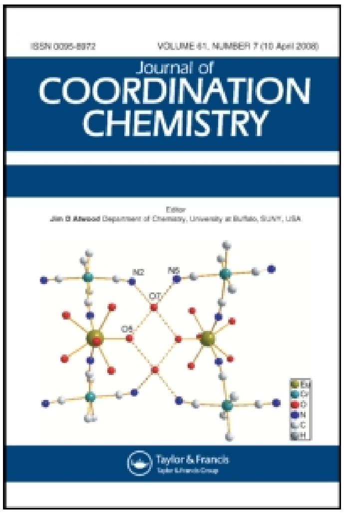

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SHORT COMMUNICATION

Carbon-13 Nuclear Magnetic Resonance Spectra Geometrical Isomers of Cobalt(III) Complexes with Diethylenetriamine and Iminodiacetate Ion.

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Carbon-13 nmr spectra are reported for s-facial, uns-facial, and meridonial isomers of $[Co(dien)_3]Cl_3$ and $[Co(dien)(IDA)]Cl$, and the s-fac and uns-fac isomers of $K[Co(IDA)_2]$. The nmr peaks are assigned, the spectra clearly reflecting the symmetry of the individual isomers.

INTRODUCTION

Bis(tridentate) complexes of cobalt(III) with diethylenetriamine and/or iminodiacetate ion can exist, theoretically, in three geometrical isomeric forms. For $[Co(dien)_2]^{3+}$ and $[Co(dien)(IDA)]^+$ ions (dien = diethylenetriamine and IDA = iminodiacetate ion) all three isomers shown in Figure 1 have been isolated.[1,2,3] Only the s-facial (C_{2h}) and u-facial (C_2) forms of $[Co(IDA)_2]^-$ ion have been isolated.[5]

Although the simplified structure of the meridonal isomer (Figure 1) of $[Co(dien)_2]^{3+}$ would suggest that it is not dissymmetric and therefore not optically active, it has been resolved into its optical isomers and circular dichroism spectra measured.[1,2,3] Keene,[1,2] Searle,[1,2] and Mason,[1] have attributed the relatively weak CD intensities ($\Delta\epsilon_{max} \sim 0.2$) to the presence of chelate rings of both δ and λ conformations for each of the dien ligands, resulting in a chiral orientation of the NH bonds of the secondary nitrogens of dien.

We report the measurement of ^{13}C nmr spectra in D_2O of the geometric isomers of $[Co(dien)_2]^{3+}$, $[Co(dien)(IDA)]^+$, and $[Co(IDA)_2]^-$, which were isolated as previously reported.[1–5] Spectra were obtained as previously reported.[6,7]

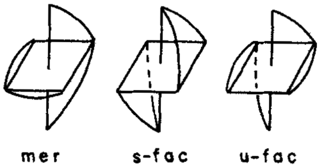

FIGURE 1 The three geometrical isomers of bis(tridentate) complexes.

RESULTS AND DISCUSSION

Figure 2 shows a stick diagram of the resonance positions and relative intensities for each of the isomers and for the ligands dien and Na_2IDA. It may be noted that the resonances of the carboxylate carbons of IDA are unusually intense for non-protonated carbons. The assignments of resonances in different regions of the spectra are shown at the top of the figure and are obtained by correlation with the results of similar investigations on complexes of Co(III) with ethylenediamine-N, N′-diacetate (EDDA),[6] trimethylenediamine-N, N′-diacetate (TNDDA),[6] and ethylenediamine-N, N′-diacetate-N, N′-di-3-propionate (EDDDA)[7] ions and on pure amines[8].

The most simple spectra are those of the s-fac isomers. There are only two carbon peaks for the s-fac (C_{2h}) isomers of $[Co(dien)_2]^{3+}$ and of $[Co(IDA)_2]^-$, indicating that, for each case, the two ligands are equivalent and the two chelate rings of each ligand are equivalent. The mixed complex ion *s-fac-*$[Co(dien)(IDA)]^+$ has only a mirror plane dividing the two halves of each ligand. Accordingly, there are two carbon peaks for each ligand.

For the uns-fac isomers of $[Co(dien)_2]^{3+}$ and $[Co(IDA)_2]^-$ the two ligands are equivalent, in each case, because of the C_2 axis, but the two halves of each ligand are not equivalent, giving a four peak spectrum. The shift nonequivalences (resonance separations for pairs of carbons which are equivalent for the free ligands or the s-fac complexes) are

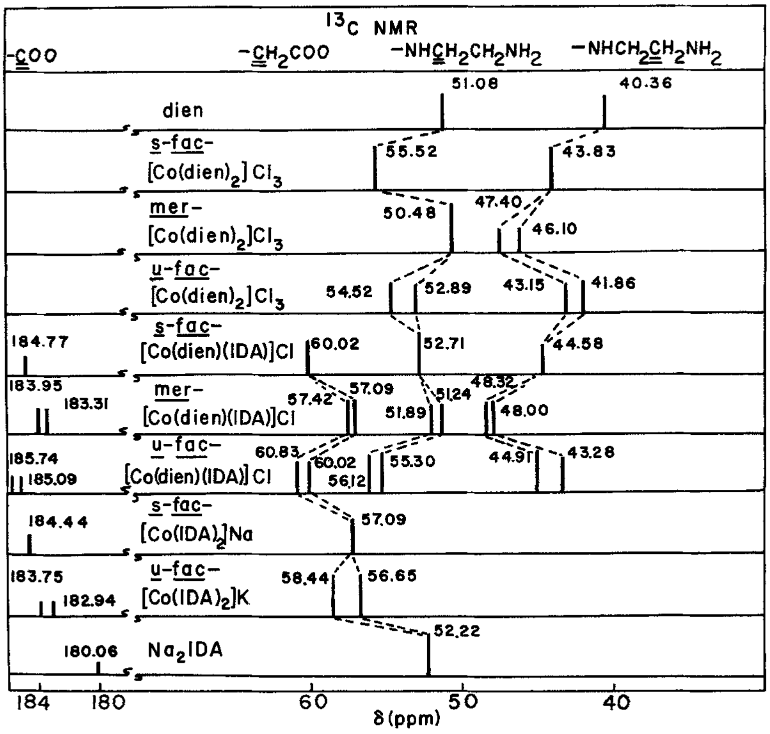

FIGURE 2 ^{13}C nmr spectra of geometrical isomers of Co(III) complexes of dien and IDA.

greatest for the u-fac isomers. The *uns-fac*-[Co(dien)(IDA)]$^+$ (C_1 symmetry) shows four carbon peaks for each ligand.

The two chelate rings of dien must have λ,λ, or δ,δ, or δ,λ conformations and a chiral orientation of the secondary N-H bond. Assuming that the dien ligands are equivalent for *mer*-[Co(dien)$_2$]$^{3+}$, there is a C_2 axis relating the two ligands. For λ,λ or δ,δ conformations all carbons of one dien are nonequivalent. For the δ,λ conformation the two chelate rings of one dien ligand are related by a mirror plane, but this same mirror plane does not extend through the other dien ligand. The chemical environments of the pairs of carbon atoms related by the mirror plane differ as a result of the unsymmetrical disposition of the other dien ligand relative to these pairs of carbon atoms. Figure 2 shows the presence of two resonances, at 47.40 and 46.10 ppm (downfield from external TMS dissolved in benzene), associated with the two pairs of carbon atoms adjacent to the primary nitrogens. The difference in environment of the four inner carbons, though, is insufficient for *mer*-[Co(dien)$_2$]$^{3+}$ to give rise to shift nonequivalences. Perhaps these carbons are equivalent because they are far enough removed from the effect of the other dien ligand. This interpretation would favor the claim[1,2] that the two chelate rings of each dien have opposite (δ and λ) conformations. This is the arrangement of the two meridional diamine chelate rings expected[9] and found[10] for *cis*-β-[Co(trien)X_2] complexes.

The dien ligand in *mer*-[Co(dien)(IDA)]$^+$ shows four resonances indicating that, in this case, all carbons are nonequivalent (as are the methylene and carbonyl carbons of IDA). The shift nonequivalence (0.32 ppm) for the outer carbons is less than that for *mer*-[Co(dien)$_2$]$^{3+}$. It seems that for the dien ligand, in proceeding from *mer*-[Co(dien)$_2$]$^{3+}$ to *mer*-[Co(dien)(IDA)]$^+$, there is a smaller difference in environment for one pair of carbons while the other pair senses a greater difference. Perhaps the great effect on the inner carbon atoms of dien in the latter complex could be the result of the influence of the lone pairs of the coordinated oxygens, which are directed more toward these carbons than toward the carbons adjacent to the primary amines. Of course, the low symmetry (C_1) of *mer*-[Co(dien)(IDA)]$^+$ is reflected in the shift nonequivalences of IDA also.

It is worth noting that the positions of all resonances of carbon nuclei in the metal complexes are at lower field (lower shielding) than in the pure ligand, with the notable exceptions of those resonances corresponding to the inner carbons of dien in *mer*-$[Co(dien)(IDA)]^+$ and *mer*-$[Co(dien)_2]^{3+}$ which are at nearly the same or slightly higher field. It is well known from ^{13}C nmr studies of organic compounds[8] that high field shifts relative to normal resonance positions for particular types of carbon atoms are observed commonly when those atoms are under unusual steric strain. This could well be the case for the inner carbons of the dien ligand in the meridional complexes. Meridional isomers are expected to be somewhat more strained than facial isomers, and it is reasonable to suggest that the pairs of inner carbons feel more of the strain than do the outer carbons, although not necessarily a greater difference in chemical environment (shift nonequivalence).

This study was undertaken to investigate the correlation of structures of bis(tridentate) metal complexes with their spectra. It is clear that those complexes of similar geometry give rise to similar spectra. The ^{13}C spectra are found to be more simple, well-defined, and unambiguous in terms of peak position and resolution compared to pmr spectra. The use of this method in the study of inorganic stereochemistry also offers another advantage over pmr in that it allows investigation of the spectra of the atoms which actually form the framework of the structures of the complexes, rather than the (hydrogen) atoms which are merely bonded to the framework.

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