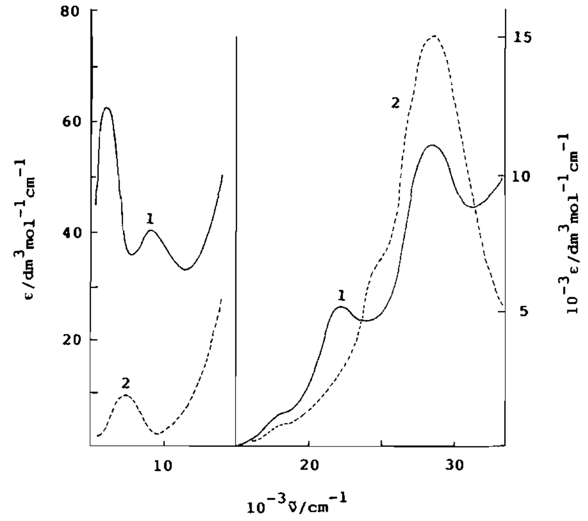

Fig. 3. Electronic spectra of the Co–Sn complex in dmf (trace 1) and in pyridine (trace 2).

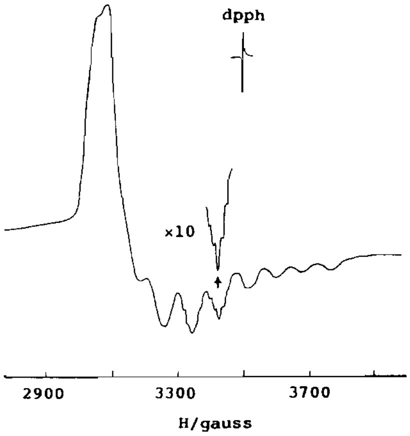

Fig. 4. ESR spectrum of the Co–Sn complex measured in frozen pyridine solution at liquid nitrogen temperature.

but we have recently found that oxygenous solvents such as dmf and dmso have a low affinity to planar cobalt(II) like [Co(salen)] [4c]; i.e. [Co(salen)] retains a planar configuration in dmf and dmso at room temperature and the coordination of dmf or dmso molecules only occurs at lowered temperature.

In pyridine solution the Co–Sn complex showed two near IR bands at 5900 and 9200 cm^{-1} and a visible band near 17900 cm^{-1}. The spectral feature in the near IR region resembles that of [Co(salen)py] determined on a powder sample [20]. Therefore, pyridine coordinates to the axial site of the cobalt(II) of the Co–Sn complex to afford a five-coordination around the cobalt though this is not the case for the Cu–Sn complex.

ESR spectra

Low-spin cobalt(II) complexes may adopt either of two distinct electronic structures $(d_{yz})^1$ and $(d_{z^2})^1$. The two electronic structures can be diagnosed on the basis of ESR spectra [21]. Planar complexes of Schiff bases like [Co(salen)] assume the $(d_{yz})^1$ ground state and show a rhombic pattern of ESR spectrum with $g_x \gg 2.0 > g_z > g_y$ and a large eight-lined hyperfine structure due to the cobalt nucleus ($I_{Co} = 7/2$) on the g_x signal [22]. The $(d_{z^2})^1$ ground state occurs for species with one or two base(s) at the axial site(s) and gives an axial pattern of the ESR spectrum with $g_\parallel \sim 2.0$ and $g_\perp > 2.0$ and a large hyperfine structure on the $g_\parallel$ component [23].

The ESR spectrum of the Co–Sn complex measured in a frozen pyridine solution at liquid nitrogen temperature is given in Fig. 4. It shows an axial pattern of $g_\parallel$ 2.02 and $g_\perp$ 2.28, and a hyperfine structure due to the cobalt nucleus ($I_{Co} = 7/2$) is imposed on the $g_\parallel$ component. The hyperfine coupling constant was evaluated at 84.8 gauss. This spectral feature is characteristic of low-spin cobalt(II) which possesses one unpaired electron on the d_{z^2} orbital. A noticeable feature of the spectrum is a five-lined superhyperfine structure imposed on each component of the $g_\parallel$ signal, indicating that both of the axial sites of the cobalt(II) ion are occupied by pyridine molecules ($I_N = 1$). The superhyperfine coupling constant is 13.9 gauss. Together with the electronic spectral result discussed above, it is found that the Co–Sn complex forms a monopyridine adduct at room temperature and a dipyridine adduct at liquid nitrogen temperature. This tendency is indeed the case of [Co(salen)] and its homologs [21]. Thus, the steric effect of the methyl groups attached to the tin(IV) is not pronounced enough to hinder the coordination of pyridine molecule at the axial site of the neighbouring cobalt(II). It appears that the cobalt(II) ion has a high affinity towards nitrogenous ligating groups and prefers a five- or six-coordination in pyridine in overcoming the steric effect from the methyl groups.

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