

symmetry to allow proposing of the scheme of Figure 10 is consistent with crystal structure results²⁴ (which indicate that the deviation from T_d in $\text{Ni}[(\text{C}_6\text{H}_5)_3\text{P}]\text{Cl}_2$, which is isomorphous to $\text{Co}[(\text{C}_6\text{H}_5)_3\text{P}]\text{Cl}_2$, is very pronounced) and with the absence of an observed strong charge-transfer band just to the blue side of about $17,000\text{ cm}^{-1}$. This reconciliation as well as the good correspondence of our formulation with experiment as seen from Tables IV, VI, and VII lend credibility to the underlying model.

Inspection of Figures 1 and 2 of ref 14 and comparison with our Tables IV, VI, and VII indicate that the present model provides an improvement over previous work. Gaussian fitting of poorly resolved spectra adds to the utility of the model. Where distortion in terms of bond angles and lengths from tetrahedral symmetry is pronounced, a choice between the constant charge-variable ligand distance approach¹⁴ and our variable charge-tetrahedral geometry method might be necessary since the former model may be more physically meaningful. Crystallographic studies, whenever available, should aid this choice. To some extent, geometric distortions are also taken into account by the empirical nature of the parameter Ds' in the present model. The structure of $\text{Co}(\text{apy})_2\text{Cl}_2$ can be inferred from the data for the isostructural²⁵ compound $\text{Zn}(\text{apy})_2\text{Cl}_2$. The crystallographic results show that neither model has much correspondence to

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the solid-state structure. However, the situation with respect to the solution species may be somewhat better. For the $\text{Co}(\text{apy})_2\text{Cl}_2$ complexes, therefore, there is little difference in physical significance between the two approaches with regard to molecular geometry assumed. However, if the remarkably good fit to experimental data obtained with the present model is interpreted as attesting to the validity of the assumptions underlying the model, namely, the dominant role of the relative effective charges residing at the sites of the two types of ligands in a given complex over relative bond lengths and angles, then the effective ligand charges play an even more significant role in determining spectral structure than has been heretofore appreciated. Such a role is at least partly accounted for more explicitly in the present approach than in previous weak-field methods. Undoubtedly, a combination of variation in ligand charges and positions represents a still better treatment. Unfortunately, the increased number of required parameters renders such a method impractical in view of the sparsity of observed electronic transitions.

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Registry No. $\text{Co}(\text{apy})_2\text{Cl}_2$, 19747-33-2; $\text{Co}(\text{apy})_2\text{Br}_2$, 19747-34-3; $\text{Co}(\text{apy})_2\text{I}_2$, 19747-35-4; $\text{Co}(\text{apy})_2(\text{NCS})_2$, 20002-46-4.

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Cobalt(III) Complexes Containing Optically Active Tartaric Acid

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Three monomeric species of the type $[\text{Co}(\text{en})_2\text{tart}]$, where en is ethylenediamine and tart is an anion of D- or L-tartaric acid, have been isolated. Two of the species are ionic and involve different types of coordination of a dinegative tartrate ion in a chelate ring. The third species is neutral and contains a trinegative tartrate ion. The compounds have been characterized using circular dichroism and electronic and infrared absorption spectra as well as proton nmr spectra.

Introduction

Recently it has been shown^{1,2} that coordinated hydroxy acid anions can induce very pronounced effects on the observed circular dichroism spectra of certain cobalt(III) complexes. In an extension of these studies we have now prepared certain monomeric complexes containing an optically active tartrate anion. The interest in these complexes arose from the fact that the coordinated ligand had a side chain with additional functional groups which could be influential in the stereochemistry of the product obtained.

Several years ago the preparation of a monomeric species with the general formula $[\text{Co}(\text{en})_2\text{tart}]\text{Br}$ was reported.³ However the species was shown to be a mixture of two diastereoisomers and no good separation was obtained. More recently some further results have been reported⁴ on the

preparation of a monomeric species in solution but again a mixture of diastereoisomers was present. Later workers, however, were successful in isolating and characterizing a dimeric species containing a bridging tartrate ion.⁵ We have now isolated three monomeric species with the general formula $[\text{Co}(\text{en})_2\text{tart}]^{n+}$ and report our findings in this paper.

Experimental Section

Reaction of Equimolar Quantities of Carbonatobis(ethylenediamine)cobalt(III) Chloride and Tartaric Acid. A mixture of 1.0 g of $[\text{Co}(\text{en})_2\text{CO}_3]\text{Cl}$, 0.5 g of optically active tartaric acid, and 10–15 ml of water was refluxed on a steam bath for 4 hr. The mixture was then transferred to an evaporating dish and evaporated to dryness on the steam bath. The reddish solid obtained was ground with absolute ethanol, filtered, washed with ether, and dried under a heat lamp; yield 1.2 g.

A concentrated aqueous solution of the above product was spotted on 1-mm tlc plates of Camag DS-O silica gel and developed with water. Three bands separated, the last of which was pink and was only a minor component of the mixture. Bands 1 and 2 (red and purple,

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respectively) were extracted with water and solid products were obtained by evaporating the filtered solutions to dryness at room temperature in an airstream. The solids obtained were rechromatographed three times to obtain better separation. The isolated solids were then washed and dried *in vacuo* at room temperature.

Anal. (for band 1). Calcd for $[\text{Co}(\text{en})_2(\text{C}_4\text{H}_3\text{O}_6)]\text{Cl}$: C, 26.50; H, 5.56; N, 15.45, Cl, 9.77. Found: C, 26.59; H, 5.60; N, 15.54; Cl, 9.70; molar conductivity $146 \text{ mho cm}^2 \text{ mol}^{-1}$. *Anal.* (for band 2). Calcd for $[\text{Co}(\text{en})_2(\text{C}_4\text{H}_3\text{O}_6)] \cdot \text{H}_2\text{O}$: C, 27.91; H, 6.15; N, 16.28. Found: C, 27.94; H, 6.26; N, 16.10.

Reaction of $[\text{Co}(\text{en})_2\text{CO}_3]\text{ClO}_4$ and Tartaric Acid in a 2:1 Molar Ratio. Reaction conditions were identical with those used above with the exception that only half the amount of tartaric acid was used; yield 0.9 g. After filtration of some water-insoluble material, chromatographic separation as above showed four bands; bands 1 and 2 were minor and corresponded to racemic $[\text{Co}(\text{en})_3]^{3+}$ and an aquated cobalt(III) species, respectively. Bands 3 and 4 were predominant and repeated chromatographs gave the following products. *Anal.* (for band 3). Calcd for $[\text{Co}(\text{en})_2(\text{C}_4\text{H}_3\text{O}_6)]\text{ClO}_4$: C, 22.52; H, 4.73; N, 13.13; Cl, 8.31. Found: C, 22.31; H, 4.87; N, 13.30; Cl, 8.41; molar conductivity $123 \text{ mho cm}^2 \text{ mol}^{-1}$. *Anal.* (for band 4). Calcd for $[\text{Co}(\text{en})_2(\text{C}_4\text{H}_3\text{O}_6)] \cdot 2.5\text{H}_2\text{O}$: C, 25.88; H, 6.52; N, 15.09. Found: C, 25.34; H, 6.57; N, 15.14.

$[\text{Co}(\text{NH}_3)_4\text{tart}]\text{Cl}$ was prepared by previously reported methods.⁶ The solid produced by this method contained a mixture of species and was purified by passing a solution of the product through a chromatography column using Sephadex G-10 as the adsorbent. Two main fractions were obtained, corresponding to $[\text{Co}(\text{NH}_3)_4\text{tart}]^+$ and $[\text{Co}(\text{NH}_3)_4\text{tart}]$, respectively. The aqueous fractions were taken to dryness in each case in order to obtain the solid species. The CD and electronic spectral data obtained for those compounds were consistent with values reported by Gillard and Price.⁷

Absorption spectra were recorded on a Beckman DK-1 recording spectrophotometer and circular dichroism spectra were obtained using a Durrum-Jasco ORD/UV-5/CD-1 spectropolarimeter. Infrared spectra were recorded on a Beckman IR-10 spectrophotometer as KBr disks. Nmr spectra were recorded on Varian T-60 or HA-100 spectrometers using deuterium oxide as solvent with sodium 2,2-dimethyl-2-silapentanesulfonate (NaDSS) as an internal reference. Microanalyses were performed by Alfred Bernhardt, Elbach, West Germany.

Results and Discussion

Nature of the Complexes. The species prepared may be regarded as further members of the series $[\text{Co}(\text{en})_2\text{ha}]^{n+}$ where en is ethylenediamine and ha is a coordinated hydroxy acid anion. Previously prepared members of the series¹ have shown that the hydroxy acid coordinates through an oxygen of the carboxylate group and the α -hydroxyl group which becomes deprotonated. This same type of chelate ring is also believed to be present in those tartaric acid complexes which showed a large Cotton effect in the visible region of the spectrum. For free tartaric acid the $\text{p}K_a$ values of the carboxylic acid groups are rather similar and much lower than the $\text{p}K_a$ of the hydroxyl group. However, on coordination the proton of the hydroxyl group becomes much more acidic and is readily lost. Hence formation of the chelate ring through a carboxylic acid and an α -hydroxyl group results in the loss of two protons from the tartaric acid molecule and it functions as a dinegative anion. The remaining uncoordinated carboxylate group is still rather acidic and retention of its proton will be strongly dependent upon reaction conditions.

The products isolated from the reaction of equimolar quantities of $[\text{Co}(\text{en})_2\text{CO}_3]^+$ and tartaric acid exhibit the acid functioning both as a dinegative anion and a trinegative ion. The species $[\text{Co}(\text{en})_2(\text{C}_4\text{H}_3\text{O}_6)]\text{Cl}$ obtained from band 1 using thin-layer chromatography appears to be a simple monomeric species in which the tartrate ion acts as a bidentate chelating agent with a free carboxylic acid group. Sup-

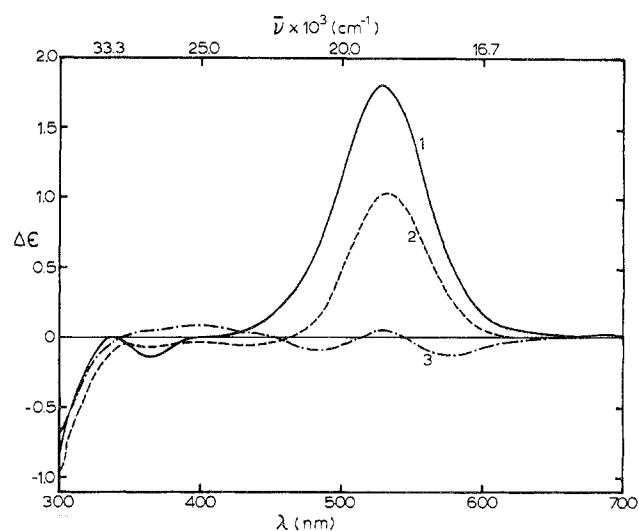


Figure 1. Circular dichroism spectra of $[\text{Co}(\text{en})_2(\text{D}(-)\text{-OOCCHOCHOHCOOH})\text{Cl}]$ (1), $[\text{Co}(\text{en})_2(\text{D}(-)\text{-OOCCHOCHOHCOO})]$ (2), and $[\text{Co}(\text{en})_2(\text{D}(-)\text{-OOCCHOHCHOHCOO})]$ (3).

port for this comes from the analytical and conductivity data reported in the Experimental Section. Moreover, infrared spectra clearly show the presence of both free COOH and coordinated COO^- with bands at 1718 and 1628 cm^{-1} , respectively.

In contrast the species isolated from band 2 contains tartaric acid as a trinegative ion which gives rise to the neutral species $[\text{Co}(\text{en})_2(\text{C}_4\text{H}_3\text{O}_6)]$. Conductivity measurements are consistent with a nonelectrolyte and the infrared spectrum shows no absorption around 1700 cm^{-1} but only a broad band at approximately 1620 cm^{-1} . Hence this species may be regarded as the deprotonated version of the complex isolated from band 1.

In both cases the tail of the ligand may be regarded as a side chain attached to the asymmetric carbon of the chelate ring. As in the case of the lactate and pantoate complexes reported earlier, the chelate ring would not be expected to be greatly puckered due to the planar character of the coordinated carboxylate group. However, the δ conformation might be slightly favored in the case of the D acid since the side chain can adopt an equatorial position on the slightly puckered ring.

The CD spectra of the species isolated from the reaction mixture using D(-)-tartaric acid are shown in Figure 1. On the basis of the large positive CD peak in the visible region of the spectrum each complex is assigned the Λ overall configuration. Further support comes from the fact that upon treatment with ethylenediamine, $\Lambda\text{-}[\text{Co}(\text{en})_3]^{3+}$ is produced. When L(+) tartaric acid is used, compounds are obtained which give mirror-image CD curves of those in the figure and hence can be designated as having the Δ configuration.

For the majority of complexes containing optically active ligands, the configurational effect is by far the strongest contributor to the observed circular dichroism. For complexes such as these the combined contributions of the conformational and vicinal effects are usually quite small. However, for the hydroxy acid complexes previously studied it was found^{1,2} that the vicinal effect due to the coordinated optically active acid was quite significant and was considerably enhanced relative to the values observed for the $[\text{Co}(\text{NH}_3)_4\text{-ha}]^+$ species where it is the sole effect. A significant vicinal effect appears to obtain for the tartrate complexes also. Unfortunately a quantitative curve for the vicinal effect cannot be obtained since only one isomer was separated for each

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Table I

Sample ^a	Absorption		CD	
	λ , nm	ϵ_{\max} , $M^{-1} \text{ cm}^{-1}$	λ , nm	$\Delta\epsilon$, $M^{-1} \text{ cm}^{-1}$
Λ -[Co(en) ₂ (D(-)-C ₄ H ₄ O ₆)]Cl	508	118	526	+1.79
	353	138	364	-0.13
Δ -[Co(en) ₂ (D(-)-C ₄ H ₄ O ₆)]	516	135	532	+1.05
	356	162	420	-0.05
[Co(en) ₂ (D(-)-C ₄ H ₄ O ₆)]ClO ₄			360	-0.07
	518	116	575	-0.13
	350	162	529	+0.05
			485	-0.08
[Co(NH ₃) ₄ (D(-)-C ₄ H ₄ O ₆)]NO ₃ ^b (in 0.1 M H ⁺)			400	+0.08
	513	80.2	554	+0.35
	(513)	(67)	(555)	(+0.34)
	350	114	490	-0.61
			(490)	(-0.66)

^a The complexes containing L(+)-tartaric acid gave virtually mirror-image CD curves. ^b Values in parentheses are from ref 7.

acid. However, by using the curves for the configurational effect of the similar complexes containing lactic and pantoic acid, an approximation for the vicinal effect of the tartrate complexes can be estimated. In both cases a very pronounced vicinal effect curve is obtained and shows values which are comparable to those reported for the pantoate complex.¹ Both the coordinated pantoate and tartrate ligands have long tails capable of hydrogen bonding with the NH₂ groups of the ethylenediamine ligands and similarity of their configurational and vicinal effect curves would be anticipated. The very significant vicinal effect observed in these complexes can again be attributed to the relatively large energy separation of the component d-d transitions compared to analogous amino acid complexes, resulting in a smaller net cancelation of circular dichroism intensity.

The species isolated from bands 1 and 2 are closely related in character and differ only in the nature of the free carboxylic acid group. It is not surprising that a mixture of the two species would be formed under the reaction conditions used and that they could be readily separated using thin-layer chromatography due to the differences in charge. The CD intensity of the neutral species isolated from band 2 is diminished by approximately 40% compared to the ionic compound and this may be primarily due to the shift in the component absorption bands for this compound. As seen in Table I, the main band is shifted to longer wavelengths in the neutral compound. Acidification of an aqueous solution of the neutral compound produces a spectrum quite similar to that for the ionic species and the spectral change is reversible. Similar reversible changes have been observed for the analogous tetraammine complexes⁷ and from the CD and visible spectra it is readily apparent that a shift in energy of the component absorption bands occurs.

It is interesting to note that for D(-)-tartaric acid, both of the products isolated have the Λ configuration. No evidence of a species with the Δ configuration was observed. However, this is not necessarily proof that the Λ species were formed stereoselectively but may only be due to selectivity in precipitation from the reaction mixture. Molecular models indicate that D(-)-tartaric acid can coordinate favorably with either the Λ or Δ configuration of ligands. However, for the Λ isomer the tail is more favorably oriented for hydrogen bonding between the carbonyl oxygen of the carboxylate group and one of the NH₂ groups on an ethylenediamine ligand. Thus there could be some extra stability associated with this particular diastereoisomer upon crystallization. For the Δ configuration some distortion of the chelate ring is necessary for hydrogen bonding to occur.

Recently workers have reported⁵ the isolation of a dimeric

species from mixtures of tartaric acid and a [Co(en)₂CO₃]⁺ salt. The species isolated was represented as [Co(en)₂tart-Co(en)₂]²⁺ and was assigned the Δ configuration about each cobalt atom when L(+)-tartaric acid was used. In an attempt to obtain the dimeric species, a reaction mixture containing a cobalt:tartaric acid ratio of 2:1 was prepared. The solid isolated from the filtered reaction mixture gave two major bands on chromatographing on silica gel which were labeled bands 3 and 4, respectively. Band 4 gave a species which was identical with that of band 2 in the earlier preparation and corresponded to the species Λ -[Co(en)₂(C₄H₃O₆)]. Band 3 gave a species which contained the ionic cation [Co(en)₂(C₄H₄O₆)]⁺ but was not similar to the ionic species isolated above. The absorption maximum was shifted to longer wavelengths while the CD spectrum showed a markedly different pattern and was significantly reduced in intensity as shown in Figure 1. This species is believed to involve the tartaric acid as a bidentate ligand also but coordination is through the two carboxylate groups on the ligand. Support for this comes from the fact that the infrared spectrum shows no absorption characteristic of a free carboxylate group and has only a broad band around 1620 cm⁻¹. The low intensity of the CD bands would be consistent with a weaker and more flexible chelate ring as has been previously observed for a similar complex derived from glutamic acid.⁸ However the tartrate species appears to be a mixture of the Λ and Δ diastereoisomers as evidenced by nmr studies (*vide infra*). Hence the low intensity and different patterns are probably only the result of cancelation effects of the two isomers. It is interesting to note that there is a lack of preference for either configuration when both carboxylate groups are coordinated.

The nmr spectra of these complexes are complicated due to the fact that the species are readily soluble only in H₂O or D₂O. The proton resonances of the tartrate ligand occur very close to the HOD signal and are generally quite broad. The most complicated spectrum is that of the species [Co(en)₂(C₄H₄O₆)]ClO₄ where six peaks of varying magnitudes are observed in this region. This is consistent with a mixture of the two diastereoisomers as indicated above. Each diastereoisomer should exhibit an AB pattern corresponding to the two nonequivalent protons on the tartrate ligand. Overlap of the signals from the two diastereoisomers could give rise to the observed pattern.

The Λ -[Co(en)₂(C₄H₄O₆)]Cl species which has a free CO-OH group shows a simple AB pattern with chemical shifts

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δ_A 4.35 and δ_B 4.08 ppm and $J_{AB} = 13$ Hz. This is consistent with the expected nonequivalence of the tartrate protons. For the neutral species $[\text{Co}(\text{en})_2(\text{C}_4\text{H}_4\text{O}_6)]$ the same type of pattern is also observed but is shifted slightly upfield by 0.07 ppm. For both complexes it is envisaged that coordination occurs through a carboxylate group and a deprotonated hydroxyl group. Hence such similarity of the nmr spectra would be anticipated. Moreover, the species $[\text{Co}(\text{NH}_3)_4(\text{C}_4\text{H}_4\text{O}_6)]\text{Cl}$ where such coordination has been shown previously⁷ shows a similar AB pattern also with δ_A 4.35 and δ_B 4.14 ppm. This pattern was maintained in acidic or neutral solution with only a slight shift as above and hence further support is given for the nature of the ethylenediamine analogs.

Thus in this study a series of monomeric species have been isolated from mixtures of $[\text{Co}(\text{en})_2\text{CO}_3]^+$ and tartaric

acid. For the D(-) acid the Λ configuration was found while for the L(+) acid the Δ configuration was obtained. These configurations are in agreement with those obtained for the dimeric species⁵ obtained earlier from mixtures of those reactants. Hence the exact nature of the product obtained is strongly dependent on the method of preparation but a similar asymmetric bias is imposed for each type of complex.

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Registry No. Λ - $[\text{Co}(\text{en})_2(\text{D}(-)\text{-C}_4\text{H}_4\text{O}_6)]\text{Cl}$, 52032-32-3; Λ - $[\text{Co}(\text{en})_2(\text{D}(-)\text{-C}_4\text{H}_4\text{O}_6)]$, 52022-19-2; $[\text{Co}(\text{en})_2(\text{D}(-)\text{-C}_4\text{H}_4\text{O}_6)]\text{-ClO}_4$, 52022-20-5; $[\text{Co}(\text{NH}_3)_4(\text{D}(-)\text{-C}_4\text{H}_4\text{O}_6)]\text{NO}_3$, 52019-97-3; $[\text{Co}(\text{en})_2\text{CO}_3]\text{Cl}$, 15842-50-9; $[\text{Co}(\text{en})_2\text{CO}_3]\text{ClO}_4$, 15155-12-1.

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Spin Delocalization in Square-Planar Spin-Triplet Benzene- and Toluenedithiolatocobaltate(III)

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The nature of the ground state and electron delocalization in tetrabutylammonium bis(benzenedithiolato)cobaltate(III) and the corresponding toluene compound has been investigated by far-infrared- and nmr spectroscopy and by measurement of paramagnetic susceptibility. The results are shown to be consistent with a spin-triplet ground state, as predicted by a molecular orbital calculation on the benzenedithiolate. The degeneracy of the ground state is lifted by a zero-field splitting of about 35 cm^{-1} . Of the singly occupied orbitals d_{z^2} and d_{yz} , the latter is considerably delocalized over the ligands.

Introduction

Tetrabutylammonium bis(1,2-benzenedithiolato)cobaltate(III), $\text{Bu}_4\text{NCo}(\text{bdt})_2$, and tetrabutylammonium bis(3,4-toluenedithiolato)cobaltate(III), $\text{Bu}_4\text{NCo}(\text{tdt})_2$, are two of the few d^6 transition metal complexes having a triplet ground state.¹⁻⁸ Although five- and six-coordinate complexes are known,^{1,2} most compounds of this type have a planar four-coordination. Examples are iron(II) phthalocyanine,³ bis(biuretato)cobaltate(III),⁴ bis(aminobenzethiolato)cobaltate(III),⁵ bis(maleonitriledithiolato)cobaltate(III),^{6,7} and the bis(benzenedithiolato)cobaltates.^{7,8}

Assignments of the ground-state configuration of the MS_4 chromophores in general are few,⁹ uncertain,^{10,11} and con-

flicting^{10,12-14} although the molecular structures are known. Recently it was even suggested¹⁴ that the ground state of the $\text{Co}(\text{tdt})_2^-$ species is actually a spin singlet, the well-established paramagnetism of this compound being caused by a low-lying excited triplet state. Nmr and far-infrared data are conspicuously lacking.

Therefore we have investigated these systems in order to obtain detailed information about the electronic ground state. We have selected magnetic susceptibility and far-infrared techniques to obtain zero-field splittings and g values. Proton nmr shifts were recorded at several temperatures for information about the spin density on the ligands and for correlation with a molecular orbital calculation.

Experimental Section

Benzene-1,2-dithiol was prepared as described in the literature.¹⁵ Toluene-3,4-dithiol (Merck) was used without further purification. $\text{Bu}_4\text{NCo}(\text{bdt})_2$ and the toluene analog were prepared according to the method of Baker-Hawkes⁸ and recrystallized three times from CH_2Cl_2 and acetone. The compounds were checked for purity by elemental analyses carried out under supervision of W. J. Buys at the Microanalytical Department of the Institute for Organic Chemistry, TNO Utrecht, The Netherlands.

Nmr spectra were recorded on a Varian XL-100 spectrometer, fitted

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