Preparation of Chromium(III) and Cobalt(III) Complexes with *d,l*-α-Phenylalanine-*N,N*-diacetic Acid[1]

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The following chromium(III) and cobalt(III) complexes with PADA (*d,l*-α-phenylalanine-*N,N*-diacetic acid) were prepared: $K[Cr(OH)pada(H_2O)]\cdot 5H_2O$ (violet) (I), $K[Cr(OH)pada(H_2O)_2]\cdot 3H_2O$ (green)(II), $(enH_2)_{1/2}[Cr(OH)pada(H_2O)_2]$ (green) (III), [Cr pada(*o*-phen)]$\cdot H_2O$ (brown) (IV), $K_2[Cr(ox)pada]\cdot 2H_2O$ (violet) (V), $K[Co(OH)pada(H_2O)]\cdot 5H_2O$ (blue-violet) (VI), and $K_2[Co_2(OH)_2(pada)_2]$ (brown-pink) (VII). On the basis of electronic spectra in both aqueous solution and solid state, it was found that PADA behaves toward central metal as a quadridentate ligand in complexes I, IV, V, VI, and VII; in other words, unlike the case of nitrilotriacetic acid (NTA), nitriloisopropionicdiacetic acid (NIPDA) and *l*-leucine-*N,N*-diacetic acid (LDA), PADA did not give different coordinating structures to the respective complexes in solid state and aqueous solution. From thermal analysis with derivatograph in the reaction processes of complex VI, it was found that the complex liberates one mole of coordinating water at about 170—180°C, resulting in the formation of the diol complex VII.

The authors have studied the preparation and properties of the chromium(III) and cobalt(III) complexes with NTA,[2,3] NIPDA,[4] LDA,[5] NPDA,[6] and AEDA.[7] Continuing these studies, we tried to prepare the corresponding complexes with PADA. The rational formulas of the chelating agents concerned are given in Table 1. In spite of a similar frame in these agents, the coordinating behaviors somewhat differ from each other due to differences in the fine structures and in the chemical properties such as acid dissociation constants. For instance, the ligands forming three five-membered chelate rings such as NTA, NIPDA, and LDA act toward metals as either N–O_3, N–O_2, or O_3 type, whereas the ligands forming two five- and one six-membered chelate rings such as NPDA and AEDA do not act as O_3 type.

If one of hydrogen atoms in a methylene group in NTA is substituted by a more bulky radical such as benzyl group, it is expected that the coordinating behaviors considerably differ from NTA, NIPDA, and LDA probably due to the stronger steric effect of the ligand substituted as above. The main purpose of the present work is to prepare PADA and the complexes therewith in order to confirm the above expectation.

When the ligands NTA and its analogues act as a quadridentate toward metal, the remaining *cis* sites are occupied by H_2O and OH^- in an aqueous medium. Therefore, an olation process expressed by the following scheme is expected in appropriate thermal conditions:

$$2[M(OH)L(H_2O)]^- \xrightarrow[-2H_2O]{} [L\ M(OH)_2M\ L]^{2-},$$

where M and L denote central metals such as chromium(III) or cobalt(III) and the quadridentate ligands, analogues of NTA, respectively. Another purpose of this study is to find a consistency between the diol complex thermally obtained as above and that directly prepared.

Table 1. Rational formula and abbreviation of chelating agents

Rational formula	Chelate ring	R	Chelating agent
R CHCOOH N–CH_2COOH CH_2COOH	5, 5, 5	H	NTA[a]
		CH_3	NIPDA[a]
		$CH_2\cdot CH(CH_3)_2$	LDA[a]
		$CH_2\cdot C_6H_5$	PADA[a]
$CH_2CH_2\cdot R$ N–CH_2COOH CH_2COOH	5, 5, 6	COOH	NPDA[a]
		SO_3H	AEDA[a]

a) NTA, Nitrilotriacetic Acid;[2] NIPDA, Nitriloisopropionicdiacetic Acid;[4] LDA, *l*-Leucine-*N,N*-diacetic Acid;[5] PADA, *d,l*-α-Phenylalanine-*N,N*-diacetic Acid; NPDA, Nitrilopropionicdiacetic Acid;[6] AEDA, β-Aminoethylsulfonic-*N,N*-diacetic Acid.[7]

Experimental

Preparation of d,l-*α-Phenylalanine*-N,N-*diacetic Acid.* Sixteen grams of *d,l*-α-phenylalanine was dissolved in 100 m*l* of water containing 7 g of potassium hydroxide, and 100 m*l* of aqueous solution containing 19 g of monochloroacetic acid was dropwise neutralized with 20 g of potassium hydrogen carbonate. The latter solution should be added gently and carefully, or else the deposition of *d,l*-α-phenylalanine takes place. The mixed solution was heated on a water bath, 30 m*l* of water containing 12 g of potassium hydroxide being added. Heating was continued for one hour in order to complete the condensation reaction. After the resulting solution was cooled to room temperature, the pH of the solution was adjusted to 2—3 by adding concentrated hydrochloric acid. White powdered crystals were easily obtained. Recrystallization of the crude product was carried out by dissolving it in potassium hydrogen carbonate solution and by adjusting the pH of the solution to 2—3. Yield 10 g.

Found: N, 4.99; C, 55.55; H, 5.85%. Calcd for $N(CH(CH_2C_6H_5)COOH)(CH_2COOH)_2$: N, 4.80; C, 55.13; H, 5.89%.

Preparation of Complexes. Preparative procedures of the complexes are schematically shown in Table 2.

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[1] Presented in part at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, March, 1969.

[2] A. Uehara, E. Kyuno, and R. Tsuchiya, This Bulletin, **40**, 2317 (1967).

[3] *Idem., ibid.*, **40**, 2322 (1967).

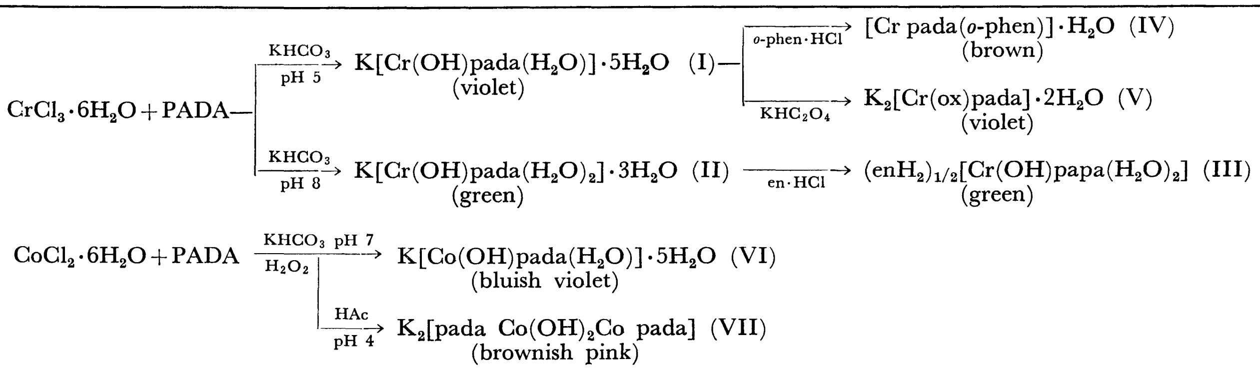
[4] *Idem., ibid.*, **41**, 2393 (1968).

[5] *Idem., ibid.*, **43**, 414 (1970).

[6] *Idem., ibid.*, **41**, 2385 (1968).

[7] *Idem., ibid.*, **42**, 2835 (1969).

TABLE 2. PREPARATIVE SCHEME FOR CHROMIUM(III) AND COBALT(III) PADA COMPLEXES



*Potassium Hydroxo-*d,l-*α-phenylalanine-*N,N-*diacetatoaquochromate(III) Pentahydrate,* $K[Cr(OH)pada(H_2O)]\cdot 5H_2O$ *(I):* Two hundred milliliters of water containing 14 g of PADA was neutralized with 6 g of potassium hydroxide. The solution was added to 100 m*l* of water containing 13 g of chromium(III) chloride hexahydrate, and the mixture was heated on a water bath until the color of the solution turned violet. After the pH of the solution was carefully adjusted to 5, the solution was concentrated to about 200 m*l* and left to stand in a refrigerator. Violet crystals were obtained which were recrystallized from water. Yield 4 g.

Found: N, 2.84; C, 31.60; H, 5.06%. Calcd for $K[Cr(OH)pada(H_2O)]\cdot 5H_2O$: N, 2.96; C, 31.91; H, 4.83%.

*Potassium Hydroxo-*d,l-*α-Phenylalanine-*N,N-*diacetatodiaquochromate(III) Trihydrate,* $K[Cr(OH)pada(H_2O)_2]\cdot 3H_2O$ *(green) (II):* The preparative procedure was the same as for complex I until the violet solution was obtained. When the pH of the solution was carefully adjusted to 8, the color turned green. The resulting solution was left to stand in a refrigerator. Green crystals were obtained which were recrystallized from water. Yield 1.5 g.

Found: N, 2.94; C, 32.78; H, 4.83%. Calcd for $K[Cr(OH)pada(H_2O)_2]\cdot 3H_2O$: N, 3.10; C, 32.90; H, 5.13%,

*Ethylenediammonium Hydroxo-*d,l-*α-phenylalanine-*N,N-*diacetatodiaquochromate(III),* $(enH_2)_{1/2}[Cr(OH)pada(H_2O)_2]$ *(green) (III):* Four and a half grams of complex II was dissolved in 100 m*l* of water containing 4 g of ethylenediamine hydrochloride. A gradual concentration on a water bath soon produced green crystals which were recrystallized from water. Yield 2.5 g.

Found: N, 3.39; C, 40.61; H, 5.31%. Calcd for $(enH_2)_{1/2}[Cr(OH)pada(H_2O)_2]$: N, 3.12; C, 40.67; H, 5.72%.

d,l-*α-Phenylalanine-*N,N-*diacetato-*o-*phenanthrolinechromium(III) Monohydrate,* $[Cr\ pada(o\text{-}phen)]\cdot H_2O$ *(brown) (IV):* Five grams of complex I was dissolved in a 200 m*l* of water, and then 2 g of *o*-phenanthroline was added to the solution. The pH of the solution was adjusted to *ca.* 5, and the solution was warmed on a water bath until the color turned brown. From the cooled solution brown crystals were obtained which were recrystallized from water. Yield 2 g.

Found: N, 7.96; C, 55.83; H, 4.10%. Calcd for $[Cr\ pada(o\text{-}phen)]\cdot H_2O$: N, 7.61; C, 56.16; H, 3.92%.

*Potassium Oxalato-*d,l-*α-phenylalanine-*N,N-*diacetatochromium(III) Dihydrate,* $K_2[Cr(ox)pada]\cdot 2H_2O$ *(violet) (V):* Five grams of complex I was dissolved in 100 m*l* of water containing 0.5 g of potassium hydroxide and 1.5 g of oxalic acid. When the solution was heated on a water bath, the color gradually turned from violet to bright violet. The solution was left to stand in a refrigerator for several days. Violet crystals were obtained which were recrystallized from water. Yield 1 g.

Found: N, 2.64; C, 33.83; H, 3.01%. Calcd for $K_2[Cr(ox)pada]\cdot 2H_2O$: N, 2.83; C, 33.41; H, 2.82%.

*Potassium Hydroxo-*d,l-*α-phenylalanine-*N,N-*diacetatoaquocobaltate(III) Pentahydrate,* $K[Co(OH)pada(H_2O)]\cdot 5H_2O$ *(blue-violet) (VI).* Seven grams of PADA was dissolved in 200 m*l* of water containing 6 g of potassium hydroxide. Six grams of cobalt(II) chloride hexahydrate was dissolved in 50 m*l* of water. The latter was added little by little under magnetic stirring. The two solutions must not be mixed in the reverse order, otherwise the deposit of PADA is formed. The pH of the mixed solution was carefully adjusted to 6—7, and a few milliliters of hydrogen peroxide solution was added in order to oxidize cobalt(II) ion. As soon as the solution turned violet, it was stored in a refrigerator. Bluish-violet crystals were obtained. Since the solution sometimes turned from violet to brownish pink when the pH was not adequately adjusted, it had to be kept violet in order to obtain the desired complex. Recrystallization was carried out from water. Yield 1.5 g.

Found: N, 2.82; C, 30.11; H, 5.10%. Calcd for $K[Co(OH)pada(H_2O)]\cdot 5H_2O$: N, 2.79; C, 31.17; H, 5.03%.

*Potassium μ-Dihydroxobis(*d,l-*α-phenylalanine)-*N,N-*diacetatodicobaltate(III),* $K_2[pada\ Co(OH)_2Co\ pada]$ *(brown-pink) (VII):* The compound was prepared from the filtrate after the crystals of complex VI were removed as precipitate. After the pH of the filtrate was adjusted to 3—4, the resulting solution was gently heated on a water bath until the color of the solution turned brownish pink. On cooling, brownish pink crystals were obtained. Purification of the crystals was carried out from water. Yield 1 g.

Found: N, 3.60; C, 39.84; H, 3.33%. Calcd for $K_2[pada\ Co(OH)_2Co\ pada]$: N, 3.56; C, 39.73; H, 3.33%.

Instruments. The instruments used in the present work are the same as described previously.[6]

Results and Discussion

IR Spectra. IR spectra for the complexes were measured in a Nujol-mull state. It is known that characteristic bands for free and coordinated carboxylic acid generally appear at ~1750 and ~1640 cm^{-1}, respectively, in aminopolycarboxylic acid complexes.[8] Since the complexes prepared in the present work showed a band near ~1640 cm^{-1}, it is obvious that the carboxylate groups in the complexes are all coordinated.

Molar Conductivity and Magnetic Moment. Molar

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[8] D. H. Bush and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **75**, 4574 (1953).

conductivities were measured in an aqueous solution at 25°C in order to find the type of electrolytes for the complexes. Magnetic moments were evaluated from the magnetic susceptibilities measured by the Gouy method. The results are given in Table 3.

TABLE 3. MOLAR CONDUCTIVITY (λ), MAGNETIC MOMENT (μ_{eff}) AND COAGULATION VALUE (mF)

Complex	$\lambda^{a)}$ mho cm^{-1}	mF$^{b)}$	μ_{eff} B.M. (°K)
I	125.6		3.83 (296)
II	121.3		3.86 (295)
III	148.9		3.78 (296)
IV	5.2		3.91 (296)
V	254.3		3.85 (296)
VI	121.2	5.7	dia. (295)
VII	154.8	0.5	dia. (295)

a) 10^{-3} mol/l aqueous solution was used at 25°C.
b) $Fe(OH)_3$ sol was used.

The values of the molar conductivities for the complexes I, II, III, and VI fairly support the view that they are 1 : 1 type electrolyte. The values for the complexes IV and V indicate that the former is a nonelectrolyte and the latter, 1 : 2 type electrolyte, respectively. On the other hand, the value for complex VII may be somewhat smaller than that expected for 1 : 2 type electrolyte as $K_2[Co_2(OH)_2pada_2]$. However, the fact that the coagulation value for VII measured by using ferric oxide hydrosol was 0.5 milliformol will support 1 : 2 type for VII.

The values of the magnetic moments for complexes I—V were in the region of 3.8—3.9 B.M., while the magnetic susceptibilities for complexes VI and VII showed that they are diamagnetic. This indicates that the central metals chromium and cobalt in complexes are both tervalent.

Electronic Spectra. It has often been pointed out that the ligands NTA,[2] NIPDA,[4] and LDA,[5] forming three five-membered chelate rings can act as a terdentate ligand of O_3 and N–O_2 as well as a quadridentate ligand of N–O_3 type. Though PADA also has three five-membered chelate rings as in the above three ligands, how does it behave toward metals?

Figure 1 shows the spectra for complex I in aqueous solution and solid state together with those for the corresponding NTA complex $K[Cr(OH)nta(H_2O)]\cdot 2H_2O$. The former two spectra closely resemble that for NTA-complex in solid state but not in aqueous solution, indicating that the coordinating structure of complex I is the same as that for NTA-complex in solid state. It has been assigned that NTA, NIPDA, and LDA act as a quadridentate (N–O_3) in a solid and as a terdentate (O_3) in a solution. In the case of PADA, no such phenomenon could be detected.

Figure 2 contains the spectra for complexes II and III in aqueous solution, together with that for the corresponding NTA complex, $K[Cr(OH)nta(H_2O)_2]\cdot 3H_2O$. Since their spectra are substantially similar, it will be accepted that PADA acts as a terdentate ligand in complexes II and III. Though PADA can act toward metals as both a quadridentate and terdentate, as seen in complexes I, II, and III, the coordinating manner does not change as extensively as that in NTA, NIPDA, or LDA. This may be due to the stronger steric hindrance by a large radical (benzyl radical) in PADA.

The absorption spectra for complexes VI and VII in aqueous solution are given in Fig. 3. Inamura

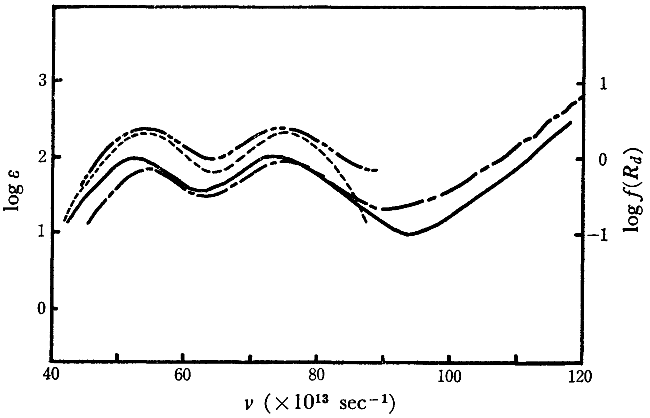

Fig. 1. Electronic spectra for complex I in an aqueous solution (———), in a solid state (— — —) and $K[Cr(OH)nta(H_2O)]\cdot 2H_2O$ in an aqueous solution (——), in a solid state (----).

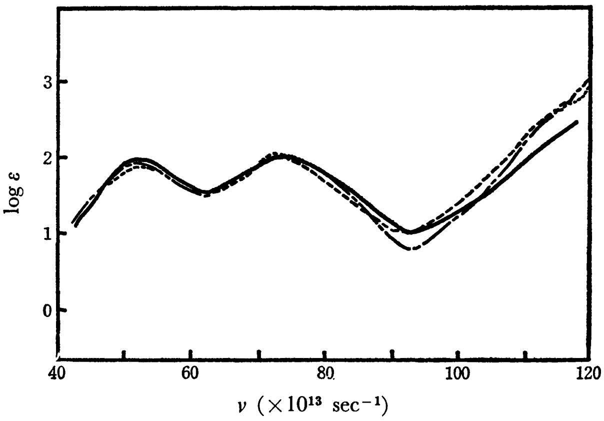

Fig. 2. Electronic spectra for complexes II (----), III (— — —) and $K[Cr(OH)nta(H_2O)_2]\cdot 3H_2O$ (——).

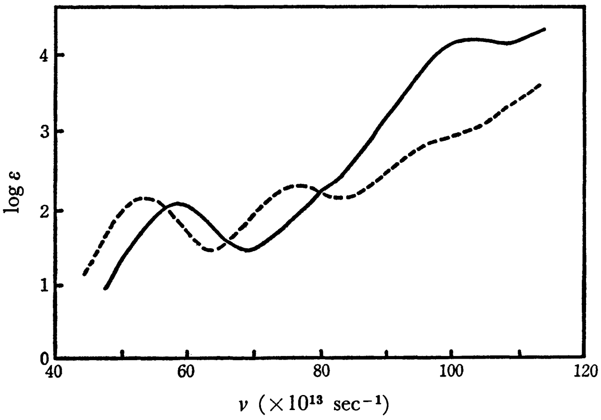

Fig. 3. Electronic spectra for complexes VI (----) and VII (——).

and Kondo[9] have reported that the spectra for the ol-ammine cobalt(III) complexes containing bridged OH groups show no distinct second d-d band, but a band due to bridged OH groups at 90—100×10^{13} (c/s). As an example, it can be shown that K$_2$[nta-Co(OH)$_2$Co nta] gives a band at near 100×10^{13} (c/s).[10] As seen from the figure, complex VII does now show such a distinct second band as in the case of complex VI, but a band at 100×10^{13} (c/s) appears predominantly. From these results, complex VII is considered to be a diol complex.

The derivatogram for complex VI is given in Fig. 4.[11] Two steps corresponding to the loss of 4 moles and one mole of water are observed in the temperature ranges of 40—90 and 90—110°C, respectively. The DTA curve in the above two steps shows the endothermic reaction. Although the mass loss corresponding to one mole of water is also detected at 170—180°C, the reaction is shown to be exothermic in spite of liberation of water. At this step, the color of the sample turned from bluish violet to brownish pink. The spectrum for complex VI picked up at 180°C in the intermediate course of the derivatograph is given in Fig. 5, together with those for complexes VI and VII. The spectrum observed for the sample obtained in the thermal process is found to be similar to that of complex VII. It is also deduced from the results that the diol complex was formed by heating complex VI.

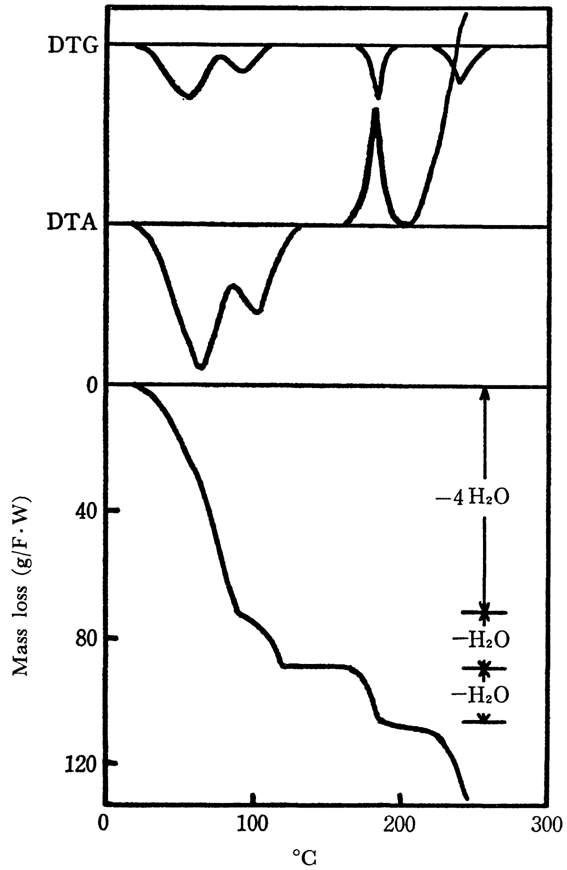

Fig. 4. Derivatogram for complexes VI.

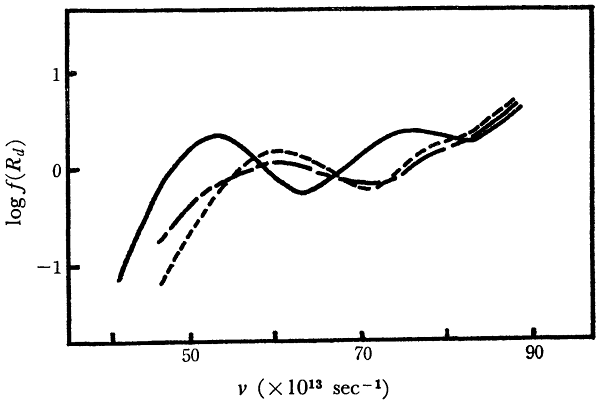

Fig. 5. Electronic spectra for complex VI (——), complex VII (----) and the sample of complex VI picked up at 180°C during heating (–·–).

TABLE 4. ABSORPTION MAXIMA

Complex	ν_1 ($\log \varepsilon_1$)	ν_2 ($\log \varepsilon_2$)	Complement
I	53.38 (1.86)	73.53 (1.98)	
II	52.17 (1.81)	73.35 (1.89)	
III	51.46 (1.93)	72.64 (1.95)	
IV	56.07 (1.98)	75.64 (2.19)	86.21 (2.97)[a)] 109.1 (4.21)[a)]
V	54.05 (1.89)	74.26 (1.92)	
IV	53.48 (2.19)	76.53 (2.35)	
VII	59.41 (2.09)	b)	~105 (~4.10)[c)]

a) The specific bands due to the coordinating *o*-phenanthlorine.

b) The band can not be clearly detected because of the strong overlap owing to the specific band of the bridging OH groups.

c) The specific band due to the bridging OH groups. The band is not clearly detected because of its broadening.

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9) Y. Inamura and Y. Kondo, *Nippon Kagaku Zasshi*, **74**, 627 (1953).

10) M. Mori, M. Shibata, E. Kyuno, and Y. Okubo, This Bulletin, **31**, 940 (1958).

11) R. Tsuchiya, A. Uehara, and E. Kyuno, This Bulletin, **44**, 701 (1971).