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Nickel(II) Compounds Containing Racemic and Optically Active 2-Amino-1-propanol

GER NIEUWPOORT, JAN KOEK and JAN REEDIJK*

Department of Chemistry, Gorlaeus Laboratories, State University Leiden, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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*Nickel(II) compounds with (*R,S*)-2-amino-1-propanol and (S)-2-amino-1-propanol are described and compared with the corresponding compounds containing 1-amino-2-propanol isomers. The compounds have the formula* $Ni(paH)_n(anion)_2$*, with n = 2, 3, paH = (*R,S*)-2-amino-1-propanol and (S)-2-amino-1-propanol; the anions are* F^-*,* Cl^-*,* Br^-*,* NO_3^- *and* NCS^-*. It proved to be impossible to prepare copper(II) coordination compounds containing the neutral ligands. Infrared and ligand field spectra have been used to obtain information about the coordination of the ligand and the structure of the compounds. Circular dichroism spectra show as expected the most stable absolute configuration for the tris-chelates,* i.e. *Λ(δδδ), to be present. For the bis-chelate compounds the circular dichroism spectra and the IR spectra indicate the structure of the compounds. The comparison of the 1-amino-2-propanol and 2-amino-1-propanol compounds show the presence of some remarkable differences in stoichiometry and structure.*

Introduction

Studies on the differences in coordination chemistry of racemic and optically active ligands have been performed increasingly during the last years [1–3]. In previous papers from this laboratory the coordination chemistry of the isomers of 1-amino-2-propanol (apH) has been described [1–3]. According to the IR spectra of the compounds the ligand coordinates either monodentately *via* the nitrogen atom or bidentately *via* the nitrogen and oxygen atoms [1, 2]. The results obtained from the IR spectra were confirmed by the ligand field spectra of the Ni(II) compounds by comparing the experimental Dq value with the Dq value calculated using the rule of average environment [1]. The circular dichroism spectra of the S-apH compounds also agreed with this picture [2].

The range of ligands has now been extended to the corresponding 2-amino-1-propanol isomers, *i.e.* (*R,S*)-2-amino-1-propanol (RS-paH) and (*S*)-2-amino-1-propanol (S-paH). The properties and structures of these compounds will be compared with those of the corresponding RS-apH and S-apH compounds. In this paper the synthesis of nickel(II) coordination compounds with RS-paH and S-paH will be described, together with the study of their IR, ligand field and CD spectra. It turned out to be impossible to prepare copper(II) coordination compounds containing the neutral ligand paH. All products prepared with copper(II) salts and paH isomers contain deprotonated ligands, but it was not possible to obtain well defined and reproducible products. This behaviour most likely is related to the higher acidity of primary alcohols (paH) compared to secondary alcohols (apH) [4] and the increased steric hindrance between methyl protons and the amine protons in paH *vs.* the hydroxy proton in apH (see Fig. 1). This apparently results in differences in the stability of the apH and paH Cu(II) compounds.

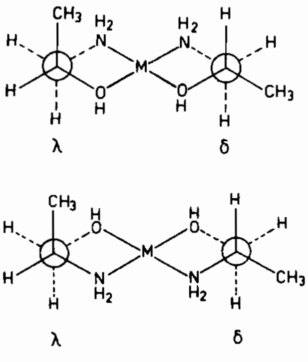

Fig. 1. Conformational isomers of coordinates (*S*)-1-amino-2-propanol (upper part) and (*S*)-2-amino-1-propanol (lower part).

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*Author to whom correspondence should be addressed.

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TABLE I. Analyses, Colours and Melting Points (°C) of the Nickel(II) Compounds Containing paH.

No.	Compound	Metal		Halogen		Colour	M.p.
		%Found	%Calc.	%Found	%Calc.		
1	$NiF_2(RS\text{-}paH)_2$	24.1	23.8			l. green	>240
2	$NiF_2(S\text{-}paH)_2$	24.1	23.8			l. green	>240
3	$NiCl_2(RS\text{-}paH)_2$	21.2	21.0	24.9	25.4	green	230
4	$NiCl_2(S\text{-}paH)_2$	20.7	21.0	25.2	25.4	green	230
5	$NiBr_2(RS\text{-}paH)_2$	16.3	15.9	42.5	43.4	l. green	190
6	$NiBr_2(S\text{-}paH)_2$	16.2	15.9	44.3	43.4	l. green	172
7	$Ni(NO_3)_2(RS\text{-}paH)_2$	17.5	17.6			green	161
8	$Ni(NCS)_2(RS\text{-}paH)_2$	17.8	18.1			green	195[d]
9	$Ni(NCS)_2(S\text{-}paH)_2$	17.7	18.1			green	195[d]
10	$[Ni(RS\text{-}paH)_3]Cl_2$	16.7	16.5	19.8	20.0	green	192
11	$[Ni(S\text{-}paH)_3]Cl_2$	16.5	16.5	19.9	20.0	green	201
12	$[Ni(RS\text{-}paH)_3]Br_2$	12.9	13.2	35.4	36.0	l. blue	219
13	$[Ni(S\text{-}paH)_3]Br_2$	13.0	13.2	35.5	36.0	l. blue	199
14	$[Ni(RS\text{-}paH)_3](NO_3)_2$	14.1	14.4			blue	186
15	$[Ni(S\text{-}paH)_3](NO_3)_2$	14.2	14.4			blue	186

Experimental

Starting Materials and Syntheses

The hydrated metal salts, (*R,S*)-2-amino-1-propanol and (*S*)-2-amino-1-propanol ($[\alpha]_D^{20}$ = +15 °C) were used as commercially available. The coordination compounds have been prepared from the anhydrous metal salts and the ligands in the proper stoichiometric ratio using absolute ethanol as a solvent, as described previously for the other (apH) compounds [1].

Analyses and Physical Measurements

Metal analyses were carried out complexometrically [5, 6]. Halogens were determined using the method of Volhard [6]. Carbon, hydrogen and nitrogen analyses were performed by Dr. F. Pascher (Mikroanalytisches 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 or CsCl pellets. No decomposition reactions were observed in KBr and CsCl.

Diffuse reflectance spectra were recorded on a Beckman DK-2A spectrophotometer with MgO as a reference. Transmission spectra were recorded on a Beckman DK-2A spectrophotometer as methanolic solutions using methanol as a reference.

The circular dichroism spectra of the methanolic solutions were recorded on a CNRS-Roussel-Jouan Dichrographe III.

The X-ray powder diffraction patterns were recorded on a Philips diffractometer using Cu-Kα radiation.

Results and Discussion

General

The new compounds are listed in Table I, together with the colours, melting points and some of the analytical data. The paH compounds do not crystallize easily, just as found for the apH compounds, and the addition of sodium-dried diethyl ether is necessary to start the precipitation. The intermolecular hydrogen bonding with the solvent apparently resists the necessary ordering for the crystallization and single crystals suitable for X-ray diffraction could not be obtained. Most of the compounds listed are hygroscopic and moisten in air.

Infrared Spectra

The most important frequencies of the ligand absorptions observed in the coordination compounds are listed in Table II. In all compounds hexacoordination occurs, as follows from the ligand field spectra (*vide infra*). The spectra of the racemic compounds are very similar to the spectra of the optically active compounds.

The IR spectra of the nitrate compounds give indications about the coordination of the nitrate group, because of differences in symmetry for ionic,

TABLE II. The IR Spectra of the Compounds $NiX_2(paH)_n$ (cm^{-1}).

No.	Compound	ν_{CN}	ν_{CO}	ν_{MN}	ν_{MO}	ν_{MX}
	Free ligand[a]	1150	1060			
1	$NiF_2(RS\text{-}paH)_2$	1112vs	1055vbr	440s 340s	260vs 222m	380s 320s
2	$NiF_2(S\text{-}paH)_2$	1112vs	1055vbr	451s 350vs	270vs 235s	380s 320s
3	$NiCl_2(RS\text{-}paH)_2$	1106s	1040br	430s 349vs	255s 220vs	280sh 240s
4	$NiCl_2(S\text{-}paH)_2$	1106s	1040br	433s 344vs	255s 220vs	280sh 240sh
5	$NiBr_2(RS\text{-}paH)_2$	1105s	1030vbr	442vs 348s	280s 265s	223vs
6	$NiBr_2(S\text{-}paH)_2$	1103s	1030vbr	440vs 345vs	280s 265s	222vs
7	$Ni(NO_3)_2(RS\text{-}paH)_2$	1104s	1040s 1050s	440s 345vs	249s 225vs	290s
8	$Ni(NCS)_2(RS\text{-}paH)_2$	1100s	1025br	430s 340m	262vs 220m	375w 245vs
9	$Ni(NCS)_2(S\text{-}paH)_2$	1100s	1025br	430s 340m	264vs 221m	375w 245vs
10	$[Ni(RS\text{-}paH)_3]Cl_2$	1109vs	1060s 1043vs	438vs 351vs	268sh 230vs	
11	$[Ni(S\text{-}paH)_3]Cl_2$	1108vs	1060s 1045s	435vs 347s	265sh 235vs	
12	$[Ni(RS\text{-}paH)_3]Br_2$	1104vs	1059s 1042s	442vs 345s	270s 223vs	
13	$[Ni(S\text{-}paH)_3]Br_2$	1103vs	1059vs 1041vs	432s 349s	268s 222vs	
14	$[Ni(RS\text{-}paH)_3](NO_3)_2$	1110vs	1062vs 1047vs	441vs 347s	271s 221vs	
15	$[Ni(S\text{-}paH)_3](NO_3)_2$	1110vs	1062vs 1047vs	440vs 340vs	275s 222vs	

[a] The FIR vibrations of the ligand occur as weak bands at 378, 275, 245 and 208 cm^{-1}.

monodentate or bidentate nitrate groups. Unfortunately, the number of ligand bands in the 1200–1400 cm^{-1} region is so large that symmetry changes of the NO_3^- ion cannot be deduced from this region. Lever *et al.* [7] have used the number and relative positions of the nitrate combination frequencies in the 1700–1800 cm^{-1} region to distinguish the various coordination modes of the nitrate group. Ionic nitrates give rise to a single, sharp band near 1750 cm^{-1}. This absorption is always strong relative to the possible other NO_3 absorptions in this region by coordinated nitrate groups and is quite distinctive [7]. The frequencies and relative intensities of the nitrate combination bands ($\nu_1 + \nu_4$), listed in Table III, show ionic nitrate to be present in the nitrate compounds *7*, *14* and *15*. In compound *7* the presence of ionic nitrate is evident, but the observation of two combination bands at 1745 and 1720 cm^{-1} suggest that a weakly coordinating bidentate nitrate is also present. Usually a bidentately coordinating nitrate gives rise to two fairly weak combination bands separated by 38–56 cm^{-1} [7]. If the interaction between the metal and the bidentate nitrate group is weakened, a decrease in this splitting may be expected. The difference in the combination bands of 25 cm^{-1} for compound *7* is small compared to the 54 cm^{-1} found for the RS-apH analogue [1] suggesting a somewhat weaker coordination of the nitrate in compound *7*, or a somewhat different coordination geometry.

The thiocyanate frequencies are characteristic of monodentate N-coordinated thiocyanate (see Table III) [8].

Hydrogen bonding of the ligand with the anion or with other ligands does not allow the use of the ν_{NH} and ν_{OH} vibrations to obtain information about the coordination. Conclusions must therefore be drawn from other vibration bands. Suitable for this purpose are the ν_{CN}, ν_{CO}, ν_{MN} and ν_{MO} vibrations. In all compounds relatively intense and sharp ν_{MN} and ν_{MO} vibrations are found, indicating bidentate coordinating ligands (*vide infra*). The ν_{CN} absorption

TABLE III. The Nitrate and Thiocyanate Vibrations in the Ni(II) Compounds Containing paH.

No.	Compound	Nitrate combination band $\nu_1 + \nu_4$ (cm^{-1})		
7	$Ni(NO_3)_2(RS\text{-}paH)_2$	1755; 1745; 1720		
14	$[Ni(RS\text{-}paH)_3](NO_3)_2$	1760		
15	$[Ni(S\text{-}paH)_3](NO_3)_2$	1760		
		Thiocyanate vibrations		
		ν_{CN}	ν_{CS}	ν_{CNS}
8	$Ni(NCS)_2(RS\text{-}paH)_2$	2100vs	774s	464s
9	$Ni(NCS)_2(S\text{-}paH)_2$	2100vs	772s	460s

shifts to lower wavenumbers in all compounds. In the tris-chelate compounds the absorption due to ν_{CO} is split. One band, at about 1040 cm^{-1}, is shifted to lower wavenumbers compared to 1060 cm^{-1} in the free ligand due to the coordination of the oxygen and the breaking of the intramolecular hydrogen bond in the ligand. Another vibration, at about 1060 cm^{-1}, would be expected to have a similar shift to lower wavenumbers, but has in addition a high-field shift, due to hydrogen bonding between the OH-group and the anion.

In the bis-chelate compounds only one broad ν_{CO} band, shifted to lower wavenumbers, can be seen, with the exception of *7* which shows two sharp ν_{CO} vibrations indicating a different hydrogen-bonding pattern. The observed shifts of the ν_{CN} and ν_{CO} vibrations in these compounds are in fair agreement with the strength of the hydrogen bonding formed by the anion and the ligand. The positions of the ν_{CN} and ν_{CO} vibrations indicate the strength of the hydrogen bond to decrease in the following order: $F^- > NO_3^- > Cl^- > Br^- > NCS^-$. The IR spectra of the tris-chelate compounds indicate these compounds to be mutually isomorphous (see Table II). X-ray powder diffractograms show, however, that only compounds *10–13* are X-ray isomorphous. In the FIR region only the ν_{MN} and ν_{MO} vibrations are observed for these compounds, in contrast with the ν_{MX} vibrations in the bis-chelates (*vide infra*). The frequencies of the ν_{MN} and ν_{MO} vibrations are in good agreement with the frequencies found in the corresponding apH compounds [1, 2], as well as with those of the ethylenediamine compounds [9, 10] and propanediol compounds [11], although the ν_{MO} frequencies of our compounds are rather low. For a tris-chelate compound two geometrical isomers are possible, *i.e.* facial and meridional. In the facial isomer all nitrogen and oxygen atoms are in *cis*-positions to each other. In the meridional isomer two nitrogen and two oxygen atoms are in mutual *trans*-positions. Based on symmetry considerations the facial isomer (C_3-symmetry) is expected to show the two ν_{MN} and two ν_{MO} vibrations [10]. The meridional isomer (C_1-symmetry) is expected to exhibit three ν_{MN} and three ν_{MO} vibrations [10]. In all compounds two ν_{MN} and two ν_{MO} vibrations are indeed present, suggesting the structure to be facial, although a meridional structure cannot be entirely excluded on the basis of the spectra only. X-ray powder diffractograms of the bis-chelate compounds show that the compounds are not isomorphous. The assignment of the vibrations in the FIR region is complicated, but a tentative assignment is shown in Table II. Because the ν_{MN} vibrations are expected to occur at about the same frequencies for the different compounds, they can easily be assigned. Independent of the anion, in all compounds two strong ν_{MN} vibrations are present, suggesting *cis*-positions for the amine groups.

The frequencies of the ν_{MN} and also the ν_{MO} vibrations observed for the bis-chelates are in good agreement with the frequencies of the tris-chelates. As was found in the apH compounds, the ν_{MO} vibration is probably coupled with ligand vibrations [1, 2]. The ν_{MX} frequencies are in good agreement with the ν_{MX} frequencies observed for the apH compounds [1, 2] and they fall in the range observed for terminal Ni–X stretching bands [9, 10].

In the fluoride compounds *1* and *2* two strong ν_{MX} and two strong ν_{MO} vibrations are observed suggesting that both the ligands and the anions are in *cis*-positions. In the other bis-chelate compounds two strong ν_{MO} and only one strong ν_{MX} vibration are observed. Because all halogens and thiocyanate are terminal and the ν_{MX} frequencies are not expected to occur below 200 cm^{-1} [10], *trans*-positions of the ligands and the anions, with *cis*-positions of the amine and hydroxy groups, are most likely. In the nitrate compound *7* the nitrate is probably, albeit weakly, bidentate or asymmetrically coordinated

TABLE IV. Diffuse Reflection Spectra of Ni(II) Compounds Containing paH.

No.	Compound	Band maxima (cm^{-1})			Dq (cm^{-1})	
		$^3T_{2g} \leftarrow {}^3A_{2g}$	$^1E_g, {}^3T_{1g} \leftarrow {}^3A_{2g}$	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$	Exp.	Calc.[a]
1	$NiF_2(RS\text{-}paH)_2$	7850(sh)	14900(sh)	27320	990(eq)	
		9880	16250			
2	$NiF_2(S\text{-}paH)_2$	7800(sh)	14810(sh)	27400	1010(eq)	
		10100	16390			
3	$NiCl_2(RS\text{-}paH)_2$	9220	14940	25300	920	910
4	$NiCl_2(S\text{-}paH)_2$	9210	15050	25010	920	910
5	$NiBr_2(RS\text{-}paH)_2$	9170	14290	25000	915	905
6	$NiBr_2(S\text{-}paH)_2$	9150	14090	25000	915	905
7	$Ni(NO_3)_2(RS\text{-}paH)_2$	9610	16000	26670	960	970
8	$Ni(NCS)_2(RS\text{-}paH)_2$	9660	16000	25000	965	970
9	$Ni(NCS)_2(S\text{-}paH)_2$	9615	16130	25000	960	970
10	$[Ni(RS\text{-}paH)_3]Cl_2$	10000	16950	27780	1000	1000
11	$[Ni(RS\text{-}paH)_3]Cl_2$	9890	16950	27000	990	1000
12	$[Ni(RS\text{-}paH)_3]Br_2$	10020	16390	27200	1000	1000
13	$[Ni(S\text{-}paH)_3]Br_2$	10010	16390	27200	1000	1000
14	$[Ni(RS\text{-}paH)_3](NO_3)_2$	9880	16390	27780	990	1000
15	$[Ni(S\text{-}paH)_3](NO_3)_2$	9990	16670	26670	1000	1000

[a] Dq_{calc} has been obtained by taking 1130 cm^{-1} for ethylenediamine, 875 cm^{-1} for 1,2-propanediol, 730 cm^{-1} for Cl^-, 715 cm^{-1} for Br^- and 900 cm^{-1} for NCS^- and bidentate NO_3^-.

TABLE V. Ligand Field and Circular Dichroism Parameters of Nickel S-paH Compounds in Methanol (about 0.08 mol/l).

No.	Compound	Ligand Field $10^{-3}\,\bar{\nu}$ (cm^{-1}) (ϵ)[a]	Circular Dichroism	
			$10^{-3}\,\bar{\nu}$ (cm^{-1})	$\Delta\epsilon$[a]
2	$NiF_2(S\text{-}paH)_2$	9.45(8)		
		15.87(8)	15.63	+0.0069
			17.86	+0.0050
		25.62(17)	24.04	+0.0031
			27.32	+0.0084
4	$NiCl_2(S\text{-}paH)_2$	9.19(10)		
		14.82(8)	15.06	+0.0008
			16.08	−0.0008
			17.95	+0.0027
		25.52(17)	23.75	+0.0022
			27.47	+0.0079
6	$NiBr_2(S\text{-}paH)_2$	9.26(11)		
		15.38(9)	14.81	+0.0008
			15.85	−0.0009
			17.86	+0.0009
		25.38(18)	24.04	+0.0037
			27.17	+0.0063
9	$Ni(NCS)_2(S\text{-}paH)_2$	9.60(9)		
		15.63(8)	15.63	−0.0044
			24.27	+0.0022
		26.04	27.47	+0.0020
11	$[Ni(S\text{-}paH)_3]Cl_2$	9.93(10)		
		16.50(9)	15.48	+0.0367

(continued overleaf)

TABLE V. *(continued)*

No.	Compound	Ligand Field $10^{-3}\ \bar{\nu}\ (\mathrm{cm}^{-1})\ (\epsilon)^a$	Circular Dichroism	
			$10^{-3}\ \bar{\nu}\ (\mathrm{cm}^{-1})$	$\Delta\epsilon^a$
			18.18	+0.0135
		27.40(17)	27.55	+0.0347
13	$[\mathrm{Ni(S\text{-}paH)_3}]\mathrm{Br_2}$	9.90(10)		
		16.53(10)	15.48	+0.0421
			18.18	+0.0145
		27.47(18)	27.55	+0.0359
15	$[\mathrm{Ni(S\text{-}paH)_3}](\mathrm{NO_3})_2$	9.93(9)		
		16.53(9)	15.58	+0.0320
			18.18	+0.0142
		27.47(16)	27.55	+0.0325
			32.79^b	+0.0040

[a] In $\mathrm{l^{-1}\ mol\ cm^{-1}}$. [b] Absorption due to nitrate [17].

(*vide supra*). Therefore, the ligands have to be in mutual *cis*-positions. In compound *7* two ν_{MN} and two ν_{MO} vibrations are found indicating the hydroxy and amine groups are in *cis*-positions. Only one ν_{MX} vibration is observed just as found for the analogous apH compound. The use of FIR to characterize the nitrate coordination has been controversial and a rule, which is simple to apply, is not yet available [10].

Ligand Field Spectra

To obtain information about the coordination of the Ni(II) ion ligand field spectra have been recorded. The band maxima, assignments and ligand field parameters of the diffuse reflection spectra are listed in Table IV. The Ni(II) compounds show three absorptions fitting, more or less, the Tanabe-Sugano diagram for octahedral nickel(II) [12]. A deviation from the pure $\mathrm{O_h}$ symmetry is observed in all spectra. The first (low energy) and second absorption band are relatively broad and asymmetric. Decreasing the temperature makes the asymmetry even more pronounced. The spectra of the fluoride compounds *1* and *2* show shoulders on the first and second absorption band, indicating a somewhat lower symmetry although a splitting is not observed. This could be further evidence for a *cis*-orientation of the F-ions. The experimental Dq values are compared with the Dq values calculated using the rule of average environment [13]. For this calculation the Dq values of ethylenediamine, 1,2-propanediol and the anions quoted in the literature are used [11, 12, 14] (see Table V). According to the IR spectra all ligands have to be bidentately coordinated. In the bis-chelate compounds all anions are assumed to be monodentately coordinated, with the exception of the nitrate in compound *7*. The experimental and calculated Dq values agree well. This confirms the *cis*-positions of the amine and OH-groups proposed above (based on IR spectra), because *cis*-distortions of the coordination geometry are expected to have smaller splittings of the absorption bands than *trans*-distortions will.

The band maxima of the transmission spectra in methanol are listed in Table V. The position of the low-energy band is very close to the solid-state value reported in Table IV. It is in good agreement with the supposed bidentate coordination of the ligand in solution. The position of the first absorption band (lowest energy) of the bis-chelate compounds in methanol does not contain useful information on whether the anion or methanol completes the octahedral coordination sphere. Conductivity measurements at varying concentrations may resolve this question.

Circular Dichroism Spectra

In coordination chemistry, CD spectra are known to yield information about the absolute configuration of the ligand and the preferred configuration of the metal compound. In octahedral metal compounds four sources of dissymmetry can exist [15]:

i: Inherent dissymmetry within the $\mathrm{ML_6}$-entity, when it is 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 centers in the coordination ligands.

In the tris-chelate compounds of S-paH all four sources influence the symmetry. To the *cis*-bis-chelates only effects *ii, iii* and *iv* contribute, whereas

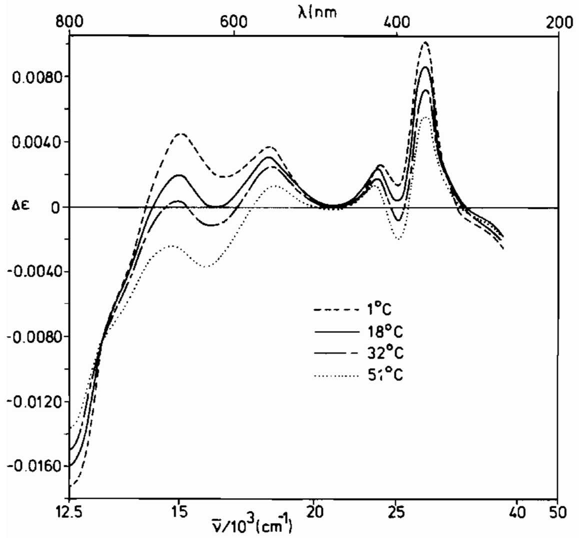

Fig. 2. The circular dichroism spectra of NiCl$_2$(S-paH)$_2$ at temperatures between 1 and 51 °C (0.08 mol/l).

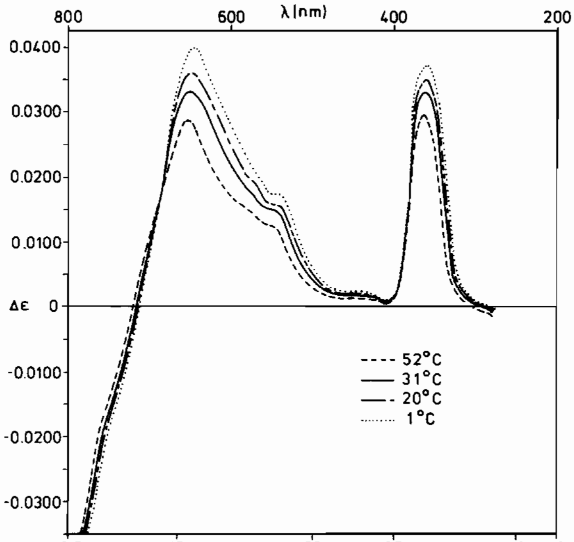

Fig. 3. The circular dichroism spectra of [Ni(S-apH)$_3$]Cl$_2$ at temperatures between 1 and 52 °C (0.08 mol/l).

in the *trans*-bis-chelates only sources *iii* and *iv* have contributions. Coordinated S-paH can occur in two conformations, *i.e.* δ and λ (See Fig. 1, lower part). The δ-conformation is the more favourable one for coordinated S-paH, because of the equatorial position of the methyl group [16].

The CD spectra of the nickel bis-chelates and tris-chelates (see Table V and Figs. 2 and 3) are very similar, resembling the spectra of the S-apH compounds [2] and the spectra of [Ni(1-pn)$_3$]$^{2+}$ [17]. A reasonable agreement between the maxima of the absorptions of the CD and the ligand field is observed. In the CD spectra of the bis-chelate compounds the shortest-wavelength band is split compared to the transmission spectra. The splitting probably originates from the lowering of the symmetry in the bis-chelate compounds.

The absence of the splitting in the transmission spectra shows that CD spectra are more sensitive to detect lowering of the symmetry. The narrower absorption bands in the CD spectra are responsible for this. The splitting in the shortest wavelength band did also not occur in the CD spectra of the bis-(S-apH) compounds.

For the tris-chelate compounds the positive CD band at about 16.5 kK and the negative charge-transfer band at about 35 kK clearly indicate a Λ-configuration for the tris-chelates, which can now be assigned as $\Lambda(\delta\delta\delta)$ [17]. This configuration corresponds to the most stable isomer for tris-chelates of S-paH. In this configuration the methyl groups are all equatorial and the ligands have the *lel*-orientation in which the carbon-carbon bond of the chelate ring is nearly parallel to the three-fold rotation axis.

Comparison of the $\Delta\epsilon$ values of the tris- and bis-chelates (see Table V) shows the $\Delta\epsilon$ values of the tris-chelate compounds to be much larger than the $\Delta\epsilon$ values of the bis-chelate compounds. Taking into account the number of ligands, a *cis*-position of the ligands in the bis-chelate compounds would result in a $\Delta\epsilon$ value of approximately 2/3 of the $\Delta\epsilon$ value of a tris-chelate compound. The $\Delta\epsilon$ of the chloride and bromide compounds *4* and *6*, however, is much smaller, *i.e.* less than 25% of the $\Delta\epsilon$ value of *11* and *13*, respectively, indicating that the ligands must occur in *trans*-positions. This conclusion is in agreement with the results of the FIR spectra, which indicated *trans*-positions for the anions and *cis*-positions for the amine and hydroxy groups. From Table V it can be seen that the $\Delta\epsilon$ value of the shortest wavelength band of compound 2 is larger than the $\Delta\epsilon$ value of the other bis-chelate compounds. In this case there is a difference with the CD of the S-apH compounds, where the fluoride compounds have much lower $\Delta\epsilon$ values, probably caused by the formation of aggregated species in solution. Assuming that compound *2* also forms significant amounts of aggregated species in solution, the $\Delta\epsilon$ value is in agreement with the ligands to be in *cis*-positions, as suggested from the FIR spectra and the ligand field spectra.

The spectrum of the thiocyanate compound *9* differs from the other bis-chelate compound and the $\Delta\epsilon$ values are much smaller. The different CD spectrum, which was found for the S-apH compounds [2], might indicate a coordinated NCS anion in solution.

The difference in $\Delta\epsilon$ values between the tris- and bis-chelate compounds may also indicate the configurational effect to be more important in S-paH than in

S-apH compounds. Another effect which can influence the $\Delta\epsilon$ values of the *trans*-bis-compounds is the induction of asymmetry at the coordinated amine and hydroxy groups through stereoselective hydrogen bonding [18], which is likely to be more important in the *trans*-bis-compounds than in the tris-compounds. Comparison of the $\Delta\epsilon$ values of the S-paH and S-apH compounds [2] shows the $\Delta\epsilon$ values of the S-paH compounds to be much larger, in agreement with Co(III) amino-alcohol compounds [18]. The size of the contribution of the induced rotational strength due to vicinal dissymmetry 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 [19]. The difference in the $\Delta\epsilon$ values between the S-paH and S-apH compounds indicates that the vicinal dissymmetry is enhanced when the asymmetric centre is next to a coordinated amine group in stead 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 OH group [18]. Compounds *4* and *11* have also been studied at temperatures between 1 and 52 °C (see Figs. 2 and 3). The differences in the $\Delta\epsilon$ values observed cannot be explained simply on the basis of solvent contraction. The apparent presence of isodichroic points is indicative of an equilibrium between the δ and the λ conformation of S-paH. The energy difference between such conformations has been calculated to be about 8–15 kJ/mol [20], depending on the force field used. It can be seen from Figs. 2 and 3 that the $\Delta\epsilon$ of the bis-chelate compound has a larger variation with the temperature than the tris-chelate compound. This can be explained by the fact that an axial methyl group in a *trans*-bis-chelate induces less steric hindrance than an axial methyl group in tris-chelate compounds.

From Fig. 3 a shift in the CD maximum towards longer wavelengths can be seen for the tris-chelate compounds. For the bis-chelate compounds shifts to longer and to shorter wavelengths can be observed in Fig. 2. In the literature [21] a shift to longer wavelengths has been explained by the decrease in dielectric constant of the solvent with increasing temperatures. This in turn increases electrostatic and ion-dipole interactions, which will strengthen the axial metal–ligand bond causing the shift towards longer wavelengths. The simultaneous presence of shifts to longer and to shorter wavelengths (see Fig. 2) is in contradiction with this explanation. Moreover, the explanation seems improbable because changes in dielectric constant of the solvent cannot be expected to influence the electrostatic and ion–dipole interactions, this would strengthen the axial metal–ligand bond, since these interactions are located in the vacuum of the metal compound environment. Probably these effects have to be explained by changes in the vibronic interactions with varying temperatures.

Comparison between the apH and the paH Compounds

The comparison of the coordination chemistry of compounds with apH and paH isomers show some remarkable and interesting differences. First, 'normal' copper coordination compounds of formula $CuX_2(paH)_n$, in which X = F, Cl, Br or NO_3 and n = 1, 2 or 3, cannot be prepared. This must be related to the higher acidity of primary alcohols (paH) compared to secondary alcohols (apH) [4]. Furthermore in paH compounds an increased steric hindrance exists between the methyl protons and the amine protons compared with the methyl protons and the OH-protons in apH compounds, resulting in more stable coordination compounds with RS-apH and S-apH.

Secondly, monodentate coordination of apH can occur, whereas paH coordinates bidentately in all nickel compounds found so far. A possible explanation for this behaviour is the difference between steric interactions in monodentate N-coordinated apH and monodentate N-coordinated paH. In apH the amine group is attached to a primary carbon in contrast to paH where the amine group is attached to a secondary carbon, resulting in an enhanced steric repulsion in the paH compounds. Only a breaking of the intramolecular N–H···O hydrogen bond can reduce this steric repulsion, but this will result in a bidentate coordination. A further difference which must be noted is the absence of mono-chelate compounds of S-paH compared to S-apH. The cause of this has not been investigated.

Concluding Remarks

The present study has shown that the coordination chemistry of RS-paH and S-paH is very similar. However, in contrast to $Ni(NO_3)_2(RS\text{-}paH)_2$, a compound $Ni(NO_3)_2(S\text{-}paH)_2$ could not be prepared. This strongly suggests that the *trans*-bis-compounds of the racemic ligand, which have a higher symmetry than the *trans*-bis-compounds of the optically active ligand, are more stable. For the nickel tris-chelates the configuration $\Lambda(\delta\delta\delta)$ appears to be most abundant. According to the FIR spectra the tris-chelates occur as the facial isomers. From the CD spectra and the FIR spectra, the ligands in the nickel bis-chelates have been found to occupy *trans*-positions with the amine and hydroxy groups in *cis*-positions. Only $NiF_2(S\text{-}paH)_2$ seems to have all donor atom pairs in *cis*-positions. In MeOH solution coordinated S-paH occurs as an equilibrium between the δ and λ conformation, with the δ conformation being the most abundant one. For S-paH compounds the configurational effect becomes more important than the S-apH compounds.

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