norbornadiene and quadricyclene.

The absence of norbornadiene dimers among the photoproducts of reaction 1 is noteworthy, since there is ample precedent for facile thermal[10,11] and photochemical[12] cycloadditions of norbornadiene in the presence of transition metal compounds. The role generally ascribed to the metal in such intermolecular addition processes is that of a template binding two (or more) proximal norbornadiene molecules, which subsequently react to form the dimer. Thus the availability of at least two coordination sites on the metal appears to be a key prerequisite for dimerization. Our data suggest that CuCl possesses little residual bonding affinity beyond that employed in forming the ClCu–NBD complex. The reluctance of this latter species to expand its coordination number,[13] either by simple addition of a second norbornadiene molecule or by oxidative addition, precludes the occurence of dimerization. Consequently, valence isomerization (Figure 2) emerges as the predominant chemical pathway for utilizing the excitation energy of the absorbed photon. Indeed it is our feeling that CuCl may be prototypal of a class of transition metal compounds which can specifically effect this transformation.[14]

Finally, we wish to note that a solar energy storage system based upon the norbornadiene–quadricyclene interconversion possesses several attractive features: (i) Norbornadiene is prepared from relatively inexpensive starting materials (acetylene and cyclopentadiene). (ii) The specific energy storage capacity, ~230–260 cal/g of quadricyclene produced,[15] is 3–4 times greater than that of water-based sensible heat systems. (iii) Sunlight is stored as chemical rather than thermal energy, thus preluding the need for extensive insulation of the storage medium. (iv) Energy may be stored indefinitely, since reversion of quadricyclene to norbornadiene is negligibly slow at room temperature. Addition of appropriate transition metal catalysts,[16] however, effects rapid reversion with release of the excess energy.

The above characteristics make a norbornadiene-based system particularly promising for applications utilizing low-grade (~100 °C) heat such as the heating and cooling of buildings and hot water preparation.[17] Further work aimed at developing a viable energy storage system based upon reaction 1 is underway, including the search for transition metal–norbornadiene complexes which absorb more strongly in the wavelength region of available solar energy.

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Registry No. CuCl, 7758-89-6; norbornadiene, 121-46-0; quadricyclene, 278-06-8.

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Crystal Structure of Niobium Tetrachloride

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We wish to report the first accurate detailed determination of the structure of $NbCl_4$. Niobium tetrachloride has been reported as being both monoclinic[1,2] and orthorhombic,[3] while its structure has been described[4] as similar to that of α-NbI_4.[5] McCarley[3] found $NbCl_4$ was not isomorphic with α-NbI_4 but he was unable to obtain a suitable single crystal due to twinning and disorder problems. Other workers[1,6] have had similar difficulties with niobium halides.

Suitable crystals of niobium tetrachloride were synthesized by the reaction of niobium pentachloride (5 g) with niobium metal (0.5 g) in a sealed and evacuated Pyrex ampule (15 cm long and 20 mm in diameter). The ampule was positioned in a tube furnace so that the pentachloride, when liquid, covered the metal. The reactants were maintained at a uniform temperature of 300 °C throughout the week long reaction. At the completion of the reaction, the walls of the ampule were covered with dark brown niobium tetrachloride in quantitative yield. This method of preparation differs from that previously reported[3,7] in which the metal and pentachloride were separated and a temperature gradient of 250 to 400 °C was used. The air-sensitive product was handled in an inert atmosphere throughout all manipulations.

The crystal chosen, a needle with well-defined faces, was wedged in a Lindemann glass capillary under dry N_2 and placed on a Syntex $P\bar{1}$ autodiffractometer equipped with a graphite monochromated Mo Kα radiation source. The Syntex procedure, which included partial rotation photographs along each of the reciprocal axes, revealed a monoclinic lattice with cell dimensions $a = 8.140$ (5), $b = 6.823$ (4), $c = 8.852$ (6), $\beta = 91.92$ (5), $V = 491.4$ (5).[8] Data were collected for $^1/_4$ of the sphere from $3° \leq 2\theta \leq 50°$ using a scan time to background time ratio of 0.67. Stability of the intensities was indicated throughout the data collection from two standard reflections monitored after every 50 observations. The data

Table I. Positional Parameters for $NbCl_4$

Nb(1)	0	0.221 98 (8)	0
Cl(1)	0.028 13 (12)	0	0.213 20 (11)
Cl(2)	−0.278 92 (11)	0.243 71 (16)	0.023 02 (10)
Cl(3)	0.024 48 (12)	0.5	0.187 34 (11)

Table II. Thermal Parameters for $NbCl_4$[a]

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Nb(1)	0.005 79 (14)	0.005 26 (21)	0.004 61 (11)	0	0.000 33 (6)	0
Cl(1)	0.009 57 (18)	0.006 42 (33)	0.004 75 (15)	0	−0.000 12 (11)	0
Cl(2)	0.006 12 (18)	0.009 60 (27)	0.010 66 (17)	0.000 51 (12)	0.001 17 (12)	0.000 02 (12)
Cl(2)	0.009 89 (19)	0.006 23 (32)	0.004 95 (16)	0	0.000 20 (12)	0

[a] The anisotropic temperature parameters are of the form $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

Table III. Interatomic Distances

Nb(1)-Nb(1)[a]	3.029 (2)	Nb(1)-Cl(3)	2.523 (1)
Nb(1)-Nb(1)[b]	3.794 (2)	Cl(2)-Cl(2)[a]	3.326 (3)
Nb(1)-Cl(1)	2.425 (1)	Cl(2)-Cl(2)[b]	3.497 (3)
Nb(1)-Cl(2)	2.291 (2)		

[a] *x*, −*y*, *z*. [b] *x*, 1−*y*, *z*.

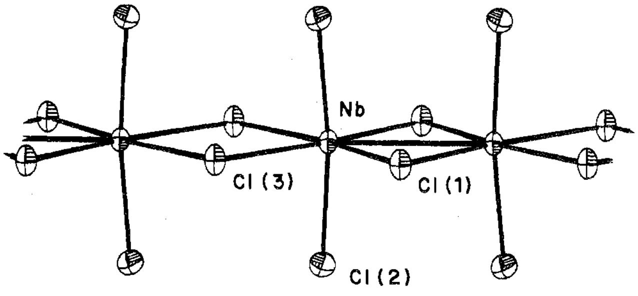

Figure 1. A section of the linear chain of $NbCl_4$. The thermal ellipsoids represent 50% probability. The short niobium–niobium distance is 3.029 (2) Å while the long niobium–niobium distance is 3.794 (2) Å.

were corrected for Lorentz–polarization and absorption (μ = 43.33 cm^{-1}) and merged to yield 476 independent reflections with $I \geq 2\sigma(I)$. The systematic absence $h + k + l = 2n + 1$ is consistent with space groups *I*2, *Im*, *I*2/*m*. Assuming four $NbCl_4$ units per cell the calculated density is 3.17 g/cm^3, in agreement with preliminary observations.

The centrosymmetric space group, *I*2/*m*, was confirmed by the successful least-squares refinement of the model. Initial isotropic least-squares refinement converged with R_1[9] = 0.118, with subsequent anisotropic refinement resulting in nonpositive definite thermal ellipsoids. However, refinement with the inclusion of isotropic secondary extinction[10] resulted in R_1 = 0.0532, with subsequent anisotropic refinement, which included terms for anomalous dispersion of Nb and Cl yielding R_1 = 0.026 and R_2 = 0.041. The final positional parameters are listed in Table I, and the final anisotropic thermal parameters are given in Table II. A diagram showing a single chain of $NbCl_4$ is presented in Figure 1, while the accompanying interatomic distances are given in Table III. The bond angles are given below (vida infra).

The most noticeable feature of this one-dimensional chain structure is that the metal atoms are drawn together alternately in pairs indicating metal–metal bonding. The short niobium–niobium distance is 3.029 (2) Å while the long distance is 3.794 (2) Å. The metal–metal bond also results in alternating bridging chloride distances of 2.523 (1) Å and 2.425 (1) Å while the terminal axial chloride is 2.291 (2) Å. As can be seen from Figure 1, the metal–metal bond also causes a distortion of the octahedral symmetry about the niobium atoms, with repulsion of the axial chlorides away from the bonded niobiums resulting in a Cl(2)–Nb–Cl(2) angle of 187.42 (6)°.

The corrected molar susceptibility at room temperature, extrapolated to $1/H = 0$, is 76 × 10^{-6} cgs/mol. This is considerably less than the expected value of 450 × 10^{-6} cgs/mol for niobium(IV) (d^1) in an octahedral field with a spin–orbit coupling constant of 800 cm^{-1} and is consistent with the presence of the metal–metal bond.

It is of interest to compare the structure of $NbCl_4$ to that of $NbCl_5$,[6] which exists as a dimeric molecule. Niobium(V) has a ground state electron configuration of d^0 and is therefore not expected to participate in metal–metal bond formation. In Nb_2Cl_{10} the lack of a metal–metal bond is readily apparent as there is a separation of 3.951 (2) Å between metal centers, a distance even longer than the nonbonded metal–metal distance in the tetrachloride. In addition, the bridging niobium chloride distance of 2.555 (6) Å in niobium pentachloride is longer than either of the two bridging distances in the tetrachloride. Although the axial chloride distance of 2.302 (5) Å is not significantly larger than the 2.291 (1) Å distance found in $NbCl_4$, the longer niobium–chloride distances in the pentachloride indicate that the oxidation state of the metal is not the major factor determining bond distances in these systems. One would expect that a higher metal oxidation state would have shortened the metal–halide distances.

Our results for $NbCl_4$ show many similarities to the structure of α-NbI_4,[5] which also forms a metal–metal bonded chain structure. Both structures are composed of hexagonal close-packed halide lattices with the niobium atoms occupying $^1/_4$ of the octahedral holes. In $NbCl_4$ the three crystallographically independent angles Cl(1)–Nb–Cl(1), Cl(2)–Nb–Cl(2), Cl(3)–Nb–Cl(3) are 102.69 (7), 172.58 (6), and 82.51 (6)°, respectively, while the corresponding angles in α-NbI_4 are 105.7 (2), 169.3 (1), and 82.2 (2)°. It is also found that multiplication of all Nb–Nb and Nb–Cl distances in $NbCl_4$ by a proportionality factor found to be 1.137 gives the corresponding Nb–Nb and Nb–I distances for α-NbI_4 to within 3%. These results suggest that both systems, although composed of different close-packed atoms, are equally distorted by the influence of the metal–metal bonded chain structure. It also follows that the dimensional differences between these two structures are almost entirely due to the size differences between the halides in the two close-packed halide lattices. An examination of the crystal structure of $NbBr_4$ is in progress.

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Registry No. $NbCl_4$, 13569-70-5.

Supplementary Material Available: Listing of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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