$[M_2S_2(\mu\text{-}S)_2(S_4)_2]^{2-}$ and S^{2-} in eq 6 also may proceed via an induced internal redox pathway, since elemental sulfur, like the organic disulfides in eq 7, would be expected to act as an electron acceptor. However, complications arising from the sulfur/sulfide/polysulfide equilibria do not readily allow the initial steps of the reaction in eq 6 to be determined. Thus, whether reductions of the W(VI) or Mo(VI) atoms are in fact initiated by the interaction of the MS_4^{2-} ion with elemental sulfur as an external oxidant or whether they are induced by another means[39] will require further study.

Regardless of mechanism, the dramatic reorganizations that occur about the tungsten and molybdenum centers under relatively nonforcing conditions on going from two tetrathiometalate ions to one $M_2S_{12}^{2-}$ or $Mo_2S_8^{2-}$ anion bespeak the facile redox and bond making/breaking processes accessible to tungsten and molybdenum sulfide compounds. The ever-increasing number of molybdenum–sulfur and tungsten–sulfur complexes that is observed as well as the important role metal sulfides play in solid-state catalysis and metalloenzymatic processes undoubtedly derives in part from these diverse redox and bonding capabilities. Reactions that utilize and more fully explore properties of transition-metal–sulfur compounds will be reported in forthcoming publications.

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Note Added in Proof. Single-crystal X-ray diffraction experiments reveal $(NEt_4)_2Mo_2S_{12}$ to be isostructural with **1**.[32]

Registry No. **1**, 98991-17-4; **2**, 98991-19-6; **3**, 92389-51-0; **4**, 98991-20-9; **5**, 97591-84-9; $(NEt_4)_2Mo_2S_8$, 88335-52-8; $Mo_2S_4[S_2CN(i\text{-}Bu)_2]_2$, 36539-30-7; $(NEt_4)_2W_2O_2(\mu\text{-}S)_2(S_2)_2$, 98991-22-1; $(NEt_4)_2W_2S_8$, 98991-24-3; $(NH_4)_2WS_4$, 13862-78-7; $(NH_4)_2MoS_4$, 15060-55-6; PPh_3, 603-35-0; S, 7704-34-9.

Supplementary Material Available: Final anisotropic thermal parameters (Table VI), bond distances and angles for the NEt_4^+ cations (Table VII), ORTEP drawings of the NEt_4^+ cations (Figures II–IV), least-squares plane of basal sulfur atoms (Table VIII), and structure factors (13 pages). Ordering information is given on any current masthead page.

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Contribution No. 7191 from the Arthur Amos Noyes Laboratory,
California Institute of Technology, Pasadena, California 91125

Chemistry and Spectroscopy of Binuclear Platinum Diphosphite Complexes

Chi-Ming Che,[1a] Leslie G. Butler,[1b] Paula J. Grunthaner,[1c] and Harry B. Gray*

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Modifications have been made to the procedure for the preparation of $K_4[Pt_2(pop)_4]\cdot 2H_2O$ (pop = $P_2O_5H_2$) in order to obtain material that is not contaminated by partially oxidized platinum species. Several other pure salts (Na^+, Ba^{2+}, Bu_4N^+, Ph_4As^+) of $Pt_2(pop)_4^{4-}$ also have been obtained. Oxidation of $Pt_2(pop)_4^{4-}$ in the presence of ligands yields $d^7,d^7\text{-}Pt_2(pop)_4X_2^{4-}$ (X = Cl, Br, I, NO_2, SCN) and $\text{-}Pt_2(pop)_4L_2^{2-}$ (L = H_2O, nicotinamide, pyridine). The influence of axial ligands on the electronic structure of the $Pt^{III}\text{–}Pt^{III}$ unit has been studied by UV–vis and X-ray photoelectron spectroscopy. It is inferred that the X (or L) perturbation of the Pt–Pt dσ interaction increases according to $H_2O < Cl^- < Br^- < NO_2^- < SCN^- \sim I^-$.

Introduction

The spectroscopic and photochemical properties of the intensely luminescent, binuclear platinum(II) diphosphite complex, $Pt_2(pop)_4^{4-}$ (pop = $P_2O_5H_2$),[2,3] have attracted great interest in recent years.[4-8] It is now well established by spectroscopic experiments that the $^3A_{2u}(d\sigma)^2(d\sigma^*p\sigma)$ excited state of this d^8,d^8 complex ($^1A_{1g}(d\sigma)^2(d\sigma^*)^2$ ground state) possesses a relatively strong Pt–Pt bond, as predicted by theory,[5] and the $d\sigma^*p\sigma$ triplet is versatile in a chemical sense, being at the same time a very powerful reductant[5a] and a strong oxidant.[7b]

The discovery that $Pt_2(pop)_4^{4-}$ is readily oxidized by a variety of reagents to give discrete binuclear Pt^{III} complexes[9,10] as well as oligomeric mixed-valence species[11] prompted the UV–vis and X-ray photoelectron spectroscopic investigation that is reported

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(1) (a) Department of Chemistry, University of Hong Kong, Hong Kong. (b) Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804. (c) Jet Propulsion Laboratory, Pasadena, CA 91109.

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here. The availability of several closely related d^7,d^7-Pt^{III} complexes ($^1A_{1g}(d\sigma)^2$ ground state) has allowed us systematically to probe axial ligand effects on a Pt–Pt single bond. And in connection with this work, we have modified the standard procedure[2,3,12] for the preparation of the potassium salt of $Pt_2(pop)_4^{4-}$ in order to obtain crystalline material that is not contaminated by partially oxidized platinum diphosphite oligomers.

Experimental Section

Materials. Deionized water was used throughout the experiments. K_2PtCl_4 was purchased from Johnson and Matthey Co., Ltd. Na_2PtCl_4 was purchased from Alfa Products. All chemicals used were reagent grade.

$K_4[Pt_2(pop)_4]\cdot 2H_2O$. This material was prepared using a modification of Roundhill's procedure.[12] A 0.8-g sample of K_2PtCl_4 and 3.0 g of H_3PO_3 in 4–5 mL of water were heated for 3 h in a boiling water bath with continuous stirring in a 10-mL beaker covered with a glass slide. A pale yellow solution was obtained. The solution was then evaporated to dryness in an oven at 100 °C for 2–3 h. (Evaporation in an inert atmosphere or under a stream of nitrogen was sometimes used to improve the yield of the reaction.) Yellow solids (sometimes contaminated with a green material) were then obtained. The solid was washed with methanol and acetone to remove unreacted H_3PO_3. The product was purified by dissolving it in a minimum amount of degassed water folowed by the quick addition of methanol (first) and acetone (later). Pale yellow, fluorescent, microcrystalline $K_4[Pt_2(pop)_4]\cdot 2H_2O$ was obtained in 30–40% yield. Large yellow crystalline plates were formed by slow evaporation of a deoxygenated aqueous solution. While the platinum diphosphite complexes are fairly stable in deionized water, the diphosphite ligand is subject to slow hydrolysis, leading to degradation of the platinum complex. The purity of the sample was checked by ^{31}P NMR. No peaks assignable to phosphoric acid, phosphate, or binuclear platinum(III) diphosphite species were observed in the NMR spectrum of $K_4[Pt_2(pop)_4]\cdot 2H_2O$. *Note*: The partially oxidized impurity was not observed when *cis*-$Pt(NH_3)_2Cl_2$ was used as the starting material. ^{31}P NMR: δ 66.14, $^1J(^{31}P$–$^{195}Pt)$ = 3073 Hz.

$Na_4[Pt_2(pop)_4]\cdot nH_2O$ was prepared from Na_2PtCl_4 by using the procedure given above. Yellow prismatic crystals were formed during the melt reaction. The species also was purified as described above for the potassium salt. There was no visible evidence of a partially oxidized impurity.

$[Bu_4N]_4[Pt_2(pop)_4]$. Solid tetrabutylammonium chloride was added to a deoxygenated aqueous solution of $Pt_2(pop)_4^{4-}$ (0.5 g in 10 mL H_2O) until a yellowish green fluorescent crystalline solid precipitated. The mixture was cooled and filtered and then the solid product was washed with diethyl ether and dried in vacuum at room temperature.

$Ba_2[Pt_2(pop)_4]$ was prepared by the slow addition of $Ba(ClO_4)_2$ or $Ba(NO_3)_2$ (2 g) to a deoxygenated aqueous solution of $Pt_2(pop)_4^{4-}$ (0.4 g in 20 mL of H_2O). Yellow crystalline plates appeared upon standing. The barium salt is slightly soluble in water but very insoluble in most organic solvents.

$[Ph_4As]_4[Pt_2(pop)_4]$. A deoxygenated aqueous solution of tetraphenylarsonium chloride (1 g in 20 mL H_2O) was added to a deoxygenated solution of $Pt_2(pop)_4^{4-}$ (0.15 g in 50 mL H_2O). A yellow microcrystalline solid appeared upon standing.

$K_4[Pt_2(pop)_4Cl_2]\cdot 2H_2O$ was prepared as described previously.[9] ^{31}P NMR: δ 27.96, $^1J(^{31}P$–$^{195}Pt)$ = 2085 Hz.

$K_4[Pt_2(pop)_4Br_2]$.[9] A 0.4-g sample of $Pt_2(pop)_4^{4-}$ and 0.5 g of KBr in 20 mL of H_2O were treated with 3–4 mL of bromine water. Additional KBr (~2 g) was added to the solution. Orange microcrystalline $K_4[Pt_2(pop)_4Br_2]$ formed upon cooling and standing. The material was recrystallized by dissolving it in a minimum amount of water followed by the addition of KBr. Yield: 60–70%. ^{31}P NMR: δ 24.01, $^1J(^{31}P$–$^{195}Pt)$ = 2100 Hz.

$[Ph_4As]_4[Pt_2(pop)_4I_2]$.[9] A 0.6-g sample of $[Ph_4As]_4[Pt_2(pop)_4]$ in 100 mL of acetonitrile was treated with excess iodine. The resulting solution was left to stand for several hours and then concentrated to 25 mL. Addition of ether to the solution yielded a microcrystalline solid in high yield (70%). ^{31}P NMR: δ 18.20, $^1J(^{31}P$–$^{195}Pt)$ = 2200 Hz.

$K_4[Pt_2(pop)_4(SCN)_2]$. A 0.4-g sample of $K_4[Pt_2(pop)_4]$ and 2 g of KNCS in 20 mL of H_2O were left to stand in air for 2 days. (The reaction time may be reduced to ~$^1/_2$ h by the addition of 2 mL of 30% H_2O_2.) Orange crystals came out slowly with a yield of about 40–60%. The crude material was recrystallized by dissolving it in hot water (~70 °C). Anal. Calcd for $K_4[Pt_2(pop)_4(SCN)_2]\cdot 2H_2O$: C, 1.88; N, 2.19; P, 19.44. Found: C, 1.96; N, 1.98; P, 19.00. IR: ν(NCS) 2120 cm^{-1}. Crystal structure: SCN^- is S-bonded.[13] ^{31}P NMR: δ 25.00, $^1J(^{31}P$–$^{195}Pt)$ = 2210 Hz.

Table I. UV–Vis Spectral Data[a]

species	λ_{max}/nm (ϵ_{max}/cm^{-1} M^{-1})	
$Pt_2(pop)_4(H_2O)_2^{2-}$ [b]	245 (25 000)	320 br
$Pt_2(pop)_4Cl_2^{4-}$	282 (48 400)	345 (8190)
		390
$Pt_2(pop)_4Br_2^{4-}$	305 (55 400)	345 (11 780)
$Pt_2(pop)_4(NO_2)_2^{4-}$	312 (22 000)	360 sh (12 100)
		470 br (650)
$Pt_2(pop)_4I_2^{4-}$ [c]	338 (42 930)	435 (15 930)
$Pt_2(pop)_4(SCN)_2^{4-}$	337 (43 600)	367 sh
		480 br (740)
$Pt_2(pop)_4BrCl_4^-$	296 (38 700)	350 (9500)

[a] Aqueous solution at 25 °C unless noted otherwise. [b] $Pt_2(pop)_4(H_2O)_2^{2-}$ was prepared by photolysis of $Pt_2(pop)_4^{4-}$ in 0.1 M H_2SO_4. [c] Acetonitrile solution.

$K_4[Pt_2(pop)_4(NO_2)_2]$ was prepared by essentially the same procedure as $K_4[Pt_2(pop)_4Br_2]$ except that KNO_2 was used. (The reaction may be accelerated by the addition of phosphoric acid (0.1 g) or H_2O_2.) Anal. Calcd for $K_4[Pt_2(pop)_4(NO_2)_2]\cdot 2H_2O$: N, 2.24; P, 19.82. Found: N, 1.94; P, 19.47. IR: $\nu(NO_2)$ 820, 1420 cm^{-1}. Crystal structure: NO_2^- is N-bonded.[13] ^{31}P NMR: δ 29.30, $^1J(^{31}P$–$^{195}Pt)$ = 2250 Hz.

$K_4[Pt_2(pop)_4BrCl]$. Prepared by the addition of 1 g of KCl to an aqueous solution of $Pt_2(pop)_4Br_2^{4-}$ (0.3 g in 15 mL of H_2O). The course of the reaction was followed by UV–vis spectroscopy. When the absorption at 308 nm (the $d\sigma \rightarrow d\sigma^*$ transition of $Pt_2(pop)_4Br_2^{4-}$) disappeared (and a new peak grew in at 297 nm), the solution was cooled in an ice bath. Typical reaction time was about 2 h. $K_4[Pt_2(pop)_4BrCl]$ was recrystallized by dissolving a sample of crude product in water followed by the subsequent addition of ethanol or acetone. Yield of the final product was 50–60%. Anal. Calcd for $K_4[Pt_2(pop)_4BrCl]$: P, 19.45; Br, 6.27; Cl, 2.78. Found: P, 19.23; Br, 6.01; Cl, 2.92.

Physical Measurements. Electronic absorption spectra were measured at room temperature on a Cary 17 spectrometer. Infrared spectra were measured with a Beckman IR 4240 spectrometer. ^{31}P NMR spectra were recorded on the Bruker 500-MHz spectrometer at the Southern California Regional NMR Facility; they are referenced to 85% H_3PO_4/D_2O (external standard, H_3PO_4; internal standard, $Pt_2(pop)_4^{4-}$). NMR data are reported with positive high frequency shifts.

X-ray photoelectron spectra (XPS) were obtained on powdered samples that were dispersed on a Vaseline-coated silicon surface. Measurements were made at 250 K by using a modified Hewlett-Packard 5950A photoelectron spectrometer. An electron flood gun was not employed. Core electron binding energies were referenced to aliphatic C1s at 285.0 eV.

Results and Discussion

$K_4[Pt_2(pop)_4]\cdot 2H_2O$ and Related Compounds. Crystalline $K_4[Pt_2(pop)_4]\cdot 2H_2O$, obtained by slow evaporation of a deoxygenated aqueous solution, is yellow. The dark green crystals reported previously[3] contain a strongly absorbing blue species as an impurity. In our preparations we have found that incomplete hydrolysis of $PtCl_4^{2-}$ prior to the evaporation of the melt enhances the formation of the blue material. Also, addition of a small amount of KCl during the crystallization of $K_4[Pt_2(pop)_4]\cdot 2H_2O$ yields a dark green crystalline solid. The absorption spectrum of one of the dark green crystals exhibits an intense band at about 550 nm that is polarized parallel to the Pt–Pt axis.[5b] This band, which is absent in the pure yellow crystalline form of $K_4[Pt_2(pop)_4]\cdot 2H_2O$ (crystallographically the same as the green material),[5b] most likely is attributable to a $\sigma \rightarrow \sigma^*$ transition of the sort observed in mixed-valence rhodium isocyanide oligomers.[14] Indeed, each of the partially oxidized 1-D materials $K_4[Pt_2(pop)_4X]\cdot 2H_2O$ (X = Cl, Br, I) has an absorption in this region.[11a]

On the basis of these observations, we conclude that in the presence of air and chloride ion (present due to the incomplete removal of HCl during the evaporation of the K_2PtCl_4/H_3PO_3 melt), $Pt_2(pop)_4^{4-}$ is slowly oxidized (the UV–vis absorption spectrum of an aqueous solution of the dark green crystals shows

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Table II. XPS Data[a]

species	Pt(4f$_{7/2}$)	halide	P(2p)	O(1s)
$K_4[Pt_2(pop)_4]\cdot 2H_2O$	73.7 (0.2)		133.7 (0.2)	533.6 (0.2)
$K_4[Pt_2(pop)_4Cl_2]\cdot 2H_2O$	75.1 (0.2)		133.9 (0.2)	533.7 (0.2)
$K_4[Pt_2(pop)_4(SCN)_2]\cdot 2H_2O$	74.8 (0.1)		133.5 (0.2)	532.8 (0.3)
$K_4[Pt_2(pop)_4Br_2]$	74.5 (0.1)	69.2 (0.3)[b]	133.5 (0.2)	532.8 (0.3)
$[Ph_4As]_4[Pt_2(pop)_4I_2]$	73.7 (0.3)	620.0 (0.3)[c]	133.8 (0.4)	532.7 (0.3)
$K_4[Pt_2(pop)_4(NO_2)_2]\cdot 2H_2O$	74.3 (0.2)		133.4 (0.2)	532.6 (0.2)

[a] Energies (error limits) in eV. [b] Br(3d). [c] I(3d$_{3/2}$).

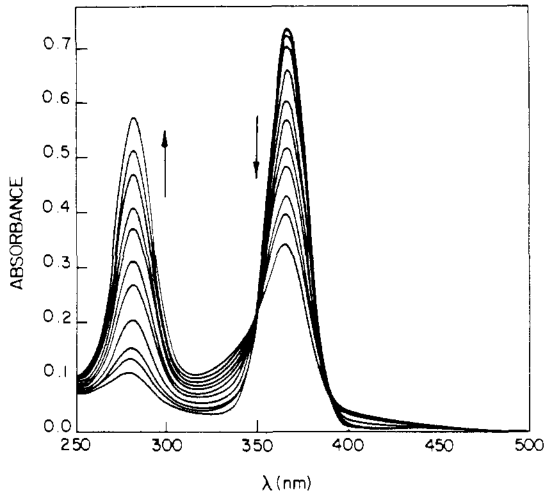

Figure 1. Absorption spectral (UV–vis) changes accompanying the oxidation of $Pt_2(pop)_4^{4-}$ in air-saturated, aqueous 1 M KCl solution. Reaction time: ~3 h.

that some $Pt_2(pop)_4Cl_2^{4-}$ is present). Partially oxidized $Pt_2(pop)_4Cl^{4-}$ units are readily incorporated into $K_4[Pt_2(pop)_4]\cdot 2H_2O$, because chloride fits in the vacant site between $Pt_2(pop)_4^{4-}$ units (both $K_4[Pt_2(pop)_4]\cdot 2H_2O$ and $K_4[Pt_2(pop)_4Cl]\cdot 2H_2O$ crystallize in space group *P4/mbm*).[11]

Reactions of Na_2PtCl_4 with phosphorus acid also proceed in essentially the same way as for K_2PtCl_4 except that the $Na_4[Pt_2(pop)_4]\cdot nH_2O$ product is not contaminated by darkly colored oxidized species.[15] Other uncontaminated salts (Ba^{2+}, Bu_4N^+, Ph_4As^+) also have been obtained.

Binuclear Pt^{III} Complexes. Thermal oxidation of $Pt_2(pop)_4^{4-}$ to $Pt_2(pop)_4Cl_2^{4-}$ requires several hours in 1 M KCl solution with excess O_2 present (Figure 1). A number of other oxidants (H_2O_2, $IrCl_6^{2-}$, IO_3^-) also convert $Pt_2(pop)_4^{4-}$ to $Pt_2(pop)_4X_2^{4-}$ or $Pt_2(pop)_4L_2^{2-}$ in the presence of nucleophiles X^- (Cl^-, Br^-, I^-, NO_2^-, SCN^-) or L (H_2O,[16] nicotinamide, pyridine).[17]

With the exception of $Pt_2(pop)_4I_2^{4-}$, the UV–vis absorption spectra of the Pt^{III} complexes are dominated by two types of bands (Table I): one is an intense $d\sigma \rightarrow d\sigma^*$ system[9] in the region 245–345 nm ($\epsilon \sim (3\text{-}5) \times 10^4$ cm^{-1} M^{-1}); the other is a broad absorption in the region 320–370 nm ($\epsilon \sim 8 \times 10^3$ cm^{-1} M^{-1}) that is usually associated with $d\pi^* \rightarrow d\sigma^*$ transitions.[9]

The nature of the axial ligand strongly influences the $d\sigma \rightarrow d\sigma^*$ transition energy in d^7,d^7 binuclear complexes.[18,19] For the platinum(III) diphosphite complexes, $E(d\sigma \rightarrow d\sigma^*)$ decreases in the order $H_2O > Cl^- > Br^- > NO_2^- > SCN^- \sim I^-$. This is exactly the reverse of the σ trans effect order,[20] which is reasonable, because ligand σ donation into dσ* should weaken the Pt–Pt dσ bond. The energetic range of the $d\sigma \rightarrow d\sigma^*$ transition as the axial ligand is varied from H_2O to SCN^- is much larger for Pt^{III} than for Rh^{II} (11 000 vs. 7000 cm^{-1}),[19] which may logically be attributed to the greater ligand character in the dσ(M–M) bond in the platinum complexes.[21]

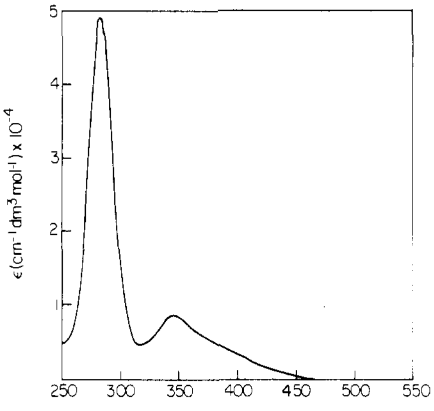

Figure 2. Absorption spectrum of $K_4[Pt_2(pop)_4Cl_2]\cdot 2H_2O$ in aqueous solution at room temperature.

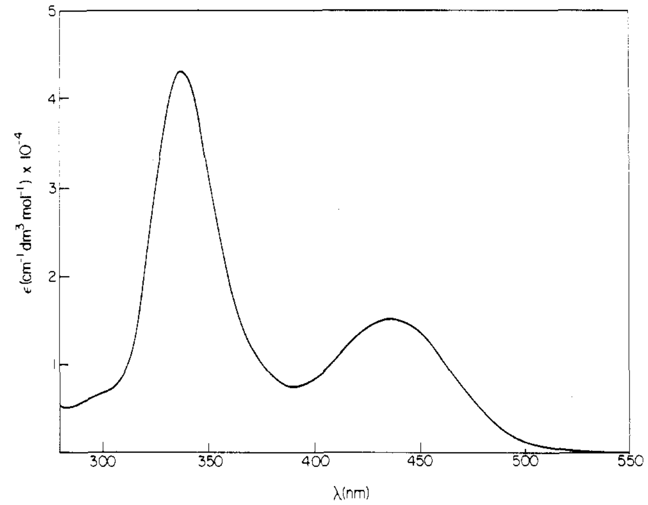

Figure 3. Absorption spectrum of $[Ph_4As]_4[Pt_2(pop)_4I_2]$ in acetonitrile solution at room temperature.

The lower energy absorption system of $Pt_2(pop)_4Cl_2^{4-}$ is broad and highly asymmetric (Figure 2). Analogous absorptions in the spectra of d^7,d^7-Rh^{II} complexes have been assigned to $\delta^* \rightarrow d\sigma^*$ and $d\pi^* \rightarrow d\sigma^*$ transitions,[19] yielding a δ*, dπ* splitting of ~2300 cm^{-1}. A larger splitting of the broad system is observed in the

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(15) Preliminary Weissenberg photographs of a single crystal of $Na_4[Pt_2(pop)_4]\cdot nH_2O$ indicate that it is orthorhombic rather than tetragonal as found for $K_4[Pt_2(pop)_4]\cdot 2H_2O$. Although we have not done a complete structure determination of $Na_4[Pt_2(pop)_4]\cdot nH_2O$, it appears that it is sufficiently different from $K_4[Pt_2(pop)_4]\cdot 2H_2O$ to discourage halide trapping, thereby simplifying the preparation of a pure Pt^{II} diphosphite species (Butler, L. G., unpublished results).

(16) A photochemical route to $Pt_2(pop)_4(H_2O)_2^{2-}$, however, is preferred: Photolysis of $Pt_2(pop)_4^{4-}$ in air-saturated 1 M $HClO_4$ or 1 M H_2SO_4 gives the Pt^{III} aquo species. Although the same initial product is obtained from H_2O_2 oxidation in water, degradation of the binuclear complex occurs, especially when the reaction time is prolonged (Che, C.-M.; Cho, K.-C.; Chan, W.-S.; Gray, H. B., to be submitted for publication).

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(21) Both charge-transfer and electron-repulsion effects contribute to the $d\sigma \rightarrow d\sigma^*$ transition energy.[19] Thus it is probable that the perturbation on the Pt–Pt bond energy is much smaller than the spectral shift for any given pair of binuclear Pt^{III} species.

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spectrum of $Pt_2(pop)_4Cl_2^{4-}$, which could mean that some of the intensity in the low-energy region is attributable to $d\pi^*(\delta^*) \rightarrow d\sigma^*$ triplet absorptions.

When the energy of the σ donor orbital of the axial ligand is comparable to that of $5d_{z^2}(Pt)$, a more complex $\sigma \rightarrow d\sigma^*$ spectrum is expected. In this case, two occupied σ levels (one derived from $d\sigma(Pt_2)$, the other from $\sigma(X{\cdots}X)$) can participate in relatively low-energy $\sigma \rightarrow d\sigma^*$ transitions. The electronic spectrum of $Pt_2(pop)_4I_2^{4-}$ exhibits intense bands at 338 and 435 nm that are attributable to delocalized $\sigma(Pt,I) \rightarrow d\sigma^*$ transitions (Figure 3). A similar pattern of $\sigma \rightarrow d\sigma^*$ transitions also has been observed in the spectra of binuclear rhodium(II) isocyanide complexes with I^- axial ligands.[19]

X-ray Photoelectron Spectra (XPS). Previous studies have established that the platinum $4f_{7/2}$ binding energy increases about 1.1 eV/unit increase in the formal oxidation state of platinum (ligand effects are sometimes as large, ca. 0.8 eV).[22,23] XPS results for several of the platinum diphosphite complexes are given in Table II. In accord with expectation, there is roughly a 1-eV increase in platinum $4f_{7/2}$ binding energy in going from Pt^{II} to Pt^{III}. The order of $Pt(4f_{7/2})$ energies does not parallel $E(d\sigma \rightarrow d\sigma^*)$, because it reflects a balance of σ and π electronic effects at each Pt center. The $Pt(4f_{7/2})$ energies of complexes containing axial ligands (SCN^-, NO_2^-) that can participate in π back-bonding are higher than would be expected if only σ-donor bonding occurred. Again, the results for $Pt_2(pop)_4I_2^{4-}$ indicate strong mixing of $d\sigma(Pt_2)$ and $\sigma(I{\cdots}I)$ orbitals; here the electron density at each "Pt^{III}" center must be unusually large.

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Contribution from the Institut für Anorganische und Analytische Chemie, Freie Universität Berlin, D-1000 Berlin 33, West Germany, and Institut für Physikalische und Theoretische Chemie, Universität Tübingen, D-7400 Tübingen 1, West Germany

Preparation, ^{19}F NMR Spectroscopy, and Electron Diffraction Study of *N*-(Trifluoromethyl)methanimines

Dieter Lentz*[1a] and Heinz Oberhammer[1b]

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Hydrogen halide addition to trifluoromethyl isocyanide results in the formation of both isomers of the compounds $CF_3N{=}CHF$, $CF_3N{=}CHCl$, and $CF_3N{=}CHBr$. The ratios of the isomers as determined by NMR spectroscopy are 15.4:1 ($CF_3N{=}CHF$), 6.7:1 ($CF_3N{=}CHCl$), and 3.8:1 ($CF_3N{=}CHBr$) ($\Delta G = 6.8 \pm 0.5$, 4.7 ± 0.5, and 3.3 ± 0.5 kJ/mol, respectively). The free enthalpies of activation of isomerization were determined by variable-temperature NMR studies. Electron diffraction studies of $CF_3N{=}CHF$ and $CF_3N{=}CHCl$ show that the *E* isomers predominate. All of these methanimines dimerize slowly, forming the corresponding aminomethanimines $CF_3N{=}C(H)N(CF_3)(CF_2H)$, $CF_3N{=}C(H)N(CF_3)(CCl_2H)$, and $CF_3N{=}C(H)(CF_3)(CBr_2H)$. Addition of pentafluorosulfur bromide to trifluoromethyl isocyanide yields the pentafluorothio-substituted methanimine CF_3-$N{=}C(Br)SF_5$.

Introduction

Methanimine, $HN{=}CH_2$, is an exceedingly unstable compound.[2] Derivatives with electronegative substituents, such as fluorine,[3] chlorine,[4] or CF_3 groups[5] however, are much more stable. In our studies on the reactivity of trifluoromethyl isocyanide,[6] we were interested in the α-addition reactions of this compound. In 1892 Nef reported that the α-additions of hydrogen halides to isocyanides at −15 °C yield the salts of the halomethanimines.[7] Due to the lower basicity of trifluoromethyl-substituted nitrogen compounds there seemed a chance that hydrogen halide addition would stop at the halomethanimine. The present paper describes our work on the reactions of the hydrogen halides HF, HCl, and HBr with CF_3NC, which give rise to $CF_3N{=}CHF$, $CF_3N{=}CHCl$, and $CF_3N{=}CHBr$. All of these methanimines may exist in the isomeric forms shown in Figure 1. Two of these methanimines, $CF_3N{=}CHF$ and $CF_3N{=}CHCl$, have been described previously in a German patent,[8] but no information about their isomeric forms has been given.

Table I. Correlation Coefficients with Values Larger than 0.6

	HCl[a]	HF[b]		HCl	HF
CF/N—C		−0.68	CX/FCF		−0.67
CF/N=C	−0.81		FCF/NCX	0.61	0.70
CF/CX		−0.84	FCF/*l*(F··F)		−0.72
CF/FCF	0.86	0.80	CNC/NCX		−0.66
CF/NCX	0.73		CNC/tilt	−0.71	−0.82
CF/*l*(CF)	−0.70		CNC/*l*(F··F)		0.71
N=C/FCF	−0.70		NCX/tilt		0.81
N=C/NCX	−0.87		NCX/*l*(CF)	−0.81	
N=C/*l*(CF)	0.84				

[a] For $CF_3N{=}CHCl$. [b] For $CF_3N{=}CHF$.

Experimental Section

Materials. HCl (Merck) was dried over Sicapent (P_2O_5/SiO_2 Merck). The compounds HBr,[9] CF_3NCF_2,[5] $(CF_3)_2NH$,[10] CF_3NC,[6] SF_5Br,[11] and

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