Vol. 3 №. 3 TRANSACTIONS OF NFsoc Aug. 1993

# EFEECT OF METALLIC CATIONS ON Si-O BONDS IN SILICATES①

Yin, Zhoulan Gao, Xiaohui
*Central-South University of Technology, Changsha 410083, China*

## ABSTRACT

The effect of metallic cations on the Si-O(br) bond and the Si-O(ter) bond was studied with CNDO/2 MO calculations. The characteristics of them were discussed, which were found to vary with the bonding and coordination situation of oxygen as well as the effect of metallic cations on oxygen. The conclusions obtained may be well used in the fields of mineralogy, geochemistry, silicate materials, pyrometallurgy and so on.

**Key words:** silicates Si-O bonds metallic cations quantum chemistry

## 1 INTRODUCTION

Over the past thirty years important advances have been made using computational quantum chemistry to study bonding mechanisms, the bond length and bond angle variations, and the physico-chemical properties of silicates as Gibbs[1] and Gao[2] have commented. The effect of tetraheral angles on the Si-O bond overlap population for isolated tetrahedra was studied with EHMO[3]. Then the same MO calculations were completed[4] to classify and order the bond length variations for isolated and polymerized tetrahedral ions. Meagher *et al* [5] studied the silica polymorphs quartz, cristobalite and coesite with CNDO/2 calculations for $H_{12}Si_5O_{16}$ clusters. The trends of bond length and bond angle variations in studying the bonding forces in framework structure were explored and systematically analyzed using the results of non-empirical MO calculations for a variety of representative molecules[6].

There exist three types of chemical bonds in silicates-Si-O(br) bond, Si-O(ter) bond and O-M bond. The O-M bond is ionic and can be dealt with classical electrostatic theory. The other two are polar. They dominate the structures and properties of silicates. Their relative strength has been investigated with *ab initio* calculations, which explains some properties of silicates[7]. The effect of metallic cations on Si-O bonds, however, has not been studied theoretically and systematically so far with the exception of some work of De Jong *et al* [8, 9]. The object of this work is to investigate the effect of cations on Si-O(br) and Si-O(ter)bonds through semi-empirical CNDO/2 MO calculations for four clusters modeling the silicate tetrahedral linkage and the coordination of cations.

## 2 COMPUTATIONAL DETAILS

Because of the "location of electrons in silicates"[7], we need not take large silicate molecules as calculation models. Usually a cluster of two $SiO_4^{4+}$ with a common corner is quite enough to represent clearly the properties of chemical bonds in the framework of polymerized silicates. In fact, much work have been done with the similar models in sili-

---

① Manuscript received June 20, 1992

cates[1,8~10]. Dangling bonds must be taken into account when clusters isolated from crystal are used as calculation models. It is suitable to saturate them with hydrogen atoms.

As metallic cations can coordinate either to O(br) or O(ter), four clusters with $C_{2v}$ symmetry shown in Fig. 1 are taken as models, where M and M′ represent such elements as H(H′), Li, Na, K, Rb, Be, Mg, Ca, Sr, Al, Ga, In, Sn, Pb, Sc, Ti, Mn, Fe, Co, Ni, Cu, Zn and Au. The necessary bonding parameters are taken from Popel *et al* [11]. Those unknown are estimated with prolongation. Bond distance and bond angles are illustrated in Fig. 1 The distance between metallic cations and oxygen is selected as the sum of their ionic radii.

Cluster (a) is the standard molecule for comparison. Clusters (b), (c) and (d) are used to study the change of chemical bonds when metallic cations coordinate respectively to O(br) and both O(br) and O(ter).

When a silicon atom is replaced by an aluminum atom in above clusters, clusters modeling aluminosilicates are obtained, with which the properties of Al-O and Si-O bonds in aluminosilicates can also be discussed.

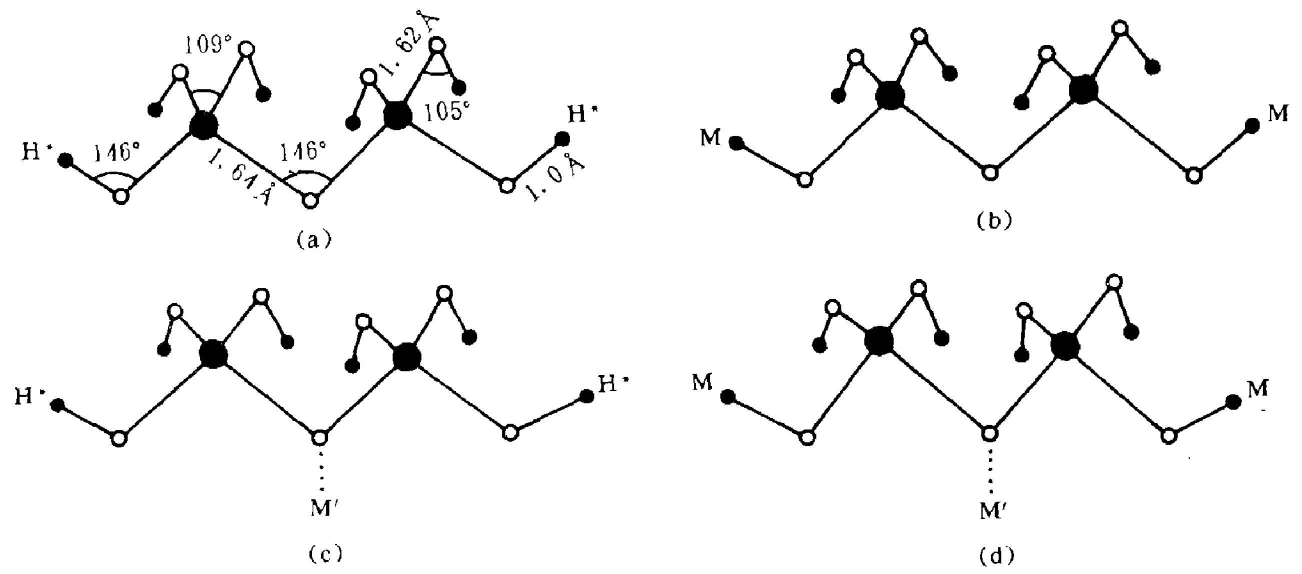
The total energy $E_T$ of any system can be broken up into the sum of biatomic energies and monoatomic ones in CNDO/2 calculations[7]:

$$E_T = \sum^{A,B} \varepsilon_{AB} + \sum^{A} \varepsilon_A$$

where $\varepsilon_{AB}$ represents the relative strength of different chemical bonds, especially the variation of chemical bonds with the environment in homologous molecules. So CNDO/2 program with the breaking-up of the total energy was adopted in our study.

## 3 EFFECT OF METALLIC CATIONS ON Si-O(br) BOND

The calculation results of clusters (a) and (b) are listed in Table 1 where $\varepsilon_{Si\text{-}O(terM)}$ represents the biatomic energy of silicon and O(ter) which bonds with metallic cations, and where $\varepsilon_{Si\text{-}O(terH)}$ represents that of silicon and O(ter) which bonds with hydrogen ion. From the first raw data of cluster (a) it can be seen that $\varepsilon_{Si\text{-}O(terH)}$ (−0.6558au) is different from $\varepsilon_{Si\text{-}O(terH^*)}$ (−0.7497au), which is elucidated to originate from the different Si-O-H angle and Si-O-H* angle. It also shows that $\varepsilon_{Si\text{-}O(terH)}$ and $\varepsilon_{Si\text{-}O(terH^*)}$ are more positive



(a) (b) (c) (d)

Fig. 1 Calculation Models

●—H; ○—O; ⬤—Si

than $\varepsilon_{Si\text{-}O(br)}$ ($-0.8069$au) though the bond distance of silicon and O(ter) is taken to be slightly shorter than that of silicon and O (br), which verifies our conclusion that the Si-O(br) bond is more stable than the Si-O (ter) bond[7].

When considering the configuration of cluster (a) and $\varepsilon_{O(ter)H}$, $\varepsilon_{Si\text{-}O(terH)}$ and $\varepsilon_{Si\text{-}O(M)}$, it is discovered that the difference between $\varepsilon_{Si\text{-}O(terH)}$ and $\varepsilon_{Si\text{-}O(terH')}$ is large as the Si-O-H angle is greatly different from the Si-O-$H^*$ angle. With the Si-O-$H^*$ angle being 146°, $\varepsilon_{Si\text{-}O(terH')}$ and $\varepsilon_{Si\text{-}O(br)}$ are approximately the same. Therefore the different strength of Si-O bond is due to the different coordination angle of oxygen. That is also why $\varepsilon_{Si\text{-}O(br)}$ is different from $\varepsilon_{Si\text{-}O(terH)}$

From the bonding mechanism of silicates, we know that an oxygen atom with a larger coordination angle will supply a larger fraction of *s* orbital for bonding and thus increase the stability of bonding electrons. The same phenomenon occurs in the O-H bond with a different Si-O-H angle. So we can get the idea that the coordination angles of oxygen play an important part in the stability of silicates, especially that of polymerized silicates.

The calculation results of cluster (c) are listed in Table 2 which indicates the change of the nearest Si-O(br) bond when O(br) is coordinated with metallic cations.

Comparing the first raw data of cluster (a) in Table 1 and the data in Table 2, it is noticed that the Si-O(br) bond in cluster (a) is the strongest when O(br) is bicoordinated. Any cation approaching O(br) as its third coordinator will weaken the Si-O(br) bond, and therefore break up the Si-O chain and reduce the polymerization of silicates. If O(br) is further coordinated with a fourth coordinator, the Si-O(br) bond will be weakened more greatly. For example, the last raw data in Table 2 show that when O(br) is coordinated with two sodium atoms, $\varepsilon_{Si\text{-}O(br)}$ is much more positive than that when O(br) is coordinated with only one sodium atom. Therefore large amounts of metal oxides in molten polymerized silicates or silica may depolymerize them or even make orthosilicates form. Quartz is formed only when metallic cations are extremely short.

**Table 1 Calculation results of clusters (a) and (b)**

| M | $\varepsilon_{Si\text{-}O(br)}$ | $\varepsilon_{Si\text{-}O(terM)}$ | $\varepsilon_{Si\text{-}O(terH)}$ | $\varepsilon_{O\text{-}M}$ | $\varepsilon_{O\text{-}H}$ |
|---|---|---|---|---|---|
| H | −0.8069 | −0.7497 | −0.6558 | −0.7916 | −0.7283 |
| Na | −0.7681 | −0.8520 | −0.5842 | −0.3341 | −0.7226 |
| K | −0.7371 | −0.8409 | −0.5479 | −0.1012 | −0.7173 |
| Mg | −0.7830 | −0.8080 | −0.6137 | −0.4755 | −0.7257 |
| Ca | −0.7429 | −0.8381 | −0.5530 | −0.5229 | −0.7182 |
| Al | −0.7924 | −0.7709 | −0.6312 | −0.6328 | −0.7269 |
| Fe | −0.7943 | −0.7900 | −0.6266 | −1.0249 | −0.6266 |

Table 2 also shows that hydrogen weakens the Si-O(br) bond most strongly of all the cations coordinating to O(br). It reduces $\varepsilon_{Si\text{-}O(br)}$ from $-0.8069$au to $-0.3325$au. This means that hydrogen will break Si-O chain most easily when coordinating to O (br). So, of all the silicates in nature, there exists no polymerized silicate where hydrogen is the third or fourth coordinator of O (br). Even no mineral can be found where hydrogen is the coordinator of O(br) or O (ter). Only in the form of $OH^-$ or $H_2O$ can hydrogen exist in natural silicate minerals.

When coordinating to O (br), transition metallic cations weaken the Si-O (br) bond strongly in the sequence of Cu>Ni>Co>Fe>Mn>Ti>Sc. Therefore they enter with difficulty into high-polymerized silicates in the sequence of reversed order.

Alkaline-earth metallic cations weaken the Si-O(br) bond to a smaller extent when coordinating to O (br) and thus enter into high-polymerized silicate more easily than transition metallic cations.

**Table 2　Calculation results of cluster(c)**

| M | $\varepsilon_{Si-O(br)}$ | $\varepsilon_{Si-O(ter)}$ | M | $\varepsilon_{Si-O(br)}$ | $\varepsilon_{Si-O(terr)}$ |
|---|---|---|---|---|---|
| H | −0.3325 | −0.7781 | Sc | −0.6148 | −0.6484 |
| Li | −0.5816 | −0.6450 | Ti | −0.5862 | −0.6485 |
| Na | −0.6550 | −0.6427 | Mn | −0.4722 | −0.6304 |
| K | −0.7639 | −0.6442 | Fe | −0.4532 | −0.6457 |
| Rb | −0.7958 | −0.6463 | Co | −0.4325 | −0.6452 |
| Be | −0.4386 | −0.6578 | Ni | −0.4098 | −0.6414 |
| Mg | −0.5940 | −0.6535 | Cu | −0.3513 | −0.6215 |
| Ca | −0.7510 | −0.6433 | Zn | −0.7351 | −0.6487 |
| Sr | −0.7733 | −0.6434 | Sn | −0.6342 | −0.6704 |
| Al | −0.5746 | −0.6579 | Pb | −0.6992 | −0.6633 |
| Ga | −0.6782 | −0.6573 | Au | −0.7163 | −0.6112 |
| In | −0.6318 | −0.6652 | Na | −0.5988 | −0.6138 |

Of all cations, alkline metallic cations weaken the Si-O(br) bond the least when coordinating to O(br). Cations of larger atomic radii and smaller electronegativities have less effect on the Si-O(br) bond. Therefore alkaline metallic cations enter into high-polymerized silicates such as the frame silicates more easily than transition or alkaline-erath metallic cations, which agrees with their behaviours in magma.

If a silicon atom is replaced by an aluminum atom in cluster(c), a cluster of aluminosilicate is obtained. Calculation results of it are listed in Table 3. It shows that the Si-O(br) bond in alumino-silicates is slightly stronger while the Al-O (br) bond is much weaker than the Si-O(br) bond in silicates when M does not coordinate to O(br), which verifies that the Si-O(br) bond in aluminosilicates is more difficultly broken up than that in silicates while Al-O(br) in aluminosilicates is quite easily broken up[12]. When coordinating to O(br) in aluminosilicates, metallic cations weaken the Si-O(br) bond as in silicates. They also greatly weaken the Al-O(br) bond. The effect of transition metallic cations on the bonds is relatively greater.

**Table 3　Effect of metallic cations on Si-O and Al-O bonds in aluminosilicates**

| M | $\varepsilon_{Si-O(br)}$ | $\varepsilon_{Si-O(br)}$ | $\varepsilon_{Si-O(ter)}$ | $\varepsilon_{Si-O(ter)}$ |
|---|---|---|---|---|
| — | −0.8259 | −0.4781 | −0.6307 | −0.4412 |
| Li | −0.4660 | −0.3407 | −0.7261 | −0.4716 |
| Na | −0.5527 | −0.4012 | −0.5995 | −0.4300 |
| K | −0.6648 | −0.3819 | −0.6018 | −0.4626 |
| Rb | −0.7283 | −0.4814 | −0.5932 | −0.4595 |
| Be | −0.4160 | −0.0812 | −0.6578 | −0.4780 |
| Mg | −0.6023 | −0.2072 | −0.6425 | −0.4707 |
| Ca | −0.7754 | −0.3657 | −0.6170 | −0.4523 |
| Mn | −0.3898 | −0.2156 | −0.6024 | −0.4592 |
| Fe | −0.4797 | −0.1217 | −0.6467 | −0.4506 |
| Co | −0.2573 | −0.1900 | −0.6068 | −0.4662 |
| Ni | −0.4359 | −0.0814 | −0.6482 | −0.4672 |
| Cu | −0.4301 | −0.0345 | −0.6235 | −0.4458 |
| Zn | −0.7525 | −0.3459 | −0.6226 | −0.1589 |
| Pb | −0.6870 | −0.2833 | −0.6421 | −0.4768 |
| Al | −0.1811 | −0.3116 | −0.6110 | −0.4972 |
| Ga | −0.6586 | −0.3685 | −0.6220 | −0.4778 |
| In | −0.6615 | −0.2659 | −0.6511 | −0.4889 |
| Sc | −0.6159 | −0.2753 | −0.6696 | −0.4999 |
| Sn | −0.5799 | −0.2258 | −0.6607 | −0.5028 |
| Fe(Ⅲ) | −0.3976 | −0.1668 | −0.6546 | −0.4823 |
| Au | −0.7175 | −0.3289 | −0.6195 | −0.4276 |

The calculation results of cluster(d) are listed in Table 4. It shows that when O(br) and O(ter) are both coordinated with metallic cations, the strength of the Si-O(br) bond is still determined by metallic coordinators of O(br). For example, when hydrogen, sodium and aluminum coordinate to O(br), they weaken the Si-O(br) bond in the sequence of H > Al > Na as in cluster(c). The effect on the Si-O(br) bond of different cations coordinating to O(ter) tends to be roughly the same in most cases. There are two main reasons that different metallic coordinators of O(br) weaken the Si-O(br) bond to different extent. One is that metallic cations may capture the bonding electrons of O(br). Cations that possess larger electronegativity $X$ will act more strongly so that they

**Table 4 The calculation results of cluster(d)**

| M' | M | $\varepsilon_{Si-O(br)}$ | $\varepsilon_{Si-O(nbrH)}$ | $\varepsilon_{Si-O(nbrM)}$ |
|---|---|---|---|---|
| H | Na | −0.4238 | −0.6022 | −0.8417 |
| H | K | −0.4020 | −0.5791 | −0.8172 |
| H | Mg | −0.4351 | −0.6233 | −0.8289 |
| H | Ca | −0.4058 | −0.5810 | −0.8116 |
| H | Al | −0.3381 | −0.6059 | −0.7261 |
| H | Fe | −0.3453 | −0.5958 | −0.7369 |
| Na | Na | −0.6502 | −0.5857 | −0.8033 |
| Na | K | −0.6440 | −0.5479 | −0.6858 |
| Na | Mg | −0.6532 | −0.6022 | −0.7670 |
| Na | Ca | −0.6435 | −0.5667 | −0.7324 |
| Na | Al | −0.6591 | −0.6297 | −0.7494 |
| Na | Fe | −0.6615 | −0.6221 | −0.7558 |
| Al | Na | −0.5514 | −0.5963 | −0.8386 |
| Al | K | −0.5242 | −0.5671 | −0.8103 |
| Al | Mg | −0.5534 | −0.6193 | −0.7833 |
| Al | Ca | −0.1906 | −0.5749 | −0.7471 |
| Al | Al | −0.5683 | −0.6237 | −0.7514 |
| Al | Fe | −0.5688 | −0.6339 | −0.7723 |

reduce the population number on the Si-O(br) bond more and weaken the Si-O(br) bond more. As is shown in Fig. 2, $\varepsilon_{Si-O(br)}$ goes up with the increase of $X$. The other is that metallic coordinators of O(br) may reduce the fraction of the $s$ orbital of O(br) which bonds with silicon and therefore decrease the stability of electrons of the Si-O(br) bond.

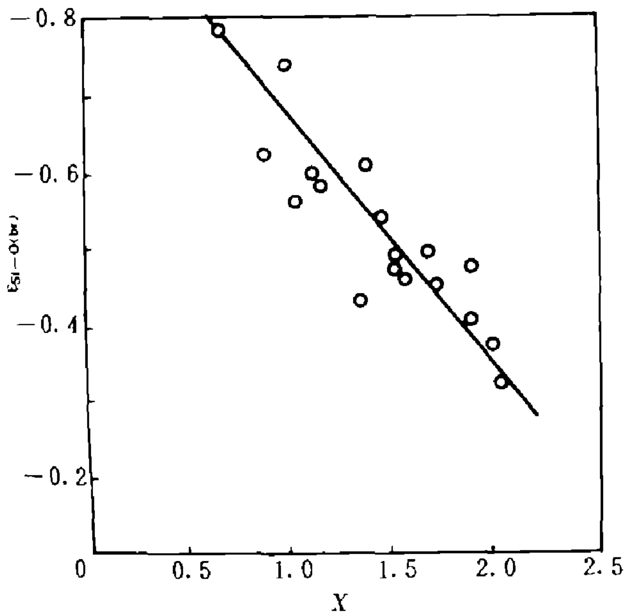


**Fig. 2** The relationship between $\varepsilon_{Si-O(br)}$ and $X$

From the above discussions, we can conclude that the main reason for the weakness of the Si-O(br) bond is the increase of the coordination number of O(br).

## 4 EFFECT OF METALLIC CATIONS ON O(ter)

There are two kinds of coordination in this case. One is that metallic cations coordinate only to O(ter). The other is that metallic cations coordinate to both O(ter) and O(br).

In the first case as is illustrated in cluster(b), we can see from Table 1 that when metallic cations coordinate to O(ter) where the Si-O-M angle is 146°, those of smaller electronegativities such as alkaline and alkaline-earth cations decrease $\varepsilon_{Si-O(ter)}$ to less than $\varepsilon_{Si-O(br)}$. Even cations of larger electronegativities such as hydrogen and iron decrease $\varepsilon_{Si-O(ter)}$ to close to $\varepsilon_{Si-O(br)}$. Therefore metallic cations will coordinate to O(ter) prior to O(br), especially O(ter) with a larger Si-O-M angle, and the remaining cations then coordinate to O(br) in molten silicates. Only in this way can the silicates exist most steadily with the exception of when silicon in polymerized silicate framework is replaced by such atoms as aluminum, boron etc. Cations which do not strongly weaken the Si-O(br) bond may enter into the framework and coordinate to O(br) prior to O(ter) because of the charge equilibrium demand.

It is necessary to point out that the effect of metallic cations on the bond connected to an adjacent bond of them can be neglected. For example, $\varepsilon_{O-H}$ is almost the same whichever metallic cation O(ter) is coordinated with. This again proves our conclusion of "the location of electrons in silicates"[7].

In the second case as is illustrated in

cluster(d), we get the idea by comparing the results of Table 1 and Table 4 that when O(ter) is coordinated with metallic cations, the further coordination on O(br) does not affect the Si-O(ter) bond greatly.

## 5 CONCLUSIONS

(1) The characteristics of different Si-O bonds in silicates depend mainly on the bonding situation of oxygen. When O(br) and O(ter) are both bicoordinated and the Si-O-H angle is smaller than or equal to the Si-O-Si angle, the Si-O(br) bond is stronger than the Si-O(ter) bond. When the coordination number of O(br) increases, the Si-O(br) bond is weakened. Therefore only on certain conditions is the Si-O(br) bond stronger than the Si-O(ter) bond. In molten silicates where the Si-O-Si angle is much larger than the Si-O-H angle, the Si-O(br) bond is usually considered to be more stable than the Si-O(ter) bond.

(2) Metallic cations coordinating to O(br) will weaken the Si-O(br) bond. Cations of larger electronegativities will act more strongly.

(3) The Al-O(br) bond is much less stable than the Si-O(br) bond in aluminosilicates. Metallic cations coordinating to O(br) will weaken the Si-O(br) and the Al-O(br) bonds strongly.

(4) If O(br) is coordinated with a fourth coordinator, the Si-O(br) bond and the Al-O(br) bond will be weakened further. Therefore enough metallic cations are necessary for the depolymerization of the molten silicic radical-framework.

(5)The strength of the Si-O(ter) bond and the Al-O(ter) bond depends on the Si-(Al)-O-M angle greatly with the larger angle resulting in a stronger bond. Coordinators of O(ter) do not affect the Si-O(br) bond and the Al-O(br) bond greatly. Coordinators with smaller electronegativities of O(ter) with larger Si-O-M angles will strengthen the Si-O(ter) and Al-O(ter) bonds.

(6) Metallic cations coordinating to either O(br) or O(ter) can only affect the adjacent bonds. Their effect on the bonds connected to the adjacent bonds can be neglected.

### REFERENCES

1 Gibbs, G A. American Mineralogist, 1982, 67: 421-450.

2 Gao, X H. J Cent South inst Min Metall, 1985, 46:9-17.

3 Louisnathan, S J *et al*. American Mineralogist, 1972, 57: 1643-1663.

4 Gibbs, G V *et al*. American Mineralogist, 1972, 57: 1578-1613.

5 Meagher, E P *et al*. Physics and Chemistry of Minerals, 1979, 4: 11-21.

6 Geisinger, K L *et al*. Physics and Chemistry of Minerals, 1985, 11: 266-283.

7 Gao, X H *et al*. J Cent South Inst Metall, 1990, 21: 441-446.

8 De Jong, B H *et al*. Geochimica et Cosmochimica Acta, 1980, 44: 491-511.

9 De Jong, B H *et al*. Geochimica et Cosmochimica Acta, 1980, 44: 1627-1642.

10 Newton, M D *et al*. Physics and Chemistry of Minerals, 1980, 6: 221—246.

11 Pople, J A *et al*. Approximate Molecular Orbital Theory. McGraw-Hill, 1970.

12 Gao, X H. *Inorganic Chemistry*, 1987, 3: 58-68.