Structure and Properties of Diaquabis(methylthioacetato)cobalt(II), $[Co(C_3H_5SO_2)_2(H_2O)_2]$, and Its Anhydride

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The crystal and molecular structure of the title complex has been determined by the X-ray diffraction method. The crystal was triclinic, space group $P\bar{1}$, $a=6.750(2)$, $b=9.214(4)$, $c=5.206(2)$ Å, $\alpha=102.57(6)$, $\beta=103.44(6)$, $\gamma=100.70(3)°$, $Z=1$, $D_x=1.702(3)$, $D_m=1.72(3)$ mg m^{-3}, μ(Mo $K\alpha$)$=1.89$ mm^{-1}, and the final R value was 0.034 for 1175 reflections. The molecular arrangement has a center of symmetry and a distorted octahedron is formed around the central cobalt(II) atom; each methylthioacetato ligand forms a chelate ring by coordinating through a sulfur atom and a carbonyl oxygen atom, and two water molecules also coordinate to the central metal. Its amorphous anhydride as well as the other type anhydride, which resembles the bis(propylthioacetato)cobalt(II) hexamer in its infrared and visible spectra, is obtained by the dehydration process.

Alkylthioacetato complexes have interesting properties and they have been studied by many authors. We have already reported about their syntheses and spectroscopic properties.[1-5] Yamasaki also studied them,[6] and Pettit has shown the formation constants of their silver complexes.[7,8] More recently, many kinds of complexes containing the multi-dentates of this type of ligand were synthesized and actively investigated by Jones and others.[9-14]

One of the special properties of this type of complexes is the formation of a polymer-type structure, where the ligand bridges metal atoms. The hexamer of bis(propylthioacetato)cobalt(II) and bis(isopropylthioacetato)copper(II) dihydrate are the examples.[15,16] In the case of phenoxyacetato complexes of copper(II), the same type of the hexamer was already reported by Carruthers;[17] however, it was also shown that the ligand was able to form complexes with other structures.[18-21]

In the case of alkylthioacetato complexes, only a few structural reports have been published yet. We judge from the syntheses that the most stable form of the alkylthioacetates of cobalt(II), nickel(II), and copper(II) is the dihydrate, $ML_2\cdot 2H_2O$ (some of which may be the diaqua complexes; here HL=alkylthioacetic acid), which are easily obtained from the aqueous solution. Therefore, we have started the structural research of this type of complexes. Although powder or fiber-like crystals of them were easily obtained, the formation of the single crystals suitable for the X-ray diffraction study was not easy. The single crystals of the title complex, obtained after many attempts, were used for its crystal and molecular structure determination.

The structural changes between the diaqua complex and the anhydride complex are also shown in the later part of this paper.

Experimental

Syntheses of Diaquabis(methylthioacetato)cobalt(II); $[Co(CH_3\cdot S\cdot CH_2\cdot CO_2)_2(H_2O)_2]$. The ligand was obtained by the slight modification of the method of Larsson:[22] a condensation reaction between dimethyl sulfate (in place of methyl iodide) and mercaptoacetic acid in the presence of sodium hydroxide in aqueous medium. The crude cobalt(II) complex was obtained by the reaction between cobalt(II) chloride and the sodium salt of the ligand in aqueous solution in the presence of a little sodium hydrogencarbonate. Then the concentrated aqueous solution of the complex was left standing for several weeks at 6 °C, and the crystals came out. Although many large crystals which looked like single crystals under microscopic observation were obtained, almost all of them consisted of many needle-like crystals in parallel, so they gave broad spots on Weissenberg photographs. From the 37 samples tried, only 2 crystals were obtained which could be used to obtain the diffraction data. Analyses of the complex. Found: Co, 19.38; C, 23.61; H, 4.61%, magnetic moment 4.8_2 BM** (per 1 mol of cobalt). Calcd for $CoC_6H_{14}S_2O_6$, Co, 19.31; C, 23.61; H, 4.62%.

Dehydration of Diaquabis(methylthioacetato)cobalt(II). When the title complex was heated to 140—150 °C for a few hours in air, the dark-red powder anhydride was obtained, this is amorphous, judging from the X-ray powder pattern. Analyses of the product. Found: Co, 21.90; C, 26.65; H, 3.84%, magnetic moment 4.9_0 BM** (per 1 mol of cobalt). Calcd for $CoC_6H_{10}S_2O_4$: Co, 21.89; C, 26.77; H, 3.74%. When the product was heated at 150 °C continuously, it decomposed slowly.

When the title complex was dehydrated by evaporating its benzene–ethanol mixed solvent solution two times, and then its benzene solution about five times (at 80 °C using rotary vacuum evaporator), another type of anhydride was obtained. (To complete the dehydration process, preferably, the anhydride obtained by the above mentioned process is to be kept in refluxed *p*-xylene for several hours.) The product was red-violet powder. Analyses Found: Co, 21.78; C, 27.15; H, 3.71%, magnetic moment 4.8_2 BM** (per 1 mol of cobalt). Calcd for $Co_6C_{36}H_{60}S_{12}O_{24}$: Co, 21.89; C, 26.77; H, 3.74%. As shown later, their infrared and visible spectroscopic properties of this anhydride resemble those of the bis(propylthioacetato)cobalt(II) hexamer *p*-xylene adduct,[15] and it is tentatively named as the hexamer-type anhydride.

X-Ray Measurement. The single crystals obtained were needle-like ones and were pale-red in color; they were stable in air. As they were too brittle, a crystal $0.4\times0.2\times0.2$ mm in size was used for X-ray measurement, without any additional reshaping process.

** 1 BM$=9.274078(36)\times10^{-24}$ J T^{-1}.

The crystallographic data are as follows: $CoC_6H_{14}S_2O_6$, F.W.=305.24, triclinic, space group $P\bar{1}$, a=6.750(2), b=9.214(4), c=5.206(2) Å, α=102.57(6), β=103.44(6), γ=100.70(3)°, Z=1, D_x=1.702(3), D_m=1.72(3) mg m^{-3}, μ(Mo $K\alpha$)=1.89 mm^{-1}. The reflections within the range of $2\theta < 60°$ were collected on a Philips 1100 automated four-circle diffractometer, using Mo $K\alpha$ radiation (0.7107 Å) and applying the ω—2θ scan technique. The 1175 independent reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the structure refinement. The intensities were corrected for Lorentz and polarization factors, but no correction was made for absorption and extinction.

All the calculations were carried out on a HITAC 8700/8800 computer at the Computer Center of The University of Tokyo, using the local version of UNICS program.[23] The atomic scattering factors were taken from the tables.[24]

Structure Determination. The structure was solved by the heavy-atom method. The positions of the cobalt and sulfur atoms were deduced from a three-dimensional Patterson map, and all the other non-hydrogen atoms were successively located by Fourier syntheses; their positions and their thermal parameters were refined by a repeated block-diagonal least squares method. Then the positions of all hydrogen atoms were obtained from a difference Fourier synthesis, and were also refined. In the last cycle of the refinement with anisotropic temperature factors for all non-hydrogen atoms, all the parameter shifts were less than one-third of the corresponding standard deviations. The final R value was 0.034.[25]

The Other Measurements. Magnetic moments of the solid powder samples were measured using a Gouy balance, at 25 °C.

The simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) were carried out with Rigaku Denki M-8075 using a sample weighing 10 mg in each operation, with the heating rate of 10 °C min^{-1} in air, using α-alumina as the reference.

The infrared spectra of the samples were obtained by means of a JASCO infrared spectrophotometer, type 403G, using Nujol and hexachloro-1,3-butadiene mull.

The visible absorption spectra of the samples were obtained by a Hitachi 124 spectrophtometer, and their reflectance spectra by the same instrument using the appropriate attachment.

Results and Discussion

The final atomic parameters are listed in Table 1,[26] the atomic distances and the bond angles in Table 2. A perspective drawing of the complex and the numbering scheme of atoms are shown in Fig. 1, and a projection of the structure along b^* in Fig. 2. The crystal consists of discrete molecules of $[Co(CH_3\cdot S\cdot CH_2\cdot CO_2)_2(H_2O)_2]$, except for weak hydrogen bondings. The molecules has a center of symmetry, occupied by a cobalt atom. As shown in Fig. 1, the central metal in this complex is in a deformed octahedral environment, elongated in both the coordinated sulfur atom directions. Methylthioacetato ligand forms a five-membered chelate ring, coordinating through a sulfur atom and a carbonyl oxygen atom. Two water molecules also coordinate to the cobalt atom. The value of the magnetic moment of the complex shows no interaction between cobalt atoms.

The Co–S distance is 2.531(1) Å, which is almost the same as that in the bis(propylthioacetato)cobalt(II) hexamer,[15] and which is slightly longer than that of the four, five or six-membered ring chelate dithiolato complexes of cobalt(II).[27–29] As the sum of the covalent bond radii (Pauling) of Co(II) and S is 2.36 Å, the Co–S bond of this chelate is a little weaker than that of the common sulfur-coordinated cobalt(II) complexes. The distance C(1)–O(1) (where O(1) of the ligand coordinates to Co), is 1.278(3) Å; this is longer than C(1)–O(2): 1.228(4) Å. Therefore, the carboxyl group of the ligand is in rather a covalent character in the chelate, because the bond length C(1)–O(1) and C(1)–O(2) should be about equal when it has the ionic character.

The coordinated water molecule forms hydrogen bonds with the O(1) atom of the complex which is

Table 1. Final atomic coordinates ($\times 10^4$ for non-hydrogen atoms, and $\times 10^3$ for hydrogen atoms) and isotropic temperature factors (B/Å^2) with estimated standard deviations in parentheses

	x	y	z	B_{eq}/Å$^{2a)}$
Co	0	0	0	1.4
S	437(1)	2744(1)	−283(1)	2.6
O(1)	−2045(3)	595(2)	2133(4)	2.6
O(2)	−3945(3)	2196(2)	3395(4)	3.2
O(W)	2397(3)	596(2)	3634(4)	3.0
C(1)	−2751(4)	1787(3)	2091(5)	2.3
C(2)	−2101(4)	2774(3)	262(6)	2.9
C(3)	2115(5)	3925(3)	3034(7)	3.8
	x	y	z	B_{iso}/Å^2
H(1)	−200(5)	392(3)	109(6)	3.0(7)
H(2)	−309(5)	234(4)	−157(7)	3.5(7)
H(3)	354(6)	391(4)	297(8)	4.7(8)
H(4)	204(6)	503(4)	332(8)	4.9(9)
H(5)	169(6)	331(4)	442(8)	5.3(9)
H(W1)	366(5)	106(4)	373(7)	4.3(8)
H(W2)	226(5)	22(4)	486(7)	3.8(8)

a) The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression: $B_{eq}=\frac{4}{3}(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{12}ab\cos\gamma+B_{13}ac\cos+\beta+B_{23}bc\cos\alpha)$. The B_{ij}'s are defined by: exp $[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})]$.

Table 2. Interatomic distance (l/Å) and bond angles (ϕ/°) with estimated standard deviations in parentheses

Co–S	2.531(1)	C(1)–C(2)	1.533(4)
Co–O(1)	2.042(2)	C(2)–S	1.805(3)
Co–O(W)	2.066(3)	C(3)–S	1.807(4)
O(1)–C(1)	1.278(3)	O(W)···O(2)^{I}	2.685(3)
O(2)–C(1)	1.228(4)	O(W)···O(1)^{II}	2.702(3)
S–Co–O(1)	82.03(6)	O(2)–C(1)–C(2)	117.0(3)
S–Co–O(W)	93.29(5)	C(1)–C(2)–S	115.0(2)
O(1)–Co–O(W)	90.05(8)	C(2)–S–C(3)	99.6(1)
Co–O(1)–C(1)	123.0(2)	Co–S–C(2)	91.2(1)
O(1)–C(1)–C(2)	118.4(3)	Co–S–C(3)	105.8(1)
O(1)–C(1)–O(2)	124.6(3)		

Key to symmetry operations: I. $1.0+x$, y, z; II. $-x$, $-y$, $1.0-z$.

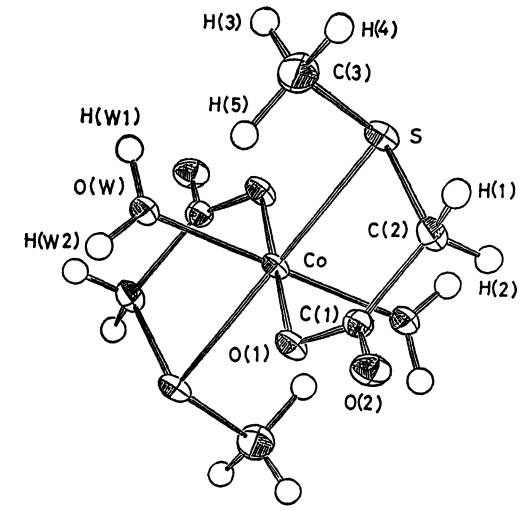

Fig. 1. A perspective drawing of the title compound with their numbering scheme of atoms.

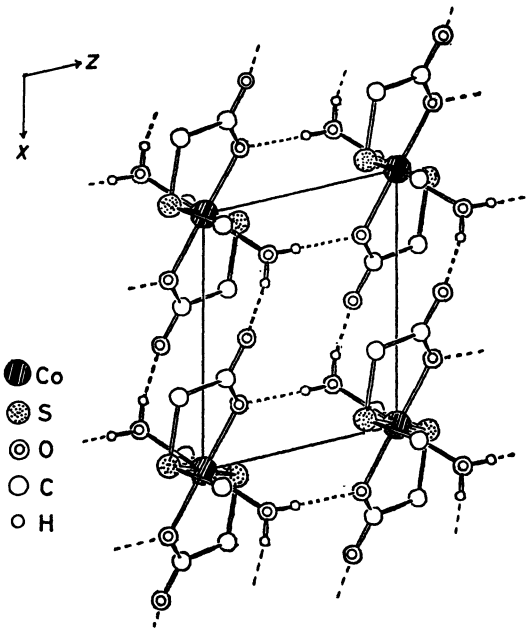

Fig. 2. Crystal packing diagram projected along b^*.

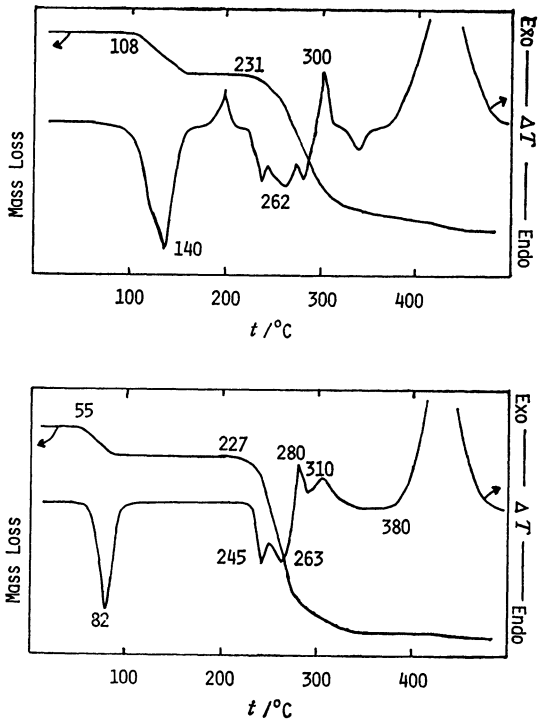

Fig. 3. Thermogravimetric and differential thermal analysis curves of a) diaquabis(methylthioacetato)-cobalt(II) (upper), and b) diaquabis(propylthioacetato)cobalt(II) (lower) (10 °C min^{-1}).

located next in the c-axis direction, as well as with the O(2) atom of the complex next in the a-axis direction. The crystal preferably grows in the c-axis direction, and a needle-like one is commonly obtained. The crystal cleaved along both of (100) and (010) planes, although the cleavage along the former plane must break hydrogen bondings between complexes.

The results of the simultaneous TG and DTA of [diaquabis(methylthioacetato)cobalt(II)] and of [diaquabis(propylthioacetato)cobalt(II)] are shown in Fig. 3. Their general features resemble each other, although the methylthioacetate is dehydrated in the higher temperature region. At the second step, a drastic mass loss occurs at about 230—300 °C in both cases. Their DTA curves show that several endo- and exo-thermal reactions occur in this region, and the complexes are completely decomposed into some tar-like materials. The TG curve of the methylthioacetate shows a plateau between 140—230 °C. The anhydride corresponding with this region is an "amorphous anhydride" obtained by heating the diaqua complex at about 140—150 °C; this fact was determined from the X-ray powder pattern. From the propylthioacetate, the same type of anhydride was also obtained by the same process, but by heating at a lower temperature (100—110 °C).

When diaquabis(propylthioacetato)cobalt(II) was dehydrated by evaporation together with a benzene–ethanol mixture, and then with benzene, the obtained product was the amorphous anhydride; this has similar spectroscopic properties to those of the one obtained by heating the solid diaqua complex in air. However, when the amorphous anhydride was dissolved in some non-polar solvent, such as benzene, carbon tetrachloride, or xylene, and dried at room temperature, the anhydride hexamer or its organic solvent adducts were obtained. Its hexamer *p*-xylene adduct, used for the crystallographic analysis, was obtained by the gradual dissolution of petroleum ether into a xylene solution of the amorphous anhydride at room temperature.[15]

The infrared spectra of diaquabis(methylthioacetato)-cobalt(II), its amorphous anhydride, and its hexamer-type anhydride form, and those of diaquabis(propylthioacetato)cobalt(II) and its anhydride hexamer (*p*-xylene adduct), are all shown in Fig. 4. Although the wave number of each corresponding peak differs in some extent, the general features of the spectra of their diaqua complexes, and of the spectra of their hexamer or hexamer-type anhydride, are almost identical in the

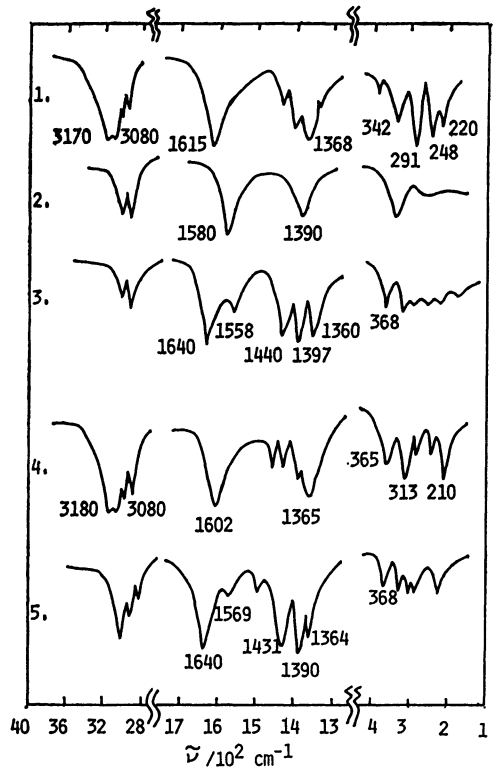

Fig. 4. Infrared spectra of the complexes. 1—3) Bis(methylthioacetato)cobalt(II); 1) diaqua complex, 2) amorphous anhydride, 3) hexamer-type anhydride. 4, 5) Bis(propylthioacetato)cobalt(II); 4) diaqua complex, 5) hexamer *p*-xylene adduct.

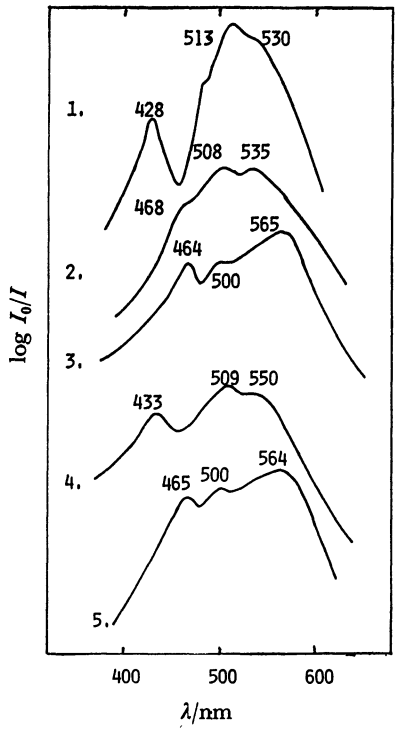

Fig. 5. Reflectance spectra of the complexes. 1—3) Bis(methylthioacetato)cobalt(II); 1) diaqua complex, 2) amorphous anhydride, 3) hexamer-type anhydride. 4, 5) bis(propylthioacetato)cobalt(II); 4) diaqua complex, 5) hexamer *p*-xylene adduct.

wave number region shown. The ν(O–H) peaks of both diaqua complexes appear at about 3100 cm^{-1} (split into 2 peaks), which is lower than those of common crystalline water in metal complexes. This fact is explained by the coordination of water to the central metal, as shown by the structure analysis of the title complex, diaquabis(methylthioacetato)cobalt(II). The wave numbers of ν_{as}(COO) and of ν_s(COO) are characteristic of each type of the complexes. In the case of both diaqua complexes, these peaks appeared at 1602 or 1615 and 1365 or 1368 cm^{-1}, those of the hexamer appeared as a strong ν_{as}(COO) peak at 1640 cm^{-1} (with a small one at 1569 or 1558 cm^{-1}), and the characteristic triplet ν_s(COO) peaks with the maxima at 1431 or 1440, 1390 or 1397, and 1364 or 1360 cm^{-1}. (The causes of the splitting and the shift of the peaks have not been analysed in detail, yet. At this stage, only the correspondence of those peaks in their general features was shown). As shown in Fig. 4, the amorphous anhydride of the methylthioacetate shows infrared spectral peaks different from those of either the diaqua complex or the hexamer-type one, in their maximum wave numbers as well as in their shapes. The far-infrared spectra of both types of complexes, diaqua and hexamer-type, also show characteristic patterns.

The reflectance spectra of these products are shown in Fig. 5. As in the case of infrared spectra, the spectra of the diaqua complexes of cobalt(II) methylthioacetate and of propylthioacetate are almost identical. Moreover, those of their hexamer-type anhydrides exhibit the same features.

From these infrared and reflectance spectral results, the diaqua complexes and the hexamer-type anhydrides of the methylthio- and propylthioacetate are likely to have the same types of structure. Their amorphous anhydrides have a structure different from the other two. It is likely to be in a polymer-type structure, but this is not yet clarified.

Although the hexamer of the propylthioacetate of cobalt(II) is soluble in many non-polar organic solvent, the methylthioacetate cannot be dissolved in benzene, xylene, toluene, or carbon tetrachloride at ambient temperature. The 1,1,2,2-tetrachloroethane solution of the methylthioacetate, stable at room temperature, can be obtained when its anhydride (hexamer-type one) is heated with the solvent and cooled.

The hexamer-type anhydride of methylthioacetate and propylthioacetate, dissolved in some non-polar organic solvent, show spectral patterns similar in their features. These patterns are similar to their reflectance spectra, too. Consequently, the hexamer structure shown by the crystallographic analysis of the propylthioacetate is kept in the solution, and the methylthioacetate complex is likely to have the same of a very similar structure in both its solid and its solution state. Beer's law is followed in the concentration region of 0.04—0.01 mol dm^{-3} (per monomer cobalt(II) complex). The high absorption coefficients of peaks, as well as the complicated splittings, correspond to the deformation from the octahedral configuration to an approximately

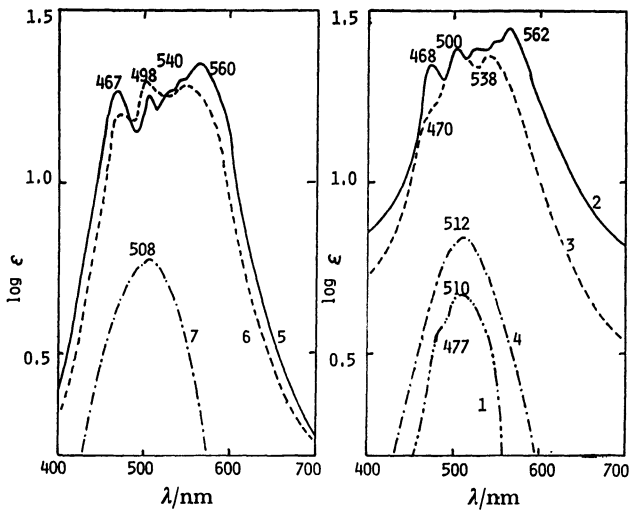

Fig. 6. Absorption spectra of the complexes in solution. 1) Cobalt(II) chloride hexahydrate in water, 2—4) bis(methylthioacetato)cobalt(II); 2) hexamer-type anhydride in 1,1,2,2-tetrachloroethane, 3) hexamer-type anhydride in the mixed solvent of 1,1,2,2-tetrachloroethane and ethanol (4 : 1, v/v), 4) diaqua complex in water (0.07 mol dm^{-3}), 5—7) bis(propylthioacetato)cobalt(II); 5) hexamer *p*-xylene adduct in benzene, 6) hexamer *p*-xylene adduct in the mixed solvent of benzene and ethanol (4 : 1, v/v), 7) diaqua complex in water (0.07 mol dm^{-3}).

squarepyramid one (Co–S is weak and elongated), around the cobalt(II) atoms.[15,30]

As shown in Fig. 6, when ethanol or some such slightly polar solvent was added to the solution of the hexamer-type anhydride mentioned above, the spectral pattern changed, and the destruction of the hexamer structure was suggested. The features of the spectra of their solutions in pure alcohols resemble those of their aqueous solution, although their absorption coefficients are higher.

When the diaqua complexes of both the alkylthioacetates were dissolved in water, the solutions showed neither the peak at 430 nm nor the shoulder about 530 nm, in their reflectance spectra. The spectra of their aqueous solution resemble those of the aqueous solution of cobalt(II) chloride. However, the intensities of the peak maxima of the former ones are higher than that of the latter one, when the former solutions are in higher concentrations (about 0.05—0.1 mol dm^{-3}). The absorption coefficients decrease as the concentration decreases, and the value tends to coincide with that of the hexaaquacobalt(II) ion. This fact shows that the methylthioacetate of cobalt(II) is decomposed in its aqueous solution, and that the ligand is almost completely dissociated in its dilute aqueous solution.

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