*Inorg. Chem.* **1988**, *27*, 3701–3706

Contribution from the School of Chemical Sciences, Department of Physics,
and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

# High-Pressure Spectroscopic Studies of Dihalotetrakis(pivalato)dirhenium(III) Metal–Metal Quadruply Bonded Complexes

R. T. Roginski, T. L. Carroll, A. Moroz, B. R. Whittlesey, J. R. Shapley,* and H. G. Drickamer*

*Received December 1, 1987*

The electronic absorption spectra of $Re_2(piv)_4Cl_2$ and $Re_2(piv)_4Br_2$ (piv = $O_2CCMe_3$) have been measured as a function of pressure in the crystalline solids and for the molecules dissolved in PMMA (poly(methyl methacrylate)). High-pressure infrared absorption spectra have been measured for the crystalline solids dispersed in mineral oil over the range 700–1800 cm$^{-1}$. The major feature appearing in the electronic spectra is the growth in intensity of a band lying on the low-energy side of the $\delta \rightarrow \delta^*$ excitation. This growth starts at the lowest pressures, while only above ~40 kbar is any decrease in intensity of the $\delta \rightarrow \delta^*$ excitation observed. In the region above 25–30 kbar new peaks appear in the IR spectrum at 1134, 1280, and 1697 cm$^{-1}$ for the bromide and at 1142, 1286, and 1697 cm$^{-1}$ for the chloride. After consideration of alternative possibilities, the changes in the spectra are assigned to a molecular isomerization, in which the axial halide ligands move to radial positions and force two of the bidentate pivalate ligands to become monodentate.

## Introduction

Quadruple metal–metal bonds in compounds such as $[(n\text{-}Bu)_4N]_2[Re_2Cl_8]$ are responsible for the eclipsed configuration of the halves of the molecule.[1] This eclipsed conformation may be modified by incorporating bridging ligands of varying "bite size" (e.g., in $Mo_2Cl_4(dmpe)_2$).[2] Pressure has been shown to cause isomerization of the torsional type in crystalline $[(n\text{-}Bu)_4N]_2[Re_2X_8]$ (X = Br, I),[3] apparently due to increased repulsion between the eclipsed halide ligands. The balance between inter- and intramolecular forces in determining the effects of pressure (pressure-tuning spectroscopy) has been discussed recently.[4]

$Re_2(piv)_4Cl_2$ (piv = $O_2CCMe_3$) is a molecule possessing a bridged quadrupole metal–metal bond. The bridging pivalate ligands are eclipsed, and the two chloride ligands reside in axial positions. If the *tert*-butyl groups are ignored, the symmetry of the molecule approaches $D_{4h}$. $Re_2(piv)_4Cl_2$ crystallizes in the $I4/m$ space group with $Z = 2$.[5] The rhenium–rhenium bond distance is 2.236 Å. $Re_2(piv)_4Br_2$ has the same molecular and crystal structure as its chloride counterpart, with a Re–Re distance of 2.234 Å.[5] We report the effect of pressure on the visible and infrared spectral features of $Re_2(piv)_4Cl_2$ and $Re_2(piv)_4Br_2$, both as crystalline solids and in a polymer matrix. The changes observed are interpreted as resulting from a molecular isomerization.

## Experimental Section

$Re_2(piv)_4Cl_2$ and $Re_2(piv)_4Br_2$ were prepared by the method of Collins, Cotton, and Gage[5] and were analyzed by the University of Illinois School of Chemical Sciences Microanalytical Laboratory. Anal. Calcd for $Re_2(C_4H_9CO_2)_4Cl_2$: C, 28.37; H, 4.28. Found: C, 28.36; H, 4.29. Calcd for $Re_2(C_4H_9CO_2)_4Br_2$: C, 25.65; H, 3.87. Found: C, 25.74; H, 3.61.

The optical absorption spectra were taken in a gasketed diamond anvil cell (DAC); the ruby fluorescence method of pressure calibration was used. Polycrystalline electronic spectra were taken with Nujol, Fluorolube, and cesium chloride used as pressure-transmitting media, with no discernible difference in the results. Electronic spectra were also taken of the two compounds dissolved in poly(methyl methacrylate) (PMMA). The tetrapivalate compound was first dissolved in dichloromethane, and enough PMMA was added to bring the weight ratio of compound to polymer equal to approximately 0.25. This converts to a mole ratio for $Re_2(piv)_4Cl_2$ (and for the bromide counterpart) of about 0.03 (based on a monomer unit of methyl methacrylate). The light source was provided by a 100-W quartz tungsten halogen lamp and was dispersed by a Kratos $^1/_4$-m monochromator. Light was detected by EMI 9658 and 9684 photomultiplier tubes and an Ortec photon-counting system. Full details of the optical system may be found elsewhere.[6] The resulting spectra were fit with a series of symmetric Gaussian peaks by means of a computer program that varied the values of each peak's height, location, and full width at half-maximum in order to achieve the minimum variance.

The infrared absorption spectra were taken in a gasketed DAC employing type IIA diamonds. Nujol was used exclusively as the pressure-transmitting medium. Spectra were obtained on a Nicolet 7199 Fourier Transform infrared spectrometer with an 800-cm$^{-1}$ HgCdTe detector and a Perkin-Elmer 4X beam condenser. An XYZ mount was used to position the DAC at the focus. Pressure was measured by the ruby fluorescence calibration method. All data for both the visible and infrared regions were both reversible and reproducible.

**Table I**

| | normalized area of low-energy peak ($\delta \rightarrow \delta^*$ = 1.00) | area fraction of low-energy peak | |
|---|---|---|---|
| | | *P* = 1 atm | *P* = 75 kbar |
| $Re_2(piv)_4Cl_2$—crystalline | 0.21 | 0.17 | 0.51 |
| $Re_2(piv)_4Br_2$—crystalline | 0.47 | 0.32 | 0.60 |
| $Re_2(piv)_4Cl_2$—polymer | 0.25 | 0.20 | 0.53 |
| $Re_2(piv)_4Br_2$—polymer | 0.50 | 0.33 | 0.53 |

## Results

Figure 1 shows the electronic spectrum of polycrystalline $Re_2(piv)_4Cl_2$ at three different pressures. Two bands are resolved in the range 14000–22000 cm$^{-1}$. The position of the higher energy band assigned as the $\delta \rightarrow \delta^*$ ($^1A_{1g} \rightarrow {}^1A_{2u}$) transition,[7] is at 20290 cm$^{-1}$ at atmospheric pressure. Both bands shift between 600 and 800 cm$^{-1}$ to lower energy over 70 kbar. Figure 2 shows the electronic spectrum of the polycrystalline bromide at three different pressures. The spectrum is very similar to that of the chloride, with the initial positions of the first two bands shifted approximately 500 cm$^{-1}$ to lower energy.

Figures 3 and 4 and Table I show the effects of pressure on the areas of the first two peaks in the electronic absorption spectra of the bromide and chloride on a quantitative basis. The area of the lower energy peak of $Re_2(piv)_4Cl_2$ increases by a factor of approximately 3.5 over 75 kbar, while the area of the $\delta \rightarrow \delta^*$ transition decreases to about 0.7 times the atmospheric pressure value. Thus, the lower energy peak, which has a fractional area of 0.17 at atmospheric pressure (basis = area of lower energy peak + area of $\delta \rightarrow \delta^*$ peak), accounts for about 51% of the area under the first two bands at 75 kbar. The changes for the bromide are slightly less: the fractional area of the low-energy peak (lep) increases from 0.32 to 0.60 over 75 kbar. Although some data have been included for pressures above 75 kbar, the accuracy of the absolute areas may be somewhat questionable due to reversible spreading of the gasket hole.

The electronic spectrum of $Re_2(piv)_4Br_2$ in a PMMA matrix is shown in Figure 5. The atmospheric-pressure spectrum in the polymer is qualitatively similar (with some rather minor differences) to the polycrystalline spectrum; this is seen by observing

---

* To whom correspondence should be addressed at the School of Chemical Sciences.

(1) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.
(2) Campbell, F. L., III; Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1985**, *24*, 177.
(3) Carroll, T. L.; Shapley, J. R.; Drickamer, H. G. *J. Am. Chem. Soc.* **1985**, *107*, 5802.
(4) Drickamer, H. G. *Acc. Chem. Res.* **1986**, *19*, 329.
(5) Collins, D. M.; Cotton, F. A.; Gage, L. D. *Inorg. Chem.* **1979**, *18*, 1712.
(6) Jurgensen, C. W.; Drickamer, H. G. *Phys. Rev. B* **1984**, *30*, 7202.
(7) Martin, D. S.; Huang, H. W.; Newman, R. A. *Inorg. Chem.* **1984**, *23*, 699.

0020-1669/88/1327-3701$01.50/0

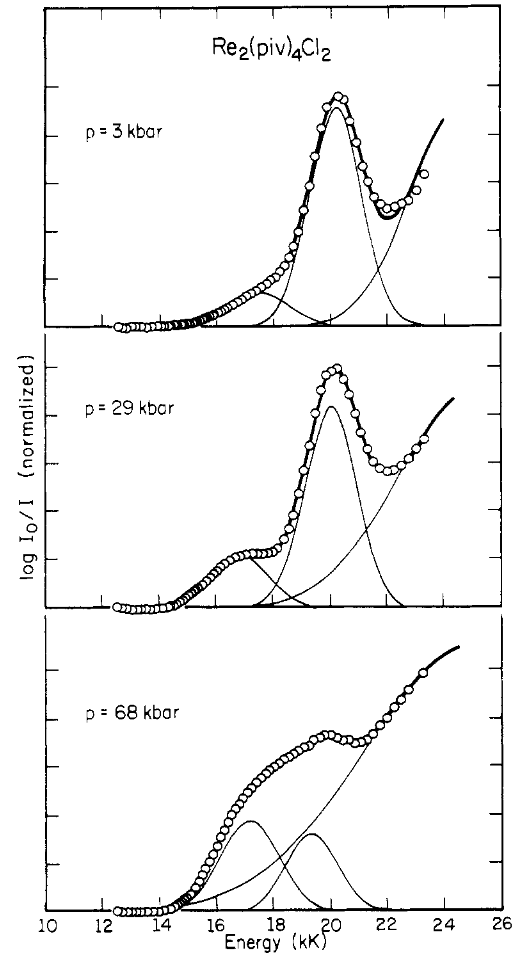


**Figure 1.** Polycrystalline visible spectra of Re$_2$(piv)$_4$Cl$_2$ at three pressures.

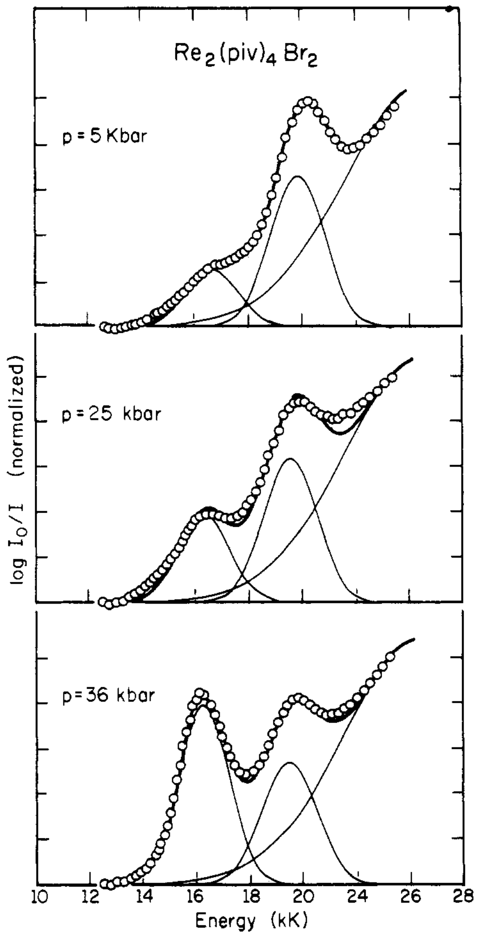


**Figure 2.** Polycrystalline visible spectra of Re$_2$(piv)$_4$Br$_2$ at three pressures.

the area fractions in Table I, which are virtually identical. This is also true for the chloride. The shifts of the two peaks are identical with what is seen in the solid state. Figures 6 and 7 show the areas of the two peaks of interest as a function of pressure. We have chosen to present the data in terms of the areas of the individual peaks in Figures 3, 4, 6, and 7, rather than using area fractions, to emphasize the increase of the intensity of the low-energy peak, which is not necessarily at the expense of the intensity of the $\delta \rightarrow \delta^*$ transition. The area fraction of the lep for the bromide is approximately twice that for the chloride and is independent of the medium. At 75 kbar, the area fraction of the lep is about 0.55, regardless of the halide ligand or the medium. Although Figures 3, 4, 6, and 7 suggest slight growth in the lep at lower pressures, we will focus on the major change that occurs above ca. 25 kbar.

The polycrystalline infrared spectra of the chloride and bromide for the region 700–1800 cm$^{-1}$ as a function of pressure are shown in Figures 8 and 9, respectively. The features present at atmospheric pressure correspond reasonably well to the infrared spectrum of polycrystalline sodium pivalate, Na(C$_4$H$_9$CO$_2$).[8] The peak located at 1208 cm$^{-1}$ is assigned as a carbon–carbon skeletal mode characteristic of *tert*-butyl groups.[9] The C–O antisymmetric and symmetric stretches[5] are located in the region of the broad absorption by Nujol and thus are not observed. Three new peaks appear in the spectrum (1134, 1280, and 1697 cm$^{-1}$) at approximately 25 kbar and grow continuously with increasing pressure for the bromide. The same changes occur for the chloride (peak locations 1142, 1286, and 1697 cm$^{-1}$), with the exception that the three new peaks are first observed at approximately 30 kbar. In each case the major changes in intensity of the new infrared peaks occur over the same pressure range as the major changes in intensity of the low-energy peak in the electronic spectra (30–60 kbar for the chloride; 25–50 kbar for the bromide).

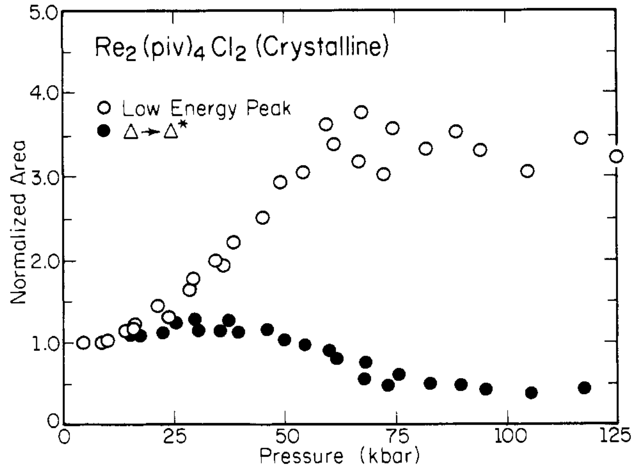


**Figure 3.** Area of the low-energy peak (normalized to 1 atm) and of the $\delta \rightarrow \delta^*$ peak in polycrystalline Re$_2$(pic)$_4$Cl$_2$ as a function of pressure.

The visible and infrared spectra of Re$_2$(OAc)$_4$Cl$_2$ (OAc = acetate) also were measured as a function of pressure. The visible spectrum of the tetraacetate is very similar to that of the tetrapivalates yet exhibited little or no change in band intensities up to 100 kbar. The infrared spectrum showed no new bands in the region 700–1800 cm$^{-1}$ up to 100 kbar.

## Discussion

It is clear that the spectral changes induced by increasing pressure occur in parallel for both Re$_2$(piv)$_4$Cl$_2$ and Re$_2$(piv)$_4$Br$_2$.

---

(8) Spinner, E. *J. Chem. Soc.* **1964**, 4217.
(9) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Chapman & Hall: London, 1975.

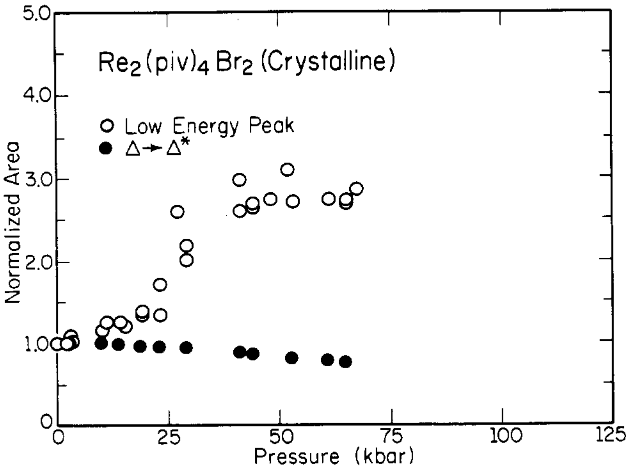


**Figure 4.** Area of the low-energy peak (normalized to 1 atm) and of the $\delta \rightarrow \delta^*$ peak in polycrystalline $Re_2(piv)_4Br_2$ as a function of pressure.

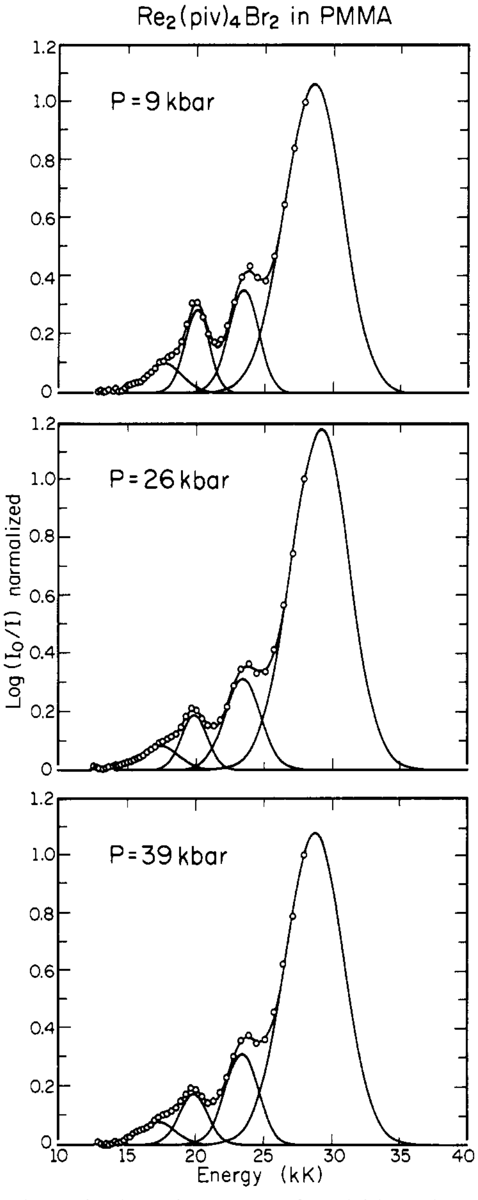


**Figure 5.** Electronic absorption spectra of $Re_2(piv)_4Br_2$ in a PMMA matrix at three pressures.

Furthermore, the electronic spectra for either the molecules in the crystal or the molecules isolated in a polymer matrix are very similar, which makes it doubtful that we are dealing with intermolecular electronic interactions. This rules out two possible explanations for the electronic spectral changes alone, namely, excitonic behavior that increases with increasing pressure or a very large increase in spin–orbit coupling with pressure.[10] The latter also is contraindicated by the lack of changes in the spectra of $Re_2(OAc)_4Cl_2$ with increasing pressure. The best explanation for

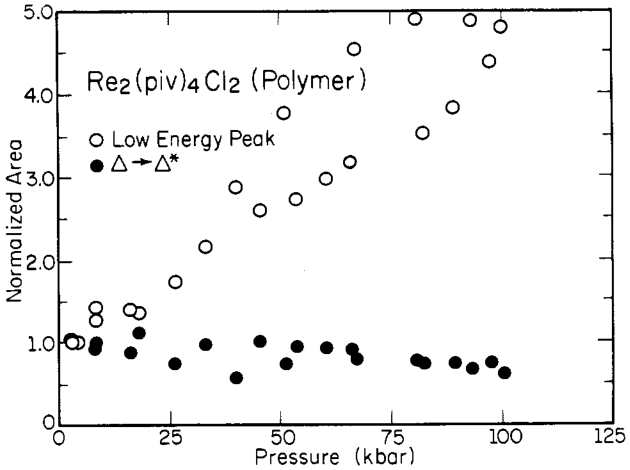


**Figure 6.** Area of the low-energy peak (normalized to 1 atm) and of the $\delta \rightarrow \delta^*$ peak of $Re_2(piv)_4Cl_2$ in a PMMA matrix as a function of pressure.

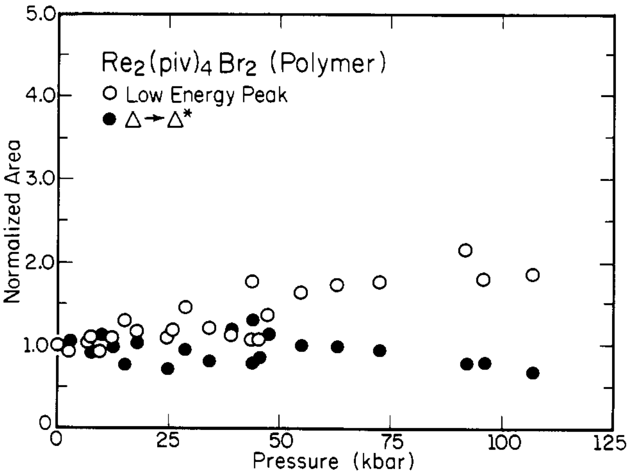
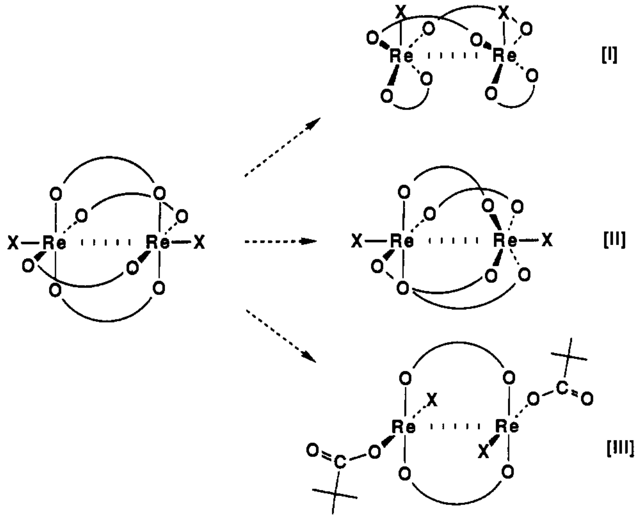


**Figure 7.** Area of the low-energy peak (normalized to 1 atm) and of the $\delta \rightarrow \delta^*$ peak of $Re_2(piv)_4Br_2$ in a PMMA matrix as a function of pressure.

**Scheme I**



---

(10) Stephens, D. R.; Drickamer, H. G. *J. Chem. Phys.* **1961**, *35*, 429.

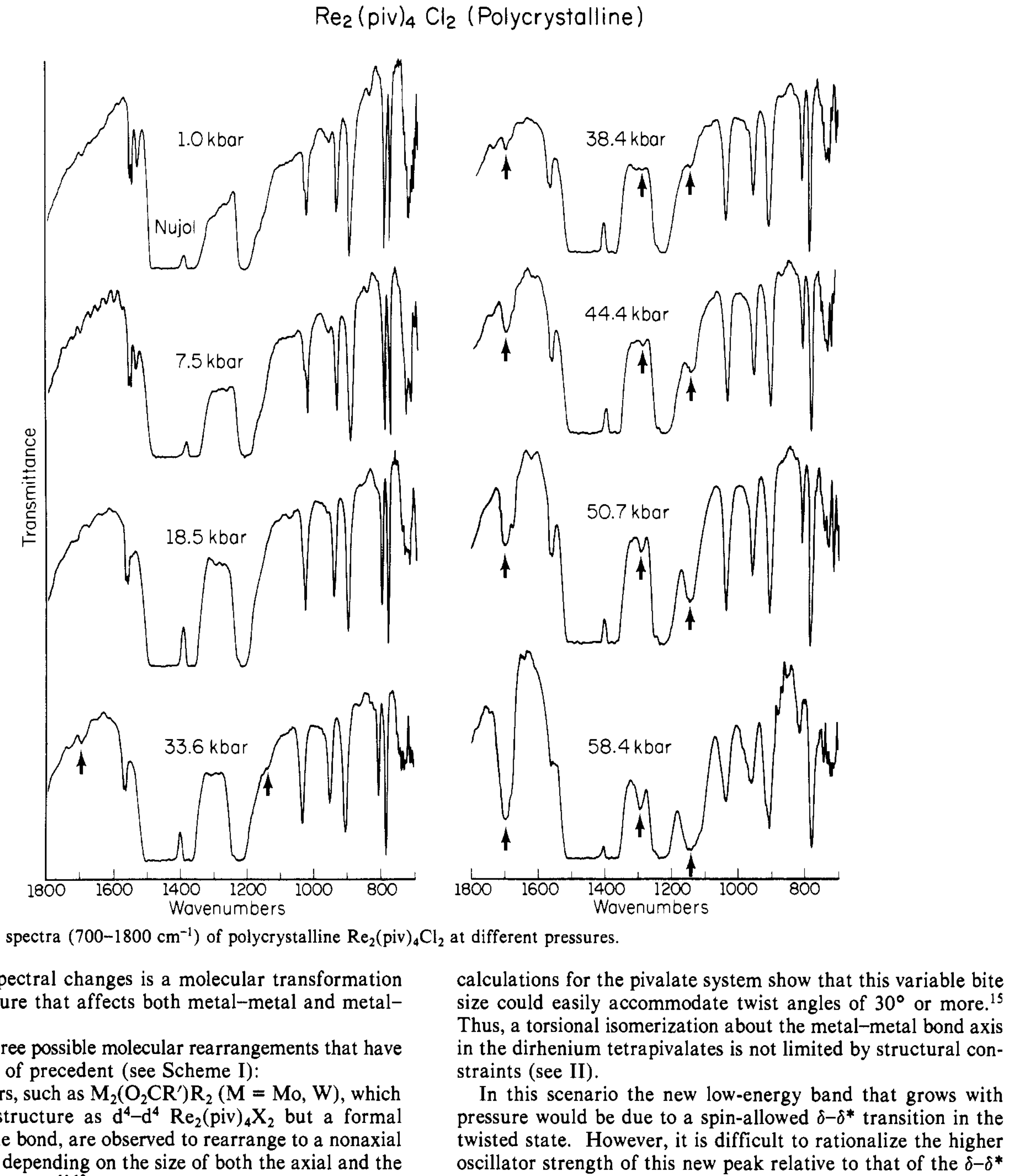


**Figure 8.** Infrared spectra (700–1800 cm$^{-1}$) of polycrystalline $Re_2(piv)_4Cl_2$ at different pressures.

the concurrent spectral changes is a molecular transformation induced by pressure that affects both metal–metal and metal–ligand bonding.

We consider three possible molecular rearrangements that have various elements of precedent (see Scheme I):

(a) d$^3$–d$^3$ dimers, such as $M_2(O_2CR')R_2$ (M = Mo, W), which have the same structure as d$^4$–d$^4$ $Re_2(piv)_4X_2$ but a formal metal–metal triple bond, are observed to rearrange to a nonaxial structure (see I), depending on the size of both the axial and the carboxylate alkyl groups.[11,12] However, this type of rearrangement has never been observed for d$^4$–d$^4$ quadruply bonded dimers. Furthermore, consideration of the Walsh diagram developed for the d$^3$–d$^3$ situation[12] makes it clear that, with the addition of two more electrons, a rearrangement of this type should be prohibitively destabilizing.

(b) It is known that the steric requirements of certain bridging ligands, i.e. diphos, can induce torsional transformation in a quadruply bonded dimer.[2] Furthermore, Carroll et al. have shown that pressure induces a twist about the metal–metal bond axis in $[Re_2X_8]^{2-}$ (X = Br, I).[3] In various molecules, bridging carboxylate frameworks are able to conform to metal–metal distances ranging from less than 2.1 Å[13] to nearly 2.9 Å,[14] and simple geometrical calculations for the pivalate system show that this variable bite size could easily accommodate twist angles of 30° or more.[15] Thus, a torsional isomerization about the metal–metal bond axis in the dirhenium tetrapivalates is not limited by structural constraints (see II).

In this scenario the new low-energy band that grows with pressure would be due to a spin-allowed $\delta$–$\delta^*$ transition in the twisted state. However, it is difficult to rationalize the higher oscillator strength of this new peak relative to that of the $\delta$–$\delta^*$ excitation of the eclipsed form. Furthermore, although the lower symmetry of the *tert*-butyl group for a twisted form would likely lead to changes in the skeletal modes associated with the hydrocarbon moiety, it is unlikely that these changes would lead to the appearance of a strong new band as high as 1700 cm$^{-1}$ in the IR spectrum.

Thus, we come to the third possible rearrangement and the one that we think provides a satisfactory explanation for all of our observations, namely, rearrangement from a diaxial configuration of the two halide ligands to a diradial configuration with concomitant change in two of the pivalate ligands from bidentate bridging to monodentate (see III). The $\delta$–$\delta^*$ transition for an isomer of this sort is expected both to occur at lower energy and to be more intense.[16] Furthermore, the new IR band at 1697 cm$^{-1}$ is clearly assignable to the C–O double bond of a monodentate pivalate, and the new band appearing near 1300 cm$^{-1}$ is

---

(11) Chisholm, M. H.; Clark, D. L.; Huffman, J. C.; Van Der Sluys, W. G.; Kober, E. M.; Lichtenberger, D. L.; Bursten, B. E. *J. Am. Chem. Soc.* **1987**, *109*, 6796.

(12) Chisholm, M. H.; Clark, D. L.; Huffman, J. C.; Van Der Sluys, W. G. *J. Am. Chem. Soc.* **1987**, *109*, 6817.

(13) Cotton, F. A.; Norman, J. G., Jr. *J. Coord. Chem.* **1971**, *1*, 161.

(14) Moreland, J. A.; Doedens, R. J. *J. Chem. Soc. Chem. Commun.* **1974**, 28.

(15) At 30° twist the calculated O···O distance (bite size) has increased to 2.469 Å.

(16) Hopkins, M. D.; Gray, H. G.; Miskowski, V. M. *Polyhedron* **1987**, *6*, 705.

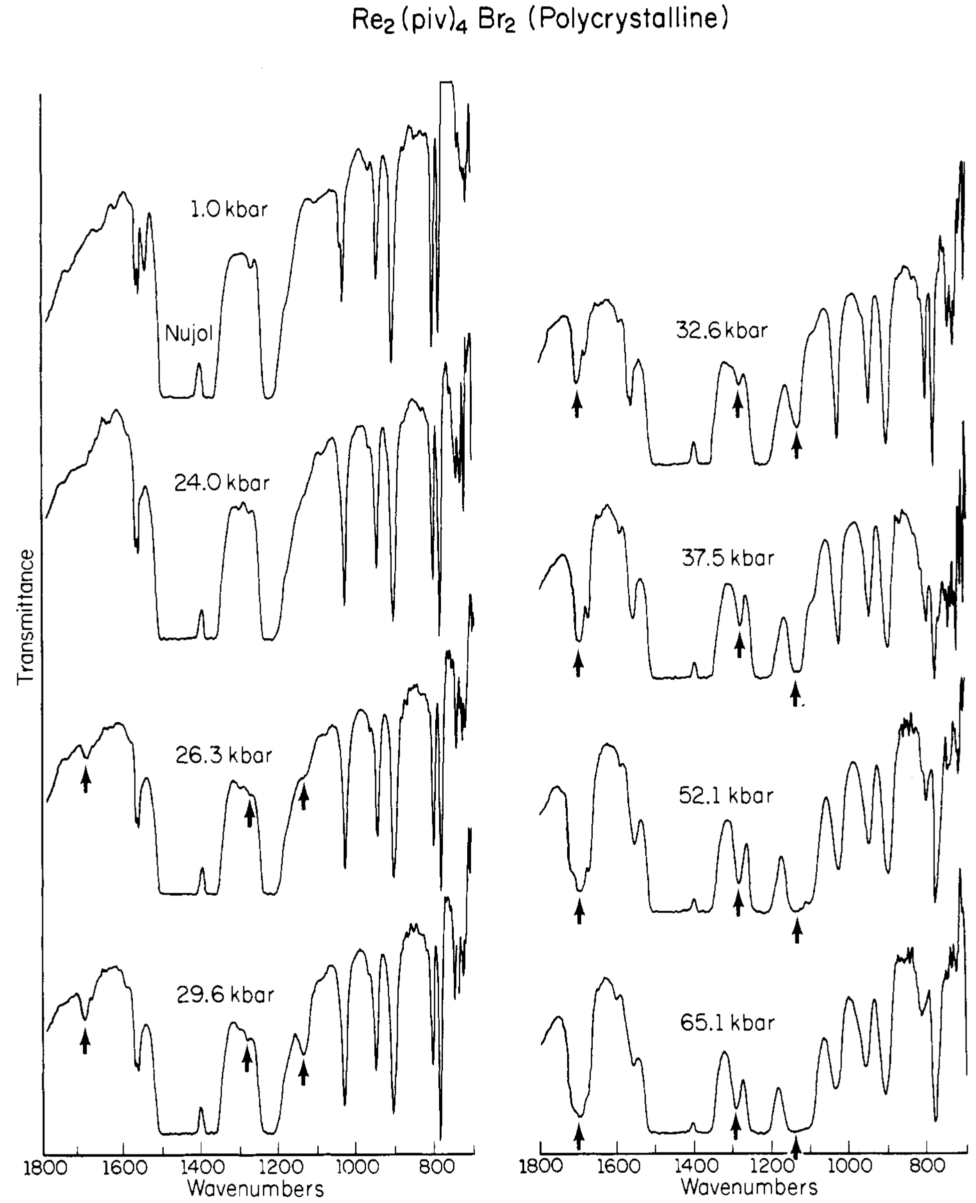


**Figure 9.** Infrared spectra (700–1800 cm$^{-1}$) of polycrystalline $Re_2(piv)_4Br_2$ at different pressures.

consistent with the corresponding C–O single bond.[17] The fact that no changes were observed in the spectra of the tetraacetate suggests that the transformation is driven by steric interactions involving the bulky pivalate ligands. In this regard it is noteworthy that the rearrangement occurs at slightly lower pressures for the polycrystalline bromide than for the chloride.

Further support for rearrangement to structure III can be derived from several sources. (a) The dimethyl analogue of the tetraacetate dichloro complex adopts a diradial structure similar to III, except for weak, axial C=O···Re interactions.[18] (b) It has been demonstrated that phosphorus ligand adducts of $M_2(O_2CCF_3)_4$ (M = Mo,[19] W[20]) can adopt either the diaxial structure or the diradial structure equivalent to III but that the latter is favored for smaller, more basic phosphines.[20,21] (c) Treatment of $Mo_2(O_2CCF_3)_4$ with bromide or iodide leads to isolable axial diadducts $Mo_2(O_2CCF_3)_4X_2^{2-}$, but the electronic spectra of the precursor solutions suggest the presence of radial species (by the appearance of strong, lower energy transitions).[22] (d) It might appear that rearrangement to III is a rather drastic structural change to occur reversibly in the solid state. However, the rearrangement of $\alpha$-$Mo_2Cl_4(dppe)_2$ to $\beta$-$Mo_2Cl_4(dppe)_2$, which also occurs in the solid state,[23] involves a possible related change in the bidentate ligands from chelating at a single metal center to bridging the two metals. (e) Finally, we note that a theoretical analysis of various geometries for $M_2L_{10}$ complexes, including molecules closely related to $Re_2(piv)_4Cl_2$ and $Re_2(piv)_4Br_2$, suggests a possible pathway for the rearrangement from diaxial to diradial configurations.[24]

The leveling observed in Figures 3 and 4 seems to indicate that the extent to which the geometrical transformation occurs may be different in the polycrystalline state, as this leveling is not readily seen in the results for the molecules dispersed in a PMMA matrix (Figures 6 and 7). It is possible that this transformation actually occurs at grain boundaries or some other crystalline defects. This

---

(17) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley: New York, 1977.

(18) (a) Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 1063. (b) Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1979**, 409.

(19) (a) Cotton, F. A.; Lay, D. G. *Inorg. Chem.* **1981**, *20*, 935. (b) Girolami, G. S.; Andersen, R. A. *Inorg. Chem.* **1982**, *21*, 1318.

(20) Santure, D. J.; Huffman, J. C.; Sattelberger, A. P. *Inorg. Chem.* **1985**, *24*, 371.

(21) Girolami, G. S.; Mainz, V. V.; Andersen, R. A. *Inorg. Chem.* **1980**, *19*, 805.

(22) Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1983**, *22*, 1327.

(23) Agaskar, P. A.; Cotton, F. A. *Inorg. Chem.* **1986**, *25*, 15.

(24) Shaik, S.; Hoffman, R.; Fisel, C. R.; Summerville, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4555.

raises the question whether the weak feature seen at 16 500 cm$^{-1}$ in a single-crystal study of Re$_2$(piv)$_4$Cl$_2$[7] was due to the presence of very small amounts of the rearranged form. Similar weak, low-energy bands have been observed in the solution spectra of several dirhenium tetracarboxylate bromides and iodides.[25]

In summary, the changes seen in the visible and infrared spectra for Re$_2$(piv)$_4$Cl$_2$ and Re$_2$(piv)$_4$Br$_2$, both in the polycrystalline state and in a polymer matrix, indicate that pressure induces a molecular transformation leading to radial halide ligands and two monodentate pivalate ligands.

**Acknowledgment.** This work was supported in part by the Materials Science Division of the Department of Energy under Contract DE-AC02-76Er01198 and in part by the Division of Materials Research of the National Science Foundation under Grant DMR 86-12860. We acknowledge helpful comments from Dr. Basil Swanson in arriving at the interpretation of our results.

---

(25) Srinivasan, V.; Walton, R. A. *Inorg. Chem.* **1980**, *19*, 1635.

---

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

# Determination of Magnetic and Structural Properties in Solids Containing Antiferromagnetically Coupled Metal Centers Using NMR Methods. Magneto-Structural Correlations in Anhydrous Copper(II) *n*-Butyrate

Gordon C. Campbell and James F. Haw*

*Received March 18, 1988*

A new approach to the investigation of magneto-structural correlations in solids containing antiferromagnetically coupled transition-metal centers is described that illustrates the potential of NMR spectroscopy in such work. In this contribution we report the results of a variable-temperature (VT) $^{13}$C cross-polarization magic-angle-spinning (CP/MAS) NMR investigation of anhydrous copper(II) *n*-butyrate, [Cu(C$_3$H$_7$COO)$_2$]$_2$. Isotropic shifts are found to be primarily contact in origin, and a statistical analysis of their temperature dependence allows the calculation of singlet-triplet energy level separations ($-2J$), diamagnetic shifts ($\delta_{\mathrm{dia}}$), and electron-nucleus hyperfine coupling constants ($A$), which are shown to give insight into the mechanisms of electron delocalization along the superexchange pathway. Signal multiplicity can be related to compound structure, which was determined by using X-ray crystallography. The title compound is triclinic and has a space group of $P\bar{1}$ with $a$ = 9.035 (2) Å, $b$ = 5.192 (2) Å, $c$ = 11.695 (3) Å, $\alpha$ = 85.88 (2)°, $\beta$ = 95.04 (2)°, $\gamma$ = 109.32 (2)°, $Z$ = 1, and $V$ = 515.2 (3) Å$^3$; the final weighted $R$ value for 2169 reflections was 0.048.

## Introduction

Solid copper(II) carboxylates, Cu$_2$(RCO$_2$)$_4$L$_n$ with $n$ = 0 or $n$ = 2, are prototypical examples of transition-metal complexes that contain two or more antiferromagnetically coupled metal centers.[1] Much emphasis has been placed on the development of magneto-structural correlations in these systems,[2] as reflected by the description of magnetic coupling between Cu(II) centers that appears in the literature. Originally thought to be the result of direct Cu-Cu bonding, either $\delta$[3] or $\sigma$,[4] the antiferromagnetic interaction is now recognized to be propagated through the electronic orbitals of ligands bridging the metal centers in what is termed the superexchange pathway.[5] Much current research is directed toward the development of a more complete understanding of magnetic superexchange, but achievement of this goal has been hampered (in part) by the limited number of spectroscopic methods amenable to solid transition-metal complexes.

Recently, though, the potential of solid-state NMR methods has been demonstrated by preliminary variable-temperature studies of copper(II) carboxylates that revealed temperature-dependent chemical shifts and line widths.[6] Up until now these results have been primarily qualitative in nature. We demonstrate here that suitable solid-state NMR experiments can effectively probe the superexchange pathway and allow the quantitative measurement of electron-nucleus hyperfine coupling constants, structurally significant chemical shifts, and singlet-triplet energy level separations for a representative member of this class. This is a natural extension of some of our previous work on the cross-polarization magic-angle-spinning (CP/MAS) NMR of paramagnetic solids.[7]

## Experimental Section

**Compound Preparation and NMR Methods.** Anhydrous copper(II) *n*-butyrate, Cu$_2$(C$_3$H$_7$CO$_2$)$_4$, was prepared by using standard literature methods[8] and packed into a Kel-F NMR rotor. Spectroscopic studies were carried out on approximately 0.3 g of powder. All variable-temperature[9] $^{13}$C CP/MAS NMR spectra were obtained at 25.02 MHz on a Chemagnetics M-100S spectrometer with a 1-ms cross-polarization contact time and a repetition delay of 1 s. Magic-angle-spinning rates used typically ranged between 4 kHz at ambient temperatures and 2.5 kHz at cryogenic temperatures. A total of 400 transients were collected at each temperature and multiplied by an exponential weighting function of 50 Hz before transforming. Spectral assignments were facilitated by the interrupted decoupling experiment.[10] Statistical analyses of tem-

**Table I.** Crystallographic Data for Anhydrous Copper(II) *n*-Butyrate

| | |
|---|---|
| chem formula | fw 475.5 |
| C$_{16}$H$_{28}$O$_8$Cu$_2$ | space group $P\bar{1}$ |
| $a$ = 9.035 (2) Å | $T$ = 20 °C |
| $b$ = 5.192 (2) Å | $\lambda$ = 0.7107 Å |
| $c$ = 11.695 (3) Å | $\rho_{\mathrm{obsd}}$ = 1.55 g cm$^{-3}$, $\rho_{\mathrm{calcd}}$ = 1.53 g cm$^{-3}$ |
| $\alpha$ = 85.88 (2)° | $\mu$ = 21.1 cm$^{-1}$ |
| $\beta$ = 95.04 (2)° | rel transmission factors 0.464-1.000 |
| $\gamma$ = 109.32 (2)° | $R(F_o^2)$ = 0.039 |
| V = 515.2 (3) Å$^3$ | $R_w(F_o^2)$ = 0.048 |
| $Z$ = 1 | |

---

* To whom correspondence should be addressed.

(1) (a) Jotham, R. W.; Kettle, S. F. A.; Marks, J. A. *J. Chem. Soc., Dalton Trans.* **1972**, 428. (b) Melnik, M. *Coord. Chem. Rev.* **1982**, *42*, 259. (c) Folgado, J. V.; Ibanez, R.; Coronado, E.; Beltran, D.; Savariault, J. M.; Galy, J. *Inorg. Chem.* **1988**, *27*, 19. (d) Thompson, L. K.; Lee, F. L.; Gabe, E. J. *Inorg. Chem.* **1988**, *27*, 39.

(2) Willett, R. D., Gatteschi, D., Kahn, O., Eds. *Magneto-Structural Correlations in Exchange Coupled Systems*; Reidel: Boston, MA, 1985.

(3) Figgis, B. N.; Martin, R. L. *J. Chem. Soc.* **1956**, 3837.

(4) Forster, L. S.; Ballhausen, C. J. *Acta Chem. Scand.* **1962**, *16*, 1385.

(5) Gerloch, M.; Harding, J. H. *Proc. R. Soc. London, A* **1978**, *360*, 211.

(6) (a) Haw, J. F. Presentation at the 28th Rocky Mountain Conference, Denver, CO, 1986. (b) Campbell, G. C. Presentation at the 28th Experimental NMR Conference, Asilomar, CA, 1987. (c) Campbell, G. C. Presentation at the 29th Rocky Mountain Conference, Denver, CO, 1987. (d) Walter, T. H.; Oldfield, E. *J. Chem. Soc., Chem. Commun.* **1987**, 646.

(7) (a) Haw, J. F.; Campbell, G. C. *J. Magn. Reson.* **1986**, *66*, 558. (b) Campbell, G. C.; Crosby, R. C.; Haw, J. F. *J. Magn. Reson.* **1986**, *69*, 191.

(8) Martin, R. L.; Waterman, H. *J. Chem. Soc.* **1957**, 2545.

(9) Haw, J. F.; Campbell, G. C.; Crosby, R. C. *Anal. Chem.* **1986**, *58*, 3172.

0020-1669/88/1327-3706$01.50/0