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Registry No. $Fe(N_2)_5$, 92763-10-5; $Fe(N_2)_4$, 92763-11-6; $Fe(N_2)_3$, 92763-12-7; $Fe(N_2)_2$, 92763-13-8; $Fe(N_2)$, 43060-89-5.

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Chiral Metal Complexes. 17.[1] Cocrystallization of Four Diastereoisomers: A Second Example

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Recently the crystal structure of [Co(acac)(*R*-dqpn′)]ClO_4 was described[4] as comprising equal amounts of Δ-β and Λ-β cations with positional disorder of the pn methyl group. Another isomerism was present in that the nitrogen α or β to the asymmetric carbon could be deprotonated. Nevertheless, only two doublets due to these methyl groups were observed in the ^1H NMR spectrum of the complex and its conjugate acid, and this was interpreted as arising from a facile rearrangement of the diastereomer population in solution.

Since we have found that Co(III) complexes of the related ligand *R*-picpn (3-(*R*)-methyl-2,6-di-2-pyridyl-2,5-diazahexane) adopt a number of topologies[5] and that four diastereomers of $[Co(R,S\text{-picpn})(S\text{-alaninate})]^{2+}$ cocrystallize in the perchlorate salt as determined crystallographically,[6] we were prompted to reexamine the dqpn complex. High-resolution NMR studies show that four diastereomers persist in solution, and the original structure indeed is the second case of four cocrystallized isomers of this kind. Several other conclusions concerning related complexes may be drawn as a result.

Experimental Section

The complex [Co(acac)(*R*-dqpn′)]ClO_4 was obtained analytically pure by using previously published procedures.[4,7] In ethanol $\Delta\epsilon_{620} = +3.80\ M^{-1}\ cm^{-1}$, $\Delta\epsilon_{470} = -7.08\ M^{-1}\ cm^{-1}$, $\log \epsilon_{490} = 3.52$, $\log \epsilon_{307} = 3.97$, and $\log \epsilon_{262} = 4.38$, in agreement with reported values.[4] NMR spectra were recorded at 360 MHz on a Bruker WM-360 spectrometer, and CD and electronic spectra were obtained on a Beckman DK 2A spectrophotometer and a CNRS Jobin-Yvon Dichrographe III. All spectra were recorded at 298 K.

Results and Discussion

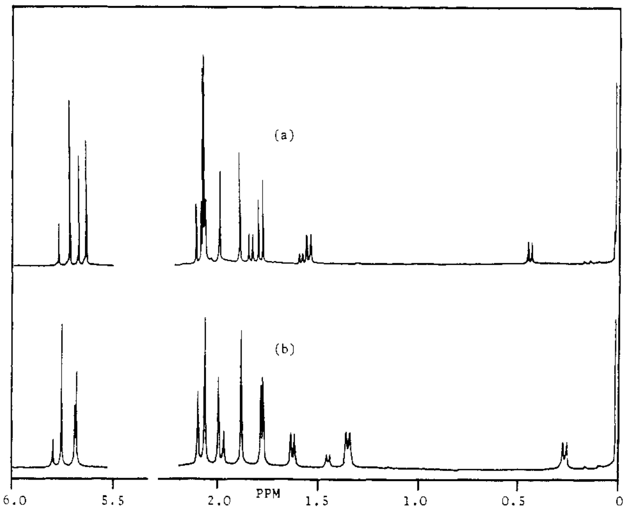

Figure 1. 360-MHz ^1H NMR spectra of the aliphatic region of Δ,Λ-β-*exo,endo*-[Co(acac)(*R*-dqpn′)]ClO_4 dissolved in (a) acetone-d_6 and (b) Me_2SO-d_6.

The 360-MHz ^1H NMR spectra of the complex (Figure 1) shows that four diastereomers persist in Me_2SO-d_6 and acetone-d_6 solution. Four dqpn methyl doublets and four acac H(3) singlets are clearly resolved in both solvents. Seven acac methyl singlets are observed in Me_2SO-d_6, the largest comprising overlapping signals (by integration) from the most and least predominant diastereoisomers. In acetone-d_6, six such singlets are observed, the others being obscured by solvent peaks. Data are tabulated in Table I. The four diastereoisomers are present in unequal amounts, the relative concentrations being 0.17:0.78:0.49:0.55 ± 0.04 by integration. This distribution is remarkably similar to that found for "positional disorder" of the methyl groups in the solid-state structure of [Co(acac)(*R*-dqpn′)]ClO_4 (0.18:0.82:0.41:0.59). This leads to the conclusion that no reequilibration of diastereomers in solution occurs, and a consideration of the population permits assignment of signals to unique isomers.

Since the complex must contain equal amounts of Δ and Λ species, the two with relative concentrations 0.17 and 0.78 must be of the same hand. Reference to the crystal structure shows that the methyl group in the Δ-β-endo isomer[6] is the most shielded by a quinoline ring, and we assign the highest field doublet to this species. The isomer distribution automatically indicates the resonances belonging to the Δ-β-exo complex. It was originally argued[4] that since the high-field doublet "disappears" in DCl, this signal is due to the a methyl group adjacent to the deprotonated nitrogen. This implies that *two* such signals should be present, contrary to our findings. It is however true that the trigonal nitrogen in the Δ-β isomers confers an inflexibility in the central chelate ring that forces the dqpn methyl group in the endo isomer closer to a shielding quinolyl ring. Protonation relieves this strain and is discussed below. Chemical shift differences in the Λ isomers are subtle, but the distribution of isomers in solution compared to that in the solid state is so striking that we conclude that the least concentrated Λ isomer is the endo one.

The question arises as to whether the observed isomer distribution reflects chiral discrimination energies for the various complex cations. It is possible, but we do not claim this to be true because in neither our nor the previous preparation[4] was the whole amount of complex isolated nor was it demonstrated that equilibrium was established. The cocrystallization of four diastereoisomers in the lattice of [Co(acac)(*R*-dqpn′)]ClO_4, only the second reported such phenomenon to our knowledge, may simply be due to crystal-packing effects. However, ^1H NMR results[4] on the related complexes [Co(acac)(dqen′)]ClO_4 and [Co(acac)(*R,R*-dqchxn′)]ClO_4, where dqen and dqchxn are the 1,2-diaminoethane and 1,2-diaminocyclohexane analogues of dqpn, indicate that certain discriminatory factors are important in complexes of this type.

When the former is dissolved in 12 M DCl, four acac methyl signals are observed. If the integrity of the coordination sphere is retained, this pattern must be generated by two diastereo-

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(1) Part 16: Goodwin, T. J.; Williams, P. A.; Vagg, R. S. *Inorg. Chim. Acta* **1984**, *86*, L73.

(2) University College.

(3) Macquarie University.

(4) Suzuki, T. M.; Ohba, S.; Sato, S.; Saito, Y.; Saito, K. *Inorg. Chem.* **1983**, *22*, 2048. dqpn is the monodeprotonated form of *N,N′*-di-8-quinolyl-(*R*)-1,2-diaminopropane; acac is the monodeprotonated form of pentane-2,4-dione.

(5) (a) Chambers, J. A.; Goodwin, T. J.; Mulqi, M. W.; Williams, P. A.; Vagg, R. S. *Inorg. Chim. Acta* **1983**, *75*, 241. (b) Chambers, J. A.; Mulqi, M. W.; Williams, P. A.; Vagg, R. S. *Inorg. Chim. Acta* **1984**, *81*, 55.

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Table I. 360-MHz ^{1}H NMR Data[a] for the [Co(acac)(dqpn′)]$^+$ Diastereoisomers

isomer	acac[b] CH$_3$	acac[b] CH′$_3$	acac[b] CH	dqpn[b] CH$_3$	acac[c] CH$_3$	acac[c] CH′$_3$	acac[c] CH	dqpn[c] CH$_3$
Δ-β-exo	1.973	1.761	5.633	1.820 (J = 6.78)	1.998	1.772	5.683	1.626 (J = 6.74)
Δ-β-endo	2.092	1.783	5.670	0.437 (J = 6.77)	2.102	1.784	5.691	0.266 (J = 6.66)
Λ-β-exo	*d*	1.875	5.715	1.536 (J = 6.83)	2.067	1.882	5.755	1.352 (J = 6.62)
Λ-β-endo	*d*	1.977	5.770	1.573 (J = 5.79)	2.067	1.973	5.797	1.452 (J = 5.71)

[a] Chemical shifts in ppm relative to Me$_4$Si as internal standard; coupling constants in Hz. [b] In acetone-d_6. [c] In Me$_2$SO-d_6. [d] Obscured by solvent signals.

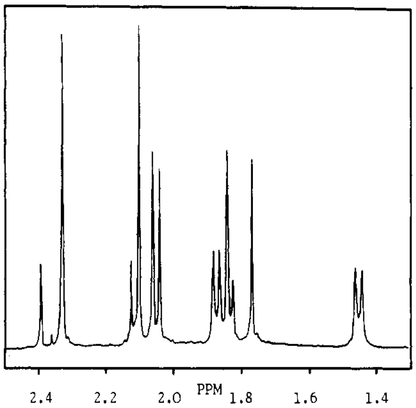

Figure 2. 360-MHz ^{1}H NMR spectrum of the methyl region of Δ,Λ-β-*exo*,*endo*-[Co(acac)(*R*-dqpn′)]ClO$_4$ dissolved in 6.0 M DCl.

mers (and their mirror images) and these must be the species that have opposite absolute configuration for the nitrogen atom remote from the fold of the tetradentate. Reference to the reported[4] spectra of the latter complex in acetone-d_6 and 12 M DCl shows that only two such singlets are found. This observation is in accord with the conformational requirements of the *R*,*R*-chxn section of the ligand. Furthermore, the results show that under the conditions used to isolate [Co(acac)(*R*,*R*-dqchxn′)ClO$_4$, stereospecific coordination is enforced. This is analogous to findings for related Co(III) complexes of *N*,*N*′-di-2-picolyl-(*R*,*R*)-1,2-diaminocyclohexane.[8]

With these conclusions in mind, we recorded the 360-MHz ^{1}H NMR spectrum of [Co(acac)(*R*-dqpn′)]ClO$_4$ in 6 M DCl, the aliphatic region of which is shown in Figure 2. Eight diastereomers are possible for β-[Co(acac)(*R*-dqpn)]$^{2+}$, of which only four are observed. Clearly the conformational preference, together with steric influences, dictates each isomer's preferred topology. In DCl solution eight separate acac methyl singlets are observed. Integration of the other signals arising from dqpn methyl resonances allows these to be assigned to corresponding isomers; two of these signals overlap at 1.872 ppm. Furthermore, the diastereoisomer distribution in 6 M DCl is found to be 0.23:0.76:0.48:0.52 ± 0.04, which is the same within experimental error as that for the deprotonated analogues. We thus conclude that no redistribution of the coordination spheres occurs. Assignments of chemical shifts in Table II are in accordance with this isomer distribution.

Table II. 360-MHz ^{1}H NMR Data[a] for the [Co(acac)(*R*-dqpn)]$^{2+}$ Diastereoisomers in 6.0 M DCl

isomer	acac CH$_3$	acac CH′$_3$	dqpn CH$_3$
Δ-β-exo	2.059	1.768	1.831 (J = 5.53)
Δ-β-endo	2.038	1.839	1.872 (J = 6.25)
Λ-β-exo	2.327	2.100	1.450 (J = 6.74)
Λ-β-endo	2.392	2.123	1.872 (J = 6.25)

[a] Chemical shifts in ppm relative to DSS as internal standard; coupling constants in Hz.

The dqpn methyl resonance of the Δ-β-exo complex shifts to lower field upon protonation. Molecular models show that if the in-plane amine nitrogen adopts the *R* configuration, the methyl group would still be significantly shielded. We thus conclude that the Δ-β-*endo*-*S*,*S*-[Co(acac)(*R*-dqpn)]$^{2+}$ ion forms stereospecifically with respect to the *R*,*S* isomer by virtue of the fact that no dqpn methyl resonances occur above 1.4 ppm. In contrast, the Δ-β-exo complex cannot adopt the *S*,*S* arrangement because of severe repulsive interactions between the methyl group, lying equatorially, and H(7) of the adjacent quinolyl ring. Quite the same interaction is evident in models of the Λ-β-endo complex, which is that species least populated in the crystal structure of the four [Co(acac)(*R*-dqpn′)]$^+$ diastereomers. This may in fact be the reason for its low relative concentration. However, the *R*,*R* nitrogen arrangement minimizes the contact, and ligand strain, while allowing the dqpn methyl group to lie equatorially.

The fourth and most populous isomer is the Λ-β-*exo*-[Co(acac)(*R*-dqpn)]$^{2+}$ ion, and it also is found to form stereospecifically with respect to nitrogen configurations in acid solution. Least strain in the tetradentate is suggested by molecular models to be in the *R*,*R* isomer, and we conclude that this complex ion has that configuration. Thus, the isomer distribution can be ascribed in these circumstances to steric effects in the tetradentate, especially due to the requirements of the optically active (*R*)-1,2-diaminopropane fragment.

Finally, we wish to emphasize that no redistribution of the coordination spheres of the diastereoisomers occurs in neutral or acidic solution. The four cocrystallized diastereoisomers persist in solution. We are continuing our studies on these and related complexes aimed at an understanding of the chiral discriminations responsible for the isomeric distributions observed.

Registry No. Δ-β-*exo*-[Co(acac)(*R*-dqpn′)]ClO$_4$, 92542-44-4; Δ-β-*endo*-[Co(acac)(*R*-dqpn′)]ClO$_4$, 92542-46-6; Λ-β-*exo*-[Co(acac)(*R*-dqpn′)]ClO$_4$, 92542-42-2; Λ-β-*endo*-[Co(acac)(*R*-dqpn′)]ClO$_4$, 92473-49-9; Δ-β-*exo*-[Co(acac)(*R*-dqpn)]$^{2+}$, 92542-47-7; Δ-β-*endo*-[Co(acac)(*R*-dqpn)]$^{2+}$, 92542-48-8; Λ-β-*exo*-[Co(acac)(*R*-dqpn)]$^{2+}$, 92542-49-9; Λ-β-*endo*-[Co(acac)(*R*-dqpn)]$^{2+}$, 92542-50-2.

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Preparation and Characterization of *trans*-Diiodotetra-*tert*-butoxytungsten(VI): The First Structurally Well-Characterized W^{VI}–I Bonds

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The hexa-*tert*-butoxyditungsten molecule[1a,b] has proved to be an extraordinarily versatile reactant, as attested by the

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