Stereoselective Association between Acetylacetonatobis(ethylenediamine)-cobalt(III) Cation and Malonate Anion as Studied by the Rate of Amine Hydrogen Exchange[1]

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Summary The rate of amine hydrogen exchange for acetylacetonatobis(ethylenediamine)cobalt(III) {[Co(acac)en)$_2$]$^{2+}$} in the presence of malonate ion indicates that the malonate ion associates with the complex from the side opposite to acac and hydrogen bonds only to trans hydrogens in the direction approximately parallel to the two-fold axis of the complex.

A FEW studies[2] on diamagnetic metal complexes have shown the presence of ion-pair structures in solution. We have measured the rate of amine hydrogen exchange for [Co(acac)(en)$_2$]$^{2+}$ in the absence and presence of malonate ion and have obtained information on the structure of the ion-associated pair, [Co(acac)(en)$_2$]$^{2+}$ ···· mal^{2-}.†

The rate of amine hydrogen exchange was determined by measuring the n.m.r. signal intensities of trans and cis (to acac) NH$_2$ groups at suitable time intervals at 36·4 °C. For [Co(acac)(en)$_2$]$^{2+}$, signal assignment follows easily from the magnetic anisotropy of the Co^{3+} ion;[3] cis NH$_2$ resonates at a field lower than trans NH$_2$. In the absence of mal^{2-}, plots of ln(intensity) vs. time were linear for both cis and

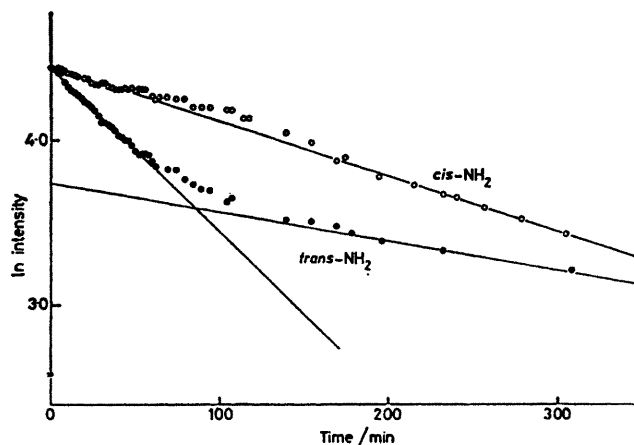trans NH$_2$. The plots‡ with mal^{2-} are shown in Figure 1. The plots for trans NH$_2$ are curved, which contrasts with the straight line for cis NH$_2$. Analysis of the rate data for trans NH$_2$ led to two rate constants $k_{t(f)}^{mal}$ and $k_{t(s)}^{mal}$. These results, along with those without mal^{2-}, are given in the Table.

The two rates for trans NH$_2$ imply that mal^{2-} shows a discrimination between the two hydrogens of the trans NH$_2$. A molecular model shows that trans NH$_2$ has two kinds of hydrogens, H$_A$ {approximately parallel to the two-fold axis of [Co(acac)(en)$_2$]$^{2+}$} and H$_B$, and that the two carboxy groups of mal^{2-} can hydrogen-bond only to H$_A$ (see Figure 2). It is reasonable for electrostatic reasons that mal^{2-} should approach the complex from the side opposite to acac along the two-fold axis because of the negative charge on acac. It is known that the rate of deuterium exchange at the amine hydrogens is proportional to the concentration of OH$^-$ ion[2] and is affected by added salts.[4,5] Although the values of $k_{t(f)}^{mal}/k_c^{mal}$ and k_t°/k_c° are almost equal (2·40 and 2·49, respectively), $k_{t(f)}^{mal}$ and k_c^{mal} are ca. 4 times as large as k_t° and k_c°, respectively. This implies that mal^{2-} acts as a general base catalyst to the same extent on cis NH$_2$, trans H$_B$, and probably trans H$_A$. The rate of exchange of trans H$_A$ is not accelerated by mal^{2-} but is reduced by a factor of 0·84. It is highly likely that the smaller value of $k_{t(s)}^{mal}$ compared to k_t° results from a hydrogen bond between H$_A$
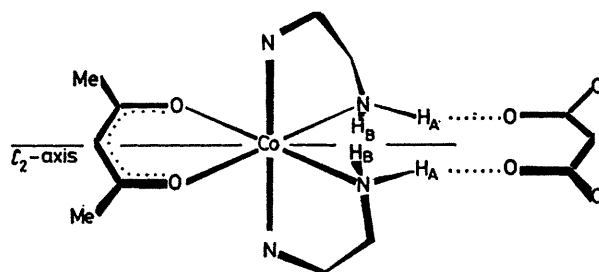

FIGURE 1. Plots of ln(intensity) vs. time for cis (○) and trans (●) NH$_2$ of [Co(acac)(en)$_2$]$^{2+}$ in the presence of mal^{2-}.

FIGURE 2. Proposed structure for the ion-associated pair, [Co(acac)(en)$_2$]$^{2+}$ ... mal^{2-}. H$_A$ is approximately parallel to the C_2-axis. The malonate ion approaches from the side opposite to acac along the C_2-axis and hydrogen bonds only to H$_A$.

TABLE. Second-order rate constants for amine hydrogen exchange (s^{-1} mol^{-1}) for [Co(acac)(en)$_2$]$^{3+}$.[a]

	Apparent pH	k_c°	k_t°		k_t°/k_c°	
Without mal^{2-}	6·72	1·58 × 10^4	3·93 × 10^4		2·49	

	Apparent pH	k_c^{mal}	$k_{t(f)}^{mal}$	$k_{t(s)}^{mal}$	$k_{t(s)}^{mal}/k_c^{mal}$	$k_{t(s)}^{mal}/k_c^{mal}$
With mal^{2-}	5·26	6·42 × 10^4	1·54 × 10^5	3·30 × 10^4	2·40	5·14 × 10^{-1}

[a] k_c° and k_t° are the rate constants for cis and trans NH$_2$ exchange in the absence of mal^{2-}. k_c^{mal} and $k_{t(f)}^{mal}$ or $k_{t(s)}^{mal}$ are the rate constants for cis and trans NH$_2$ exchange in the presence of mal^{2-}, respectively, and f and s in parentheses indicate the faster and slower rates of trans NH$_2$ exchange.

† A saturated solution of [Co(acac)(en)$_2$]I$_2$ was used; the concentration of mal^{2-} is five times that of the complex.

‡ Abbreviations used: Hacac = acetylacetone; en = ethylenediamine; H$_2$mal = malonic acid.

and mal^{2-}. We conclude that H_A exchanges with deuterium much slower than *cis* NH_2 and *trans* H_B owing to the stereoselective association, assisted by the hydrogen bond as depicted in Figure 2.

This method appears promising for studying ion-pair complexes in solution.

[1] For previous article in the series, 'Proton Magnetic Resonance Spectra of Metal Ammine Complexes' see U. Sakaguchi, K. Morito, and H. Yoneda, *Chem. Letters,* in the press.

[2] For n.m.r. techniques for paramagnetic metal complexes, see, *e.g.*, G. N. La Mar in 'NMR of Paramagnetic Molecules,' eds. G. N. La Mar, W. Dew. Horrocks, Jr., and R. H. Holm, Academic Press, New York, 1973, ch.10.

[3] U. Sakaguchi, K. Maeda, and H. Yoneda, *Bull. Chem. Soc. Japan,* 1976, **49**, 397, and references cited therein.

[4] H. Yamatera and M. Fujita, *Bull. Chem. Soc. Japan,* 1967, **42**, 3043.

[5] M. Iida, Ph.D. Thesis, Nagoya University, 1976.