N,N-Dimethylethylenediamine(ethylenediamine)palladium(II) iodide, $[Pd(udmen)(en)]I_2$, was presumably produced by the reaction between 1 g of $Pd(en)I_2$ and 3 drops of udmen in 50 ml of water as described above. When, however, the pale yellow solid product was filtered and exposed to air, it decomposed to form a hard resinous black solid which could not be characterized.

Acknowledgment.—This work was supported by the Robert A. Welch Foundation and the U. S. Atomic Energy Commission.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN 60680

Cobalt(III) Complexes of β-Aminoethyliminodiacetic Acid

BY MARILYN W. S. CHU, DEAN W. COOKE, AND CHUI FAN LIU

Received December 20, 1967

Complexes of various branched-chain tetradentate ligands in which the chain is bifurcated at a donor atom such as β,β′,β″-triaminotriethylamine[1-3] and nitrilotriacetic acid[4,5] have been made and their stereochemistries were studied. However, chelates of this type containing nonidentical arms have never been made before. In the present investigation complexes of one such ligand, β-aminoethyliminodiacetic acid (H_2AEIDA), have been prepared with cobalt(III) and ethylenediamine. Two geometric isomers designated *cis* or *trans*, according to the position of the acetic acid chains with respect to each other, are possible and these have been separated and characterized by essentially the same methods used by Legg and Cooke.[6]

Experimental Section

Preparation of β-Aminoethyliminodiacetic Acid Sulfate (($H_2AEIDA)SO_4$).—This ligand was prepared by the method of Schwarzenbach.[7] *Anal.* Calcd for $C_6H_{12}N_2O_4 \cdot H_2SO_4$: C, 26.27; H, 5.14; N, 10.22. Found: C, 25.49; H, 4.66; N, 9.92.

Preparation and Separation of *trans*- and *cis*-(CoAEIDAen)Cl.—$(H_2AEIDA)SO_4$ (2.1944 g, 8×10^{-3} mol) in 20 ml of water was mixed with $Ba(OH)_2 \cdot 8H_2O$ (5.0480 g, 16×10^{-3} mol) in 20 ml of water and to the mixture was added carbonatotetramine sulfate[8] (2.0958 g, 4×10^{-3} mol) in 70 ml of water. The mixture was heated on a steam bath for 23 hr. After cooling, the barium sulfate precipitate was filtered. To the filtrate was added ethylenediamine dihydrochloride (1.0642 g, 8×10^{-3} mol) and the solution was heated on a steam bath for 10 hr. The resulting dark red solution was deposited on a column (diameter 5.5 cm) containing about 400 ml of Dowex 50-WX8 resin (50–100 mesh) in the sodium form. After thoroughly washing with water the column was eluted with 0.5 *N* sodium perchlorate solution at a rate of 1.8 ml/min. Two red bands separated. The large first red band and the small second red band were collected separately. After evaporating to a small volume, these were washed with alcohol and the first band yielded 0.4860 g of the *trans* complex. *Anal.* Calcd for *trans*-$(CoAEIDAen)ClO_4$: C, 24.47; H, 4.62; N, 14.26; Cl, 9.03. Found: C, 24.42; H, 4.65; N, 14.18; Cl, 8.97.

A portion of the *trans*-$(CoAEIDAen)ClO_4$ (0.306 g) was converted to the chloride by passing the solution through an anion-exchange column containing Dowex 2-X8 in the chloride form. The complex obtained weighed 0.275 g. *Anal.* Calcd for *trans*-$(CoAEIDAen)Cl \cdot 3H_2O$: C, 25.11; H, 6.32; N, 14.64. Found: C, 25.06; H, 6.23; N, 14.76.

The solution of the second band was evaporated to dryness. The sodium perchlorate was removed by washing with ethanol. Recrystallization of the residue in water gave 0.190 g of the *cis* isomer. Part of the isomer was converted to the chloride in the same way as the *trans* isomer. *Anal.* Calcd for *cis*-$(CoAEIDAen)Cl \cdot 2H_2O$: C, 26.35; H, 6.08; N, 15.26. Found: C, 26.46; H, 6.09; N, 15.49.

Analyses.—The C, H, N, and Cl analyses were done by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

Visible Spectra.—These spectra were recorded at room temperature using a Cary Model 11 spectrophotometer for 10^{-2} *M* solutions in 1-cm cells.

Proton Nuclear Magnetic Resonance Spectra.—These spectra were recorded on a Varian A-60 spectrometer (60 Mc/sec) at about 35°, the internal temperature of the probe. For the *cis* compound a spectrum was also taken on a Varian HA-100 spectrometer (100 Mc/sec) at ambient temperature to get better resolution. D_2O was used as solvent. For the *trans* compound 1 drop of concentrated D_2SO_4 was added to shift the HDO peak downfield about 2 ppm to facilitate the integration of adjacent sample peaks. NaTMS was used as an internal reference.

Results and Discussion

The first band from the column is assigned the *trans* configuration on the basis of visible absorption and proton magnetic resonance spectra. The order of column elution agrees with the results of other investigations on *trans* and *cis* isomers utilizing monodentate ligands[9,10] and on similar CoN_4O_2 systems with multidentate ligands.[6,11]

As summarized in Table I, the two isomers exhibit typical spectra for *trans* and *cis* isomers of this type.[12] In the visible region the *trans* complex shows a shoulder on the high-energy side of the first absorption band while the *cis* isomer exhibits only broadening. The shift in the main peak of the first absorption band from that of the parent compound (using the data for Co-

TABLE I

VISIBLE ABSORPTION SPECTRA[a]

Complex	Spectral bands ($\bar{\nu}$)		
	I_a	I_b	II
trans-(Co(en)-AEIDA)$Cl \cdot 3H_2O$	1.894 (144)[b]	2.237 sh (38)	2.801 (175)
cis-(Co(en)-AEIDA)$Cl \cdot 2H_2O$	1.789 sh (24)[c]	2.008 (107)	2.801 (117)

[a] All $\bar{\nu}$ in $cm^{-1} \times 10^{-4}$. [b] Extinction coefficients (ϵ) in parentheses. [c] The wavelengths for the shoulders are determined assuming a symmetrically shaped curve for the main peaks.

---

(1) F. G. Mann and W. J. Pope, *J. Chem. Soc.*, 482 (1926).

(2) S. E. Rasmussen, *Acta Chem. Scand.*, **13**, 2009 (1959).

(3) G. A. Barclay and A. K. Barnard, *J. Chem. Soc.*, 2540 (1958).

(4) G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 331 (1948).

(5) G. Schwarzenbach, E. Kampitsch, and R. Steiner, *ibid.*, **28**, 828 (1945).

(6) J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **4**, 1576 (1965).

(7) G. Schwarzenbach, G. Anderegg, W. Schneider, and H. Senn, *Helv. Chim. Acta*, **38**, 1147 (1955).

(8) H. F. Walton, "Inorganic Preparations," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1948, p 91.

(9) E. L. King and R. R. Walters, *J. Am. Chem. Soc.*, **74**, 4471 (1952).

(10) J. T. Hougen, K. Schug, and E. L. King, *ibid.*, **79**, 519 (1957).

(11) J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **5**, 594 (1966).

(12) J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p 187.

$(en)_3^{3+}$ [6]) in the *trans* case was about 1.9 times that of the *cis* which agrees quite well with the simple crystal field prediction for monodentate complexes of this type. The theory predicts that the *cis* compound due to a lack of an effective center of symmetry should have a greater intensity than the *trans* isomer. The greater intensity of the *trans* isomer as observed here agrees with the results of Legg and Cooke[11] on similar complexes with iminodiacetic acid. As discussed by Ballhausen[13] the d-d transitions in the *trans* case gain intensity through the dissymmetry introduced by asymmetrical ligand vibrations.

The acetate and ethylenediamine methylene proton resonance peaks for the two isomers are summarized in Table II. The amine protons exchanged too rapidly for these peaks to be observed. The substituted and unsubstituted ethylenediamine methylene protons exhibit a complicated resonance in the 2.3–3.7-ppm region. Owing to the positioning of the acetate rings, the two methylene protons are in different chemical environments and an ab quartet is expected for each different acetate ring. The structure of each of the isomers is given in Figure 1. In the *trans* isomers the two acetate rings are equivalent and one quartet appears in the acetate proton region. For the *cis* isomer both acetate rings are different and two overlapping quartets are observed. These quartets are separated somewhat in the 100-Mc spectrum.

TABLE II

RESONANCE FREQUENCY ASSIGNMENT AND INTEGRATION VALUES FROM THE PMR SPECTRA OF THE *trans*- AND *cis*-TETRADENTATE CHELATE COMPLEXES[a]

	trans-(Co(en)AIEDA)Cl·3H₂O		*cis*-(Co(en)AEIDA)Cl·2H₂O		
Assignment	Res freq, ppm	No. of H's	Res freq, ppm		No. of H's
$-(CH_2COO)_2$	4.61 4.34 4.15 3.87	4.23	4.43 4.15 4.12 3.82	4.43 4.12 4.08 3.76	4.25
$>NCH_2CH_2N<$	3.57 ↓ 2.5	7.77		3.74 ↓ 2.34	7.75

[a] All frequencies on low-field side of NaTMS.

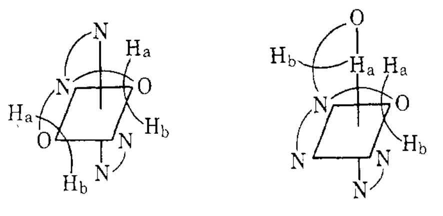

Figure 1.—Orientation of acetate ring protons in *trans*- and *cis*-Co(en)AEIDA.

The chemical shifts for the acetate ring protons for the two isomers calculated according to Jackman[14] are shown in Table III. For the *trans* isomer the acetate proton pointing upward toward the AEIDA ethylene backbond is designated H_b, and the other, H_a. The chemical shifts of these protons are comparable to the average values of 3.97 and 4.30 ppm found by Legg and Cooke[11] for *trans*-Co(dien)MIDA and can be explained by the anisotropy of the CN bond. The H_a will be shielded by the en ring of the tetradentate, and the H_b will be deshielded, so that H_a will occur at higher fields. For the *cis* isomer it is impossible to assign the different quartets to specific acetate rings. Apparently the different orientations of the neighboring groups result in each acetate group having similar chemical environment.

TABLE III

CHEMICAL SHIFTS (PPM) OF ACETATE RING PROTONS OF *trans*- AND *cis*-Co(en)AEIDA

trans-(Co(en)AEIDA)Cl		*cis*-(Co(en)AEIDA)Cl	
δ_a	δ_b	δ_a	δ_b
4.06	4.43	4.05	4.21
		4.02	4.18

Acknowledgments.—Financial support of this investigation by the National Institutes of Health is gratefully acknowledged.

[13] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 186.

[14] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1964, p 89.

Contribution from the Department of Chemistry,
University of Maryland, College Park, Maryland 20740

The Oxidation of Tris(1,10-phenanthroline)iron(II) Ion by Aqueous Chlorine[1a]

By Bassam Z. Shakhashiri and Gilbert Gordon[1b]

Received February 23, 1968

The oxidation of iron(II) species by chlorine may proceed through a two-electron step to form an iron(IV) intermediate

$$Fe(II) + Cl_2 \rightleftarrows Fe(IV) + 2Cl^- \qquad (1)$$

$$Fe(IV) + Fe(II) \longrightarrow 2Fe(III) \qquad (2)$$

or through a one-electron step to form a chlorine radical intermediate

$$Fe(II) + Cl_2 \rightleftarrows Fe(III) + Cl_2^- \qquad (3)$$

$$Fe(II) + Cl_2^- \longrightarrow Fe(III) + 2Cl^- \qquad (4)$$

In this note we wish to report the results of our study of the oxidation of tris(1,10-phenanthroline)iron(II)

[1] (a) Part of the thesis presented by B. Z. Shakhashiri to the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1967. (b) Department of Chemistry, University of Iowa, Iowa City, Iowa 52240.