The Apparent Flexibility of Bonds in Paddlewheel-Type Compounds

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Introduction

Since the existence of multiple metal−metal bonds was first recognized over 30 years ago, the paddlewheel motif has been one of the most prevalent structural types observed. In compounds of this type, the strength of the metal−metal bond is commonly assessed (at least partly) on the basis of its length; often arguments for or against particular electronic configurations are based on this parameter.[1] However, a recent study[2] has appeared to cast some doubt on this approach: A statistical analysis of coordination compounds revealed that Ru−Ru bonds may deform up to 0.03 Å due to "packing effects". This has prompted us to examine the issue as it relates to the metal−metal multiple bond present in paddlewheel-type structures, both those that contain three-atom bridges between the two metal atoms and those that do not. As a representative compound for complexes with three-atom bridges $Ru_2(chp)_4Cl$ (chp = 2-chloro-6-hydroxypyridinate anion) was chosen since it is known in a variety of different crystalline forms.[3] For the compounds with no bridges $Re_2Cl_8^{2-}$ was chosen since it too is known in many crystalline forms with differing counterions.[4]

Data Analysis

The methodology followed for data analysis is similar to that used in ref 2 and can be summarized as follows. A data set was constructed for each bond type, viz. Ru−Ru, Ru−Cl, Ru−N, Ru−O, Re−Re, and Re−Cl. For each data set an unweighted average was obtained ($\langle x_i\rangle = \sum x_i/n$) and differences from the mean calculated ($\Delta_i = \langle x_i\rangle - x_i$). A standard deviation was then calculated for each set ($\sigma^2 = \sum\Delta_i^2/(n-1)$).

An estimate of the variance due to packing forces was then calculated assuming that $\sigma^2_{tot} = \sigma^2_e + \sigma^2_p$, where σ_e represents the deviations observed due to the inherent uncertainties associated with the crystallographic experiment, and σ_p the differences due to packing effects. In order not to underestimate σ_p, it was assumed that σ_e is of the order of the average standard uncertainty (su) for the parameter in question. It is further assumed that no chemically significant deviation is present, since within each set only data relevant to one compound are used.

Data from one early structural determination of a compound containing $Re_2Cl_8^{2-}$ was excluded due to the very large su's found for that determination.[5]

Results and Discussion

Figure 1 is a plot representing the deviation from the mean within each type of bond, with error bars obtained from crystallographic su's. Immediately apparent is that the M−M bonds appear to show the smallest deviation among all data sets. The numerical values obtained are listed in Table 1. The values of σ_p = 0.001 Å for the Ru−Ru bond and σ_p = 0.006 Å for the Re−Re bond are reasonable, and the difference between the two is easily rationalized. One would expect a compound where the metal−metal bond is cocooned inside a stabilizing shroud of three atom ligands, as in $Ru_2(chp)_4Cl$, to be less susceptible to deformation, both because the ligands themselves will help resist the change and because the M−M bond lies protected within a space insulated from any direct contacts with neighboring molecules. Conversely, the Re−Re bond in $Re_2Cl_8^{2-}$ is both susceptible to direct influence by neighboring molecules and lacks the three-atom bridges. From Figure 1 it is also apparent that one of the observations for Re−Re distances deviates significantly from the rest. While this may be a genuine outlier, we have no reason to doubt the structural determination and it is possible that this bond length represents the longest Re−Re separation possible for $Re_2Cl_8^{2-}$. If this datum is excluded from the set, a new value of σ_p = 0.004 is obtained.

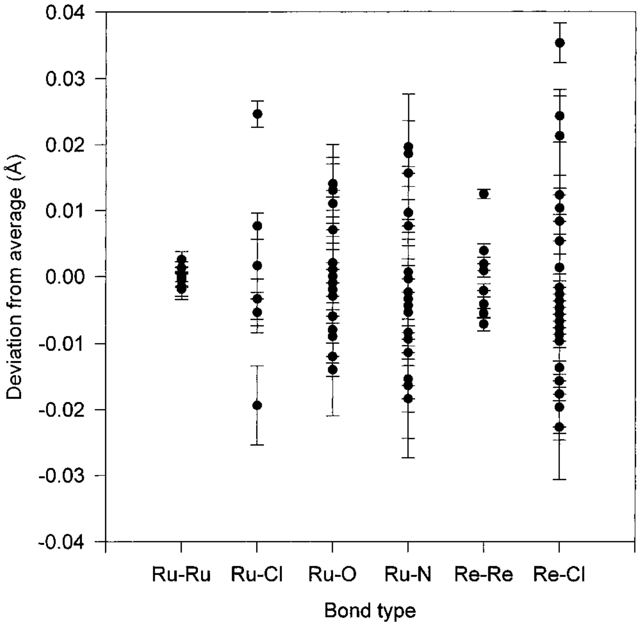

Figure 1. Distribution of bond lengths about average.

For the M−L bonds, the following results were obtained: Ru−O, 0.005 Å; Ru−N, 0.008 Å; Ru−Cl, 0.014 Å; Re−Cl, 0.019 Å. Again we see that the bidentate chp^- ligand forms rather more rigid bonds than the unidentate Cl^-, but all numbers are in the same range. Additionally, the flexibility parameter for the halide is similar whether it resides in an axial position, as for $Ru_2(chp)_4Cl$, or in an equatorial position, as in $Re_2Cl_8^{2-}$. However, the Re−Cl bond parameter may be overestimated since in many of the compounds used there is a partial disorder of the $Re_2Cl_8^{2-}$ quasicube in the lattice. This is observed as one or two additional positions of the Re_2 unit in the structure. While it is possible to model the disordered dimetal unit, the additional positions of the halides cannot be resolved at the resolution used in routine structural determinations. This may cause a very slight apparent elongation of the Re−Cl bonds in the final structures but not enough to be significant in the present study.

Comparison of Present Study with Previous Results. Most of the results obtained in this study are in good agreement with those reported by Martín and Orpen.[2] The largest differences appear in the Ru−N and M−M bonds. The discrepancy in the Ru−N parameter may be simply explained by the fact that in

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[1] See, for example: Cotton; F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*, 2nd ed.; Oxford University Press: Oxford, U. K., 1992.

[2] Martín, A.; Orpen, A. G. *J. Am. Chem. Soc.* **1996**, *118*, 1464.

[3] Yokochi, A. Ph.D. Dissertation, Texas A & M University, 1997.

[4] See, for example: Cotton, F. A.; Matonic, J. H.; Silva, D. O. *Inorg. Chim. Acta* **1995**, *234*, 115 and references therein.

[5] This is the structure reported in *J. Struct. Chem.* **1963**, *4*, 49, where the Re−Re distance is determined to be 2.22(2) and the Re−Cl distance is found to be 2.43(3).

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Table 1

	Ru−Ru	Ru−Cl	Ru−O	Ru−N	Re−Re	Re−Cl
av bond length (Å)	2.2835	2.4344	1.9980	2.0974	2.2202	2.3317
SD of bond lengths ($\times 10^{-3}$ Å)	1.5	13.6	8.3	11.5	6.3	18.6
mean su of bond lengths ($\times 10^{-3}$ Å)	1.3	3.1	6.4	7.8	1.0	4.0
no. observations	7	7	21	21	8	36
σ_p for this bond type ($\times 10^{-3}$ Å)	0.9	13.2	5.3	8.5	6.2	18.1
σ_p reported in ref 2 ($\times 10^{-3}$ Å)	36.2	9.8	13.4	39.6		
suggested force constant (mdyn/Å)	3	0.9	2.5	2.5	4.12	2.73

our case the observations are taken from a bidentate ligand, while in the more general study it is likely that many of the data came from compounds with unidentate N donors. The comparison of our M−M bond parameters with those previously reported are more difficult to explain since, even for $Re_2Cl_8^{2-}$, where the M−M bond is unbuttressed, there still is an order of magnitude difference in the two estimates. It is therefore likely that the difference is not merely of a structural nature but may have a chemical origin behind it. We suggest that in the previous case the great majority of the Ru−Ru bonds used are from compounds of the Ru_3L_{12} type, where there are relatively long single bonds between the metal atoms. These are much weaker bonds and undoubtedly less resistant to deformation.

We next reexamine the question of whether there is a linear relationship between the force constants for bonds of a certain type and their susceptibility to deformation by packing effects. Since the force constants used to prepare Figure 3 of ref 2 seem a bit large, we made new estimates.

With no accurate assignment of the vibrational spectrum for $Ru_2(chp)_4Cl$, we shall obtain a force constant from an empirical bond length−force constant relationship.[6] From these equations, and using an average Ru−Ru length of 2.2835 Å, we obtain $F_{Ru-Ru} \simeq 3$ mdyn/Å. This compares favorably with the value of 2.59 mdyn/Å reported[7] for $Ru_2(O_2CH)_4Cl_2^-$. For $Ru_3(L)_{12}$ the Ru−Ru distance is usually ~2.80 Å and this yields a force constant of ~1 mdyn/Å, in excellent agreement with the reported value of 0.82 mdyn/Å reported for $Ru_3(CO)_{12}$.[8] For an axial Ru−Cl bond, we may assume that this bond is similar in strength in all the molecules. Based on the reported vibrational frequencies for $Ru_2(O_2CR)_4Cl$ (R = H, Me, Et, Pr),[7,9] where all bands attributed to ν_{Ru-Cl} fall between 160 and 210 cm^{-1}, a value of ~0.8 mdyn/Å is reasonable.[10] Force constants for the Re−Re and Re−Cl bonds in $Re_2Cl_8^{2-}$ have been determined and are available in the current literature. These have values of $F_{Re-Re} = 4.12$ mdyn/Å and $F_{Re-Cl} = 2.73$ mdyn/Å, and are in excellent agreement with those calculated from the empirical relations.[6b] Since Martín and Orpen's report also included some Pt−L bonds, these too are included in this work. Calculating Pt−P and Pt−Cl force using the same empirical relationship applicable to Re−Cl bonds[6b] we get $F \simeq 2.7$ mdyn/Å (assuming $r_{P--P} \simeq r_{Pt-Cl}$ 2.3 Å). Finally, we can estimate the force constant for an Ru−O bond from the vibrational data provided for $Ru_2(O_2CH)_4Cl_2^-$, where $\nu_{a_{1g}}(Ru-O) = 430$ cm^{-1}, yielding a force constant of ~2.5 mdyn/Å.[11] The Ru−N bond should be slightly weaker. An estimate of the force constant for the bond between a monodentate amine and a ruthenium atom can be extracted from the series of compounds $[Ru(NH_3)_5(N_2)][X]_2$ (X = Cl^-, Br^-, I^-, BF_4^-, PF_6^-),[12] where the ν_{Ru-N} fall in the range between 435 and 388 cm^{-1} yielding a value of ~1.5 mdyn/Å.

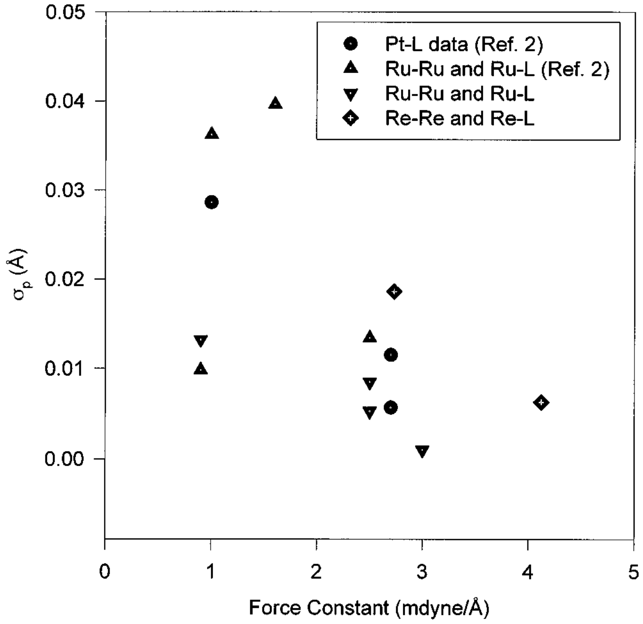

Figure 2. σ_p vs force constant.

The results obtained by using these new force constants are given in Figure 2. While the correlation is not strong between force constant and σ_p, at least a general trend is established where those bonds with the larger force constant do have smaller σ_p, and vice versa.

Conclusions

We suggest that a value for the susceptibility to deformation of a metal−metal bond in compounds where strong bonding occurs between the metal atoms should be ~0.005 Å, while values of ~0.01 Å for the M−L bonds are reasonable. Therefore, even a slight change in metal−metal distance, say in the order of 0.005 Å, should be considered real and may therefore have an underlying chemical significance.

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Supporting Information Available: Tables containing the raw data used as well as statistical results from these are available (4 pages). Ordering information is given on any current masthead page.

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(10) Using $F = (\nu^2\mu) \times 5.9 \times 10^{-7}$, ν in cm^{-1}, μ in amu's and with a value of 35.5 (= Cl).

(11) Using $F = {}^1/_2(\nu^2\mu) \times 5.9 \times 10^{-7}$, ν in cm^{-1}, μ in amu's and with a value of 45 (= O_2CH).

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