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Temperature-Dependent Nuclear Magnetic Resonance Spectrum of Cyclooctatetraenecyclopentadienylcobalt

BY SEI OTSUKA AND A. NAKAMURA

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Rapid valence tautomerism of cyclooctatetraenetricarbonyliron (**1**) is known to occur in solution.[1-3] The X-ray[1] and the infrared[2] analyses of **1** indicated that the tautomers have the 1,3-butadienetricarbonyliron-type structure. Valence tautomerism in **1** is very rapid even at −60° as evidenced by the appearance of a single, sharp nmr peak.[4]

In the related cobalt complex, cyclooctatetraenecyclopentadienylcobalt (**2**), the cyclooctatetraene coordinates to cobalt as 1,5-diene as indicated by the nmr spectrum having three peaks in a ratio of 4:5:4.[5] A marked difference in the modes of bonding of the cyclooctatetraene (COT) moiety to the metals is thus apparent.

There are some examples[6] of diolefincyclopentadienylcobalt complexes involving 1,3-diene coordination. Hence, the valence tautomers of **2** might contain the 1,3-diene coordination group at higher temperatures, at least as a transient species. The nmr spectrum of **2** at 70° gave rise to only a minor change as compared to the room-temperature spectrum. Line broadening of the peaks due to the COT protons was observed. At 100°, this broadening became very extensive and the peaks were almost disappearing.

These peaks reappeared on lowering the temperature to 70° and approximate to the uppermost curve as shown in Figure 1. This clearly assures the reversibility of the line broadening. The spectrum at 133° showed peaks at τ 4.36, 5.12, 5.36, 5.70, and 5.90, in approximate relative intensity of 7:15:10:9:7, respectively. The peaks at τ 5.70 and 5.90 can be assigned as due to the C_5H_5 and C_8H_8 protons of $[(C_5H_5)Co]_2C_8H_8$ (**3**), respectively (lit.[7] τ 6.1, 6.3).

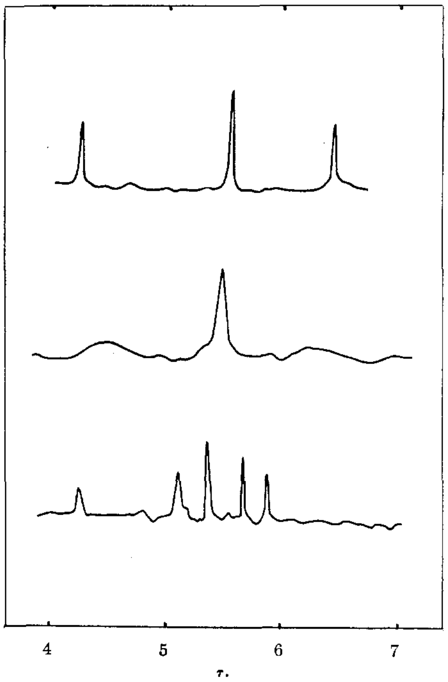

Figure 1.—Nmr spectrum of $(C_5H_5)Co(C_8H_8)$: top curve, room temperature; middle curve, 100°; bottom curve, 133°.

The formation of this binuclear compound (**3**) is not unexpected since the disproportionation of **2** was observed under the condition of the nmr measurement. A similar disproportionation was recently reported for tetracarbonylcyclooctatetraenemolybdenum.[8]

The peaks at τ 5.36 are due to C_5H_5 protons of **2**. New appearance of the peak at τ 5.12 and absence of the peaks at τ 4.25 and 6.48, originally present in the room-temperature spectrum of **2**, indicate the valence tautomerism to be occurring at 133° as expected. The position of the new peak is found quite near the average position (τ 5.17) of the two room-temperature peaks if the correction of the downfield shift (τ 0.22)[9] is made for raising the temperature (see Table I). The peak at τ 4.36 may be due to free C_8H_8 (lit.[7] τ 4.2) released by the reaction forming $[(C_5H_5)Co]_2C_8H_8$. This nmr observation is believed to be the first one of the valence tautomerism in COT complexes having a 1,5-diene as a coordinating site. Possibly the valence tautomerism occurs between the two different 1,5-diene structures only. Alternatively, the tautomerism may involve 1,3-diene coordination as an intermediate for the two 1,5-diene forms as mentioned above. However, no distinction between the two possibilities can be made from the present nmr information.

TABLE I
NMR DATA FOR $(C_5H_5)Co(C_8H_8)$ IN τ VALUES

	C_8H_8 protons	C_5H_5 protons
Room temperature	4.25, 6.48	5.58
133°	512	5.36
		$\Delta\tau$ 0.22

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[9] The reason for this temperature shift could not be ascertained.

Olefin complexes having more than one mode of coordination have the possibility to exhibit valence tautomerism in a certain temperature range. Valence tautomerism in the COT complexes of platinum, palladium, and rhodium is thus expected at high temperatures.

Experimental Section

Materials.—Cyclooctatetraenecyclopentadienylcobalt was prepared and purified by the published procedure.[5] Identification of the compounds recovered from the nmr measurements at 133° was made by comparison of the infrared spectra and the melting points with those of the authentic samples of **2** and **3**.

The nmr spectra were obtained in *p*-xylene under nitrogen by a Jeol JNM-4H-100 instrument working at 100 Mc. The data are calibrated by the ring and methyl proton resonances of *p*-xylene as an internal standard.

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Cobalt(III) Complexes of 1,3-Bis(2′-aminoethylamino)propane

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In a recent paper, Bosnich, Poon, and Tobe[1] have reported the preparation of several complexes of cobalt(III) with the macrocylic tetradentate ligand, 1,4,8,11-tetraazacylotetradecane (cyclam). Since all of these complexes, including [Co(cyclam)Cl$_2$]Cl, yield visible spectra bearing close similarity to the spectra of the corresponding *trans*-bis(ethylenediamine)cobalt(III) complexes, they have been assigned the *trans* configuration. Attempts to prepare complexes having the *cis* configuration were unsuccessful. Conversely, in the case of the linear tetradentate ligand, triethylenetetramine (trien), $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$, the *cis*-$\alpha$ isomer of [Co(trien)Cl$_2$]Cl was quite easily prepared[2] a number of years ago, and it was not until recently that the *cis*-β[3] and *trans*[4] isomers were successfully prepared.

Since cyclam and trien exhibit opposed stereochemical behavior, the present work was conducted to examine some of the stereochemistry of a tetradentate ligand intermediate between trien and cyclam. The ligand we have used is 1,3-bis(2′-aminoethylamino)-propane (beap), $NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$, which was first synthesized by van Alphen[5] in 1936. This ligand differs from trien by having a trimethylene bridge between ethylenediamine residues rather than an ethylene bridge, and, in contrast to cyclam, it is a straight-chain tetramine.

Experimental Section

Preparation of 1,3-Bis(2′-aminoethylamino)propane.—With only slight modification, the procedure described by van Alphen[5] was employed in preparing the ligand. To a cold, constantly stirred solution of 1,3-dibromopropane (300 g) in ethanol (500 ml) was added ethylenediamine (500 g). Upon complete addition of ethylenediamine, the solution was warmed to 50° for 1 hr. Solid KOH (400 g) was then added slowly, and the mixture was warmed another 0.5 hr. After filtering off KBr, the remaining ethylenediamine, 1,3-dibromopropane, and ethanol were removed by distillation. The solution was then cooled, filtered, and fractionally distilled under vacuum using a Todd 12.5-mm glass-pack fractionation column. The desired product was collected at 185–186° with a pressure of 35 mm. Only the center fraction of distillate was used in the following syntheses.

Preparation of *trans*-[Co(beap)Cl$_2$]Cl.—$CoCl_2 \cdot 6H_2O$ (24 g) was dissolved in water (250 ml) and 1,3-bis(2′-aminoethylamino)-propane (16 g) was added slowly with stirring. Air which had been passed through a dilute NaOH solution and dried was bubbled through the solution for 24 hr. Concentrated HCl (15 ml) was then added, and the resulting green solution was evaporated to near dryness on a steam bath. The large green crystals which formed were filtered, recrystallized from dilute HCl, washed with ethanol and ether, and heated *in vacuo* overnight at 100°.

Anal. Calcd for [Co(C$_7$H$_{20}$N$_4$)Cl$_2$]Cl: C, 25.85; H, 6.19; N, 17.24; Cl, 32.8. Found: C, 26.01; H, 6.30; N, 17.08; Cl, 32.7.

Aqueous Molar Conductivity.—The value expected for a uni-univalent electrolyte[6] was 96–115 ohm^{-1} cm^2 mole^{-1}; found: 97 ohm^{-1} cm^2 mole^{-1}.

Preparation of *cis*-[Co(beap)Cl$_2$]Cl.—*trans*-[Co(beap)Cl$_2$]Cl (5 g) was dissolved in hot water (20 ml) and placed on a steam bath. Anhydrous sodium carbonate (1.5 g) was added, and the red solution was heated 0.5 hr. NaBr (4 g) was added, and air was passed over the hot solution to reduce the volume. An amorphous-appearing material formed when near dryness had been reached. This was dissolved in 95% ethanol, and a pink material separated upon addition of ether. The pink material was filtered, washed successively with cold ethanol and ether, and air dried. One gram of this material was dissolved in concentrated HCl (15 ml). After heating for 5 min, butyl alcohol (100 ml) was added and a purple residue was formed with addition of ether. This material was filtered and washed with absolute methanol until the wash showed no green coloration due to the *trans* isomer which was also formed to a slight extent. The purple complex was washed immediately with ether and dried at 100°.

Anal. Calcd for [Co(C$_7$H$_{20}$N$_4$)Cl$_2$]Cl: C, 25.85; H, 6.19; N, 17.24; Cl, 32.8. Found: C, 25.74; H, 6.24; N, 17.07; Cl, 32.8.

Aqueous Molar Conductivity.—The value expected for a uni-univalent electrolyte[6] was 96–115 ohm^{-1} cm^2 mole^{-1}; found: 106 ohm^{-1} cm^2 mole^{-1}.

Analysis.—Carbon, hydrogen, and nitrogen analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Potentiometric titrations were employed in chloride analysis using a Beckman expandomatic pH meter equipped with silver wire and saturated calomel electrodes. Solutions were adjusted to pH 8 with 0.01 *N* NaOH for total chloride titrations. A standard solution of silver nitrate was used as the titrant.

Visible and Infared Spectra.—Visible spectra were determined using a Beckman DB spectrophotometer equipped with a recorder. Standard silica cells (1 cm) were used. Measurements were made on aqueous solutions immediately after preparation. Conductivity measurements show that aquation rates are slow enough so that very little aquation occurs prior to spectral measurements. Infrared data were obtained on a Perkin-Elmer Model

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