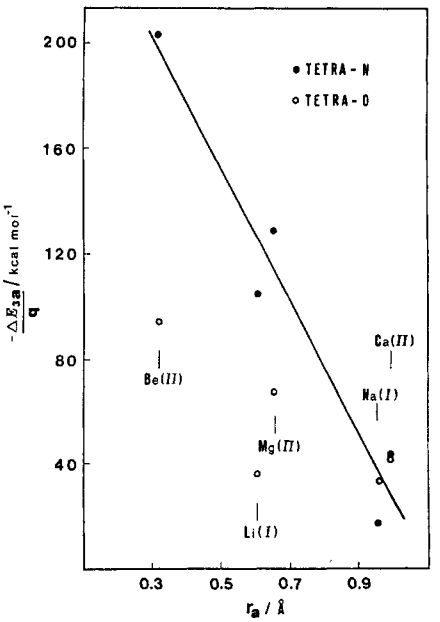

Figure 4. Charge-normalized stabilization energies of metal complexes with macrocyclic ligands vs. ionic radii.

Table IV. Calculated Stabilization Energies between the Metal Ions and the Cyclic Ligands (ΔE_{3a}) Compared to Calculated Hydration Energies per Water Molecule in the Octahedrally Coordinated First Hydration Shell ($\Delta E_{calcd}{}^{O_h}$) (kcal mol^{-1})

ions	$4\Delta E_{calcd}{}^{O_h}$ [a]	$\Delta E_{3a}{}^{N_4}$	$\Delta E_{3a}{}^{O_4}$
Li(I)	−88.4	−122.7	−52.3
Na(I)	−61.6	−34.6	−59.0
Be(II)	−421.6	−407.2	−192.3
Mg(II)	−202.0	−268.5	−150.8
Ca(II)	−187.6	−103.8	−151.6

[a] Value taken from ref 17.

If binding energies for the cyclic (eq 2a) and noncyclic (eq 2b and 2c) ligands are compared, it can be seen that the electronic structure of a closed ring system is apparently very much in favor of electron density rearrangements upon metal binding, similar to the "electronic chelate effect" observed for two noncyclic ligands forming a ring system via hydrogen bonds.[16]

In Table IV, ΔE_{3a} is compared with calculated binding energies per water molecule in an octahedrally coordinated first hydration shell ($\Delta E_{calcd}{}^{O_h}$), computed with the same basis set as used in our work.[17] It can be assumed that the metal ion in the complex will be hydrated by only two water molecules,[18–24] because of steric reasons. In this case, four water molecules from the first hydration shell will be released upon complexation; i.e., the metal ion is supposed to form an energetically stable complex whenever $\Delta E_{3a} > 4\Delta E_{calcd}{}^{O_h}$. Our data predict, therefore, enthalpy-stabilized metal complexes ($\Delta E \simeq \Delta H < 0$) in aqueous solution only for Li(I) and Mg(II) with the tetraaza ligand but no such cases for the tetraoxa ligand.

Unfortunately, no experimental data for these specific complexes have been reported yet. It is obviously not sufficient to consider only hydration and the complexation energies of the metal ion, as entropy effects might have another considerable influence.[25] However, a similar prediction based on energies only was made by Fukui et al.,[23] using the CNDO/2 method (generally unsuitable for metal complexes[26–28] in calculations on complexes of alkali-metal ions with O_4 ligands.

Recent investigations by Clay[29] have shown that, for one and the same metal ion, differences in complex stability can be explained merely on the basis of the difference of hydration enthalpies in a series of macrocyclic ligands. This indicates that the principal results obtained in our investigation on the two model compounds (N_4 and O_4 cyclic ligands) should have a general validity even for higher analogues of these ligands, if metal ion and ligand character do not differ too much.

Acknowledgment. Financial support for S.V.H. by the Austrian Federal Government is gratefully acknowledged.

(16) Rode, B. M. *Chem. Phys. Lett.* **1974**, *26*, 350.
(17) Rode, B. M.; Reibnegger, G. J.; Fujiwara, S. *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 1268.
(18) Martin, L. Y.; Sperati, C. R.; Busch, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 2968.
(19) Vitiello, J. D.; Billo, E. J. *Inorg. Chem.* **1980**, *19*, 3477.
(20) Fabbrizzi, L. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1857.
(21) Fabbrizzi, L. *Inorg. Chem.* **1977**, *16*, 2667.
(22) Anichini, A.; Fabbrizzi, L.; Paoletti, P. *Inorg. Chim. Acta* **1977**, *24*, L21.
(23) Yamabe, T.; Hori, K.; Akagi, K.; Fukui, K. *Tetrahedron* **1975**, *35*, 156.
(24) Hinz, F.; Margerum, D. W. *Inorg. Chem.* **1974**, *13*, 2941.
(25) Pullman, B. "Intermolecular Interactions: From Diatomics to Biopolymers"; Wiley-Interscience: New York, 1978.
(26) Russegger, P.; Lischka, H.; Schuster, P. *Theor. Chim. Acta* **1972**, *24*, 191.
(27) Rode, B. M. *Monatsh. Chem.* **1975**, *106*, 339.
(28) Rode, B. M.; Sagarik, K. P. *Chem. Phys. Lett.* **1982**, *88*, 337.
(29) Clay, R. M. Third European Symposium on Macrocyclic Compounds, Scotland, August, 1984.

Notes

Contribution from the Department of Chemistry, North-Eastern Hill University, Shillong 793003, India

Alkali-Metal and Ammonium Peroxyfluoroborates. First Synthesis of Peroxyfluoroborate Complexes

Mihir K. Chaudhuri* and Bimalendu Das

Received July 19, 1984

It has been known for quite some time that orthoboric acid reacts in solution[1] with hydrogen peroxide giving peroxyboric acid, which most probably contains the $[B_2(O_2)_2(OH)_4]^{2-}$ anion. Alkali-metal salts of this anion are also known and constitute an important oxidizing component in many washing powders. The commercially most important compound in this context is $Na_2B_2(O_2)_2(OH)_4 \cdot 6H_2O$. No heteroligand peroxyborate is known to our knowledge. As a part of our program of synthesis, structural assessment, and studies of reactivities of peroxy compounds of metals,[2] we have extended our investigation to boron and expected that the results obtained would provide internally consistent data regarding the effect of heteroligands on the stability of peroxyborate systems. In this report we present an account of the synthesis and assessment of structures of the first examples of heteroligand peroxyborates of the types $A_2B(O_2)F_3 \cdot 4H_2O$ (A = Na or K) and $(NH_4)_2B_2(O_2)_3F_2$.

(1) (a) Greenwood, N. N. "The Chemistry of Boron"; Pergamon Press: Elmsford, NY, 1975; Vol. 8, p 887. (b) Hansson, A. *Acta Chem. Scand.* **1961**, *15*, 934.
(2) Chaudhuri, M. K.; Ghosh, S. K. *Polyhedron* **1982**, *1*, 553; *Inorg. Chem.* **1982**, *21*, 4020; *Inorg. Chem.* **1984**, *23*, 534; *J. Chem. Soc., Dalton Trans.* **1984**, 507. Bhattacharjee, M. N.; Chaudhuri, M. K.; Dutta, Purkayastha, R. N. *J. Chem. Soc., Dalton Trans.* **1985**, 409.

0020-1669/85/1324-2580$01.50/0

Table I. Analytical Data, Molar Conductance Values, and Structurally Significant IR Bands of $A_2B(O_2)F_3 \cdot 4H_2O$ (A = Na or K) and $(NH_4)_2B_2(O_2)_3F_2$

compd	molar conductance, Ω^{-1} cm^2 mol^{-1}	% found (% calcd) A or N	B	O_A[a]	F	IR, cm^{-1}	assignt
$(NH_4)_2B_2(O_2)_3F_2$	234	14.47 (14.62)	11.64 (11.28)	51.2 (50.07)	19.75 (19.82)	1050 (s, br)	ν_{B-F}
						850 (m)	ν_{O-O}
						3155 (m)	ν_3
						3045 (s)	ν_1
						1400 (s)	ν_4
$Na_2B(O_2)F_3 \cdot 4H_2O$	270	45.35 (45.98)	5.21 (4.96)	14.8 (14.69)	27.11 (26.16)	1060 (s)	ν_{B-F}
						860 (m)	ν_{O-O}
						3450 (m)	ν_{O-H}
						1640 (m)	δ_{H-O-H}
$K_2B(O_2)F_3 \cdot 4H_2O$	255	31.54 (31.27)	4.52 (4.32)	13.2 (12.8)	23.12 (22.79)	1050 (s)	ν_{B-F}
						860 (m)	ν_{O-O}
						3450 (m)	ν_{O-H}
						1640 (m)	δ_{H-O-H}

[a] Peroxy oxygen.

Experimental Section

The chemicals used were all reagent grade products. Infrared spectra were recorded on a Perkin-Elmer Model 125 spectrophotometer separately in KBr and in Nujol media. Molar conductance measurements were made by using a Philips PR 9500 conductivity bridge at 23 °C, with the concentration of each of the solutions being maintained at 10^{-3} M. The pH of the reaction solutions was measured with a Systronics Type 335 digital pH meter and also with pH indicator (BDH) paper.

Synthesis of $Na_2B(O_2)F_3 \cdot 4H_2O$, $K_2B(O_2)F_3 \cdot 4H_2O$, and $(NH_4)_2B_2(O_2)_3F_2$. General Procedure. To a suspension of 2.0 g (32.34 mmol) of boric acid in ca. 15 cm^3 of water was added alkali-metal hydroxide or ammonium hydroxide (AOH; A = Na, K, or NH_4) solution, under constant magnetic stirring, first to completely dissolve the boric acid and then to raise the pH of the medium to 9. While the sodium hydroxide or potassium hydroxide was added as 20% solution, the ammonium hydroxide was added as its 25% solution. An amount of 6.0 cm^3 (120 mmol) of 40% HF solution was added, and the resultant mixture was stirred for ca. 5 min. The pH of the resulting solution was adjusted to 9 by the addition of alkali-metal or ammonium hydroxide solution, and the mixture was cooled in an ice–water bath for ca. 15 min, followed by the addition of 14 cm^3 (123.4 mmol) of 30% hydrogen peroxide. The solution was cooled in the ice–water bath for ca. 10 min under slow magnetic stirring, and the pH of the solution was raised once again to 9 by adding AOH solution. Addition of a nearly equal volume of ethanol to the above solution produced white crystalline alkali-metal or ammonium peroxyfluoroborate in a very high yield. The compound thus obtained was separated by filtration, washed three times with ethanol, and finally dried in vacuo over concentrated sulfuric acid.

The yields of $Na_2B(O_2)F_3 \cdot 4H_2O$, $K_2B(O_2)F_3 \cdot 4H_2O$, and $(NH_4)_2B_2(O_2)_3F_2$ were 6.5 g (92%), 6 g (74%), and 4.5 g (72%), respectively.

Elemental Analyses. Boron was estimated gravimetrically, after the peroxy oxygen was expelled, as nitron tetrafluoroborate.[3] The peroxide content in each of the compounds was determined by redox titration with a standard potassium permanganate solution.[4] Sodium and potassium were estimated by the methods described in our earlier papers.[2] Nitrogen and fluoride analyses were obtained from Amdel, Australian Microanalytical Service, Port Melbourne, Victoria 3207, Australia. Fluoride in the $Na_2B(O_2)F_3 \cdot 4H_2O$ compound was also estimated gravimetrically as lead chloride fluoride PbClF.[5] All analytical data, molar conductance values, and structurally significant IR band positions and their assignments are summarized in Table I.

Results and Discussion

Synthesis. The reaction of orthoboric acid with hydrogen peroxide produces the peroxyborate species $[B_2(O_2)_2(OH)_4]^{2-}$ in solution,[1] and the alkali-metal salts of the complex ion are prepared from the reaction of borates with hydrogen peroxide. The sodium salt can also be prepared from the reaction of boric acid with sodium peroxide. Further it is well-known from the familiar chemistry of boron that fluoride reacts with trivalent boron rather easily.[6] Thus it was expected that under the appropriate conditions both peroxide (O_2^{2-}) and fluoride (F^-) ligands may be made to coordinate to boron in the presence of each other to produce heteroligand peroxyborate complexes.

The role of pH in the synthesis of such compounds have been emphasized[2] recently. Accordingly the reactions of boric acid with alkali-metal or ammonium hydroxide, 40% HF, and 30% H_2O_2 solutions were conducted at pH 9, which gave rise to the formation of the complex ions $[B(O_2)F_3]^{2-}$, in the case where the alkali-metal hydroxide was either NaOH or KOH, and $[B_2(O_2)_3F_2]^{2-}$, in the case of NH_4OH. The complex ions were isolated as $Na_2B(O_2)F_3 \cdot 4H_2O$, $K_2B(O_2)F_3 \cdot 4H_2O$, and $(NH_4)_2B_2(O_2)_3F_2$ in very high yields by the addition of ethanol, which facilitated precipitation. The peroxyfluoroborate formation reactions are best monitored through peroxy oxygen estimation. This is accomplished by isolating a small amount of the sample from the reaction mixture, followed immediately by the estimation of active oxygen. It must be emphasized that a pH 9 reaction medium is very conducive to the formation and isolation of the compounds. Our attempts to explore the possibility of synthesis of peroxyfluoroborates at a lower pH (3 or 4) were in vain. The compounds thus obtained were found to contain very low levels of peroxide.

Characterization and Assessment of Structure. The peroxyfluoroborates are all white crystalline stable products and can be stored in sealed polyethylene bags. Their stabilities can be ascertained by periodic estimation of peroxide. The peroxide content in each of the compounds was estimated by titration with a standard potassium permanganate solution. The results obtained thereof and those of the analyses of other constituents of the compounds (Table I) suggest the stoichiometry of $B:O_2^{2-}:F^-$ as 1:1:3 in each of the Na^+ and K^+ salts and 2:3:2 in the NH_4^+ salt. Accordingly, the compounds have been formulated as $Na_2B(O_2)F_3 \cdot 4H_2O$, $K_2B(O_2)F_3 \cdot 4H_2O$, and $(NH_4)_2B_2(O_2)_3F_2$. The peroxyfluoroborates do not melt up to 300 °C; however, the $(NH_4)_2B_2(O_2)_3F_2$ compound volatilizes at about 165 °C. Pyrolytic studies reveal that while all the compounds start losing peroxy oxygen at ca. 130 °C, the Na^+ and K^+ salts also start expelling water at nearly the same temperature. The compounds are stable and permit molar conductance measurements. The molar conductances of the newly synthesized compounds have been found to lie between 230 and 270 Ω^{-1} cm^2 mol^{-1} in very good agreement with their formulas. A slightly higher value in the case of the Na^+ salt might be due to the presence of a trace of impurity, presumably sodium fluoride, arising from its low solubility.

The most significant feature of IR spectra of the peroxyfluoroborates are the absorptions at ca. 1050 and ca. 860 cm^{-1}, which have been assigned to the ν_{B-F}[7] and ν_{O-O}[2,8] modes respectively originating from the presence of coordinated fluoride and peroxide ligands. The position of ν_{O-O} suggests a strong possibility

(3) Vogel, A. I. "A Text Book of Quantitative Inorganic Analysis"; Longmans, Green and Co.: New York, 1962; p 578.
(4) Reference 3, p 295.
(5) Reference 3, p 269.
(6) Reference 1a, p 956.
(7) Greenwood, N. N. *J. Chem. Soc.* **1959**, 3811.
(8) Griffith, W. P. *J. Chem. Soc.* **1963**, 5345, **1964**, 5248. Griffith, W. P.; Wickins, T. D. *J. Chem. Soc. A* **1968**, 397.

of the O_2^{2-} ligand being bonded to the boron center in a triangular bidentate (C_{2v}) manner,[2,8] and the complex anion $[B(O_2)F_3]^{2-}$ may be a pentacoordinated monomer; however, the possibility that the complex ion is tetrahedral with a terminal O–O group cannot be ruled out. The IR spectrum of the complex anion $[B_2(O_2)_3F_2]^{2-}$ shows a pattern generally similar to that of the $[B(O_2)F_3]^{2-}$ species, except for much greater broadening of the band at 1050 cm^{-1}. It is believed that the stereochemistry of boron in the $[B_2(O_2)_3F_2]^{2-}$ ion is tetrahedral, which is attained through coordination of one O_2^{2-} ligand in a triangular bidentate fashion, one terminal F^- ligand, and one end of a bridging O–O ligand. An alternate structure of the dimer, similar to that found for $NaBO_3 \cdot 4H_2O$, with two O–O bridges connecting the two boron atoms (i.e., a six-membered B_2O_4 ring), is also possible irrespective of the mode of coordination of the third peroxide group. In view of the structural study of the complex anion $[B_2(O_2)_2(OH)_4]^{2-}$, the latter structure appears more likely. The two extra bands at 3450 (m) and 1640 (m) cm^{-1} in the case of the Na^+ and K^+ salts were assigned to the ν_{O-H} and δ_{H-O-H} modes of uncoordinated water.[9] The broad nature of the ν_{O-H} band in each case indicates a fair possibility of hydrogen bonding through F···H···F interactions. The bans at 1400 (s), 3045 (s), and 3155 (m) cm^{-1} in the spectrum of $(NH_4)_2B_2(O_2)_3F_2$ have been attributed to the ν_4, ν_1, and ν_3 modes of NH_4^+.

Thus, it is evident from the present work that, under the appropriate conditions, peroxyfluoroborates can be prepared and such complexes are appreciably stable.

Acknowledgment. The authors are grateful to the Department of Atomic Energy for generous financial support (Grant No. 37/16/82G) and to the reviewers of the paper for valuable suggestions.

Registry No. $(NH_4)_2B_2(O_2)_3F_2$, 96455-71-9; $Na_2B(O_2)F_3$, 96455-72-0; $K_2B(O_2)F_3$, 96455-73-1.

(9) Bhattacharjee, M. N.; Chaudhuri, M. K.; Dasgupta, H. S.; Khathing, D. T. *J. Chem. Soc., Dalton Trans.* **1981**, 2587.

Contribution from the Institut für Anorganische Chemie, Universität Bern, CH-3000 Bern 9, Switzerland

Preparative Uses of Hexaaquaruthenium(II): Synthesis of Phosphine Complexes

Owen H. Bailey and Andreas Ludi*

Received September 25, 1984

While the chemistry of ruthenium(II) is vast, many of its complexes fall within two main classifications—chemical complexes containing simple amines as well as π-accepting heterocycles and molecules containing the wealth of soft ligands associated with organometallic chemistry. $RuCl_3 \cdot 3H_2O$ ultimately serves as the source of ruthenium in the preparation of many of the compounds within both of these classes. Although the versatility of this starting material is a matter of record, it does suffer two important limitations: (1) a reduction is required in order to obtain Ru(II) species; (2) the reaction must proceed in the presence of chloride ions. Hexaaquaruthenium(II) salts may function as alternative starting points for systems where it is desired to avoid either or both of these conditions. The structure of this ion is known,[1] the lability of the aqua ligands has been studied,[2] and a range of solvents is allowed depending upon the choice of anion. The utility of $[Ru(H_2O)_6](tos)_2$ (tos = *p*-toluenesulfonate) in the preparation of complexes containing nitrogenous ligands has been described previously.[3]

Experimental Section

Reagents. All solution manipulations were performed under argon by using Schlenk-type apparatus. Solvents were purified and dried by standard procedures and saturated with argon prior to use. $[Ru(H_2O)_6](tos)_2$[1] and $[Ru(H_2O)_3(C_6H_6)](tos)_2$[4] were prepared by literature methods. All other reagents were used as commercially supplied.

Physical Measurements. ^1H, $^{13}C\{^1H\}$, and ^{31}P NMR spectra were obtained on Bruker WP-80 CW and Varian XL-100 spectrometers, respectively. ^1H and ^{13}C chemical shifts are referenced to Me_4Si; ^{31}P chemical shifts are referenced relative to 85% H_3PO_4 with positive ppm values being downfield. IR and UV–vis spectra were obtained with Perkin-Elmer 599B and 551S spectrophotometers, respectively. Solution conductivities were measured in CH_3NO_2 (κ = 0.73 $\mu\Omega$) at seven concentrations (10.2–0.77 mM) with a Philips PW 9505 conductivity bridge. Results were treated according to the method recommended by Geary.[5]

Preparations. $Ru(H_2O)_2(THF)_2(tos)_2$. $[Ru(H_2O)_6](tos)_2$ (0.500 g, 0.907 mmol) was suspended in 25 mL of THF and stirred for 72 h. The pale pink solid was isolated by filtration, rinsed with THF, and dried under vacuum (78% yield). Anal. Calcd for $C_{22}H_{34}O_{10}S_2Ru$: C, 42.37; H, 5.49; S, 10.28; H_2O, 5.78. Found: C, 42.37; H, 5.43; S, 10.20; H_2O, 5.69.

$Ru(H_2O)_2(PPh_3)_2(tos)_2$. Method A. $[Ru(H_2O)_6](tos)_2$ (2.00 g, 3.63 mmol) and PPh_3 (1.95 g, 7.43 mmol) were suspended in 40 mL of THF and stirred for 24 h. The deep red solution was filtered, reduced in volume by half, and treated with 30 mL of diethyl ether. When the mixture was cooled to −30 °C, a scarlet crystalline solid formed. This solid was collected by filtration and dried under vacuum (80% yield). Anal. Calcd for $C_{50}H_{48}O_8P_2S_2Ru$: C, 59.82; H, 4.82; P 6.17; S, 6.39; H_2O, 3.59. Found: C, 59.84; H, 5.00; P, 6.10; S, 6.21; H_2O, 3.56.

Method B. $Ru(H_2O)_2(THF)_2(tos)_2$ (0.362 g, 0.581 mmol) and PPh_3 (0.304 g, 1.16 mmol) were stirred in 25 mL of THF for 24 h, producing a deep red solution. Treatment of this solution as described above resulted in isolation of $Ru(H_2O)_2(PPh_3)_2(tos)_2$, as shown by comparison of its infrared spectrum with that of an authentic sample.

$Ru(dppe)_2(tos)_2$. When a suspension of 1.00 g (1.81 mmol) of $[Ru(H_2O)_6](tos)_2$ and 1.45 g (3.64 mmol) of $Ph_2PCH_2CH_2PPh_2$ (dppe) in 40 mL of THF was stirred for 24 h, a yellow solid gradually precipitated. This solid was isolated by filtration and crystallized from a $CHCl_3/C_6H_6$ mixture (40% yield). Anal. Calcd for $C_{66}H_{62}O_6P_4S_2Ru \cdot 0.5H_2O$: C, 63.46; H, 5.08; P, 9.92; S, 5.13; H_2O, 0.72. Found: C, 63.45; H, 5.06; P, 9.57; S, 5.16; H_2O, 0.81.

***cis*-$RuH_2(dppe)_2$.** A suspension containing 0.800 g (0.645 mmol) of $Ru(dppe)_2(tos)_2$ and 0.18 g (3.3 mmol) of $NaAlH_4$ in 35 mL of THF was stirred for 1 h at room temperature. During this period the yellow metal complex reacted, yielding a colorless solution containing a white precipitate. The solid was removed by filtration and the filtrate reduced in volume to 5 mL. When the filtrate was cooled to −30 °C, a white crystalline solid formed. This solid was isolated by filtration and dried under vacuum.

$Ru(PPh_3)(C_6H_6)(tos)_2$. A suspension of 2.50 g (4.34 mmol) of $[Ru(H_2O)_3(C_6H_6)](tos)_2$ and 2.30 g (8.78 mmol) of PPh_3 in 40 mL of THF was stirred for 24 h, producing an orange solid. The mixture was warmed, yielding a red solution, which was filtered hot. When the solution was cooled to 5 °C, an orange microcrystalline solid formed, which was isolated by filtration, rinsed with cold THF, and dried under vacuum (80% yield). Anal. Calcd for $C_{38}H_{35}O_6PS_2Ru$: C, 58.23; H, 4.50; P, 3.95; S, 8.18. Found: C, 58.16; H, 4.65; P, 3.94; S, 8.35; H_2O, <0.3.

$RuH_2(PPh_3)(C_6H_6)$. A solution containing 1.00 g (1.28 mmol) of $Ru(PPh_3)(C_6H_6)(tos)_2$ in 50 mL of THF was slowly added with stirring to a suspension of $NaAlH_4$ (0.36 g, 6.6 mmol) in 20 mL of THF. Reaction was rapid with formation of a white precipitate and a pale yellow solution. The solid was removed by filtration and the clear filtrate reduced in volume of 5 mL. Addition of diethyl ether and cooling to −30 °C resulted in the formation of a yellow microcrystalline solid, which was isolated by filtration and dried under vacuum.

Results and Discussion

$[Ru(H_2O)_6](tos)_2$ Derivatives. The high solubility of $[Ru(H_2O)_6]^{2+}$ in a variety of weakly coordinating solvents together

(1) Bernhard, P.; Bürgi, H.-B.; Hauser, J.; Lehmann, H.; Ludi, A. *Inorg. Chem.* **1982**, *21*, 3936.
(2) Bernhard, P.; Helm, L.; Rapaport, I.; Ludi, A.; Merbach, A. E. *J. Chem. Soc., Chem. Commun.* **1984**, 302.
(3) Bernhard, P.; Lehmann, H.; Ludi, A. *J. Chem. Soc., Chem. Commun.* **1981**, 1216.
(4) Bailey, O. H.; Stebler, M.; Beck, U.; Ludi, A., presented at the Second International Conference on the Chemistry of the Platinum Group Metals, 1984.
(5) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

0020-1669/85/1324-2582$01.50/0