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Transition Metal Complexes of Tetraethylenepentamine. II. Some Acidotetraethylenepentamine Complexes of Cobalt(III) and Chromium(III)[1]

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The following new acidotetraethylenepentamine complex compounds of cobalt(III) and chromium(III) have been prepared and characterized by chemical analyses and infrared spectra: α-[Co(tetren)Cl]Z_2 (Z = ClO_4, 0.5Zn$(SCN)_4$, 0.5$CoCl_4$), α-[Co(tetren)Br]$ZnBr_4$, α-[Co(tetren)OH]$(ClO_4)_2$, α-[Co(tetren)OH_2]$(ClO_4)_3$, α-[Co(tetren)ONO]$ZnCl_4$, α-[Co(tetren)N_3]$ZnCl_4$, α-[Co(tetren)NCS]Z_2 (Z = 0.5$ZnCl_4$, 0.5Zn$(SCN)_4$), β-[Co(tetren)Cl]Z_2 (Z = ClO_4, 0.5Zn$(SCN)_4$), β-[Co(tetren)Br]$ZnBr_4$, β-[Co(tetren)NCS]Z_2 (Z = 0.5$ZnCl_4$, 0.5Zn$(SCN)_4$), α-[Cr(tetren)Cl]Z_2 (Z = Cl, 0.5$ZnBr_4$), and α-[Cr(tetren)NCS]$(SCN)_2$, where α and β refer to geometrical isomers. The visible absorption spectra of these complexes have been obtained and compared with the spectra of the related $M(NH_3)_5X^{n+}$ (M = Co, Cr) ions. Circular dichroism measurements on (−)-β-[Co(tetren)Cl]$ZnCl_4$ show that the absolute configuration is L. Double isomerization (both linkage and geometric) occurs readily in the solid state for α-[Co(tetren)ONO]$ZnCl_4$, which isomerized to β-[Co(tetren)NO_2]$ZnCl_4$.

In the first paper[2] of this series we have described the preparation, properties, and geometric configuration of α-[Cr(tetren)Cl]$ZnCl_4$ and of α- and β-[Co(tetren)Cl]$ZnCl_4$, containing the straight-chain quinquedentate ligand tetraethylenepentamine,[3] and presented evidence that the α and β isomers probably have structures I and II, respectively (Figure 1).

In the present paper we report the preparation and properties of 18 new acidotetraethylenepentamine complex compounds of cobalt(III) and chromium(III). Their visible absorption spectra are compared with the spectra of the related $M(NH_3)_5X^{n+}$ (M = Co, Cr) ions. Confirmation of the absolute configuration of (−)-β-[Co(tetren)Cl]$ZnCl_4$ is also reported.

Experimental Section

Pure β-[Co(tetren)NO_2]$ZnCl_4$, α- and β-[Co(tetren)Cl]$ZnCl_4$, and mixtures of the latter two isomers were prepared as previously described for use as parent compounds in synthesizing some of the new compounds below. The synthesis and resolution of (−)-β-[Co(tetren)Cl]$ZnCl_4$ was as given earlier.[2] All other chemicals were reagent grade.

α-Chlorotetraethylenepentaminecobalt(III) Tetrachlorocobaltate(II).—Method A described earlier[2] was used to prepare Co(tetren)Cl^{2+} ion. However, the solution was not cooled during oxidation with H_2O_2.[4] Bright blue crystals of α-[Co(tetren)Cl]$CoCl_4$ crystallized from the HCl solution on evaporation to 150 ml (total heating time about 3 hr). The crystals were washed with 95% ethanol, then with methanol, and air dried; yield, 15%.

Anal. Calcd for [Co(tetren)Cl]$CoCl_4$: C, 19.83; H, 4.78; Co, 24.4; Cl, 36.58. Found: C, 19.75; H, 4.70; Co, 24.5; Cl, 36.50.

These crystals dissolved in 0.1 *F* $HClO_4$ to give a red solution with a visible absorption spectrum characteristic of the α-Co(tetren)Cl^{2+} ion[2] after correction for the absorption due to the $Co(OH_2)_6^{2+}$ formed from the $CoCl_4^{2-}$ anion.

α- and β-Chlorotetraethylenepentaminecobalt(III) Perchlorate.—The α and β isomers of [Co(tetren)Cl]$ZnCl_4$ were separately dissolved in the minimum amount of 80° 0.2 *F* $HClO_4$ (5 g/200 ml) and $NaClO_4\cdot H_2O$ (10 g/200 ml) was added. The rose-red perchlorate salts that crystallized on cooling for several hours in an ice bath were washed with 95% ethanol and air dried; yield, 60–70%.

Anal. Calcd for [Co(tetren)Cl]$(ClO_4)_2$: Co, 12.2; Cl (ligand), 7.4. Found, α isomer: Co, 12.4; Cl (ligand), 7.2. Found, β isomer: Co, 12.3; Cl (ligand), 7.2.

On heating at 5°/min both isomeric salts darkened at 230–240° and melted with nonviolent decomposition at *ca.* 265°.

α- and β-Chlorotetraethylenepentaminecobalt(III) Tetrathiocyanatozincate(II).—The α and β isomers of [Co(tetren)Cl]$ZnCl_4$ were separately dissolved in 80° 0.2 *F* CH_3CO_2H (1 g/150 ml) and a solution of 3 g of KSCN in 20 ml of water was added to the hot solution. The rose-red tetrathiocyanatozincate(II) salts crystallized immediately. The product was filtered from the cooled solution, washed with three 10-ml portions of ice water, then with 95% ethanol, and air dried; yield, 95–100%.

Anal. Calcd for [Co(tetren)Cl]Zn$(SCN)_4$: C, 24.79; H, 3.99; N, 21.68; Co, 10.12; SCN, 40.00. Found, α isomer: C, 24.34; H, 4.38; N, 21.54; Co, 10.00. Found, β isomer: N, 21.8; Co, 10.2; SCN, 39.82.

α- and β-Bromotetraethylenepentaminecobalt(III) Tetrabromozincate(II).—Starting with separate portions of an isomeric mixture of α- and β-[Co(tetren)Cl]$ZnCl_4$, methods G and F were used,[2] except that $ZnBr_2$ and HBr replaced the $ZnCl_2$ and HCl. Violet crystalline salts were obtained; yield, 70–80%.

Anal. Calcd for [Co(tetren)Br]$ZnBr_4$: C, 13.51; H, 3.26; N, 9.85; Co, 8.30; Br, 56.18. Found, α isomer: C, 13.87; H, 3.37; Co, 8.10; Br, 56.14. Found, β isomer: C, 13.45; H, 3.40; N, 9.88; Co, 8.45; Br, 56.22.

α-Azidotetraethylenepentaminecobalt(III) Tetrachlorozincate(II).—Isomerically pure α- or β-[Co(tetren)Cl]$ZnCl_4$ (1 g) was dissolved in 20 ml of 0.2 *F* CH_3CO_2H and 3 g of NaN_3 was added. The solution was heated at 80° for 15–20 min, then cooled to *ca.* 25°, and 100 ml of 1:1 2-propanol–methanol was added to precipitate the pink product. The salt was recrystallized from a minimum volume (*ca.* 20 ml) of 0.1 *F* HCl containing *ca.* 2 g of $ZnCl_2$, by addition of 100 ml of 1:1 2-propanol–methanol; yield, 60%.

Anal. Calcd for [Co(tetren)N_3]$ZnCl_4$: C, 19.39; H, 4.68; Co, 11.9; Cl, 28.62. Found: C, 19.48; H, 4.86; Co, 12.0; Cl, 28.75.

α-Isothiocyanatotetraethylenepentaminecobalt(III) Tetrathiocyanatozincate(II).—A mixture of α- and β-[Co(tetren)Cl]$ZnCl_4$ (1.5 g) was dissolved in 180 ml of water and 20 ml of 2 *F* NaOH was added. The solution was warmed at 80° for 10 min to hydrolyze off the chloro ligand completely and was then made acid (pH 5) by dropwise addition of glacial acetic acid. Twenty

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[2] D. A. House and C. S. Garner, *Inorg. Chem.*, **5**, 2097 (1966).

[3] $H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$; abbreviation, tetren.

[4] If pure tetren were used, there would not be an excess of $CoCl_2$ in the synthesis, and 24 g of $CoCl_2\cdot 6H_2O$ should then be added in place of the $ZnCl_2$ during the final heating.

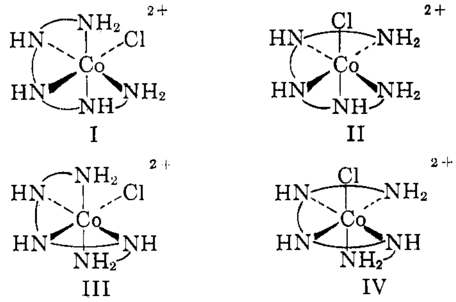

Figure 1.—Possible geometric isomers of $Co(tetren)Cl^{2+}$.

milliliters of an aqueous solution containing 5 g of KSCN was added to the solution at *ca.* 25° and the reaction mixture was allowed to stand to anate. Sparingly water-soluble, orange crystal clusters separated from the solution after 4 days. The product was washed with three 10-ml portions of ice water, then with 2-propanol, and air dried; yield, 65%.

Anal. Calcd for $[Co(tetren)NCS]Zn(SCN)_4$: C, 25.85; H, 3.84; Co, 9.76; SCN (from complex anion), 38.46. Found: C, 25.72; H, 4.27; Co, 9.78; SCN (from complex anion), 38.60.

This compound is readily soluble in dimethylformamide, acetone, methanol, and ethanol, but cannot be recrystallized from boiling water without isomerization to the β form.

β-Isothiocyanatotetraethylenepentaminecobalt(III) Tetrathiocyanatozincate(II).—Isomerically pure β-$[Co(tetren)Cl]ZnCl_4$ (1.5 g) was dissolved in 200 ml of 0.2 *F* CH_3CO_2H, and 5 g of KSCN was added. The red solution, together with the crystalline precipitate of β-$[Co(tetren)Cl]Zn(SCN)_4$ (*vide ante*) that formed, was heated about 1 hr at 80° until a clear orange solution was obtained. Sparingly water-soluble, orange featherlike crystals of the product deposited on cooling. The crystals were washed with three 10-ml portions of water, then with 2-propanol, and air dried; yield, 80%.

Anal. Calcd for $[Co(tetren)NCS]Zn(SCN)_4$: C, 25.85; H, 3.84; Co, 9.76; SCN (from complex anion), 38.46. Found: C, 25.72; H, 4.21; Co, 9.60; SCN (from complex anion), 38.52.

The solubility properties of this salt are similar to those of the α-isomeric salt.

α- and β-Isothiocyanatotetraethylenepentaminecobalt(III) Tetrachlorozincate(II).—Isomerically pure α- and β-$[Co(tetren)NCS]Zn(SCN)_4$ salts (1 g) from the above two preparations were each dissolved in separate 50-ml portions of acetone, and 10 ml of 12 *F* HCl was added to each. The orange chloride salts crystallized on cooling in an ice bath and were washed with acetone and air dried. The chloride salts were converted to the tetrachlorozincate(II) salts by dissolution in 20 ml of 0.1 *F* HCl and pouring this solution into 200 ml of 2-propanol containing 5 g of $ZnCl_2$ and 1 ml of 12 *F* HCl. Orange crystals were deposited on standing overnight at *ca.* 25°; these were removed by filtration, washed with 2-propanol, and air dried; yield, 75–80%.

Anal. Calcd for $[Co(tetren)NCS]ZnCl_4$: C, 21.05; H, 4.52; N, 16.37; Co, 11.5; Cl, 27.62. Found, α isomer: C, 20.96; H, 4.77; N, 16.07; Co, 11.6; Cl, 27.83. Found, β isomer: C, 21.02; H, 4.69; N, 16.5; Co, 11.7; Cl, 27.52.

α-Hydroxotetraethylenepentaminecobalt(III) Perchlorate.—A mixture of α- and β-$[Co(tetren)Cl]ZnCl_4$ (2 g) and 2.4 g of Ag_2O were suspended in 50 ml of water. The mixture was warmed at 60° for 15 min and then filtered. Five grams of $NaClO_4 \cdot H_2O$ was added to the filtrate, and the orange solution was then evaporated at *ca.* 25° to about 10 ml under a slow stream of air. Orange rhombs were deposited, and these were washed with 95% ethanol and then with methanol; yield, 60–70%.

Anal. Calcd for $[Co(tetren)OH](ClO_4)_2$: Co, 12.7. Found: Co, 12.9.

When the compound was heated at 5°/min, it darkened at 180° and melted at 270° with nonviolent decomposition.

When this compound was dissolved in 0.1 or 1 *F* $HClO_4$, it gave a visible absorption spectrum the same as that of α-$[Co(tetren)OH_2](ClO_4)_3$ (*vide infra*).

α-Aquotetraethylenepentaminecobalt(III) Perchlorate.—The procedure for the synthesis of the hydroxo complex was repeated except that after filtration, the solution was made acid (pH 2) with $HClO_4$ before adding the $NaClO_4 \cdot H_2O$. Orange crystal clusters were obtained; yield, 50%.

Anal. Calcd for $[Co(tetren)(OH_2)](ClO_4)_3$: Co, 10.44. Found: Co, 10.55.

Heating the compound at 5°/min caused it to darken at 180° and to melt with nonviolent decomposition at 270°.

When the salt was dissolved in 1 *F* NaOH and its visible absorption spectrum taken immediately, the spectrum of α-$[Co(tetren)OH](ClO_4)_2$ (*vide ante*) was found.

α-Nitritotetraethylenepentaminecobalt(III) Tetrachlorozincate(II).—Isomerically pure α-$[Co(tetren)Cl]ZnCl_4$ (1 g) was added to 22 ml of 1.5 *F* NH_4OH and warmed at 80° for *ca.* 5 min to complete the base hydrolysis. The clear orange solution was cooled in ice and made acid (pH 5) with 12 *F* HCl, and 2.5 g of $NaNO_2$ was added. The solution was allowed to stand for 30 min at room temperature and then 2 g of $ZnCl_2$ was added, followed by 150–200 ml of 1:1 2-propanol–methanol. Orange crystals were deposited in 1 hr from the solution cooled in an ice bath and were washed with methanol; yield, 50%.

Anal. Calcd for $[Co(tetren)ONO]ZnCl_4$: C, 19.24; H, 4.64; N, 16.83; Co, 11.8; Cl, 28.39. Found: C, 19.22; H, 4.29; N, 16.62; Co, 11.7; Cl, 28.15.

α-Chlorotetraethylenepentaminechromium(III) Chloride.—Crude α-$[Cr(tetren)Cl]Cl_2$ (2 g) was synthesized as described for the pink crystalline intermediate in the preparation of α-$[Cr(tetren)Cl]ZnCl_4$ reported earlier[2] and dissolved in 20 ml of 12 *F* HCl at *ca.* 25°. This orange-red solution was slowly poured into 400 ml of acetone. On stirring and cooling the mixture in ice, red-violet crystals of the chloride salt crystallized. These were filtered off after 1 hr, washed with acetone, and then air dried; yield, 90%.

Anal. Calcd for $[Cr(tetren)Cl]Cl_2$: C, 27.64; H, 6.67; N, 20.14; Cr, 14.95; Cl, 30.59. Found: C, 27.63; H, 6.66; N, 19.9; Cr, 14.90; Cl, 30.70.

α-Chlorotetraethylenepentaminechromium(III) Tetrabromozincate(II).—This salt was prepared in the same way as α-$[Cr(tetren)Cl]ZnCl_4$[2] except for substituting HBr and $ZnBr_2$ for the HCl and $ZnCl_2$. The product is orange; yield, 85%.

Anal. Calcd for $[Cr(tetren)Cl]ZnBr_4$: C, 14.45; H, 3.50; N, 10.60; Cr, 7.87; halogen, 53.59. Found: C, 15.07; H, 3.94; N, 10.15; Cr, 8.00; halogen, 53.50.

α-Isothiocyanatotetraethylenepentaminechromium(III) Thiocyanate.—Crude $[Cr(tetren)Cl]Cl_2$ (1 g, *vide ante*) was dissolved in 10 ml of water containing 3 g of KSCN, and the solution was heated at 80° for 15 min. The hot solution was filtered to remove a small amount of unknown material, and on cooling the filtrate to *ca.* 25° orange-yellow crystals of product formed. These were filtered off, washed with three 10-ml portions of ice water and then with 2-propanol, and air dried; yield, 90%.

Anal. Calcd for $[Cr(tetren)NCS](SCN)_2$: C, 31.79; H, 5.58; N, 26.97; Cr, 12.52. Found: C, 31.73; H, 5.66; N, 27.0; Cr, 12.35.

Attempt to Improve Yield in Synthesis of α- and β-Chlorotetraethylenepentaminecobalt(III) Tetrachlorozincate(II).—The yield in the synthesis of α- and β-$[Co(tetren)Cl]ZnCl_4$ and of α-$[Cr(tetren)Cl]ZnCl_4$ described in our first paper[2] was only 15%, apparently due to the use of commercial tetraethylenepentamine later found to contain only about 20% of this pentamine. In an effort to improve the yield we increased twofold the proportion of amine used in method A.[2] Chemical analyses and the infrared spectrum of the product showed that it contained considerable amounts of $[Co(dien)(en)Cl]ZnCl_4$ formed from the diethylenetriamine (dien) and ethylenediamine (en) impurities in the commercial amine. Attempts to purify the amine by crystallizing the pentahydrochloride[5] without first distilling the commercial amine gave only an oil.

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(5) H. B. Jonassen, F. W. Frey, and A. Schaafsma, *J. Phys. Chem.*, **61**, 504 (1957).

Table I

Some Assigned and Characteristic Infrared Frequencies[a] (cm^{-1}) of [M(tetren)X]Z (M = Cr, Co) Compounds (KBr Disk)

Compounds	NH$_2$ stretch				NH$_2$ bend		Other specific assignments
α-[Cr(tetren)Cl]Cl$_2$	3200 s	3150 s	3070 s	3015 s	1560 s		
α-[Cr(tetren)Cl]ZnCl$_4$[2]	3260 s	3215 s	3175 s	3125 s	1550 s		
α-[Cr(tetren)Cl]ZnBr$_4$	3220 s	3220 s	3160 s	3120 s	1566 s		
α-[Cr(tetren)NCS]Zn(SCN)$_4$	3240 s	3200 s	3130 s	3100 s	1577 s		2060 vs[b] 2050 vs[b]
α-[Co(tetren)Cl]ZnCl$_4$[2]	3255 s	3215 s	3165 s	3130 s	1565 s		
α-[Co(tetren)Cl](ClO$_4$)$_2$	3260 s	3230 s	3200 s	3120 s	1565 s		
α-[Co(tetren)Cl]CoCl$_4$	3255 s	3220 s	3170 s	3135 s	1564 s		
α-[Co(tetren)Cl](SCN)$_2$	3270 s	3200 s	3120 s	3095 s	1564 s		2090 vs[b]
α-[Co(tetren)Br]ZnBr$_4$	3250 s	3210 s	3155 s	3125 s	1561 s		
α-[Co(tetren)N$_3$]ZnCl$_4$	3270 s	3220 s	3190 s	3140 s	1576 s		2085 vs[c] 2025 vs[c]
α-[Co(tetren)NCS]Zn(SCN)$_4$	3260 s	3240 s	3200 s	3110 s	1570 s		2090 vs[b]
α-[Co(tetren)NCS]ZnCl$_4$	3280 s	3220 s	3100 s	3030 s	1550 s		2100 vs[b]
α-[Co(tetren)OH](ClO$_4$)$_2$	3310 s	3260 s	3230 s	3090 m	1603 s		3582 s[d] 1636 s[d]
α-[Co(tetren)OH$_2$](ClO$_4$)$_3$	3280 s	3250 s	3200 s	3140 s	1585 s		3420 m[d] 1610 m[d]
α-[Co(tetren)ONO]ZnCl$_4$[e]	3260 s	3210 s	3160 s	3130 s	1570 s		1475 s[f] 1315 s[f] 1040 s[f] 824 m[f]
β-[Co(tetren)Cl]ZnCl$_4$[2]					1589 m	1560 s	
β-[Co(tetren)Cl](ClO$_4$)$_2$					1588 m	1570 s	
β-[Co(tetren)Cl]Zn(SCN)$_4$					1585 m	1563 s	2090 vs[b]
β-[Co(tetren)Br]ZnBr$_4$					1582 m	1563 s	
β-[Co(tetren)NCS]Zn(SCN)$_4$					1590 m	1564 s	2090 vs[b]
β-[Co(tetren)NCS]ZnCl$_4$					1598 m	1572 s	2100 vs[b]
β-[Co(tetren)NO$_2$]ZnCl$_4$					1580 m	1560 s	1410 s[g] 1323 s 815 s[g]

[a] Intensities estimated as follows: vs, very strong; s, strong; m, medium. [b] C≡N stretch. [c] N≡N stretch. [d] OH vibrations. [e] Spectrum essentially the same in Nujol mull. [f] ONO vibrations. [g] NO$_2$ vibrations.

Spectral Measurements.—The infrared spectra were determined in KBr disks using a Perkin-Elmer Model 421 spectrophotometer. Visible absorption data were obtained by dissolving each compound in 0.1 *F* HClO$_4$ (except for the hydroxo complex, where 1 *F* NaOH was used) at 20–25° and immediately taking the spectrum (aquation occurs only slowly) with a Cary Model 15 recording spectrophotometer, using matched 10.00-cm quartz cells with the reference cell filled with water. The circular dichroism of (−)-β-[Co(tetren)Cl]ZnCl$_4$ freshly dissolved in 0.1 *F* HClO$_4$ in a 5.00-cm strain-free cell was measured with a Durrum Jasco Model ORD/UV/CD/5 spectropolarimeter.

Chemical Analyses.—Chromium, cobalt, chlorine, carbon, hydrogen, and nitrogen were determined as described previously.[2] The complex cobalt and chromium cations were decomposed by boiling in peroxydisulfate solution. Bromide was determined gravimetrically as the silver salt, the complexes being decomposed with hot 0.5 *F* NaOH for 15 min and then acidified with HNO$_3$; excess AgNO$_3$ was added, and the solution was heated to coagulate the precipitate. Free thiocyanate was determined gravimetrically as the silver salt.

Results

Infrared Spectra.—Comparison of the infrared spectra of the new compounds with the infrared spectra[2] of α- and β-[Co(tetren)Cl]ZnCl$_4$ and of α-[Cr(tetren)Cl]ZnCl$_4$ led readily to the assignments of the α and β configurations[2] given for the new compounds. The new salts of the chlorotetraethylenepentamine complexes gave infrared spectra essentially the same as for the tetrachlorozincate(II) salts,[2] except for frequencies associated with the various complex anions of the salts. The major differences in the infrared spectra of α- and β-[Co(tetren)Cl]ZnCl$_4$ have been given in the first paper of this series,[2] and some of these observed differences in the spectra of the new compounds reported here are evident from the relevant frequencies listed in Table I. Other bands at lower frequencies also permit isomeric characterization, but these are sometimes obscured by bands from the acido ligand X or the anion Z where these consist of two or more atoms, and hence are not listed.

In general, the α isomers have four distinct bands of nearly equal intensity in the NH$_2$ stretching region (3000–3300 cm^{-1}), whereas the bands for the β isomers in this region are less well resolved and have several shoulders. In the NH$_2$ bending region (1550–1600 cm^{-1}) the α isomers have one sharp band whereas the β isomers show two bands.[6]

Selbin[7] has listed the infrared bands for the coordinated NO$_2$ in Co(tetren)NO$_2^{2+}$ salts of unassigned configuration. His complex appears to be the β isomer, since the reported nitro bands agree with the nitro bands listed for our β-[Co(tetren)NO$_2$]ZnCl$_4$, which is assigned the β configuration on the basis of the two NH$_2$ bending vibrations at 1560 and 1580 cm^{-1} (see Table I) and the fact that the nitro compound gives[2] β-[Co(tetren)Cl]ZnCl$_4$ on treatment with 12 *F* HCl and excess ZnCl$_2$. We also observe splitting of the 1323- and 1410-cm^{-1} NO$_2$ bands, but this may arise from overlay by bands from the tetraethylenepentamine ligand, as there are strong absorptions in this region in β-[Co(tetren)Cl]ZnCl$_4$.[2] There is a medium intensity absorption at 552 cm^{-1} in the NO$_2$ wagging region. However, both α- and β-[Co(tetren)ZnCl$_4$ show bands in this region from the amine ligand.

The nitrito complex, α-[Co(tetren)ONO]ZnCl$_4$, exhibits a band at 1040 cm^{-1} characteristic of ONO stretching, which is normally absent in nitro complexes.[8]

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[6] Similar results were obtained for the α and β geometric isomers of *cis*-[Co(triethylenetetramine)X$_2$]Z compounds by D. A. Buckingham and D. Jones, *Inorg. Chem.*, **4**, 1387 (1965), and used to make assignments of α and β configurations to some related diacidotriethylenetetramine complexes of cobalt(III) and chromium(III) by D. A. House and C. S. Garner, *J. Am. Chem. Soc.*, **88**, 2156 (1966).

[7] J. Selbin, *J. Inorg. Nucl. Chem.*, **17**, 84 (1961).

[8] See D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, **3**, 1389 (1964), for a summary of the evidence for distinguishing nitro from nitrito compounds based on infrared and electronic spectra.

TABLE II

VISIBLE ABSORPTION MAXIMA AND MINIMA OF α- AND β-M(tetren)X^{n+} AND $M(NH_3)_5X^{n+}$ (M = Co, Cr) IN AQUEOUS SOLUTION AT 20–25°[a]

Complex	λ_{max}, mμ	λ_{min}, mμ	λ_{max}, mμ	λ_{min}, mμ	λ_{max}, mμ	λ_{min}, mμ
α-Co(tetren)Cl^{2+} [b,c]	522 (109)		480 (105) sh[d]	417 (37.5)	362 (103)	328 (43.6)
β-Co(tetren)Cl^{2+} [b c]	525 (98.6)	508 (97.3)	480 (101)	415 (37.2)	360 (107)	332 (64.5)
$Co(NH_3)_5Cl^{2+}$ [e]	534 (50.1)		467 (11.0) sh[d]		364 (46.8)	
α-Co(tetren)Br^{2+} [c]	548 (132)		480 (100) sh[d]	423 (48.1)		
β-Co(tetren)Br^{2+} [c]	550 (121)	495 (97.8)	480 (98.0)	422 (46.5)		
$Co(NH_3)_5Br^{2+}$ [e]	552 (57.6)		470 (11.5) sh[d]		310 (831) sh[d]	
α-Co(tetren)NCS^{2+} [c]	490 (219)			415 (50.8)		
β-Co(tetren)NCS^{2+} [c]	487 (318)			412 (71.7)		
$Co(NH_3)_5NCS^{2+}$ [f,g]	497 (186)			430 (35.5)	357 (398) sh[d]	
α-Co(tetren)N_3^{2+} [c]	508 (490)			432 (117)		
$Co(NH_3)_5N_3^{2+}$ [f]	519 (257)					
β-Co(tetren)NO_2^{2+} [c]	460 (207)			397 (51.6)		
?-Co(tetren)NO_2^{2+} [h]	460 (224)				328 (1820)	
$Co(NH_3)_5NO_2^{2+}$ [i]	458 (219)				325 (1700)	
$Co(NH_3)_5NO_2^{2+}$ [f]	458 (100)				325 (1660)	
α-Co(tetren)ONO^{2+} [c]	475 (164)			428 (106)	358 (872)	
$Co(NH_3)_5ONO^{2+}$ [f]	491 (72.4)			434 (32)	361 (276)	
α-Co(tetren)OH^{2+} [c]	490 (149)			417 (51)	348 (147)	
$Co(NH_3)_5OH^{2+}$ [j]	503 (62.5)			425 (20)	370 (70.8)	360 (69)
α-Co(tetren)OH_2^{3+} [c]	472 (122)			405 (33.0)	350 (85.3)	
$Co(NH_3)_5OH_2^{3+}$ [k,l]	485 (48)				340	
α-Cr(tetren)Cl^{2+} [b]	495 (118)			422 (45.4)	375 (82.0)	
$Cr(NH_3)_5Cl^{2+}$ [m]	512 (36)				375 (39)	
$Cr(NH_3)_5Cl^{2+}$ [n]	515 (38)		452 (7.9) sh[d]		376 (43.7)	
$Cr(NH_3)_5Cl^{2+}$ [o]	511 (34.6)				375 (33.9)	
α-Cr(tetren)NCS^{2+} [c]	515 (125)		435 (33.7)		388 (63.2)	360 (43.0)
$Cr(NH_3)_5NCS^{2+}$ [f]	490 (83.1)				370 (52.5) sh[d]	
$Cr(NH_3)_5NCS^{2+}$ [o]	488 (66)				362 (47)	

[a] Everywhere numbers inside parentheses are the molar absorbancy indices a_M (extinction coefficient ϵ) in M^{-1} cm^{-1}, defined by the relation $A = \log (I_0/I) = a_M cd$, where c is the molarity of the complex and d is the optical path in centimeters. [b] Reference 2; in 0.1 F $HClO_4$. [c] This research; in 0.1 F $HClO_4$, except in 1 F NaOH for the hydroxo complex. [d] sh = shoulder. [e] M. Linhard and M. Weigel, *Z. Physik. Chem.*, **11,** 308 (1957); apparently in water. [f] M. Linhard, H. Siebert, and M. Weigel, *Z. Anorg. Allgem. Chem.*, **278,** 287 (1955); apparently in water. [g] A. v. Kiss and D. v. Czegledy, *ibid.*, **235,** 407 (1938); apparently in water. [h] J. Selbin, *J. Inorg. Nucl. Chem.*, **17,** 84 (1961); complex of unknown configuration (infrared spectrum of perchlorate salt suggests it is the β isomer), in water. [i] R. C. Brasted and C. Hirayama, *J. Phys. Chem.*, **63,** 780 (1959); in water. [j] "Gmelins Handbuch der anorganischen Chemie," Kobalt, Teil B, Vol. 58, Verlag Chemie, Germany, 1964, p 404; apparently in water. [k] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Ltd., London, 1962, p 293; medium not stated. [l] R. I. Colmar and F. W. Schwartz, *J. Am. Chem. Soc.*, **54,** 3204 (1932); apparently in water, [m] M. A. Levine, T. P. Jones, W. E. Harris, and W. J. Wallace, *ibid.*, **83,** 2453 (1961); apparently in aqueous solution. [n] M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, **266,** 49 (1951); apparently in water. [o] R. Tsuchida, *Bull. Chem. Soc. Japan*, **13,** 388 (1938); apparently in water.

The bands at 824, 1315, and 1475 cm^{-1} may also be ascribed to ONO vibrations, and these disappear and are replaced by bands at 815, 1323, and 1410 cm^{-1} on isomerization to the nitro complex. There is a medium band at 1402 cm^{-1} in the nitrito complex which could arise from a possible impurity of nitro complex, but the band may simply arise from overlay of amine bands, since there is a 1401-cm^{-1} band of medium intensity in the spectrum of α-[Co(tetren)Cl]$ZnCl_4$.[2] The α configuration of the tetraethylenepentamine ligand in [Co(tetren)ONO]$ZnCl_4$ is assigned chiefly on the basis of the single band at 1570 cm^{-1} (see Table I) and the fact that this compound gives mainly α-[Co(tetren)Cl]$ZnCl_4$ on treatment with hydrochloric acid.

Visible Absorption Spectra.—Wavelengths and molar absorbancy indices of the absorption maxima and minima in the range 320–700 mμ for solutions of the M(tetren)X^{n+} (M = Co, Cr) cations in 0.1 F $HClO_4$ are given in Table II, together with those reported earlier for the related $M(NH_3)_5X^{n+}$ cations. These spectral parameters for the new salts of α- and β-Co(tetren)Cl^{2+} and α-Cr(tetren)Cl^{2+} agree within 2% with those we reported[2] earlier for their tetrachlorozincate(II) salts.

Circular Dichroism of (−)-β-[Co(tetren)Cl]$ZnCl_4$.—Figure 2 displays the circular dichroism of this complex, together with its optical rotatory dispersion and absorption spectrum.[2]

Discussion

In the visible absorption spectra (see Table II) of these acidotetraethylenepentamine complexes the absorption maxima are shifted to shorter wavelengths and have greater intensities than for the corresponding acidopentaammine complexes, except for α-Cr(tetren)NCS^{2+} (the maxima of which are shifted to longer wavelengths) and β-Co(tetren)NO_2^{2+} (the maxima and intensities of which are comparable to those of $Co(NH_3)_5NO_2^{2+}$). In other respects the spectra of the analogs in these two classes of complexes are similar as would be expected from the fact that in each class the chromophore is MN_5X.

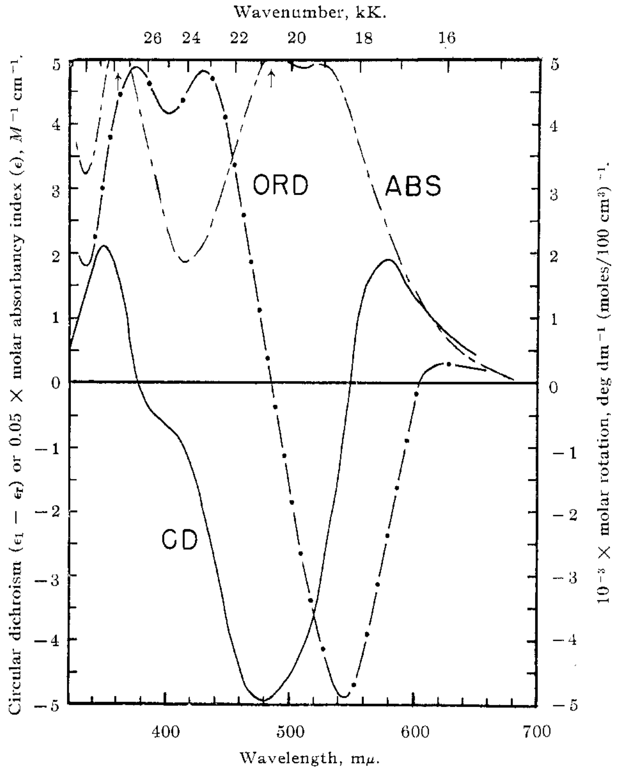

Figure 2.—Circular dichroism (CD), optical rotatory dispersion (ORD), and visible absorption spectrum (ABS) of $(-)$-β-[Co(tetren)Cl]$ZnCl_4$ in 0.1 *F* $HClO_4$ at 20–25°; absorption maxima offscale are at 360 mμ (a_M = 107 M^{-1} cm^{-1}) and 480 mμ (a_M = 101 M^{-1} cm^{-1}). The ordinates of the ORD curve of Figure 2 of paper I of this series[2] are in error by a factor of two and should be as given here.

Inasmuch as some transition metal nitrito complexes rapidly isomerize or aquate in aqueous solution, it is worthy of note that α-Co(tetren)ONO^{2+} exhibits rapid changes in the visible absorption spectrum upon dissolution in water or dimethylformamide, although the spectrum in 0.1 *F* $HClO_4$ shows essentially no change in 5 min at room temperature.

An interesting aspect of the syntheses reported here for the α- and β-M(tetren)X^{n+} complexes is that the particular isomeric configuration of the amine ligand appears to be sensitive to the nature of the acido ligand X. With X = Cl, Br, and NCS, both α and β isomers are formed. The α form of the isothiocyanato complex converts to the β form upon crystallization from hot water.[9] With X = H_2O, OH, N_3, and ONO, only α isomers have been obtained, and with X = NO_2 (and SO_3, according to preliminary evidence), only β isomers were found. The infrared spectra show that there is no isomerization in the conversion of α- and β-[Co(tetren)Cl]$ZnCl_4$ to the perchlorate and tetrathiocyanatozincate and the change of α- and β-[Co(tetren)NCS]Zn$(NCS)_4$ to the tetrachlorozincate(II) salts. The infrared spectra of the azido complex and the [Co(tetren)Cl]$ZnCl_4$ derived from it[10] indicate that only the α configuration is produced, even when β-[Co(tetren)Cl]$ZnCl_4$ is used to make the azido complex.

An interesting double isomerization (both linkage and geometric) is afforded by α-[Co(tetren)ONO]$ZnCl_4$. Spontaneous isomerization to β-[Co(tetren)NO_2]$ZnCl_4$[2] occurs in the solid state in about 4 days at *ca.* 25°, or in 1 hr at 110°. This is evidenced by change from the characteristic orange color of cobalt(III) nitrito complexes to the yellow color typical of cobalt(III) nitro complexes, and from the change in infrared spectrum (see Table I), which reveals the simultaneous conversion from α to β configuration as well as the change from nitrito to nitro linkage. Formation of unstable nitrito forms of transition metal complexes, observed for $M(NH_3)_5ONO^{n+}$ where M = Co(III), Rh(III), Ir(III), and Pt(IV),[11] has generally been considered[11–13] as arising from attack by N_2O_3 on $M(NH_3)_5OH^{2+}$ intermediate without rupture of the M–O bond. The unstable nitrito complex then rearranges intramolecularly to the thermodynamically more stable nitro isomer. Where stable nitrito complexes are formed, as for M = Cr(III) and various nitrito amine and pyridine complexes of Ni(II),[14] the stability of the nitrito form has been considered as steric in origin,[14] with the angular nitrito ligand presumably offering less steric hindrance from the amine or ammine groups than would be expected for the bulkier nitrogen-coordinated nitro ligand. However, for Cr(III) nitrito complexes the effect may arise predominantly from the inherently greater strength of Cr–O bonds as compared with Cr–N bonds. Both of the above effects may be operative in the isomerization of α-[Co(tetren)ONO]$ZnCl_4$ to β-[Co(tetren)NO_2]$ZnCl_4$, the formation of the thermodynamically more stable nitro complex leading to steric rearrangement of the amine ligand due to the sterically bulky nitro ligand.

Regarding the absolute configuration of $(-)$-β-[Co(tetren)Cl]$ZnCl_4$, tentatively assigned[2] as L on the basis of its optical rotatory dispersion (ORD), we may now confirm this assignment by the circular dichroism (CD) evidence given in Figure 2, which shows a negative CD band at the long-wavelength minimum of the ORD curve. This assignment is based on the relationship of β-Co(tetren)Cl^{2+} to *cis*-α-Co(trien)Cl_2^{+}, as outlined in the first paper[2] of this series, using assumptions essentially the same as those made by Sargeson and Searle[15] for relating the absolute configurations of *cis*-α- and *cis*-β-Co(trien)X_2^{n+} to *cis*-Co(en)$_2X_2^{n+}$. The L configuration corresponds to structure II, Figure 1.

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[9] The isomeric conversion is visually readily apparent if the tetrathiocyanatozincate(II) salts are crystallized inasmuch as the α isomer forms orange crystal clusters, whereas the β isomer forms orange feathery crystals. Infrared or visible absorption spectra are required to distinguish the α and β isomers of the chloro or bromo complexes, on the other hand.

[10] By heating at 80° with 12 *F* HCl and excess $ZnCl_2$ for 15 min.

[11] See F. Basolo and G. S. Hammaker, *Inorg. Chem*., **1**, 1 (1962), and references therein.

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Preparation and Characterization of Tris(diacetamido)chromium(III) and Tris(dibenzamido)chromium(III)

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The new compounds tris(diacetamido)chromium(III), $Cr(C_4H_6O_2N)_3$, and tris(dibenzamido)chromium(III), $Cr(C_{14}H_{10}O_2N)_3$, have been synthesized. Infrared and visible–ultraviolet spectral comparisons suggest that these compounds are structurally analogous to $Cr(acac)_3$ and $Cr(dbm)_3$. The values of *Dq* for the β-diketo and the diamido ligands with Cr(III) are found to be essentially the same. It is concluded that Cr–O π bonding, as it is normally considered to effect *Dq*, cannot be extensive in $Cr(daa)_3$, $Cr(dba)_3$, $Cr(acac)_3$, or $Cr(dbm)_3$.

Introduction

Diacetamide ($CH_3CONHCOCH_3$) and other related amides should be capable of forming metal chelate complexes either in the parent amide form or in the anionic form obtained by removal of the amide hydrogen in a suitable chemical process. This is a property exhibited by only a limited number of ligands, *e.g.*, H_2O and OH^-, NH_3 and NH_2^-. Ionic complexes derived from diacetamide,[1,2] dibenzamide,[3] and other C-alkyl, N-alkyl, and N-phenyl diamides[4] are now known. In 1913, Ley and Werner[5] isolated a compound which analyzed for $Cu(C_6H_5CONCOC_6H_5)_2 \cdot 2H_2O$. To our knowledge this is the only reported neutral transition metal complex derived from a diamide although the nature of attachment of water has not been clearly defined. We wish to report in this paper the syntheses and some physical properties of the new compounds, tris(diacetamido)chromium(III), $Cr(C_4H_6O_2N)_3$, $Cr(daa)_3$, and tris(dibenzamido)chromium(III), $Cr(C_{14}H_{10}O_2N)_3$, $Cr(dba)_3$.

The nature of bonding in these compounds will be discussed in the light of infrared and ultraviolet–visible spectral data. Inasmuch as the diamide, diamido, and β-diketo chelate linkages are isoelectronic and isostructural, the physical properties of these different ligand systems should bear strong relationsips to each other.

Experimental Section

Melting points reported below are uncorrected.

Reagents.—N-Benzoylbenzonitriliumtetrachlorozincate, prepared by the method of Freudenberg,[6] was hydrolyzed over ice and extracted with a saturated solution of sodium bicarbonate to remove residual benzoic acid. The dibenzamide was then extracted from the mixture with 5% sodium hydroxide solution followed by a neutralization of the extract with concentrated hydrochloric acid. The crude product was purified by Soxhlet extraction with diethyl ether to yield a colorless solid (mp 147–148.5°). Diacetamide was prepared by the method of Durrell, Young, and Dresdner[7] and purified by vacuum distillation (mp 78–80°).

Anhydrous chromium(III) chloride was prepared in the laboratory.[8] Chloroform, *n*-hexane, and diethyl ether were used as received from J. T. Baker Chemical Co. (Baker Analyzed reagent). Benzene (Baker Analyzed reagent) was distilled azeotropically to remove the bulk of the water and then drawn through an 18-in. column of activated alumina as needed. Tetrahydrofuran (Matheson Coleman and Bell) was distilled from calcium hydride and redistilled from lithium aluminum hydride directly into the reaction vessels.

Tris(diacetamido)chromium(III).—A slurry of the sodium salt of diacetamide in 150 ml of tetrahydrofuran was prepared from diacetamide (9.1 g, 0.09 mole) and sodium (2.07 g, 0.09 mole). The mixture was heated at reflux and the extent of reaction was monitored by the collection of evolved hydrogen gas; the reaction time to near completion was about 2 days. Anhydrous chromium(III) chloride (4.75 g, 0.03 mole) was added and the mixture was refluxed under nitrogen for 12 hr. At the end of the reflux period the THF was removed under vacuum and the residue was extracted repeatedly with boiling dry benzene to yield a maroon solution. Unreacted anhydrous chromium(III) chloride (0.35 g) was recovered from the reaction residue. The benzene solution was evaporated under vacuum and the resultant maroon solid was transferred under nitrogen to a sublimation apparatus and sublimed at 100° and a pressure of 0.05 mm. The yield was 1.35 g. The sample was further purified by dissolving in diethyl ether, adding 2 vol. of *n*-hexane, filtering, and chilling the filtrate to obtain maroon crystals (mp 180–180.5°). *Anal.* Calcd for $CrC_{12}H_{18}N_3O_6$: C, 40.91; H, 5.15; N, 11.93. Found: C, 41.16; H, 5.06; N, 12.05.

Tris(dibenzamido)chromium(III).—Dibenzamide (10.2 g, 0.045 mole) was dissolved in THF (100 ml) containing finely divided sodium (1.0 g, 0.045 mole). The solution became red-orange and the reaction was assumed complete with the dis-

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