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Fluorinated Ligands. I. Chelating Behavior of 1-Amino-3,3,3-trifluoro-2-propanol with Copper(II) Ion and Preparation of Copper(II)-, Cobalt(III)-, and Nickel(II) Complexes*

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In the reaction of 1-amino-3,3,3-trifluoro-2-propanol (LOH) with cupric ion in aqueous solutions two kinds of complex species were found to be formed: One was a complex ion of $[Cu(LO)(H_2O)_2]^{+1}$, which was of major abundance in the solutions where mole ratio of the ligand to the metal ion was less than 3, and the other was an inner complex of $[Cu(LO)_2]$ predominating in the solutions which contained a large excess of the ligand or a small amount of alkali. The structures of the species in the solution phases were assigned by the spectral data. Chelate compounds of inner complex type, $[Cu(LO)_2(H_2O)]$, $[Co(LO)_3]$, and $[Ni(LO)_2]$, were synthesized from the present ligand and corresponding metal ion. These are insensitive to moisture in the air. Structures of the chelates are discussed on the basis of spectroscopic observations.

In connection with studies on coordinating behaviors of hydroxyl group of aminoalcohols and of their *N*-alkylated derivatives, various preparative and spectral studies have been carried out. In the early preparative studies by Hieber and Levy[1] and by Brintzinger and Hase,[2] the isolated products were complex salts containing the neutral ligands accompanied by counter anions. Complex formation with copper(II) in aqueous solution was studied by means of the spectroscopic method by Ojima and Sone,[3] who concluded that a tetraaminocopper(II) complex, $[Cu(amine)_4]^{+2}$, was formed in the region of lower concentration of the ligand, which behaved therein as a monodentate ligand, and that an increase in the ligand concentration or an addition of a strong base afforded a 1:2 (Cu: ligand) inner complex chelate. These complexes, however, could not be isolated as a stable form from such solutions. Yoneda and Kida[4] also isolated a neutral trisethanolaminecoblat(III), $[Co(NH_2CH_2CH_2O)_3]$, from a strongly alkaline aqueous solution. Subsequently Kida[5] obtained copper(II) chelates of inner complex type, $[Cu(NH_2CH_2CH_2O)_2(H_2O)]$ and $[Cu(NH_2CH(C_6H_5)CH(C_6H_5)O)_2]$, from anhydrous alkaline ethanol solutions. In every case, the isolated metal chelates of inner complex type were unstable and readily affected by moisture.

In this paper, we discuss the chelating behavior of

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[1] W. Hieber and E. Levy, *Z. Anorg. Allgem. Chem.*, **219**, 225 (1934).

[2] H. Brintzinger and B. Hase, *ibid.*, **252**, 293 (1944).

[3] H. Ojima and K. Sone, *ibid.*, **309**, 110 (1961).

[4] H. Yoneda and S. Kida, *J. Amer. Chem. Soc.*, **82**, 2139 (1960).

[5] S. Kida, *Nippon Kagaku Zasshi*, **85**, 428 (1964).

1-amino-3,3,3-trifluoro-2-propanol [$CF_3CH(OH)CH_2NH_2$; LOH] with copper ion in aqueous phases and the structures of copper(II)-, cobalt(III)-, and nickel(II) chelates of the present ligand in solid phase, in comparison with some other ethanolamine type ligands.

Experimental

Apparatus. All melting points measured were uncorrected. Visible absoprtion and reflectance spectra were measured with a Hitachi ESP-2 and a Hitachi EPU-2 spectrophotometers, respectively. The IR spectra were recorded with a JASCO DS-403G spectrophotometer. Molecular weights were determined on a Vapor Pressure Osmometer (Mechrolab Inc.) with 2-methyloxine as a standard substance for the copper complex in absolute ethanol, and *p*-bromonitrobenzene for the nickel complex in absolute methanol. Copper(II) acetate monohydrate (an extrapure grade from the Wako Pure Chemicals Co., Ltd.) was used without further purification for the reaction equilibrium study in aqueous media.

Synthesis of 1-amino-3,3,3-trifluoro-2-propanol. The aminofluoropropanol hydrochloride was prepared according to Jones.[6] Into a solution of the hydrochloride in as a small amount of water as possible, was added a saturated aqueous sodium bicarbonate up to pH 8. The freed aminopropanol was extracted with ethylether. The ethereal solution was dried and concentrated slowly on a water bath to give precipitates, which were recrystallized from ethylether, melting at 97—98°C.

Found: C, 27.77; H, 46.6; N, 8.22; Cu, 10.82%. Calcd for $C_3H_6ONF_3$: C, 27.95; H, 4.65; N, 10.82%.

Synthesis of Bis(1-amino-3,3,3-trifluoro-2-propanolato)copper(II) Monohydrate. One gram of copper acetate monohydrate was dissolved into 50 m*l* of water containing 1.3 g of the ligand, and then 0.2 M aqueous sodium hydroxide was added slowly up to pH being 8. The solution was kept at about 40°C for 12 hr on a water bath. The resulting mixture, when cooled to 0°C, gave a red-violet crystalline precipitate, which was recrystallized from an ethyl acetate-ethanol mixture, to give red-purple needles decomposing at 199—200°C.

Found: C, 21.44; H, 3.60; N, 8.22; Cu, 18.81%; mol wt, 324. Calcd for $C_6H_{12}O_3N_2F_6Cu$: C, 21.38; H, 3.56; N, 8.30; Cu, 18.81%; mol wt, 337.5.

Synthesis of tris(1-amino-3,3,3-trifluoro-2-propanolato)cobalt(III). One and three tenth gram of cobaltous perchlorate was added into 20 m*l* of ethanol containing 0.32 g of the ligand and then 0.2 M aqueous sodium hydroxide was added slowly into the mixture until its pH became 9. The solution was maintained at about 50°C on a water bath for about 24 hr. A pink powdery precipitate, which was obtained from the resulting mixture when cooled to 0°C, was washed with ethanol, and then dried *in vacuo*, decomposing at 240°C. The product was insoluble in donating solvents such as ethanol and water, whereas being soluble in inert organic solvents such as benzene.

Found: C, 24.52; H, 3.45; N, 9.99; Co, 13.63%. Calcd for $C_9H_{15}O_3N_3F_9Co$: C, 24.38; H, 3.39; N, 9.48; Co, 13.29%.

Synthesis of bis(1-amino-3,3,3-triffuoro-2-propanolato)nickel(II). A saturated ethanol solution of 0.45 g of nickel(II) perchlorate was added into a saturated ethanol solution of 0.32 g of the ligand. Light-blue crystals which precipitated immediately, were collected by filtration and recrystallized from ethanol, to give light-blue plates decomposing at 170—173°C. The complex was insoluble in an inert organic solvent such as benzene, while being soluble in a donating solvent such as methanol.

Found: C, 22.62; H, 3.48; N, 8,87% mol wt (in methanol), 312. Calcd for $C_6H_{10}O_2N_2F_6Ni$: C, 22.81; H, 3.18; N, 8.88; mol wt, 314.89.

Paper Electrophoresis. Paper electrophoresis of the copper complex was performed in a solvent immersion method on a filter paper strip soaked in a 0.1 M sodium chloride electrolyte. Potential applied between both ends (14 cm distant) was 640 V (45.7 V/cm) and current 3 mA. A copper spot of the fluoro-ligand complex did not migrate when the potential was applied for 5 min, while those of bis(ethylenediamine)copper(II) perchlorate and of copper(II) perchlorate travelled 20 mm respectively toward the negative electrode in 5 min under the same operation conditions. Diphenyl-carbazone was used as a chromogenic indicator for copper ion.

Results and discussion

Spectrophotometric Studies on the Chelating Behavior of the Ligand (LOH) with Copper(II) Ion. Figure 1 shows absorption spectra of aqueous solutions containing copper(II) ion and various amouts of the ligand (LOH). When the mole ratio of copper ion to the ligand in the solution is less than 1:2 (Cu:LOH), copper(II) ion precipitates in a form of hydroxide. A 1:3 (Cu:LOH) mixture gives a clear solution showing an absorption peak at 14500 cm^{-1}. An increase in the ligand concentration causes a blue shift of the absorption peak up to 16600 cm^{-1} until the mole ratio becomes as much as 1:6. Further increase in the ligand concentration does not produce any more shift in the absorption band. The 1:6 or 1:8 solution shows the absorption curve superimposable to that of the red-violet copper chelate in aqueous solution phases which is shown in Fig. 3. Figure 2 indicates that an addition of an equimole of aqueous sodium hydroxide to the 1:1 (Cu:LOH) mixture results in dis-

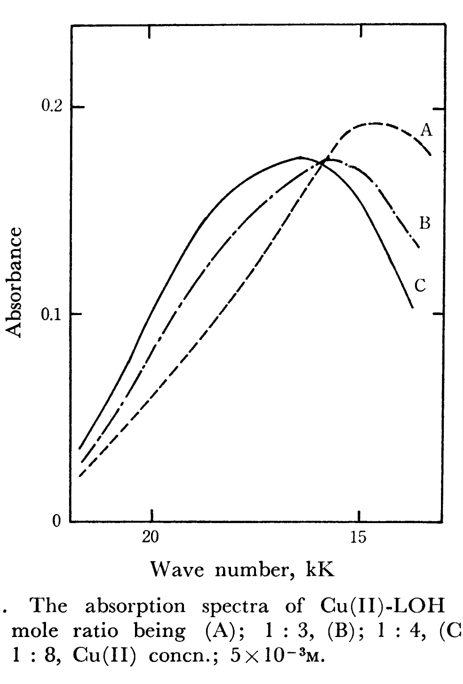

Fig. 1. The absorption spectra of Cu(II)-LOH mixture, the mole ratio being (A); 1 : 3, (B); 1 : 4, (C); 1 : 6, and 1 : 8, Cu(II) concn.; 5×10^{-3}M.

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[6] R. C. Jones, *J. Amer .Chem. Soc.*, **70**, 143 (1948).

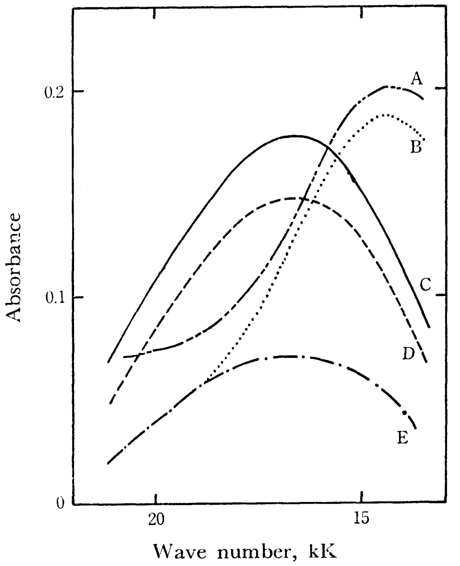

Fig. 2. The absorption spectra of a $Cu(LO)_2(H_2O)$-Cu(II) (1 : 1) mixture (A), and of Cu(II)-LOH-NaOH mixtures, the mole ratio being (B), 1 : 1 : 1, (C); 1 : 4 : 5, (D); 1 : 2 : 5 and (E); 1 : 2 : 2, Cu(II) concn.; 5×10^{-3}M.

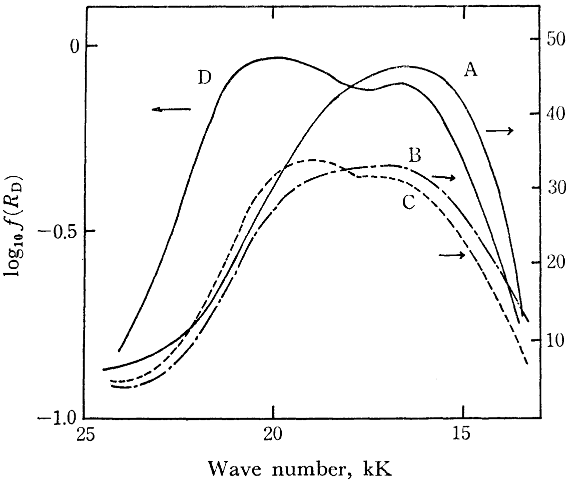

Fig. 3. The absorption spectra in water (A), methanol (B) and ethanol (C), and the reflectance spectrum (D) of $Cu(LO)_2(H_2O)$.

solution of the precipitates of copper hydroxide, giving a clear blue solution, an absorption peak of which is at 14500 cm^{-1} in good agreement with that of the 1 : 3 mixture in Fig. 1. Dissolution of the solid copper chelate, $Cu(LO)_2(H_2O)$, in an equimole of aqueous copper acetate also gives a blue solution showing the absorption curve B in Fig. 2, absorption maximum of which is also in good agreement with the above 1 : 3 mixture in Fig. 1. This value of the absorption peak corresponds to that of a 1 :1 copper chelate of ethylenediamine at 15200 cm^{-1} [7] or that of *N*-hydroxyethylethylenediamine at 14500 cm^{-1},[8] and is most likely to be ascribed to the formation of a 1 : 1 (Cu : LO^{-1}) chelate in the aqueous solutions. An ddition of alkali into the 1 : 2 (Cu : LOH) mixture in which precipitates of copper hydroxide are formed, affords a clear red-violet solution, which shows an absorption peak at 16600 cm^{-1}, as illustrated by Curve E in Fig. 2, in agreement with that of the 1 : 6 mixture in Fig. 1. Further addition of alkali or the ligand does not produce any shift of the absorption band.

In a region of the mole ratio higher than 1 : 6, the 1 : 2 inner complex is formed. An excess of the ligand is likely to play a role of an agent deprotonating from the hydroxyl group upon the chelate formation. Presence of the 1 : 2 inner complex is also indicated by the results of high voltage paper electrophoresis, which show that the copper chelate is of zero charge in aqueous media. In contrast with isopropanolamine which produced a 1 :2 chelate in a region of the mole ratio higher than 1 : 10,[3] the present ligand readily forms the neutral 1 : 2 chelate under much milder conditions.

Complexing behavior of the present fluoro-ligand, therefore, seems to be quite different from that of an ordinary ethanolamine type ligand. The latter causes precipitation of copper hydroxide in a 1 :3 (Cu :ligand) aqueous mixture and gives a tetraammine type complex in a range of mole ratio slightly higher than 1 : 4, forming no 1 : 1 chelate.[3] The trifluoromethyl group affects the donating power of the adjacent hydroxyl group presumably by its strong electron-withdrawing effect, favoring the dissociation of proton from hydroxyl oxygen. Consequently chelate formation with copper ion is more easily attained.

Spectral Studies on the Chelate Compounds of Copper(II)-, Cobalt(III)-, and Nickel(II) ions. IR spectral results on the ligand and its metal chelates are summarized in Table 1, including assignments of the bands according to Brannon.[9] The free ligand shows a broad band diffused between 3200 and 2400 cm^{-1} due to a strongly hydrogenbonded hydroxyl group, and a sharp doublet at 3330 and 3280 cm^{-1} related to a primary amino group involved in the hydrogen bonding. The hydrochloride of the ligand shows also a broad strong band centered at 3220 cm^{-1} due to a hydroxyl group, N–H stretching bands due to the ammonium group being probably hidden under the hydroxyl absortion.

Copper Complex, $Cu(LO)_2(H_2O)$. IR spectrum of the copper chelate shows a prominent absorption band spread over from 3260 to 3100 cm^{-1} due to lattice water in agreement with the result of elemental analysis, N–H absorptions again being hidden under the strong water band. The absorption peak due to ν(C–F) is observed at 1123 cm^{-1}. Figure 3 shows the visible reflectance and absorption spectra of the chelate in some donating solvents respectively. The reflectance spectrum exhibits an absorption peak and a shoulder at 20200 and about 16600 cm^{-1} respectively, indicating a square planar structure with respect to the central metal ion in the chelate molecule.[10,11]

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[7] H. B. Jonassen and T. H. Dexter, *J. Amer. Chem. Soc.*, **71**, 1553 1949).

[8] J. L. Hall and W. E. Dean, *ibid.*, **80**, 4183 (1958).

[9] D. G. Brannon, R. H. Morrison, J. L. Hall, G. L. Humphrey, and D. N. Zimmerman, *J. Inorg. Nucl. Chem.*, **33**. 981 (1971).

[10] J. P. Fackler, Jr., F. A. Cotton, and D. W. Barnum, *Inorg. Chem.*, **2**, 97 (1963).

[11] A. E. Martell, R. L. Belford, and M. Calvin, *J. Ionrg. Nucl. Chem.*, **5**, 170 (1958).

TABLE 1. CHRACTERISTIC IR FREQUENCIES FOR LIGAND AND ITS METAL CHELATES[a)]

Compound	ν(OH)	ν_a(NH)	ν_s(NH)	$\delta(NH_2)$	ν(CN)	ν(CF)	ν(CC)
LOH	3200—2400 m	3330 m	3280 m	1612 m	1160 s	1135 s	1076 m
LOH.HCl	3220 s, br	b)	b)	1602 m	1161 s	1150 s, sh	1120 m
$Cu(LO)_2.H_2O$	3260—3100 s	b)	b)	1620 s	1165 s	1123 s	1100 s
$Co(LO)_3$		3300 m	3220 m	1616 m	1165 s	1120	1100 s
$Ni(LO)_2$		3400 w	3376 w	1600 m	c)	c)	c)

a) In Nujol mulls. Frequencies are given in K(cm^{-1}). Intensity designations: w, weak; m, medium; s, strong; br, broad; sh, shoulder.
b) Obscured by hydroxyl bands.
c) Unable to be assigned due to much complicated spectrum in these region.

On the other hand, the paper electorphoresis of the chelate indicates that the complex is present as a zerocharged, neutral complex in aqueous media. Combined with the result of molecular weight determination, these observations indicate consistently the copper chelate to be an inner complex type, excluding a possibility of an ion-pair type complex such as $[Cu(LO)(LOH)]^+[OH]^-$.

Absorption spectrum in water shows at 16400 cm^{-1} a broad peak, which is at much lower wave-number with a narrower half-band width than those of the corresponding band observed in the solid reflectance spectrum. These spectral evidences indicate an existence of axial ligation of the solvent molecules on the planar tetracoordinate copper chelate to form the penta- or hexacoordinations.[12,13)]

While the spectral characteristics in methanol and in ethanol in the region between 15000 and 21000 cm^{-1} are rather resemblant to those observed in the reflectance spectrum, and the effect of axial ligation of the solvent molecules in such alcohol solutions is, therefore, considered to be in a small extent, though comparisons of the absorption intensities suggesting the slightly stronger effect of methanol than that of ethanol.

Cobalt complex, $Co(LO)_3$. A strong IR absorption band at 3220 cm^{-1} due to ν(O–H) of the present aminofluoropropanol hydrochloride disappears in the spectrum of the cobalt chelate, while the absorption peak due to ν(C–F) remains at 1120 cm^{-1}. Curve A in Fig. 4 shows the spectrum of the chelate in a benzene solution. Two absorption maxima at 25200 and 18200 cm^{-1} indicate an octahedral hexacoordination structure in respect to the central cobalt(III) ion.[14)] The solubility of the chelate in inert organic solvents also supports to be of an inner complex type.

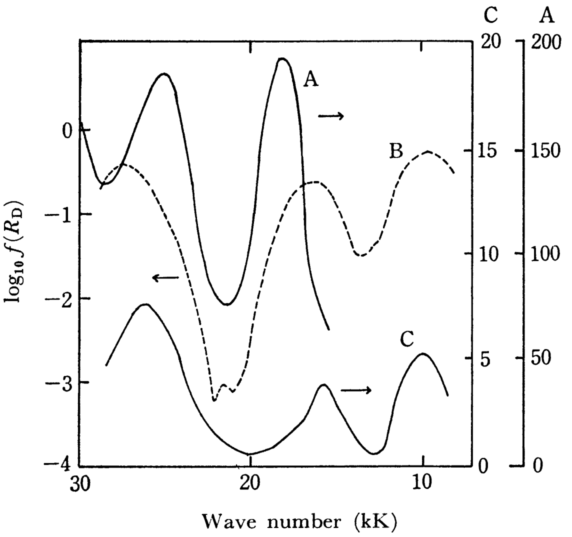

Fig. 4. The absorption spectrum of $Co(LO)_3$ in benzene (A), and the reflectance (B), and absorption (C) spectra of $Ni(LO)_2$

Nickel Complex, $Ni(LO)_2$. Curve B in Fig. 4 shows the reflectance spectrum of the nickel chelate. General feature of three absorption peaks at 27000, 16200, and 9700 cm^{-1} indicates[15)] an octahedral coordination structure of the chelate in respect to the central metal ion, whereas the analytical data indicate the mole ratio of 1:2 for nickel ion to the ligand and the IR spectrum shows no absorption band due to hydroxyl group or water. The nickel chelate is, therefore, considered to be of a polymeric structure at least in a solid phase. On the other hand, the chelate takes a monomeric form in a donating solvent such as methanol. The absorption spectrum in the solvent, as shown in the curve C of Fig. 4, indicates an octahedral coordination structure regarding the central metal ion. Therefore solid polymeric chelate complex cleaves to give a monomeric form by donating of two molecules of methanol upon dissolution.

The metal chelates of the present ligand were isolated as stable forms without any precautions, forming a striking contrast to those of monoethanolamine which were highly sensitive to moisture.

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12) L. L. Funck and T. R. Ortolano, *Inorg. Chem.*, **7**, 567 (1968).

13) a) I. Yoshida, Y. Oono, H. Kobayashi, and K. Ueno, This Bulletin, **45**, 174 (1972).
b) D. P. Graddon and K. B. Heng, *Aust. J. Chem.*, **24**, 1059 (1971).

14) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publish, Inc., New York, (1966), p. 875.

15) F. A. Cotton and G. Wilkinson, *ibid.*, p 881.