

Niobium Cluster Compounds with Transition Metals: $K_2Mn[Nb_6Cl_{18}]$

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A new quaternary niobium cluster chloride, $K_2Mn[Nb_6Cl_{18}]$, has been synthesized in a sealed quartz tube from stoichiometric amounts of $NbCl_5$, niobium metal, KCl , and $MnCl_2$ at $720^\circ C$. The structure, as determined by single-crystal X-ray diffraction, is rhombohedral, space group $R\bar{3}$ (No. 148) with $Z = 3$ and has lattice parameters $a = 914.01$ (4) pm, $c = 2522.9$ (2) pm (hexagonal setting). The structure refinement based on F^2 yielded $wR2 = 0.040$. (For comparison, a refinement based on F values yielded $R1 = 0.016$). The structure contains isolated $[Nb_6Cl_{18}]^{4-}$ clusters, separated by K^+ and Mn^{2+} cations, being located in an anticubeoctahedral and octahedral chloride coordination environment, respectively. © 1996 Academic Press, Inc.

INTRODUCTION

The structure of the $[Nb_6Cl_{18}]^{4-}$ ion is well known from many compounds (1). A representative number of compounds, such as Nb_6Cl_{14} (2) or $K_4[Nb_6Cl_{18}]$ (3), were characterized many years ago. More recently we obtained the new compounds $M[Nb_6Cl_{15}]$ (4), $M_4[Nb_6Cl_{18}]$ (5), and $M_2Li_2[Nb_6Cl_{18}]$ (6) with $M = In, Tl$. It has been shown, however, that M can also be a lanthanoid metal in other compounds with Nb_6Cl_{18} units. These compounds occur with two structure types, that of $CsLn[Nb_6Cl_{18}]$ ($Ln =$ all lanthanoides except Eu) with the space group $P\bar{3}1c$ and that of the general formula $M_xLn[Nb_6Cl_{18}]$ which crystallize in the $R\bar{3}$ space group, where the M (alkali metal) position can be fully occupied, half-filled, or empty ($x = 2$ (only for $Ln = Eu^{2+}$), 1, 0) (7, 8).

It is important to note that the compounds $Ln[Nb_6Cl_{18}]$ ($Ln = Lu, Tm, Er, Ho, Dy, or Y$) (7) represent less common examples of niobium clusters containing only 15 electrons in metal–metal bonding states (like Nb_6F_{15}), leading to paramagnetic behavior. Our present studies have revealed a niobium halide cluster compound that for the first time contains a transition metal as a counterion. The role of transition metals as interstitial atoms inside of

TABLE 1
Data Collection and Structure Determination Parameters
for $K_2Mn[Nb_6Cl_{18}]$

Space group, Z	$R\bar{3}$ (No. 148), 3
Lattice parameters (pm) ^a	$a = 914.01$ (4) $c = 2522.9$ (2)
ρ_{calc} (gcm ⁻³)	3.61
Formula weight (gmol ⁻³)	1328.7
Crystal size (mm ³)	$0.11 \times 0.23 \times 0.27$
μ (mm ⁻¹)	5.5
Data collection	Siemens-Stoe, AED 2
Radiation	$MoK\alpha$ ($\lambda = 71.069$ pm)
Temperature (°C)	20
Scan method	$2\theta - \omega$, "learnt profile"
2θ range (°)	$4.8 < 2\theta < 60.1$
Corrections applied	Polarization, Lorentz, Absorption (20 Ψ -scans)
Measured reflections	3517
Unique reflections	1185
$F_0 > 4\sigma(F_0)$	1072
Transmission coeff. range	0.18–0.26
R_{ave} . ($F_0 > 0$)	0.04
Number of variables	43
$R1^b$	0.016
$wR2^c$	0.040
Max. shift (esd)	<0.0005
Largest residue peak (e ⁻ /Å ³)	0.5

^a Diffractometer data.

^b $R1 = \sum||F_0| - |F_c|| / \sum|F_0|$, for $F_0 > 4\sigma(F_0)$.

^c $wR2 = [\sum\{w(F_0^2 - F_c^2)^2\} / \sum\{w(F_0^2)^2\}]^{1/2}$, for all reflections.

M_6X_{12} -type clusters has been widely explored in the zirconium and rare-earth halide cluster chemistry, of which $Na[Zr_6Cl_{14}Mn]$ and $Zr_6Cl_{14}Fe$ are recent examples (9).

EXPERIMENTAL

Synthesis. The new compound $K_2Mn[Nb_6Cl_{18}]$ was prepared from the reaction of stoichiometric quantities of $NbCl_5$ (99.99%, Alfa), Nb powder (99.99%, Alfa), KCl (99.99%, Alfa), and $MnCl_2$ (anhydrous, 99.99%, Alfa) in

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TABLE 2
Atomic Positions in $K_2Mn[Nb_6Cl_{18}]$ (Hexagonal Setting)

Atom	Wyckoff position	x/a	y/b	z/c	U_{eq} (pm ²) (21)
K	6c	$\frac{2}{3}$	$\frac{1}{3}$	0.05561 (4)	385 (3)
Mn	3a	0	0	0	138 (2)
Nb	18f	0.29106 (2)	0.46393 (2)	0.11937 (1)	93 (1)
Cl1	18f	0.09664 (6)	0.47891 (6)	0.05541 (2)	151 (1)
Cl2	18f	0.04971 (6)	0.24163 (6)	0.16739 (2)	145 (1)
Cl3 ^a	18f	0.24584 (6)	0.21318 (7)	0.05865 (2)	162 (1)

^a Outer chloride atoms.

high yields (about 90%, the binary Nb_3Cl_8 was obtained as side product). Reactions were performed in evacuated and sealed quartz tubes at 720°C for 3 days. The heating and cooling rates were 50°C per hour. The reaction product was obtained as a dark green (almost black) well crystalline powder, containing gemlike crystals varying between 0.1 and 0.5 mm in size, showing olive green color when ground. Crystals of $K_2Mn[Nb_6Cl_{18}]$ do not show any change when they are exposed to air for several days, but the crystalline powder dissolves in hot water to produce an intense green solution, caused by the $[Nb_6Cl_{12}]^{2+}$ ion. Starting with this ion, it has been shown recently that new compounds with six terminal pseudohalide ligands, e.g., $[Nb_6Cl_{12}(N_3)_6]^{4-}$, can be obtained (10).

$K_2Mn[Nb_6Cl_{18}]$ was characterized by X-ray powder patterns (monochromated $CuK\alpha$ radiation) obtained with an automated Phillips diffractometer and silicon as an internal standard. Lattice parameters were determined from 17 indexed lines for the trigonal cell: $a = 913.8$ (2) pm, $c = 2523.1$ (5) pm.

Magnetic measurements. Magnetic susceptibility measurements were performed (66.5 mg of the powdered sample of selected crystals of $K_2Mn[Nb_6Cl_{18}]$, sealed in a Pyrex ampoule under dry Ar) using an MPMS 5 SQUID-based variable temperature susceptometer, between room temperature and 2 K, under magnetic fields of 100, 1000, and 10000 Oe. The contribution of the Pyrex ampoule was

subtracted from the total magnetic moment. A diamagnetic correction was performed according to Ref. (11).

Structural studies. Single crystals of $K_2Mn[Nb_6Cl_{18}]$ were sealed in thin-walled glass capillaries in a glove box under dry argon atmosphere. Oscillation photographs were taken to check the crystal quality. Intensity data of a selected crystal were collected at room temperature with a four-circle diffractometer (Siemens-Stoe AED 2) using graphite-monochromated $MoK\alpha$ radiation. The unit cell dimensions of $K_2Mn[Nb_6Cl_{18}]$ were calculated by least-squares refinement on setting angles of 25 reflections. Reflection data of half an Ewald sphere were collected, and 20 Ψ -scans were used for an empirical absorption correction, to be applied in the data reduction process. Decay of the crystal was virtually absent during the measurement. Only reflections resulting from the R condition were found to be systematically absent, and therefore possible space groups were $R3$, $R\bar{3}$, $R32$, $R3m$, and $R\bar{3}m$.

The structure was solved in the trigonal space group $R\bar{3}$ with the aid of the direct methods of the SHELXS-86 program (12) that provided all atomic positions correctly (attempts to refine the structure in higher symmetry space groups were unsuccessful). The structure refinement was performed straightforwardly, using the SHELXL-93 (13) program. The scattering factors f' and f'' were taken from Ref. (14). After the anisotropic refinement of all atoms (43 parameters) the reliability factors were satisfactory

TABLE 3
Anisotropic Displacement Parameters (pm² (21)) in $K_2Mn[Nb_6Cl_{18}]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K	414 (4)	414 (4)	326 (5)	207 (2)	0	0
Mn	143 (2)	143 (2)	126 (3)	72 (1)	0	0
Nb	100 (1)	96 (1)	85 (1)	50 (1)	-1 (1)	-4 (1)
Cl1	182 (2)	167 (2)	127 (2)	105 (2)	-55 (2)	-45 (2)
Cl2	145 (2)	104 (2)	152 (3)	37 (2)	27 (2)	-9 (2)
Cl3 ^a	184 (2)	151 (2)	151 (2)	82 (2)	-18 (2)	-42 (2)

^a Outer chloride atoms.

TABLE 4
Important Bond Distances in $K_2Mn[Nb_6Cl_{18}]$

Atoms	Distance range (pm)	Mean (pm)
Nb–Nb	293.2 (1)–293.3 (1)	293.3
Nb–Cl ⁱ	244.7 (1)–246.2 (1)	245.4
Nb–Cl ^a	261.5 (1)	261.5
Mn–Cl	258.3 (1)	258.3
K–Cl	343.3 (1)–346.2 (1)	344.5

Note. Nb–Clⁱ (i = inner) or Nb–Cl^a (a = outer).

with $R1 = 0.021$ (based on F values, all data) and $wR2 = 0.040$ (based on F^2 values, all data). The calculated final difference map was flat with the highest electron density residual being smaller than $0.5 e^-/\text{\AA}^3$. Further details regarding data collection and refinement parameters are listed in Table 1.

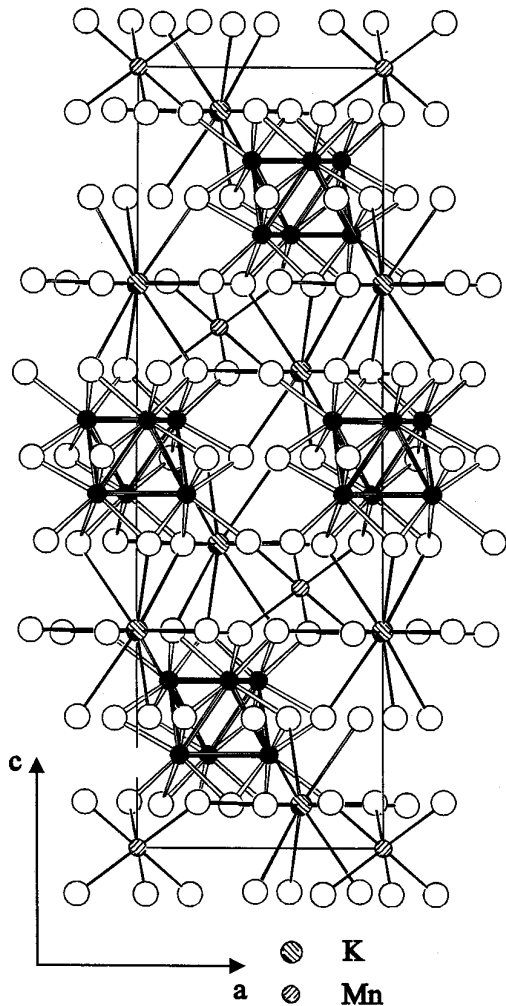


FIG. 1. The crystal structure of $K_2Mn[Nb_6Cl_{18}]$ ([010] section), containing $(Nb_6Cl_{12})Cl_6^+$ clusters (Nb, black spheres; Cl, empty spheres).

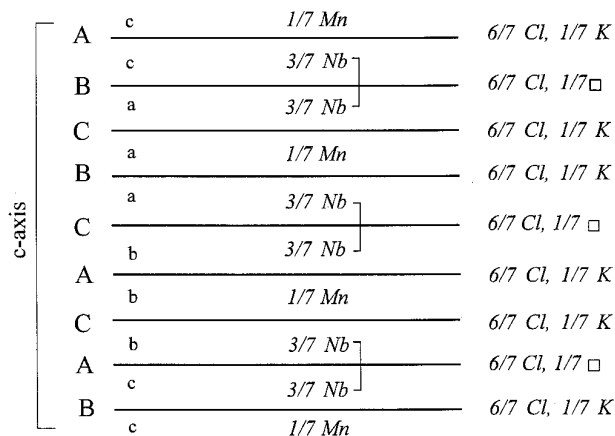


FIG. 2. Packing scheme of the $K_2Mn[Nb_6Cl_{18}]$ structure.

The positional, isotropic-equivalent, and anisotropic thermal parameters consistent with the hexagonal setting of the cell are given in Tables 2 and 3, while important atomic bond distances are listed in Table 4.

RESULTS AND DISCUSSION

The structure of $K_2Mn[Nb_6Cl_{18}]$ is isotypic with the structure of $Cs_2Eu[Nb_6Br_{18}]$ (15). The structure is also the same as for the stuffed cluster compounds $Cs_2Zr[Zr_6I_{18}C]$ (16) and $Cs_2Lu[Lu_6Cl_{18}C]$ (17). The completely occupied alkali site of the title compound is in clear contrast to the 50% occupancy in the $CsLu[Nb_6Cl_{18}]$ (18) structure.

The three-dimensional structure can be described on the basis of $[Nb_6Cl_{12}Cl_6]^+$ ions, where i and a denote the inner halides (bridging edges of the niobium cluster) and outer halides, respectively. These units are interlinked by K^+ and Mn^{2+} ions (Fig. 1). The Mn^{2+} ions are bonded to 6 exo-Cl^a (Cl3), belonging to 6 different clusters, forming almost regular $MnCl_6$ octahedra, with the Mn–Cl distance of 258.3 (1) pm and deviations from the ideal (90°) Cl–Mn–Cl bond angles of no more than $0.26 (2)^\circ$. This bond distance is somewhat longer than the corresponding distance reported for $MnCl_2$ (254.8 (2) pm) (19). The K^+ environment of 3 symmetry is nearly anticubeoctahedral, formed by 12 chloride ions, with average K–Cl distances of 344.4 pm.

In a more general view the structure may be described in terms of close-packed chloride layers. Two-thirds of these layers have one-seventh of the chloride atoms substituted by potassium. In the other one-third of the layers, one-seventh of the chloride positions are vacant and coincide with the cluster centers. Niobium atoms occupy three-sevenths of the octahedral voids between two-thirds of the $(chh)_3$ close packed chloride layers (Fig. 2).

The Nb–Nb distances (mean 293.3 pm) are in agreement with $[Nb_6Cl_{18}]^+$ clusters (mean values: 291 pm (3) to 293

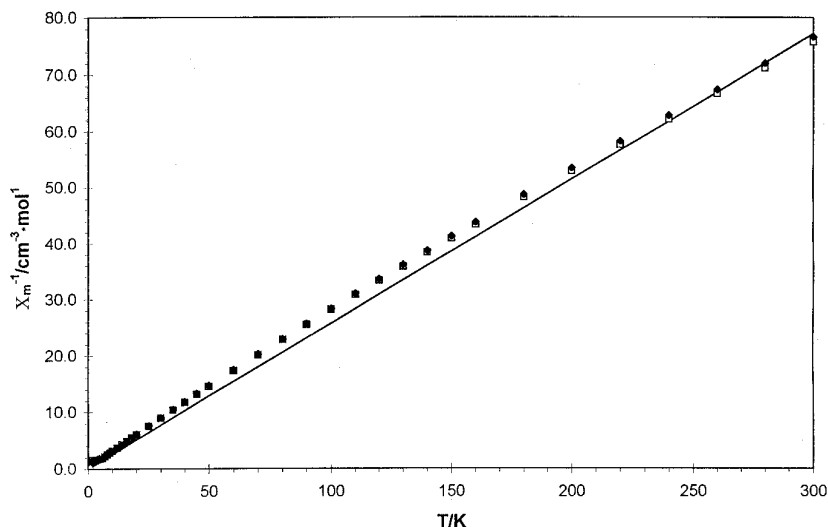


FIG. 3. χ^{-1} versus temperature plot for $\text{K}_2\text{Mn}[\text{Nb}_6\text{Cl}_{18}]$ (at 10 kOe, zero field cooled, \square , measured; \blacklozenge , corrected) compared with Curie behavior (line).

pm (5)) and consequently manganese is present as Mn^{2+} , as confirmed by magnetic studies.

Measurements revealed field-independent (100, 1000, 10000 Oe) magnetism, consistent with paramagnetic Curie–Weiss behavior as shown in Fig. 3. The effective magnetic moment at 300 K and 10 kOe of $5.63 \mu_{\text{B}}$ per manganese is close to the expected spin-only value of high spin Mn^{2+} ($5.9 \mu_{\text{B}}$). A slight reduction in the Landé factor g , as measured by electron paramagnetic resonance experiments in other niobium halides (20), would explain a magnetic moment below the spin-only value. Magnetic coupling effects, however, were virtually absent in $\text{K}_2\text{Mn}[\text{Nb}_6\text{Cl}_{18}]$. For comparison we performed a magnetic measurement of $\text{Nb}_6\text{Cl}_{14}$ (also 16 electrons in niobium states per cluster). The nearly temperature-independent paramagnetic susceptibility value of $\text{Nb}_6\text{Cl}_{14}$ was found to be very small (in the order of 10^{-4} emu per mol $\text{Nb}_6\text{Cl}_{14}$) and therefore not considered for the correction of the $\text{K}_2\text{Mn}[\text{Nb}_6\text{Cl}_{18}]$ data.

A more recent work by the authors on the chemistry of other transition metals with alkali metal halides, niobium halides, and niobium metal shows that $\text{K}_2\text{Mn}[\text{Nb}_6\text{Cl}_{18}]$ is the first example of a rather large family of transition metal niobium halides.

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REFERENCES

1. C. Perrin and M. Sergent, *Eur. J. Solid State Chem.* **28**, 933 (1991).
2. A. Simon, H. G. von Schnering, H. Wöhrle, and H. Schäfer, *Z. Anorg. Allg. Chem.* **339**, 155 (1965).
3. A. Simon, H. G. von Schnering, and H. Schäfer, *Z. Anorg. Allg. Chem.* **361**, 235 (1968).
4. H. Womelsdorf, H.-J. Meyer, and A. Lachgar, *Z. Anorg. Allg. Chem.* in press; A. Simon, *Angew. Chem. Int. Ed. Engl.* **27**, 159 (1988); R. P. Ziebarth and J. D. Corbett, *J. Am. Chem. Soc.* **109**, 4844 (1987).
5. B. Baján and H.-J. Meyer, *Z. Naturforsch. B* **50**, 1373 (1995).
6. A. Lachgar and H.-J. Meyer, *J. Solid State Chem.* **110**, 15 (1994).
7. S. Ihmaïne, C. Perrin, and M. Sergent, *Acta Crystallogr. Sect. C* **43**, 813 (1987); *Acta Crystallogr. Sect. C* **45**, 705 (1989).
8. S. Ihmaïne, C. Perrin, O. Peña, and M. Sergent, *J. Less-Common Met.* **137**, 323 (1988).
9. J. Zhang and J. D. Corbett, *J. Solid State Chem.* **109**, 265 (1994).
10. O. Reckeweg and H.-J. Meyer, *Z. Naturforsch. B* **50**, 1377 (1995).
11. P. W. Selwood, "Magnetochemistry," 2nd ed., p. 69–82, 781. Interscience Publishers, New York/London, 1956.
12. G. M. Sheldrick, "SHELXS-86: Program for Crystal Structure Determination." Univ. Göttingen, F.R.G., 1986.
13. G. M. Sheldrick, "SHELXL-93: Program for Crystal Structure Refinement." Univ. Göttingen, F.R.G., 1993.
14. "International Tables for X-ray Crystallography," Vol. C. Kluwer, Dordrecht, 1992.
15. S. Cordier, C. Perrin, and M. Sergent, *Z. Anorg. Allg. Chem.* **619**, 621 (1993).
16. M. W. Payne and J. D. Corbett, *J. Solid State Chem.* **102**, 553 (1993).
17. H. M. Artelt, T. Schleid, G. Meyer, *Z. Anorg. Allg. Chem.* **618**, 18 (1992).
18. S. Ihmaïne, C. Perrin, and M. Sergent, *Acta Crystallogr. Sect. C* **45**, 705 (1989).
19. J. D. Tornero and J. Fayos, *Z. Kristallogr.* **192**, 147 (1990).
20. R. A. Mackay and R. F. Schneider, *Inorg. Chem.* **6**, 549 (1967).
21. R. X. Fischer and E. Tillmanns, *Acta Crystallogr. Sect. C* **44**, 775 (1988).