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Chiral Metal Complexes.
19[†]. Chiral Discrimination between Diastereoisomers of [(2,4-Pentanedionato)(N,N′-di-8-quinolyl-1,2-diaminoethane)cobalt(III)]

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Abstract

The 360 MHz ^1H NMR spectrum of a synthetic isomeric mixture of Δ,Λ-β-[Co(dqen)(acac)]$^{2+}$ ions (where dqen is N,N′-di-8-quinolyl-1,2-diaminoethane and acac is the 2,4-pentanedionate anion) has been measured in 6 M DCl. Two sets of completely resolved signals have been assigned uniquely to the Δ-β-(S,S) and Δ-β-(R,S) diastereoisomers, together with their enantiomeric forms, where R and S refer to the absolute configuration of the two amine nitrogen atoms of the tetradentate dqen ligand. Integration of the spectrum permits the calculation of the chiral discrimination energy difference between the two forms of the complex cation at 298 K. This quantity emerges as only 0.44 kJ mol^{-1} in favour of the Δ-β-(S,S) isomer. The results are discussed with reference to other similar complexes, especially those in which the geometry of the in-plane amine nitrogen atom of the coordinated tetradentate is determined by the steric requirements of substituents on the aliphatic backbone of the dqen ligand.

Introduction

It has been shown recently that the complex[#] Δ,Λ-β-*exo,endo*-[Co(R-dqpn′)(acac)]ClO_4 consists of four co-crystallised diastereoisomers in the solid state and that these species persist in solution [2, 3]. The trigonal in-plane nitrogen atoms of the diastereoisomers may be protonated (or deuterated) to yield the complex cations Δ,Λ-β-*exo,endo*-[Co(R-dqpn)(acac)]$^{2+}$. Of the eight diastereoisomers possible in this system only four are present in solution, as evidenced by high resolution ^1H NMR measurements of the complex dissolved in 6 M DCl. These four isomers retain the geometrical isomerism and absolute configuration at the metal centres of the original N-deprotonated species. Thus the protonation (deuteration) process at the amine nitrogen atoms is stereospecific. A similar result is found also for the related dqchxn complex [3]. In contrast Suzuki and coworkers [2] reported a doubling of the number of CH_3 singlet resonances attributable to the acac ligands in the NMR spectrum of the dqen′ complex when it is deuterated. This effect can only be due to the fact that deuteration of the in-plane amine nitrogen results in both R and S absolute configurations for that atom.

In order to precisely evaluate the chiral discrimination energy between these two sets of dqen isomers we have measured the ^1H NMR spectrum of the isomeric mixture using a high frequency instrument. The results of our study, which are detailed below, permit us to comment on the relative magnitudes of the discriminations involved between various diastereoisomers in related complex mixtures, particularly those containing the substituted congeners of dqen mentioned above.

Experimental

Δ,Λ-[Co(dqen′)(acac)]$ClO_4 \cdot 0.5C_6H_6$

This complex was prepared according to the method reported in the literature [2] except that in our hands a benzene *hemi*-solvate form was isolated. [*Anal.*: Calc. for $C_{28}H_{27}N_4O_6ClCo$: C, 55.1; H, 4.5; N, 9.2%. Found: C, 55.0; H, 4.5; N, 9.5%]. The presence of the benzene of solvation is clearly evident

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[#] R-dqpn = N,N′-di-8-quinolyl-R-1,2-diaminopropane; dqen and dqchxn are the 1,2-diaminoethane and *trans*-1,2-diaminocyclohexane analogues of dqpn, respectively; the primed ligand notations represent the mono-N-deprotonated derivatives of the parent tetradentates; acac = 2,4-pentanedionate anion; trien = 1,4,7,10-tetraazadecane; glyH = glycine.

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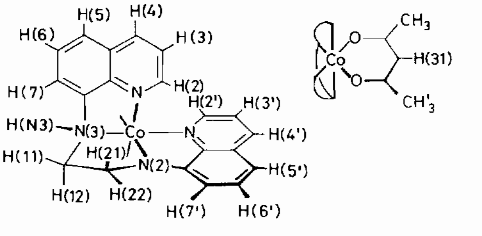
in NMR spectra of the complex in acetone-d_6, and integration of these signals confirms the 2:1 stoichiometry.

The ^{1}H NMR spectra were measured at 360 MH and 298 K in acetone-d_6 and 6 M DCl using a Bruker WM-360 instrument. TMS and DSS were used respectively for internal reference, and chemical shifts are reported in ppm relative to these.

Results and Discussion

NMR data for the deprotonated Δ,Λ-β-[Co(dqen′)(acac)]$^+$ complex cations in acetone-d_6 are given in Table I and the numbering scheme for the protons involved is shown in I. The spectrum of the complex is shown in Fig. 1.



I

TABLE I. ^{1}H NMR Data[a] for Δ,Λ-β-[Co(dqen′)(acac)]$^+$.

Proton	Chemical Shift (δ)	Coupling Constant (J_{ij})		
		i	j	$\lvert J_{ij}\rvert$
H(2)	6.95	2	3	5.21
H(3)	7.49	2	4	1.55
H(4)	8.66	3	4	8.39
H(5)[b]	8.20	5	6	7.93
H(6)	8.02	5	7	<0.05
H(7)[b]	8.47	6	7	8.18
H(2′)	8.43	2′	3′	5.05
H(3′)	7.77	2′	4′	1.49
H(4′)	8.45	3′	4′	8.35
H(5′)[c]	6.88	5′	6′	7.72
H(6′)	7.34	5′	7′	<0.05
H(7′)[c]	6.70	6′	7′	6.92
H(N3)	8.74	N3	11	<0.05
H(11)	3.52	N3	12	4.27
H(12)	4.21	11	12	11.64
H(21)	2.99	11	21	3.71
H(22)	3.18	11	22	<0.05
H(31)	5.73	12	21	12.60
CH_3	2.09	21	22	12.55
CH'_3	1.86	12	22	5.63

[a] Chemical shifts in ppm (±0.05) relative to TMS as internal standard and coupling constants in Hz (±0.005). The spectrum was recorded in acetone-d_6 at 298 K. [b, c] We do not distinguish between these pairs of protons.

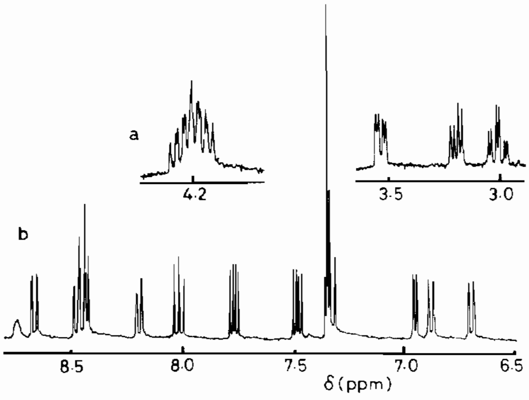


Fig. 1. 360 MHz ^{1}H NMR spectrum of Δ,Λ-β-[Co(dqen′)(acac)]$^+$ in acetone-d_6. (a) Resonances associated with the ethane bridge. (b) Aromatic region.

The fact that only one proton in the aliphatic region of the complex shows significant coupling to H(N3), together with the results of spin-decoupling experiments, uniquely defines the resonances associated with the diaminoethane bridge in the ligand. Application of the Karplus relationship and a study of molecular models of the complex permit the assignment of individual resonances. The β-topology is confirmed by the observation of distinct signals for all individual protons in the complex ion. The aromatic proton signals have been assigned using spin-decoupling experiments and by comparison with the spectra of related complexes [4]. Signals arising from H(5′), H(6′) and H(7′) are assumed to occur at higher field strength relative to corresponding protons on the other quinoline ring because of their proximity to the deprotonated N(2) atom. We do not differentiate between the two acac methyl groups in assigning their resonances at 1.86 and 2.09 ppm.

When Δ,Λ-β-[Co(dqen′)(acac)]$ClO_4 \cdot 0.5C_6H_6$ is dissolved in 6 M DCl much of the aromatic region of its ^{1}H NMR spectrum is obscured by the broad HDO resonance. However, the aliphatic region of the spectrum is well resolved (Fig. 2). Four methyl singlet

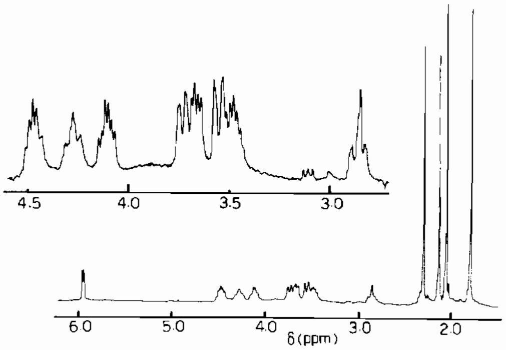


Fig. 2. 360 MHz ^{1}H NMR spectrum in the aliphatic region of Δ,Λ-β-[Co(dqen)(acac)]$^{2+}$ in 6 M DCl.

resonances, two H(31) singlets and eight separate multiplets corresponding to the diaminoethane bridge of the tetradentate ligand are seen. This pattern of signals clearly arises from the presence of two sets of diastereoisomers in solution, Δ-β-(S,S)- and Δ-β-(R,S)-$[Co(dqen)(acac)]^{2+}$, together with their enantiomeric forms. The R,S terminology refers to the absolute configurations of N(2) and N(3) respectively.

A series of spin-decoupling experiments demonstrated that the signals at 2.86, 3.56, 3.74 and 4.27 ppm were due to the protons in the ethane bridge of one diastereoisomer and those at 3.48, 3.66, 4.11 and 4.47 ppm to the other. These experiments also allowed all of the coupling constants in the pairs of diastereoisomers to be deduced unambiguously. Chemical shift and coupling constant data are gathered together in Table II. Again an inspection of molecular models and the application of the Karplus relationship to the data permits the assignment of resonances to individual diastereoisomers.

TABLE II. ^{1}H NMR Data[a] for the N-Deuterated Complexes.

	Δ-β-(R,S)	Δ-β-(S,S)
H(11)	3.56	3.48
H(12)	4.27	4.47
H(21)	2.86	3.66
H(22)	3.74	4.11
$J_{11,12}$	13.07	11.90
$J_{11,21}$	2.90	5.63
$J_{11,22}$	<0.05	12.13
$J_{12,21}$	12.84	<0.05
$J_{12,22}$	3.12	5.50
$J_{21,22}$	12.51	11.76
$J_{N3,11}$	<0.05	<0.05
$J_{N3,12}$	<0.05	5.50
H(31)	5.95	5.94
CH_3	2.29	2.04
CH'_3	2.12	1.78

[a] Chemical shifts in ppm (±0.05) relative to DSS as internal standard. Absolute values of coupling constants in Hz (±0.005).

The rigidity of the two outer chelate rings formed by the tetradentate in turn forces a locked and quite rigid conformation in the central chelate ring when both inner nitrogen atoms are protonated. This is particularly noticeable in the Δ-β-(R,S) isomer. The obvious mirror-image relationship applies here as well and is taken as understood in the remainder of this discussion. Furthermore, in this isomer, but not in Δ-β-(S,S)-$[Co(dqen)(acac)]^{2+}$, atom H(21) is constrained to lie directly over the quinolyl ring adjacent to the fold of the ligand and in an unusually close proximity to it. Therefore it must experience considerable electronic shielding, and for this reason we have assigned the resonance at 2.86 ppm to this proton. Spin-decoupling and coupling-constant relationships serve to uniquely define individual resonances in the remainder of the ethane bridge for the Δ-β-(R,S) diastereoisomer as those given in Table II. The resonances for the corresponding protons in the Δ-β-(S,S) isomer were assigned in a similar way. All signals arising from the acac ligands in the diastereoisomers also were able to be assigned from a careful integration of the spectrum.

At equilibrium, in 6 M DCl at 298 K, the concentrations of the diastereoisomeric pairs are not equal. Integration of the aliphatic ethane bridge resonances, as well as those due to the acac ligands, gives a value of 0.84 for the ratio $[\Delta$-β-$(R,S)]/[\Delta$-β-$(S,S)]$. The diastereoisomer which has the same (S) absolute configuration at the inner nitrogen atoms N(2) and N(3) is thus thermodynamically more stable with respect to its congener by some 0.44 kJ mol^{-1} under these conditions. Such a low value for the chiral discrimination energy involved is comparable with those reported [5, 6] for both β_1- and β_2-$[Co(trien)(gly)]^{2+}$ which are either 0.4 or 5.4 kJ mol^{-1} in favour of that β-isomer in which the secondary nitrogen atoms have the same absolute configuration.

The results indicate clearly why only four of the eight possible diastereoisomers are observed for the related complex Δ,Λ-β-*exo,endo*-$[Co(R\text{-}dqpn)(acac)]^{2+}$ under the same conditions [3]. Numerous studies have been directed towards an understanding of the equatorial preference for a substituent in five-membered chelate rings [7, 8]. This energetic preference is of the order of 8–10 kJ mol^{-1}, a quantity which obviously would greatly outweigh that associated with varying the absolute configuration at N(2). This fact is particularly relevant to the R-dqpn complexes since the methyl group is able to lie in an equatorial position with minimum strain for limited combinations of the absolute configurations of N(3), the metal centre and the dqpn tetradentate topology [3]. Alternative combinations of these possible configurations should only result from the introduction of other more significant steric interactions.

Finally, with reference to the above conclusions, we wish to draw attention to the isomer distribution in related complexes of dqchxn. It was observed that when $[Co(R,R\text{-}dqchxn')(acac)]ClO_4$ is dissolved in either acetone-d_6 or 12 M DCl only two methyl singlets due to the acac ligand are present in the ^{1}H NMR spectra [2]. This result shows that these deprotonated or deuterated complexes are formed stereospecifically, assuming the β geometry, and such a result is in accord with the stereochemical requirements of the 1R,2R-diaminocyclohexane fragment of the tetradentate ligand. On the basis of the CD spectrum in the π–π^* region it was suggested [2] that the complex, when protonated, adopts the Λ absolute configuration. This prediction is consistent with the stereospecificity found for Co(III) complexes of the related ligand N,N′-di-(2-pyridyl)-1R,2R-diaminocyclohexane [9].

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