

bonds (1.703 and 1.690 Å) of a tbp. But the angles O(1)–P–O(3) (145.2°) and O(2)–P–O(4) (160.1°) give priority to a description of this geometry in terms of an rp. A simple consideration (Holmes, 1974) of the size of these two angles in relation to the values of the idealized geometries yields a 75% rp for this compound. An analogous criterion for a quantification of the geometry (Wunderlich, 1976) can be gained from a least-squares plane defined by the atoms O(1), O(2), O(3), and O(4). This is the basis of an ideal rp or tp with the four atoms coplanar (average distance  $\langle d \rangle = 0$ ). In the case of an ideal tbp these atoms occupy the top, the bottom and two equatorial sites and cannot be coplanar. But they will all have identical distances from a best plane of exactly  $\frac{1}{4}$  the averaged equatorial bond lengths. With these as two ends of a scale ( $\langle d \rangle = 0$  and a maximum of  $\langle d \rangle = \frac{1}{4}\langle P-O \rangle_{eq}$ ) it is possible to classify every intermediate geometry by a criterion involving the positions of four ligands of the central atom. In the title compound, the four O atoms have an averaged distance of 0.100 Å from the corresponding least-squares plane and the averaged equatorial bond length is 1.650 Å. Thus, this geometry is 0.100/0.4125 = 0.24 away from the ideal rp and can be called 76% rp.

Many of the bond lengths and bond angles of the five-membered rings, the condensed benzene rings and the extra phenyl group show considerable deviations from standard values but they agree with those of other structures of this type, e.g. the analogous phenoxyphosphorane (Sarma, Ramirez & Marecek, 1976).

#### References

- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71–98. Birmingham: Kynoch Press.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- HOLMES, R. R. (1974). *J. Am. Chem. Soc.* **96**, 4143–4149.
- SARMA, R., RAMIREZ, F. & MARECEK, J. F. (1976). *J. Org. Chem.* **41**, 473–479.
- WIEBER, M., FOROUGH, K. & KLINGL, H. (1974). *Chem. Ber.* **107**, 639–643.
- WUNDERLICH, H. (1974). *Acta Cryst.* **B30**, 939–945.
- WUNDERLICH, H. (1976). Third European Crystallographic Meeting, Zurich, Switzerland. Abstract 0 54 D.
- WUNDERLICH, H. & MOOTZ, D. (1974). *Acta Cryst.* **B30**, 935–939.

## SHORT COMMUNICATIONS

*Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.*

*Acta Cryst.* (1978). **B34**, 344–346

**Bond distances in rhodium tribromide, RhBr<sub>3</sub>, by the X-ray absorption technique.** By JOSEPH REED\* and P. EISENBERGER, *Bell Laboratories, Murray Hill, New Jersey 07974, USA*

(Received 11 July 1977; accepted 15 August 1977)

The interatomic bond distances in RhBr<sub>3</sub> have been determined by extended X-ray absorption fine structure (EXAFS) measurements of the K-shell absorption edges of rhodium and bromine. The analysis yields a Rh–Br distance of 2.49 (1) Å based on the Rh edge data. The Br edge data yield 2.48 (1) Å for the Br–Rh bond and a Br–Br distance of 4.85 (1) Å.

#### Introduction

In soluble transition-metal catalysts, the strength of the interatomic metal-to-ligand bond is of the utmost importance. A ligand, *L*, must frequently be dissociated in order to make a coordination site available, and the important factor then is the stability of the interatomic *M–L* bond (Henrici-Olivé & Olivé, 1971). Rhodium trihalides have been shown to be active catalysts in the reduction of fumaric acid in aqueous acetate solutions at 25 °C and 1 atm hydrogen (Ipatieff & Tronev, 1935). Nevertheless, structural determinations which would help to elucidate the way in which rhodium trihalides

function as catalysts have not been attempted to date. One possible reason could be the extreme difficulty in obtaining X-ray quality single crystals owing to the deliquescent nature of RhX<sub>3</sub>, where X = Cl, Br.

This study reports on the interatomic bond distances in RhBr<sub>3</sub>, where a novel technique, extended X-ray absorption fine structure (EXAFS), was used. This technique does not rely on single crystals and has been used previously to determine interatomic distances in iron–sulfur proteins (Shulman, Eisenberger, Blumberg & Stombaugh, 1975), in copper salts in aqueous solutions (Eisenberger & Kincaid, 1975), and in polymer-bound rhodium(I) catalysts (Reed, Eisenberger, Teo & Kincaid, 1977). This present study is part of a larger effort in developing structural confidence in the use of EXAFS as a complement to single-crystal X-ray crystallography.

\* To whom correspondence should be addressed. Present address: Exxon Res. & Eng. Co., Linden, New Jersey 07036, USA.

### Experimental

We measured the photo-absorption  $K$  edges of Rh and Br in  $\text{RhBr}_3$  using the tuneable X-ray synchrotron source at the Stanford Synchrotron Radiation Project, Stanford University. The instrumentation has been described previously (Kincaid & Eisenberger, 1975).

The measurements of the intensity,  $I_0$ , of the incident X-ray radiation passing through one ionization chamber ( $\text{He} + \text{N}_2$ ), then transmitted through the sample and finally to a second ionization chamber ( $\text{N}_2$ ) allows the relationship  $\mu x = \ln(I_0/I)$ , where  $\mu$  is the linear absorption coefficient,  $x$  is the absorber thickness, and  $I$  is the transmitted intensity, to be plotted against the photon energy.

The data in this paper were taken on crystalline  $\text{RhBr}_3$  purchased from Matty Bishops. The sample was sealed between two thin layers of Kapton tape which is transparent to the X-rays and protects the deliquescent sample from air.

The theoretical basis for the EXAFS effect has been advanced by several groups (Lee & Beni, 1977; Stern, Sayers & Lytle, 1975; Ashley & Doniach, 1975; Lee & Pendry, 1975). In addition, the various methods of data analysis are found in articles by Stern, Sayers & Lytle (1975), Citrin, Eisenberger & Kincaid (1976), Teo, Lee, Simons, Eisenberger & Kincaid (1977) and Lee, Teo & Simons (1977).

The data for  $\text{RhBr}_3$  where Rh is the absorber and for  $\text{RhBr}_3$  where Br is the absorber are shown in Fig. 1, where  $\mu x$  is plotted against photon energy. The threshold energy,  $E_{\text{th}}$ , was chosen in a systematic way for both Rh and Br edges as the maximum of the first oscillation.

The subsequent data analysis included background removal for the Rh and Br EXAFS (Fig. 2), use of the Fourier transform technique (Fig. 3), and curve fitting of the Fourier-filtered data (Fig. 4) based on transferability of theoretical phase shifts (Citrin, Eisenberger & Kincaid, 1976) and of theoretical amplitudes (Teo, Lee, Simons, Eisenberger & Kincaid, 1977). It has previously been shown that theoretical phase shifts,  $\varphi_j$ , and amplitudes,  $f_j$ , can be used to accurately predict interatomic distances to  $\pm 0.01 \text{ \AA}$  in known structures (Citrin, Eisenberger & Kincaid, 1976).

Our results are based on fitting a single frequency for the Rh and the Br EXAFS in  $\text{RhBr}_3$  to the function

$$\frac{\Delta\mu}{\mu} = \sum_j \frac{N_j |f_j(k, \pi)|}{R_j^2 k} \exp(-2\sigma^2 k^2) \times \sin[2kR_j + \varphi_j(k)], \quad (1)$$

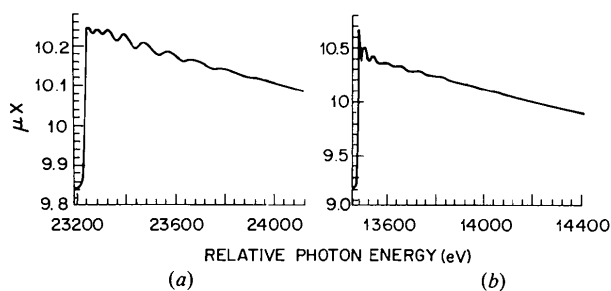


Fig. 1. Plots of  $\mu x$  (absorption coefficient  $\times$  thickness) vs photoelectron kinetic energy  $E$ . (a) Measured  $K$  edge of Rh in  $\text{RhBr}_3$  and (b) measured  $K$  edge of Br in  $\text{RhBr}_3$ .

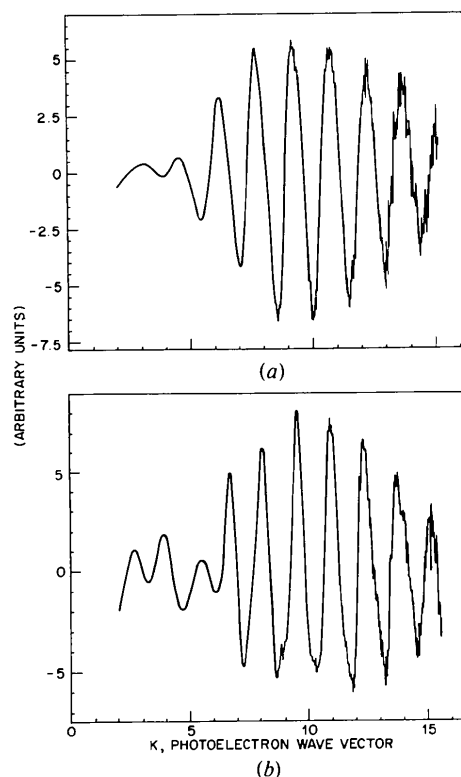


Fig. 2. EXAFS data for  $\text{RhBr}_3$  (a) where Rh is the absorber, background removed, and (b) where Br is the absorber, background removed.

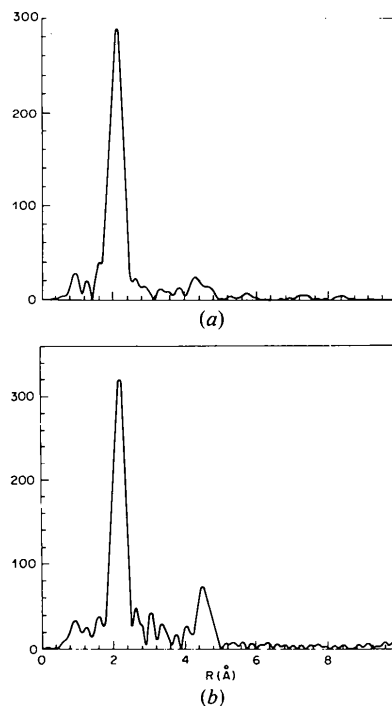


Fig. 3. Fourier transform of the EXAFS data of  $\text{RhBr}_3$  (a) where Rh is the absorber and (b) where Br is the absorber. The peak at 2.1 is Rh-Br and at 4.5 is Br-Br.

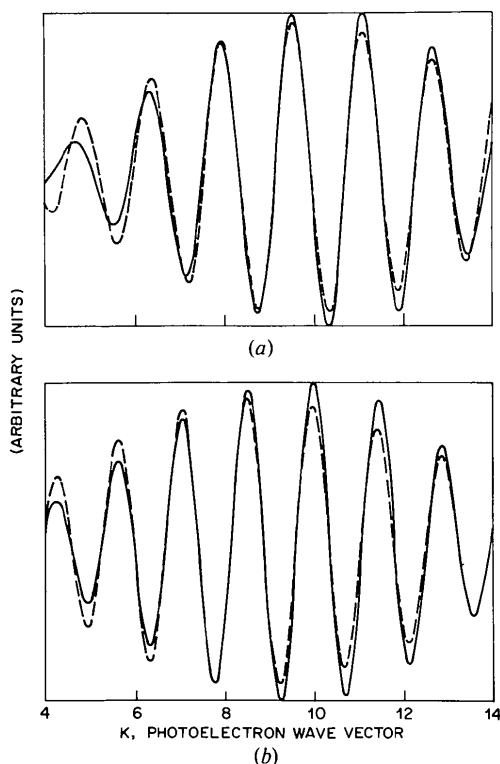


Fig. 4. The fit (---) of the EXAFS data (—) of  $\text{RhBr}_3$  after being Fourier filtered (a) where Rh is the absorber and (b) where Br is the absorber.

where  $N_j$  is the number of scattering atoms  $j$  at a distance  $R_j$  to the absorbing atom with a Debye–Waller-like temperature factor  $\exp(-2\sigma_j^2 k^2)$ .  $\varphi_j(k)$  and  $f_j(k, \pi)$  are an energy-dependent phase shift and an electron back-scattering form factor. The  $k$  wavevector of the emitted photoelectron is given by

$$k = \sqrt{\frac{2m(E - E_{\text{th}})}{\hbar^2}},$$

where  $E_{\text{th}}$  is the absorption threshold energy for the atoms and  $E$ , the photon energy, is varied. For the Br edge data, Fig. 3(b) clearly shows that two distances are present. By using the appropriate filter and transforming back into  $k$  space one can individually fit the Br–Rh and the Br–Br contribution.

### Results and discussion

The results of the fitting technique are summarized in Table 1. This fitting function gives a Rh–Br interatomic distance of 2.49 (1) Å when the absorber is rhodium and 2.48 (1) Å when the absorber is bromine. The fit of the data is shown in Fig. 4. The analysis also gives a Br–Br distance of 4.85 (1)

Table 1. Interatomic bond distances (Å) in  $\text{RhBr}_3$

	Rh edge	Br edge
Rh–Br	2.49 (1)	2.48 (1)
Br–Br		4.85 (1)
$\sigma$ (Rh–Br)	0.07	0.07
$E_0$ (eV)	23260	13484

Å. The absence of any significant intensity or phase distortion of the Br–Br signal in Fig. 3(b) is a strong indication that the atoms are arranged in a *cis* configuration. Previous studies on the *trans* configuration where one atom shadows another (*i.e.* the Rh would be between two bromines) have all shown significant amplitude and phase distortions (unpublished results). The technique and results reported herein demonstrate the practical application of EXAFS to the solution of structural problems. This analysis technique supplements single-crystal X-ray diffraction as another tool for the resolution of structural problems for which X-ray crystallography could not or has not been applied.

We thank Drs B. M. Kincaid, B. K. Teo and P. A. Lee for their technical assistance and helpful discussions. We are also grateful to B. Chambers and A. Simons for programming assistance.

### References

- ASHLEY, C. A. & DONIACH, S. (1975). *Phys. Rev. Sect. B*, **11**, 1279–1288.
- CITRIN, P. H., EISENBERGER, P. & KINCAID, B. M. (1976). *Phys. Rev. Lett.* **36**, 1346–1349.
- EISENBERGER, P. & KINCAID, B. M. (1975). *Chem. Phys. Lett.* **36**, 134–136.
- HENRICI-OLIVÉ, G. & OLIVÉ, S. (1971). *Angew. Chem. Int. Ed. Engl.* **10**, 105–115.
- IPATIEFF, V. V. & TRONEV, V. G. (1935). *C.R. (Dokl.) Acad. Sci. URSS*, **1**, 622–624.
- KINCAID, B. M. & EISENBERGER, P. (1975). *Phys. Rev. Lett.* **34**, 1361–1364.
- LEE, P. A. & BENI, G. (1977). *Phys. Rev. Sect. B*, **15**, 2862–2883.
- LEE, P. A. & PENDRY, J. B. (1975). *Phys. Rev. Sect. B*, **11**, 2795–2811.
- LEE, P. A., TEO, B. K. & SIMONS, A. L. (1977). *J. Am. Chem. Soc.* **99**, 3856–3859.
- REED, J., EISENBERGER, P., TEO, B. K. & KINCAID, B. M. (1977). *J. Am. Chem. Soc.* **99**, 5217.
- SHULMAN, R. B., EISENBERGER, P., BLUMBERG, W. E. & STOMBAUGH, N. A. (1975). *Proc. Natl Acad. Sci. USA*, **72**, 4003–4007.
- STERN, E. A., SAYERS, D. E. & LYTLE, F. W. (1975). *Phys. Rev. Sect. B*, **11**, 4836–4846.
- TEO, B. K., LEE, P. A., SIMONS, A. L., EISENBERGER, P. & KINCAID, B. M. (1977). *J. Am. Chem. Soc.* **99**, 3854–3856.