

Figure 8. Optical rotation of 30 mM (+)₅₈₉[Co(en)₃]³⁺ ion (—) and of 30 mM (+)₅₈₉[Co(en)₃]³⁺ ion in the presence of 10 mM racemic [Ni(acac)₃]⁻ ion (- - -).

4.3. However, the absorption spectrum of Na[Ni(acac)₃] in solution at a pH of 4.3 is identical with that obtained in neutral solution, so the observed spectral changes are not a result of the slightly acidic pH of the solution.

The [Ni(acac)₃]⁻ System with (+)_D[Co(en)₃]³⁺. When the environment substance, (+)₅₈₉[Co(en)₃]³⁺, is used with Na-

[Ni(acac)₃] as a Pfeiffer effect system, the ORD curve of the (+)₅₈₉[Co(en)₃]³⁺ complex shows a nonsymmetrical change, and the crossover point for the Cotton effect is not the same in both cases (Figure 8). Therefore, it is proposed that this is a true Pfeiffer effect system utilizing one enantiomer of a complex ion as an environment substance, which results in the enrichment of one enantiomer of an octahedral, six-coordinate complex anion.¹³

Acknowledgment. The authors wish to express their appreciation to the National Science Foundation for a research grant which contributed significantly to the progress of this investigation.

Registry No. [Zn(QS)₂]²⁻, 41133-46-4; (+)₅₈₉[Co(en)₃]³⁺, 27228-84-8; *d*-CinHCl, 24302-67-8; [Ni(acac)₃]⁻, 31147-73-6; *l*-brucine hydrochloride, 5786-96-9.

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Contribution No. 2406 from Central Research & Development Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Preparation of the Paramagnetic Alkyls Cp₂NbMe₂ and (MeCp)₂TaMe₂ and Some Six- and Eight-Coordinate Phosphine Derivatives of Nb(IV)

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Received July 26, 1976

AIC605464

Reactions of Cp₂NbCl₂ and (MeCp)₂TaBr₂ (Cp = π-C₅H₅ and MeCp = π-C₅H₄Me) with MeLi in ether give the paramagnetic alkyls Cp₂NbMe₂ and (MeCp)₂TaMe₂ as red crystalline solids. Magnetic moments and ESR spectral data are given. The niobium complex violently decomposes at ~130 °C liberating 1.3–1.5 mol of methane/mol of complex. Convenient preparations of NbCl₄ and NbCl₄(THF)₂ (THF = tetrahydrofuran) are described. Reactions of the tetrahydrofuran complex with triethyl- and trimethylphosphine give NbCl₄L₂. Using chelating phosphines the eight-coordinate complexes NbCl₄(R₂PCH₂CH₂PR₂)₂ (R = Me, Et) are isolated as magnetically dilute, blue crystalline solids.

Introduction

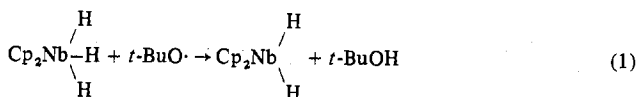
The tetrahalides of niobium in the +4 oxidation state are polymeric, insoluble, diamagnetic, and rather unreactive materials. Nevertheless, a number of adducts of NbX₄ have been isolated^{1,2} either by the slow reaction of ligands with the tetrahalides or by reduction of the pentahalides in the presence of excess ligand. We were interested in finding a more convenient route to niobium(IV) complexes and in this paper describe a good preparation of NbCl₄(THF)₂ and some phosphine derivatives of the types NbCl₄L₂ (L = PMe₃, PEt₃) and NbCl₄L₄ (where L₂ = R₂PCH₂CH₂PR₂, R = Me, Et).

Few organometallic derivatives of niobium(IV) and tantalum(IV) have been prepared. Seigert and deLiefde Meijer³ reported the preparation of Cp₂NbPh₂ and recently Klaus⁴ has reported the preparation of Nb(CH₂Ph)₂Cl₂ from NbCl₅ and Mg(CH₂Ph)₂. Preparations of the two paramagnetic com-

plexes Cp₂NbMe₂ and (MeCp)₂TaMe₂ are now reported.

Results and Discussion

A. Some Organometallic Chemistry Of Nb(IV) and Ta(IV). In a recent ESR study⁵ we observed the formation of the paramagnetic dihydride Cp₂NbH₂ by the reaction of Cp₂NbH₃ with photochemically generated *tert*-butoxy radicals according to eq 1. The complex exhibited a beautiful ESR spectrum



in solution at -80 °C. The resonance consisted of ten lines due to coupling of the electron with ⁹³Nb (*I* = 9/2, 100% abundance) and each of these lines was split into a triplet due to hyperfine coupling of the electron with two hydrogen atoms.

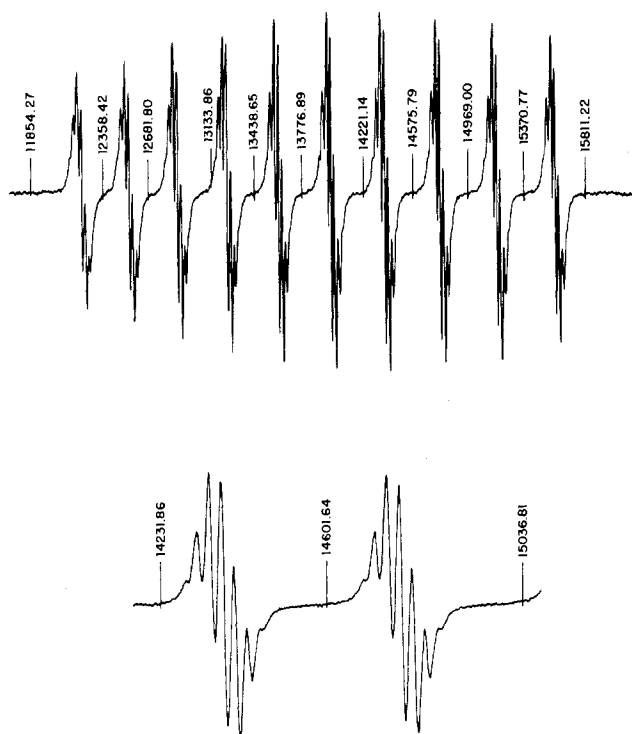


Figure 1. ESR spectrum of Cp_2NbMe_2 and the central multiplet ($M_I = \pm 1/2$) at higher resolution. The proton NMR field markers are given in kilohertz.

On warming of the compound to room temperature the spectrum rapidly collapsed due to decomposition of Cp_2NbH_3 .

The addition of MeLi or MeMgBr to a suspension of Cp_2NbCl_2 in ether at -80°C gives the ESR spectrum shown in Figure 1. The 70-line spectrum centered at $g = 1.9984$ may be attributed to that of Cp_2NbMe_2 . Ten lines arise from ^{93}Nb coupling ($\langle a_{\text{Nb}} \rangle = 88.8\text{ G}$) and each of these is split into seven lines due to hyperfine coupling with six equivalent hydrogen atoms on the two methyl groups ($\langle a_{\text{H}} \rangle = 6.3\text{ G}$). Using CD_3MgI only the ^{93}Nb coupling is discernible. Since the spectrum did not decay on warming to room temperature we attempted to isolate the complex.

The slow addition of an ether solution of MeLi to a suspension of Cp_2NbCl_2 in ether at 0°C gives a dark red solution. Removal of the solvent by rotary evaporation gives a dark solid from which Cp_2NbMe_2 can be extracted with pentane and isolated as a red-brown crystalline solid. The ESR spectrum is identical with that shown in Figure 1. The magnetic moment, determined in benzene by the Evans technique,⁶ is $1.5\ \mu_{\text{B}}$. This moment is somewhat lower than the spin-only value of $1.73\ \mu_{\text{B}}$ expected for an electron in an orbitally nondegenerate ground state. The high-resolution mass spectrum shows a peak for the parent ion at $m/e\ 253.0306$ (calculated for $\text{NbC}_{15}\text{H}_{16}\ m/e\ 253.0309$).

Cp_2NbMe_2 may be carefully sublimed at 80°C , 10^{-4} mmHg, but higher temperatures must be avoided. During one sublimation the bath temperature was raised to 130°C and at this temperature a small explosion occurred liberating a gas. We have examined this decomposition by careful pyrolysis at 130°C . The results of three experiments indicate that 1.3–1.5 mol of gas is liberated per mole of Cp_2NbMe_2 . The gas was analyzed by GC-MS and was comprised of 96–98% methane with a small amount of ethylene (1–2%). It is interesting that no ethane was observed, in contrast to the pyrolysis of platinum(IV)-methyl complexes that gives only ethane.⁷ The reaction may well proceed via α -hydrogen abstraction from one methyl group by another, as has been observed recently by Schrock,⁸ to give polymeric methylene-bridged complexes.

Alternatively, abstraction of a hydrogen from a cyclopentadienyl group may occur to give C_5H_4 groups similar to those observed in niobocene.⁹

The reaction of methyl lithium with $(\pi\text{-MeCp})_2\text{TaBr}_2$ ¹⁰ gave $(\text{MeCp})_2\text{TaMe}_2$ as a dark red, waxy solid. It may be readily sublimed at 90°C , 10^{-4} mmHg. No explosive decomposition was observed as for the niobium compound. The ESR spectrum of $(\text{MeCp})_2\text{TaMe}_2$ shows only an eight-line spectrum due to coupling of the electron with ^{181}Ta ($I = 7/2$, 100% abundance). No hyperfine coupling to the hydrogens is observed because of much broader line widths associated with tantalum. The magnetic moment in benzene ($1.1\ \mu_{\text{B}}$) is considerably lower than the spin-only moment.

An x-ray structure of Cp_4Nb has not been reported although it is often formulated as having two η^5 - and two η^1 -cyclopentadienyl rings. In view of the narrow line widths and hyperfine coupling constants observed in the spectrum of Cp_2NbMe_2 we recorded the spectrum of $(\text{C}_5\text{H}_5)_2\text{Nb}(\sigma\text{-C}_5\text{H}_5)_2$ hoping to see coupling to the two hydrogens on the σ -bonded carbon. However using extremely dilute solutions and a variety of temperatures, no hyperfine coupling was observed.

B. Some Coordination Chemistry of Niobium(IV). The preparation of NbCl_4 is generally conducted in hot tubes using temperature gradients^{11,12} to separate products. The reaction involves the reduction of NbCl_5 with a variety of reducing agents such as Nb metal,¹² aluminum foil or powder,¹³ red phosphorus,¹⁴ or niobium trichloride. We have found that NbCl_4 can easily be prepared in a thick-walled Carius tube at 250°C using excess freshly sublimed NbCl_5 and high-purity Al powder. The unreacted NbCl_5 and AlCl_3 are then removed by sublimation. Unfortunately, reactions of the insoluble material are very slow and the magnetic moments of derivatives obtained from the compound are low.¹⁵ We have now developed a route to the more reactive complex $\text{NbCl}_4(\text{THF})_2$.¹³

Gut and Perron¹⁶ found that $\text{NbCl}_4(\text{NCMe})_3$ could easily be prepared by the aluminum reduction of NbCl_5 in acetonitrile. This reaction can easily be extended to the synthesis of the tetrahydrofuran derivative in large quantities and in reasonably good yield. The reduction of NbCl_5 with excess aluminum powder in acetonitrile gives a dark orange solution of $\text{NbCl}_4(\text{NCMe})_3$. The solution is simply filtered, the MeCN is removed by rotary evaporation, and the mass is stirred in tetrahydrofuran to give $\text{NbCl}_4(\text{THF})_2$ as an insoluble pale yellow powder. It is filtered and washed with copious amounts of THF to remove $\text{AlCl}_3(\text{THF})$. Although $\text{NbCl}_4(\text{THF})_2$ is quite insoluble, the coordinated tetrahydrofuran is very labile and is easily displaced by trialkylphosphine ligands to form six- and eight-coordinate complexes.

The addition of PMe_3 to a suspension of $\text{NbCl}_4(\text{THF})_2$ in THF under nitrogen gives a transient dark green solution from which precipitated a red-brown crystalline solid analyzing as $\text{NbCl}_4(\text{PMe}_3)_2$. It could not be redissolved in the presence of excess phosphine to give a green solution. The magnetic moment was measured to 4.2 K using a Faraday balance and μ_{eff} at room temperature was found to be $0.50\ \mu_{\text{B}}$. The low moment and insolubility would indicate that there may be considerable metal-metal interaction.

The reaction of PEt_3 with $\text{NbCl}_4(\text{THF})_2$ in THF gives $\text{NbCl}_4(\text{PEt}_3)_2$ as an orange crystalline solid. It slowly decomposes on standing at room temperature in the drybox under an inert atmosphere.

The chelating diphosphine $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ reacts slowly with NbCl_4 and rapidly with $\text{NbCl}_4(\text{THF})_2$ to give $\text{NbCl}_4(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2$ as a dark blue crystalline solid. The ESR spectrum in toluene is shown in Figure 2. It consists mainly of a ten-line spectrum due to ^{93}Nb coupling ($\langle a_{\text{Nb}} \rangle = 150.2\text{ G}$) and hyperfine coupling to four phosphorus atoms

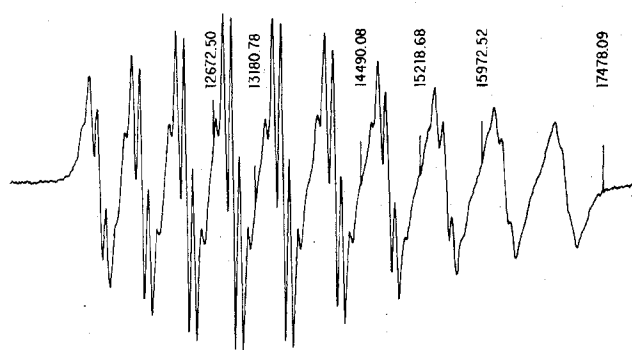


Figure 2. ESR spectrum of $\text{NbCl}_4(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2$ in toluene. The proton NMR field markers are given in kilohertz.

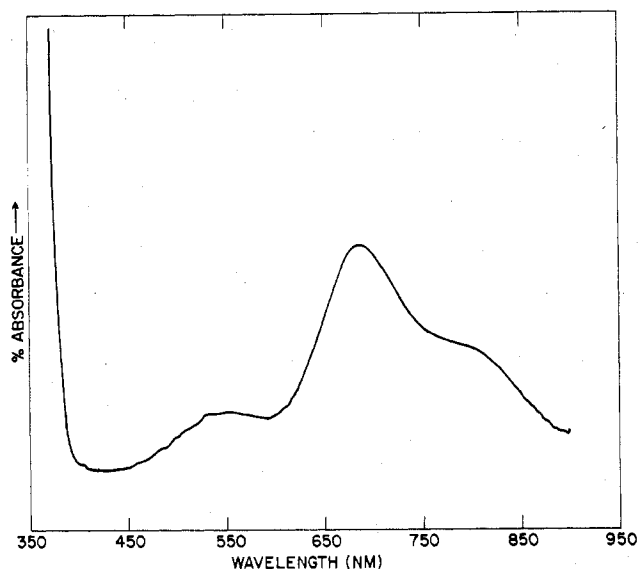


Figure 3. Visible spectrum of $\text{NbCl}_4(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)_2$ in CH_2Cl_2 .

($a_p = 22.0$ G). The room-temperature effective magnetic moment of $\text{NbCl}_4(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2$ in dichloromethane solution is $1.9 \mu_B$ and it is one of the few Nb(IV) complexes that is magnetically dilute. Similarly the reaction of $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$ with $\text{NbCl}_4(\text{THF})_2$ gave a dark blue crystalline complex whose magnetic moment is $1.9 \mu_B$. The electronic spectrum in CH_2Cl_2 shows three bands in the visible region as shown in Figure 3. Similar spectra have been observed for other eight-coordinate complexes of niobium(IV) containing chelating ligands such as 1,8-bis(dimethylarsino)naphthalene,¹⁷ β -diketonates,^{16,18} and chelating diarsines.^{19,20} The compounds have been assigned a dodecahedral structure.

Experimental Section

All reactions and manipulations were performed under an atmosphere of dry nitrogen in a Vacuum Atmospheres drybox. Solvents were dried over molecular sieves (Linde 4A) and sparged with nitrogen prior to use. Anhydrous NbCl_5 and Al powder were obtained from Research Organic/Research Inorganic Chemical Co.

$\text{Cp}_2\text{NbCl}_2^3$ and $(\text{MeCp})_2\text{TaBr}_2^{10}$ were prepared by known methods. Microanalyses were performed by the Physical and Analytical Section of this department.

A. Preparation of Cp_2NbMe_2 . MeLi (16 ml of a 1.72 M solution, 27.2 mmol) was added dropwise to a stirred solution of Cp_2NbCl_2 (4.0 g, 13.6 mmol) in ether at 0°C . After the addition was completed, the flask was warmed to room temperature and the solution was magnetically stirred for 1 h. The ether was removed by rotary evaporation to give a dark red solid. The compound was dissolved in pentane, the mixture was filtered, and the solvent was evaporated slowly to give large, dark red-brown crystals; yield 1.95 g (57%). The compound may be sublimed at 80°C , 10^{-4} mmHg; however caution

must be taken since it explodes at 128°C . Anal. Calcd for $\text{NbC}_{12}\text{H}_{16}$: C, 56.93; H, 6.37. Found: C, 56.62; H, 6.24. Visible spectrum (THF): 402 nm, ϵ $30 \text{ cm}^{-1} \text{ l}^{-1} \text{ mol}$; 475 nm, ϵ $33 \text{ cm}^{-1} \text{ l}^{-1} \text{ mol}$. Magnetic moment (C_6H_6): $\chi_M^{\text{cor}} = 977.1 \times 10^{-6} \text{ emu/mol}$; $\mu_{\text{eff}}^{303} = 1.5 \mu_B$. ESR spectrum (toluene): $g = 1.998$; $\langle a_{\text{Nb}} \rangle = 88.8 \text{ G}$; $\langle a_{\text{H}} \rangle = 6.3 \text{ G}$.

B. Preparation of $(\text{MeCp})_2\text{TaMe}_2$. To a suspension of $(\text{MeCp})_2\text{TaBr}_2$ (2.1 g, 4.20 mmol) in ether was added LiMe (4.43 ml of a 1.9 M solution, >8.42 mmol). After stirring of the mixture for 1 h the ether was removed by rotary evaporation to give a dark red solid. The solid was dissolved in pentane and filtered from the LiBr, and the pentane was removed to give deep red crystals which were sublimed at 90°C , 10^{-4} mmHg; yield 1.3 g (84%), mp $100\text{--}102^\circ\text{C}$. Anal. Calcd for $\text{TaC}_{14}\text{H}_{20}$: C, 45.54; H, 5.46. Found: C, 45.03; H, 5.45. Visible spectrum (THF): 448 nm, ϵ $667 \text{ cm}^{-1} \text{ l}^{-1} \text{ mol}$. Magnetic moment (C_6H_6): $\chi_M^{\text{cor}} = 509.86 \times 10^{-6} \text{ emu/mol}$; $\mu_{\text{eff}}^{303} = 1.1 \mu_B$. ESR (toluene): $g = 1.993$; $\langle a_{\text{Ta}} \rangle = 93 \text{ G}$; line width 17 G.

C. Pyrolysis of Cp_2NbMe_2 . A sample of Cp_2NbMe_2 (0.220 g) was placed in a 100-ml round-bottom flask and evacuated. The flask was sealed and slowly heated to 150°C . The compound exploded and covered the inside of the flask with a red-brown solid. The flask was transferred to a vacuum line and the gas volume was measured using a Toepler pump. The results of three experiments indicated that 1.3–1.5 mol of gas was liberated per mole of Cp_2NbMe_2 . The gas sample was analyzed by GC-MS and found to contain 96–98% CH_4 and 1–2% $\text{CH}_2=\text{CH}_2$.

D. Preparation of Tantalum Tetrachloride. Tantalum pentachloride (40.0 g) and aluminum powder (1.142 g) were placed in a thick-walled Carius tube of approximately 200-ml capacity, sealed under vacuum, and heated to 250°C for 48 h in a fluidized sand bath. The tube was cooled and taken into the drybox, and the olive green solid was placed in a sublimator. The sublimator was connected to a vacuum line and the unreacted TaCl_5 and AlCl_3 were sublimed at 10^{-4} mmHg and 200°C over 24 h. The olive green powder remaining was TaCl_4 . The yield was 37.0 g (85%).

E. Preparation of Niobium Tetrachloride. Freshly sublimed NbCl_5 (50.0 g) was placed in a 200-ml thick-walled Carius tube with 1.66 g of aluminum powder. The tube was sealed under vacuum and heated to 250°C for 48 h in a fluidized sand bath. The tube was then cooled to give a dark brown crystalline solid. The contents were transferred to a sublimator and the unreacted NbCl_5 and AlCl_3 were sublimed at 10^{-4} mmHg, 200°C for 24 h. The yield of NbCl_4 was 37 g (85%).

F. Preparation of $\text{NbCl}_4(\text{THF})_2$. Niobium pentachloride (240 g, 0.88 mol) was added to a suspension of 8 g of aluminum powder in 1 l. of acetonitrile. The mass was stirred for 2 h and filtered to give a dark orange-brown solution and a pale, yellow-green solid. The acetonitrile was then removed by rotary evaporation to give a reddish brown solid. The solid was suspended in ~ 1 l. of THF and the mass was vigorously stirred for ~ 3 h. The color of the complex turned to a pale yellow. It was then filtered, washed with copious amounts of THF and then pentane, and dried under vacuum. The yield of $\text{NbCl}_4(\text{THF})_2$ was 167.4 g (50%); mp 110°C dec. Anal. Calcd for $\text{NbCl}_4\text{O}_2\text{C}_8\text{H}_{16}$: C, 25.36; H, 4.26; O, 8.44, Cl, 37.42. Found: C, 25.37; H, 4.30; O, 8.23; Cl, 37.46.

G. Preparation of $\text{NbCl}_4(\text{PET}_3)_2$. To a suspension of $\text{NbCl}_4(\text{THF})_2$ (2.0 g, 5.28 mmol) in THF was added 2 equiv of triethylphosphine (1.25 g). The solution rapidly turned dark orange and after being magnetically stirred for 20–25 min the solution was filtered and the solvent was removed by rotary evaporation to give a sticky, red-brown solid. The solid was dissolved in toluene and filtered, and pentane was added. A small amount of a black solid separated so the solution was filtered again and cooled to -40°C overnight. Large, bright orange crystals separated. These were filtered, washed with pentane, and dried. The solid turns dark on standing under nitrogen in the drybox; mp $130\text{--}132^\circ\text{C}$. Anal. Calcd for $\text{NbCl}_4\text{P}_2\text{C}_{12}\text{H}_{30}$: C, 30.60; H, 6.42; P, 13.15. Found: C, 29.55; H, 6.44; P, 13.90.

H. Preparation of $\text{NbCl}_4(\text{PMe}_3)_2$. To a magnetically stirred suspension of $\text{NbCl}_4(\text{THF})_2$ (2.0 g, 5.28 mmol) in dichloromethane was added 2 equiv of trimethylphosphine (0.8 g). The solution initially turned green and a dark red-orange crystalline compound precipitated from solution. The addition of 2 equiv of trimethylphosphine had no effect. The red solid was filtered and washed with dichloromethane. The yield was 1.82 g; mp 125°C dec. Anal. Calcd for $\text{NbCl}_4\text{P}_2\text{C}_6\text{H}_{18}$: C, 18.63; H, 4.69; P, 16.01. Found: C, 18.46; H, 4.68; P, 17.26. A similar reaction in tetrahydrofuran gave the same product.

I. Preparation of $\text{NbCl}_4[\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2]_2$. NbCl_4 (3.0 g, 12.78 mmol) was suspended in 200 ml of THF and $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ (3.84 g, 25.59 mmol) was added. The flask was stoppered and magnetically stirred for 48 h in the drybox to give a purple solution. The solution was filtered and the residue was washed until the washings were colorless. The THF was removed by rotary evaporation to give purple crystals which were filtered and washed with ether. The yield was 6.68 g (98%), mp $>300^\circ\text{C}$. The analytical sample was recrystallized from THF and ether at -40°C to give large purple crystals. Anal. Calcd for $\text{NbCl}_4\text{P}_4\text{C}_{12}\text{H}_{32}$: C, 26.94; H, 6.03; Cl, 26.51; P, 23.16. Found: C, 27.03; H, 6.18; Cl, 26.61; P, 23.75. ESR (toluene): $g = 1.962$; $\langle a_{\text{Nb}} \rangle = 150.2\text{ G}$; $\langle a_{\text{P}} \rangle = 22.0\text{ G}$. Magnetic moment (CH_2Cl_2): $\chi_{\text{M}} = 1575.7 \times 10^{-6}\text{ emu/mol}$; $\mu_{\text{eff}}^{303} = 1.9\mu_{\text{B}}$. Visible spectrum (CH_2Cl_2): 550 (ϵ 31), 686 (ϵ 74), 805 nm (ϵ 48).

J. Preparation of $\text{NbCl}_4(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)_2$. To a suspension of $\text{NbCl}_4(\text{THF})_2$ (2.76 g, 7.27 mmol) in tetrahydrofuran was added $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$ (3.0 g, 14.55 mmol). The solution rapidly turned dark blue. After being stirred for 30 min the solution was filtered and pentane was added. The solution was cooled to -40°C overnight to give dark blue crystals. They were filtered and washed with pentane; yield 3.06 g. Anal. Calcd for $\text{C}_{20}\text{H}_{48}\text{Cl}_4\text{NbP}_4$: C, 37.11; H, 7.47. Found: C, 37.56; H, 7.35. Magnetic moment (CH_2Cl_2): $\chi_{\text{M}}^{\text{cor}} = 1469.0 \times 10^{-6}\text{ emu/mol}$; $\mu_{\text{eff}}^{\text{cor}} = 1.9\mu_{\text{B}}$. Visible spectrum (CH_2Cl_2): 555 (ϵ 43), 700 (ϵ 65), 825 nm (ϵ 38).

Acknowledgment. I am grateful to Professor J. Kochi (University of Indiana) and Dr. P. J. Krusic for recording the ESR spectra and to Drs. G. W. Parshall, F. N. Tebbe, U. Klabunde, and R. A. Schunn for helpful discussions and supplying samples of Cp_2NbCl_2 and $(\text{MeCp})_2\text{TaBr}_2$.

Registry No. Cp_2NbMe_2 , 54373-66-9; $(\text{MeCp})_2\text{TaMe}_2$, 54474-29-2; $\text{NbCl}_4(\text{THF})_2$, 61247-57-2; $\text{NbCl}_4(\text{PEt}_3)_2$, 61202-63-9; $\text{NbCl}_4(\text{PMe}_3)_2$, 61202-64-0; $\text{NbCl}_4[\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2]_2$, 61202-65-1; NbCl_4 -

$(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)_2$, 61202-66-2; Cp_2NbCl_2 , 12793-14-5; $(\text{MeCp})_2\text{TaBr}_2$, 61202-67-3; TaCl_4 , 13569-72-7; NbCl_4 , 13569-70-5; TaCl_5 , 7721-01-9; NbCl_5 , 10026-12-7.

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Optical Activity of the ${}^4A_2 \rightleftharpoons {}^2E$ Transitions in $\text{Cr}(\text{en})_3^{3+}$

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Received August 17, 1976

AIC605969

Circular dichroism (CD)/absorption and circularly polarized emission (CPE)/total emission spectra are reported for $\text{Cr}(\text{en})_3^{3+}$ in the region of the spin-forbidden ${}^4A_{2g} \rightleftharpoons {}^2E_g$, ${}^2T_{1g}$ intraconfigurational d-d transitions. All spectra are reported for $(-)_546[\text{Cr}(\text{en})_3\text{Cl}_3]$ dissolved in 2:1 ethylene glycol-water solution at room temperature. The absorption and emission anisotropy factors associated with the ${}^4A_{2g} \rightleftharpoons {}^2E_g$ transitions are found to be of similar magnitude (and of identical sign), indicating similar structures of the $\text{Cr}(\text{en})_3^{3+}$ system in the ground (${}^4A_{2g}$) and emitting (2E_g) states. A theoretical model is developed for calculating the optical activity of the ${}^4A_{2g} \rightarrow {}^2E_g$, ${}^2T_{1g}$, ${}^4T_{2g}$, and ${}^4T_{1g}$ transitions in the trigonal-dihedral (D_3) $\text{Cr}(\text{en})_3^{3+}$ complex. This model treats both spin-orbit interactions and noncubic (trigonal) ligand field interactions as perturbations upon the cubic, non-spin-orbit coupled states of a Cr^{3+} ion in an octahedral ligand environment. The experimentally observed chiroptical properties of $\text{Cr}(\text{en})_3^{3+}$ are discussed and compared with respect to the theoretically calculated results.

Introduction

Co^{3+} and Cr^{3+} complexes of trigonal-dihedral (D_3) symmetry have played a central role as model systems in both experimental and theoretical investigations of natural optical activity in coordination compounds. In most cases the spin-allowed d-d and near-ultraviolet charge-transfer transitions have been the focus of attention in these investigations. Recently, Kaizaki, Hidaka, and Shimura¹ have reported the circular dichroism (CD) spectra associated with the low-energy spin-forbidden d-d transitions in a series of tris-chelate Cr^{3+} complexes. The CD/absorption intensities of these transitions are considerably weaker (by several orders of magnitude) than those associated with their spin-allowed counterparts. The primary mechanism whereby the spin-forbidden transitions

acquire intensity (CD and absorption) is through spin-orbit coupling of the low-lying doublet excited states to nearby quartet excited states. Kaizaki, Hidaka, and Shimura¹ employed this mechanism to give a semiquantitative account of their experimental results.

In the present study we examine in some detail the mechanism for generating optical activity in the low-energy spin-forbidden transitions (d-d) of trigonal-dihedral (D_3) Cr^{3+} complexes. Of special interest is the optical activity associated with the ${}^4A_2 \rightleftharpoons {}^2E$ transition. We present experimental data for both the CD and the circularly polarized emission (CPE) of this transition in $\text{Cr}(\text{en})_3^{3+}$ ($\text{en} = \text{ethylenediamine}$). $\text{Cr}(\text{en})_3^{3+}$ exhibits a relatively weak phosphorescence in aqueous solution at room temperature which is partially circularly