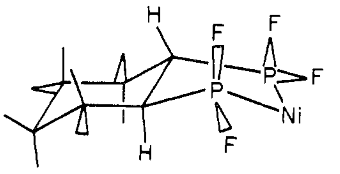
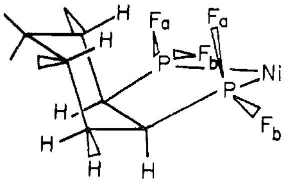
to the dominant,[3] coordinated trans ligand isomer, structure **1**. Inspection of models indicates that, in structure **1**, the four fluorine nuclei will interact equivalently with the ring protons, especially given rapid ring inversion on the NMR time scale, giving a single chemical shift for all four nuclei. The two small doublets are assigned to the coordinated cis ligand isomer, structure **2**. In this case, rapid ring inversion leads always to two sets of two fluorine nuclei (labeled a and b) which interact differently with the ring protons. It is noteworthy that no evidence for a cis–trans isomer mixture was observed in the NMR spectra (either ^{19}F or ^{31}P) of the uncoordinated ligand.[3] A complex multiplet was observed in the ^{19}F spectrum of the ligand which showed no temperature dependence and which was entirely consistent with the presence of a single isomer. The free ligand spectrum consisted of a mirror image about the center point, each half containing nine resolved lines in a pattern completely reminiscent of the spectra of other F_2PMPF_2 species.[6] Further unambiguous resolution of the eight expected doublets[6] was not achieved due, likely, to coupling with the ring protons. On this basis, it appears either that some ring isomerization occurred during the reaction or that whatever minor component of cis isomer may have been present in the ligand (<10%) was preferentially coordinated. The latter interpretation seems suspect in that more steric crowding is apparent in the cis ligand complex, **2**, than in the trans ligand complex. The spectra do not allow analysis of the isomer mixture of complexes, i.e., bis[*cis*-, bis[*trans*-, and bis[*cis*,*trans*-1,2-bis(difluorophosphino)cyclohexane]nickel(0).



1



2

The 100.1-MHz proton NMR spectrum of bis[1,2-bis(difluorophosphino)cyclohexane]nickel(0) gives a complex multiplet at δ 2.12 with benzene as the internal reference (free ligand, δ 1.97, broad peak).

The solid-phase infrared spectrum of the complex consists of the following bands (cm^{-1}) with some tentative assignments as shown: 2895 vs (ν_{CH}), 2835 vs (ν_{CH}), 1435 s (δ_{CH_2}), 1326 w, 1301 w, 1267 w, 1179 w, 1164 w, 1063 m, 1040 w, 988 w, 865 m, sh, 779 vs, br (ν_{PF}), 710 vs (ν_{PF}), 604 w, 506 m, 483 w, 373 w. Absorptions in the CO region were not observed. The coordinated ligand P–F stretch is seen at 779 cm^{-1} as compared to the free ligand P–F stretch at 799 cm^{-1} suggesting,[5] as expected, a significant $d\pi$–$d\pi$ bonding interaction between phosphorus and nickel.

The mass spectrum contains two intense fragments, one which corresponds to the parent ion at *m/e* 498 [$(NiP_4F_8C_{12}H_{20})^+$, 100%] and one at *m/e* 278 [$(NiP_2F_4C_6H_{10})^+$, 35%] which represents the loss of one bis(difluorophosphino)cyclohexane moiety from the molecule. In both cases, the nickel isotope envelope was present and consistent. Only two other peaks of relative intensity greater than 5% were observed: *m/e* 138 ($P_2F_4^+$ and $NiC_6H_8^+$, 10%) and 82 ($C_6H_{10}^+$, 6%). The formulation as a coordination monomer was confirmed by vapor pressure osmometry.

The mild conditions required for the complete displacement of CO from $Ni(CO)_4$ are in contrast to those required for displacement by PF_3[7] and illustrate the effective combination of π-acceptor and chelating character in this ligand.

Acknowledgment. The support of the U.S. Army Research Office—Durham and Research Corp. is gratefully acknowledged. We thank Mr. A. Srinivasan for assistance in obtaining NMR data.

Registry No. $Ni(P_2F_4C_6H_{10})_2$, 56488-42-7; $Ni(CO)_4$, 13463-39-3.

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Contribution from the Departments of Chemistry and
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Facile Separation of the Cis Isomers of Dicyclohexyl-18-crown-6[1]

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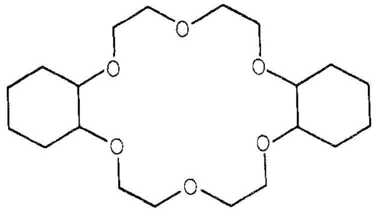
Since crown ethers were first reported by Pedersen,[3] they have been used extensively as cation complexing agents.[4,5] Owing to its ready availability and favorable solubility characteristics, dicyclohexyl-18-crown-6 (I)[3] has found the most use in recent years.[5] When compound I is produced from the catalytic hydrogenation of dibenzo-18-crown-6, two of the possible five isomers of dicyclohexyl-18-crown-6 are produced and have been identified structurally as the cis-syn-cis[7,8] (Ia) and cis-anti-cis[8,9] (Ib) isomers. We have found that the two isomers of I have markedly different ligating properties toward mono- and divalent cations in aqueous and polar, nonaqueous solvents.[10,11] For a given cation, Ia usually has a larger equilibrium constant of formation than does Ib. As expected, Ag^+ reacts in water both with Ia ($\log K = 2.3$)[12] and with Ib ($\log K = 1.6$);[10] however, the reaction with Ia is almost entirely due to favorable entropy effects, $\Delta S = +11$ eu,[11] while the reaction with Ib is almost entirely due to favorable enthalpy effects, $\Delta H = -2.1$ kcal/mol.[10]



Ia, cis-syn-cis isomer
Ib, cis-anti-cis isomer

The two cis isomers of dicyclohexyl-18-crown-6 have been separated by column chromatography on Woelm alumina (activity grade I) using *n*-hexane–diethyl ether solvent mixtures as eluents.[10,11] This separation is costly and very time consuming and yields about 20–30% of each isomer. We have developed a new separation technique which takes advantage of the great solubility differences between the $Pb(ClO_4)_2$ and OH_3ClO_4 complexes of Ia and Ib

$$\mathrm{Ia + Ib + Pb(ClO_4)_2 \xrightarrow{H_2O} [PbIb][ClO_4]_2 \cdot H_2O(s) + [PbIa]^{2+}}$$

$$\mathrm{Ia + Ib + HClO_4 \xrightarrow{H_2O} [OH_3Ia][ClO_4](s) + [OH_3Ib]^{+}}$$

Nearly all of Ib precipitates from solution as the lead perchlorate complex with essentially no contamination by Ia. Similarly, nearly all of Ia precipitates from solution as the oxonium perchlorate complex with essentially no contamination by Ib.[13]

The procedure outlined below can be modified in several ways. The oxonium complex can be precipitated first followed by the lead complex. Mercury(II) or thalium(I) perchlorate can be used instead of the lead(II) perchlorate. Only one isomer need be precipitated from solution as either the lead or oxonium complex; after the excess Pb^{2+} or OH_3^+ is removed, the other isomer can be obtained by concentrating the aqueous solution and then extracting with *n*-hexane. *None of the perchlorate complexes described in this paper could be detonated using either heat or percussion*; notwithstanding, the perchlorate complexes were handled with due care.

Experimental Section

The isomer mixture of dicyclohexyl-18-crown-6 (10.0 g)[14] was added to 1.0 l. of distilled water at 60°C. After the cyclic ether melted, the mixture was allowed to cool to room temperature with vigorous stirring. The dissolution took 10–20 hr. A solution of lead perchlorate, prepared by dissolving 14.4 g of lead carbonate (J. T. Baker) in a mixture of 14.8 g of 70% perchloric acid (Mallinckrodt) and 15 ml of water, was then added to the cyclic ether solution which was stirred for an additional 60 min to complete crystallization. The resulting lead perchlorate complex of Ib was filtered to yield 9.7 g of the colorless crystals.

The filtrate, containing mostly isomer Ia, was treated with hydrogen sulfide gas (Matheson) until the precipitation of lead sulfide was complete. The solid PbS was filtered off, and enough 70% perchloric acid (about 45 ml) was added to the filtrate to start the precipitation of the oxonium perchlorate complex of isomer Ia. The solution was stirred for 15 min and an additional 15 ml of 70% perchloric acid was added to ensure complete precipitation of the solid. The mixture was stirred for an additional 1 hr and then filtered to yield 6.4 g of the colorless crystals of the oxonium perchlorate complex.

Pure Ia and Ib were isolated as follows. The lead perchlorate complex was dissolved in 60 ml of reagent *N*,*N*-dimethylformamide (Eastman). Water (60 ml) was added to this solution and hydrogen sulfide gas was bubbled through it until precipitation of lead sulfide was completed. Immediately thereafter, 60 ml of acetone (Eastman) was added, the PbS was filtered off, and the solvents were removed from the filtrate under vacuum. To the resulting viscous oil was added 60 ml of water, and this mixture was extracted with three 250-ml portions of *n*-hexane (Matheson Coleman and Bell). The combined *n*-hexane extracts were dried over anhydrous magnesium sulfate (Mallinckrodt) and filtered. The *n*-hexane was removed under vacuum, and the solid was recrystallized from *n*-hexane. The yield was 3.9 g (39%) of colorless crystals of Ib, mp 83–84°C (high-melting polymorph).

The oxonium perchlorate complex was dissolved in 50 ml of acetone and then 150 ml of water was added. This solution was extracted with *n*-hexane and treated exactly as above. The product was recrystallized from *n*-hexane or diethyl ether (Mallinckrodt) to yield 4.4 g (44%) of colorless crystals of Ia, mp 61–62°C.

Registry No. Ia, 15128-65-1; Ib, 15128-66-2; $[PbIb][ClO_4]_2$, 56468-35-0; $[OH_3Ia][ClO_4]$, 39671-97-1.

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Correspondence

Reconciliation of Apparently Contradictory Assignments of Charge-Transfer Transitions in Acidopentacyanocobaltate(III) and Acidopentaamminecobalt(III) Complexes. Inferences about Photoprocesses and Charge-Transfer Energetics[1]

AIC50046V

Sir:

In a recent report to this journal Miskowski and Gray[2] have commented that the lowest energy absorption bands assigned as charge transfer to metal (CTTM) transitions in acidopentacyanocobaltate(III) complexes occur at energies only 2–4 kK greater than the corresponding CTTM transitions of acidopentaaminecobalt(III) complexes. On casual consideration this observation seems to belie the common experience that pentacyanocobaltates are much more difficult to reduce than the corresponding pentaammines. More careful considerations demonstrate that concern with the similarity of energies of transitions assigned as CTTM in these families of complexes is well founded. (1) Straightforward application of the semiemperical expression (1) which Jorgensen[3–5] has

$$\tilde{\nu}_{\max} = 30(\chi_L - \chi_M) + 10Dq + \delta_{SP} + aB \qquad (1)$$

proposed to correlate the energies of CTTM transitions suggests that similar transitions in $Co(CN)_5X^{3-}$ and $Co(NH_3)_5X^{2+}$ complexes should differ by approximately 7 kK.[6,7] (2) The minimum excitation energy required to generate redox products is given by (2). The only large difference in the

$$Co^{III}L_5(N_3^-) \xrightarrow[H_2O]{\Delta H^\circ{}_1} \{Co^{III}L_5OH_2,N_3^-\} \xrightarrow{\Delta H^\circ{}_{IP'}} \{Co^{II}L_5,\cdot N_3\} \qquad (2)$$

overall energetics of the cyano and ammine complexes must arise from the different contributions of the $Co(CN)_5OH_2^{2-}$–$Co(CN)_5^{3-}$ and $Co(NH_3)_5OH_2^{3+}$–$Co(NH_3)_5^{2+}$ couples; the respective enthalpy contributions can be estimated to be 20.5[8] and about 10 kK mol^{-1}.[9] (3) Many of the acidopentacyanocobaltates have been shown to exhibit photoredox behavior following CTTM excitation.[10,11] In the course of some of our studies,[10,12] originally stimulated by Basolo and coworkers' discovery[13] of a photochemical process involving nitrene intermediates, we have made some observations on photoredox processes in $Co(CN)_5N_3^{3-}$. We have found the threshold energy for significant photoredox behavior to be about 7 kK greater for $Co(CN)_5N_3^-$ (Figure 4[14]) than for $Co(NH_3)_5N_3^{2+}$.[15] Thus these three different lines of consideration seem to substantiate the expectation of considerably different energies for CTTM transitions in pentaammine and pentacyano complexes of cobalt(III). Yet the absorption features in question are very similar in both families of complexes,[2] and the observation of appreciable photoredox (forming $Co^{II}L_5$ and $\cdot X$) upon irradiation of these absorption