Cobalt(III), Nickel(II), Copper(II) and Zinc(II) Triflate Compounds Containing Aminopropanol Isomers

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*The synthesis and characterization of tris-chelate compounds of cobalt(III), nickel(II), copper(II) and zinc(II) triflate containing (*R,S*)-1-amino-2-propanol (RS-apH), (*S*)-1-amino-2-propanol (S-apH), (*R,S*)-2-amino-1-propanol (RS-paH) and (*S*)-2-amino-1-propanol (S-paH) is described. The compounds have the formulae* $[M(LL)_3](T)_2$ *(*$M = Ni^{2+}, Zn^{2+}$*; LL = apH and paH;* $T = CF_3SO_3^-$*),* $[Co_2(ap)_3(apH)_3]T_3$, $[Cu(ap)(apH)]_2T_2$, $[Cu_3(Rs\text{-}ap)_2(RS\text{-}apH)_6]T_4$, $[Cu_2(S\text{-}pa)(S\text{-}paH)_5]T_3$ *(*$T = CF_3SO_3^-$*). Infrared spectra of the Co(III) and Cu(II) compounds indicate the presence of strong O···H···O hydrogen bonding in the solid state. Ligand field spectra and infrared spectra of the Ni(II) and Zn(II) compounds indicate that the different ligand isomers yield different geometrical isomers (meridional and facial). Circular dichroism spectra strongly suggest that the Co(III) and Ni(II) tris-chelates have the theoretically expected* $\Lambda(\delta\delta\delta)$ *absolute configuration. Differences in the occurrence for the tris-chelate coordination for 1-amino-2-propanol and 2-amino-1-propanol compounds have been related to the longer M–O distances compared to the M–N distances in the 1-amino-2-propanol compounds.*

Introduction

This paper is part of an investigation on the differences in coordination chemistry between compounds with racemic and optically active ligands. Such differences have been reported in the literature, but in most cases adequate explanations have not been given. An example is the formation of crystals of compounds containing 1,2-propanediamine in which the conformation of the two ligands is $\delta\lambda$, although $\delta\delta$ (and $\lambda\lambda$) are calculated to be more favourable conformations in energy [1]. Another example is the difference in stoichiometric composition between compounds with racemic and optically active 1,2-propanediol [2]. These examples show the differences associated with the optical activity of the ligand to be important factors for the complex formation. The compounds with the ligands (*R,S*)-amino-2-propanol (RS-apH) and (*S*)-1-amino-2-propanol (S-apH) have been prepared and described [3]. Also the differences between the crystal structures of $Ni(NCS)_2(RS\text{-}apH)_2$ and $Ni(NCS)_2(S\text{-}apH)_2$ have been investigated [3c]. It was shown that the driving force for the differences between both structures is neither determined by the hydrogen bonding nor by the intermolecular contacts. Instead of the intermolecular factors, which are identical for both structures, the intramolecular geometry is related to the small intramolecular differences between the structures.

During the preparation of compounds with RS-apH [3a] and S-apH [3b], tris-chelates with the anions F^-, Cl^-, Br^-, NO_3^- and NCS^- could not be isolated. The compounds with Cl^-, Br^- and NO_3^- of formula $M(L)_3X_2$ have a structure with one bidentate ligand, two monodentate N-coordinated ligands and two axially coordinated anions [3a]. All attempts to obtain tris-chelates of RS-apH and S-apH with the non- or very weakly coordinating anions BF_4^-, $SbCl_6^-$, $InCl_4^-$ and SiF_6^{2-} have so far failed. Succesfull attempts to prepare tris-chelate compounds by using the very weakly coordinating anion $CF_3SO_3^-$ are described in this paper. As ligands RS-apH, S-apH, (*R,S*)-2-amino-1-propanol (RS-paH) and (*S*)-2-amino-1-propanol (S-paH) have been used. The magnetic behaviour of the copper(II) triflate compounds in relation to their proposed dimeric structure and the crystal structure of $[Cu_3(RS\text{-}pa)_2(RS\text{-}paH)_6](CF_3SO_3)_4$ have been described elsewhere [4].

In this paper the properties of cobalt(III), nickel(II), copper(II) and zinc(II) triflate compounds will be described, together with their IR, ligand field and CD spectra. The Cu(II) and Co(III) compounds contain both neutral and deprotonated ligands, suggesting the presence of strong O···H···O

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TABLE I. Analyses, Colours and Melting Points of the Metal Compounds Containing Aminopropanol Isomers.

No.	Compound	Metal		Colour	M.p. (°C)
		%Found	%Calc.		
1	$[Co_2(RS\text{-}ap)_3(RS\text{-}apH)_3](CF_3SO_3)_3$	11.6	11.6	purple	208
2	$[Co_2(S\text{-}ap)_3(S\text{-}apH)_3](CF_3SO_3)_3$	11.7	11.6	purple	205
3	$[Ni(RS\text{-}apH)_3](CF_3SO_3)_2$	10.0	10.1	l. blue	210
4	$[Ni(S\text{-}apH)_3](CF_3SO_3)_2$	10.0	10.1	l. blue	199
5	$[Ni(RS\text{-}paH)_3](CF_3SO_3)_2$	10.0	10.1	l. blue	221
6	$[Ni(S\text{-}paH)_3](CF_3SO_3)_2$	10.0	10.1	l. blue	221
7	$[Cu(RS\text{-}ap)(RS\text{-}apH)]_2(CF_3SO_3)_2$	17.3	17.6	blue	182
8	$[Cu(S\text{-}ap)(S\text{-}apH)]_2(CF_3SO_3)_2$	17.3	17.6	blue	175
9	$[Cu_3(RS\text{-}pa)_2(RS\text{-}paH)_6](CF_3SO_3)_4$	14.0	13.8	blue	110
10	$[Cu_2(S\text{-}pa)(S\text{-}paH)_5](CF_3SO_3)_3$	12.5	12.4	blue	116
11	$[Zn(RS\text{-}apH)_3](CF_3SO_3)_2$	10.9	11.1	white	165
12	$[Zn(S\text{-}apH)_3](CF_3SO_3)_2$	10.9	11.1	white	169
13	$[Zn(RS\text{-}paH)_3](CF_3SO_3)_2$	10.9	11.1	white	170
14	$[Zn(S\text{-}paH)_3](CF_3SO_3)_2$	10.9	11.1	white	189

No.	Compound	Carbon[a]		Hydrogen		Nitrogen	
		%Found	%Calc.	%Found	%Calc.	%Found	%Calc.
1	$[Co_2(RS\text{-}ap)_3(RS\text{-}apH)_3](CF_3SO_3)_3$	25.20	24.91	5.15	5.08	8.35	8.30
5	$[Ni(RS\text{-}paH)_3](CF_3SO_3)_2$	22.98	22.69	4.71	4.67	7.05	7.21
7	$[Cu(RS\text{-}ap)(RS\text{-}apH)]_2(CF_3SO_3)_2$	22.91	23.24	4.77	4.74	7.67	7.74
9	$[Cu_3(RS\text{-}pa)_2(RS\text{-}paH)_6](CF_3SO_3)_4$	24.29	24.27	5.07	5.09	8.17	8.09
10	$[Cu_2(S\text{-}pa)(S\text{-}paH)_5](CF_3SO_3)_3$	24.60	24.63	5.19	5.22	8.26	8.21
11	$[Zn(RS\text{-}apH)_3](CF_3SO_3)_2$	22.36	22.44	4.67	4.62	7.19	7.14

[a] Carbon, hydrogen and nitrogen analyses have been carried out for a few representative compounds.

hydrogen bonds [4]. It appeared to be possible to isolate only well-defined Co(III) compounds with neutral apH isomers. Also, Cu(II) compounds containing only neutral paH ligands could not be prepared [5]. This behaviour might be related to a difference in stability between the apH and paH compounds caused by a greater acidity of primary alcohols (paH) compared to secondary alcohols (apH) [6] and to the increased steric hindrance between the methyl protons and the amine protons in paH compounds *vs.* the methyl protons and the hydroxy proton in apH compounds.

Experimental

Synthesis

The hydrated metal salts, (*R,S*)-1-amino-2-propanol, (*R,S*)-2-amino-1-propanol and (*S*)-2-amino-1-propanol ($[\alpha]_D^{20}$ = +15 °C) were used as commercially available. (*S*)-1-amino-2-propanol was prepared using published methods [7].

The compounds were synthesized by adding a solution of the metal salt in absolute ethanol, containing an excess of triethyl orthoformate for dehydration, to a solution of the ligand in absolute ethanol. After mixing the two solutions, addition of dry diethyl ether to a concentrated solution started the precipitation. The solids were isolated by filtration and washed with sodium-dried diethyl ether, followed by drying *in vacuo* at room temperature.

Analyses and Physical Measurements

Metal analyses were carried out complexometrically [8, 9]. Halogens were determined using the method of Volhard [9]. Carbon, hydrogen and nitrogen analyses were performed by Dr. F. Pascher (Mikro-analytisches Laboratorium, Buschstrasse 54, D-5500 Bonn 1, BRD). Infrared spectra were recorded on a Perkin-Elmer model 580 spectrophotometer as nujol mulls and as KBr pellets.

Diffuse reflectance spectra were recorded on a Beckman DK-2A with MgO as a reference. Transmission spectra were recorded on a Beckman DK-2A

TABLE II. The IR Spectra of the Metal Compounds Containing Aminopropanol Isomers (cm^{-1}).

No.	Compound^a	ν_{CN}	ν_{CO}	ν_{MN}	ν_{MO}
1	$[Co_2(RS\text{-}ap)_3(RS\text{-}apH)_3](CF_3SO_3)_3$	1132s	1082s; 1061s	467s; 350s	290vs; 241m
2	$[Co_2(S\text{-}ap)_3(S\text{-}apH)_3](CF_3SO_3)_3$	1130s	1081s; 1061s	468s; 350s	288vs; 240s
3	$[Ni(RS\text{-}apH)_3](CF_3SO_3)_2$	1104s	1072s	447s; 388s; 350vs	259m; 240s; 215vs
4	$[Ni(S\text{-}apH)_3](CF_3SO_3)_2$	1106s	1072s	448s; 387s; 350s	260m; 240,; 216s
5	$[Ni(RS\text{-}paH)_3](CF_3SO_3)_2$	1107vs	1050vs	440vs; 396m; 350vs	280s; 228sh; 214s
6	$[Ni(S\text{-}paH)_3\text{-}(CF_3SO_3)_2$	1106vs	1065sh; 1048vs	440vs; 355vs	275s; 220vs
7	$[Cu(RS\text{-}ap)(RS\text{-}apH)]_2(CF_3SO_3)_2$	1121vs	1075s; 1059m	427s; 350s	266vs; 210m
8	$[Cu(S\text{-}ap)(S\text{-}apH)]_2(CF_3SO_3)_2$	1120s	1075s; 1056m	424vs; 350s	267vs; 210m
9	$[Cu_3(RS\text{-}pa)_2(RS\text{-}paH)_6](CF_3SO_3)_4$	1113s	1075sh; 1062s	A,B^b: 432vs; 390sh; 349s	285sh; 255m; 209s
				C^b: 409vs	303s
10	$[Cu_2(S\text{-}pa)(S\text{-}paH)_5](CF_3SO_3)_3$	1112s	1070s; 1057m	438vs; 382s; 351m	287s; 260sh; 200vs
11	$[Zn(RS\text{-}apH)_3](CF_3SO_3)_2$	1105s	1078s; 1060sh	440s; 400m; 351vs	260m; 240sh; 210vs
12	$[Zn(S\text{-}apH)_3](CF_3SO_3)_2$	1105s	1078s; 1053s	440s; 400m; 350vs	260m; 238sh; 210vs
13	$[Zn(RS\text{-}paH)_3](CF_3SO_3)_2$	1111vs	1067vs; 1045sh	436s; 350s	260s; 210vs
14	$[Zn(S\text{-}paH)_3](CF_3SO_3)_2$	1112vs	1069vs; 1046s	438vs; 351s	265sh; 211vs

^{a}Free ligand bands are assigned in references 3 and 5. ^{b}Compound 9 contains two differently coordinated copper ions (see reference 4).

as methanol solutions and using methanol as a reference. The circular dichroism spectra were recorded using a CNRS-Roussel-Jouan Dichrographe III in methanolic solutions. The NMR spectra were recorded with a JEOL PS-100 spectrometer in the Fourier transform-mode, operating at 100 MHz.

Results and Discussion

General

The compounds prepared are listed in Table I, together with their analyses, colours and melting points. The compounds containing the triflate ion could be prepared more easily than other apH^3 and paH^5 compounds. The compounds are not hygroscopic and can be stored in air without decomposition.

X-ray powder diffractograms show the pairs of compounds *3* and *4*, *6* and *14* and *7* and *8* to be mutually X-ray isomorphous.

Infrared Spectra

The most relevant infrared bands originating from the ligand in the coordination compounds are listed in Table II.

In the IR spectra the $\nu_{as}(SO)_3$, at about 1170–1180 cm^{-1}, and the $\nu_{as}(CF)_3$, at about 1280–1290 cm^{-1}, would indicate possible coordination by the triflate group [10]. These vibrations should be split when the triflate group is coordinated as a result of the lowering of the symmetry of the triflate. In the IR spectra of the present compounds ν_{as}-$(CF)_3$ gives rise to absorptions in a region with many ligand vibrations. The $\nu_{as}(SO)_3$ vibration can be clearly observed on the other hand. This $\nu_{as}(SO)_3$ absorption is sometimes broad, possibly indicating hydrogen bonding of the triflate group, but clear splittings were not observed. Thus, in all compounds the triflate group is at best weakly coordinating. In compounds *7*, *8* and *9* however a (semi-)coordination cannot be excluded according to the stoichiometry and the known preference of copper for weakly coordinating axial ligands.

The presence of both protonated and deprotonated ligands usually gives rise to strong O···H···O hydrogen bonding [11]. The IR spectra of such very strong hydrogen bonds display extremely broad bands that can have a width of 1000 cm^{-1} or more [12]. When the hydrogen bond distances are in the range of 2.40–2.45 Å the IR spectra show such broad bands below 1600 cm^{-1} [12, 13]. In agreement with the hydrogen bonds observed in compound *9* with a O·····O distance of about 2.40 Å [4] the IR spectrum shows a broad band in the area 1500–800 cm^{-1}. The IR spectrum of compound *9* also shows medium-strong combination bands at about 2400 and 1850 cm^{-1}, assigned to combination bands involving the O–H stretching or deformation vibrations, which are forbidden under the selection rules valid for the symmetrical hydrogen bonding [13, 14]. This indicates that the O···H···O

TABLE III. Diffuse Reflection Spectra of the Ni(II) Triflate Compounds Containing Aminopropanol Isomers.

No.	Compound	Assignments for octahedral geometry		
		$^3T_{2g} \leftarrow {}^3A_{2g}$	^1E_g, $^3T_{1g} \leftarrow {}^3A_{2g}$	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$
3	$[Ni(RS\text{-}apH)_3](CF_3SO_3)_2$	9300; 10850(sh)	16950	27550
4	$[Ni(S\text{-}apH)_3](CF_3SO_3)_2$	9350; 10800(sh)	16900	27550
5	$[Ni(RS\text{-}paH)_3](CF_3SO_3)_2$	9400; 10550(sh)	16700	27200
6	$[Ni(S\text{-}paH)_3](CF_3SO_3)_2$	10100	16850	27400

bonds are not completely symmetrical, in agreement with the observed proton positions in the crystal structure of compound *9* [4].

The IR spectrum of compound *10* also shows a broad band from about 1500–800 cm^{-1} and weak combination bands at about 2400 and 1900 cm^{-1}, indicating the presence of a similar hydrogen bond with O····O distances comparable to those of compound *9*.

The IR spectra of the compounds *1, 2, 7* and *8* show a very broad band from about 2000–400 cm^{-1}, again indicating strong O···H···O hydrogen bonding. Probably the hydrogen bonding has O····O distances of similar length as compound *9*. The presence of only one single (broad) absorption may indicate that the hydrogen bonds are nearly symmetrical in compounds *1, 2, 7* and *8* [13, 14].

In all compounds the ν_{CO} and ν_{CN} vibrations can be expected to show a shift to lower wave numbers, as a result of the coordination of the ligand and also a shift to higher wave numbers as a result of hydrogen bonding. In compounds *1, 2, 7* and *8* where all hydroxy groups are part of a strong O···H···O hydrogen bond the ν_{CN} is found at the highest wave numbers, possibly due to a dominant effect of the strong hydrogen bonding with the triflate groups. In most compounds the ν_{CO} absorption appears as a split band. This splitting is probably caused by differences in hydrogen bonding.

Far-Infrared Spectra

The $M(AB)_3$ entity has two geometrical isomers. The facial isomer (C_3-symm.) has all A and B atoms in *cis*-positions. The meridional isomer (C_1-symm.) has two A and two B atoms in *trans*-positions. Based on symmetry considerations the facial isomer is expected to show two ν_{MN} and two ν_{MO} vibrations [15]. The meridional isomer is expected to show three ν_{MN} and three ν_{MO} vibrations [15].

The FIR spectra of compounds *1* and *2* show two strong ν_{MN} and two strong ν_{MO} vibrations, suggesting that the compounds have a facial geometry. This, together with the strong O···H···O hydrogen bonding indicated by IR (*vide supra*), strongly suggests that compounds *1* and *2* have a structure similar to the related compound $[Co_2(Eta)_3(EtaH)_3](ClO_4)_2 \cdot \frac{1}{2}H_2O$, in which EtaH = ethanolamine [11]. This structure has tris-chelate coordinated dinuclear cations joined face to face by three strong O···H···O bonds with a short O·····O distance of about 2.42 Å. The structure proposed for the X-ray isomorphous compounds *7* and *8*, which consists of O···H···O hydrogen-bonded dimers of square-planar coordinated copper ions with the amine and hydroxy groups in *cis*-positions [4, 16], is in good agreement with the FIR spectra which show two strong ν_{MN} and two strong ν_{MO} vibrations, suggesting *cis*-positions for the amine and hydroxy groups.

The crystal structure of compound *9* shows two differently coordinated copper atoms [4]. The crystal structure shows copper atoms A and B to have the meridional isomers. Copper C has two ligands with *trans*-positions of the hydroxy and the amine groups. A tentative assignment of the ν_{MN} and ν_{MO} vibrations, in agreement with the crystal structure, is given in Table II.

The FIR spectrum of compound *10* shows three ν_{MN} and threee ν_{MO} vibrations, indicative for the meridional isomer [15].

The IR and FIR spectra of the nickel and zinc compounds are very similar. The FIR spectra of compounds *3, 4, 5, 11* and *12* show three ν_{MN} and three ν_{MO} vibrations, indicative of the meridional isomer. Compounds *6, 13* and *14* show only two ν_{MN} and two ν_{MO} vibrations, suggesting facial isomers for these compounds. The X-ray isomorphism of compounds *6* and *14* is in good agreement with this assignment. All paH tris-chelates, described in this paper and elsewhere [5], occur as the facial isomer (with the exception of compound *5*) while all apH tris-chelates with triflate as anion occur as the meridional isomer.

Ligand Field Spectra

The ligand field maxima of the copper compounds *7* and *8* (17200 cm^{-1}) are indicative of a square-planar coordination with at best weak axial ligands. The ligand field maxima of *9* and *10* (15400 cm^{-1})

TABLE IV. Ligand Field Maxima and Circular Dichroism Parameters of the Metal Compounds Containing S-apH and S-paH in Methanol.

No.	Compound	Ligand field $10^{-3}\ \bar{\nu}$ (cm^{-1}) (ϵ)	Circular dichroism $10^{-3}\ \bar{\nu}$ (cm^{-1})	Circular dichroism $\Delta\epsilon$[a]
2	$[Co_2(RS\text{-}ap)_3(RS\text{-}apH)_3](CF_3SO_3)_3$[b]	19.19(161)	17.79	+1.442
			19.92	−1.943
			24.63	+0.287
4	$[Ni(S\text{-}apH)_3](CF_3SO_3)_2$[c]	10.08(9)		
		16.75(10)	15.63	+0.0150
			17.86	+0.0082
		27.55(17)	27.62	+0.0166
6	$[Ni(S\text{-}paH)_3](CF_3SO_3)_2$[c]	10.08(9)		
		16.64(9)	15.50	+0.0251
			17.86	+0.0118
		27.32(16)	27.47	+0.0294
8	$[Cu(S\text{-}ap)(S\text{-}apH)]_2(CF_3SO_3)_2$[d]		13.37	−0.0121
		16.05(77)	16.58	+0.0868
10	$[Cu_2(S\text{-}pa)(S\text{-}paH)_5](CF_3SO_3)_3$[d]		11.82	+0.0858
		15.85(73)	15.60	−0.0433
			17.86	+0.0682
			19.34	+0.0344
			22.94	−0.0139
			25.19	−0.0567

[a] In $l^{-1}\cdot mol\cdot cm^{-1}$. [b] About 0.01 mol/l. [c] About 0.03 mol/l. [d] About 0.05 mol/l.

are indicative for a tetragonally Jahn-Teller distorted coordination. The ligand field spectra of the Co(III) compounds are similar. Both compounds show absorption maxima at 16000 and 26100 cm^{-1}. The observed bands are in good agreement with spectra of related Co(III) compounds containing protonated and deprotonated amino alcohols and an octahedral geometry for Co(III). The geometrical isomers can be distinguished by their ligand field spectra. The first band of the meridional isomer (C_1-symmetry) should split to a much greater extent than that of the facial isomer (C_3-symmetry) [17]. The first absorption band, which is nearly symmetrical for compounds *1* and *2*, again suggests that the facial isomer is present, in good agreement with the FIR spectra and the crystal structure of the related compound $[Co_2(Eta)_3(EtaH)_3](ClO_4)_2\cdot \frac{1}{2}H_2O$ [11a].

The band maxima and assignment of the ligand field parameters of the diffuse reflection spectra of the nickel(II) compounds are listed in Table III. In these compounds the coordination is octahedral. The Ni(II) compounds have three absorptions fitting the Tanabe-Sugano diagram of octahedral Ni(II) [18]. The deviation from the pure O_h symmetry is clearly visible in the spectra of the compounds *3, 4* and *5*. The first absorption band shows a shoulder at about 10800 cm^{-1}. The spectrum of compound *6* shows sharp and symmetric absorptions. The position of the first absorption band is in good agreement with the tris-chelate coordination of the ligand [1]. The ligand field spectra of the four nickel compounds agree with the FIR spectra, which indicated compounds *3, 4* and *5* to be meridional and compound *6* to be facial. The band maxima of the transmission spectra of the optically active compounds in methanol are listed in Table IV. The position of the first absorption band (low energy) is in good agreement with tris-chelate coordination of the ligand in solution.

Circular Dichroism Spectra

In coordination chemistry, CD spectra are known to give information about the absolute configuration of the ligand and the preferred configuration of the metal compound. In octahedral metal compounds four sources of dissymmetry exist [19]:

i) Inherent dissymmetry within the ML_6 entity, if trigonally distorted.

ii) Configurational dissymmetry, due to a chiral arrangement of chelating systems around the metal atom.

iii) Conformational dissymmetry, due to chiral conformations of individual chelate rings.

iv) Vicinal dissymmetry, due to chiral centres in the coordinated ligands.

The tris-chelate compounds of S-apH and S-paH have contributions from all four sources. Coordinated

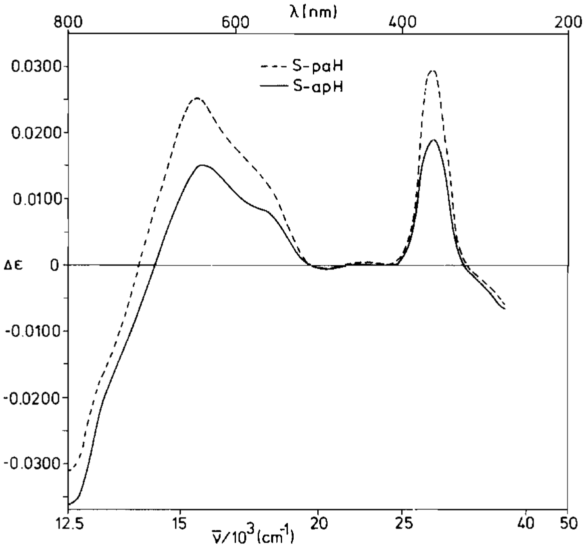

Fig. 1. The circular dichroism spectra of the compounds $[Ni(S\text{-}apH)_3](CF_3SO_3)_2$ and $[Ni(S\text{-}paH)_3](CF_3SO_3)_2$ in methanol (0.03 mol/l).

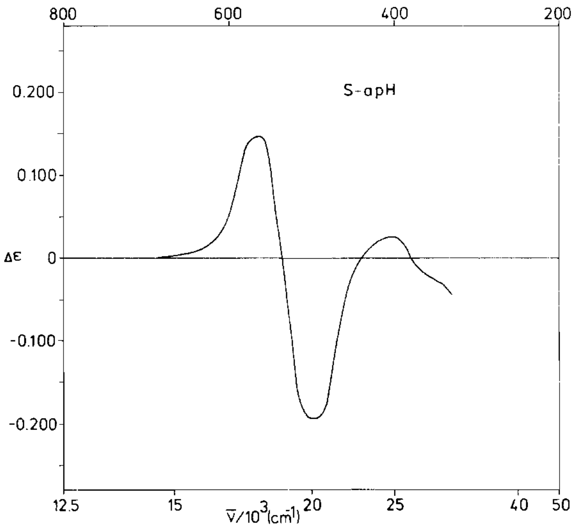

Fig. 3. The circular dichroism spectra of the compound $[Co_2(S\text{-}ap)_3(S\text{-}apH)_3](CF_3SO_3)_3$ in methanol (0.01 mol/l).

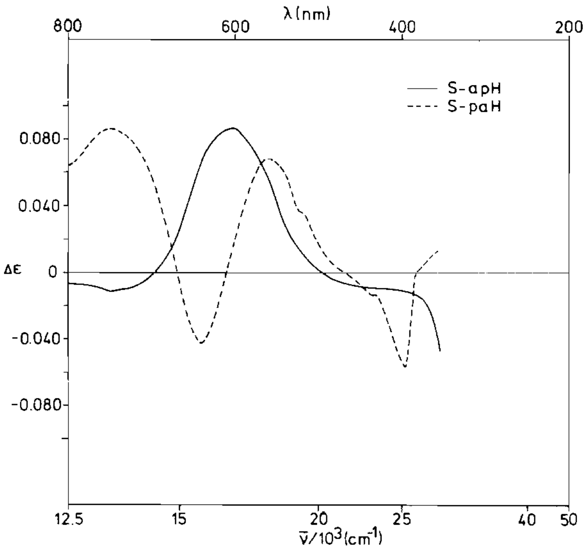

Fig. 2. The circular dichroism spectra of the compounds $[Cu(S\text{-}ap)(S\text{-}apH)]_2(CF_3SO_3)_2$ and $[Cu_2(S\text{-}pa)(S\text{-}apH)_5](CF_3SO_3)_3$ in methanol (0.05 mol/l).

S-apH and S-paH occur in two conformations, *i.e.* δ and λ. For coordinated S-apH and S-paH the δ conformation is the more favourable one, because of the equatorial position of the methyl group [20].

The CD spectra of the compounds are shown in Figs. 1–3 and the CD parameters are listed in Table IV. The CD spectra of the present compounds are compared with the CD spectra of the S-apH [2] and S-paH compounds [5]. The spectra of the present nickel(II) compounds (*3*, *4*, *5* and *6*) are very similar to the spectra of other nickel(II) compounds containing S-apH [2], S-paH [5] and 1-propanediamine [21]. Reasonable agreement between the maxima of the absorptions in the CD and the ligand field is observed. The positive CD band at about 16000 cm^{-1} and the negative charge transfer band at about 35000 cm^{-1} both indicate a Λ-configuration [21]. Thus, together with the equatorial position of the methyl group, the absolute configuration can now be assigned to Λ(δδδ). This is the most stable isomer for tris-chelates of S-apH and S-paH. As in the CD spectra of other nickel(II) compounds containing S-apH and S-paH [2, 5], the Δε values of the S-paH compounds are larger than those of the S-apH compounds, in agreement with the Δε values of Co(III) amino alcohol compounds [22]. The size of the contribution to the induced rotational strength due to vicinal asymmetry depends on the donor group of the ligand. The effect decreases as the number of atoms between the donor group and the asymmetric centre increases [23]. The difference in the Δε values between the S-apH and S-paH compounds indicates that the vicinal asymmetry is enhanced when the asymmetric centre is next to a coordinated amine group instead of a coordinated hydroxy group. At least part of this effect originates from the asymmetry in the adjacent nitrogen in paH, which is caused by the interaction between the amine protons and the methyl group. This contribution is minimized for apH, where substitution is adjacent to the hydroxy group [22].

TABLE V. Structural Data of the Amino Alcohol, Diol and Diamine Compounds.

No.	Compound^a	M–X (Å)		X–M–X (°)	Bite (Å)	Reference
	Diols					
15	$CuCl_2(eg)$	1.958;	1.996	79.1	2.52	25
16	$CuCl_2(eg)\cdot½H_2O$	2.004;	1.968	79.9	2.55	25
17	$[Cu(eg)_3]SO_4$	1.975;	2.335	77.6^b	2.71	26
		1.957;	2.023	81.2	2.59	
		2.030;	2.320	78.9^b	2.77	
18	$[Ni_2Cl_2(pg)_4]Cl_2$	2.04;	2.09	78.6	2.62	27
	Diamines					
19	$[Cu(en)_3]SO_4$	2.15		80.9	2.79	28
20	$Cu(NCS)_2(en)_2$	2.01;	1.99	85.0	2.70	29
21	$Cu(NO_3)_2(en)_2$	2.044;	2.012	86.2	2.77	30
22	$Cu(ClO_4)_2(pn)_2$	2.017^b;	2.027^b	86.3^b	2.76^b	31
23	$[Ni(en)_3](NO_3)_2$	2.13		81.9	2.79	32
24	$[Ni(en)_3]SO_4$	2.124		82.1	2.79	33
25	$[Ni(en)_3](B(C_6H_5)_4)_2\cdot3(CH_3)_2SO$	2.14;	2.12	81.7	2.79	34
		2.18;	2.11	80.8	2.78	
		2.16;	2.17	79.8	2.78	
26	$Ni(NCS)_2(en)_2$	2.095^b;	2.109^b	82.0^b	2.76^b	35
27	$Ni(en)(H_2O)_4$	2.058;	2.073	83.6	2.75	36
28	$Ni(NCS)_2(pn)_2$	2.06		81.1	2.68	37
	Amino alcohols					
29	$CuCl_2(RS\text{-}apH)$	O: 2.02;	N: 2.02	82.1	2.65	38
		2.01;	1.90	83.1	2.59	
		2.02;	1.95	82.4	2.62	
30	$Ni(NCS)_2(RS\text{-}apH)_2$	O: 2.107;	N: 2.075	82.1	2.75	3
31	$Ni(NCS)_2(S\text{-}apH)_2$	O: 2.102;	N: 2.071	83.6	2.78	3
		2.092;	2.072	81.1	2.71	
32	$[Cu_3(RS\text{-}pa)_2(RS\text{-}paH)_6](CF_3SO_3)_4$	1.956	2.015	82.6	2.62	4
		2.460	2.035	75.6	2.78	
		2.462	2.016	76.9	2.81	
		1.862	1.957	86.5	2.62	
		1.967	2.023	83.1	2.65	
33	$[Cu(Eta)(Eta')]_2(NO_3)_2$	O: 1.960;	N: 1.985	84.9	2.66	16
		1.955	1.995	85.0	2.67	
		1.966	1.987	84.6	2.66	
		1.948	1.988	84.9	2.66	
34	$Ni(NCS)_2(Eta)_2$	O: 2.14;	N: 2.10	80.8	2.75	37

[a] The used abbreviations are: eg = 1,2-ethanediol; pg = 1,2-propanediol; en = 1,2-ethanediamine; pn = 1,2-propanediamine; Eta = ethanolamine and Eta$'$ = ethanolamine in which the hydroxy group is deprotonated. [b] These values have been calculated from the atomic positions given in the references.

A reasonable agreement between the positions of the absorption maxima in the CD and transmission spectra of the Cu(II) compounds is found. The CD spectrum of compound *8* shows three absorptions, of which the shortest wavelength band is partly masked by the charge-transfer transition. The observed three absorptions are in good agreement with the tetragonally distorted structure [4, 16] of compound *8*. As can be seen from the CD spectrum of compound *10*, the greater resolution in the CD spectrum and the differences in sign of the transitions makes the CD spectra more sensitive for lowering of the symmetry to C_1. In the CD spectrum of *10* four transitions with positive and negative signs occur. This is typical for the meridional isomer, found in the FIR spectrum reported above. The CD spectrum of compound *2* resembles the CD spectra of related Co(III) compounds containing various protonated and deprotonated amino alcohols [17]. According to the ^{1}H NMR spectra of compounds *1* and *2*, which show a signal at 14.9 ppm relative to TMS, the strong O···H···O hydrogen bonding is also present in solution [11].

The ligand field spectrum of compound *2* shows two absorptions, *i.e.* the $^{1}T_{1g} \leftarrow {}^{1}A_{1g}$ and $^{1}T_{2g} \leftarrow {}^{1}A_{1g}$. Both absorption bands contain two components. In the $^{1}T_{2g} \leftarrow {}^{1}A_{1g}$ transition the $^{1}A_{1} \leftarrow {}^{1}A_{1}$ is magnetic dipole-forbidden, and only the $^{1}E \leftarrow {}^{1}A_{1}$ is magnetic dipole-allowed. This suggests that the absorption in the CD spectrum at about 24.5 kK is due to the $^{1}E \leftarrow {}^{1}A_{1}$ transition. The $^{1}T_{1g} \leftarrow {}^{1}A_{1g}$ transition splits in two magnetic dipole allowed components, *i.e.* $^{1}E \leftarrow {}^{1}A_{1}$ and $^{1}A_{2} \leftarrow {}^{1}A_{1}$. In the CD spectrum these components have positive and negative signs respectively.

The absolute configuration around the Co(III) is Λ, according to the empirical rule formulated by Saito [1]. In agreement with the preference for the equatorial position of the methyl group, the absolute configuration is Λ(δδδ), which has the lel-orientation corresponding to the most stable configuration.

The Possibility of Tris-Chelates with Aminopropanols

Tris-chelate compounds of general formula $[M(LL)_3](anion)_2$ are known for the ligands ethanediol, 1,2-propanediol, ethanediamine, 1,2-propanediamine and ethanolamine. Tris-chelates have also been found for 2-amino-1-propanol (paH) [5], in contrast with the compounds prepared with 1-amino-2-propanol (apH) having one bidentate ligand, two monodentate N-coordinated ligands and two axially coordinated anions [3]. Tris-chelates of apH arc only found with triflate as anion. The apparent reluctance of the apH compounds forming tris-chelates is now discussed in relation with the bite distances of the apH, paH and similar diol and diamine compounds. To understand the differences in coordination a literature study of crystal structures has been carried out. Due to the large number of structures available for the ethanediamine compounds, a selection of more or less similar structures was made. The results for copper(II) and nickel(II) compounds have been summarized in Table V.

Since an equatorial substitution of methyl groups in ethanediol, ethanediamine and ethanolamine is known not to influence the conformation [24], the corresponding ethane and propane compounds can easily be compared. An important factor in the coordination of five-membered ligand rings is the bite size of the ligands. The bite size *b* is defined as the intramolecular distance between the donor atoms (X = N or O) in the bidentate ligand (see Fig. 4). It is evident from Fig. 4 that a simple goniometric relation exists between M–X, X–M–X angle and *b*, *i.e.* $b^2 = (M-X)^2 + (M-X')^2 - 2\cdot(M-X)(M-X')\cdot\cos(X-M-X')$.

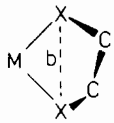

Fig. 4. The five-membered ring formed by a coordinated bidentate ligand and the metal ion. The bite distance *b* is indicated.

It is evident that the bite distance of a diol compound will be smaller (and that of a diamine compound will be larger) than the bite distance of the amino alcohol compounds, because of the larger C–N distance compared to the C–O distance. It can be seen from Table V that the bite distances of the diol compounds are indeed the smallest, those of the diamines are the largest, whereas those of the amino-alcohol compounds are intermediate. It must be noted here that in some cases the copper tris-chelates have somewhat larger bite distances due to the tetragonal Jahn-Teller deformation.

Smaller bite distances, such as in the diol compounds, are more favourable for tris-chelate coordination, because of decreased interligand repulsions. Comparing the bite distances in the copper diamine compounds *19, 20, 21* and *22* it is seen that the bite distances in *20, 21* and *22*, having two ligands in *trans*-positions, are longer than in the diol compounds as a result of increased X–M–X angles. This increase is not possible for the tris-chelate compound *19*, because of strong inter-ligand repulsions. To minimize this repulsion the M–N distances have increased. This is the apparent origin of the relatively long M–N distance in the tris-chelate compounds *19, 23, 24* and *25* compared to the other diamine compounds (see Table V).

Differences in ring geometry can be related to the difference in occurrence of tris-chelate diol, diamine and aminopropanol compounds. The diol compounds have shorter bite and shorter M–X distances and smaller X–M–X angles compared with the aminopropanol compounds (see Table V), resulting in smaller inter-ligand repulsions. It is, therefore, easier to obtain tris-chelate coordination in the diol compounds.

The diamine, the apH and the paH compounds have (more or less) similar X–M–X angles (see Table V). To decrease the inter-ligand repulsions in the diamine compounds the M–N distance increases and in the tris-chelate diamine compounds the M–N distances are longer than usual. The M–O distances in the apH compounds are longer than the M–N distances. This atypical behaviour is not found in paH compounds (see Table V). The probable cause is the position of the methyl group (at the hydroxy side of the ligand in apH compounds and at the amine side in paH compounds), which is forced more to the outside in both apH and paH compounds. In order to realize tris-chelate coordination for apH and paH compounds the metal–ligand distances have to increase, as was found for the diamine compounds. Because of this elongation and the longer M–O distance in apH compounds, the oxygen atom of apH will be a weaker donor atom than a coordinating anion, resulting in the mixed bidentate/monodentate coordination of the ligands.

An additional argument for the more frequent occurrence of paH tris-chelates, compared to apH tris-chelates, is the less favourable steric hindrance for monodentate N-coordinated paH compared to monodentate N-coordinated apH. In apH the amine group is attached to a primary carbon atom, in contrast to paH where the amine group is attached to a secondary carbon atom, resulting in an enhanced steric repulsion in the paH compounds. Only a breaking of the intramolecular N–H···O hydrogen bond of the monodentate coordinated ligand can reduce this steric repulsion, but this will result in a bidentate coordination of the ligand.

Concluding Remarks

The present study has shown that tris-chelate compounds of apH can be prepared with triflate as anion, in contrast with other anions such as F^-, Cl^-, Br^-, NCS^-, NO_3^-, BF_4^-, $SbCl_6^-$, $InCl_4^-$ and SiF_6^{2-}. The reason for this behaviour might be that the triflate group is a very large, non-dissociating, very weakly coordinating anion, which possesses very good hydrogen bonding possibilities to stabilize the crystal lattice.

According to the FIR spectra, all apH tris-chelates are likely to have the meridional isomer, while all paH tris-chelates, except $[Ni(S\text{-}paH)_3](CF_3SO_3)_2$, have the facial isomer. Not only differences in geometrical isomer are observed for the compounds prepared with triflate as anion, but also different stoichiometric compositions for the copper compounds. The CD spectra confirm the results of the FIR spectra and show for the nickel and cobalt compounds the most stable absolute configuration to be present, *i.e.* $\Lambda(\delta\delta\delta)$.

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References

1 Y. Saito, 'Inorganic Molecular Dissymmetry', Springer Verlag (1979).

2 D. Knetsch, 'Diols as Ligands', Ph.D. Thesis, State University Leiden (1976).

3 a) G. Nieuwpoort and W. L.Groeneveld, *Recl. Trav. Chim. Pays-Bas, 99,* 394 (1980).
b) G. Nieuwpoort and J. Reedijk, *ibid., 100,* 378 (1981).
c) G. Nieuwpoort and G. C.Verschoor, *Inorg. Chem., 20,* 4079 (1981).

4 G. Nieuwpoort, G. C. Verschoor and J. Reedijk, *J. Chem. Soc. Dalton,* in press.

5 G. Nieuwpoort, J. Koek and J. Reedijk, *Inorg. Chim. Acta,* in press.

6 R. T. Morrison and R. N.Boyd, 'Organic Chemistry', Allyn and Bacon Inc., 3rd Edition (1978).

7 G. Nieuwpoort, J. Brussee and J.Reedijk, *Inorg.Chim. Acta, 68,* 131 (1983).

8 A. I. Vogel, 'A Textbook of Quantitative and Inorganic Analysis.

9 G. Schwarzenbach, 'Die Komplexometrische Titration', Enke Verlag Stuttgart (1965).

10 M. G. Miles, G. Doyle, R. P. Cooney and R. S. Tobias, *Spectrochim. Acta, 25A,* 1515 (1969).

11 a) J. A. Bertrand, P. Gary Eller, E. Fujita, M. O. Lively and D. G. VanDerVeer, *Inorg. Chem., 18,* 2419 (1979).
b) J. A. Bertrand, T. D. Black, P. Gary Eller, F. T. Helm and R. Mahmood, *Inorg. Chem., 15,* 2965 (1976).

12 J. Emsley, D. J. Jones and R. Kuroda, *J. Inorg. Nucl. Chem., 43,* 2243 (1981).

13 D. Hadzi and B. Orel, *J. Mol. Struct., 18,* 227 (1973).

14 A. Bertoluzza, P. Monti, M. A. Montelli and M. A. Battaglia, *J. Mol. Struct., 73,* 19 (1981).

15 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds', 3rd edition, Wiley–Interscience (1978).

16 J. A. Bertrand, E. Fujita and D. G. VanDerVeer, *Inorg. Chem., 19,* 2022 (1980).

17 K. Ohashi, J. Fujita, B. Shimoyana and K. Saito, *Bull. Chem. Soc. Jpn., 41,* 2422 (1968).

18 J. Reedijk, P. W. N. M. van Leeuwen and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas, 87,* 129 (1968).

19 F. S.Richardson, *Chem. Rev., 79,* 17 (1979).

20 E. J. Corey and J. C. Bailar Jr., *J. Am. Chem. Soc., 81,* 2620 (1959).

21 M. J. Harding, S. F. Mason and B. J. Peart, *J. Chem. Soc. Dalton,* 955 (1973).

22 C. J. Hawkins, 'Absolute configuration of metal complexes', Wiley–Interscience (1971).

23 C. J. Hawkins, G. A. Lawrance and J. A. Palmer, *Austr. J. Chem., 31,* 2399 (1978).

24 a) S. R.Niketic and K. Rasmussen, *Acta Chem. Scand., A32,* 391 (1978).
b) L. J. DeHayes and D. H. Busch, *Inorg. Chem., 12,* 1505 (1973).

25 B. M. Antti, *Acta Chem. Scand., A30,* 405 (1976).

26 B. M. Antti, B, K. S. Lundberg and N. Ingri, *ibid., 26,* 3984 (1972).

27 B. M. Antti, *ibid., A29,* 76 (1975).

28 D. L.Cullen and E. C. Lingafelter, *Inorg.Chem., 9,* 1858 (1970).

29 B. W. Brown and E. C. Lingafelter, *Acta Cryst., 17,* 254 (1964).

30 P. Jose, L. M. Pant and A. B. Biswas, *ibid., 17,* 1145 (1964).

31 A. Pajunen and M. Lehtonen, *Suom. Kemisti, B45,* 43 (1972).

32 J. D. Korp and I.Bernal. *Acta Cryst., B36,* 560 (1980).

33 M. Ul-Haque, C. N.Caughlan and K. Emerson, *Inorg. Chem., 9,* 2421 (1970).

34 R. E. Cramer and J. T. Huneke, *ibid., 17,* 365 (1978).

35 B. W. Brown and E. C. Lingafelter, *Acta Cryst., 16,* 753 (1963).

36 G. J. McDougall and R. D. Hancock, *J. Chem. Soc. Dalton,* 654 (1980).

37 A. G. Shvelashvili, M. A. Porai-Koshits, A. I. Kvitashivili, B. M. Sochedrin and M. G. Tavberidze, *Zh. Strukt. Khimi., 15,* 313 (1974).

38 G. Nieuwpoort, A. J. de Kok and C. Romers, *Recl. Trav. Chim. Pays-Bas, 100,* 177 (1981).