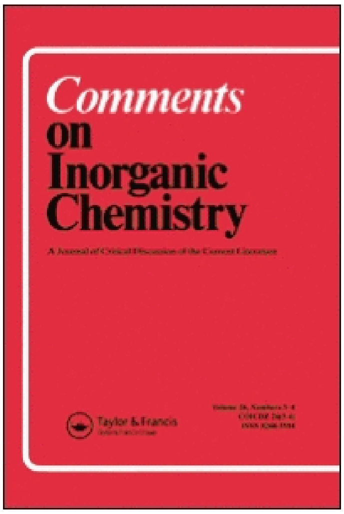

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Superheated Solvent Media for Organometallic (Poly)Chalcogenide Cluster Synthesis

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Solvothermal reactions in superheated aqueous and nonaqueous solvent media have led to many new metal-carbonyl chalcogenido clusters. This efficient synthetic technique, usually applied to synthesize solid state materials, is also surprisingly useful in preparing molecular clusters in crystalline form. Thus, many of the often laborious purification and separation procedures which are associated with conventional solution methods can be avoided. This method holds substantial promise for the exploratory synthesis of inorganic/organometallic compounds. In this short account we intend to focus on the contributions of the solventothermal technique to the organometallic polytelluride cluster chemistry.

Keywords: *solvothermal reactions, hydrothermal synthesis, metal clusters, chalcogenide complexes*

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INTRODUCTION

There has been intense research activity on the synthesis of both soluble[1–7] and solid state[8] metal chalcogenides during the past several years. Though some of the work is driven by the applications aspects of metal chalcogenides,[9,10] the majority of research has been exploratory in nature, mainly because chaclogenide chemistry is astoundingly rich and variegated. This is more true of the heavier congeners, Se and Te, among the chalcogens, particularly since the explorations of the chemistry of these elements could not keep pace with the activities on the lighter brethren sulfur.[1,2a,11] However, this aspect has already been stressed and, fittingly enough, considerable progress has been made to narrow the existing gaps. Numerous compounds displaying novel modes of coordination and bonding by Se_x^{2-} and Te_x^{2-} have been synthesized. Using soluble Zintl phases A_2Q_x(A = alkali cation; Q = S, Se, Te; X = 2–6) which provide the valuable Q_x^{2-} synthons in polar solvents, such as dimethylformamide, acetonitrile, etc., a large number of homoleptic polychalcogenide complexes of the transition and main-group metal atoms have been synthesized. Almost in parallel with these developments, there was also a surge of activity in the area of organometallic chalcogenide complexes and clusters which predominantly contain cyclopentadienide and carbon monoxide ligands as ancillaries. Thus, investigations on molecular complexes formed by metal ions with polychalcogenido ligands form an important part of chalcogenide research. This field was reviewed a few years ago.[1–3]

Until recently, solventothermal processes involved almost exclusively solid state compounds, both for the synthesis of new materials and for crystal growth of useful materials. No particular attention has been paid to producing discrete molecular compounds, and when they have been encountered it has been primarily by accident. Since the solventothermal technique is a great tool for exploratory synthesis and the most interesting developments in coordination and cluster chemistry continue to come from new compounds, it seems logical to extend this technique to such chemistry. Hydrothermal synthetic conditions have been recently applied to oxidative decarbonylation chemistry with polychalcogenide ligands,[1] a well-known reaction which gives rise to interesting metal chalcogenido clusters.[2]

Together with the molten salt technique,[8,12] the hydrothermal method has also provided a soft route for the synthesis of metastable polychalcogenide compounds having extended solid state structures. Initially, the hydrothermal route had been applied in this laboratory to prepare a whole family of interesting molybdenum polyselenido cluster compounds,[13] but it quickly became apparent that hydrothermal chemistry could be extended to reactions between alkali metal chalcogenides and metal carbonyl compounds. The existence of several interesting molecules such as $Fe_2Q_2(CO)_6$ ($Q = S$[14], Se[15], Te[16]), $[W_6Te_8(CO)_{18}]^{2-}$,[17] $Fe_2Ru_2Te_2(CO)_{11}$,[18] $(\eta^5\text{-}C_5H_5)Mo_2Fe_xTe_2(CO)_7$ ($x = 1, 2$),[19] among others, prepared via the oxidative decarbonylation[2b] of metal carbonyls with Se_x^{2-} and Te_x^{2-} ligands, by conventional synthetic techniques, provided a good foundation and reference base with which to judge the value of a hydrothermal twist in this type of reaction. The chalcogen atoms S, Se, and Te are widely known to favor the formation and stabilization of large clusters as attested to by the isolation of the giant metal selenido clusters such as $Cu_{70}Se_{35}(PEt_3)_{22}$ and $Cu_{146}Se_{73}(PPh_3)_{30}$.[7] High nuclearity organometallic clusters stabilized by main-group ligands are relevant in the area of homogeneous catalysis.[20]

Our investigations involving the application of the solvothermal technique have resulted in a variety of interesting metal-carbonyl chalcogenido clusters. The hydrothermal results are so interesting that expanding the solventothermal technique to other types of coordination and cluster compounds (not necessarily only chalcogenido ones) seemed compelling, especially for systems which have been already well investigated by more traditional solution approaches at ambient temperature and pressure. In this short account we intend to focus on the contributions of the solventothermal technique to the organometallic cluster chemistry.

SOLVOTHERMAL SYNTHESIS OF METAL-CARBONYL CHALCOGENIDO CLUSTERS

Hydrothermal conditions provide a useful path for crystal growth,[21] and currently the technique is being increasingly applied to the synthesis of inorganic solids.[21,22] Success of the method hinges on the improved solvent properties and high reactant mobilities obtained in superheated water. Reactions may also be carried out at or above supercritical temperatures, but this need not always be the case. Many interesting solids are routinely prepared at subcritical temperatures. In fact, most of these materials are only kinetically stable and tend to transform to more thermodynamically stable phases by the time critical or supercritical temperatures are reached. The hydrothermal technique using either sub- or super-critical conditions differs from conventional solution methods for the synthesis and/or crystallization of compounds at near-ambient temperatures primarily because viscosity of the liquid is lower under hydrothermal conditions. Thus, diffusion processes are faster and crystals may form at a higher rate. Because of these reasons, this technique has received overwhelming favor for crystal growth and the production of many important inorganic materials.[23]

Use of sparingly soluble starting materials is permitted to a considerable extent in hydrothermal synthesis. In hydrothermal reactions for the preparation of inorganic materials, a *mineralizer* is added to increase the solubility of substrates.[21] Many inorganic ions are effective mineralizers, Cl^- and CO_3^{2-} being the most common in the formation of natural crystals such as SiO_2 under geological conditions. In many instances the solvent may be the actual mineralizer itself. Since a minimum solubility of 2–5% for the least soluble component is required for many hydrothermal preparations, use of nonaqueous solvents, i.e., solvothermal reactions, may be quite useful in the cases where the required solubility is not easy to achieve in an aqueous medium. Of course, non-aqueous solvents can also enable new reaction pathways (probably a richer collection) and can afford new reaction types and products, different from those obtained from water.

It is useful to discuss here a few practical aspects of performing the solvothermal reactions highlighted in this account. The oxidative decarbonylation reactions between metal carbonyl compounds and A_2Q_x, in the presence of bulky cationic templates such as R_4E^+ (R, an alkyl group for E = N and a phenyl group for E = P) can be carried out in thick-walled sealed glass ampoules. Existence of templating effects in solvothermal reactions is an established fact.[24] Typically, about 500 mg of the $M_i(CO)_j/A_2Q_x/R_4E^+$ mixture in variable molar ratios provides a convenient and useful starting amount for laboratory scale preparations in sealed, ampoules containing 0.2–0.5 mL of the chosen solvent so as to give a filling of approximately 20–40%. Reactions are carried out at ~10–30 degrees above the boiling point of the solvent used. At higher temperatures, decomposition of the organic cation becomes a problem. This decomposition involves nucleophilic attack of the alkyl groups by the highly reactive Te_x^{2-} and Se_x^{2-} ligands, according to Eqs. (1) and (2). The least robust cations with respect to Eqs. (1) and (2) are the alkylammonium species, which can decompose at >140°C. The Ph_4P^+ cation, however, survives at much higher temperatures. If this decomposition occurs to a significant extend, the production of volatile organic compounds in the ampoule can cause an explosion which could release various noxious fumes. Therefore, it is strongly recommended that the reactions be performed inside a hood.

$$R_4N^+ + Te_x^{2-} \longrightarrow RTe^- + R_3N \qquad (1)$$

$$RTe^- + R_4N^+ \longrightarrow R_2Te + R_3N \qquad (2)$$

The preparative procedures can be optimized by varying the reaction parameters such as reactant ratio, temperature, and duration. Isolation of compounds involves only washing the solid product with suitable solvents in most cases. Purity and yield are generally good.

The reactions of polychalcogenide anions with metal carbonyls may lead to either carbonyl-containing clusters or completely decarbonylated binary anions:

$$Fe(CO)_5 + Te_2^{2-} \longrightarrow [Fe_8Te_{10}(CO)_{20}]^{2-} \qquad (3)$$

$$Mn_2(CO)_{10} + Se_4^{2-}(\text{excess}) \longrightarrow [Mn(Se_4)_2]^{2-} \qquad (4)$$

Although most reactions are *oxidative decarbonylations*,[2b] some decarbonylation processes involve only substitution. An example of such a metathetical reaction[2] is

$$Cr(CO)_6 + Te_4^{2-} \longrightarrow [Cr(Te_4)(CO)_4]^{2-} \qquad (5)$$

Because the oxidative decarbonylation does not eliminate all the CO ligands from the starting material – in fact it is our experience that the remaining carbonyl groups are tenaciously bound to the oxidized metal centers – we are able to obtain discrete molecular species rather than solid state materials. The CO groups act as terminal ligands preventing growth to an infinite system. Therefore, we could assert that this type of reaction almost ensures the formation of molecular species.

Reactions in Superheated Aqueous Media

The first reaction attempted under hydrothermal conditions is illustrated in Eq. (6),

$$Ru_3(CO)_{12} + 5Na_2Te_2 + 6Ph_4PCl \xrightarrow[\text{65hours}]{\text{0.5mL } H_2O,\,110^\circ C} (PH_4P)_2[Ru_6Te_{14}(CO)_{12}] \qquad (6)$$

in which a hexanuclear ruthenium cluster was produced.[25] The corresponding iron compound $(Ph_4P)_2[Fe_6Te_{14}(CO)_{12}]$ was also prepared in 90% yield.[26] The only impurity found to be present was well-formed crystals of elemental Te which can be removed from the product by gravity separation in bromoform. The molecular structures of these $[M_6Te_{14}(CO)_{12}]^{2-}$ (**1**) clusters with an idealized S_6 symmetry contain octahedral arrays of Fe or Ru atoms upheld by a central Te_2^{2-} fragment. The Te atoms in this unit each bind to three metal centers, forming an M_3Te-TeM_3 ethane-like fragment with staggered conformation. Similar bonding features, observed previously in the $[W_6Te_8(CO)_{18}]^{2-}$ (**2**) cluster,[17] are not known for any molecular species containing S_2^{2-} or Se_2^{2-} ligands. Interestingly, this particular Te_2^{2-} bonding environment is found in pyrite-type structures.[25,27] The structure of $[Ru_6(Te_2)_7(CO)_{12}]^{2-}$ is peculiar in that its central $[Ru_6(Te_2)_7]^{2-}$ core is reminiscent of an excised fragment of the $RuTe_2$ pyrite-type lattice (see Fig. 1). The mid-point of the central Te unit is situated at the octahedral center with six Ru atoms being its immediate neighbors. This is the Te_2^{2-} environment found in pyrite. It is tempting to speculate that this cluster core could be acting as the nucleus for crystallite growth of bulk $RuTe_2$ pyrite. Recently there have been attempts to elaborate on such relationships between structures of metal chalcogenide clusters and infinitely extended lattices of parent solid-state compounds.[28]

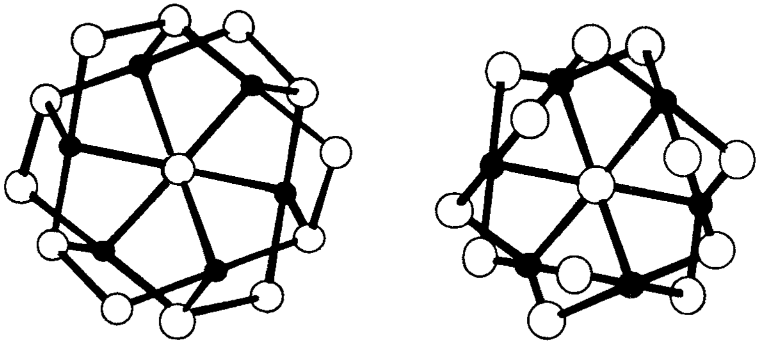
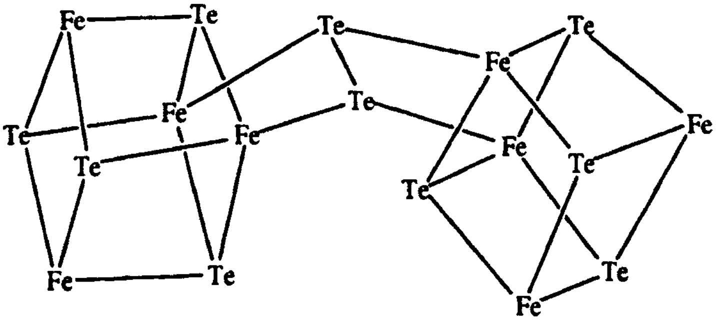


FIGURE 1 Comparison between the $[Ru_6(Te_2)_7]^{2-}$ core (left) and a small core fragment of $RuTe_2$ (right)

The compound $[Fe_8Te_{10}(CO)_{20}]^{2-}$,[29] (**3**) can be obtained both via a conventional reaction between $Fe(CO)_5$ and $(Ph_4P)_2Te_4$ in dimethylformamide at ambient conditions, and by hydrothermal synthesis.[30] The cluster anion **3** consists of two approximate "Fe_4Te_4" cubane-like clusters bridged by a μ_2-Te_2^{2-} ligand. The octahedral geometry around the iron centers in **3** distinguishes this cluster from the iron-sulfur clusters of similar core structures.[31] The cluster $[Fe_6Te_{14}(CO)_{12}]^{2-}$ was not found to form, however, when $Fe(CO)_5$ was the starting carbonyl compound. Use of solid $Fe_3(CO)_{12}$ in place of liquid $Fe(CO)_5$ perhaps gives a better handle on controlling the required reaction stoichiometry which appears to be a crucial factor in solvothermal preparation of metal-carbonyl chalcogenido clusters.



COMPOUND (**3**)

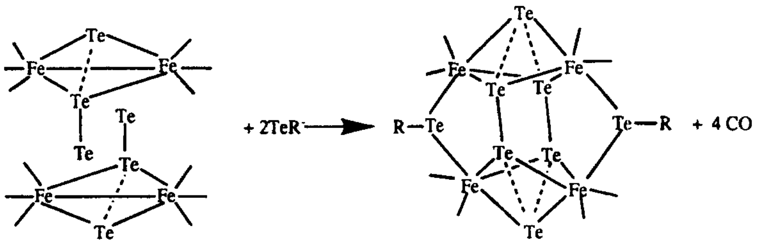
The other iron species prepared hydrothermally at 130°C is $Cs[HFe_3Te(CO)_9]$ (**4**)[32] from a reaction mixture consisting of $Fe_3(CO)_{12}$ and Cs_2Te_3 (4:1 molar ratio) in 0.2 mL H_2O. The $[HFe_3Te(CO)_9]^-$ cluster was previously reported[33] to have formed in solution via the protonation of $[Fe_3Te(CO)_9]^{2-}$. The structure of **4** contains a "Fe_3Te" tetrahedron in which one of the Fe-Fe edges is bridged by the hydrido ligand as indicated by its significant shortness compared with the other two Fe-Fe bonds. The presence of the hydrido ligand can also be detected from the high-field shifted ^1H NMR signal of **4** in solution.

The hydrothermal reactions of at 110°C of $Mo(CO)_6$, Na_2Te_2 and Ph_4PCl gives the cluster anion $[Mo_6Te_8(CO)_{18}]^{2-}$ which has not been prepared via the conventional routes, to our knowledge. This cluster is isostructural to its W analog mentioned above.[17]

Homometallic Clusters

The solvothermal chemistry of the $M_x(CO)_y/O_x^{2-}/R_4E^+$ system appears to be richer in alcoholic medium because, under certain conditions, the solvent participates in side reactions giving rise to new ligands which *in-situ* proceed to incorporate in the final products. At first, this may seem an undesirable complication which would be hard to control, but given the formation of pure products in high yields, the good reproducibility of these reactions, and the novel structural features found in the products, the solvent participation could be appreciated as a synthetic tool and exploited as such.

Two novel tetranuclear cluster anions $[M_4Te_6(TeMe)_2(CO)_8]^{2-}$ (M = Fe, **5a**; M=Ru, **5b**) form in 80% yield in methanol from the reaction of one equivalent of $M_3(CO)_{12}$ with five equivalents of Na_2Te_2 in the presence of a suitable organic quaternary ammonium salt.[35] Use of the Ph_4P^+ cation resulted in the isolation of $[Fe_2Te_3(CO)_6]^{2-}$ (**6**) which forms in the early stages of the reaction when mild conditions were used. This species was previously prepared by the solution route as the $(K\text{-crypt})^+$ salt.[36]



Two $[Fe_2Te_3(CO)_6]^{2-}$ (**6**) ions

An $[Fe_4Te_6(TeR)_2(CO)_8]^{2-}$ ion
(R = Me, **5a**; R = Et, **7**)

SCHEME 1

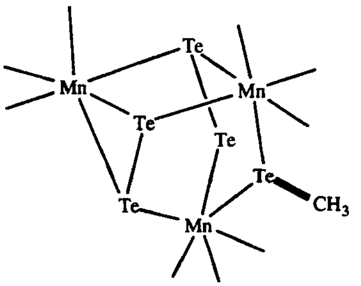
The transition metal atoms in **5** form a rectangle whose shorter and longer arms are bridged by μ_2-Te^{2-} and μ_2-$TeMe^-$ ligands, respectively. Two μ_2,μ_2-η^2-Te_2^{2-} ligands bridge all four atoms of the "M_4" rectangle, from above and below, to complete the highly symmetrical (D_{2h}) cluster anion **5**. The structural motif of **5a** can be thought of as originating from the fusion of two $[Fe_2Te_3(CO)_6]^{2-}$ anions (Scheme I). In **6** the metal atoms are held together by μ_2-Te^- and μ_2,η^1-Te_2^{2-} ligands. The two dimeric anions approach each other in a centrosymmetric fashion so that the dangling tellurium atom belonging to the ditelluride ligand in **6** forms two new Fe-Te bonds with the Fe atoms of the other anion to transform the μ_2,η^1-Te_2^{2-} ditelluride to a μ_2,μ_2-η^2-Te_2^{2-} ligand. A carbonyl ligand on each of the metal atoms of **6** may now be putatively assumed to have been replaced by incoming μ_2-$TeMe^-$ ligands. The above proposal is reasonable because we isolate **6** only in the early stages of these reactions or at lower temperatures (e.g., 80°C instead of 100°C). In fact, $(Ph_4P)_2[Fe_2Te_3(CO)_6]$ converts to $(Ph_4P)_2[Fe_4Te_6(TeMe)_2(CO)_8]$ upon heating in MeOH with Na_2Te_2 at 110°C, suggesting that **6** is an intermediate species in the formation of $[Fe_4Te_6(TeR)_2(CO)_8]^{2-}$ (*vide infra*).

What is interesting in the formation of **5** is the unanticipated methylation of the Te^{2-} anion which gives rise to the Te-Me^- ligands. Hydrothermal reactions of $Fe(CO)_5$[29] as well as $M_3(CO)_{12}$ (M = Fe,[26] Ru[25]) with Na_2Te_2 in the presence of the Ph_4P^+ cation lead to the formation of **3** and **1**, respectively, which are not methylated. The methyl groups in **5** most likely come from methanol, which is the reaction medium, and not from CO or the organic cations. This view is strongly supported by the isolation of $[Fe_4Te_6(TeEt)_2(CO)_8]^{2-}$ (**7**) when the reaction is carried out in ethanol[26] and also by the fact that **5** cannot be made in the absence of methanol. The $[Fe_4Te_6(TeEt)_2(CO)_8]^{2-}$ cluster is exactly isostructural to (**6**).

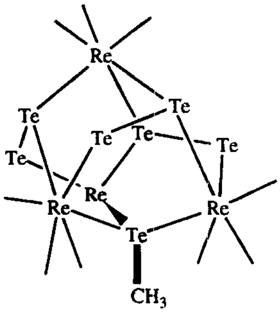
Similar methylation processes have also been observed in reactions involving organometallic compounds of the group 7 elements Mn and Re. The methanothermal reactions of $Mn_2(CO)_{10}$ with Na_2Q_2 (Q = S, Se, Te) at 80°C in the presence of the Ph_4P^+ cation gave the novel cluster anions $[Mn_3Q_4(QMe)(CO)_9]^{2-}$ (**8**) at 80°C.[34, 1] Rather interestingly, all three compounds crystallize in different space groups; nevertheless, all of them have the same molecular structure. Also the $[Mn_3S_4(SH)(CO)_9]^{2-}$ cluster containing the hydrosulfido ligand forms under certain conditions. There are two dichalcogenide ligands in the cluster anion, one of them of the μ_3-η^2Q2 type, while the other a μ_2,μ_2-η^2-Q_2 ligand. The manganese atoms are in the formal oxidation state of 1+ and these have idealized C_{3v} local symmetry for their individual $M(a)_3(b)_3$ octahedral coordination environments. These compounds react further with methanol to form the completely methylated $[Mn_2(QMe)_3]^-$ anions.[34] For rhenium, a reaction between $(\eta^5\text{-}C_5H_5)Re(CO)_3$ and Na_2Te_2 under the same conditions was found to give yet another novel cluster anion $[Re_4Te_6(TeMe)(CO)_{12}]^{3-}$ (**9**).[1,34] The structure of the cluster anion possesses a pseudo-three-fold axis which passes through the methylated tellurium atom and the unique Re atom. The reaction does not involve oxidation of Re atoms.

The production of $MeTe^-$ and $EtTe^-$ ligands appears to result from a nucleophilic displacement of the alcohol's hydroxyl group by Te^{2-} and Te_x^{2-} anions in solution under the operating conditions (see Eq. (7)). The reason this reaction is unanticipated is that it normally occurs in reverse, where the hard OH^- ion replaces the soft heavy main group element from the coordination sphere of carbon. Therefore Eq. (7) becomes an equilibrium under solvothermal conditions:

$$RCH_2OH + Te^{2-} \longleftrightarrow RCH_2Te^- + OH^- \qquad (7)$$



(**8**)



(**9**)

The alkylation of telluride ions, under the solventothermal conditions, adds a new dimension to this chemistry. The clean and reproducible nature of such reactions should lead to interesting new mixed ligand Metal/Te/RTe clusters inaccessible by other means.

Under similar conditions which lead to $[Fe_4Te_6(TeMe)_2(CO)_8]^{2-}$, but at slightly lower temperatures, a new cluster which does not posses a $MeTe^-$ ligand was identified. Solutions of this species readily display six ^{125}Te NMR signals (see Table II). Identical spectra are also observed for solutions aged for ca. 20 h as well. But when the acetone-D_6 solution is

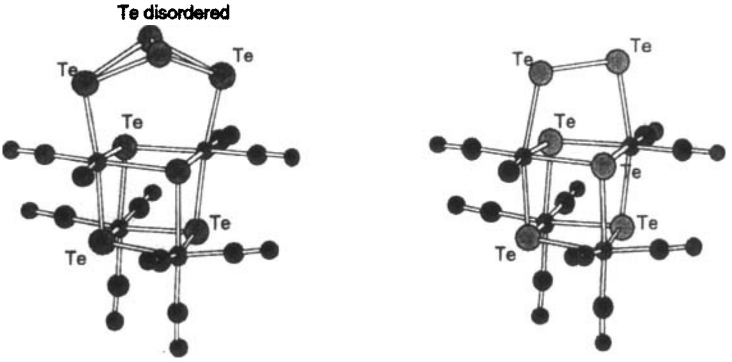


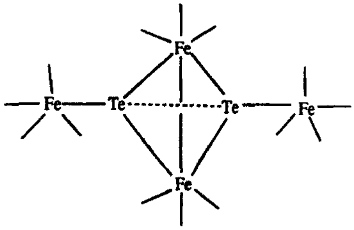
FIGURE 2 The two anionic clusters (10a) and (10b) which occupy the same crystallographic site in the lattice

allowed to stand for several days, the double cubane cluster $(Ph_4P)_2[Fe_8Te_{10}(CO)_{20}]$ **(3)**[29] crystallizes out. These results suggest that solutions of the above-mentioned compound are moderately stable and also that the species present in solution have an "Fe_4Te_4" cubane-type core. This view is corroborated by single crystal x-ray analysis which clearly indicates the presence of such a core structure. However, the structure has a disordered region of electron density which could be modeled in terms of partially occupied Te_2^{2-} and Te_3^{2-} fragments. Thus a reasonable formulation of the cluster compound is $(Ph_4P)_2[Fe_4Te_4(Te_2)_{0.6}(Te_3)_{0.4}(CO)_{10}]$ **(10)**.[37] Furthermore, the tellurium atom from the tritelluride fragment, which is not connected to the iron centers, appears to be disordered between two positions related by a crystallographic 2-fold axis. These structural considerations suggest $[Fe_4Te_4(Te_2)_{0.6}(CO)_{10}]^{2-}$ **(10a)** and $[Fe_4Te_4(Te_3)_{0.4}(CO)_{10}]$ **(10b)** to exist for 60% and 40% of the time, respectively. We must note that the structural disorder within the Te_3^{2-} fragment, as well as between the Te_2^{2-} and Te_3^{2-} ligands, brings the corresponding Te atoms too close together (<0.4 Å) in this part of the structure. This close proximity is beyond the resolution of our, relatively good, diffraction data (~0.8 Å), and this prevented us from achieving a good refinement of the positions of these disordered atoms (see Fig. 2). Ideally, the two chemically different species **10a** and **10b** would have seven different types of tellurium environments. Either we missed one of the ^{125}Te signals or, more likely, two of the tellurium signals have fortuitously the same chemical shift. Despite the fact that additional work is needed to clarify the solution behavior of this compound, these results further corroborate the richness and complexity of the iron carbonyl chemistry with telluride ligands and also denote the special stability of the "Fe_4Te_4" cubane core in this chemistry.

In contrast to the tellurium-rich conditions (1:5 molar ratios of $M_3(CO)_{12}$ and Te_2^{2-}) used in the solvothermal preparations of hexa- and tetra-nuclear clusters of iron and ruthenium, tellurium-poor ratios have also been explored. Crystals of the compound $(Ph_4P)_2[Fe_4Te_2(CO)_{14}]$ (**11**) were obtained in good yield by reacting two equivalents of $Fe_3(CO)_{12}$ with one equivalent of Na_2Te_2 in MeOH at 80°C.[32] Depending on the reactant ratio and reaction time used, the product was sometimes found to be contaminated with known complexes $(Ph_4P)_2[Fe_3Te(CO)_9]$ (**12**)[33] and $(Ph_4P)_2[Fe_5Te_4(CO)_{14}]$ (**13**).[30] The structure of the $[Fe_4Te_2(CO)_{14}]^{2-}$ anion in **11** consists of a central "Fe_2Te_2" tetrahedron (more correctly a butterfly since the Te-Te distance is not a full single bond *(vide infra)*, which is connected to two "$Fe(CO)_4$" units through its tellurium atoms. The Te-Te distance of 3.225(2) Å is, however, long for a Te-Te single bond, though it is considerably shorter than the van der Waals separation of *ca.* 4 Å between two tellurium atoms. This compound has iron atoms both in zero as well as +1 oxidation states. Corresponding to this fact, Fe-Te distances for the "$Fe(CO)_4$" fragment are somewhat longer (by 0.05 Å) compared to those for the central "$Fe_2Te_2(CO)_6$" butterfly fragment. Thus it exemplifies a mixed-valence compound with localized oxidation states.

The ruthenium analogues of the tellurium-poor compounds (**4**) and (**11**) could not be obtained. But two structurally interesting compounds, namely, $(Ph_4P)_2[Ru_4Te_2(CO)_{10}]$ (**14**) and $(Ph_4P)_2[Ru_5Te(CO)_{14}]$ (**15**), containing "Ru_xTe_y" octahedra as their cores, have been prepared under methanothermal conditions at 80°C.[40] While the former was obtained using a 4:3:18 mixture of $Ru_3(CO)_{12}$, Na_2Te_2, and Ph_4PBr, the latter was obtained from a 3:1:3 mixture of the same reactants. It was also possible to make $(Ph_4P)_2[Ru_3Te(CO)_9]$ (**16**), which is analogous to the corresponding iron compound (**11**).[33]

Structurally, the anions $[Ru_4Te_2(CO)_{10}]^{2-}$ and $[Ru_5Te(CO)_{14}]^{2-}$ belong to a rather extensive class of clusters consisting of a plane of four transition metal atoms capped on both faces by either two main-group element ligands or, in fewer instances, by one main-group element lig-



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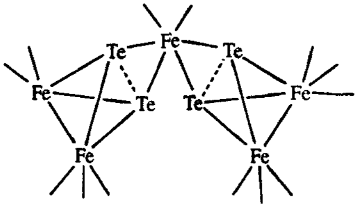

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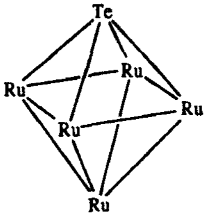

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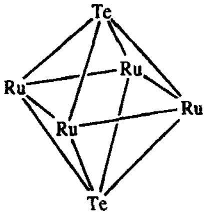


(15)

and and a fifth metal atom.[41] The Overall geometry of the six-atom cores in both cases is octahedral with tetragonal distortions. Two of the CO groups in **14** are present in the symmetrical bridging mode on two opposite edges of the "Ru_4" rectangle; the other eight are terminal. The bridged Ru-Ru bonds are shorter by 0.225 Å compared with the other two in the rectangle. In contrast to this, the central "Ru_4" plane in **15** is bridged on two adjacent edges asymmetrically by two carbonyl ligands. All the eight Ru-Ru bond distances are close to the average Ru-Ru bond distance of 2.8541(4) Å in $Ru_3(CO)_{12}$.[42] This is probably a reflection of the fact that all the ruthenium atoms in **15** are still in the zero oxidation state as in $Ru_3(CO)_{12}$, despite the entry of the (μ4-Te)$^{2-}$ ligand to impart two negative charges to the cluster. Apparently, there is little shortening effect due to the asymmetric carbonyl bridges on the metal atom cluster.

Two interesting clusters were reported to form from methanothermal synthesis, $[Co_{11}Te_8(CO)_{10}]^{2-}$ (**17**) and $[Co_4Te_2(CO)_{11}]$ (**18**) from the reaction of $Co_2(CO)_8$, Na_2Te_2 and Ph_4PCl.[43] The former features an unprecedented metal-telluride core with pentagonal prismatic symmetry. There is a prism of ten cobalt atoms which encapsulates a single Co atom in the center. The encapsulate Co center serves as a common vertex for five nearly regular Co_5Te face-sharing octahedra, which make up

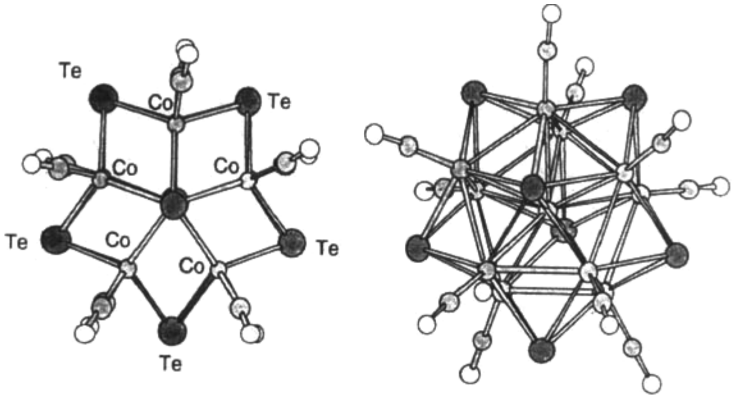
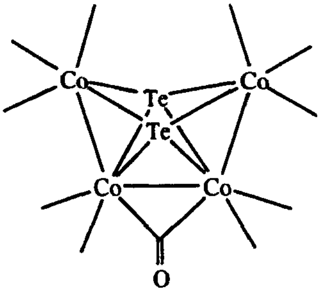


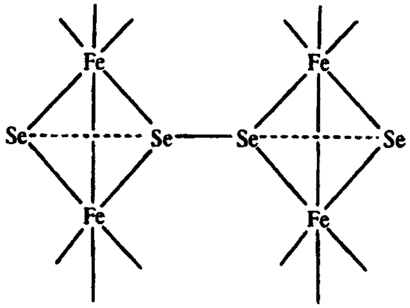
FIGURE 3 Two views of the $[Co_{11}Te_8(CO)_{10}]^{2-}$ cluster (**17**). The view on the right shows the encapsulated Co atom, adapted from Ref. 43

the entire "$Co_{11}Te_8$" core (see Fig. 3). The mean oxidation of the Co atoms is +1.09 and Co-Co bonds exist in this cluster. The cluster $[Co_4Te_2(CO)_{11}]$ is neutral, and this is the first time a neutral species is known to have form and crystallized from a solvothermal reaction medium despite the fact that the Ph_4P^+ counter ion was present in solution. The trapezoidal arrangement of the Co atoms in **18** is reminiscent of a partially closed pentagon of cobalt atoms and may imply that this smaller cluster is an early intermediate of $[Co_{11}Te_8(CO)_{10}]^{2-}$.



(**18**)

Although not the focus of this article, corresponding solvothermal reactions with polyselenides and polysulfides are also productive. A conventional solution reaction of $Fe(CO)_5$ with Na_2Se_5 in DMF yielded the mononuclear complex anion $[Fe_4(Se_4)_2(CO)_2]^{2-}$ which is analogous to the corresponding ruthenium compound prepared in a similar manner.[34,38] Application of the methanothermal method to the $Fe(CO)_5/Se_2^{2-}$ system, on the other hand, led to the isolation[34] of the double butterfly cluster anion $[Fe_4Se_4(CO)_{12}]^{2-}$ (**19**) for which sulfur analogue exists.[39] This cluster consists of two "$Fe_2Se_2(CO)_6$" units, structurally similar to $Fe_2Q_2(CO)_6$ (Q = S, Se, Te)[14–16] and also to the "$Fe_2Te_2(CO)_6$" butterfly fragment of **11**.



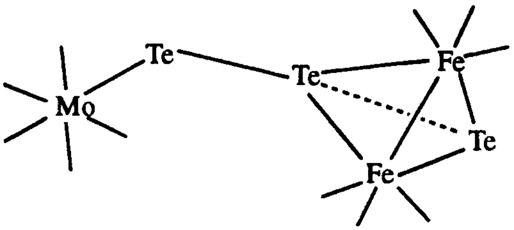
(19)

The noteworthy structural features of **19** are the considerably long (2.467(7) Å) Se-Se single bond in the bridging diselenide and the almost nonbonding Se-Se unit of the "$Fe_2Se_2(CO)_6$" butterflies. It appears likely that the Se valence electrons in this cluster anion are delocalized to some extent among the four selenium atoms. An "$Fe_2Se_3(CO)_6$" fragment having structure similar to **6** can be seen in **19**, though an iron selenide (or sulfide) complex analogous to **6** is currently unknown.

Heterometallic clusters

Following the facile and clean synthesis of several homometallic iron and ruthenium clusters via the solvothermal route, it was logical to attempt the preparation of heterometallic clusters utilizing the same method. The presence of two different metals in the reaction mixture would probe the possibility for mixed-metal clusters and test the thermodynamic and kinetic stability of the corresponding homometallic species. Several neutral heterometallic tellurido carbonyl compounds, some of which have already been referred to, were in existence prior to the present work.[14,15] Anionic heterometallic carbonyl tellurido clusters, on the other hand, were not known until we initiated these hydrothermally performed reactions. It was indeed possible to obtain several interesting compounds as described below.

The compounds $(Ph_4P)_2[Fe_2MTe_3(CO)_{11}]$ (M = Mo, W) (**20**) was made utilizing a 1:2:5:8 reaction mixture of $Fe_3(CO)_{12}$, $M(CO)_6$, Na_2Te_2, and Ph_4PBr in methanol at 80°C.[44] It was not possible to obtain **20** as the sole product in the reaction, but the large chunky crystals of this species (accounting for about 40% of the whole product) could be easily separated from the rest under microscopic observation. For the preparation of the corresponding tungsten compound, a 2:3:5:8 mixture of the reactants was used. This compound was obtained pure in 75% yield. Compound **20** and its tungsten analogue appear to be substitution products of $M(CO)_6$ where the sixth CO ligand is replaced by the dangling tellurium atom belonging to $[Fe_2Te_3(CO)_6]^{2-}$ (**6**) which is available *in situ* initially. Despite the substitution by an anionic fragment, the Mo (or W) atom does not undergo oxidation during the reaction. Due to the conversion of the μ_2-η^1-Te_2^{2-} ligand in **6** to the μ_3-η^2-Te_2^{2-} ligand in **18**, several structural changes take place. The Fe-Fe bond becomes shorter, while the Te-Te bond becomes longer; and most significantly, the Te(Te^{2-})-Te(Te_2^{2-}) distance gets shortened by 0.15 Å. Though this Te-Te separation of 3.175(3) Å is still too long for a Te-Te single bond (*ca.* 2.8 Å), it may imply significant bonding effects.



(20)

The presence of short Te-Te contacts is not peculiar to compound **20** alone. Several of the known telluride clusters show short Te-Te contacts. For example, in the tetranuclear iron and ruthenium clusters, the analogous parameters range from ca. 3.25 to 3.42 Å. Table I shows some additional data.

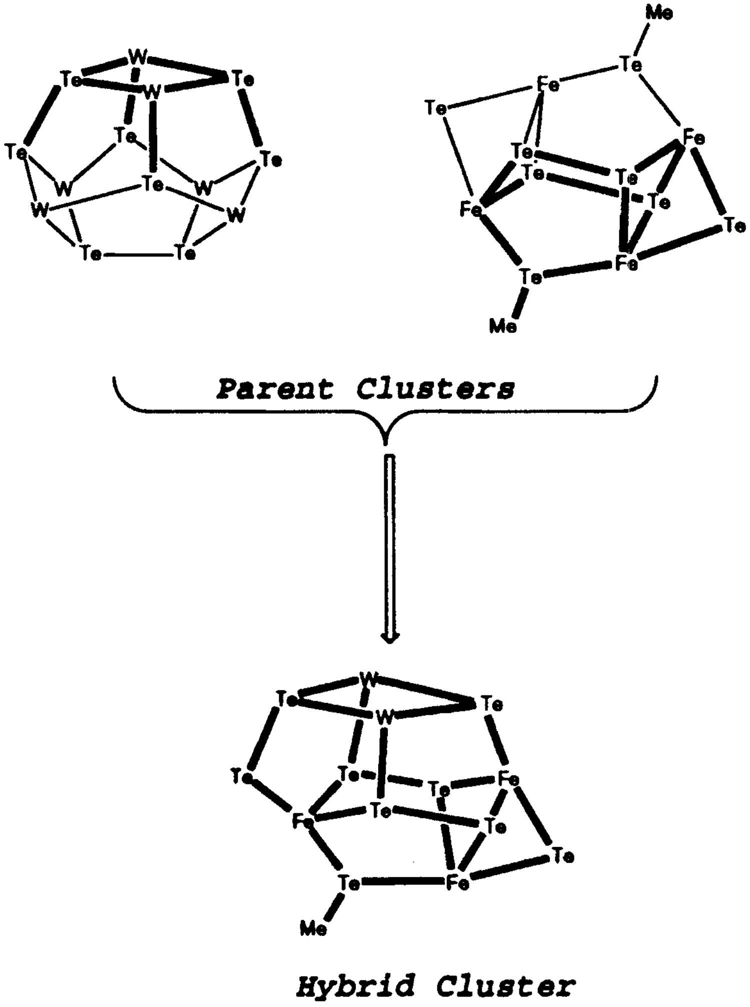
TABLE I Te-Te contacts in selected metal-carbonyl tellurido clusters

Compound	*Te···Te contact (Å)*	*Reference*
$[Fe_4Te_2(CO)_{14}]^{2-}$ **(11)**	3.225(2)	32
$[Fe_5Te_4(CO)_{14}]^{2-}$ **(13)**	3.152(2)	30
$[Fe_2Te_3(CO)]^{2-}$ **(6)**	3.23(2)[a]	36
$Fe_2Te_2(CO)_6$	2.71	16
$[Fe_8Te_6(CO)_{24}]^{2-}$ **(20)**	3.267(2), 3.123(2)	45

[a] This structure determination was rather inaccurate. But a similar distance has been found independently (Das and Kanatzidis, unpublished work).

Theoretical calculations on several solid-state compounds indicate that such short Te···Te contacts are indeed bonding in nature,[41] though the bond orders are considerably smaller than 1.0. In the present situation, electron withdrawal by the π-acceptor CO ligands from the electron-rich Te_x^{2-} ligands via the metal center probably facilitates bonding interactions among geometrically close telluride fragments and result in a tendency for catenation. In a way, we can view this electronic effect, which shortens the Te-Te distances, as the beginning of an oxidative coupling event of two different Te_x^{2-} anions.

A larger, tellurium-rich cluster $Na(Et_4N)_2[Fe_3W_2Te_8(TeMe)(CO)_{12}$ (**21**) was isolated from a reaction mixture of $Fe_3(CO)_{12}$, W(CO)6, Na_2Te_2, and Et_4NCl in 1:2:6:6 molar ratio.[44] This remarkable trianionic, cage-like cluster presents a beautiful example of a hybrid between two known homometallic structures, viz., $[Fe_4Te_6(TeMe)_2(CO)_8]^{2-}$ (**5a**)[35] and $[W_6Te_8(CO)_{18}]^{2-}$ (**2**)[17](**Scheme II**). The unsymmetrical, polyhedral cluster anion **21** with triangular, rhombic, and pentagonal faces has its telluride ligands in a variety of coordination modes.[44] In addition, one tellurium atom is methylated similarly with **5**. Because of the presence of a W-W single bond (3.089(1) Å), each of the W atoms is seven coordinate. The formal oxidation states of Fe and W in **21** are +2 and +1, respectively, in accord with the corresponding oxidation states in the parent clusters mentioned above.



SCHEME 2

The synthesis and study of heterometallic clusters containing chalcogens or other main groups elements, regardless of how they are made, is still a budding new area, and a lot remains to be done. Undoubtedly, the solvothermal technique has a great role to play in the preparation of heterometallic carbonyl chalcogenide clusters. Synthetic possibilities for mixed-metal compounds are very promising and should be pursued. The fact that a mixture of the two parent homometallic clusters is not obtained suggests that these reactions are entropically favored and thus, by varying the reaction conditions, it should be possible to prepare other interesting mixed-metal clusters which may not be easily accessible through the conventional solution route. Early/late transition metal combinations should be particularly interesting.

Properties of Compounds

Under the conditions of our preparative methodology, most of the compounds discussed in this account can be obtained as well-formed crystals in 10^2 mg scale. All compounds were found to be soluble in polar solvents such as dimethyl formamide and dimethyl sulfoxide. Their solubilities were generally low in acetonitrile, methanol, dichloromethane, etc. Solutions are stable in an inert atmosphere, but they decompose in air forming dark solutions and black precipitates. One interesting point to note is the high solubility of $Cs[HFe_3Te(CO)_9]$ in diethyl ether which was found to be helpful during isolation of this species. The surprising solubility of this salt in ether suggests that there is substantial cation/anion interaction in solution, so much so as to behave as a single neutral molecule. Infrared spectroscopy in solution and in the solid state indicates that in some cases the compounds rearrange in solution, most likely undergoing reorganization or even dissociation. For example, $[Fe_4Te_6(TeMe)_2(CO)_8]^{2-}$ (**5a**) displays three carbonyl stretching vibrations in solution compared to the expected two observed in the solid state. Rather inexplicably, the DMSO-D_6 solution of the compound also exhibits four ^{125}Te NMR resonances at 351, –519, –657, and -795 ppm.[35] On the basis of the observed structure, only three signals are to be expected. The ^{125}Te NMR spectra for most of the other compounds have been obtained as well, and the chemical shifts were found to span an extremely broad range of ppm values in compliance with results found for other compounds having tellurium atoms. Chemical shift data on ^{125}Te NMR spectra of some metal-carbonyl tellurido compounds are listed in Table II.

TABLE II ^{125}Te NMR spectral data for metal-carbonyl tellurido clusters

Cluster	*Solvent*	*NMR Signals(ppm)*[*]
$Fe_4Te_6(TeMe)_2(CO)_8]^{2-}$	acetone-d_6	351, –591, –657, –795
$[Fe_2Te_3(CO)_6]^{2-}$	DMSO-D_6	241, –32, –613
$[Fe_4Te_2(CO)_{14}]^{2-}$	CD_2Cl_2	-195
$[Fe_4Te_4(Te_2)_{0.6}(Te_3)_{0.4}(CO)_{14}]^{2-}$	DMSO-D_6	13, –542, –581, -1850, –1858, –1995
	Acetone-d_6	38, –550, –599, -1836, –1848, –1986
$[Ru_4Te_2(CO)_{10}]^{2-}$	acetone-d_6	-990
$[Ru_5Te(CO)_{14}]^{2-}$	CD_2Cl_2	667
$[Fe_2MoTe_3(CO)_{11}]^{2-}$	DMSO-D_6	159, –600, –703
$[Fe_2WTe_3(CO)_{11}]^{2-}$	DMSO-D_6	149, –635, –712
$Fe_3W_2Te_8(TeMe)(CO)_{12}]^{3-}$	DMSO-D_6	1368, 1114, 590, 428 273, 169, –527

[*] The signals were referenced to a signal for $TeCl_4$ (D_2O/HCl) at $\delta = 1237$ ppm with respect to Me_2Te.

CONCLUDING REMARKS

The most intriguing feature of hydro(solvo)thermal reactions is the concomitant growth of single crystals of the products. Under hydro(solvo)thermal conditions, the chemical reaction is combined with a transport process. The latter can facilitate crystallization of the reaction product. Generally, both solubility and crystallization process are improved by the presence of a complexing agent-a "mineralizer" in geological terminology. In the above reactions, dichalcogenide ligands act as reagents as well as mineralizers. The advantage of hydrothermal technique in these organic salts is that a particular cluster is removed from solution as soon as it is formed (due to insolubility of organic salts of clusters in water or methanol), and thus kinetic products are more likely to be isolated. In the classical ambient pressure approach, where an organic polar solvent is used, clusters must remain in solution a much longer time before crystallization, thereby allowing for enough time to reach thermodynamically stable products (despite the lower temperature involved).

It is apparent that the solvothermal technique can provide a useful and convenient avenue for the preparation of *molecular* inorganic as well as organometallic compounds. This account is meant to promote the technique and to encourage researchers in the field of cluster and organometallic chemistry to try it. The clean and reproducible nature of such reactions promises the discovery of not only many interesting compounds but also new fundamental reaction chemistry. Applicability of the method does not have to be restricted only to the $M_i(CO)_j/Q_x^{2-}$ system. As an illustration, the interesting hydrothermal reaction involving $Fe_3(CO)_{12}$, $NaAsO_2$, $Na_2S_2O_4$, and Ph_4PBr may be mentioned here.[46] This reaction has been found to lead to the formation of the pseudotetrahedral $[Fe_2(AsS)(CO)_6]^-$ cluster anion that is isostructural and isoelectronic with the well-studied compound $Fe_2S_2(CO)_6$.[14,47] The same reaction without the use of $Na_2S_2O_4$ gave an arsenido cluster $[Fe_3As(CO)_9]^{3-}$ resulting obviously from the reduction of $NaAsO_2$ to arsenide species. The incorporation of main group elements into transition metal clusters often introduces unique structural features and unusual reactivities. This result points to new directions in this kind of hydrothermal research activity involving other main group elements with the use of proper starting materials.

Eventually, an intriguing direction in this research would be to produce well-defined organometallic solid state materials. These novel solids would combine the elegant reactivity and selectivity control possible by organometallic molecules (e.g., reactivity in homogeneous media) with the robustness and bulk properties of inorganic solids.

Acknowledgments

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