ment based on a hexagonally packed structure of identical SWCNTs would favor a structure whose faces consisted of close-packed SWCNTs. This would include a hexagonal cross section but could equally well be any cross section consisting of 120° facets. We are unable to take a diffraction pattern along the crystal length, but the projected shapes of the crystals and the contrast in the HRTEM images indicate that faceting of the SWCNT crystals does indeed occur as seen at the ends of the crystals in Fig. 3A.

HRTEM investigations were performed on several crystals, including one that is ~750 nm long and ~40 nm in diameter with a curved end cap (Fig. 4A). Higher magnification images show the internal structure at the apex (Fig. 4B) and at the base of the crystal (Fig. 4C). Figure 4B shows the perfect regular arrangement of 1.6-nm-diameter SWCNTs in a bundle with no evidence of inhomogeneity or defect. This structural perfection was a characteristic of all nanotubes produced using this technique.

The perfection of the crystals of SWCNTs and the observation that they are all physically identical within any given crystal containing up to several thousand individual nanotubes are unexpected from the point of view of previous results and synthetic approaches in the field. Nevertheless, the expected, most stable arrangement of a nanotube crystal, as shown here, follows general thermodynamic expectations of a minimum-energy configuration over an extended array of tubes in close contact. Minimization of energy also implies that all tubes be identical and straight, permitting maximization of the van der Waals interactions, minimization of strain, and a hexagonally packed lattice.

Our results provide evidence of faceting of SWCNT crystals. The role of weak forces such as applied magnetic fields and the spatial localization of the reactants appear be essential to direct the self-assembly process. The approach we have discussed shows that nanostructuring of reactants in the solid-state reaction of C_{60} and Ni is a key feature to the formation of SWCNTs organized into a bulk crystalline material.

References and Notes

1. S. Iijima, *Nature* **354**, 56 (1991).
2. M. M. J. Treacy, T. W. Ebbesen, J. M. Gibson, *Nature* **381**, 678 (1996).
3. S. J. Tans, R. M. Verschueren, C. Dekker, *Nature* **393**, 40 (1998).
4. "Every 18 months, processing power doubles while cost holds constant," G. Moore, Intel Corporation, 1965.
5. H. Dai, J. H. Hafner, A. G. Rinzler, D. T. Colbert, R. E. Smalley, *Nature* **384**, 147 (1996).
6. Ph. Poncharal, Z. L. Wang, D. Ugarte, W. A. de Heer, *Science* **283**, 1513 (1999).
7. J. Kong *et al.*, *Science* **287**, 622 (2000).
8. P. G. Collins, K. Bradley, M. Ishigami, A. Zettl, *Science* **287**, 1801 (2000).
9. A. C. Dillon *et al.*, *Nature* **386**, 377 (1997).
10. Q. H. Wang *et al.*, *Appl. Phys. Lett.* **72**, 2912 (1998).
11. S. Fan *et al.*, *Science* **283**, 512 (1999).
12. C. J. Lee *et al.*, *Appl. Phys. Lett.* **75**, 1721 (1999).
13. P. Kim, C. M. Lieber, *Science* **286**, 2148 (1999).
14. A. Thess *et al.*, *Science* **273**, 483 (1996).
15. S. Iijima, T. Ichihashi, *Nature* **363**, 603 (1993).
16. D. S. Bethune *et al.*, *Nature* **363**, 605 (1993).
17. See, for example, X. F. Zhang *et al.*, *J. Cryst. Growth* **130**, 368 (1993).
18. M. Terrones *et al.*, *Nature* **388**, 52 (1997).
19. J. Li, C. Papadopoulos, J. M. Xu, M. Moskovits, *Appl. Phys. Lett.* **75**, 367 (1999).
20. L. Henrard *et al.*, *Eur. Phys. J. B* **13**, 661 (2000).
21. N. Hamada, S. I. Sawada, A. Oshiyama, *Phys. Rev. Lett.* **68**, 1579 (1992).
22. J. Brugger *et al.*, *Microelectron. Eng.* **53**, 403 (2000).
23. R. Lüthi *et al.*, *Appl. Phys. Lett.* **75**, 1314 (1999).
24. R. Kuozo, M. Terauchi, M. Tanaka, *Jpn. J. Appl. Phys.* **31**, L1484 (1992).
25. R. Saito, G. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998).
26. R. R. Meyer *et al.*, *Science* **289**, 1324 (2000).
27. C.-H. Kiang *et al.*, *Phys. Rev. Lett.* **81**, 1869 (1998).
28. CrystalKit was written by Roar Kilaas, Total Resolution, 20 Florida Avenue, Berkeley CA, USA.

29. This work has partially been supported through the European Union and the Swiss Federal Office for Education and Science by the Information Society Technologies–Future Emerging Technology (IST-FET) projects ATOMS and BUN. We thank J. Brugger for his help in developing the original sieve technology and F. Diederich for useful discussions. J.W.S. acknowledges support by the Swiss National Science Foundation and thanks the Institut für Festkörperforschung (Forschungszentrum Jülich, Germany) for use of the 4000FX microscope.

28 November 2000; accepted 23 March 2001

10.1126/science.1057823
Include this information when citing this paper.

Reaction-Controlled Phase-Transfer Catalysis for Propylene Epoxidation to Propylene Oxide

Xi Zuwei,* Zhou Ning, Sun Yu, Li Kunlan

The epoxidation of olefins with H_2O_2 was performed with a tungsten-containing catalyst. This insoluble catalyst forms soluble active species by the action of H_2O_2, and when the H_2O_2 is used up, the catalyst precipitates for easy recycling. Thus, the advantages of both homogeneous and heterogeneous catalysts are combined in one system through reaction-controlled phase transfer of the catalyst. When coupled with the 2-ethylanthraquinone/2-ethylanthrahydroquinone redox process for H_2O_2 production, O_2 can be used for the epoxidation of propylene to propylene oxide with 85% yield based on 2-ethylanthrahydroquinone without any co-products. This approach avoids the problematic co-products normally associated with the industrial production of propylene oxide.

Propylene oxide is used for making polyurethane, unsaturated resins, surfactants, and other products, and market demand for it has been increasing over the years. Its current worldwide production capacity is around 4.5 million metric tons per year. There are two industrial methods for propylene oxide production: the chlorohydrin method and the Halcon method. In the chlorohydrin method, large amounts of Cl_2 are consumed, which gives rise to serious problems of equipment corrosion and environmental pollution. In the Halcon method, autoxidation of ethylbenzene or isobutane is used to make alkylhydroperoxide, which acts as an oxidant for catalytic epoxidation of propylene to propylene oxide, together with a large amount of co-products. Thus, the Halcon process is a very complicated one and needs heavy capital investment.

The oxidation of propylene to propylene oxide without any co-products in a more environmentally friendly way has been an important objective for many chemists. Although O_2 is an inexpensive and clean oxidant, heterogeneous catalytic epoxidation of propylene with O_2 usually gives poor selectivity because of the high reaction temperature (*1*, *2*). H_2O_2 is also a clean oxidant, and the TS-1 zeolite catalyst for propylene epoxidation with H_2O_2 in methanol solution has high catalytic activity and selectivity (*3*). Moreover, the TS-1 zeolite can be easily separated and reused. However, this method has not yet been commercialized because of the relatively high cost of H_2O_2 when used to produce a low-priced commodity chemical such as propylene oxide. Some researchers have used the redox reaction of 2-ethylanthraquinone (EAQ)/2-ethylanthrahydroquinone (EAHQ), with O_2 as the oxidant, to produce H_2O_2 in situ, which then undergoes propylene epoxidation in the presence of TS-1 zeolite (*4*). However, because of the restriction imposed by the properties of the TS-1 zeolite (*5*), its reaction medium in the EAQ/EAHQ system is more complicated than that of the normal industrial

---

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian 116023, People's Republic of China.

*To whom correspondence should be addressed. E-mail: huangw@dicp.ac.cn

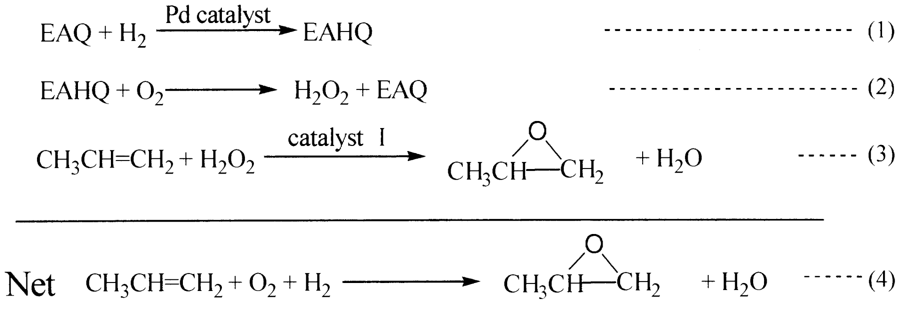
EAQ/EAHQ (polymethylbenzenes plus trialkylphosphate) system for H_2O_2 production, thus resulting in a substantial decrease in reaction efficiency (*6*).

Homogeneous catalytic epoxidation of propylene can also take place under mild conditions with metalloporphyrin or $EuCl_3$ being used as the catalyst and O_2 as the oxidant in the presence of a reductant (such as propanal or Zn powder) (*7*, *8*). This approach can give high selectivity, but the utilization efficiency of the reductant is low, and a large amount of low-valued co-products is produced. Both the activity and selectivity of homogeneous catalytic epoxidation of liquid olefins with H_2O_2 are excellent when using metalloporphyrin or salts of heteropolyacids as the catalyst (*9–11*). However, the selectivity of homogeneous catalytic epoxidation of propylene with H_2O_2 in an aqueous/oil biphasic system is limited because propylene oxide is highly water-soluble and hydrolyzes (*12*). Furthermore, there is a problem common in homogeneous catalytic systems: the difficulty of catalyst separation and reuse.

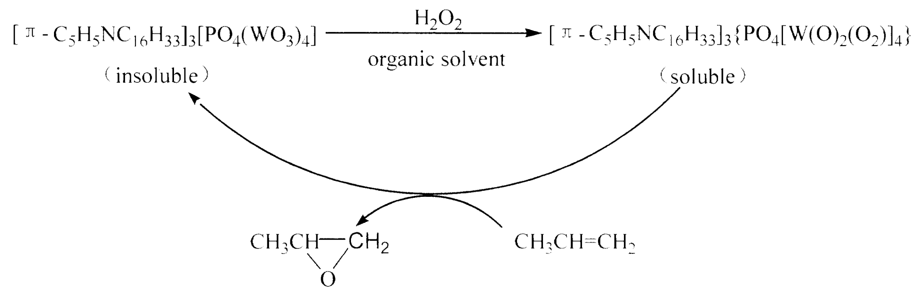
We have designed and synthesized a catalyst system based on quaternary ammonium heteropolyoxotungstates. This system can be used for homogeneous catalytic epoxidation of olefins, using H_2O_2 as the oxidant, and exhibits high conversion and selectivity as well as excellent catalyst stability. After reaction, the catalyst can be filtered and reused just like a heterogeneous catalyst. Therefore, this catalytic system possesses the advantages of both homogeneous and heterogeneous catalysts. In this system, $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PO_4(WO_3)_4]$ (catalyst I) gives the best activity and selectivity for epoxidation. For example, when catalytic epoxidations of olefins were performed at 35°C with H_2O_2 in a chloride-free solvent/aqueous biphasic system, the conversions were 100 and 98.4% based on H_2O_2 and the selectivities were 89.6 and 87.6% for 1-hexene and cyclohexene (*13*), respectively. We have coupled the catalytic epoxidation of propylene with H_2O_2 to the EAQ/EAHQ redox process for H_2O_2 production. Thus, the O_2 can be used for epoxidation of propylene. The reaction is shown in Scheme 1.

After the oxidation of EAHQ to H_2O_2 and EAQ, the catalytic epoxidation of propylene in this system was carried out at 65°C for 6 hours, with a propylene conversion of 89% based on EAHQ; a selectivity for propylene oxide of 95% (that is, a yield of 85% based on EAHQ); and a turnover number of 382 (*14*). A small amount of propylene glycol was generated as a by-product.

When using either 30% H_2O_2 or the H_2O_2 generated by the oxidation of EAHQ to carry out the epoxidation of olefins, catalyst I precipitates from the reaction medium after epoxidation and can be recovered and reused. In an aqueous/oil biphasic system, catalyst I itself is not soluble in the oil phase, but it dissolves slowly under the action of H_2O_2, which subsequently leads to homogeneous catalytic epoxidation of olefins. During the reaction, the system gradually changes from turbid to clear. When the H_2O_2 is used up, catalyst I precipitates gradually. As a result, the system becomes turbid again, indicating completion of the epoxidation. This phenomenon manifests a solid-liquid-solid phase transfer of catalyst I, which is controlled by the reaction, and so we refer to these catalysts as "reaction-controlled phase transfer catalysts."



Scheme 1.



Scheme 2.

After the catalytic epoxidation of propylene in the medium of the EAQ/EAHQ system, catalyst I is self-precipitated with a 90% recovery yield (by weight). As shown in Table 1, the catalytic activity and selectivity of the recovered catalysts were practically the same as those of the fresh catalyst, indicating the excellent stability of catalyst I.

The industrial process of the EAQ/EAHQ redox system for H_2O_2 production is a closed-loop cycling process, so the net effect, as shown in Eq. 4, is that the reaction only consumes O_2 (air), H_2, and propylene, and produces propylene oxide with high selectivity. Because catalyst I can be recycled, this method for the epoxidation of propylene to propylene oxide without any co-products is more environmentally friendly and economical.

Venturello and co-workers reported the synthesis of tetraalkylammonium heteropolyperoxotungstates for the epoxidation of olefins, such as $[(C_6H_{13})_4N]_3\{PO_4[WO(O_2)_2]_4\}$. The coordination number of the W atom with oxygen atoms is seven in this molecule (*15*). This compound is soluble in organic solvents. Both catalyst I and the recovered catalyst in this study are insoluble in organic solvents, and analysis results show that they do not contain any active oxygen. After dissolving catalyst I in CH_2Cl_2 under H_2O_2, the solvent was eliminated by vacuum and a solid was obtained. The active oxygen of this solid was determined to be 3.3% (by weight) (*16*), which is equivalent to the structure of $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3\{PO_4\text{-}[W(O)_2(O_2)]_4\}$ (compound II). Compound II is soluble in organic solvents and is an active species for the epoxidation of olefins. When all of the H_2O_2 is consumed, compound II returns to catalyst I and precipitates from the solution. Therefore, the mechanism for the reaction-controlled phase-transfer catalyst I can be described as in Scheme 2.

Why is catalyst I insoluble in organic solvents, whereas compound II is soluble? Infrared spectra (Fig. 1) show that both catalyst I and the recovered catalyst do not have a peroxo-bond absorption peak ν(O-O) at 840 cm^{-1} (ν, stretching vibration), but they do

Table 1. Recycling of catalyst I for the epoxidation of propylene. Reaction conditions were as follows. Fresh catalyst: EAHQ = 1: 200 (molar ratio) at 65°C for 5 hours. The catalyst was recovered by centrifugation and used in the next reaction without addition of fresh catalyst. The others were the same as in (*14*). The conversion of propylene was based on EAHQ, and the selectivity to propylene oxide was based on propylene.

Catalyst	C_3H_6:EAHQ (molar ratio)	Conversion (%)	Selectivity (%)
Fresh	2.5:1	91	94
Cycle 1	2.7:1	87	96
Cycle 2	2.4:1	90	92

have a clear ν_{as}(W-O-W) peak at 890 cm^{-1} (ν_{as}, asymmetric ν) (*17*). However, compound II has a ν(O-O) peak at 840 cm^{-1} but no visible ν_{as}(W-O-W) peak at 890 cm^{-1}. These results suggest that the W atom in catalyst I with intramolecular O atoms is not enough for its coordination number, so this W atom will interact with O atoms of another molecule (forming a W-O-W bond), thus forming complicated polymeric structures, which gives rise to its insolubility in organic solvents. When catalyst I reacts with H_2O_2 to form the peroxo bond, the coordination number of the W atom with intramolecular O atoms increases, and the intermolecular interaction (W-O-W) decreases, which leads to a dramatic reduction of intermolecular bonds. As a result, compound II becomes soluble in organic solvents. Moreover, the structure of the quaternary ammonium cation (for example, the number of carbon atoms) also has a substantial effect on catalyst solubility, as shown in Table 2. Catalyst III, containing a small tetrapropyl ammonium ion, was insoluble in the reaction system during the epoxidation, so both the conversion and selectivity were low: only 60.6 and 60.2%, respectively. Catalyst I is a reaction-controlled phase-transfer catalyst with high catalytic activity and selectivity. Although catalyst IV also has good catalytic performance, it was totally soluble in the reaction system during and after the epoxidation, because it contains a big octadecyl benzyl dimethyl ammonium ion. This makes catalyst IV difficult to recover. Therefore, the structure of the quaternary ammonium cation has an important effect on forming a reaction-controlled phase-transfer catalyst and on its catalytic performance.

Besides epoxidation of lower olefins with H_2O_2 generated from the EAQ/EAHQ redox process, this catalytic system can also be applied to the epoxidation of other olefins (such as linear terminal olefins, internal olefins, cyclic olefins, styrene, and allyl chloride) with 30% H_2O_2. Excellent catalytic activity and selectivity, as well as the same property of reaction-controlled phase-transfer catalysis, were also observed in the epoxidation of such olefins.

The concept of a reaction-controlled phase-transfer catalyst can be summarized as follows: The catalyst itself is insoluble in the reaction medium, but under the action of one of the reactants, it can form soluble active species that subsequently react with another reactant to selectively generate the desired product. When the former reactant is used up, the catalyst returns to its original structure and precipitates from the reaction medium, which can then be easily separated and reused, thus providing a useful approach to the difficult problem of the separation of homogeneous catalysts.

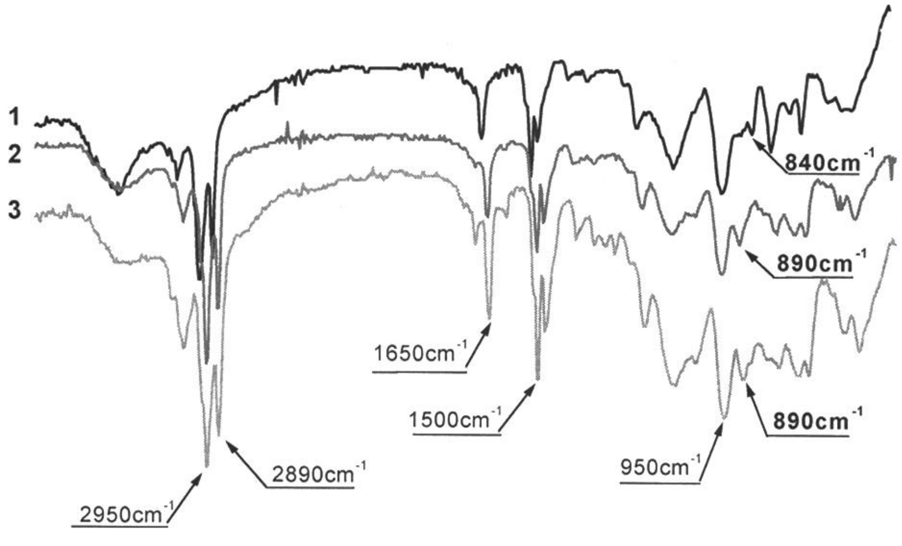


Fig. 1. Infrared spectra of catalyst I, compound II, and recovered catalyst. 1: $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3\{PO_4[W(O)_2(O_2)]_4\}$ (compound II). 2: $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PO_4(WO_3)_4]$ (catalyst I). 3: Recovered catalyst of I.

Table 2. The effect of the ammonium ion of catalysts on cyclohexene epoxidation with H_2O_2. Catalyst III = $[(C_3H_7)_4N]_3[PO_4(WO_3)_4]$. Catalyst IV = $[C_{18}H_{37}N(CH_2Ph)(CH_3)_2]_3[PO_4(WO_3)_4]$. Reaction conditions were as follows. Solvent: 16 ml of CH_2ClCH_2Cl at 35°C for 1.5 hours. The others were the same as in (*13*). The conversion of cyclohexene was based on H_2O_2, and the selectivity to cyclohexene oxide was based on cyclohexene.

Catalyst	During epoxidation	After epoxidation	Conversion (%)	Selectivity (%)
III	Insoluble	Insoluble	60.6	60.2
I	Soluble	Insoluble	90.6	96.7
IV	Soluble	Soluble	96.5	85.8

References and Notes

1. M. F. Portela *et al.*, *Catal. Today* **1**, 101 (1987).
2. G. Z. Lu, X. B. Zuo, *Catal. Lett.* **58**, 67 (1999).
3. M. G. Clerici, G. Bellussi, U. Romano, *J. Catal.* **129**, 159 (1991).
4. P. Ingallina, M. G. Clerici, L. Rossi, *Stud. Surf. Sci. Catal.* **92**, 31 (1995).
5. The diameter of the pore of TS-1 zeolite is about 0.6 nm. Linear molecules and mononuclear aromatic compounds can diffuse to TS-1 active sites and be oxidized. In order to avoid these reactions, 2-methylnaphtalene and diisobutylcarbinol, whose molecules have a cross-section diameter greater than 0.6 nm, are used as the medium. Methanol is necessary for the epoxidation of propylene catalyzed by TS-1 zeolite.
6. In industrial production of H_2O_2, after several cycles of the EAQ/EAHQ redox system, the degree of hydrogenation can be 75 to 80%, and the concentration of hydroquinone is 0.4 to 0.45 mol/liter. However, in (*4*), when the degree of hydrogenation is 100%, the concentration of hydroquinone is only about 0.13 mol/liter.
7. J. Haber, T. Mlodnicka, *J. Mol. Catal.* **54**, 451 (1989).
8. I. Yamanaka, K. Nakagaki, K. Otsuka, *J. Chem. Soc. Chem. Commun.* **1995**, 1185 (1995).
9. J. P. Renaud, P. Battioni, J. F. Bartoli, D. Mansuy, *J. Chem. Soc. Chem. Commun.* **1985**, 888 (1985).
10. C. Venturello, R. D'Aloisio, *J. Org. Chem.* **53**, 1553 (1988).
11. Y. Ishii *et al.*, *J. Org. Chem.* **53**, 3587 (1988).
12. C. Venturello, E. Alneri, M. Ricci, *J. Org. Chem.* **48**, 3831 (1983).
13. Reaction conditions were as follows. Thirty mmol of olefin was dissolved in a mixed solvent of 16 ml of toluene and 12 ml of tributylphosphate; 10 mmol of 30% H_2O_2 and 0.05 mmol of catalyst I were then added. The reaction was conducted at 35°C and was terminated after the catalyst precipitated.
14. 12.5 g of EAQ (~50 mmol) was dissolved in a mixed solvent of 40 ml of xylene and 30 ml of tributylphosphate. In the presence of 0.1250 g of 5% Pd/C, the hydrogenation was carried out at 45°C under 1.0 MPa of H_2. The reaction was terminated when about 75% of EAQ was hydrogenated. The exact concentration of EAHQ was determined by titration. 75 ml of EAHQ solution (0.45 mol/liter) was charged into a glass reactor with vigorous stirring at 35°C under 0.1 MPa of O_2 until EAHQ was completely oxidized to EAQ and H_2O_2. The solution was transferred to a 250-ml-capacity stainless steel autoclave with a glass liner. Catalyst I [catalyst: EAHQ = 1: 450 (molar ratio)] and benzene (the internal standard) were added. 3.8 g of propylene [C_3H_6: EAHQ = 2.7: 1 (molar ratio)] was fed into the autoclave. The reaction was maintained at 65°C for 6 hours. After the reaction, the autoclave was cooled to 23°C. The gas in it was discharged, and the propylene and propylene oxide in the gas were analyzed by gas chromatography (GC) with the external standard method. The propylene and propylene oxide in the liquid were analyzed by GC with the internal standard method.
15. C. Venturello, R. D'Aloisio, J. C. J. Bart, M. Ricci, *J. Mol. Catal.* **32**, 107 (1985).
16. Active oxygen was analyzed by the improved iodometric method proposed by Venturello. For $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3\{PO_4[W(O)_2(O_2)]_4\}$: O (active) = 3.20%.
17. C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, R. Thouvenot, *Inorg. Chem.* **22**, 207(1983).
18. We are grateful to C. Zhang and X. Huang for their support of this research and to L. Lin for his valuable discussions. This work was financially supported by the National Nature Science Foundation of China (grant no. 29673042).

16 January 2001; accepted 26 March 2001