Synthesis and crystal structure of alkali metal oxo nitrido dimetallates(VI), $A_6[M_2N_4O_3]$ (A≡K, Rb, Cs; M≡Mo, W)[☆]

R. Niewa, H. Jacobs[*]

Fachbereich Chemie der Universität, D-44221 Dortmund, Germany

Abstract

Mixtures of M–MO_3 with M≡Mo, W react with an excess of alkali metal amides ANH_2 (A≡K, Rb, Cs) in autoclaves at 600 °C to yield red and yellow crystals respectively, of oxo nitrido dimetallates(VI) of general composition $A_6[M_2X_7]$ embedded in alkali metal. The alkali metal is washed out by liquid ammonia at room temperature.

The structures were determined from X-ray single-crystal data. They are monoclinic with the $K_6[Co_2O_7]$ structure type, $Z = 2$, with the following unit cell parameters:

	a (Å)	b (Å)	c (Å)	β (deg)
$K_6[Mo_2N_4O_3]$	6.721(3)	9.490(6)	9.582(4)	92.07(4)
$K_6[W_2N_4O_3]$	6.720(2)	9.473(1)	9.581(2)	91.99(2)
$Rb_6[Mo_2N_4O_3]$	6.960(2)	9.766(2)	9.827(2)	92.02(2)
$Rb_6[W_2N_4O_3]$	6.977(2)	9.768(4)	9.861(2)	91.87(2)
$Cs_6[Mo_2N_4O_3]$	7.305(2)	10.108(7)	10.204(4)	91.53(3)
$Cs_6[W_2N_4O_3]$	7.284(3)	10.045(5)	10.174(5)	91.54(3)

The title compounds contain corner-sharing double tetrahedra units $[M_2X_7]^{6-}$. The ligands X≡N, O are distributed statistically. The anions $[M_2X_7]^{6-}$ are stacked together following the motif of a distorted body-centred arrangement connected by alkali metal ions.

Keywords: Alkali metal compounds; Oxo nitrido dimetallates(VI); Crystal structure

1. Introduction

In the course of our investigations on ternary alkali metal nitrides of transition metals we reported the oxo nitrido metallates $Na_4[MoN_2O_2]$ (M≡Mo, W) [1] and $K_6[W_2N_4O_3]$ [2]. The sodium compounds contain isolated tetrahedra $[MX_4]^{4-}$, whereas for the potassium compound corner-sharing double tetrahedra $[W_2X_7]^{6-}$ are found. So we expected a higher degree of connection between the coordination tetrahedra of the transition metals in compounds with larger alkali metals. However, we found structures isotypic with that of the potassium compound. Thus we report here about the synthesis and structural characterization of all six compounds $A_6[M_2N_4O_3]$ with A≡K, Rb, Cs and M≡Mo, W.

[*]Corresponding author.

2. Experimental details

Transparent red (M≡Mo) and yellow (M≡W) crystals of $A_6[M_2X_7]$ (A≡K, Rb, Cs; 7X≡3O and 4N) are obtained by the reaction of MO_3 (MoO_3 ACS purity, WO_3 99.7%; Ventron GmbH, Karlsruhe) with the corresponding alkali metal amide (from alkali metals, K 98% Fluka AG, Neu-Ulm, Rb 99.8% Johnson Matthey GmbH, Karlsruhe, Cs reinst, Merck AG, Darmstadt and liquid ammonia, NH_3 99.999% Messer Griesheim at 80 °C and 70 bar) at 600 °C for 6 days. The reactions were carried out in autoclaves for salt melts (Inconel 625, no. 2.4856) to prevent early decomposition of ANH_2 to A, N_2 and H_2. They were closed by an Ni membrane seal and had a volume of about 6 cm^3. The solid starting materials were loaded into an Al_2O_3 crucible with a volume of about 3 cm^3 within the autoclave in a glove-box. Starting with pure MO_3 as one educt the oxo nitrido dimetallates are byproducts

Table 1
Technical and crystallographic data concerning structure determinations on $A_6[M_2N_4O_3]$ with $A \equiv K$, Rb, Cs and $M \equiv Mo$, W

	$K_6[Mo_2N_4O_3]$	$K_6[W_2N_4O_3]$	$Rb_6[Mo_2N_4O_3]$	$Rb_6[W_2N_4O_3]$	$Cs_6[Mo_2N_4O_3]$	$Cs_6[W_2N_4O_3]$
Crystal size	$0.1 \times 0.1 \times 0.25$	$0.3 \times 0.4 \times 0.4$	$0.075 \times 0.075 \times 0.1$	$0.175 \times 0.175 \times 0.25$	$0.05 \times 0.1 \times 0.15$	$0.15 \times 0.15 \times 0.2$
a (Å)	6.721(3)	6.720(2)	6.960(2)	6.977(2)	7.305(2)	7.284(3)
b (Å)	9.490(6)	9.473(1)	9.766(2)	9.768(4)	10.108(7)	10.045(5)
c (Å)	9.582(4)	9.581(2)	9.827(2)	9.861(2)	10.204(4)	10.174(5)
β (deg)	92.07(4)	91.99(2)	92.02(2)	91.87(2)	91.53(3)	91.54(3)
Volume (Å^3)	610.8	609.6	667.5	671.7	753.2	744.1
D_x (g cm^{-1})	2.885	3.848	4.024	4.868	4.821	5.684
Z	2	2	2	2	2	2
Space group	$P2_1/n$	$P2_1/n$ (Pn)	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
Radiation	Ag Kα	Mo Kα	Ag Kα	Ag Kα	Ag Kα	Ag Kα
$1/\mu$ (mm)	0.116	0.078	0.054	0.048	0.073	0.062
Absorption correction	–	–	ψ scan	ψ scan	ψ scan	ψ scan
Θ_{min}, Θ_{max} (deg)	3, 35	1, 35	3, 40	3, 30	3, 35	3, 35
h, k, l	±12, -16 to $+2$, ±16	±10, -1 to $+15$, ±15	-14 to $+1$, ±20, ±20	±10, ±14, -14 to $+1$	±15, ±9, -9 to 0	±15, ±9, -9 to 0
Independent reflections	5225	2818	6194	3664	2485	2614
$F_o^2 > 3\sigma F_o^2$	1576	2057	1037	1684	1140	1172
Variables	71	71 (137)	71	71	71	71
R_{int}	3.7	3.6 (3.6)	3.9	6.7	6.5	9.8
R/R_w ($w=1$)	4.1/5.0	4.1/4.9 (4.9)	4.4/5.5	4.9/5.7	6.3/7.3	4.9/5.4
Extinction coefficient	1.4×10^{-7}	3.9×10^{-7} (−)	5.8×10^{-8}	7.4×10^{-8}	1.8×10^{-7}	1.1×10^{-8}
Largest peak in final difference map (Å^{-3})	1.3	5.1 (1.6)	2.0	5.9	5.1	3.9

All measurements were done in the scan mode Ω–2Θ and with a graphite monochromator.
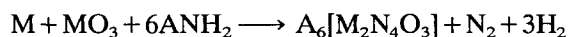
Table 2
Atomic coordinates and isotropic thermal displacement parameters B (Å^2) for $A_6[M_2X_7]$ with $A \equiv K$, Rb, Cs, $M \equiv Mo$, W and $7X \equiv 4N$, 3O (solutions in $P2_1/n$, X(1) in site 2c, all other atoms in site 4e)

	$K_6[Mo_2N_4O_3]$	$K_6[W_2N_4O_3]$	$Rb_6[Mo_2N_4O_3]$	$Rb_6[W_2N_4O_3]$	$Cs_6[Mo_2N_4O_3]$	$Cs_6[W_2N_4O_3]$
x(M)	0.94660(8)	0.94713(5)	0.9514(2)	0.95146(8)	0.9553(2)	0.95598(8)
y(M)	0.14213(6)	0.14131(3)	0.1380(1)	0.13717(6)	0.1331(2)	0.1322(1)
z(M)	0.63360(6)	0.63315(3)	0.6315(1)	0.63068(6)	0.6282(2)	0.62722(9)
B(M)	0.844(5)	0.640(4)	0.76(1)	0.807(6)	0.94(2)	1.03(1)
x[A(1)]	0.2522(3)	0.2523(3)	0.2543(2)	0.2537(2)	0.2538(2)	0.2536(1)
y[A(1)]	0.0236(2)	0.0234(2)	0.0229(2)	0.0230(2)	0.0247(2)	0.0246(2)
z[A(1)]	0.0508(2)	0.0497(3)	0.0532(2)	0.0518(2)	0.0545(1)	0.0529(2)
B[A(1)]	1.73(3)	1.46(3)	1.57(2)	1.75(2)	1.84(2)	1.56(3)
x[A(2)]	0.3798(3)	0.3839(4)	0.3846(3)	0.3871(2)	0.3850(2)	0.3884(2)
y[A(2)]	0.1539(2)	0.1533(3)	0.1501(2)	0.1506(2)	0.1485(2)	0.1481(2)
z[A(2)]	0.4319(2)	0.4309(3)	0.4257(2)	0.4248(2)	0.4205(2)	0.4182(2)
B[A(2)]	2.27(3)	2.04(4)	1.96(3)	2.08(3)	2.02(3)	1.77(3)
x[A(3)]	0.8718(3)	0.8756(4)	0.8777(2)	0.8798(2)	0.8806(2)	0.8832(2)
y[A(3)]	0.2062(2)	0.2095(3)	0.2117(2)	0.2135(2)	0.2170(2)	0.2194(2)
z[A(3)]	0.2820(2)	0.2810(3)	0.2818(2)	0.2802(2)	0.2794(1)	0.2778(2)
B[A(3)]	2.25(3)	1.88(4)	1.72(2)	1.84(3)	1.80(2)	1.53(3)
x[X(1)]	0	0	0	0	0	0
y[X(1)]	0	0	0	0	0	0
z[X(1)]	1/2	1/2	1/2	1/2	1/2	1/2
B[X(1)]	3.9(2)	4.7(4)	3.9(5)	3.0(4)	4.3(6)	3.5(6)
x[X(2)]	0.5692(9)	0.567(1)	0.568(2)	0.568(2)	0.567(2)	0.563(2)
y[X(2)]	0.1994(7)	0.1976(9)	0.209(1)	0.209(1)	0.216(2)	0.219(2)
z[X(2)]	0.0756(7)	0.0754(9)	0.076(1)	0.077(2)	0.075(2)	0.073(2)
B[X(2)]	2.1(1)	1.8(1)	1.9(2)	2.3(2)	2.2(3)	2.1(3)
x[X(3)]	0.682(1)	0.684(1)	0.698(2)	0.697(2)	0.715(2)	0.713(2)
y[X(3)]	0.1723(9)	0.171(1)	0.169(2)	0.165(2)	0.160(2)	0.159(2)
z[X(3)]	0.6422(9)	0.640(1)	0.643(1)	0.637(2)	0.639(2)	0.640(2)
B[X(3)]	2.5(1)	2.1(2)	1.9(3)	2.4(3)	2.2(4)	1.7(4)
x[X(4)]	0.050(1)	0.049(1)	0.054(2)	0.048(2)	0.054(2)	0.053(2)
y[X(4)]	0.0933(7)	0.093(1)	0.089(2)	0.089(2)	0.085(2)	0.078(2)
z[X(4)]	0.8057(7)	0.8046(9)	0.797(1)	0.796(1)	0.789(2)	0.784(2)
B[X(4)]	1.6(1)	1.4(1)	1.6(2)	1.5(2)	1.6(3)	2.4(4)

besides other oxides or oxynitrides which are not yet characterized.

The neat compounds $A_6[M_2X_7]$ can be prepared if an oxygen–transition metal ratio of 3:2 is chosen and reacted with an excess of ANH$_2$ (M:ANH$_2$ = 1:6). Best results are obtained with a mixture of M–MO$_3$ with a small excess of the transition metal (Mo m5N, W m5N, Johnson Matthey GmbH, Karlsruhe) (M:MO$_3$ = 1.05:1). The products may be formed according to the following reaction:

$$M + MO_3 + 6ANH_2 \longrightarrow A_6[M_2N_4O_3] + N_2 + 3H_2$$

After the reaction is carried out the crystals are embedded in solid alkali metal formed by thermal decomposition of excess alkali metal amide. The alkali metal is washed out by liquid ammonia at room temperature. The oxo nitrido dimetallates are insoluble in this solvent.

All six compounds show a high sensitivity towards moist air. Rapid hydrolysis leads to ammonia and in the case of $A \equiv K$, Rb to colourless metallates $A_2[MO_4]$ as characterized by their X-ray powder patterns. In the case of the caesium compounds, hydrolysis proceeds slowly to other metallates so we could not characterize them by their X-ray diagrams.

3. Structure determinations and discussion

Intensity data of the monoclinic crystals of all compounds were collected on a four-circle diffractometer (CAD 4, Enraf Nonius, Delft). The observed reflection conditions led to the space group $P2_1/n$ (no. 14). The structure calculations (program system SDP [3]) showed that all compounds are isotypic. In Table 1 technical and crystallographic data concerning the structure determinations are given. In all tables the data of $K_6[W_2N_4O_3]$ [2] are included for comparison. Tables 2 and 3 give atomic coordinates, isotropic and anisotropic thermal displacement parameters.

Table 3

Anisotropic thermal displacement parameters $U_{ij}(\times 10^3$ Å$^2)$ for A$_6$[M$_2$X$_7$] with A ≡ K, Rb, Cs, M ≡ Mo, W and 7X ≡ 4N, 3O (solutions in $P2_1/n$)

	K$_6$[Mo$_2$N$_4$O$_3$]	K$_6$[W$_2$N$_4$O$_3$]	Rb$_6$[Mo$_2$N$_4$O$_3$]	Rb$_6$[W$_2$N$_4$O$_3$]	Cs$_6$[Mo$_2$N$_4$O$_3$]	Cs$_6$[W$_2$N$_4$O$_3$]
U_{11}(M)	12.2(1)	10.5(1)	12.4(4)	10.9(2)	14.0(3)	15.9(2)
U_{22}(M)	10.6(1)	5.87(9)	9.7(4)	9.1(2)	6.9(7)	11.3(4)
U_{33}(M)	9.4(1)	8.11(9)	7.0(3)	10.9(2)	14.8(7)	11.7(4)
U_{12}(M)	−0.9(2)	−1.0(1)	−0.3(5)	−0.7(2)	−0.2(4)	−0.9(3)
U_{13}(M)	2.7(1)	3.11(8)	2.3(3)	2.8(1)	−3.9(4)	−1.3(2)
U_{23}(M)	−1.3(2)	−1.3(1)	−0.9(5)	−1.4(2)	−1.6(6)	−0.7(4)
U_{11}[A(1)]	19.6(6)	15.4(8)	20.9(6)	16.8(6)	22.5(4)	22.0(3)
U_{22}[A(1)]	20.5(7)	15.1(8)	21.3(6)	20.9(6)	17.4(7)	17.1(7)
U_{33}[A(1)]	26.0(7)	25.2(9)	18.0(6)	29.0(7)	29.9(7)	20.3(7)
U_{12}[A(1)]	−3.1(6)	−2.2(7)	−2.1(6)	−2.8(5)	−3.7(4)	−4.0(4)
U_{13}[A(1)]	5.9(5)	5.4(7)	4.9(5)	5.4(5)	−2.4(4)	0.5(4)
U_{23}[A(1)]	−4.3(6)	−5.2(7)	−3.2(6)	−3.3(6)	−3.3(6)	−4.3(7)
U_{11}[A(2)]	26.4(7)	24.8(9)	26.4(7)	24.4(6)	26.8(4)	27.3(4)
U_{22}[A(2)]	31.6(9)	24(1)	27.8(8)	24.9(7)	18.9(7)	18.6(8)
U_{33}[A(2)]	28.5(7)	29(1)	20.3(6)	29.8(7)	30.7(7)	21.1(8)
U_{12}[A(2)]	−5.9(7)	−6.0(9)	−4.5(7)	−4.8(6)	−3.7(5)	−2.5(5)
U_{13}[A(2)]	6.1(6)	5.6(8)	3.7(6)	3.8(6)	−5.5(4)	−1.9(4)
U_{23}[A(2)]	1.7(8)	1.9(9)	2.8(7)	1.4(7)	1.8(6)	1.7(8)
U_{11}[A(3)]	25.0(7)	19.9(9)	21.2(6)	18.7(6)	23.0(4)	23.7(3)
U_{22}[A(3)]	38.0(9)	31(1)	28.9(7)	28.3(7)	21.0(7)	20.4(8)
U_{33}[A(3)]	22.5(7)	20.2(9)	15.1(6)	22.8(7)	23.9(7)	13.6(7)
U_{12}[A(3)]	9.7(7)	7.5(9)	5.2(7)	5.5(6)	4.5(4)	4.8(4)
U_{13}[A(3)]	1.4(6)	−0.6(7)	0.3(5)	0.1(5)	−9.0(4)	−5.6(4)
U_{23}[A(3)]	5.7(7)	5.2(9)	3.3(7)	4.1(6)	2.7(5)	2.4(8)
U_{11}[X(1)]	80(8)	120(0)	70(20)	60(10)	60(10)	70(10)
U_{22}[X(1)]	41(6)	28(7)	50(10)	15(7)	10(10)	20(10)
U_{33}[X(1)]	29(4)	32(7)	30(10)	40(10)	100(20)	50(20)
U_{12}[X(1)]	−3(6)	4(9)	10(10)	−4(8)	0(10)	0(10)
U_{13}[X(1)]	15(5)	21(8)	0(10)	21(9)	−40(10)	20(10)
U_{23}[X(1)]	−7(5)	−12(6)	−10(10)	0(8)	−10(10)	0(20)
U_{11}[X(2)]	24(3)	18(3)	24(6)	16(5)	29(5)	25(4)
U_{22}[X(2)]	25(3)	18(3)	21(6)	15(5)	10(8)	30(10)
U_{33}[X(2)]	32(3)	31(4)	28(6)	55(9)	44(9)	25(9)
U_{12}[X(2)]	4(2)	2(3)	1(5)	2(4)	−2(6)	−3(6)
U_{13}[X(2)]	5(2)	−3(3)	−2(5)	6(5)	−12(6)	−15(5)
U_{23}[X(2)]	−5(2)	−13(3)	−7(5)	−1(6)	5(7)	0(10)
U_{11}[X(3)]	17(3)	12(3)	16(6)	12(5)	17(5)	17(4)
U_{22}[X(3)]	40(4)	32(5)	36(8)	26(7)	10(10)	10(10)
U_{33}[X(3)]	37(4)	38(5)	20(6)	50(10)	50(10)	40(10)
U_{12}[X(3)]	−1(3)	−2(3)	−2(6)	2(5)	−3(6)	0(5)
U_{13}[X(3)]	1(3)	3(3)	6(5)	−1(6)	−3(6)	−4(6)
U_{23}[X(3)]	4(3)	0(4)	1(6)	−13(7)	−3(9)	−10(10)
U_{11}[X(4)]	20(2)	17(3)	28(7)	24(6)	26(5)	30(5)
U_{22}[X(4)]	23(3)	20(3)	18(6)	25(6)	14(9)	20(10)
U_{33}[X(4)]	16(2)	17(3)	13(5)	9(5)	21(9)	40(10)
U_{12}[X(4)]	−6(2)	−5(3)	−1(6)	−5(5)	−4(6)	3(6)
U_{13}[X(4)]	−1(2)	0(3)	−2(5)	−1(4)	−11(5)	−3(6)
U_{23}[X(4)]	6(2)	4(3)	−1(6)	12(5)	7(7)	10(10)

The title compounds contain corner-sharing double tetrahedra units [M$_2$X$_7$]$^{6-}$ which are stacked together to form the motif of a distorted body-centred arrangement connected by alkali metal ions. In $P2_1/n$ the angle M–X(1)–M is 180° as given by symmetry. The dianions are in a staggered conformation.

As we reported for A$_6$[Ge$_2$O$_7$] (A ≡ K, Rb) [2] and as is known for a large number of dimetallates, we found large thermal displacement parameters for the bridging ligand (X(1)) in the special site 2c (see Table 2) as shown in Fig. 1.

As Jansen and Hoppe proposed for the compound K$_6$[Co$_2$O$_7$] [4] and as we showed for K$_6$[Ge$_2$O$_7$] [2], a

Table 4
Distances and angles in the compounds $A_6[M_2X_7]$ with $A \equiv K$, Rb, Cs, $M \equiv Mo$, W and $7X \equiv 4N$, 3O (solutions in $P2_1/n$)

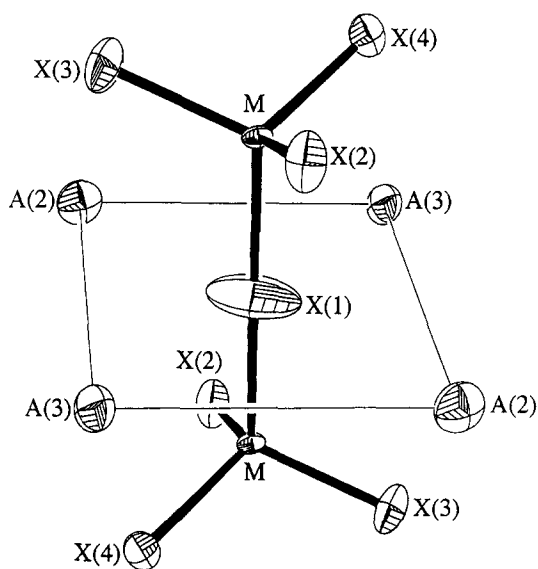|	$K_6[Mo_2N_4O_3]$	$K_6[W_2N_4O_3]$	$Rb_6[Mo_2N_4O_3]$	$Rb_6[W_2N_4O_3]$	$Cs_6[Mo_2N_4O_3]$	$Cs_6[W_2N_4O_3]$
Distances (Å)						
M–X(1)	1.903(1)	1.891(1)	1.906(1)	1.897(1)	1.911(2)	1.888(1)
M–X(2)	1.814(6)	1.820(8)	1.80(1)	1.80(1)	1.82(2)	1.78(2)
M–X(3)	1.803(7)	1.794(9)	1.80(1)	1.80(1)	1.78(1)	1.80(1)
M–X(4)	1.826(6)	1.816(9)	1.82(1)	1.81(1)	1.82(2)	1.81(2)
$2 \times$ X(1)–A(2)	3.033(2)	3.053(3)	3.160(2)	3.184(2)	3.309(1)	3.322(1)
$2 \times$ X(1)–A(3)	2.968(2)	2.987(3)	3.077(2)	3.103(2)	3.244(1)	3.254(2)
X(2)–A(1)	2.712(6)	2.687(8)	2.84(1)	2.85(1)	2.99(1)	2.99(2)
X(2)–A(1)	2.739(7)	2.719(9)	2.89(1)	2.89(1)	3.08(2)	3.09(2)
X(2)–A(2)	2.898(6)	2.942(8)	3.03(1)	3.05(1)	3.16(1)	3.17(2)
X(2)–A(3)	2.784(6)	2.813(8)	2.90(2)	2.91(1)	3.06(2)	3.09(2)
X(2)–A(3)	3.193(6)	3.183(9)	3.23(1)	3.26(2)	3.34(2)	3.30(2)
X(3)–A(1)	3.062(9)	3.06(1)	3.17(2)	3.19(2)	3.32(2)	3.32(2)
X(3)–A(2)	2.815(8)	2.80(1)	3.00(1)	2.96(2)	3.24(2)	3.22(2)
X(3)–A(2)	3.206(9)	3.18(1)	3.23(2)	3.20(2)	3.25(2)	3.22(2)
X(3)–A(3)	2.771(8)	2.76(1)	2.90(1)	2.91(2)	3.13(2)	3.07(2)
X(3)–A(1)	3.493(8)	3.51(1)	3.53(2)	3.58(2)	3.65(2)	3.63(2)
X(3)–A(2)	3.452(8)	3.48(1)	3.50(1)	3.58(2)	3.66(2)	3.64(2)
X(4)–A(1)	2.730(7)	2.728(9)	2.86(1)	2.85(1)	3.01(2)	3.00(2)
X(4)–A(1)	2.748(7)	2.756(9)	2.91(1)	2.93(1)	3.10(2)	3.11(2)
X(4)–A(2)	2.940(7)	2.929(9)	3.10(2)	3.07(1)	3.26(2)	3.31(2)
X(4)–A(3)	2.896(7)	2.903(9)	2.99(2)	3.02(1)	3.12(2)	3.09(2)
X(4)–A(3)	3.020(7)	3.025(9)	3.08(2)	3.10(2)	3.17(2)	3.15(2)
A–A	$\geqslant$3.520(2)	$\geqslant$3.518(3)	$\geqslant$3.625(3)	$\geqslant$3.631(3)	$\geqslant$3.828(2)	$\geqslant$3.758(2)
Angles (deg)						
X(1)–M–X(2)	106.6(2)	107.0(3)	107.0(4)	107.4(5)	107.4(5)	107.0(6)
X(1)–M–X(3)	110.7(3)	110.2(4)	111.0(5)	109.3(6)	109.6(7)	109.8(7)
X(1)–M–X(4)	110.5(2)	110.9(3)	110.2(5)	111.2(5)	110.8(6)	108.9(6)
X(2)–M–X(3)	109.9(3)	109.1(4)	109.5(7)	109.8(7)	109.8(8)	109.7(8)
X(2)–M–X(4)	108.9(3)	109.4(4)	109.0(6)	108.8(7)	108.7(7)	111.2(8)
X(3)–M–X(4)	110.1(3)	110.2(5)	110.1(7)	110.3(8)	110.5(8)	110.2(9)

Fig. 1. Exemplary illustration of a dianion $[M_2X_7]^{6-}$ and X(1) environment in compounds $A_6[M_2X_7]$ with $A \equiv K$, Rb, Cs, $M \equiv Mo$, W and $7X \equiv 4N$, 3O.

symmetry reduction leads, with respect to the above-mentioned problem, to the space group Pn (no. 7). In Pn the symmetry of the special position for the bridging ligand is lost and the tetrahedra are now twisted against each other. In one example, $K_6[Mo_2X_7]$, we tried to solve the structure as an inversion twin in the space group Pn (SHELXL-93 [5]). Some data are given in parentheses in Table 1. The isotropic thermal displacement parameter $B[X(1)]$ of the bridging ligand dropped particularly to 2.4(3) Å^2 in contrast to 3.9(2) Å^2 in $P2_1/n$. We found an angle Mo–X(1)–Mo of 173(2)° and a twin ratio of 0.50(4). In compounds with analogous anions $[M_2N_7]^9$ (M = Mo, W), LiBa$_4$[M$_2$N$_7$] [6] and LiBa$_4$[Mo$_2$N$_7$]BaCl$_2$ [7] the angle at the bridging ligand is about 174°. Because of the small distortion of the tetrahedra and the equivalent distribution of the twin domains we suppose a statistical, static distortion in contrast to a real twinning with large domains.

In no case could we distinguish between oxygen and nitrogen. This is analogous to results obtained by neutron diffraction on compounds such as Na$_3$[WO$_3$N] [8] and on the perovskite-type SrMoO$_{2.6}$^{15}N$_{0.4}$ [9], LaWO$_{0.6}$N$_{2.4}$

[10] and $SrTaO_2N$ [11]. So we expect statistical distribution of the ligands N and O.

The anion–alkali metal distances increase with increasing radii of the alkali metals and they are in the range of the sums of ionic radii [12] (Table 4). The environments of the alkali ions and of the ligands of M become more homogeneous with increasing alkali metal radius. So differences in distances become adjusted.

The average distances $\bar{d}(M-X_{term.}) = 1.8$ Å between transition metals and terminal ligands are 0.1 Å shorter than those $\bar{d}(M-X_{bridg.}) = 1.9$ Å to bridging ligands. This difference in bond length can be interpreted by the extended Zintl–Klemm concept [13] as in metallates containing "$[M_2O_7]$" units or the nitrido metallates with terminal and bridging ligands $Na_3[MN_3]$ ($M \equiv Mo$, W) [14,15] and $K_{14}[W_6N_{16}NH]$ [16], as we reported recently. According to this concept double-bond character to terminal atoms is expected.

Acknowledgments

References

[1] D. Ostermann, H. Jacobs and B. Harbrecht, Z. anorg. allg. Chem., 619 (1993) 1277.

[2] M. Monz, D. Ostermann and H. Jacobs, J. Alloys Comp., 200 (1993) 211.

[3] B.A. Frenz, in H. Schenk, R. Olthof-Hazekamp, H. van Konigsveld and G.C. Bassi (eds.), Computing in Crystallography, Delft University Press, Delft, 1978, p. 64.

[4] M. Jansen and R. Hoppe, Z. anorg. allg. Chem., 409 (1974) 152.

[5] G.M. Sheldrick, SHELXL-93, A Program for Crystal Structure Determination, Göttingen, 1993.

[6] P. Höhn, R. Kniep, J. Maier, Z. Naturforsch., 49b (1994) 5.

[7] A. Gudat, R. Kniep, J. Maier, Z. Naturforsch., 47b (1992) 1363.

[8] S.H. Elder and F.J. DiSalvo, submitted for publication in J. Solid State Chem.

[9] G. Liu, X. Zhao and H.A. Eick, J. Alloys Comp., 187 (1992) 145.

[10] P. Bacher, P. Antoine, R. Marchand, P. L'Haridon, Y. Laurent and G. Roult, J. Solid State Chem., 77 (1988) 67.

[11] F. Pors, P. Barcher, R. Marchand, Y. Laurent and G. Roult, Rev. Int. Hautes Tempér. Réfract., 24 (1987) 239.

[12] R.D. Shannon, Acta Crystallogr., A 32 (1976) 751.

[13] W. Bronger and P. Müller, J. Less-Common Met., 100 (1984) 241.

[14] D. Ostermann, U. Zachwieja and H. Jacobs, J. Alloys Comp., 190 (1992) 137.

[15] H. Jacobs and R. Niewa, Eur. J. Solid State Inorg. Chem., 31 (1994) 105.

[16] D. Ostermann and H. Jacobs, J. Alloys Comp., 206 (1994) 15.