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Proton Magnetic Resonance Spectra of Malonato-Containing Cobalt(III) Complexes

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The proton magnetic resonance spectra of [Co mal en_2]NO_3 and K[Co mal_2 en] were measured in D_2O. As a result, two kinds of effects due to chelation were found about the CH_2 signal of the chelating malonato ring. First, the intensity of the CH_2 signal of the malonato group was found to decrease with time and to disappear completely upon standing overnight. Second, the CH_2 signal of the malonato chelate ring in K[Co mal_2 en] was found to appear as a quartet, which suggests two kinds of hydrogen atoms in the same CH_2 group.

Introduction

High resolution nuclear magnetic resonance spectroscopy has shcwn its ability to provide informations about the structures of a large number of organic compounds, but only a few works[1] have been reported in the field of coordination chemistry. We have been interested in the studies on the proton magnetic resonance spectra of cobalt(III) ammine complexes and reported several papers on this subject.[2] In this paper we should like to report several interesting features of the proton magnetic resonance spectra of cobalt(III) complexes containing the OCC-CH_2-COO group.

Experimental Section

Materials. [Co mal en_2]NO_3 [3] was prepared from [$CoCO_3en_2$]NO_3 and malonic acid. K[Co mal_2 en]. H_2O[4] was kindly supplied by Dr. J. Hidaka, Osaka University. Both complexes were analytically pure.

N.M.R. measurements. The spectra reported here were recorded on a Varian A60 Analytical n.m.r. spectrometer. All spectra were run in D_2O, and chemical shifts were measured relative to the sodium salt of 3-(trimethylsilyl)-propane sulfonate as an internal reference.

Results and Discussion

Figure 1 shows the spectra of [Co mal en_2]NO_3 dissolved in D_2O. Curves a and b represent the spectra measured 5 and 30 minutes respectively after dissolution. The assignment of bands can be made easily by considering their intensities. The band on the high field side is assigned to the CH_2 protons of the ethylenediamine chelate ring, and the sharp peak just left of it is due to the CH_2 protons of the malonato chelate ring. The two broad bands on the low field side come from the two kinds of NH_2 groups of the ethylenediamine chelate ring. It is interesting to note that the sharp peak of the malonato CH_2 protons changed with time (see curves a and b). This suggests that the malonato CH_2 protons are replaced by deuterium. Here it must be noted that this kind of exchange did not take place in the case of sodium malonate dissolved in D_2O. In this case, even when the temperature of the solution was raised to 90°C, no appreciable decrease in signal intensity was observed. Therefore, the exchange observed in the complex must be attributed to chelation. A similar kind of decrease in signal intensity was observed in the case of K[Co mal_2 en] too. Figure 2 shows the spectra of this complex. Curves a and b represent the spectra recorded 5 and 30 minutes respectively after dissolution. The signals of CH_2 and NH_2 protons of the

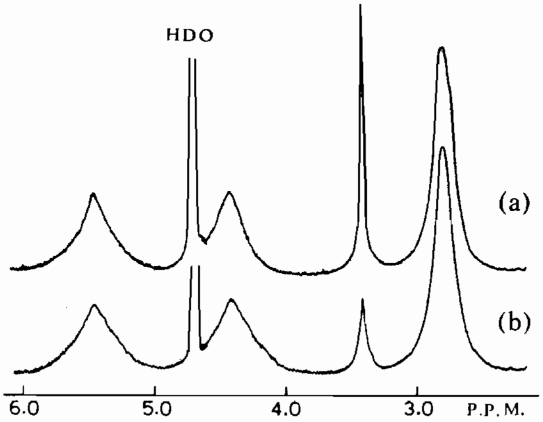

Figure 1. The p.m.r. spectra of [Co mal en_2]NO_3 in D_2O.

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Experimental Section

Preparation of the Substituted Pyridine N-Oxides. Pyridine N-oxide, 4-methoxy- and 4-methylpyridine N-oxide were obtained commercially. The 4-nitro and 4-chloro substituted ligands were prepared from pyridine N-oxide by the method of Ochiai.[16] The melting points of the two products were consistent with literature values.

Preparation of the Complexes. In general a solution of the hydrated metal perchlorate in 2,2-dimethoxypropane and absolute ethanol was stirred for three hours at room temperature, a procedure which served to dehydrate the perchlorate. The complexes were then prepared by the addition of this mixture to an excess of an ethanolic solution of the ligand. A molar ratio, ligand: perchlorate, of 10:1 was employed. The products, which generally crystallized immediately or upon standing for a short time, were filtered, washed with ethanol and dried in vacuo. For R = H, it was frequently found unnecessary to carry out the initial dehydration procedure and complexes were prepared simply by mixing warm methanol or ethanol solutions of the hydrated perchlorate and the ligand.

In the reaction with copper(II) perchlorate the use of the above conditions yielded a hexakis product for R = H, but tetrakis products with R = OCH_3, CH_3, Cl and NO_2. For the unsubstituted pyridine N-oxide, the tetrakis species was isolated by the use of stoichiometric quantities of the ligand and copper(II) perchlorate.

Analytical Data. Microanalyses for carbon, hydrogen and nitrogen were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Metal analyses were carried out following the method reported by Guerrin *et al.*[17] The analytical data are presented in Table I.

Spectral Measurements. Infrared spectra in the region 1300-250 cm^{-1} were recorded on a Perkin Elmer, Model 521, grating spectrophotometer. The samples were measured as nujol mulls supported between caesium bromide plates.

Diffuse reflectance spectra of solid samples were obtained on a Beckman DU spectrophotometer fitted with the standard reflectance attachment and employing a block of magnesium carbonate as standard.

Visible spectra were also recorded as mineral oil mulls in the region 350-1500 mμ on a Cary 14 recording spectrophotometer. The mulls were smeared on filter paper and run against a reference consisting of a similar piece of filter paper soaked in mineral oil.

Magnetic Measurements. Magnetic susceptibilities were determined by the Faraday method using equipment and procedures which have been described previously.[18] Mercury tetrathiocyanatocobaltate(II) was used as magnetic susceptibility standard[19] and diamagnetic corrections were estimated from Pascal's constants.[20]

Results and Discussion

The Complexes. For M = Fe(III), Co(II), Ni(II) and Cu(II), mixing ethanolic solutions of the ligand and

Table I. Analytical Data

Complex $[M(4\text{-}RC_5H_4NO)_6](ClO_4)_n$			Analyses							
			C		H		N		M	
M	R	n	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
Cr(III)	OCH_3	3	39.19	39.23	3.88	3.82	7.19	7.63	—	4.72
Cr(III)	CH_3	3	42.94	43.03	4.42	4.21	8.52	8.37	—	5.18
Cr(III)	H	3	38.91	39.12	3.44	3.28	8.91	9.13	—	5.65
Cr(III)	Cl	3	31.82	31.95	2.50	2.14	7.23	7.45	—	4.61
Fe(III)	OCH_3	3	39.35	39.13	3.99	3.80	7.41	7.61	5.04	5.06
Fe(III)	CH_3	3	42.73	42.86	4.19	4.20	8.08	8.33	5.76	5.54
Fe(III)	H	3	38.35	38.95	3.29	3.27	8.52	9.09	6.12	6.04
Fe(III)	Cl	3	31.68	31.85	2.05	2.14	7.48	7.42	5.05	4.94
Fe(III)	NO_2	3	30.09	30.15	2.20	2.02	13.84	14.07	4.78	4.67
Co(II)	OCH_3	2	42.72	42.86	4.20	4.17	8.45	8.34	5.86	5.85
Co(II)	CH_3	2	47.56	47.39	4.67	4.64	9.09	9.21	6.50	6.46
Co(II)	H	2	43.78	43.50	3.85	3.65	9.96	10.15	7.11	7.11
Co(II)	Cl	2	34.64	34.81	2.20	2.34	8.00	8.12	5.69	5.69
Co(II)	NO_2	2	32.70	32.82	2.32	2.20	15.16	15.31	5.37	5.37
Ni(II)	CH_3	2	47.53	47.40	4.59	4.64	9.10	9.21	6.24	6.43
Ni(II)	H	2	43.47	43.51	3.88	3.65	9.97	10.15	7.16	7.09
Ni(II)	Cl	2	35.01	34.81	2.30	2.34	7.98	8.12	5.60	5.67
Ni(II)	NO_2	2	32.86	32.82	2.36	2.20	15.10	15.31	5.36	5.35
*Cu(II)	OCH_3	2	37.79	37.77	3.81	3.67	7.12	7.34	8.21	8.33
*Cu(II)	CH_3	2	41.03	41.23	3.94	4.04	7.95	8.02	8.99	9.09
Cu(II)	H	2	43.75	43.26	3.78	3.63	10.20	10.09	7.71	7.63
*Cu(II)	H	2	37.17	37.38	3.12	3.14	8.60	8.72	9.90	9.89
*Cu(II)	Cl	2	30.71	30.77	2.16	2.07	6.87	7.18	8.08	8.14
*Cu(II)	NO_2	2	29.44	29.19	2.04	1.96	13.85	13.62	7.73	7.72

* Empirical formula $[Cu(4\text{-}RC_5H_4NO)_4](ClO_4)_2$.

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