It is interesting to note that the addition of H_2S to $[Au(CH_2)_2P(C_6H_5)_2Br]_2$ produces as the principal product the less symmetrical complex possessing four- and five-atom polysulfide bridges in good yield. In contrast, addition of H_2S to the Au^{II} benzoate derivative, $[Au(CH_2)_2P(C_6H_5)_2C_6H_5CO_2]_2$, produces a very symmetrical product containing two four-atom polysulfide bridges in nearly quantitative yield. The linear S—Au—Au—S geometry undoubtedly plays a role in determining the most stable ring size; however, the reasons underlying the preferential formation of the product containing two four-atom S bridges over that containing both four- and five-atom S bridges remain unclear at this point.

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A Molybdenum(II) Halide Cluster with (*E*)-Cinnamyl Alcoholate Ligands

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Abstract. Single crystals of disodium octa-μ_3-chloro-hexakis[(*E*)-cinnamyl alcoholato]-*octahedro*-hexamolybdate(II)–acetonitrile–(*E*)-cinnamyl alcohol (1/3/1), $Na_2[Mo_6Cl_8(OC_9H_9)_6].C_9H_9OH.3CH_3CN$, have been grown from acetonitrile. M_r = 1961·6, monoclinic, $C2/c$, a = 36·244 (7), b = 8·430 (2), c = 31·679 (5) Å, β = 127·48 (2)°, V = 7681 (3) Å^3, Z = 4, D_x = 1·696 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 1·268 mm^{-1}, $F(000)$ = 3896, T = 213 K, R = 0·0531 for 2905 independent reflections with $F_o > 4\sigma(F_o)$. The compound contains $[Mo_6Cl_8]^{4+}$-cluster units with six terminal (*E*)-cinnamyl alcoholate ligands, $d_{Mo—Mo}$ ranging from 2·596 (2) to 2·623 (2) Å, $d_{Mo—Cl}$ from 2·480 (4) to 2·508 (5) Å, $d_{Mo—O}$ from 2·012 (1) to 2·09 (2) Å. The sodium ions have distorted tetrahedral environment.

Introduction. The synthesis of salts containing octahedral Mo$_6$ clusters with methoxy, ethoxy or phenoxy ligands is well known (Nannelli & Block, 1968, 1969) and so are the crystal structures of the methoxy derivatives (Chisholm, Heppert & Huffman 1984). We are interested in the introduction of alcoholate ligands with delocalized π-electron systems into clusters. (*E*)-cinnamyl alcoholate was chosen as a simple model ligand.

Experimental. The compound was obtained by metathesis of $Na_2Mo_6Cl_8(OCH_3)_6$, prepared according to the procedure given by Nannelli & Block (1968), with (*E*)-cinnamyl alcohol. A solution of $Na_2Mo_6Cl_8(OCH_3)_6$ in (*E*)-cinnamyl alcohol was stirred at room temperature for 24 h. The methanol formed in the reaction distilled off continously under reduced pressure. Removal of excess (*E*)-cinnamyl alcohol left a yellow powder which was recrystallized from acetonitrile to form small orange columns. A suitable crystal of dimensions 0·10 × 0·17 × 0·25 mm was selected under petroleum, glued to the top of a 0·7 mm glass capillary and immediately transferred to an Enraf–Nonius CAD-4 diffractometer where it was cooled to 213 K in a cold N$_2$-gas stream. Graphite-monochromatized Mo $K\alpha$ radiation; cell parameters from 25 reflections ($19{\cdot}0 < 2\theta < 25{\cdot}2°$); systematic absences consistent with $C2/c$; total of 10 775 reflections measured with $3{\cdot}0 < 2\theta < 46{\cdot}0°$ in the range $-39 \le h \le 39$, $0 \le k \le 9$, $-34 \le l \le 34$; intensity variation of two standard reflections 1·09 ≥

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Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic displacement coefficients* (Å^2 × 10^3)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Mo(1)	2524 (1)	5840 (1)	390 (1)	36 (1)
Mo(3)	3105 (1)	7101 (1)	264 (1)	38 (1)
Cl(2)	2865 (1)	7436 (3)	− 650 (1)	46 (2)
Cl(4)	2109 (1)	10771 (3)	− 74 (1)	49 (2)
Na(*A*)*	6708 (5)	2714 (16)	3560 (5)	54 (2)
O(2)*	2069 (5)	4685 (21)	− 1213 (5)	36 (2)
O(3)	3776 (3)	6595 (10)	600 (3)	64 (2)
C(12)	2383 (4)	3642 (14)	1437 (4)	51 (3)
C(14)	2878 (3)	4548 (10)	2382 (3)	56 (3)
C(16)	3330	5842	3239	77 (4)
C(18)	2859	3562	3084	88 (5)
C(21)*	2049 (5)	5240 (24)	− 1641 (4)	45 (4)
C(23)*	1553	4145	− 2558	79 (6)
C(25)*	1055	3029	− 3497	94 (10)
C(27)*	220	3227	− 4065	95 (11)
C(29)*	672	4262	− 3171	81 (9)
C(22*A*)	1431	5088	− 2186	60 (4)
C(24*A*)*	871	3938	− 3089	51 (6)
C(26*A*)*	355	2758	− 3960	78 (9)
C(28*A*)*	57	4615	− 3653	114 (13)
C(31)	4048 (6)	7311 (18)	498 (6)	75 (4)
C(33)	4022 (5)	4859 (15)	39 (5)	59 (3)
C(35)	4419	4230	− 359	76 (4)
C(37)	4369	1604	− 696	102 (6)
C(39)	3969	2199	− 322	96 (5)
C(11*S*)*	5774 (7)	2950 (26)	3783 (8)	78 (10)
C(13*S*)*	5542	342	3321	118 (13)
C(15*S*)	5323	− 2329	2853	107 (13)
C(17*S*)*	4605	− 2702	1974	100 (12)
C(19*S*)*	4792	− 135	2397	89 (10)
C(2*L*)	5912 (6)	4924 (22)	2401 (7)	90 (5)
N(1)*	6085 (11)	2719 (38)	3680 (12)	93 (8)
C(11*L*)*	5405 (13)	4104 (44)	3573 (14)	96 (10)
Mo(2)	2286 (1)	6155 (1)	− 571 (1)	38 (1)
Cl(1)	1695 (1)	8207 (3)	− 1163 (1)	46 (2)
Cl(3)	3252 (1)	10015 (4)	406 (1)	49 (2)
Na*	6660 (5)	2791 (16)	3671 (5)	54 (2)
O(1)	2600 (2)	4017 (9)	851 (3)	43 (2)
O(2*A*)*	1948 (5)	4741 (22)	− 1235 (5)	36 (2)
C(11)	2253 (4)	3461 (14)	890 (5)	50 (3)
C(13)	2728 (4)	4444 (14)	1825 (4)	50 (3)
C(15)	3186	5739	2719	63 (3)
C(17)	3167	4753	3422	85 (5)
C(19)	2714	3459	2564	71 (4)
C(22)*	1575	4889	− 2174	60 (4)
C(24)*	1078	3784	− 3090	70 (8)
C(26)*	626	2750	− 3985	104 (11)
C(28)*	242	3982	− 3658	127 (14)
C(21*A*)*	1923 (5)	5313 (24)	− 1665 (4)	45 (4)
C(23)*A*)*	1362	4135	− 2563	79 (6)
C(25*A*)*	799	2926	− 3482	77 (8)
C(27*A*)*	− 16	3603	− 4046	90 (10)
C(29*A*)*	500	4783	− 3175	65 (7)
C(32)	4170 (5)	6302 (17)	198 (5)	70 (4)
C(34)	4136 (3)	3752 (11)	− 222 (3)	58 (3)
C(36)	4536	3156	− 596	99 (5)
C(38)	4086	1125	− 560	120 (6)
O(1*S*)*	6107 (5)	3685 (19)	3789 (6)	53 (4)
C(12*S*)*	5437	1862	3307	100 (11)
C(14*S*)*	5208	− 742	2843	70 (7)
C(16*S*)*	5021	− 3309	2419	92 (10)
C(18*S*)*	4490	− 1115	1963	93 (10)
N(2)	6126 (5)	4186 (16)	2773 (5)	84 (4)
C(21*L*)	5618 (9)	5785 (34)	1881 (11)	158 (9)
C(1*L*)*	5758 (12)	3396 (40)	3608 (13)	74 (9)

*S.o.f. = 0·5.

$I_o \geq 0.98$; ω—2θ scan with a width of (0·8 + 0·35tanθ)°, dectector-aperture width 1·8 mm + 1·05tanθ, 5310 unique reflections ($R_{\rm int}$ = 0·0321); 2905 observed reflections with $F_o > 4\sigma(F_o)$; linear absorption coefficient 1·268 mm^{-1}; no absorption correction applied. The structure was solved by direct methods (H atoms were allowed to ride on their parent C atoms at a fixed distance of $r_{\rm C—H}$ = 0·96 Å and with

Table 2. *Selected bond lengths* (Å) *and bond angles* (°)

Mo(1)—Mo(2)	2·623 (2)	Mo(1)—Mo(3)	2·596 (2)
Mo(1)—Mo(3')	2·598 (1)	Mo(2)—Mo(3)	2·623 (1)
Mo(1)—Cl(1')	2·494 (3)	Mo(1)—Cl(2')	2·489 (5)
Mo(1)—Cl(4')	2·496 (5)	Mo(2)—Cl(1)	2·492 (3)
Mo(2)—Cl(3')	2·508 (5)	Mo(2)—Cl(4')	2·483 (3)
Mo(3)—Cl(3)	2·496 (3)	Mo(3)—Cl(1')	2·490 (4)
Mo(1)—O(1)	2·020 (8)	Mo(2)—O(2)	2·086 (16)
Mo(3)—O(3)	2·022 (10)	Na—O(1*S*)	2·375 (30)
Na—O(2*A*'')	2·314 (23)	Na—N(2)	2·553 (17)
Na(*A*)—N(1)	2·464 (50)	Na(*A*)—O(2'')	2·278 (22)
Mo(1)—Mo(2')	2·596 (2)	Mo(3)—Cl(4')	2·501 (3)
Mo(2)—Mo(3')	2·607 (2)	Mo(2)—O(2*A*)	2·053 (15)
Mo(1)—Cl(3')	2·481 (3)	Na—O(1'')	2·368 (16)
Mo(2)—Cl(2)	2·504 (5)	Na(*A*)—O(1'')	2·289 (14)
Mo(3)—Cl(2)	2·480 (4)	Na(*A*)—N(2*A*)	2·441 (16)

Mo(2)—Mo(1)—Mo(3)	60·4 (1)	Mo(2)—Mo(1)—Mo(2')	90·8 (1)
Mo(2)—Mo(1)—Mo(3')	59·9 (1)	Mo(3)—Mo(1)—Mo(3')	90·3 (1)
Mo(1)—Mo(2)—Mo(3)	59·3 (1)	Mo(1)—Mo(2)—Mo(1')	89·2 (1)
Mo(1)—Mo(2)—Mo(3')	59·6 (1)	Mo(3)—Mo(2)—Mo(3')	89·5 (1)
Mo(1)—Mo([3)—Mo(2)	60·3 (1)	Mo(1)—Mo(3)—Mo(1')	89·7 (1)
Mo(1)—Mo(3)—Mo(2')	59·9 (1)	Mo(2)—Mo(3)—Mo(2')	90·5 (1)
O(1*S*)—Na—O(1'')	119·7 (7)	O(1*S*)—Na—O(2*A*'')	129·0 (10)
O(1*S*)—Na—N(2)	83·6 (7)	O(1'')—Na—N(2)	108·0 (7)
O(1'')—Na(*A*)—N(1)	123·2 (10)	O(1'')—Na(*A*)—O(2'')	92·1 (6)
O(1'')—Na(*A*)—N(2*A*)	114·6 (7)	N(1)—Na(*A*)—N(2*A*)	81·8 (9)
Mo(3)—Mo(1)—Mo(2')	60·3 (1)	Mo(1')—Mo(3)—Mo(2')	60·5 (1)
Mo(2')—Mo(1)—Mo(3')	60·7 (1)	O(1'')—Na—O(2*A*'')	94·3 (7)
Mo(3)—Mo(2)—Mo(1')	59·7 (1)	O(2*A*'')—Na—N(2)	123·1 (8)
Mo(1')—Mo(2)—Mo(3')	59·9 (1)	N(1)—Na(*A*)—O(2'')	112·0 (11)
Mo(2)—Mo(3)—Mo(1')	59·6 (1)		

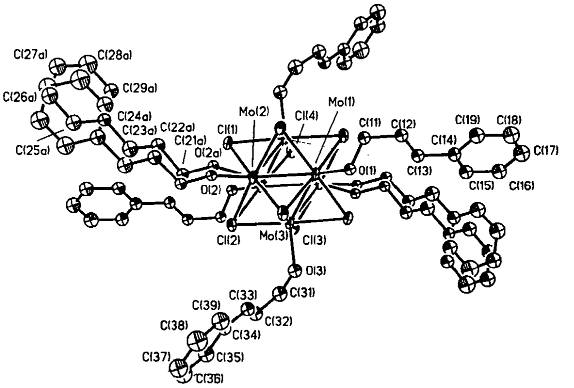

Fig. 1. View of the $[Mo_6Cl_8(OC_9H_9)_6]^{2-}$ anion. Two of the alcoholate ligands are disordered. Hydrogen atoms have been omitted for clarity.

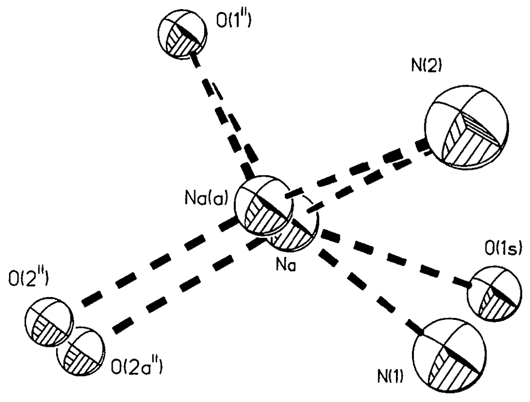

Fig. 2. Environment of the disordered sodium ion.

a fixed $U_{\rm iso}$ of 0·08 Å^2) and refined on F by the full-matrix least-squares method to $R = 0{\cdot}0531$, $wR = 0{\cdot}0421$, $w = 1/\sigma^2(F)$, $S = 1{\cdot}03$; $(\Delta/\sigma)_{\rm max} = 0{\cdot}000$; $(\Delta\rho)_{\rm max} = 0{\cdot}94$, $(\Delta\rho)_{\rm min} = -0{\cdot}56$ e Å^{-3}. All calculations were performed on a VAX 3200 using the *SHELXTL-Plus*88 package (Sheldrick, 1988); atomic scattering factors from *SHELXTL-Plus*88.

Discussion. Final atomic coordinates and equivalent isotropic atomic displacement factors are listed in Table 1.* The structure contains the centrosymmetric $[Mo_6Cl_8(OC_9H_9)_6]^{2-}$ anions shown in Fig. 1. To a first approximation the clusters together with the sodium ions form $PdCl_2$-type chains which are arranged parallel to [010] to form a hexagonal-rod packing. The $[Mo_6Cl_8]^{4+}$ core is coordinated by six terminal (*E*)-cinnamyl alcoholate ligands. Averaged values for $d_{\rm Mo—Mo} = 2{\cdot}607$ Å and $d_{\rm Mo—Cl} = 2{\cdot}493$ Å are comparable to those found for the $Mo_6Cl_{14}^{2-}$ anion in salts with monovalent organic cations like tetrabutylammonium or tetraphenylphosphonium (Perchenek & Simon, 1990), indicating that exchange of the terminal halide for alcoholate ligands does not lead to major changes of the bonding relationships in the $[Mo_6Cl_8]^{4+}$ unit; the averaged value for $d_{\rm Mo—O} = 2{\cdot}037$ Å is similar to the one in $[Mo_6Cl_8(OCH_3)_6]^{2-}$ (Chisholm, Heppert & Huffman, 1984). Individual bond lengths and angles are listed in Table 2. According to Fig. 2 the sodium ion is located in a distorted tetrahedron formed by two oxygen atoms of cluster-bonded (*E*)-cinnamyl alcoholate ligands, one nitrogen atom of a solvent acetonitrile or an oxygen atom of a solvent (*E*)-cinnamyl alcohol molecule, respectively. This disorder in the solvent coordination yields a simple explanation for the observed twofold disorder of the cluster-bonded alcoholate ligand which is nearest to those channels containing the disordered solvent molecules. The Mo—Mo distances in the cluster range from 2·596 (2) to 2·623 (2) Å. This differentiation of bond lengths is unexpected as the cluster has a closed-shell configuration with 24 electrons in metal–metal bonding states and should therefore be regular. Compounds containing distorted Mo_6 octahedra with 24 electrons have been reported before, *e.g.* $Mo_6Cl_{10}Y$ (Y = S,Se,Te), with $d_{\rm Mo—Mo}$ in $Mo_6Cl_{10}Se$ ranging from 2·598 (1) to 2·626 (1) Å (Perrin, Sergent, Le Traon & Le Traon, 1978). While the distortion of the Mo_6 octahedron in $Mo_6Cl_{10}Se$ is obviously due to interconnection of the clusters *via* bridging atoms, no such explanation can be thought of for the molecular title compound.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a complete list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54329 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Diaquabis(1,2-propanediamine)nickel(II) Dibromide Dihydrate

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Abstract. $[Ni(C_3H_{10}N_2)_2(H_2O)_2]Br_2.2H_2O$, $M_r = 438{\cdot}83$, monoclinic, $P2_1/c$, $a = 7{\cdot}510\,(9)$, $b = 16{\cdot}264\,(6)$, $c = 7{\cdot}632\,(3)$ Å, $\beta = 113{\cdot}26\,(6)°$, $V = 857\,(1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}70$ Mg m^{-3}, Mo $K\alpha$ radiation (graphite crystal monochromator, $\lambda = 0{\cdot}71073$ Å), μ(Mo $K\alpha$) = 5·77 mm^{-1}, $F(000) = 444$, $T = 293$ K. Final conventional $R = 0{\cdot}044$ for 943 observed reflections and 95 variables. The Ni—N distances, 2·106 (6) and 2·099 (6) Å, are typical for pseudo-octahedral coordination and the N—Ni—N bite angle is 83·3 (2)°. The Ni—N distances are slightly different due to the effect of the asymmetric *C*-substitution, showing a similar behaviour to the 2-methyl-1,2-propanediamine complexes.

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