5622 *Inorg. Chem.* **1996,** *35,* 5622−5626

$Nb_xRu_{6-x}Te_8$, New Chevrel-Type Clusters Containing Niobium and Ruthenium[†,‡]

Jörg Neuhausen, E. Wolfgang Finckh, and Wolfgang Tremel*

Institut für Anorganische Chemie und Analytische Chemie der Johannes Gutenberg-Universität Mainz,
Becherweg 24, D-55128 Mainz, Germany

Received July 7, 1995[⊗]

Phases of composition $Nb_xRu_{6-x}Te_8$ were prepared by reacting stoichiometric mixtures of the elements at high temperature in evacuated silica ampules. The structure of $Nb_{3.33}Ru_{2.67}Te_8$ was refined from X-ray powder data using the Rietveld method. $Nb_{3.33}Ru_{2.67}Te_8$ crystallizes isotypic with Mo_6Q_8 (Q = S, Se, Te) in the rhombohedral space group $R\bar{3}$ with the hexagonal lattice parameters $a = 10.34106(5)$ Å, $c = 11.47953(7)$ Å, and $Z = 3$. Its structure consists of M_6Te_8 mixed-metal clusters (M = Nb, Ru) which are connected by intercluster M−Te bonds to form a three-dimensional network. Metal−metal bonding in these phases is analyzed in terms of Pauling bond orders and found to be weaker compared to that in related cluster compounds. $Nb_xRu_{6-x}Te_8$ are the first representatives of Chevrel-type cluster phases with complete substitution of Mo by other metals. The chemical perspectives arising from this substitution are discussed.

Introduction

The Chevrel phases $M_xMo_6Q_8$ (M = Pb, Sn, Fe, Co, Ni, Cu, La, Eu, etc.; Q = S, Se, Te) have been studied intensively in the last two decades because of their exceptional physical properties such as superconductivity at moderately high temperatures and high critical magnetic fields as well as coexistence of magnetic order and the superconducting state.[1−3] In an effort to understand these phenomena, the structural chemistry of the Chevrel phases has been thoroughly investigated[2−5] and their electronic structures have been studied using calculations at various levels of sophistication.[3,6−11] The structure of the Chevrel phases $M_xMo_6Q_8$ consists of a three-dimensional network of Mo_6Q_8 clusters whose cavities are filled with metal atoms M. Simple electron-counting rules[2,12] reveal that compounds with valence electron concentrations (VEC) of 19−24 e^- per Mo_6 cluster can be synthesized, where phases with 22−24 cluster electrons are particularly stable. According to the results of MO studies on Mo_6Q_8 clusters,[6,7] all bonding states are occupied with 24 e^- per Mo_6 cluster. The results of band structure calculations[3,8−11] reveal the existence of a band gap for that particular electron count. Correlation of electronic structure and physical properties is possible to a certain extent. Most phases with 24 e^- per Mo_6 cluster are semiconductors, while those phases with incompletely filled valence states are metallic. However, not all of the spectacular physical properties of the Chevrel phases can be explained in such a simple manner. A rather subtle interplay between structural and electronic effects seems to govern the occurrence of superconductivity and its coexistence with magnetic order phenomena.[1−3] These effects are still not well understood. Therefore, further investigations on these materials are necessary.

From the chemist's viewpoint, the question arises as to why the existence of Chevrel-type phases should be restricted to molybdenum compounds. For example, the substitution of molybdenum by its higher homologue tungsten in Chevrel-type phases has been impossible so far. In the binary Mo_3Q_4 phases (Q = S, Se, Te) molybdenum can be partially substituted by rhenium, rhodium, or ruthenium,[13−19] whereas a complete substitution of molybdenum by other metals has not been possible so far. The synthesis of new cluster compounds such as Ta_4BTe_8,[20,21] Ta_4FeTe_4,[22] and $M_6S_{17}{}^{4-}$ (M = Nb, Ta)[23] indicates that metal chalcogenide clusters are also formed by group Vb metals. Therefore, Chevrel-type cluster compounds containing niobium and tantalum and more electron-rich metals such as rhenium, ruthenium, or rhodium are an attractive synthetic goal for a design of new cluster compounds close to the 24 e^- limit. Here we report the synthesis of phases of composition $Nb_xRu_{6-x}Te_8$ ($2.83 \leq x \leq 3.50$) and the structural characterization of $Nb_{3.33}Ru_{2.67}Te_8$ based on X-ray powder data using the Rietveld method.

Experimental Section

Synthesis. Phases of composition $Nb_xRu_{6-x}Te_8$ were prepared by reaction of stoichiometric mixtures of the elements—niobium powder (Starck, 99.99%), ruthenium powder (Heraeus, 99.9%), and tellurium powder (Merck, 99.9%)—in sealed evacuated (approximately 10^{-5} bar)

[†] This work is part of the Ph.D. Theses of J.N. and E.W.F.

[‡] Dedicated, with admiration, to Prof. H. G. von Schnering on the occasion of his 65th birthday.

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1996.

(1) Fischer, Ø. *Appl. Phys.* **1978**, *16*, 1.
(2) Yvon, K. *Curr. Top. Mater. Sci.* **1979**, *3*, 53.
(3) *Topics in Current Physics, Superconductivity in Ternary Compounds I;* Fischer, Ø., Maple, M. B., Eds.; Springer: Berlin, 1982.
(4) Chevrel, R.; Sergent, M.; Prigent, J. *J. Solid State Chem.* **1971**, *3*, 515.
(5) Corbett, J. D. *J. Solid State Chem.* **1981**, *39*, 56.
(6) Cotton, F. A.; Haas, T. E. *Inorg. Chem.* **1964**, *3*, 10.
(7) Guggenberger, L. J.; Sleight, A. W. *Inorg. Chem.* **1969**, *8*, 2041.
(8) Andersen, O. K.; Klose, W.; Nohl, H. *Phys. Rev. B: Condens. Matter* **1978**, *17*, 1209.
(9) Bullett, D. W.; *Phys. Rev. Lett.* **1977**, *39*, 664.
(10) Hughbanks, T.; Hoffmann, R. *J. Am. Chem. Soc.* **1983**, *105*, 1150.
(11) Bronger, W.; Fleischhauer, J.; Marzi, H.; Raabe, G.; Schleker, W.; Schuster, T. *J. Solid State Chem.* **1987**, *70*, 29.
(12) Yvon, K.; Paoli, A. *Solid State Commun.* **1977**, *24*, 41.
(13) Perrin, A.; Sergent, M.; Fischer, Ø. *Mater. Res. Bull.* **1978**, *13*, 259.
(14) Perrin, A.; Chevrel, R.; Sergent, M.; Fischer, Ø. *J. Solid State Chem.* **1980**, *33*, 43.
(15) Hönle, W.; Flack, H. D.; Yvon, K. *J. Solid State Chem.* **1983**, *49*, 157.
(16) Berry, F. J.; Forgan, E. M.; Gibbs, C. D. *Solid State Commun.* **1988**, *66*, 667.
(17) Berry, F. J.; Gibbs, C. D. *J. Chem. Soc., Dalton Trans.* **1991**, 57.
(18) Berry, F. J.; Gibbs, C. D.; Greaves, C. *J. Solid State Chem.* **1991**, *92*, 148.
(19) Berry, F. J.; Forgan, E. M.; Gibbs, C. D. *Solid State Commun.* **1993**, *85*, 545.
(20) Kleinke, H. Ph.D. Thesis, Universität Mainz, 1994.
(21) Kleinke, H.; Tremel, W. Manuscript in preparation.
(22) Neuhausen, J.; Finckh, E. W.; Tremel, W. *Chem. Ber.* **1995**, *128*, 569.
(23) Sola, J.; Do, Y.; Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 1706.

S0020-1669(95)00837-8 CCC: $12.00

silica tubes (length approximately 8 cm, ∅ = 6 mm). After being heated to 500 °C for 48 h in a tube furnace, the samples were reacted at 1000 °C for 10 d. The furnace was then switched off, and the samples were allowed to cool radiatively to room temperature. The fine crystalline gray products showed metallic luster. All samples prepared in this way contained small amounts of NbO_2,[24] which was presumably formed by reaction of niobium with the tube walls (SiO_2), as well as $RuTe_2$.[25] In the region $2.83 \leq x \leq 3.50$, the amount of these impurities is negligibly small (approximately 0.5 wt. % NbO_2 and $RuTe_2$). Therefore the composition of the products is assumed to be equal to the ratio of the starting materials. For compositions with $x < 2.83$ and $x > 3.50$, the amount of impurities in the products increases considerably. Since the lattice constants of the product phase vary continuously in the region $2.83 \leq x \leq 3.50$, a corresponding phase width is assumed to exist for the ternary product. No impurities could be detected by EDAX analysis performed on samples in this composition range using a Zeiss DSM 962 electron microscope equipped with a KEVEX analyzer. Single crystals of the ternary phases could not be prepared.

Structure Determination. High-quality X-ray powder diffraction data were obtained from a sample of composition $Nb_{3.33}Ru_{2.67}Te_8$. The substance was thoroughly ground (approximately 15 min) in an agate mortar and then fixed on a Kapton foil using hair spray (Gard). The sample was mounted on a Siemens D5000 powder diffractometer (transmission geometry, bent primary monochromator, Cu $K\alpha_1$ radiation, $\lambda = 1.540\,56$ Å, sollerslits (20 mm) in primary and diffracted beams, receiving slit 0.2 mm, scintillation counter). Diffraction data were collected in the angular range $10° < 2\theta < 100°$ using a $\theta-2\theta$ step-scan method (step width 0.01°, step time 60 s/step). The sample was rotated at 15 rpm to minimize texture effects.

The angular positions of diffraction maxima were accurately determined using the program PROFAN[26] employing a pseudo-Voigt function to simulate the peak shape. The first 15 strong reflections at low diffraction angles could be indexed with a hexagonal cell with a = 10.340 and 11.480 Å using the program INDP.[26] On the basis of this cell all, but two weak reflections of the diffraction profile could be indexed. These weak reflections at 26.0 and 31.28° were identified as the strongest diffraction maxima of NbO_2[24] and $RuTe_2$,[25] respectively. Refinement of lattice constants based on the angular positions of all indexed reflections using a least-squares procedure (program LATTIC[26]) yielded the values $a = 10.3406(1)$ and $c = 11.4801(2)$ Å. These lattice constants are similar to those of $Mo_{4.5}Ru_{1.5}Te_8$.[18] Furthermore, the systematic extinctions were compatible with the space group of $Mo_{4.5}Ru_{1.5}Te_8$, the binary molybdenum chalcogenides Mo_3Q_4 (Q = S, Se, Te),[2,3] and the rhombohedral Chevrel-phases.[2-5] Therefore, the new ternary phase $Nb_{3.33}Ru_{2.67}Te_8$ was assumed to be isotypic with $Mo_{4.5}Ru_{1.5}Te_8$ and Mo_3Q_4 (Q = S, Se, Te). This assumption was verified by a sucessful structure refinement using the Rietveld method.[27,28]

The atomic positions of $Mo_{4.5}Ru_{1.5}Te_8$[18] were used as a starting model for the Rietveld refinement. A common site M was used for the metal atoms. This site was assumed to be occupied by niobium and ruthenium in a ratio corresponding to the starting composition, i.e. 3.33:2.67. Since the X-ray scattering factors of both metals are similar, the relative occupation factors of the two different metal atom types could not be refined. An ordering of Nb and Ru atoms could not be detected. The structure refinement was carried out using the program PC-Rietveld Plus 1.01 (Philips).[29-31] In order to minimize a bias of the refinement results due to the presence of small amounts of the impurity phases NbO_2 and $RuTe_2$, these phases were included in the refinement. Structural parameters for NbO_2[24] and $RuTe_2$[25] were taken from the literature. The background was corrected manually. The reflection profiles were best described by a pseudo-Voigt function where the angle dependence of reflection widths was taken into account using the method of Caglioti et al.[32] Lattice parameters and scale factors for all three phases were refined, as well as parameters for zero shift and reflection asymmetry at low diffraction angles. Twelve structural parameters were refined for $Nb_{3.33}Ru_{2.67}Te_8$ including isotropic thermal parameters, while a refinement of atomic parameters for the impurity phases was not possible because of their small contribution to the total scattering power. On the basis of the scale factors obtained after refinement, the weight percentages of the impurity phases were calculated as 0.5% (NbO_2) and 0.7% ($RuTe_2$). The refinement converged to residuals of $R_B(Nb_{3.33}Ru_{2.67}Te_8) = 0.046$, $R_p = 0.074$, $R_{wp} = 0.097$, und $R_{p'} = 0.134$.[33] Figure 1 shows the observed and calculated profiles as well as a difference plot. Important crystallographic data are compiled in Table 1. Atomic parameters and important interatomic distances are given in Tables 2 and 3, respectively.

Electrical Resistivity Measurements. The electrical resistivity of a pressed and sintered pellet with a nominal composition $Nb_{3.33}Ru_{2.67}Te_8$ was investigated between 4 and 290 K with a four-probe dc technique. The sample was sputtered with gold, and gold wires were attached with a silver epoxy resin.

Results

The phases $Nb_xRu_{6-x}Te_8$ ($2.83 \leq x \leq 3.50$) crystallize isotypic with the binary molybdenum chalcogenides Mo_3Q_4 (Q = S, Se, Te).[2,3] The structure contains three crystallographically independent atom sites. The metal atoms occupy the Wyckoff positions 18f (point symmetry 1) of the space group $R\bar{3}$ (hexagonal setting) in a statistical manner, while the tellurium atoms are situated on two independent positions, 18f and 6c (point symmetry 3).

Six metal atoms form a slightly distorted octahedral M_6 unit (M = Nb, Ru) which is inscribed into a slightly distorted cube of tellurium atoms, so that the metal atoms occupy the square faces of the tellurium cube (Figure 2). This results in a nearly regular square planar coordination of the metal atoms by tellurium atoms of the same cluster. These M_6Te_8 units are connected via intercluster M−Te bonds leading to a square pyramidal Te coordination of the metal atoms. The resulting structure is depicted in Figure 3. A rotation of the cube-shaped M_6Te_8 units around the 3-fold inversion axis inside the pseudocubic rhombohedral unit cell (approximately 26°) facilitates the formation of intercluster M−Te bonds, which are of crucial importance for the stability of these compounds.[10]

According to the observed phase width for $Nb_xRu_{6-x}Te_8$ ($2.83 \leq x \leq 3.50$), the valence electron concentration per cluster (VEC)[1,3,6-12] in these phases can vary between 21.5 and 23.5 e^-/cluster. This is in good agreement with the values calculated for other Chevrel-type compounds, where phases with 19−24 cluster electrons could be synthesized. According to the deduced electron count, the samples are expected to show metallic conductivity. In fact, the results of resistivity measurements show that $Nb_{3.33}Ru_{2.67}Te_8$ is metallic in the temperature range between 4 and 290 K with a specific resistivity of 2.6 mΩcm at 290 K. No indications of superconducting behavior could be detected. These findings are in agreement with the observed pauli paramagnetism ($\chi_{mol} = 1.0 \times 10^{-3}$ emu/mol, corrected for diamagnetism) for $Nb_{3.33}Ru_{2.67}Te_8$. Detailed measurements of physical properties such as resistivity and magnetic susceptibility as a function of VEC are in progress.

Metal−tellurium bond lengths in $Nb_{3.33}Ru_{2.67}Te_8$ vary between 2.703(2) and 2.777(2) Å for intracluster interactions and

---

(24) Cheetham, A. K.; Rao, C. N. R. *Acta Crystallogr.* **1976**, *B32*, 1579.
(25) Sutarno; Knop, O.; Reid, K. I. G. *Can. J. Chem.* **1967**, *45*, 1391.
(26) Akselrud, L. G.; Percharsky, V. K. *CSD program system L'viv*, 1991.
(27) Rietveld, H. M. *Acta Crystallogr.* **1967**, *22*, 151.
(28) Rietveld, H. M. *J. Appl. Crystallogr.* **1969**, *2*, 65.
(29) Wiles, D. B.; Young, R. A. *J. Appl. Crystallogr.* **1981**, *14*, 149.
(30) Howard, C. J.; Hill, R. J. AAEC Report M112, 1986.
(31) Fischer, R. X.; Lengauer, C.; Tillmanns, E.; Ensink, R. J.; Reiss, C. A.; Fantner, E. J. *Mater. Sci. Forum* **1993**, *133−136* (Proceedings of the Second European Powder Diffraction Conference, 1992, Part 1) 287.
(32) Caglioti, G.; Paoletti, A.; Ricci, F. P. *Nucl. Instrum. Methods* **1958**, *3*, 223.
(33) Hill, R. J.; Fischer, R. X. *Ber. Dt. Min. Ges., Beiheft Eur. J. Miner.* **1989**, *1*, 70.

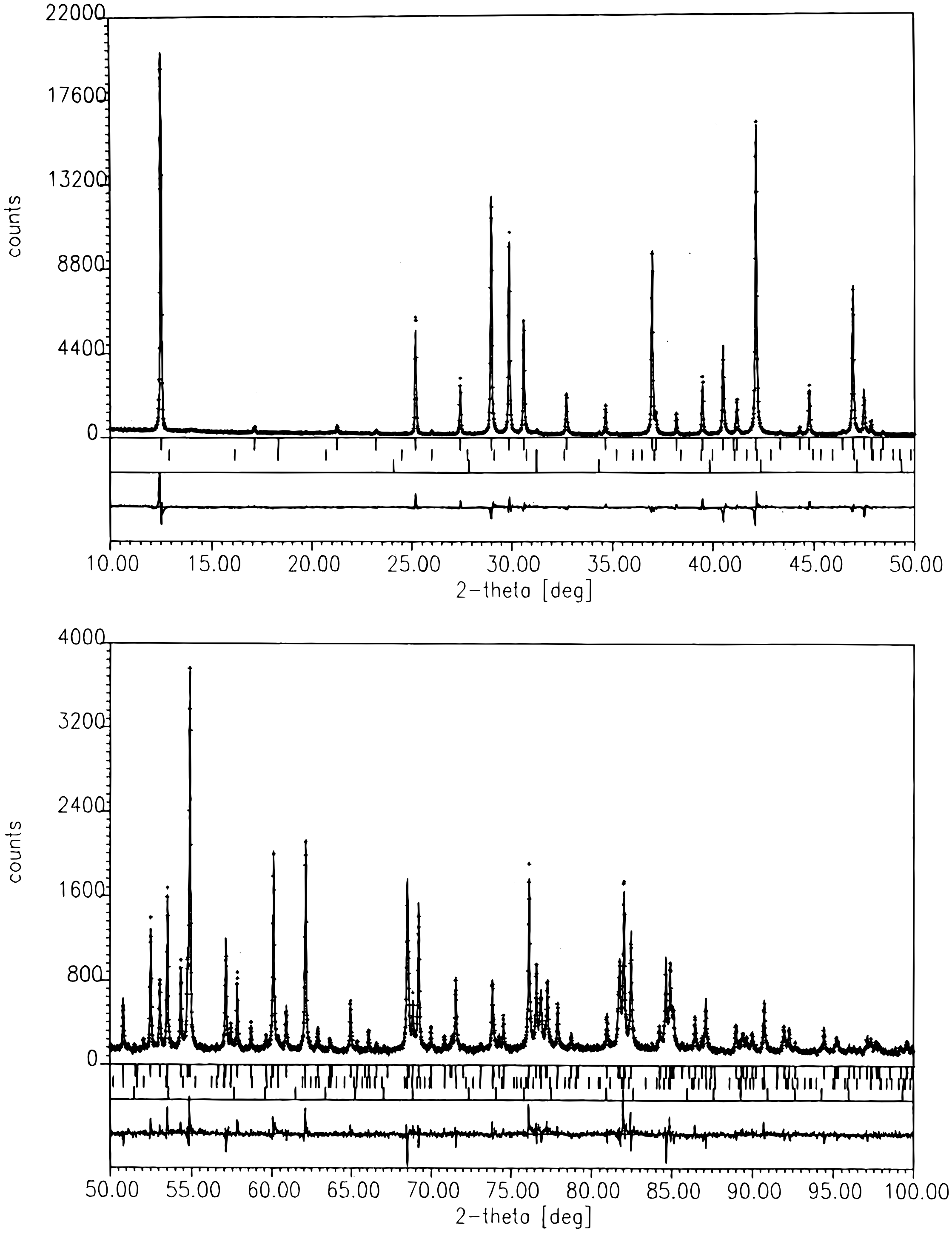

Figure 1. X-ray powder diffraction profile of $Nb_{3.33}Ru_{2.67}Te_8$. Observed and calculated intensities are represented as crosses and solid line, respectively. All possible Bragg reflections of $Nb_{3.33}Ru_{2.67}Te_8$, NbO_2, and $RuTe_2$ are indicated as tick marks. The lower part of the diagram shows a difference plot between observed and calculated intensities.

2.793(2) Å for the intercluster metal−tellurium bond. The shortest Te−Te distances are intercluster Te(1)−Te(2) contacts of 3.658(2) Å. The remaining Te−Te distances are significantly longer (3.774(2)−4.194(2) Å). There are different metal−metal interactions characterized by three metal−metal distances, d_1, d_2, and d_3. While d_1 = 2.856(3) Å and d_2 = 2.768(3) Å correspond to the metal−metal bonds nearly parallel and perpendicular to the 3-fold inversion axis *inside* a single M_6 cluster, respectively (Figure 2), d_3 = 3.665(2) Å represents the shortest metal−metal distance *between* neighboring M_6Te_8 units. Similar to the case of all isostructural compounds reported so far, a slight elongation of the M_6 octahedron parallel to the $\bar{3}$ axis is observed. The diagonal distance between metal atoms inside a M_6 cluster (d_4) amounts to 3.978(2) Å and can be regarded as nonbonding.

Discussion

The M−Te bond lengths in $Nb_{3.33}Ru_{2.67}Te_8$ (d_{M-Te}: 2.703(2)−2.793(2) Å) lie in a regime typical for a compound with a mixed-metal site and a statistical Nb:Ru occupation of ≈1:1. They can be compared with metal−tellurium separations in typical niobium and ruthenium tellurides such as $Nb_4OTe_9I_4$ (d_{Nb-Te}: 2.777(3)−3.008(3) Å),[34] $NbNi_{2.38}Te_3$ (d_{Nb-Te}: 2.714(1)−2.903(1) Å),[35] or $RuTe_2$ (d_{Ru-Te}: 2.647(3) Å).[25] The Te−Te distances (d_{Te-Te}: 3.658(2)-4.194(4) Å) are significantly shorter

Table 1. Crystal Data for $Nb_{3.33}Ru_{2.67}Te_8$

fw = 1600.0	T = 298 K
crystal system: rhombohedral	ρ_{calc} = 7.496 g/cm3
space group = $R\bar{3}$ (No. 148)	Cu $K\alpha_1$ radiation, λ = 1.540 56 Å
lattice params, hexagonal setting[a]	μ = 180.19 mm^{-1}
a_h = 10.34106(5) Å	measd angular range: 10° ≤ 2θ ≤ 100°
c_h = 11.47953(7) Å	$R_B(Nb_{3.33}Ru_{2.67}Te_8)^b$ = 0.046
V_h = 1063.13(2) $Å^3$	$R_p{}^b$ = 0.074
Z = 3	$R_{wp}{}^b$ = 0.097

[a] Rhombohedral setting: a_r = 7.0914 Å, α_r = 93.62°, V = 354.38, Z = 1. [b] $R_B = \sum_k|I_{ko} - I_{kc}|/\sum_k I_{ko}$, $R_p = \sum_i|y_{io} - y_{ic}|/\sum_i y_{io}$, $R_{wp} = [\sum_i w_i(y_{io} - y_{ic})^2/\sum_i w_i y_{io}{}^2]^{1/2}$, $w_i = 1/y_{io}$.

Table 2. Atomic Coordinates and Isotropic Thermal Parameters for $Nb_{3.33}Ru_{2.67}Te_8$, Hexagonal Setting (Standard Deviations)

atom	Wyckoff position	x/a	y/b	z/c	B, $Å^2$
M[a]	18f	0.0152(2)	0.1616(2)	0.3969(2)	0.94(3)
Te1	18f	0.3231(2)	0.2878(1)	0.4111(1)	1.18(3)
Te2	6c	0	0	0.2070(2)	1.43(6)

[a] Statistically occupied by Nb and Ru in the ratio 3.33:2.67.

Table 3. Important Interatomic Distances (Å) for $Nb_{3.33}Ru_{2.67}Te_8$ (Standard Deviations)

M–Te(1)	2.710(2)	M–M[a]	2.768(3) (2×)
M–Te(1)	2.731(2)	M–M[b]	2.856(3) (2×)
M–Te(1)	2.777(2)	M–M[c]	3.665(2)
M–Te(1)	2.793(2)	M–M[d]	3.978(2)
M–Te(2)	2.703(2)		

shortest observed Te–Te-distance: 3.658(2)

[a] d_2. [b] d_1. [c] d_3. [d] d_4, see text and Figure 2.

then the sum of the ionic radii (4.4 Å).[36] This can be explained on the basis of the strong covalent character of the compound. Similar values are found in other transition metal tellurides with highly covalent bonding such as Ta_4FeTe_4 (d_{Te-Te}: 3.800(4)–4.154(5) Å)[22] and $NbNi_{2.38}Te_3$ (d_{Te-Te}: 3.740(1)–4.223(1) Å).[35]

The intercluster Te(2)–Te(1) distance of 3.658(2) Å is significantly shorter than the remaining Te–Te contacts (d_{Te-Te}: 3.774(2)–4.194(2) Å). This distance also corresponds to the shortest Te–Te distances in the two previously characterized tellurides crystallizing in the Mo_3Q_4 structure, $Mo_{4.5}Ru_{1.5}Te_8$[18] and Mo_6Te_8.[2,3] A detailed analysis of the geometric features of the Mo_3S_4 and Mo_3Se_4 structure[5] shows that the repulsive interactions resulting from these close chalcogen–chalcogen contacts are one major cause of the elongation of the M_6 octahedron parallel to the $\bar{3}$ axis which is reflected in the occurence of different intracluster M–M bonds $d_1 > d_2$. This type of elongation is observed in $Nb_{3.33}Ru_{2.67}Te_8$ as well as in $Mo_{4.5}Ru_{1.5}Te_8$[18] and Mo_6Te_8.[2,3]

An analysis of bonding in comparison with that of other compounds crystallizing in the Mo_3Q_4 structure such as $Mo_4Ru_2Se_8$,[14,15] $Mo_{1.5}Re_{4.5}Se_8$,[15] $Mo_{4.5}Ru_{1.5}Te_8$,[18] and Mo_3Q_4, (Q = S, Se, Te)[2,3]—especially a comparison of the metal–metal bond strength—should be interesting. One way to compare the strength of metal–metal bonding in different cluster compounds was proposed by Corbett[5] on the basis of the empirical bond strength relation (1) of Pauling[36] (D_n = bond distance for a bond

$$D_n = D_1 - 0.60 \log n \qquad (1)$$

of order n, D_1 = single-bond distance, n = bond order). Single-bond distances are determined from tabulated metallic radii[37] and the valency of the metal. The sum over all bond orders for all metal–metal bonds is then divided by the number of electrons available for metal–metal bonding. In this way values of Pauling bond order per electron (PBO/e) are obtained, which lie close to 1 for many cluster compounds of group IIIb to group VIb metals in which no anion–anion repulsions (so-called matrix effects) exist.[38] Therefore, the strengths of metal–metal bonds in these compounds are comparable to the metal–metal bond strength in the metal itself considering the number of bonding electrons available. Similar calculations for the molybdenum chalcogenides Mo_3Q_4 (Q = S, Se, Te) and for all Chevrel phases MMo_6Q_8 (Q = S, Se) structurally characterized at that time yielded PBO/e values systematically lower (0.72

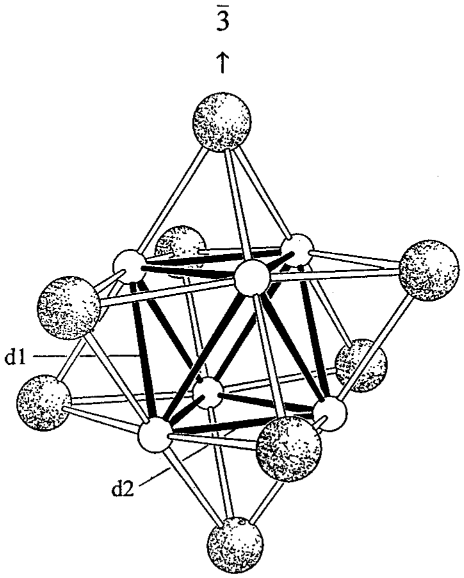

Figure 2. Perspective view of a single M_6Te_8 unit: large dotted circles, Te; small empty circles, M. Distances d_1 and d_2 and the direction of the 3-fold inversion axis are indicated.

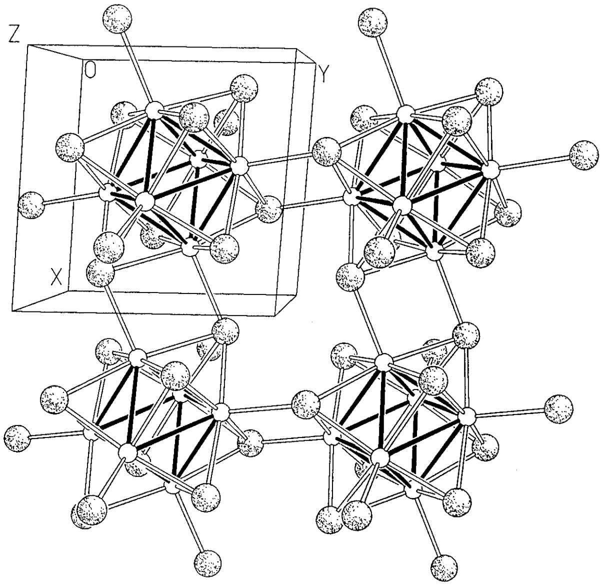

Figure 3. Perspective projection of the $Nb_{3.33}Ru_{2.67}Te_8$ structure: large dotted circles, Te; small empty circles, M = Nb, Ru. In this view, the pseudocubic rhombohedral unit cell (a_r = 7.0914 Å, α_r = 93.62°) is shown.

---

(34) Tremel, W. Habilitationsschrift, Universität Münster, 1992.
(35) Neuhausen, J.; Finckh, E. W.; Tremel, W. *Inorg. Chem.* **1995**, *34*, 3823.
(36) Pauling, L. *Die Natur der chemischen Bindung*, 3rd ed.; Verlag Chemie: Weinheim, Germany, 1968.
(37) Pearson, W. B. *The Crystal Chemistry and Physics of Metals and Alloys*; Wiley-Intersience: New York, 1972; p 151.
(38) Corbett, J. D. *J. Solid State Chem.* **1981**, *37*, 335.

$<$ PBO/e $<$ 0.84).[5] This result was ascribed to matrix effects (chalcogen−chalcogen repulsion between neighboring M_6Q_8 units).[5] A calculation of PBO/e for $Nb_{3.33}Ru_{2.67}Te_8$ results in a still lower value of 0.52. Here single-bond distances for the mixed-metal bonds were obtained from eq 1 using the weighted average of the metal radii and a valency of 6 for both metals.[36] The low PBO/e value indicates relatively weak metal−metal bonding. The tellurium matrix in $Nb_{3.33}Ru_{2.67}Te_8$ is only slightly different from that of Mo_6Te_8 (PBO/e = 0.78, erroneously given as 0.65 and 0.70 by Corbett[5] and Hönle et al.,[15] respectively). The only significant difference is the shorter intercluster Te(1)−Te(2) distance of 3.566 Å in Mo_6Te_8 when compared with $Nb_{3.33}Ru_{2.67}Te_8$ ($d_{Te(1)-Te(2)} = 3.658(2)$). This should result in a comparatively strong matrix effect in Mo_6Te_8. Therefore matrix effects are obviously not the cause of the relatively weak metal−metal bonding in $Nb_{3.33}Ru_{2.67}Te_8$ when compared to Mo_6Te_8. Presumably, differences in the electronic structure such as shifts of the metal- centered d states resulting from the existence of mixed-metal clusters could lead to weaker bonding interactions inside the clusters. This assumption is supported by the relatively low PBO/e value of 0.57 calculated for the mixed cluster compound $Mo_{4.5}Ru_{1.5}Te_8$.[18] Investigations of the electronic structure of mixed-metal clusters could be helpful in understanding these effects. The synthesis and characterization of new phases with mixed-metal clusters are desirable, as well. Here, new perspectives are revealed by the complete substitution of molybdenum by other metals in Chevrel-type phases such as $Nb_xRu_{6-x}Te_8$. Not only could sulfides and selenides $Nb_xRu_{6-x}Q_8$ (Q = S, Se) be goals of synthetic efforts but Chevrel-type compounds containing mixed (NbRe), (NbRh), (ZrRe), (ZrRu), or (ZrRh) clusters might also be prepared. The synthesis of such compounds should give new insight into the effects of electronic and structural factors on the stability and physical and chemical properties of this class of compounds.

In contrast to the known substitution by the more electron rich metals Re, Ru, and Rh,[13−19] the substitution of molybdenum by more electron deficient transition metals such as niobium facilitates a selective decrease of the cluster valence electron count. Most of the known phases with mixed-metal clusters are relatively electron rich with electron counts close to 24 e^- per M_6 unit. Since these compounds tend to be electronically saturated, intercalation reactions leading to products of type $M'_xM_6Q_8$, where additional metal atoms M′ are incorporated between the clusters and donate their valence electrons into unoccupied electronic states of the host are unlikely to occur. A decrease of VEC by substitution of molybdenum by more electron deficient metals could enhance the likeliness of reduction by intercalation reactions and thus give rise to the synthesis of a whole class of new compounds with interesting physical and chemical properties.

A remarkable property of Chevrel-type compounds containing mixed-metal clusters is their catalytic activity in the electrochemical reduction of molecular oxygen to water in an acid environment. For example, a phase of composition $Mo_{4.2}Ru_{1.8}Se_8$ shows catalytic activity comparable to that of platinum.[39] On the basis of relationships between VEC and the metal−metal bond strength inside the clusters,[2] a mechanism for this reaction has been proposed.[39] Therefore, an investigation of catalytic properties of the phases $Nb_xRu_{6-x}Te_8$ seems promising.

Acknowledgment. This work was supported by a grant from the Bundesministerium für Forschung und Technologie under Contract No. 05 5UMGAB. We are grateful to Heraeus Quarzschmelze (Dr. Höfer) and the H. C. Starck Co. (Dr. Peters) for gifts of silica tubes and niobium powder, respectively. We are also indebted to Dr. R. X. Fischer for access to the Rietveld program.

Supporting Information Available: Tables of crystallographic data and interatomic angles (2 pages). Ordering information is given on any current masthead page.

IC9508379

---

(39) Alonso Vante, N.; Jaegermann, W.; Tributsch, H.; Hönle, W.; Yvon, K. *J. Am. Chem. Soc.* **1987**, *109*, 3251.