CHEMISTRY LETTERS, pp. 19-22, 1979. Published by the Chemical Society of Japan

STEREOSELECTIVE DEUTERATION OF MALONATE METHYLENE HYDROGENS IN SOME BIS(MALONATO)COBALT(III) COMPOUNDS[1)]

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The base-catalysed hydrogen-deuterium exchange at the malonate methylenes takes place stereoselectively for $[Co(mal)_2(L)]^{n-}$, where mal = malonate ion, L = ethylenediamine, N-methylethylenediamine, glycinate ion, and sarcosinate ion, but not for cis-$[Co(mal)_2(NH_3)_2]^-$. The proton deuterated first is probably the one which is closer to the chelate L.

It is known for some time that methylene hydrogens of malonic acid chelated to cobalt(III) ion can be deuterated in deuterium oxide.[2)] We have studied the deuteration process for a number of bis(malonato)cobalt(III) complexes of the type $[Co(mal)_2(L)]^{n-}$, where L stands for ethylenediamine(en), N-methylethylenediamine (Meen), glycinate ion(gly), sarcosinate ion(sar), and cis-$(NH_3)_2$.[3)] The ^1H nmr spectra were measured at 36°C on a Varian T-60 spectrometer and pD values reported here refer to direct pH meter readings on a Hitachi-Horiba Model F-7 pH meter.

The nmr spectra of $[Co(mal)_2(en)]^-$ in D_2O taken at suitable time intervals are shown in Fig. 1. As reported previously,[2)] the malonate hydrogens give rise to an AB quartet. Let us denote the hydrogens resonating at a lower magnetic field as H_B and those at a higher field as H_A. As time passes the quartet decreases in intensity and a slightly broad singlet appears exactly at the chemical shift of A hydrogens. Since we did not observe the corresponding B singlet throughout the whole deuteration process, and since the A singlet is due to $-CH_AD-$, it is readily apparent that the B hydrogens are more activated and deuterated first. The pseudo-first-order rate constant(k_1) for the process $-CH_AH_B-$ to $-CH_AD-$ is 1.0×10^{-3} sec^{-1} at pD=6.52. The A singlet eventually vanishes after 1 day standing ($k_1=2.8\times10^{-5}$ sec^{-1} at pD=6.52), indicating that the deuteration is complete to yield the species -CDD-. The above result shows that the deuteration takes place stereoselectively.

A similar result could be obtained for the Meen compound, in which the unsymmetrical nature of the ligand was responsible for the observed two sets of an

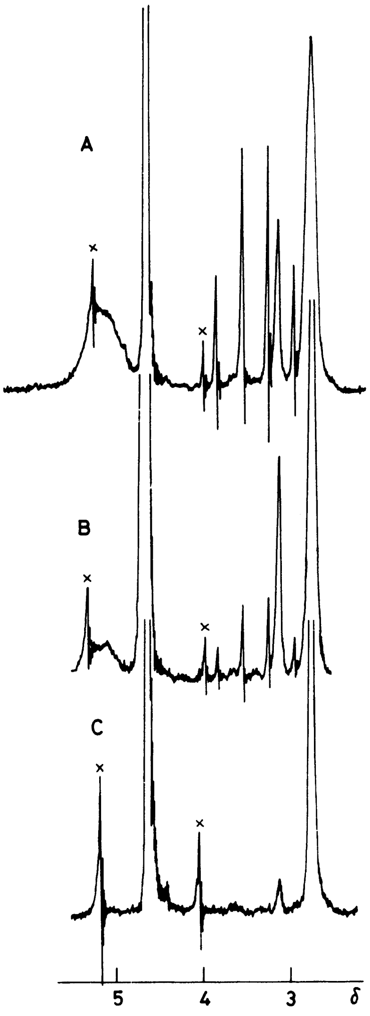


Fig. 1.(left) The spectra of $[Co(mal)_2(en)]^-$ in D_2O taken at (A) 5 min., (B) 20 min., and (C) 20 hours after dissolution. The asterisk indicates the spinning sideband of the HDO resonance.

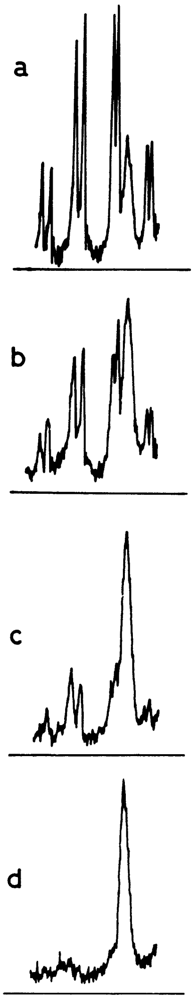
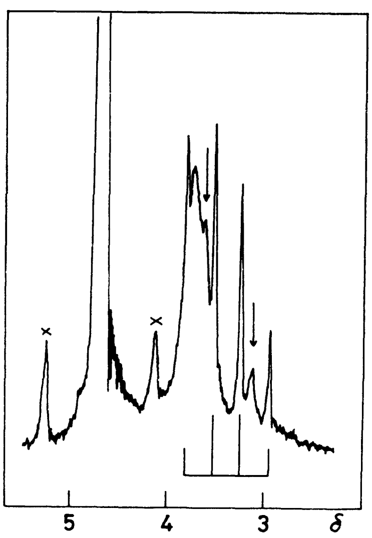


Fig. 2.(right) The spectra of $[Co(mal)_2(Meen)]^-$ in D_2O taken at (a) 7, (b) 14, (c) 26, and (d) 33 min. after dissolution. Only the malonate resonances are shown.

AB quartet. Figure 2 illustrates the malonate portion of the nmr spectra of the Meen compound. In this case, the resonance positions of H_A and $H_{A'}$ (high field hydrogens) are quite close to each other at 60 MHz, so that the A and A' singlets may overlap to give an apparent singlet. This singlet, as shown in Fig. 2(d), disappears after 1 day standing. The k_1 values for the process $-CH_2-$ to -CHD- for the high and low field quartets are 1.2×10^{-3} sec^{-1} and 1.4×10^{-3} sec^{-1}, respectively, and for the disappearance of the AA' singlet $k_1 = 4.1 \times 10^{-5}$ sec^{-1} at a solution pD value of 6.26. The malonate hydrogens in the gly and sar compounds gave rise to a singlet and an AB quartet. The deuteration of the hydrogens correponding to the AB quartet was found to be stereoselective. In the gly complex at pD=6.68, the k_1 values for the decrease of the singlet and the quartet are 1.5×10^{-3} sec^{-1} and 2.3×10^{-3} sec^{-1}, respectively, and the process -CHD- to -CDD- had the k_1 value of 7.0×10^{-4} sec^{-1}.



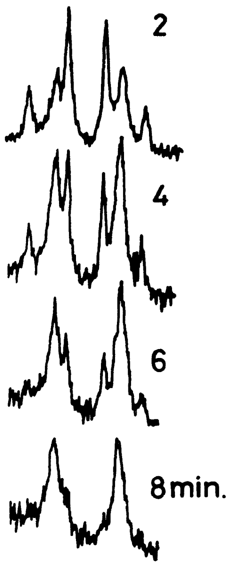


Fig. 3.(left) The spectrum of cis-$K[Co(mal)_2(NH_3)_2]$ taken 1 hour after dissolution in D_2O. The arrows indicate the singlets corresponding to the species $-CH_AD-$ and $-CDH_B-$.

Fig. 4.(right) The spectra of cis-$K[Co(mal)_2(NH_3)_2]$ plus Na_2CO_3 in D_2O taken at every 2 min.

Figure 3 presents the spectrum of cis-$K[Co(mal)_2(NH_3)_2]$ in D_2O. It is noted that both A and B singlets can be observed and in addition they are equal in intensity, implying that the deuteration is *not* stereoselective. The low field portion of the malonate quartet overlapped with the broad ammine resonance, which rendered it difficult to assess quantitatively each resonance intensity. A trace amount of Na_2CO_3 could eliminate the ammine absorption while retaining the malonate resonances. Figure 4 shows the malonate resonances of the sample solution prepared in this fashion and taken at every 2 min. The deuteration process for this system could be confirmed to exhibit little or no stereoselectivity. At pD=5.46, the rates for the disappearance of the quartet and two singlets are $k_1=1.8\times10^{-4}$ sec^{-1} and 2.4×10^{-5} sec^{-1}, respectively. The two singlets had equal rates.

The origin of the stereoselectivity exhibited by these compounds is not readily apparent as yet. The following points will, however, be noted. i) There are two types of malonate hydrogens in $[Co(mal)_2(en)]^-$, for example, because this ion possesses the C_2 symmetry axis. Of these two, one type of hydrogen atoms comes close to the NH_2 group of the en ring when the malonate ring is folded toward the en ring. We tentatively assign the hydrogens that appeared at lower magnetic fields and were deuterated first to this type of hydrogens. This is because on methylation at the en nitrogen the low field resonances suffered a greater downfield shift than did the high field resonances, suggesting that the low field hydrogens can go to the close proximity of the $N-CH_3$ group. Certainly the assignment of the fast-exchanging hydrogens to this or the other type of hydrogens must await further experimental evidence. ii) It was found from the pD dependence of the rate constant that the deuteration is base-catalysed at a pD value greater than about 5, while it is acid-catalysed at lower pD values. The results presented here concern only with the base-catalysed reaction. In the case where OD^- catalyses the deuteration, the direction of access of OD^- toward the malonate hydrogens will determine the stereoselectivity. If this direction is dictated strongly for some reasons, a high degree of selectivity will result. Now, if the malonate rings are folded toward each other, as found in the crystal of $Na(+)_{546}-[Co(mal)_2(en)]$,4) the easy access will be from the less hindered protons, which are now the protons closer to the third chelate L when the malonate rings are folded back toward the L ring. This line of reasoning leads us to propose that the hydrogens closer to the chelate L exchange faster with deuterium. This is consistent with the deduction obtained in i).

References and Notes

1) This work is Part X of "Proton Magnetic Resonance Spectra of Metal Ammine Complexes."
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3) The complexes studied in this work were prepared by the literature methods or their modifications; $[Co(mal)_2(en)]^-$ and $[Co(mal)_2(Meen)]^-$: F. P. Dwyer, I. K. Reid, and F. L. Garvan, J. Amer. Chem. Soc., 83, 1285(1961); $[Co(mal)_2(gly)]^{2-}$ and $[Co(mal)_2(sar)]^{2-}$: K. Yamasaki, J. Hidaka, and Y. Shimura, Bull. Chem. Soc. Jpn., 42, 119(1969).
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(Received October 4, 1978)