4) can be considered as satisfactorily linear.[35]

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Registry No. **1**, 79971-92-9; **2**, 77188-05-7; **3**, 79971-93-0; **4**, 79971-94-1; **5**, 79971-95-2; **6**, 79971-96-3; **7**, 79971-97-4; **8**, 79971-98-5; **9a**, 28660-76-6; **9b**, 79971-99-6; **9c**, 79972-00-2; **9d**, 79972-01-3; **10**, 79972-02-4; **11**, 79972-03-5; **12a**, 79972-04-6; **12b**, 79972-05-7; **13**, 79972-06-8; **14**, 80008-88-4; **15**, 79972-07-9; **16**, 79972-08-0; **17**, 79972-09-1; **18**, 79972-10-4; **19**, 32425-27-7; **20**, 32425-23-3; **21**, 32425-19-7; **22**, 79972-11-5; **23**, 79972-12-6; **24**, 79972-13-7; **25**, 79972-14-8; **26**, 14647-29-1; **27**, 13986-92-0; **28a**, 14873-21-3; **28b**, 14647-26-8; **28c**, 79972-15-9; **29**, 15006-86-7; **30**, 79972-16-0; **31**, 79972-17-1; **32**, 79972-18-2; **33**, 79972-19-3; **34**, 79972-20-6; **35**, 79972-21-7; **36**, 79972-22-8.

Supplementary Material Available: A table of analytical data (Table I) (2 pages). Ordering information is given on any current masthead page.

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(35) The linearity in Figure 4 is not due to fortuitous choice of two different solvents (benzene (bz) for ν_{max} and dimethylformamide (DMF) for $E°_{298}$) to generate the two axes. In a number of cases ν_{max} was determined in DMF and was found to correlate linearly with $E°_{298}$. A slight shift ($\sim$200 cm^{-1}) to lower energy which occurs in going from bz to DMF is probably due to axial coordination as in the case of pyridine solvent.[22] Representative ν_{max} values in DMF are as follows: **20**, 945; **21**, 930; **22**, 925; **23**, 915; **26**, 920; **28a**, 910; **29**, 905 nm.

Contribution from the Department of Chemistry,
Faculty of Science, Hiroshima University, Hiroshima 730, Japan

Inversion in the Direction of a Chiral Equilibrium Shift Observed in the Pfeiffer Effect of Some Mixed-Chelate Chromium(III) Complexes at the Ligand Field Excited State

KATSUHIKO MIYOSHI, YUUKO MATSUMOTO, and HAYAMI YONEDA*

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Laser irradiation of an aqueous solution of racemic $[Cr(ox)_2(phen)]^-$ or $[Cr(ox)(phen)_2]^+$ (ox = oxalate dianion and phen = 1,10-phenanthroline) at their ligand field transition regions in the presence of *d*-cinchonine or *l*-cinchonidine hydrochloride led to a relatively rapid shift in a chiral equilibrium between their two enantiomers, which was opposite in direction to that induced by the usual Pfeiffer effect of the corresponding system in the dark. This is in contrast to the observation that the direction of the equilibrium shift induced for homochelate complexes $[Cr(ox)_3]^{3-}$ and $[Cr(phen)_3]^{3+}$ was unaltered whether they were photoirradiated or not. This new finding was interpreted in terms of anisotropic expansion of these mixed-chelate Cr(III) complexes at the ligand field excited state and of the accompanying perturbation in their stereoselective interaction with *d*-cinchoninium or *l*-cinchonidinium ion.

Introduction

Several octahedral Cr(III) complexes have been partially resolved through photoexcitation at their ligand field (LF) transition regions.[1-3] In particular, the use of circularly polarized light has a great advantage in that it affords ORD and CD curves of an optically pure enantiomer. However, the optical yield practically achievable by this technique is governed by the dissymetric factor *g*, and it is low for usual Cr(III) complexes (at most 5%). On the other hand, the optical yield attained by the Pfeiffer effect,[4] an induced shift in a chiral equilibrium between two enantiomers of an initially racemic and labile metal complex under the influence of a chiral compound (called an environment substance) present in solution, depends on the efficiency of chiral discrimination effected in the diastereomeric interaction of the two enantiomers with the environment substance, so that it may amount to almost 20% in a favorable situation.[5] Furthermore, the direction of the equilibrium shift induced, i.e., the absolute configuration of the enantiomer enriched by the Pfeiffer effect, can give some information on the stereoselective interactions involved.[5-7]

In the present study, partial photoresolution of some Cr(III) complexes was attempted by irradiating these complexes with linearly polarized light at their LF transition regions in the presence of hydrochloride salts of some cinchona alkaloids in water. Interestingly enough, we found some mixed-chelate complex systems in which the chiral equilibrium was shifted upon photoirradiation toward the opposite direction to that observed in the usual Pfeiffer effect in the dark.

Experimental Section

Materials. Racemic complexes to be photoirradiated were $[Cr(ox)_3]^{3-}$, $[Cr(ox)_2(phen)]^-$, $[Cr(ox)_2(bpy)]^-$ (bpy = 2,2′-bipyridine), $[Cr(ox)(phen)_2]^+$, and $[Cr(phen)_3]^{3+}$, all of which were prepared by standard methods described in the literature,[8] and their purity was checked by absorption spectra and ion-exchange chromatography. $[Co(phen)_3]^{2+}$, used in place of $[Cr(phen)_3]^{3+}$ in the study of the Pfeiffer effect at the ground state, was prepared by mixing appropriate amounts of $CoCl_2{\cdot}6H_2O$ and phen·H_2O in water (in 1:3 mole ratio). Chiral environment substances used were commercially available *d*-(8*R*,9*S*)-cinchonine and *l*-(8*S*,9*R*)-cinchonidine hydrochlorides, both of which were recrystallized from hot water. Hydrochloride salts of *d*-(8*R*,9*S*)-quinidine and *l*-(8*S*,9*R*)-quinine, which are 6′-MeO derivtives of *d*-cinchonine and *l*-cinchonidine, respectively.[9] were also used for comparison.

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Table I. Absolute Configuration of Enriched Enantiomers and Percentage Resolution Attained by the Pfeiffer Effect[a]

complex	*d*-cinchonine[b]	*l*-cinchonidine[b]	
$[Cr(ox)_3]^{3-}$	Λ (1.0%)	Δ (0.6%)	a
$[Cr(ox)_2(phen)]^-$	Δ (1.2%)	Λ (4.1%)	b
$[Cr(ox)(phen)_2]^+$	Δ (0.3%)	Λ (0.8%)	b
$[Co(phen)_3]^{2+}$	Δ (...)	Λ (...)	b

[a] [Environment substance] = 10 mM for a and = 30 mM for **b**; [complex] = 7.0 mM. [b] Hydrochloride.

Procedure and Apparatus. An aqueous mixture of a racemic complex (in 7.0 mM) with an environment substance (in 10 or 30 mM) in a quartz cell was irradiated with the light of linear polarization emitted from an NEC GLG-2023 argon ion laser[3] operating at 488.0 or 514.5 nm (ca. 800 mW) corresponding to the first d–d transition region for the present Cr(III) complexes. The change in the CD spectrum, which developed with irradiation time, was followed with a JASCO J-40CS spectropolarimeter. When $[Cr(ox)_3]^{3-}$, $[Cr(ox)_2(phen)]^-$, and $[Cr(ox)_2(bpy)]^-$ were used as a racemic complex, the quartz cell was cooled to 10 °C to depress their equilibrium shift induced by the usual Pfeiffer effect at the ground state (their half-life of racemization in the dark is ca. 18.4, 50, and 60 min at 25 °C in water, respectively).[7a,10,11] Since $[Cr(phen)_3]^{3+}$ was found to undergo photoaquation[12] under our experimental conditions, the laser-irradiated solution was subjected to ion-exchange chromatography with aqueous NaCl as an eluant. The CD spectrum was recorded for each fraction of the effluent from the column, so that only the direction of the equilibrium shift was determined for $[Cr(phen)_3]^{3+}$. The same difficulty was encountered in the $[Cr(ox)(phen)_2]^+$–*l*-cinchonidine hydrochloride system. To determine the percentage resolution and the direction of the equilibrium shift attained, the following spectroscopic data given in the literature were employed: $\Delta\epsilon_{522} = +2.83$ for Λ-$(+)_{589}$-$[Cr(ox)_3]^{3-}$,[13] $\Delta\epsilon_{526} = +2.46$ for Λ-$(+)_{546}$-$[Cr(ox)_2(phen)]^-$,[14] $\Delta\epsilon_{513} = +2.22$ for Λ-$(+)_{546}$-$[Cr(ox)_2(bpy)]^-$,[14] $\Delta\epsilon_{499} = +2.43$ for Λ-$(+)_{589}$-$[Cr(ox)(phen)_2]^+$,[15] and $\Delta\epsilon_{457} = +2.48$ for Λ-$(+)_{546}$-$[Cr(phen)_3]^{3+}$.[14] For comparison, the usual Pfeiffer effect was examined for each system in the same manner as described previously,[5,7a] taking into account the inversion rate constant of each complex.[8c,10,11,16]

Results and Discussion

Pfeiffer Effect at the Ground State. In Table I are summarized the absolute configuration of the enantiomers enriched and the percentage resolution attained by the usual Pfeiffer effect in the dark (at the ground state) with *d*-cinchonine hydrochloride and *l*-cinchonidine hydrochloride as an environment substance in water at ambient temperature. In the last row of Table I are given the results obtained for $[Co(phen)_3]^{2+}$, because $[Cr(phen)_3]^{3+}$ is so inert[16,17] that a mutual inversion between its enantiomers does not take place without photoexcitation, but it is expected from our chemical intuition to interact with the environment substance in the same fashion as labile $[Co(phen)_3]^{2+}$ (or $[Ni(phen)_3]^{2+}$).[6,18] In short, if $[Cr(phen)_3]^{3+}$ were labile enough to undergo an inversion at the ground state, its chiral equilibrium would be shifted toward the same direction as actually found for $[Co(phen)_3]^{2+}$. In addition, the percentage resolution cannot be estimated for $[Co(phen)_3]^{2+}$, for it is too labile[19] to resolve by conventional methods, but the correlation between the CD pattern and the absolute configuration has been already established for this complex in the study of its Pfeiffer effect.[6,18,20]

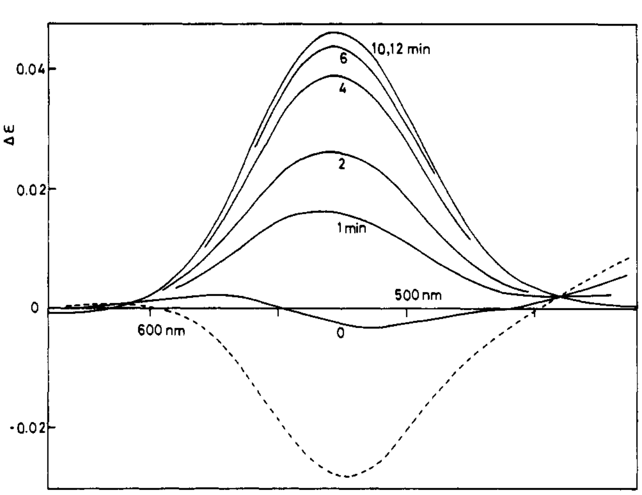

Figure 1. Change in the CD spectrum developed with irradiation time (488.0-nm laser) for the $[Cr(ox)_2(phen)]^-$ (7 mM)–*d*-cinchonine hydrochloride (30 mM) system in water. The broken curve is a CD spectrum obtained after equilibration in the dark.

Table II. Absolute Configuration of Enriched Enantiomers and Percentage Resolution Attained by the Pfeiffer Effect[a]

complex	*d*-cinchonine[b]	*l*-cinchonidine[b]	
$[Cr(ox)_3]^{3-}$	Λ (1.3%)	Δ (1.0%)	a
$[Cr(ox)_2(phen)]^-$	Λ (1.9%)	Δ (1.4%)	b
$[Cr(ox)(phen)_2]^+$	Λ (0.6%)	Δ (...)	b
$[Cr(phen)_3]^{3+}$	Δ (...)	Λ (...)	b

[a] Under laser irradiation. Experimental conditions are identical with those shown in Table I except for the $[Cr(phen)_3]^{3+}$ system where 0.6 M NaCl is added. [b] Hydrochloride.

It is evident in Table I that absolute configurations of the enantiomers enriched for the three complexes having at least one phen ligand are identical with each other, but are different from that for $[Cr(ox)_3]^{3-}$. This suggests that the stacking or hydrophobic (or π–π) interaction[5,7a] between phen ligand(s) and the quinolyl group of the environment substance plays a crucial role in chiral discrimination exhibited in the Pfeiffer effect of the three complexes. For the $[Cr(ox)_3]^{3-}$ system, on the other hand, electrostatic attraction has been proposed as an important interaction in its Pfeiffer effect with cinchona alkaloids as an environment substance.[7a]

Another finding to be noted is that the percentage resolution attained is much lower for the $[Cr(ox)(phen)_2]^+$ system than for the $[Cr(ox)_2(phen)]^-$ system. The same tendency is observed when hydrochloride salts of other cinchona alkaloids such as *d*-quinidine and *l*-quinine hydrochlorides are used as an environment substance. This is well interpreted in terms of the electrostatic repulsion inevitably expected between $[Cr(ox)(phen)_2]^+$ and the positive charge on the environment substance. In fact, if NaCl is added to neutralize the positive charge, the Pfeiffer effect is enhanced greatly for this cationic complex system.[21] On the other hand, the addition of NaCl to the $[Cr(ox)_2(phen)]^-$ system in which electrostatic repulsion is not expected leads to the diminished Pfeiffer effect, probably

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owing to reduced electrostatic attraction brought about by the accompanying increase in ionic strength of the medium.

Pfeiffer Effect at the Ligand Excited State. Now, let us turn to the experimental results obtained under photoirradiation at the ligand field (LF) transition region. Figure 1 shows how the CD intensity increases with irradiation time for the $[Cr(ox)_2(phen)]^-$–*d*-cinchonine hydrochloride system, where a very weak CD spectrum at $t = 0$ is so-called induced CD and a dotted curve is the CD spectrum obtained by the usual Pfeiffer effect after equilibration in the dark. It is seen that a stationary state is attained within 12 min, which is much shorter than the time required for equilibration in the usual Pfeiffer effect of the corresponding system (ca. 200 min at 25 °C).[5,11] This explicitly means that chiral discrimination under photoirradiation is performed at the excited state(s). Qualitatively the same situations were encountered in other systems, and both the magnitude and the shape of the CD spectra obtained at a stationary state were independent of the wavelength of irradiation light (488.0 or 514.5 nm) within our experimental errors.

From the shape and the magnitude of the CD spectra thus obtained under photoirradiation, the absolute configuration of the enriched enantiomer and the percentage resolution are estimated as before, and they are summarized in Table II, where only the absolute configuration is listed for those systems that are subjected to photoaquation (see Experimental Section). For comparison, $[Cr(ox)_2(bpy)]^-$ was also examined with *l*-cinchonidine hydrochloride as an environment substance. The results obtained at the ground and excited states were the same (with respect to the absolute configuration of the enriched enantiomer) as those listed for $[Cr(ox)_2(phen)]^-$ in Tables I and II.

The most striking finding in Table II is that the chiral equilibrium of the mixed-chelate complexes is shifted toward the opposite direction to that found in their respective Pfeiffer effects without photoexcitation, whereas the direction of the equilibrium shift induced for the homochelate complexes $[Cr(ox)_3]^{3-}$ and $[Cr(phen)_3]^{3+}$ is unaltered whether they are photoirradiated or not (see Table I).

Kane-Maguire and Langford[22] have proposed from their quenching study that photoinduced racemization of $[Cr(phen)_3]^{3+}$ and $[Cr(ox)(phen)_2]^+$ occurs through the lowest excited quartet state ($^4T_{2g}$ in O_h symmetry) prior to intersystem crossing to the thermally equilibrated doublet states (^2E_g and $^2T_{1g}$ in O_h symmetry). So that the Pfeiffer effect can be developed, the racemic complex must undergo a mutual inversion between its enantiomers. As a result, if the inversion takes place at the excited quartet state when the complex is photoirradiated at its LF transition region, chiral recognition under photoexcitation should be performed also at the quartet state. Since this excited state of a Cr(III) complex has an electronic configuration of $(t_{2g})^2(e_g)^1$ different from that $((t_{2g})^3)$ of the ground state ($^4A_{2g}$ in O_h symmetry), the complex at this thexi state is expected to be distorted with respect to the ground-state geometry.[23] That is, the Cr(III)–ligand bonds are lengthened, the complex as a whole being expanded, since one of the antibonding e_g orbitals is occupied.[24]

If the Cr(III) complex to be photoirradiated has ligands with different LF strengths as is the case with the mixed-chelate complexes examined here (C_2 symmetry), the excited quartet state is split into three components. Thus, particular Cr(III)–ligand bond(s) are preferentially lengthened (or labilized)[25] upon photoexcitation, leading to anisotropic expansion (geometrical deformation) of these complexes. In fact, Kirk et al.[26] found preferential labilization and subsequent substitution of the en ligand in both $[Cr(ox)_2(en)]^-$ and $[Cr(ox)(en)_2]^+$ upon photoexcitation at their LF transition regions. Therefore, similar anisotropic expansion is expected for the present mixed-chelate complexes $[Cr(ox)_2(phen)]^-$, $[Cr(ox)_2(bpy)]^-$, and $[Cr(ox)(phen)_2]^+$, probably with the Cr(III)–N bonds preferentially lengthened, when they are excited to the quartet state.

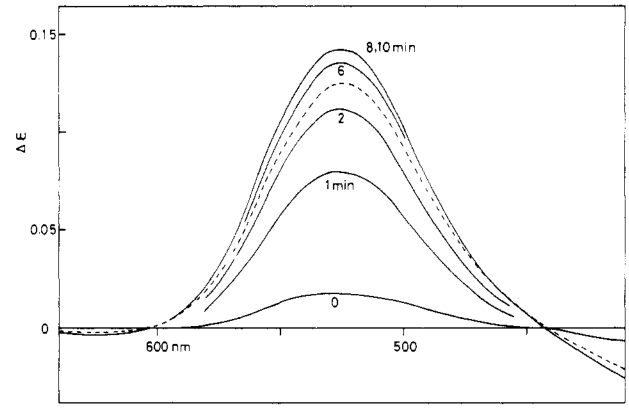

Figure 2. Change in the CD spectrum developed with irradiation time (488.0-nm laser) for the $[Cr(ox)_2(phen)]^-$ (4 mM)–*l*-quinine hydrochloride (5 mM) system in water. The broken curve is a CD spectrum obtained after equilibration in the dark.

Consequently, the inversion in the direction of the equilibrium shift observed only for the mixed-chelate complexes under photoexcitation is attributable to anisotropic expansion of these complexes. That is, we presume that the stacking or π–π interaction that dominantly contributes to chiral recognition in the present Pfeiffer effect (vide supra) is perturbed upon photoexcitation because of the accompanying geometrical deformation (particularly at the phen or bpy ligand portion(s)) of these mixed-chelate complexes, the direction of the equilibrium shift thus being inverted. However, anisotropic expansion of the complex need not necessarily lead to the inversion in the direction of the equilibrium shift, which is observed by chance when *d*-cinchonine and *l*-cinchonidine hydrochlorides are used as an environment substance. In fact, if *l*-quinine hydrochloride (6′-methoxy-*l*-cinchonidine hydrochloride) is used, Λ enantiomers of $[Cr(ox)_2(phen)]^-$, $[Cr(ox)_2(bpy)]^-$, and $[Cr(ox)(phen)_2]^+$ are enriched by the usual Pfeiffer effect just as when *l*-cinchonidine hydrochloride is used, but the the direction of the equilibrium shift is not inverted upon photoexcitation for the former two complexes (Figure 2), it being inverted only for the last complex. Essentially the same phenomena are observed when *d*-quinidine hydrochloride (6′-MeO-*d*-cinchonine hydrochloride) is used, though the equilibrium of the respective complexes is shifted toward the opposite direction at both the ground and excited states to that found with *l*-quinine hydrochloride as an environment substance. These facts lead us to suppose that chiral discrimination observed in the present Pfeiffer systems is performed by a very small difference in the stereoselective interactions of Δ and Λ enantiomers with a chiral environment substance. In any case, our experimental results presented above are taken as indirect evidence suggesting an anisotropic

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change in the geometry of the mixed-chelate Cr(III) complexes at their LF excited state.

On the other hand, the homochelate complexes $[Cr(ox)_3]^{3-}$ and $[Cr(phen)_3]^{3+}$ are expected to expand isotropically when excited to the quartet state, since all of the six Cr(III)–ligand bonds are equivalent to a good approximation. Therefore, the inversion in the direction of the equilibrium shift is not anticipated for these homochelate complexes, as is really the case (Table II), but the optical yield attained might be changed upon photoexcitation because of their isotropic expansion at the quartet state (compare the percentage resolutions attained for $[Cr(ox)_3]^{3-}$ at the ground state with those at the excited state).

Recently, some evidence has been presented suggesting that photoreaction of some Cr(III) complexes proceeds not only from the quartet state but also from the doublet states,[27] which are designated simply as the ^2E state here, and in particular, photoaquation of $[Cr(bpy)_3]^{3+}$ is believed to occur only at the doublet ^2E state.[23b,28] Photophysical and photochemical similarities[12,29,30] between $[Cr(bpy)_3]^{3+}$ and $[Cr(phen)_3]^{3+}$ imply that photoracemization of $[Cr(phen)_3]^{3+}$ as well as $[Cr(bpy)_3]^{3+}$ might take place at the ^2E state. Since the ^2E state has the same electronic configuration $((t_{2g})^3)$ as the ground state, these two states in Cr(III) complexes have virtually the same geometry.[12,23b,24] As a result, the direction of the equilibrium shift is expected not to be inverted for $[Cr(phen)_3]^{3+}$ upon photoexcitation even if only the ^2E state is a photoreactive level. In this way, our experimental results obtained for this complex are well interpreted equally by the doublet and quartet reactivity hypotheses. However, the photochemical behavior exhibited by the mixed-chelate complexes seems not to be accounted for by the doublet reactivity hypothesis alone.

Finally, it is worth noting that Kane-Maguire et al.[31] have reported only one example, to our knowledge, in which the Pfeiffer effect is applied to partial photoresolution of $[Cr(phen)_3]^{3+}$ with ((*R*,*R*)-tartrato)antimonate(III) as an environment substance in water. The direction of the equilibrium shift they attained under photoexcitation at the LF regions is the same (Δ) as that found in the usual Pfeiffer effect of labile $[Ni(phen)_3]^{2+}$ or $[Cd(phen)_3]^{2+}$.[32] This observation is consistent with our interpretation presented above.

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Registry No. $[Cr(ox)_3]^{3-}$, 15054-01-0; $[Cr(ox)_2(phen)]^-$, 21748-33-4; $[Cr(ox)_2(bpy)]^-$, 21748-32-3; $[Cr(ox)(phen)_2]^+$, 32626-76-9; $[Cr(phen)_3]^{3+}$, 15276-16-1; *d*-cinchonine hydrochloride, 5949-11-1; *l*-cinchonidine hydrochloride, 524-57-2; *d*-quinidine hydrochloride, 1668-99-1; *l*-quinine hydrochloride, 130-89-2.

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Contribution from the Department of Chemistry,
McMaster University, Hamilton, Ontario, Canada L8S 4M1

Electronic Structure of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ Studied by Photoelectron Spectroscopy and LCAO–HFS Calculations

ADAM P. HITCHCOCK,* NGUYEN HAO, NICK H. WERSTIUK, MICHAEL J. McGLINCHEY, and TOM ZIEGLER

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The He I ultraviolet photoelectron spectra of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ have been recorded and analyzed with the aid of an LCAO–HFS(Xα) calculation on $Zr(BH_4)_4$. The PE spectra of these two species are found to be essentially identical, as previously observed by Downs et al. [*J. Chem. Soc., Dalton Trans.* **1978**, 1755]. Our assignments differ in some aspects from those given previously. A qualitative scheme for the triple-bridge bonding in these molecules has been developed, which is based on an analogy with the bonding in classical d^0 tetrahedral complexes such as $TiCl_4$ and MnO_4^-. The factors determining the relative stabilities of mono-, di-, and tribridged borohydride ligands are also discussed.

Introduction

The tetrakis(tetrahydroborates) of zirconium and hafnium are volatile, covalently bonded molecular complexes, which pose interesting bonding questions. Vibrational spectroscopy,[1] electron[2,3] and neutron diffraction[4] studies, and X-ray crystallography[5] have shown that these molecules are tetrahedral with three hydrogen atoms bridging the metal atom and each boron atom. Vibrational spectroscopic studies indicate that the tetrakis(tetrahydroborates) of uranium[6] and neptunium[7] are also tetrahedral and triply bridged in the gas phase. It is also probable that tetrahydroborate derivatives of samarium[8] and thorium[9] are triply bridged.

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