

Bis(ethylenediamine)(L-2,3-diaminopropionic acid)platinum(IV) Chloride. Preparation, Resolution, and Determination of Absolute Configuration

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The reaction of K_2PtCl_4 with L-2,3-diaminopropionic acid gives dichloro(L-2,3-diaminopropionic acid)platinum(II), which is oxidized by chlorine to tetrachloro(L-2,3-diaminopropionic acid)platinum(IV). Bis(ethylenediamine)(L-2,3-diaminopropionic acid)platinum(IV) chloride, $[Pt(en)_2L-Dap]Cl_4$, is obtained by reacting ethylenediamine with tetrachloro(L-2,3-diaminopropionic acid)platinum(IV). This complex is resolved into diastereoisomers through the *d*-tartrate salt. The resolved complex can be prepared directly from the reaction of L-2,3-diaminopropionic acid on optically active *cis*-dichlorobis(ethylenediamine)platinum(IV) chloride. Based on the known absolute configuration of $(+)_365-cis-[Pt(en)_2Cl_2]Cl_2$, it is proposed that the absolute configuration of $(+)_312-[Pt(en)_2L-Dap]Cl_4$ is $\Delta(\lambda_{en}\lambda_{en}\lambda_{Dap})$ and that of $(-)_320-[Pt(en)_2L-Dap]Cl_4$ is $\Lambda(\delta_{en}\delta_{en}\lambda_{Dap})$. ORD, CD, and proton NMR spectra of the two diastereoisomers are discussed.

Introduction

Only a few optically active platinum(IV) complexes with mixed bidentate ligands have been prepared.¹ We have prepared optical diastereoisomers of bis(ethylenediamine)-(L-2,3-diaminopropionic acid)platinum(IV) chloride, $[Pt(en)_2L-Dap]Cl_4$, by two different methods. The complex can be prepared by coordinating first L-2,3-diaminopropionic acid as a bidentate ligand and then two molecules of ethylenediamine to the metal ion. It can also be prepared by the substitution reaction of *cis*- $[Pt(en)_2Cl_2]Cl_2$ with L-2,3-diaminopropionic acid.

Though it was possible, in certain cases, to assign the absolute configuration of complexes on the basis of the stereospecificity of the ligands, the relative solubilities of the diastereoisomeric salts, and the sign of the ORD or CD spectra, the x-ray structure determination² of $(+)-[Co(en)_3]^{3+}$ gave the first positive basis for the assignment of absolute configurations for cobalt(III) complexes. In the case of Pt(IV) complexes, no such basis for the absolute configuration existed until Liu and Ibérs³ determined the structure of optically active *cis*-dichlorobis(ethylenediamine)platinum(IV) chloride, $(+)_365-cis-[Pt(en)_2Cl_2]Cl_2$, by x-ray crystallographic methods. Since our compound can also be prepared directly from $(+)_365-cis-[Pt(en)_2Cl_2]Cl_2$, it is possible to assign correct absolute configurations for our resolved isomers.

As the ligand L-2,3-diaminopropionic acid is expected to have the same chelate ring conformation in both diastereoisomeric complexes, the proton NMR, ORD, and CD spectra of these complexes are of interest in regard to the interactions between the configuration of metal complex and the conformation of chelate ring.

Experimental Section

Reagents. L-2,3-Diaminopropionic acid hydrochloride (L-DapHCl) is purchased from Calbiochemical, San Diego, Calif. $[\alpha]_D$ in 1 N HCl 25.7°. Ethylenediamine (en) was obtained from Aldrich Chemical Co., Milwaukee, Wis. Platinum metals, purchased from Goldsmith Chemical and Metal Corporation, Evanston, Ill., as platinum clips, are used to make K_2PtCl_4 . Optically active *cis*-dichlorobis(ethylenediamine)platinum(IV) chloride, $(+)_365-$ and $(-)_365-cis-[Pt(en)_2Cl_2]Cl_2$, is prepared as described.⁴

Preparation of *cis*-Dichloro(L-2,3-diaminopropionic acid)platinum(II), $[Pt(L-Dap)Cl_2]$. To a solution of 4.15 g (0.010 mol) of K_2PtCl_4 in 40 ml of water is added 1.40 g (0.010 mol) of L-2,3-diaminopropionic acid hydrochloride dissolved in 30 ml of water. The dark red precipitate which separates immediately is dissolved when the solution is heated to boiling. To this boiling solution, 48.2 ml of 0.415 N KOH (0.020 mol) is added gradually. Care is taken to keep the pH below 6 until 90% of base is added. The resulting yellow solution is evaporated to dryness on a steam bath with a stream of air. The brown mass is recrystallized twice from dilute hydrochloric acid. The final yellow *cis*-dichloro(L-2,3-diaminopropionic acid)platinum(II) $[Pt(L-Dap)Cl_2]$ is washed with alcohol and ether: yield

0.77 g (21%); $[\alpha]_{420}$ in 1 N HCl 44°. Anal. Calcd for $[PtC_3H_8N_2O_2Cl_2]$: Pt, 52.71; C, 9.74; H, 2.18; N, 7.57; Cl, 19.16. Found: Pt, 52.81; C, 9.78; H, 2.22; N, 7.60; Cl, 19.15.

Oxidation of *cis*-Dichloro(L-2,3-diaminopropionic acid)platinum(II) with Chlorine. Chlorine gas is passed for 5 min through the cold solution of 0.70 g of *cis*-dichloro(L-2,3-diaminopropionic acid)platinum(II) dissolved in 70 ml of dilute hydrochloric acid. The solution is evaporated to dryness on a steam bath. The resulting yellow substance is extracted with dilute hydrochloric acid and the latter solvent is evaporated on a steam bath. The product is then extracted twice with ethanol. The bright yellow solid is filtered with the aid of ether: yield 0.88 g (96%); $[\alpha]_{434}$ in 1 N HCl 186°. Anal. Calcd for $[PtC_3H_8N_2O_2Cl_4] \cdot C_2H_5OH$: Pt, 40.04; C, 12.33; H, 2.90; N, 5.75; Cl, 29.11. Found: Pt, 40.24; C, 12.14; H, 2.62; N, 5.79; Cl, 29.05.

Preparation of Bis(ethylenediamine)(L-2,3-diaminopropionic acid)platinum(IV) Chloride, $[Pt(en)_2L-Dap]Cl_4$. A solution of 0.80 g (1.81 mmol) of tetrachloro(L-2,3-diaminopropionic acid)platinum(IV) in 15 ml of dimethylformamide is treated with 0.27 ml (4.04 mmol) of 99% ($d = 0.899$) ethylenediamine. A pale yellow solid separates immediately. The reaction mixture is allowed to stand at room temperature for 3 h. After 3 h, 30 ml of acetone containing 1 ml of concentrated HCl is added to the mixture. The precipitate is filtered and recrystallized from dilute hydrochloric acid to obtain white bis(ethylenediamine)(L-2,3-diaminopropionic acid)platinum(IV) chloride: yield 0.60 g (59%); $[\alpha]_{308}$ in 1 N HCl 134°. Anal. Calcd for $[PtC_7H_{24}N_6O_2]Cl_4 \cdot 1.5H_2O$: Pt, 33.16; C, 14.29; H, 4.63; N, 14.29; Cl, 24.10. Found: Pt, 32.69; C, 15.17; H, 4.57; N, 14.37; Cl, 23.57.

Resolution of Bis(ethylenediamine)(L-2,3-diaminopropionic acid)platinum(IV) Chloride. To a solution of 0.561 g (1.0 mmol) of $[Pt(en)_2L-Dap]Cl_4$ and 0.300 g (2.0 mmol) of *d*-tartaric acid dissolved in 30 ml of water is added 5.00 ml of 1 N LiOH (5.0 mmol). The white sticky precipitate which appears first becomes crystalline while the solution is digested on a steam bath for 15 min. The hot solution is filtered and the white crystalline product is washed with boiling water, ethanol, and ether: yield 0.16 g. Anal. Calcd for $[PtC_7H_{23}N_6O_2](C_4H_4O_6)_{1.5} \cdot 4H_2O$: Pt, 27.38; C, 21.91; H, 5.23; N, 11.80. Found: Pt, 27.41; C, 22.41; H, 4.82; N, 11.68.

The diastereoisomer is treated with a small amount of concentrated hydrochloric acid and alcohol and warmed on a steam bath. The white complex chloride is filtered and washed with alcohol and ether. It is recrystallized to constant rotation from dilute hydrochloric acid: yield 0.16 g; $[\alpha]_{312}$ in 1 N HCl 418°. Anal. Calcd for $[PtC_7H_{24}N_6O_2]Cl_4 \cdot H_2O$: Pt, 33.68; C, 14.51; H, 4.52; N, 14.51; Cl, 24.48. Found: Pt, 33.31; C, 15.05; H, 4.16; N, 14.51; Cl, 23.71.

The filtrate and washings from the above tartrate diastereoisomer are concentrated on a steam bath to yield several fractions of crystalline material. The yields are 0.10, 0.11, 0.11, and 0.18 g, respectively, the last two fractions being much more soluble than the first two. The last two fractions are converted to the chloride as described above and then fractionally crystallized from dilute hydrochloric acid. The most soluble material is recrystallized once more from dilute hydrochloric acid and washed with ethanol and ether: $[\alpha]_{320}$ in 1 N HCl -227°. Anal. Calcd for $[PtC_7H_{24}N_6O_2]Cl_4 \cdot 2H_2O$: Pt, 32.66; C, 14.08; H, 4.72; N, 14.07; Cl, 23.74. Found: Pt, 33.00; C, 14.91; H, 4.37; N, 14.06; Cl, 23.34.

Preparation of Bis(ethylenediamine)(L-2,3-diaminopropionic acid)platinum(IV) Chloride from *cis*-Dichlorobis(ethylenediamine)platinum(IV) Chloride. To a suspension of 0.105 g (0.230 mmol) of (-)₃₆₅-*cis*-dichlorobis(ethylenediamine)platinum(IV) chloride, (-)₃₆₅-*cis*-[Pt(en)₂Cl₂]Cl₂, in 2 ml of dimethylformamide, 0.065 g (0.461 mmol) of L-2,3-diaminopropionic acid and 0.46 ml of 1 N NaOH are added. When the resulting clear solution is warmed at 60 °C for 20 min, a yellow gellike precipitate is formed. After 3 h at room temperature 30 ml of acetone containing 1 ml of concentrated hydrochloric acid is added to the mixture. The white precipitate (-)₃₂₀-bis(ethylenediamine)(L-2,3-diaminopropionic acid)platinum(IV) chloride, (-)₃₂₀-[Pt(en)₂L-Dap]Cl₄, is filtered, washed with acetone, and then recrystallized from dilute hydrochloric acid: yield 0.084 g (61%); [α]₃₂₀ in 1 N HCl -263°. Anal. Calcd for [PtC₇H₂₄N₆O₂]Cl₄·2H₂O: Pt, 32.66; C, 14.08; H, 4.72; N, 14.07; Cl, 23.74. Found: Pt, 33.02; C, 14.13; H, 4.50; N, 14.20; Cl, 23.77.

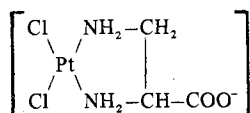
Starting with (+)₃₆₅-*cis*-dichlorobis(ethylenediamine)platinum(IV) chloride, white (+)₃₁₂-bis(ethylenediamine)(L-2,3-diaminopropionic acid)platinum(IV) chloride, (+)₃₁₂-[Pt(en)₂L-Dap]Cl₄, is obtained in a similar way: [α]₃₁₂ in 1 N HCl 430°. Anal. Calcd for [PtC₇H₂₄N₆O₂]Cl₄·2H₂O: Pt, 32.66; C, 14.08; H, 4.72; N, 14.07; Cl, 23.74. Found: Pt, 32.94; C, 14.20; H, 4.36; N, 14.22; Cl, 23.76.

Instrumental Measurements. ORD and CD spectra are obtained at room temperature using a Durrum-Jasco SS-20 spectrometer. Proton NMR spectra are recorded on a Varian A-60 spectrometer. Chemical shifts are measured with respect to sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) in D₂O solvent.

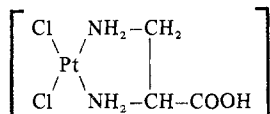
Analyses. Elemental analyses are performed by Spang Micro-analytical Laboratory, Ann Arbor, Mich., and Micro-Tech Laboratories, Inc., Skokie, Ill.

Results and Discussion

The procedure given for the preparation of bis(ethylenediamine)((*R*)-propylenediamine)platinum(IV) chloride by Dwyer and Sargeson⁵ has to be modified for the synthesis of bis(ethylenediamine)(L-2,3-diaminopropionic acid)platinum(IV) chloride because the ligand L-2,3-diaminopropionic acid has a third functional group (i.e., carboxyl group) in addition to the two amino groups for coordination. Since this carboxyl group is very acidic (pK_a is 1.33⁶), coordination of the ligand to platinum(II) through two amino nitrogens is not complete until 2 mol of base is added to 1 mol of ligand monohydrochloride. The resulting complex,



has a free carboxylate group and is very soluble in water. Therefore, the complex is isolated as the less soluble



form from acidic solution. Oxidation of the latter to [Pt(L-Dap)Cl₄] is carried out also in dilute hydrochloric acid to prevent the coordination of the ionized carboxylate oxygen to platinum(IV).

Unlike bis(ethylenediamine)((*R*)-propylenediamine)platinum(IV) ion,⁵ the bis(ethylenediamine)(L-2,3-diaminopropionic acid)platinum(IV) ion and the tartrate, either *d*-tartrate or *l*-tartrate, do not form a well-defined crystalline diastereoisomer, and a rather sticky mass is obtained so that the resolution is not possible. Successful resolution is obtained with *d*-tartaric acid in the presence of LiOH.

ORD and CD spectra of the resolved complexes (+)₃₁₂-[Pt(en)₂L-Dap]Cl₄ and (-)₃₂₀-[Pt(en)₂L-Dap]Cl₄ are shown in Figure 1. In addition to the dissociation of a proton from the amino group, which has been reported earlier,⁷ there is an additional dissociation of a proton due to the presence of

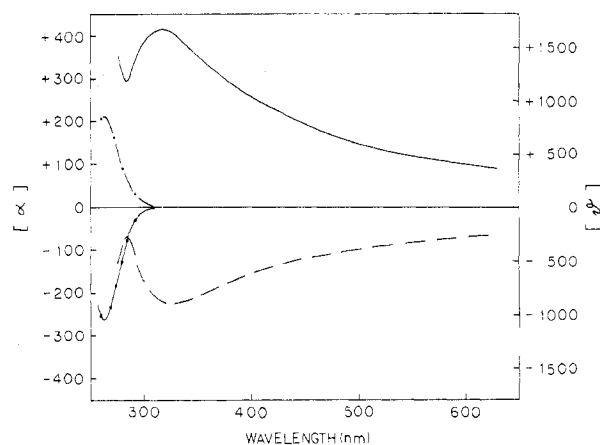


Figure 1. ORD and CD spectra of optical isomers of bis(ethylenediamine)(L-2,3-diaminopropionic acid)platinum(IV) chloride in 1 N HCl: (+)₃₁₂-[Pt(en)₂L-Dap]Cl₄, ORD (—) and CD (—●—); (-)₃₂₀-[Pt(en)₂L-Dap]Cl₄, ORD (---) and CD (- - -).

an uncoordinated carboxyl group in the Dap ligand. The spectra, therefore, are taken in 1 N HCl solution. Compared with the corresponding spectra in water, the ORD maximum shifts to higher wavelength by 10–20 nm and the molar rotation at this wavelength decreases in acidic solution. Mathieu⁸ showed in the case of (-)-[Pt(en)₃]Cl₄ that the optical rotation at the sodium D line has the opposite sign to the long wavelength CD and that the former comes from absorption at 190 nm. Larsson and his co-workers⁷ studied Pt(IV) complexes of en and *R*- and *S*-pn and showed that d-d transitions of these complexes appear as shoulders at 270 nm and 230 nm on a much stronger charge transfer band which has a peak at 188 nm. These two transitions (d-d and charge transfer) have the opposite signs in CD and it is the stronger charge transfer band which contributes predominantly to the visible optical rotation. The present Pt(IV)-diamine complexes also show visible optical rotation and a long wavelength CD peak with opposite signs.

Until recently the absolute configuration of optically active platinum(IV) complexes has been determined on the basis of stereospecific effects of the ligand with respect to the configuration of the complex, the relative solubilities of diastereoisomeric salts, and the ORD and CD spectra of the complex. Larsson and his co-workers⁷ assigned absolute configurations for platinum(IV) complexes containing ethylenediamine and optically active propylenediamine based on these criteria. Dwyer and Garvan⁹ reported that (+)-[Pt(*R*-pn)₃]⁴⁺ is the major product (over (-)-[Pt(*R*-pn)₃]⁴⁺) when hydrogen hexachloroplatinate(IV) is reacted with *R*-pn in ethanolic solution. Since the stable conformation of *R*-pn is λ, the above (+) isomer has the Δλλλ configuration,¹⁰ whereas the (-) isomer has the Δλλλ configuration, in agreement with the conformational analysis by Corey and Bailar.¹¹ In the case of cobalt(III) complexes of *R*-pn, the stereospecificity of the result obtained has been proven by x-ray crystallography. Similarly, the absolute configurations for some platinum(IV) complexes of mixed ligands containing ethylenediamine and optically active propylenediamine were assigned if the product ratio indicated preference of one isomer over the other. It should, however, be remembered that the product ratio does not necessarily reveal thermodynamic stability of different diastereoisomers. Different product ratios have been obtained for the formation of [Pt(*R*-pn)₃]⁴⁺ in dimethylformamide and in ethanol: 60:40 in dimethylformamide and 85:15 in ethanol.⁵ In other cases such as the formation of [Pt(en)₂*R*-pn]Cl₄ it is not possible to deduce absolute configuration solely on the product ratio, since approximately equal amounts of both isomers are formed. The

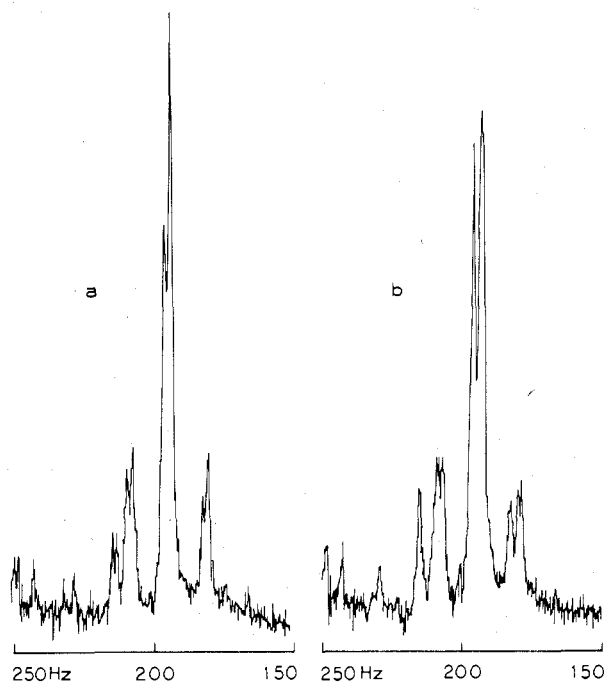


Figure 2. Proton NMR spectra of $(+)_312$ -[Pt(en)₂L-Dap]Cl₄ (a) and $(-)_320$ -[Pt(en)₂L-Dap]Cl₄ (b) with DSS as internal standard.

formation of our complex, racemic [Pt(en)₂L-Dap]Cl₄, also does not show favorable formation of one isomer over the other.

Larsson et al.⁷ concluded that the sign of the major circular dichroism band associated with the long wavelength absorption of the complex is related to the configuration of the complex and, specifically, if the sign is positive, the complex is related to $(+)$ -[Co(en)₃]³⁺ which is known from x-ray studies to have the Δ configuration. Accordingly, the CD spectra in Figure 1 show that $(+)_312$ -[Pt(en)₂L-Dap]Cl₄ has the Δ configuration and $(-)_320$ -[Pt(en)₂L-Dap]Cl₄ has the Λ configuration.

The same authors also applied Werner's less soluble diastereoisomer rule¹² and concluded that the platinum(IV) complexes of ethylenediamine and optically active propylenediamine have the same configuration as $(+)$ -[Co(en)₃]³⁺ if the less soluble diastereoisomeric salt is formed with *d*-tartrate anion. Thus, $(+)_312$ -[Pt(en)₂L-Dap]Cl₄ is expected to have the Δ configuration since it forms the less soluble salt with *d*-tartrate. This is contrary to the conclusion drawn above from CD spectra. Jaeger¹³ has stated that the Werner's less soluble diastereoisomer rule is applicable only to compounds which are isomorphous with one another. The tartrate salt of bis(ethylenediamine)(L-2,3-diaminopropionic acid)platinum(IV), analyzed as [Pt(en)₂L-Dap](tartrate)_{1.5}, is not expected to be isomorphous with the tartrate salt of bis(ethylenediamine)((*R*)-propylenediamine)platinum(IV), analyzed as [Pt(en)₂R-pn](tartrate)₂.

We propose that the absolute configuration of platinum(IV) complexes can be determined on the basis of known absolute configuration of $(+)_365$ -*cis*-dichlorobis(ethylenediamine)platinum(IV) chloride, $(+)_365$ -*cis*-[Pt(en)₂Cl₂]Cl₂. Liu and Ibers³ have determined the structure of $(+)_365$ -*cis*-[Pt(en)₂Cl₂]Cl₂ by x-ray diffraction methods. The complex has the Δ configuration and the two ethylenediamine chelate rings take λ conformations. The individual diastereoisomers of [Pt(en)₂L-Dap]Cl₄ can be prepared from the reaction of L-diaminopropionic acid on resolved [Pt(en)₂Cl₂]Cl₂ as shown in the Experimental Section. The ORD and CD spectra of bis(ethylenediamine)(L-2,3-diaminopropionic acid)platinum(IV) chloride prepared from $(+)_365$ -*cis*-[Pt(en)₂Cl₂]Cl₂ and L-Dap are exactly the same as those of resolved $(+)_312$ -[Pt(en)₂L-Dap]Cl₄. In the same way the ORD and CD

spectra of bis(ethylenediamine)(L-2,3-diaminopropionic acid)platinum(IV) chloride prepared from $(-)_365$ -*cis*-[Pt(en)₂Cl₂]Cl₂ and L-Dap match those of resolved $(-)_320$ -[Pt(en)₂L-Dap]Cl₄. This shows that the reaction occurs without any appreciable racemization. The reaction of *cis*-[Pt(en)₂Cl₂]Cl₂ with ethylenediamine or (*R*)-propylenediamine has been studied and the results support the same conclusion.¹⁴ Provided that there is no inversion at Pt(IV) during the formation of [Pt(en)₂L-Dap]Cl₄ from *cis*-[Pt(en)₂Cl₂]Cl₂, the configuration of $(+)_312$ -[Pt(en)₂L-Dap]Cl₄ is then Δ and that of $(-)_320$ -[Pt(en)₂L-Dap]Cl₄ is Λ .

In order to obtain good agreement between optical rotation at the sodium D line and the effects of conformation and configuration, Larsson et al.⁷ assumed that the ethylenediamine chelate ring does not prefer any particular conformation in the case of platinum(IV) complexes, while in the case of cobalt(III) complexes, the ethylenediamine chelate ring prefers a λ conformation in the Δ configuration and a δ conformation in the Λ configuration. They explained that the ethylenediamine chelate ring in platinum(IV) complexes may be more labile due to the large size of platinum(IV) and to the acidic properties of the complex. The x-ray result on $(+)_365$ -*cis*-[Pt(en)₂Cl₂]Cl₂,³ however, shows that the Pt-N or Pt-Cl distances are comparable to the corresponding Co-N or Co-Cl distances, and ethylenediamine prefers a λ conformation in the Δ complex configuration as in the case of cobalt(III) complexes. The heavier platinum may assume a bigger size than lighter cobalt, but the higher charge on platinum(IV) brings the ligand close to the metal, so that the platinum(IV)-ligand distance falls in the same range as the cobalt-ligand distance. Therefore, the proposed absolute configuration of $(+)_312$ -[Pt(en)₂L-Dap]Cl₄ is $\Delta_{\lambda\text{en}\lambda\text{en}\lambda\text{L-Dap}}$ and that of $(-)_320$ -[Pt(en)₂L-Dap]Cl₄ is $\Lambda_{\delta\text{en}\delta\text{en}\lambda\text{L-Dap}}$.

This is further illustrated by proton NMR spectra shown in Figure 2. Though the three chelate rings in $(+)_312$ -[Pt(en)₂L-Dap]Cl₄ take the same λ conformation, the methylene group of coordinated L-Dap is different from the methylene groups of ethylenediamine due to the dissymmetrical nature of the former ligand. Unlike the case of [Pt(en)₃]Cl₄ where a clear triplet due to Pt¹⁹⁵ is observed, Figure 2 shows that the methylene triplet is further split. The chemical shift of the methylene proton of coordinated diaminopropionic acid is lower than the chemical shift of the methylene proton of coordinated ethylenediamine. The C-C axis of diaminopropionic acid in $(+)_312$ -[Pt(en)₂L-Dap]Cl₄ is parallel to the pseudo-C₃ axis of the complex, whereas the C-C axis of diaminopropionic acid in $(-)_320$ -[Pt(en)₂L-Dap]Cl₄ is oblique to the pseudo-C₃ axis of the complex. This difference is seen in Figure 2 where the center peak of the methylene proton triplet is more clearly split in $(-)_320$ -[Pt(en)₂L-Dap]Cl₄. In both spectra the presence of a methine proton causes further splitting of methylene peaks.

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Registry No. [Pt(L-Dap)Cl₂], 25880-75-5; [Pt(L-Dap)Cl₄], 59982-43-3; [Pt(en)₂L-Dap]Cl₄, 59982-44-4; Δ - $(+)_312$ -[Pt(en)₂L-Dap](C₄H₄O₆)_{1.5}, 60018-55-5; Δ - $(+)_312$ -[Pt(en)₂L-Dap]Cl₄, 60018-56-6; Λ - $(-)_320$ -[Pt(en)₂L-Dap]Cl₄, 60018-57-7; Λ - $(-)_365$ -*cis*-[Pt(en)₂Cl₂]Cl₂, 18661-28-4; Δ - $(+)_365$ -*cis*-[Pt(en)₂Cl₂]Cl₂, 28491-18-1.

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Synthesis and Reactions of Cationic Perfluoropropyliron Carbonyl Acetonitrile Complexes

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The reaction of $n\text{-C}_3\text{F}_7\text{Fe}(\text{CO})_4\text{I}$ with silver hexafluorophosphate, AgPF_6 , in acetonitrile at room temperature affords $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})_3]\text{PF}_6$ in almost quantitative yield. A characteristic feature of the $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})_3]^+$ cation is the extreme lability of its unique CH_3CN ligand; the two mutually equivalent CH_3CN groups are much less labile. This is illustrated by the selective exchange of only the unique CH_3CN ligand with free CD_3CN and by reactions of $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})_3]\text{PF}_6$ with group 5 Lewis bases (L). The latter reactions afford only *monosubstituted* $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})_2\text{L}]\text{PF}_6$ derivatives even in the presence of excess L. The reactivity of the $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})_3]^+$ cation is compared with that of the isoelectronic *fac*- $[\text{Mn}(\text{CO})_3(\text{CH}_3\text{CN})_3]^+$ cation.

Introduction

The chemistry of the $\text{Mn}(\text{CO})_5$ group has been investigated in great detail.¹⁻³ The isoelectronic relationship between $\text{Mn}(\text{CO})_5$ and $\text{RFe}(\text{CO})_4$ (R = alkyl) would suggest that an analogous extensive chemistry might be based upon the $\text{RFe}(\text{CO})_4$ group. This has been realized in part with the use of *perfluoroalkyl* R substituents, particularly $n\text{-C}_3\text{F}_7$, on the iron moiety. Known analogues in the isoelectronic $\text{C}_3\text{F}_7\text{-Fe}(\text{CO})_4$ and $\text{Mn}(\text{CO})_5$ series include the following: (1) mononuclear iodides, $\text{C}_3\text{F}_7\text{Fe}(\text{CO})_4\text{I}^4$ and $\text{Mn}(\text{CO})_5\text{I}^5$ and corresponding derivatives formed by substitution of one or two CO groups with phosphorus^{6,7} and nitrogen^{6,8} donor ligands; (2) dinuclear iodides, $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_3\text{I}]_2^4$ and $[\text{Mn}(\text{CO})_4\text{I}]_2^9$; (3) hydrides, $\text{C}_3\text{F}_7\text{Fe}(\text{CO})_4\text{H}^{10}$ and $\text{Mn}(\text{CO})_5\text{H}^{11}$; (4) perfluorocarbon derivatives, $(\text{C}_3\text{F}_7)_2\text{Fe}(\text{CO})_4^4$ and $\text{C}_3\text{F}_7\text{-Mn}(\text{CO})_5^{12}$ and $(\text{C}_3\text{F}_7)(\text{C}_4\text{F}_7)\text{Fe}(\text{CO})_4^{13}$ and $\text{C}_4\text{F}_7\text{Mn}(\text{CO})_5^{13}$; (5) mercury derivatives, $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_4]_2\text{Hg}^{10}$ and $[\text{Mn}(\text{CO})_5]_2\text{Hg}^{14}$; (6) anions, $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_4]^-^{10,15}$ and $[\text{Mn}(\text{CO})_5]^-^{16,17}$; (7) cations, $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_2(\text{NH}_3)_3]^+^8$ and $[\text{Mn}(\text{CO})_3(\text{NH}_3)_3]^+^{18}$.

Although the preparation of cationic manganese carbonyl derivatives has received considerable attention,¹⁹⁻²¹ cationic $\text{C}_3\text{F}_7\text{Fe}$ analogues are limited to the single example cited above. In view of both the recent interest^{20,21} in cationic derivatives of $[\text{Mn}(\text{CO})_6]^+$ and our own interest²² in the synthesis and reactivity of metal carbonyl cations, we have investigated the preparation of cationic carbonyls formally derived from the unknown $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_5]^+$ cation. We report here the facile preparation of the $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})_3]^+$ cation, an isoelectronic analogue of the well-known^{20,21} *fac*- $[\text{Mn}(\text{CO})_3(\text{CH}_3\text{CN})_3]^+$ cation, as well as a series of derivatives obtained from reaction of this iron cation with various Lewis bases. In addition to extending the isoelectronic analogy between $\text{C}_3\text{F}_7\text{Fe}(\text{CO})_4$ and $\text{Mn}(\text{CO})_5$, the complexes reported herein are further examples of the relatively limited class of *cationic* fluorocarbon-metal carbonyls.²³

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of nitrogen. Microanalyses (Table I) were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points (Table I) were taken in capillaries sealed under nitrogen and are uncorrected.

Materials. All solvents (reagent grade) were dried by appropriate methods and were saturated with nitrogen prior to use. The following compounds were purchased from the indicated commercial source and were used without further purification: $n\text{-C}_3\text{F}_7\text{I}$ (PCR, Inc.);

Table I. Analytical Data and Melting Points

| Complex | Mp, °C | Elemental analyses, calcd (found), % | | |
|---|------------|--------------------------------------|----------------|----------------|
| | | C | H | N |
| $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})_3]\text{PF}_6$ | 112 dec | 24.06 (23.82) | 1.65 (1.61) | 7.65 (7.53) |
| $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})_2\text{-PPh}_3]\text{PF}_6$ | 143 dec | 42.10 (41.54) | 2.75 (2.70) | 3.64 (3.49) |
| $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})_2\text{-AsPh}_3]\text{PF}_6$ | 128 | 39.83 (39.24) | 2.60 (2.47) | 3.44 (3.32) |
| $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})_2\text{-P(OMe)}_3]\text{PF}_6$ | 143 | 22.80 (22.28) | 2.39 (2.30) | 4.43 (4.31) |
| $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})_2\text{-P(OEt)}_3]\text{PF}_6$ | 141 | 26.73 (26.92) | 3.14 (3.14) | 4.16 (4.00) |
| $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})_2\text{-P(OPh)}_3]\text{PF}_6$ | 96 | 39.63 (39.23) | 2.59 (2.54) | 3.42 (3.26) |
| $\{[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})_2]_2\text{-diphos}\}(\text{PF}_6)_2$ | 139 dec | 37.37 (37.30) | 2.56 (2.59) | 3.96 (3.81) |
| $\text{C}_3\text{F}_7\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})_2\text{I}$ | 125 dec | 22.07 (21.98) | 1.23 (1.32) | 5.72 (5.59) |

$\text{Fe}(\text{CO})_5$, PPh_3 , $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (Pressure Chemical Co.); AgPF_6 (Ozark-Mahoning Co.); P(OPh)_3 , AsPh_3 (Aldrich Chemical Co.); P(OMe)_3 , P(OEt)_3 (MC/B). Other chemicals were of reagent grade. The compound $\text{C}_3\text{F}_7\text{Fe}(\text{CO})_4\text{I}$ was prepared from $\text{C}_3\text{F}_7\text{I}$ and $\text{Fe}(\text{CO})_5$ according to the method of King.²⁴

Spectra. Infrared spectra (Table II) were obtained on a Perkin-Elmer 180 spectrometer calibrated with carbon monoxide, polystyrene, and indene. All spectra were run in KBr cells using dichloromethane as solvent.

Proton NMR spectra (Table II) were recorded at 60 MHz on a JEOL C-60-H instrument using internal TMS as reference and acetone- d_6 , dichloromethane- d_2 , or acetonitrile- d_3 as solvent. The ^{19}F NMR spectra (Table II) were obtained at 56.4 MHz on the same instrument and were recorded for <5 mol% solutions in dichloromethane or acetone. Hexafluorobenzene was used as internal reference and chemical shifts are presented relative to CFCl_3 using the conversion:²⁵

$$\delta_{\text{CFCl}_3} = \delta_{\text{C}_6\text{F}_6} + 162.9 \text{ ppm}$$

Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6 mass spectrometer at 70 eV with a chamber temperature of 200 °C and a sample temperature of 95 °C.

Preparation of $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})_3]\text{PF}_6$. A solution of AgPF_6 (6.31 g, 24.9 mmol) in 50 ml of acetonitrile was added dropwise to a solution of $\text{C}_3\text{F}_7\text{Fe}(\text{CO})_4\text{I}$ (11.1 g, 23.4 mmol) in 40 ml of acetonitrile. Immediate precipitation of AgI occurred. The solution was stirred for 1.5 h at room temperature and AgI was removed by filtration. The bright orange filtrate was evaporated to dryness in