4276 *Inorg. Chem.* **1991**, *30*, 4276-4278

Notes

Contribution from the Department of Chemistry,
University of Mississippi, University, Mississippi 38677

Spectroscopic Characterization of the Octachlorodirhenate(3−) Ion, $[Re_2Cl_8]^{3-}$

Sandra K. D. Strubinger, Charles L. Hussey,
and W. E. Cleland, Jr.*

Received February 21, 1991

Introduction

The existence of a quadruple bond between rhenium atoms in the octachlorodirhenate(III) ion, $[Re_2Cl_8]^{2-}$, was first recognized over 25 years ago. Since that time, the chemistry of dinuclear rhenium complexes possessing multiple Re–Re bonds has played a prominent role in the overall development of the field of metal–metal multiple bonds.[1-4] Indeed, $[Re_2Cl_8]^{2-}$ is a versatile precursor for the preparation of a variety of complexes with Re_2^{n+} cores (n = 8, 6, 5, 4).[1,2] While a number of dinuclear complexes possessing the Re_2^{5+} core with the $\sigma^2\pi^4\delta^2\delta^*$ electronic configuration are known, the parent chloride complex, $[Re_2Cl_8]^{3-}$, has remained elusive.

Chloroaluminate ionic liquids have been found to be excellent solvents for the study of the spectroscopic and electrochemical properties of transition-metal chloride complexes.[6] Combining aluminum chloride with a quaternary ammonium chloride salt such as 1-methyl-3-ethylimidazolium chloride (MeEtimCl) produces a molten salt or ionic liquid that is molten at room temperature. The Lewis acid–base properties of the melts can be altered by adjusting the ratio of aluminum chloride to quaternary ammonium chloride. Basic melts contain excess chloride ions, while acidic melts contain excess $Al_2Cl_7^-$ ions. Molten salts have several advantages for the study of transition-metal chloride complexes over conventional solvents such as water or acetonitrile, including the ability to obtain spectra of complexes free of hydrolysis or solvolysis product impurities. These advantages have been discussed in detail elsewhere.[6]

In a recent publication,[5] we reported on the electrochemistry and spectroelectrochemistry of rhenium(III) chloride complexes utilizing a chloroaluminate molten salt as solvent, including the first successful production of stable solutions of $[Re_2Cl_8]^{3-}$ by bulk controlled-potential electrolytic reduction of $[Re_2Cl_8]^{2-}$. In this paper, we report the optical absorption and ESR spectra of $[Re_2Cl_8]^{3-}$.

Experimental Section

Solutions of $[Re_2Cl_8]^{3-}$ were prepared by bulk electrolytic reduction of $[Re_2Cl_8]^{2-}$ according to the literature procedure.[5] Optical absorption spectra were recorded by using either a Perkin-Elmer Model 3840 Lambda Array or a Perkin-Elmer Hitachi Model 200 UV–vis spectrophotometer. Near-infrared spectra were recorded by using a Cary 17 spectrophotometer. X-Band electron spin resonance (ESR) spectra were recorded as frozen glasses at 77 K by using a Varian E4 spectrometer. ESR samples were prepared in 3-mm quartz ESR tubes which were frozen and sealed under vacuum.

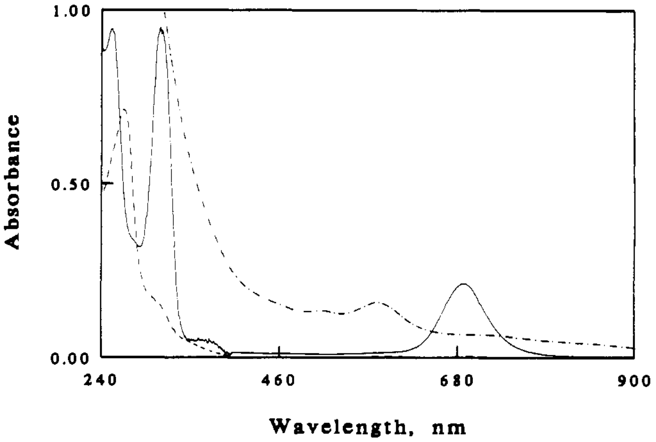

Figure 1. Absorption spectra of dimeric rhenium chloride complexes in 49.0 mol % $AlCl_3$–MeEtimCl at room temperature: (—) 9.07 × 10^{-4} M solution of $(Bu_4N)_2[Re_2Cl_8]$; (– –) 9.53 × 10^{-4} M solution of $(Bu_4N)_2$-$[Re_2Cl_8]$ after exhaustive reduction at −0.71 V; (–··–) after exhaustive reduction of a 5.73 × 10^{-3} M solution of $[Bu_4N]_2[Re_2Cl_8]$ under the same conditions. The cell path lengths were 1.00 mm.

Table I. Optical Absorption Data and Possible Assignments for $[M_2Cl_8]^{3-}$: M = Re, Tc

$[Re_2Cl_8]^{3-}$		$[Tc_2Cl_8]^{3-}$ [a]	possible
λ_{max},[b] ($10^{-2}\epsilon_M$)	ν_{max} [b]	ν_{max} [b]	assignt[a]
1468 (17.0)[c]	6.8	5.9	$\delta \rightarrow \delta^*$
708	14.1	13.6	$\pi \rightarrow \delta^*$
580 (2.8)	17.2	15.7	$\delta^* \rightarrow \pi^*$
512 (2.3)	19.5	20.0[d]	$\delta^* \rightarrow d_{x^2-y^2}$ $\delta^* \rightarrow \sigma^*$ $\delta \rightarrow \pi^*$ $\delta \rightarrow d_{x^2-y^2}$
305 (sh, 19.0)	32.7	31.4[d]	LMCT $\pi \rightarrow \pi^*$ $\pi \rightarrow d_{x^2-y^2}$
268 (75.0)	37.3	37.2	LMCT
		43.5	LMCT

[a] From ref 7. [b] λ in nm; ν in cm^{-1} × 10^{-3}. [c] Peaks in the vibrational progression at 1274, 1322, 1370, 1413, 1468 (center), 1523, 1585, 1680, 1755 nm (±3 nm). [d] Any of the given assignments are possible for this transition.

Results and Discussion

During the course of our investigation of the chemistry of rhenium chloride complexes in the basic $AlCl_3$–MeEtimCl melt,[5] we discovered that $[Re_2Cl_8]^{2-}$ exhibited a reversible one-electron reduction and that stable solutions of $[Re_2Cl_8]^{3-}$ could be prepared by electrolytic reduction of $[Re_2Cl_8]^{2-}$. The $[Re_2Cl_8]^{3-}$ ion is isoelectronic with its well-known technetium analogue, $[Tc_2Cl_8]^{3-}$. Fortunately, the spectrum of $[Tc_2Cl_8]^{3-}$ has been reported[7] along with possible assignments based on theoretical computations. The UV–vis absorption spectra of $[Re_2Cl_8]^{2-}$ and $[Re_2Cl_8]^{3-}$ are presented in Figure 1, while the near-IR spectrum of $[Re_2Cl_8]^{3-}$ is shown in Figure 2. Data from these spectra are collected in Table I along with data and possible assignments for the isoelectronic $[Tc_2Cl_8]^{3-}$ ion. Upon reduction, a subtle color change from the blue-green of $[Re_2Cl_8]^{2-}$ to the navy blue of $[Re_2Cl_8]^{3-}$ was observed. Figure 1 shows that the prominent band at 688 nm in the spectrum of $[Re_2Cl_8]^{2-}$ is completely absent from the spectrum of the reduced species and is replaced by several new features. Comparison of the spectrum of $[Re_2Cl_8]^{3-}$ to that reported for the isoelectronic $[Tc_2Cl_8]^{3-}$ ion shows that the spectra are qualitatively quite similar. Assuming that the orders of the energy levels of $[Re_2Cl_8]^{3-}$ and $[Tc_2Cl_8]^{3-}$ are approximately the

---

(1) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

(2) Cotton, F. A.; Walton, R. A. *Struct. Bonding* **1985**, *62*, 1.

(3) Cotton, F. A. *Chem. Soc. Rev.* **1983**, *12*, 35.

(4) Trogler, W. C.; Gray, H. B. *Acc. Chem. Res.* **1978**, *11*, 232.

(5) Strubinger, S. K. D.; Sun, I. W.; Cleland, W. E., Jr.; Hussey, C. L. *Inorg. Chem.* **1990**, *29*, 993.

(6) Hussey, C. L. *Pure Appl. Chem.* **1988**, *60*, 1763.

(7) Cotton, F. A.; Fanwick, P. E.; Gage, L. D.; Kalbacher, B.; Martin, D. S. *J. Am. Chem. Soc.* **1977**, *99*, 5642.

0020-1669/91/1330-4276$02.50/0

Table II. Spectroscopic Properties of Rhenium Chloride Complexes with the Re_2^{5+} Core

complex	$\delta^2\delta^* \rightarrow \delta\delta^{*2}$ [a]	$g_\parallel$ $(A_\parallel)$ [b]	$g_\perp$ $(A_\perp)$	ref
$[Re_2Cl_8]^{3-}$	1468 (1700)[c]	$g \sim 2.6$[c]		this work
$Re_2Cl_6(PEt_3)_2^-$	1525 (1200)	~2.2 (~350)	~2.4 (75–100)	8
$Re_2Cl_6(PPr_3)_2^-$	1450 (1000)	~2.2 (~350)	~2.4 (75–100)	8, 9
$Re_2Cl_6(PMePh_2)_2^-$	1475 (1100)	~2.2 (~350)	~2.4 (75–100)	8
$Re_2Cl_6(PEtPh_2)_2^-$	1475 (1000)	~2.2 (~350)	~2.4 (75–100)	8
1,3,6-$Re_2Cl_5(PMe_3)_3$	1314 (2300)	$g \sim 2.2$		10
1,2,7-$Re_2Cl_5(PMe_3)_3$	1283 (2200)	$g \sim 2.2$		10
$Re_2Cl_5(PEt_3)_3$	1460[d]			11
$Re_2Cl_5(PPr_3)_3$	1375[d]			11
$Re_2Cl_5(PMePh_2)_3$	1350			12
$Re_2Cl_5(PEtPh_2)_3$	1375 (2700)			12
$Re_2Cl_5(dppm)_2$	1530 (1700)	<2[e]	~2.2	13, 14
$Re_2(OAc)Cl_4(PPh_3)_2$	1200 (1700)	2.16	2.20	19
$Re_2(OAc)Cl_4(Ph_2Ppy)_2$	1330 (1100)	2.16	2.20	19
$Re_2(O_2CEt)Cl_4(Ph_2Ppy)_2$	1330 (1050)	2.16	2.20	19
$Re_2Cl_4(PMe_3)_4^+$	1380 (~4000)	g_{av} = 2.41–2.42		15
$Re_2Cl_4(PEt_3)_4^+$	1410		2.25 (170)	9, 16
$Re_2Cl_4(PPr_3)_4^+$	1503[f]			17
$Re_2Cl_4(PMe_2Ph)_4^+$	1360[g]	2.19 (300)	2.24 (120)	18

[a] λ, nm (ϵ_M); CH_2Cl_2 solution at room temperature unless otherwise noted. [b] *A* values in gauss; CH_2Cl_2 or CH_2Cl_2/toluene glass at −150 to −160 °C unless otherwise noted. [c] 49.0% $AlCl_3$–MeEtimCl solution. [d] Nujol mull. [e] 20 °C. [f] KBr pellet at 5 K. [g] MeCN solution.

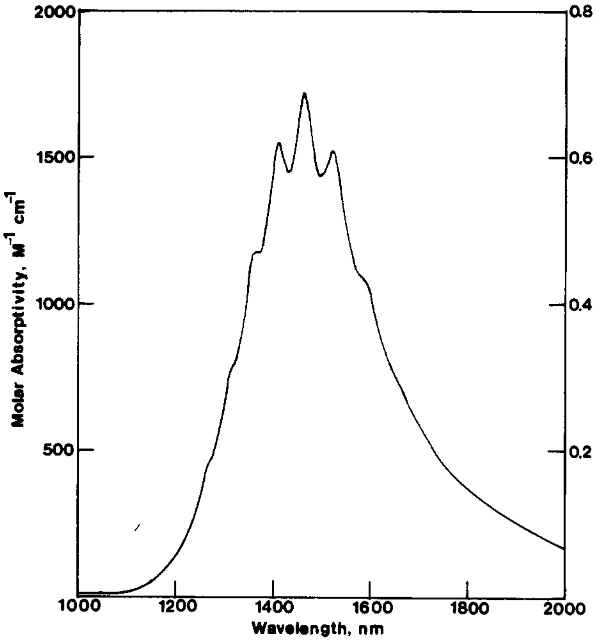

Figure 2. Near-infrared absorption spectrum of a 4.03 × 10^{-3} M solution of $[Re_2Cl_8]^{3-}$ in 49.0 mol % $AlCl_3$–MeEtimCl at room temperature. This solution was obtained by the bulk electrolytic reduction of a solution initially containing $[Re_2Cl_8]^{2-}$. The cell path length was 1.00 mm.

same, corresponding features can be tentatively assigned (Table I). The four lowest energy absorption maxima of $[Re_2Cl_8]^{3-}$ appear to have corresponding features in the spectrum of $[Tc_2Cl_8]^{3-}$. These absorptions appear with the same pattern of intensities but are generally displaced to higher energy for $[Re_2Cl_8]^{3-}$. Both species have steeply rising absorptions below 400 nm, and there appears to be less correlation of spectral features in this region. Assignments in this region are therefore more tenuous.

The near-IR spectra of a number of complexes with the Re_2^{5+} core, including a series of mixed-ligand chloro–phosphine complexes with general formulas $Re_2Cl_6(PR_3)_2^-$,[8,9] $Re_2Cl_5(PR_3)_3$,[10-14] and $Re_2Cl_4(PR_3)_4^+$,[9,15-18] as well as the carboxylate-substituted species $Re_2(O_2CR)Cl_4(PR_3)_2$,[19] have been reported. Spectroscopic data for these complexes are collected in Table II. All of the complexes can be considered derivatives of $[Re_2Cl_8]^{3-}$ and exhibit an intense band around 1400 nm (average for 19 complexes) in the near-infrared region. While all of the compounds exhibit a near-IR band, no obvious trends in the data or correlation with charge or variation in ligation can be discerned from the data. The spectrum of $[Re_2Cl_8]^{3-}$ in this region consists of an intense absorption with considerable vibrational fine structure centered around 1468 nm. The position and intensity of the band are typical of compounds with a Re_2^{5+} core (Table I); this band is assigned to the fully allowed transition $\sigma^2\pi^4\delta^2\delta^* \rightarrow \sigma^2\pi^4\delta\delta^{*2}$. The vibrational progression observed in the spectra of molecules with the Re_2^{5+} core is based on the excited-state, totally symmetric Re–Re stretching frequency. The Re–Re stretching frequency obtained for the excited state of $[Re_2Cl_8]^{3-}$ from the vibrational progression is 270 cm^{-1}. The corresponding value for the analogous $[Tc_2Cl_8]^{3-}$ ion is 320 cm^{-1}.[7] The value for $[Re_2Cl_8]^{3-}$ is quite comparable

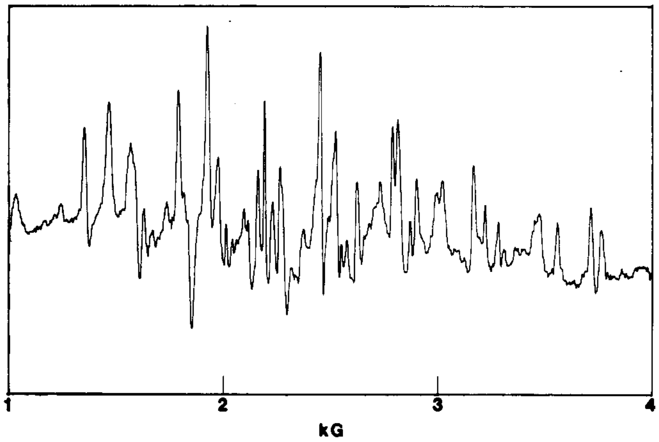

Figure 3. X-Band ESR spectrum of a 1.79 × 10^{-3} M solution of $[Re_2Cl_8]^{3-}$ in 49.0 mol % $AlCl_3$–MeEtimCl at 77 K. This solution was obtained by the bulk reduction of a solution initially containing $[Re_2Cl_8]^{2-}$.

---

(8) Dunbar, K. R.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 5.
(9) Brant, P.; Salmon, D. J.; Walton, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 4424.
(10) Cotton, F. A.; Price, A. C.; Vidyasagar, K. *Inorg. Chem.* **1990**, *10*, 5143.
(11) Hertzer, C. A.; Myers, R. E.; Brant, P.; Walton, R. A. *Inorg. Chem.* **1978**, *9*, 2383.
(12) Ebner, J. R.; Walton, R. A. *Inorg. Chem.* **1975**, *14*, 1987.
(13) Barder, T. J.; Cotton, F. A.; Lewis, D.; Schwotzer, W.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 2882.
(14) Cotton, F. A.; Shive, L. W.; Stults, B. R. *Inorg. Chem.* **1976**, *15*, 2239.
(15) Root, D. R.; Blevins, C. H.; Lichtenberger, D. L.; Sattelberger, A. P.; Walton, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 953.
(16) Cotton, F. A.; Pederson, E. *J. Am. Chem. Soc.* **1975**, *97*, 303.
(17) Bursten, B. E.; Cotton, F. A.; Fanwick, P. E.; Stanley, G. G.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 2606.
(18) Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Tomas, M.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 4950.
(19) Cutler, A. R.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 3811.

to the value of 275 cm^{-1} found from the spectra of $Re_2Cl_4(PPr_3)_4^+$.[17] A Re–Re stretching frequency of 248 cm^{-1} was observed in the $\delta \rightarrow \delta^*$ excited state of $[Re_2Cl_8]^{2-}$.[20] This finding implies a stronger excited state for $[Re_2Cl_8]^{3-}$ compared to the excited state of $[Re_2Cl_8]^{2-}$ and therefore, by analogy, a stronger ground state, even though the bond order for $[Re_2Cl_8]^{2-}$ is higher than for $[Re_2Cl_8]^{3-}$, 4.0 and 3.5, respectively. These results are consistent with the experimental and theoretical results for $Re_2Cl_4(PPr_3)_4^+$.[17] The correlation between bond order and bond strengths has been discussed.[2-4]

The X-band ESR spectrum of $[Re_2Cl_8]^{3-}$ at 77 K is shown in Figure 3. Data from the spectrum as well as for other Re_2^{5+} complexes appear in Table II. A broad, complex signal centered around 2400 G is observed. Cotton and Pedersen have presented a detailed analysis of ESR spectra of species with the $\sigma^2\pi^4\delta^2\delta^*$ configuration, such as Re_2^{5+}[16] and Tc_2^{5+}.[21] Their results indicate that the spectra of these species arise from a single unpaired electron residing in a δ^* orbital coupled to two Re atoms, each with nuclear spin $^5/_2$, or two Tc atoms, each with spin $^9/_2$. Spectra of the rhenium chlorophosphine complexes are further complicated by coupling of the electron to phosphorus. Our results are consistent with those found for other Re_2^{5+} species (Table II) and confirm the $\sigma^2\pi^4\delta^2\delta^*$ configuration. Because of the lack of sufficient resolution and its expected complexity,[8-10,16,18] we make no attempt to interpret the spectrum in any detail.

Acknowledgment. This work was sponsored by the National Science Foundation, Grant No. CHE-9016632 to C.L.H. S. K.D.S. acknowledges support through the USAF Laboratory Fellowship Program. We thank Memphis State University for use of their ESR facility.

Registry No. $[Re_2Cl_8]^{3-}$, 53260-18-7.

---

(20) Cowman, C. D.; Gray, H. B. *J. Am. Chem. Soc.* **1973**, *95*, 8177.
(21) Cotton, F. A.; Pedersen, E. *Inorg. Chem.* **1975**, *14*, 383.

Contribution from the Department of Chemistry
and Biochemistry, University of California
at Los Angeles, Los Angeles, California 90024-1569

Structural Analysis of $[Et_3NH][Cu(1\text{-}B_{10}H_9N_2)_2]$ and $[Et_3NH][1\text{-}B_{10}H_9N_2]$

Lai-Ling Ng, Bradford K. Ng, Kenneth Shelly,
Carolyn B. Knobler, and M. Frederick Hawthorne*

Received May 10, 1991

We have previously reported the synthesis and spectroscopic characterization of $[1\text{-}B_{10}H_9N_2]^-$ (**1**).[1-4] We now report the utilization of this monoanion as a ligand and the synthesis and structural characterization of a new metallaborane derivative, $[Cu(1\text{-}B_{10}H_9N_2)_2]^-$ (**2**). The structure of the monoanion **1** was previously assigned on the basis of spectroscopic data, and we have now confirmed the initial structural assignment by a single-crystal X-ray diffraction study.

Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without further purification unless otherwise stated. Triethylamine (MCB), 2,4,6-tribromoaniline (Eastman), sodium propionate (Aldrich), sodium nitrite (Mallinckrodt), fluoroboric acid (Aldrich), sodium tetrafluoroborate (Aldrich), and copper(I) chloride (Aldrich) were used without further purification. Acetonitrile was dried over CaH_2 and refluxed under nitrogen prior to use. Other solvents were used as received. ^{11}B NMR spectra were recorded on a Bruker AM500 (160.463 MHz) NMR spectrometer. The ^{11}B chemical shifts are referenced to external $BF_3\cdot OEt_2$; peaks upfield of the reference are designated as negative, and areas are given in parentheses. Infrared spectra were obtained as KBr pellets by using a Beckman Model FT 1100 FT-IR spectrometer.

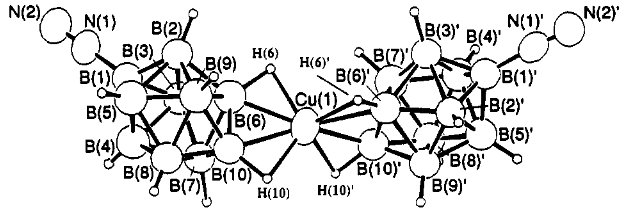

Figure 1. Structure of $[Et_3NH]\cdot$**2** with thermal ellipsoids for non-hydrogen atoms drawn at 50% probability and for hydrogen drawn artificially small.

Preparation of $[Et_3NH][1\text{-}B_{10}H_9N_2]$ ($[Et_3NH]\cdot$1). A 11.1-g (26-mmol) sample of 2,4,6-tribromobenzenediazonium tetrafluoroborate was dissolved in 200 mL of CH_3CN, and the resulting solution was added slowly to a solution of $[(Et_3NH)_2][B_{10}H_{10}]$[1-4] (8.4 g, 26.0 mmol) in 400 mL of CH_3CN maintained at 0 °C. After being stirred for 30 min, the solution was warmed to room temperature and 1 g of sodium propionate was added. After the reaction mixture was stirred overnight, CH_3CN was removed by rotary evaporation and the resulting solid was taken up in 200 mL of H_2O and extracted three times with ether. The ether fractions were combined, dried over $MgSO_4$, and evaporated to give 650 mg (10% yield) of solid residue of $[Et_3NH]\cdot$**1**. Additional product was recovered by washing the $MgSO_4$ with acetone (three times) to give a dark green solution. Evaporation of the solvent gave a dark solid, which was recrystallized in hot 95% ethanol to afford an additional 1.84 g of the product for a total yield of 39%. IR spectrum (KBr): 3124 (s), 2510 (s), 2230 (s), 1450 (m), 1400 (m), and 1135 cm^{-1} (m). ^{11}B NMR (Et_2O): 23.23 (d, 1 B), −14.70 (s, 1 B), −16.48 (d, 4 B), and −24.86 ppm (d, 4 B).

Preparation of $[(Et_3)NH][Cu(1\text{-}B_{10}H_9N_2)_2]$ ($[Et_3NH]\cdot$2). Into a 100-mL round-bottom flask equipped with a magnetic stirring bar and a reflux condenser was added CuCl (1.46 g, 14.8 mmol), 1.23 mL of 12 N HCl (14.8 mmol), and 200 mL of H_2O. To this was added $[Et_3NH]\cdot$**1** (1.84 g, 7.4 mmol) in 150 mL of acetonitrile, and the solution was gently refluxed for 2 h. After cooling, the acetonitrile was removed by rotary evaporation, and the solution was neutralized by the addition of triethylamine. The crude product mixture was extracted with ether (3 × 50 mL). The combined organic layers were then dried with brine and over $MgSO_4$, and the solvent was removed to dryness to obtain $[Et_3NH]\cdot$**2** as a light brown powder, which was then recrystallized from CH_2Cl_2/Et_2O. Clear plates having a pink coloration were obtained in 14% yield (227 mg, 0.5 mmol) after further recrystallizations. Anal. Calcd (found): C, 15.81 (15.78); H, 7.46 (6.99); B, 47.42 (46.75); N, 15.37 (15.29); Cu, 13.94 (14.11). IR spectrum (KBr): 2552 (s), 2457 (s), 2258 (s), 2218 (s), 1467 (m), 1395 (m), 1166 (m), 1134 (s), 1014 (s), and 685 cm^{-1} (m). ^{11}B NMR (Et_2O): 7.44 (d, 1 B), −7.90 (s, 1 B), −16.90 (d, 4 B), and −25.48 ppm (d, 4 B).

Solid-State Structures of $[Et_3NH]\cdot$1 and $[Et_3NH]\cdot$2. Crystallographic data, atomic coordinates, and selected bond distances and angles are reported in Tables I–V.

Results and Discussion

Milder reaction conditions for the preparation of $[Et_3NH]\cdot$**2** were investigated. The reaction of $[Et_3NH]\cdot$**1** with CuCl in the absence of added HCl did not result in the desired product. When HCl was added without bringing the solution to reflux, $[Et_3NH]\cdot$**2** formation was not observed. However, in the presence of HCl at the reflux temperature, the ^{11}B NMR spectrum of an aliquot of the reaction mixture taken after 2 h of reaction indicated an essentially quantitative conversion of $[Et_3NH]\cdot$**1** to $[Et_3NH]\cdot$**2**. The $[Et_3NH]\cdot$**2** complex is soluble in common organic solvents such as MeCN, Et_2O, and CH_2Cl_2. After 3 weeks, no degradation of the complex was observed in the presence of air and moisture.

Complexes $[Et_3NH]\cdot$**1** and $[Et_3NH]\cdot$**2** have been obtained as a brownish yellow and as a pale pink crystalline solid, respectively. In order to establish the molecular geometry of the complexes, suitable single crystals of $[Et_3NH[\cdot$**1** were grown from H_2O and

---

(1) Leyden, R. N.; Hawthorne, M. F. *Inorg. Chem.* **1975**, *14*, 2444.
(2) Hawthorne, M. F.; Olsen, F. P. *J. Am. Chem. Soc.* **1964**, *86*, 4219.
(3) Hawthorne, M. F.; Olsen, F. P. *J. Am. Chem. Soc.* **1965**, *87*, 2366.
(4) Leyden, R. N.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1973**, *95*, 2032.

0020-1669/91/1330-4278$02.50/0