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($C_7H_{20}N_4$)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($C_7H_{20}N_4$)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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(1) B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965).

(2) F. Basolo, *J. Am. Chem. Soc.*, **70**, 2634 (1948).

(3) G. H. Searle, Ph.D. Thesis, Australian National University, 1963.

(4) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 3193 (1963).

(5) J. van Alphen, *Rec. Trav. Chim.*, **55**, 835 (1936).

(6) M. M. Jones, "Elementary Coordination Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1964, p 254.

137 spectrometer using NaCl optics. Nujol mulls and KBr disks were employed in determining these spectra.

Conductivity Measurements.—Conductivity determinations were performed using an Industrial Instruments Model 16B2 conductivity bridge. Molar conductivities were determined at 25° and concentrations of 10^{-3} *M*.

Paper Chromatography.—Paper chromatograms were obtained according to the method of Stefanovic and Janjic[7] using 1 × 12 in. strips of Whatman No. 1 chromatography paper. The eluting solution consisted of concentrated HCl in water-saturated 1-butanol (5 ml of concentrated HCl/100 ml of solution).

Results and Discussion

Two isomers of [Co(beap)Cl_2]Cl have been isolated and characterized. The green isomer, which shows only one spot with paper chromatographic separation, has been assigned the *trans* configuration on the basis of its visible absorption spectrum. In its visible spectrum there is a maximum at 623 mμ and a shoulder at 410 mμ having extinction coefficients of 35.2 and 35 M^{-1} cm^{-1}, respectively. These values compare well with the spectra for the *trans* isomers of the corresponding en, trien, and cyclam complexes as shown in Table I.

TABLE I

VISIBLE SPECTRAL DATA

Complex	λmax, mμ	ε, M^{-1} cm^{-1}	λmax, mμ	ε, M^{-1} cm^{-1}
trans-[Co(en)$_2$Cl$_2$]Cl[a]	625	34.7	450	25.2
trans-[Co(trien)Cl$_2$]Cl[b]	615	36.3	454	33.9
trans-[Co(cyclam)Cl$_2$]Cl[c]	635	32	435	42
trans-[Co(beap)Cl$_2$]Cl	623	35.2	410[e]	35
cis-[Co(en)$_2$Cl$_2$]Cl[a]	540	100	390	77.6
cis-[Co(trien)Cl$_2$]Cl[d]	540	105	379	87.1
cis-[Co(beap)Cl$_2$]Cl	540	103	390[e]	85

[a] F. Basolo, *J. Am. Chem. Soc.*, **72,** 4393 (1950). [b] See ref 4. [c] See ref 1. [d] E. Kyuno and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **88,** 1120 (1966). [e] Observed as shoulders.

The other isomer, which is violet in color, is assigned the *cis* configuration. This isomer was formed in small yields from what is believed to be the carbonato complex. The visible spectrum of the *cis* isomer displays a maximum at 540 mμ having an extinction coefficient of 103. An additional shoulder is observed at 390 mμ. As indicated in Table I, these values are also in line with corresponding data for analogous *cis* complexes.

Additional evidence concerning the configurations of these complexes has been obtained through study of their infrared spectra. As with the octahedral complexes of trien, beap should give rise to *trans*, *cis*-α, and *cis*-β isomers. Since the differences in the two ligands are slight, they would be expected to yield very similar infrared spectra when coordinated in the same configuration. This expected similarity is borne out for the *trans* isomers. As with *trans*-[Co(trien)Cl_2]Cl,[8] *trans*-[Co(beap)Cl_2]Cl displays four absorption bands in the N–H stretching region of 3000–3300 cm^{-1} and yields only one band at 1600 cm^{-1} resulting from an NH_2 bending mode. The *cis* complex isolated in this study has an infrared spectrum quite similar to the *cis*-α trien complex and on this basis we have reason to believe the complex is of the *cis*-α configuration. Major factors which lead to assigning this structure include the presence of only three sharp absorptions in the N–H stretching region, the presence of only one band at 1600 cm^{-1}, and the presence of two strong absorptions in the region 990–1090 cm^{-1}. The positions and intensities of these bands correspond to those of *cis*-α trien complex and are in contrast to the spectrum of the *cis*-β trien complex where 4, 2, and 4 bands populate the respective areas.[8]

It is of interest to consider relative stabilities of the *cis*- and *trans*-[Co(beap)Cl_2]Cl isomers. Preparation of the dichloro complex by conventional air oxidation proceeds with exclusive formation of the *trans* isomer. All attempts to prepare the *cis* complex by prolonged heating of an aqueous solution of the *trans* isomer have been unsuccessful. This behavior parallels that of the corresponding cyclam complex[1] and is in strict contrast to the behavior of the trien system. In methanolic solution isomerization of *cis*-α-[Co(beap)Cl_2]Cl to the *trans* isomer proceeds to completion proving the greater stability of the *trans* isomer. Although, it is apparent that the *trans* configuration is preferred for beap complexes, the stereospecificity is not so pronounced as in the cyclam case since Bosnich, *et al.*,[1] unsuccessfully attempted to prepare *cis* cyclam complexes using methods quite similar to ours for *cis*-α-[Co(beap)Cl_2]Cl. The close similarity between the beap and cyclam systems and the marked divergence of the beap and trien systems suggest that the nature of the group(s) bridging the ethylenediamine residues, rather than linear or macrocyclic character, determines the stereochemistry.

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[7] G. Stefanovic and T. Janjic, *Anal. Chim. Acta*, **19,** 488 (1958).

[8] D. A. Buckingham and D. Jones, *Inorg. Chem.*, **4,** 1387 (1965).

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Fluoro-Containing Complexes of Chromium(III). II. The Reaction of Sodium Tetrafluoroethylenediaminechromate(III) Monohydrate with Ethylenediamine[1]

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The anion tetrafluoroethylenediaminechromate(III) was first prepared by Dahme[2,3] in 1957 and isolated as

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[1] For the first paper in this series, see J. W. Vaughn and B. J. Krainc, *Inorg. Chem.*, **4,** 1077 (1965).

[2] W. Dahme, Thesis, Bergakademie Clausthal, 1957.

[3] "Gmelins Handbuch der Anorganischen Chemie," Chrom, Part C, Vol. 52, 1965, p 274.