Octahedral Cluster Compounds in the Tungsten Bromide Chemistry: MW_6Br_{14} and $M_2W_6Br_{14}$. The Crystal Structure of CdW_6Br_{14}

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The title compounds synthesized by solid state reaction crystallize in the cubic system ($Pn\bar{3}$) and are based on isolated $[(W_6Br_8{}^i)Br_6{}^a]^{2-}$ units. For $M^{II}W_6Br_{14}$ the units are linked together by divalent cations lying at octahedral sites of apical bromines belonging to six adjacent units. In the case of $M^I{}_2W_6Br_{14}$, the cohesion of the stacking is effected by pairs of monovalent counter cations located at two alternant triangular sites of apical bromines, each of them built of three adjacent units; these two triangular sites correspond to a split octahedral one occupied by the divalent cation in the structure of $M^{II}W_6Br_{14}$. The structure of CdW_6Br_{14}, refined from single crystal X-ray diffraction data, is detailed.

INTRODUCTION

We have previously reported on the progressive condensation of the $[Mo_6L_{14}]^{n-}$ units (L = halogen or chalcogen) by halogen/chalcogen substitution around the Mo_6 cluster.[1] All the compounds of this series have been synthesized at high temperature by the techniques of solid state chemistry. The first terms of the series correspond to compounds in which the Mo_6L_{14} units are isolated, for instance MMo_6X_{14} (M = divalent cation, X = halogen),[2] while the last ones correspond to the $M_xMo_6L_8$ Chevrel phases (M = monovalent, divalent or trivalent cation, L = chalcogen) for which the clusters are connected in three directions of the space *via* metal-metal intercluster bondings.[3] Be-

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tween these two limits, we have isolated several halides and chalcohalides, mainly in the Mo-Br-S system where all possible examples have been encountered.[4-7] Most of them exhibit original crystal structures with different types of linkage between the units, involving L^{a-a}, L^{i-a} and L^{i-i} ligands according to the Schäfer notation. No Chevrel phases based on the W_6 cluster have been isolated so far, in contrast to the first terms of the series, which can be obtained with the tungsten cluster. Closely-related compounds with (W_6S_8) cores, for instance $W_6S_8(py)_6$ and $W_6S_8(PEt_3)_6$, have been synthesized using the solution chemistry techniques.[8,9] Attempts to stabilize the tungsten Chevrel phases starting from these types of organo-mineral compounds have been unsuccessful so far. Our aim is to investigate in detail the W_6 cluster solid state chemistry and to compare it with the Mo_6 cluster chemistry. We present here the crystallochemistry of $M^I_2W_6Br_{14}$ and $M^{II}W_6Br_{14}$, and details of the crystal structure of CdW_6Br_{14} refined from single crystal X-ray diffraction data.

EXPERIMENTAL

Synthesis of $M^{II}W_6Br_{14}$ and $M^I_2W_6Br_{14}$

Compounds of the two series have been synthesized from stoichiometric amounts of MBr or MBr_2, WBr_5 and W, heated in sealed silica tubes at a temperature range of 700 – 800 °C.. They crystallize in the cubic system and are isotypic with the corresponding $M^{II}Mo_6Cl_{14}$ and $M^I_2Mo_6Cl_{14}$, for which the crystal structures have been previously determined on single crystals.[2] The unit-cell variation of the compounds that we have isolated to date (M^{II} = Co, Mn, Cd, Ca, Eu, Sr; M^I = Li, Cu) is presented in Figure 1. It correlates well with the ionic radius of the counter cations.

Crystal Structure of CdW_6Br_{14}

The unit-cell constants of a CdW_6Br_{14} single crystal (parallelepiped, $0.14 \times 0.14 \times 0.09$ mm^3) have been calculated using a Nonius CAD-4 four-circle diffractometer (Mo Kα radiation) by least square refinement on a setting angle of 25 reflections with $7° < \theta < 20°$. They led to a cubic lattice ($a = 13.3126(4)$ Å, $V = 2359.3(1)$ Å^3, $Z = 4$). 3341 intensities have been measured at 295 K ($\omega - 2\theta$ technique) for $0 < h < 21$, $0 < k < 21$, $0 < l < 21$. Data have been corrected for Lorentz and polarization effects. After averaging ($R_{int} = 0.033$), 1360 independent reflections were conserved. 961 observed reflections with $I > 3\sigma(I)$ were used for refinement (34 parameters refined). $\mu = 54.14$ mm^{-1} and empirical absorption corrections were applied using the DIFABS program[10] ($T_{min} = 0.86$, $T_{max} = 1.96$). All the atoms were located by isotypy with $Cu_2Mo_6Cl_{14}$.[11] Positional parameters and the anisotropic thermal factors have been refined on F by full-matrix least-square techniques in the $Pn\overline{3}$ space group. Secondary extinction[12] has been applied (extinction coefficient : 1.9×10^{-8}). All the calculations were performed using the MOLEN package[13] on a Digital Micro VAX 3100 computer. The final reliability factor converged to $R = 0.044$, $R_\omega = 0.052$, $S = 1.019$ with $\omega = 4 F_o^2/[\sigma^2(F_o^2) + (0.05 F_o^2)^2]$ A final Fourier difference map revealed no residual peaks greater than 1 e Å^{-3}. The final atomic parameters and the interatomic distances and angles are given in Table I and Table II, respectively.

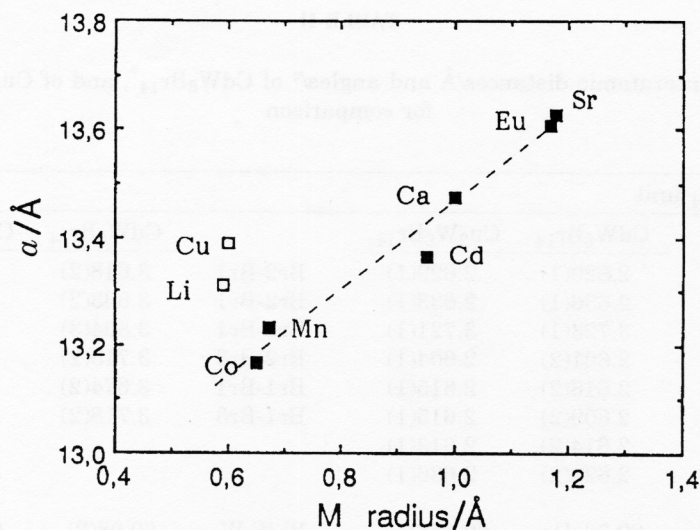Figure 1. Variation of the a unit-cell parameter *versus* the ionic radius of the M cation for the two M$^I_2$W$_6$Br$_{14}$ and M^{II}W$_6$Br$_{14}$ series. Errors are smaller than the symbol sizes.

TABLE I

Fractional atomic coordinates and equivalent isotropic displacement parameters B_{eq}/Å^2 of CdW$_6$Br$_{14}$.

Atom	Position	x	y	z	B^*_{eq}
W	24h	0.52434(4)	0.13434(4)	0.03018(4)	0.247(8)
Br1	24h	0.4220(1)	0.1870(1)	0.8715(1)	0.77(2)
Br2	24h	0.8198(1)	0.9197(1)	0.0650(2)	1.39(3)
Br3	8e	0.6398(1)	0.6398	0.6398	1.07(1)
Cd	4b	0	0	0	0.81(1)

$^*B_{eq} = 4/3 \, \Sigma_i \, \Sigma_j \, \beta_{ij} \, a_i \cdot a_j$

RESULTS

The structure of CdW$_6$Br$_{14}$ is based on the [(W$_6$Br$_8{}^i$)Br$_6{}^a$]$^{2-}$ units of D_{3d} symmetry, presented in Figure 2. These units are stacked like in rock-salt (Figure 3). The same units and the same stacking appear in the isostructural Cu$_2$W$_6$Br$_{14}$ compound, the structural refinement of which has been reported in detail elsewhere.[11]

TABLE II

Selected interatomic distances/Å and angles/° of CdW_6Br_{14}*, and of $Cu_2W_6Br_{14}$** for comparison

the W_6Br_{14} unit

	CdW_6Br_{14}	$Cu_2W_6Br_{14}$		CdW_6Br_{14}	$Cu_2W_6Br_{14}$
W-W[ii]	2.629(1)	2.629(1)	Br2-Br1	3.618(2)	3.656(2)
W-W[iii]	2.636(1)	2.633(1)	Br2-Br1	3.683(2)	3.665(2)
W-W[i]	3.723(1)	3.721(1)	Br2-Br1	3.804(3)	3.766(2)
W-Br1	2.601(2)	2.604(1)	Br2-Br3	3.715(2)	3.733(2)
W-Br1	2.616(2)	2.615(1)	Br1-Br1	3.674(2)	3.679(2)
W-Br1	2.609(2)	2.615(1)	Br1-Br3	3.718(2)	3.724(1)
W-Br2	2.614(2)	2.613(1)			
W-Br3	2.629(2)	2.636(1)			
Br1-W-Br1	89.70(4)	89.65(3)	W-W-W	60.08(2)	60.06(1)
Br1-W-Br1	178.69(7)	178.85(6)	W-W-W	59.83(3)	59.89(3)
Br1-W-Br3	90.30(4)	90.34(4)			
Br2-W-Br1	93.51(6)	92.15(5)			
Br2-W-Br1	87.56(5)	88.76(5)			
Br2-W-Br1	89.85(6)	89.26(5)			
Br2-W-Br3	90.24(5)	90.67(4)			

the cation environment

CdW_6Br_{14}		$Cu_2W_6Br_{14}$	
Cd-Br2	2.766(2)	Cu-Br2	2.378(2)
Br2-Cd-Br2	93.27(6)	Cu-Br2	3.864(2)
Br2-Cd-Br2	86.73(6)	Br2-Cu-Br2	120
Br2-Cd-Br2	180	Cu-Cu	3.062(3)
W-Cd	4.895(1)	W-Cu	4.240(1)

Symmetry codes: (i) -*x*, -*y*, -*z*, (ii) -*z*, -*x*, *y*, (iii) *z*, *x*–1, -*y*
*this work,
**Ref. 11.

These two structures differ only in the localization of the counter cation. In CdW_6Br_{14}, the cadmium lies at the origin of the unit-cell, at an octahedral site formed by six bromines belonging to six adjacent units (Figure 4a). In $Cu_2W_6Br_{14}$, the counter cation is located on the ternary axis, shifted from the origin to form Cu-Cu pairs (Cu-Cu distance = 3.062(3) Å) (Figure 4b). Each of these two copper atoms is located at two alternant triangular sites of apical bromines belonging to three adjacent units; these two triangular sites, building a Br_6 antiprism of D_{3d} symmetry, are in fact formed by splitting the octahedral site which is occupied by the cadmium in CdW_6Br_{14}.

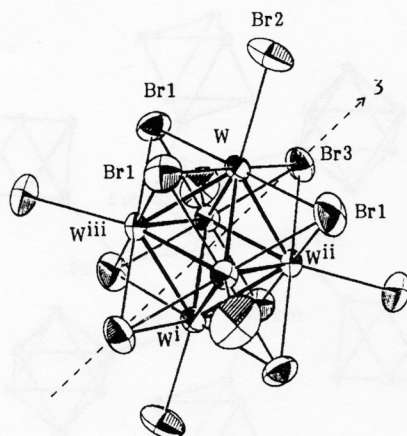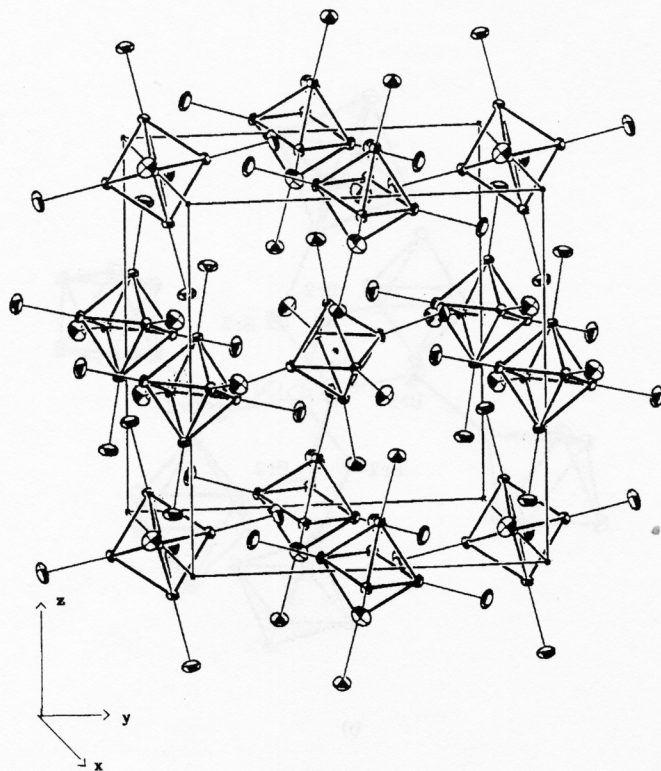Figure 2. The $[W_6Br_{14}]^{2-}$ unit. Displacement ellipsoids enclose a 95% probability.

Figure 3. The CdW_6Br_{14} unit-cell. For clarity, only the W and Br^a atoms are presented. Displacement ellipsoids enclose a 75% probability.
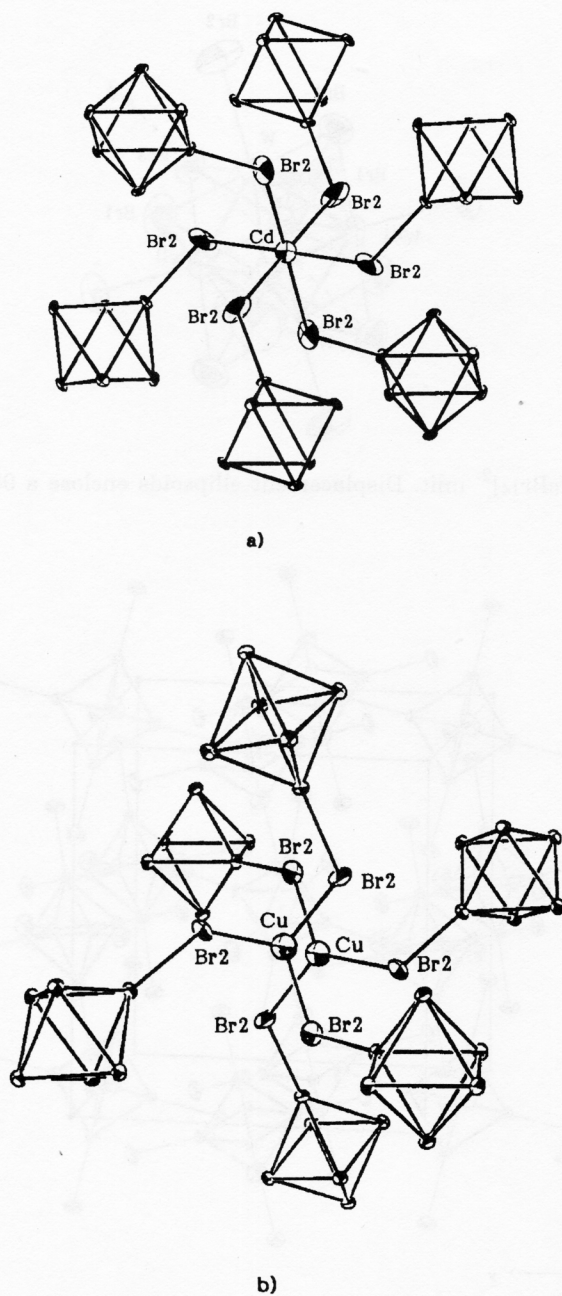
a)

b)

Figure 4. a) The cadmium environment, b) The two closest copper environment. Only the bromine atoms involved in these two coordination spheres are presented. Displacement ellipsoids enclose a 75% probability.

DISCUSSION

In the two structures, Cu$_2$W$_6$Br$_{14}$ and CdW$_6$Br$_{14}$, all the W-W and W-Br intra-unit distances are the same within the standard deviation, in good agreement with the same charge ($n = 2$) on the [W$_6$Br$_{14}$]$^{n-}$ anion. The W-W intracluster distances are similar to the corresponding distances in other tungsten octahedral cluster bromides with VEC (valence electron concentration) = 24, but smaller than in bromides with VEC = 23 (see Table III). This result is consistent with the presence of one more electron in the metal-metal bonding orbital. The W-X^a distances are longer than in compounds with VEC = 23 owing to the less important electrostatic attraction of the bromide by the more reduced W$_6$ cluster. The shortest interaction between the units appears through the Br1-Br2 contact: 3.487(2) Å and 3.509(2) Å in CdW$_6$Br$_{14}$ and Cu$_2$W$_6$Br$_{14}$, respectively, the latter being larger due to the presence of the Cu-Cu pair which increases the separation between the W$_6$Br$_{14}$ units.

A significant matrix effect appears for the bromine compounds as observed in Table III, when comparing the W-W intracluster distances in [(n-C$_4$H$_9$)$_4$N]$_2$W$_6$Br$_{14}$ and [(n-C$_4$H$_9$)$_4$N]$_2$W$_6$Cl$_{14}$: 2.635 Å and 2.607 Å, respectively. The latter distance is close to the one observed in CdMo$_6$Cl$_{14}$ and Cu$_2$Mo$_6$Cl$_{14}$: 2.607 Å and 2.611 Å, respectively,[2] indicating a similar size for the W$_6$ and Mo$_6$ cluster in the same ligand environment.

In conclusion, the first stage of our W$_6$ cluster study has enabled us to obtain easily, by solid state reaction the two M$^I_2$W$_6$Br$_{14}$ and M^{II}W$_6$Br$_{14}$ series in which the W$_6$Br$_{14}$ units are isolated. Another step involves the well known W$_6$Br$_{12}$ bromide, also prepared by solid state chemistry, in which the units are condensed in two directions of the space *via* four Br^{a-a} ligands.[16] All these tungsten bromides are isotypic to the corresponding molybdenum bromides. Attempts to isolate the next step of this progressive units condensation, by halogen/chalcogen substitution, are now in progress. The expected results, and their comparison with the corresponding molybdenum chemistry, could contribute to the explanation of the difficulty to obtain the tungsten Chevrel phases by solid state reaction.

TABLE III

Averaged distances/Å in some tungsten compounds based on
[W$_6$Br$_{14}$]$^{n-}$ and [W$_6$Cl$_{14}$]$^{n-}$ units for comparison

Compounds	Ref.	VEC	W-W intracluster	W-X^i	W-X^a
CdW$_6$Br$_{14}$	this work	24	2.632	2.614	2.614
Cu$_2$W$_6$Br$_{14}$	11	24	2.631	2.617	2.613
[(n-C$_4$H$_9$)$_4$N]$_2$W$_6$Br$_{14}$	14	24	2.635	2.628	2.587
[((C_6H$_5$)$_3$P)$_2$N]W$_6$Br$_{14}$	15	23	2.649	2.613	2.538
[(n-C$_4$H$_9$)$_4$N]$_2$W$_6$Cl$_{14}$	14	24	2.607	2.499	2.416

Supplementary Materials. – Crystallographic data (excluding structure factors which are available from the authors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-109/68-877. Copies of the data can be obtained on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (Fax: 44 (0) 1223-336033; E-mail: teched@chemcrys.cam.ac.uk).

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SAŽETAK

Oktaedarski klusteri u kemiji volframova bromida: MW_6Br_{14} i $M_2W_6Br_{14}$. Kristalna struktura CdW_6Br_{14}

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Spojevi navedeni u naslovu, priređeni reakcijama u krutom stanju, kristaliziraju u kubičnom sustavu ($Pn\overline{3}$) i temelje se na izoliranim jedinicama $[(W_6Br_8^i)Br_6^a]^{2-}$. U spojevima $M^{II}W_6Br_{14}$ te su jedinice povezane dvovalentnim kationima koji se nalaze u oktaedarskim položajima apikalnih bromovih atoma iz šest susjednih jedinica. Za spojeve $M^I_2W_6Br_{14}$ slaganje je postignuto parovima monovalentnih kationa koji su smješteni u dva naizmjenična trokutasta položaja apikalnih bromovih atoma, od kojih svaki potječe iz tri susjedne klusterske jedinice. Ova dva trokutasta položaja odgovaraju jednom pocijepanom oktaedarskom koji je zaposjednut dvovalentnim kationom u strukturi $M^{II}W_6Br_{14}$. Kristalna struktura spoja CdW_6Br_{14} određena je difrakcijom rentgenskih zraka na monokristalu.