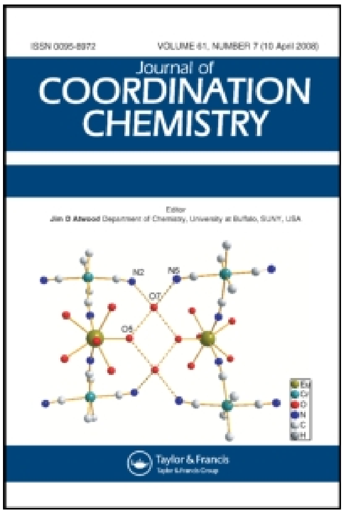

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# ASSIGNMENT OF THE GEOMETRIC ISOMERS OF BIS(L-ASPARTATO)COBALTATE(III) ION BY PROTON NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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# ASSIGNMENT OF THE GEOMETRIC ISOMERS OF BIS(L-ASPARTATO)COBALTATE(III) ION BY PROTON NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY†

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The three possible geometric isomers of bis(*L*-aspartato)-cobaltate(III) ion each give a twelve-line ABX pmr spectrum at 100 MHz. The parameters from analysis of the spectra have been used to calculate line positions and intensities which compare favorably with those observed. The conformation of the CH—$CH_2$ moiety in the flexible six-membered chelate ring is calculated from the vicinal coupling constants. The geometric configurations are assigned using the proton chemical shifts. The results are compared to those for *N,N'*-ethylenediaminedisuccinatocobaltate(III) ion.

## INTRODUCTION

The three possible geometric isomers of bis(*L*-2, 3-diaminopropionato) cobaltate(III) ion ($[Co(N)_4(O)_2]$ configuration) have been prepared and separated.[5] The *trans*(O)*cis*(αN)*cis*(βN) isomer was identified easily from the electronic absorption spectrum. The *cis*(O)*trans*(αN)*cis*(βN) and *cis*(O)*cis*(αN)*trans*(βN) isomers were correctly assigned by the method of less-soluble diastereomers and the ring-pairing method. The assignment was verified by the crystal structure[6] of the *cis*(O)*trans*(αN)*cis*(βN) isomer. The opposite assignment[5] resulted from the interpretation of CD spectra based upon the premise that, for one of the isomers, the opposite chiralities of chelate rings of different types cancel, leaving only a vicinal contribution. The vicinal, conformational, and configurational contributions are not separable from the data available, so that this approach is unreliable in this case. Subsequent study[7] of the pmr spectra of these isomers plus those of bis(*L*-2,4-diaminobutyrato)cobaltate(III) ion yielded correct assignments of all the isomers for both complexes.

The three possible isomers of bis(L-aspartato)cobaltate(III) ion ($[Co(N)_2(O)_4]$ configuration, *L*-asp$=NH_2CH(CH_2CO_2)(CO_2)^{2-}$) have been prepared and separated by ion-exchange chromatography.[8] A pmr study of these isomers was undertaken to complement the configurational assignments made from the interpretation of CD and absorption spectra[8] and is reported herein. The conformation of the CH—$CH_2$ moiety of coordinated *L*-asp has been calculated from the vicinal coupling constants obtained by analysis of the pmr spectra. The assignments of the configurations of the geometric isomers have been made from consideration of the proton chemical shifts. The results are compared to those for the similar complex ion *N,N'*-ethylenediaminedisuccinatocobaltate(III), Co(EDDS)$^-$.[9]

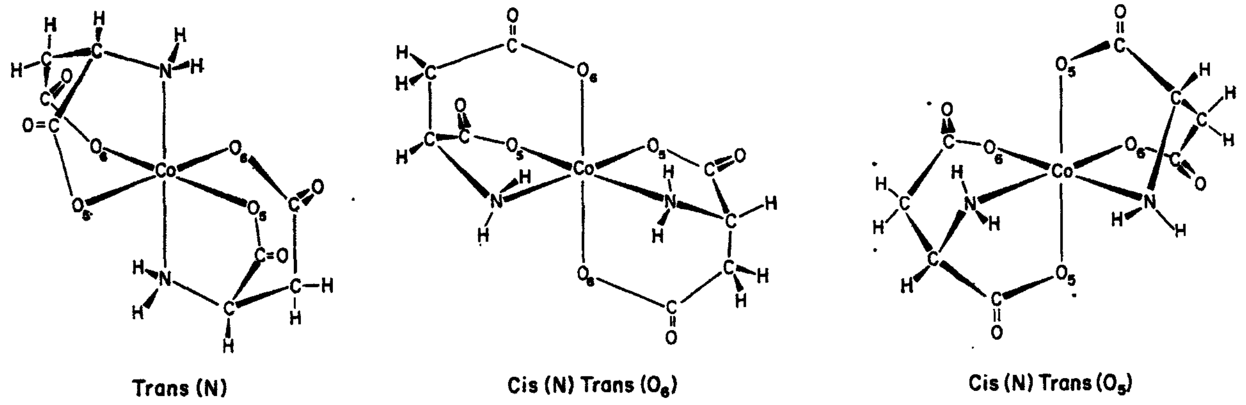
## EXPERIMENTAL SECTION

Pmr spectra were recorded on a JEOLCO NMR spectrometer at 100 MHz in the frequency sweep mode with a frequency lock on the methyl resonance of *t*-butyl alcohol (TBA) at δ1.234 ppm (with respect to DSS at 0). Solutions contained ca. 10 wt % of the lithium salts of the isomers[8] in $D_2O$ (ca. 0.5 ml) with TBA added as an internal standard.

Calculation of theoretical line positions and intensities of ABX nmr spectra were carried out using a Hewlett-Packard 2116B computer. The program incorporated the usual expressions[10] written in BASIC language. The program was tested by recalculating a known[11] theoretical spectrum.

## RESULTS AND DISCUSSION

The three geometrical isomers of Co(L-asp)$_2^-$ (Figure 1) have $C_2$ symmetry, hence the pmr



Trans (N)　Cis (N) Trans ($O_6$)　Cis (N) Trans ($O_5$)

FIGURE 1 Geometrical isomers of Co(*L*-asp)$_2$$^-$.

spectrum of any of the isomers is diagnostic of one coordinated *L*-asp dianion. Each of the isomers gives a twelve-line spectrum (Figure 2) at 100 MHz which is readily amenable to interpretation as an ABX pattern (Table I). Using the chemical shifts and coupling constants listed in Table I, theoretical line spectra were calculated which compared favorably with the observed spectra (Table II). It should be noted that the values of $J_{AB}$ in Table I calculated from the upfield and downfield components of each *AB* pattern differ by ca. 1 Hz. This discrepancy may be due to greater overlapping of the components in the *B* portion of the *AB* patterns, since $J_{BX} < J_{AX}$. The theoretical and observed spectra compare more favorably for the *X* portion which is not dependent on $J_{AB}$ (cf. Table II).

The Karplus equation[12] was applied simultaneously[13] to average vicinal coupling constants for $J_{AX}$ (5.1 Hz) and $J_{BX}$ (2.2 Hz) to yield a dihedral angle of 67° for $\phi_{BX}$.[14] While the accuracy of this result is uncertain to within ca. ±5°,[12] the conclusion that $\phi_{BX}$ is larger than $\phi_{AX}$ and that the two angles are comparable[15] is valid. These conditions are met when the $CH_2CH$ moiety is part of a conformation of the six-membered chelate ring (Figure 3) which is intermediate between the chair and boat forms. This result indicates an intermediate, time-averaged conformation of the partially-flexible six-membered chelate ring on the pmr time scale. In this time-averaged conformation the chair form is slightly favored and the C—O bond of the carbonyl group opposite the $NH_2$

TABLE I

Coupling constants and chemical shifts[a] for protons of Co(*L*-asp)$_2$$^-$

| | First eluate[8]<br>*trans*(N) | Second eluate[8]<br>*cis*(N)*trans*($O_6$) | Final eluate[8]<br>*cis*(N)*trans*($O_5$) |
|---|---|---|---|
| $\delta_A$ (ppm) | 3.199 | 3.127 | 2.943 |
| $\delta_B$ | 2.724 | 2.776 | 2.678 |
| $\delta_X$ | 4.068 | 3.611 | 3.722 |
| $J_{AB}$[b] (Hz) | 18.7 (17.9,[c] 19.5[d]) | 18.4 (17.5,[c] 19.2[d]) | 18.8 (18.4,[c] 19.2[d]) |
| $J_{AX}$[e] (Hz) | 5.2 | 5.1 | 5.0 |
| $J_{BX}$[e] (Hz) | 2.2 | 1.7 | 2.4 |
| $\delta_A$–$\delta_B$ (ppm) | 0.475 | 0.351 | 0.265 |

[a] Values are ppm downfield from TBA at $\delta$1.234 ppm (wrt DSS at 0), accuracy is ±0.005 ppm.

[b] Average of two values in parentheses, accuracy is ±1 Hz.

[c] $J_{AB}$ from downfield components.

[d] $J_{AB}$ from upfield components.

[e] Accuracy is ±0.5 Hz; signs have not been determined.

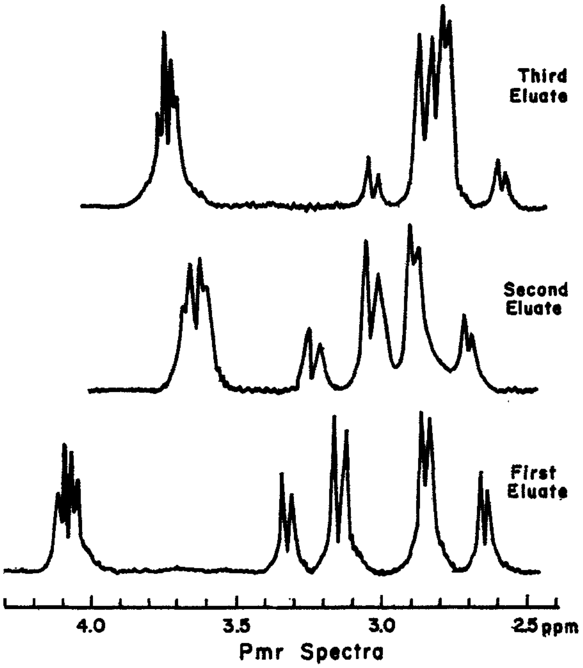


FIGURE 2 Pmr spectra of the three geometrical isomers of Co($L$-asp$)_2{}^-$.

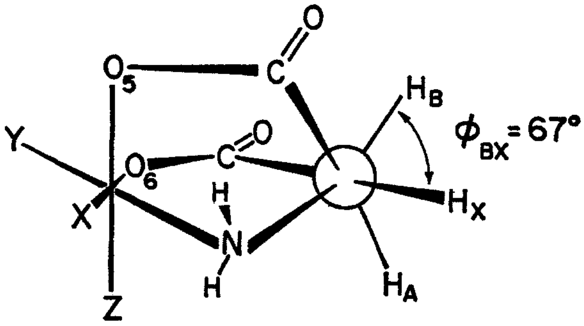


FIGURE 3 Proposed conformation of the six-membered chelate ring of coordinated $L$-asp calculated from pmr parameters. The five-membered ring is rigid and is puckered toward the six-membered ring. The oxygen donor atoms of the five- and six-membered chelate rings are designated $O_5$ and $O_6$, respectively.

group on the six-membered ring points roughly along the direction of the C—$H_B$ bond (Figure 3). The assignment of A and B to specific protons is based upon consideration of shielding effects. Proton $H_B$ lies near the plane of the adjacent carbonyl group of the six-membered ring in a shielding position[16] and it is also in a shielding region of the carbonyl group on the five-membered ring. Both of these influences are consistent with the observation that $H_B$ resonates upfield from $H_A$.

The three geometric isomers of Co($L$-asp$)_2{}^-$ can be generated by a sequence of three 120° rotations of a second tridentate $L$-asp group about the $X$, $Y$, and $Z$ positions in Figure 3. Because the ligands are pure optical isomers, the geometric configuration fixes the absolute configuration about the metal. From the pmr spectra $\delta_A$ is farthest downfield for the isomer obtained as the first eluate by ion-exchange chromatography.[8] This isomer is assigned the *trans*(N)[17] configuration since Framework Molecular Models indicate that $H_A$ lies near the line of the C–O bond of $O_6$[17] (attached at $Z$ in Figure 3) in the other ligand and hence is deshielded.[18] $H_A$ is relatively shielded by the C—O bond of $O_5$ (at $Z$ in Figure 3) in the other ligand of the *cis*(N)*trans*($O_5$) configuration assigned to the third (final) eluate[8] isomer, and $\delta_A$ is farthest upfield. $H_A$ is intermediate to these cases in the *cis*(N)*trans*($O_6$) isomer, the second eluate,[8] where it is opposite the H—N—H angle of the $NH_2$ group of the other ligand (also at Z). The same arguments can be applied to $H_X$ to explain the relative values of $\delta_X$ for the isomers except that $O_6$ is responsible for a shielding effect and $O_5$ is responsible for a deshielding effect. The groups most influencial in determining $\delta_X$ lie at $X$ in Figure 3. The chemical shift differences of $\delta_B$ for $H_B$ among the isomers are small and difficult to interpret since the two carbonyl groups of an $L$-asp ligand isolate $H_B$ more than $H_A$ or $H_X$ from effects of the other ligand.

It is instructive to compare the pmr spectra of the isomers of Co($L$-asp$)_2{}^-$ to that of Co(EDDS$)^-$, $N,N'$-ethylenediaminedisuccinatocobaltate(III).[19] When the Karplus equation is applied simultaneously to $J_{AX}$ and $J_{BX}$ for Co(EDDS$)^-$ a dihedral angle $\phi_{AX}$[21] of 65° is obtained. Since the conformations of the $L$-asp groups are the same in coordinated $L$-asp and EDDS, configurational assignments can be carried out by pmr if the effect of the ethylene bridge in Co(EDDS$)^-$ is considered. From Framework Molecular Models the ethylene bridge induces considerable strain through constriction of the N—Co—N bond angle and widening of the $O_5$—Co—$O_5$ angle in the *cis*(N)*trans*($O_6$) isomer. No strain is evident in the model of the *cis*(N)*trans*($O_5$) isomer.

The hydrogens on the ethylene bridge of Co(EDDS$)^-$ are crowded about $H_X$ so that its chemical shift is no longer a good criterion of configuration compared to the Co($L$-asp$)_2{}^-$ iso-

TABLE II

Comparison of experimental and calculated[a] pmr spectra for Co($L$-asp)$_2$$^-$

| | | First eluate[8] *trans*(N) | | | Second eluate[8] *cis*(N)*trans*(O$_6$) | | Final eluate[8] *cis*(N)*trans*(O$_5$) | |
|---|---|---|---|---|---|---|---|---|
| | Line | Obs Position[b] | Theoret Position[b] | Theoret Intensity[c] | Obs Position[b] | Theoret Position[b] | Obs Position[b] | Theoret Position[b] |
| | 1 | 2.616 | 2.601 | 0.623 | 2.669 | 2.652 | 2.570 | 2.541 |
| B | 2 | 2.637 | 2.624 | 0.643 | 2.690 | 2.671 | 2.594 | 2.567 |
| | 3 | 2.809 | 2.788 | 1.376 | 2.862 | 2.836 | 2.762 | 2.729 |
| | 4 | 2.833 | 2.811 | 1.356 | 2.882 | 2.855 | 2.785 | 2.755 |
| | 5 | 3.083 | 3.098 | 1.376 | 3.013 | 3.033 | 2.826 | 2.855 |
| A | 6 | 3.134 | 3.149 | 1.356 | 3.064 | 3.082 | 2.876 | 2.902 |
| | 7 | 3.262 | 3.285 | 0.623 | 3.188 | 3.217 | 3.009 | 3.043 |
| | 8 | 3.315 | 3.336 | 0.643 | 3.239 | 3.266 | 3.060 | 3.091 |
| | 9 | 4.032 | 4.031 | 1.000 | 3.576 | 3.577 | 3.685 | 3.685 |
| X | 10 | 4.082 | 4.082 | 1.000 | 3.626 | 3.626 | 3.735 | 3.733 |
| | 11 | 4.053 | 4.054 | 1.000 | 3.590 | 3.596 | 3.709 | 3.711 |
| | 12 | 4.105 | 4.105 | 1.000 | 3.640 | 3.645 | 3.758 | 3.759 |

[a] Data in Table I used, 100 MHz spectra.

[b] ppm downfield from TBA at $\delta$1.234 ppm (wrt DSS at O), ±.005 ppm.

[c] Intensities are similar for all three calculated spectra.

mers. Direct comparison of single proton (A or B) chemical shifts is not possible since the chemical shifts for Co(EDDS)$^-$ were measured versus an external reference.[9] A good criterion is available, however, from differences in chemical shifts, namely $\delta_A$–$\delta_B$. $H_A$ and $H_B$ are sufficiently removed from the ethylene bridge that the difference in their chemical shifts should not be adversely affected by its presence. $H_A$ and $H_B$ should still be affected by the shielding effects of the other $L$-asp group. The value of $\delta_B$–$\delta_A$ ($\delta_A$–$\delta_B$ in this work) for Co(EDDS)$^-$ is 0.23 ppm,[9] comparable to 0.265 ppm for the *cis*(N)*trans*(O$_5$) isomer in this study (cf., Table I). Neal and Rose considered the corresponding arrangement more likely for Co(EDDS)$^-$ (case I in Ref. 9).

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19. EDDS is two *L*-aspartic acid dianions linked at the N atoms by an ethylene bridge, cf., I in Ref. 9.
20. The arbitrary assignment of A and B in Ref. 9 is the reverse of that in this work, hence $\phi_{AX}$ in Ref. 9 is $\phi_{BX}$ in this work.