and Steinfeld[11] in their work on the formation of the glycinate complexes of nickel(II) calculate a rate of water loss from the monoglycinatonickelate(II) complex 13 times greater than that of the aquo nickel ion and attribute the increase to a loosening of the water molecules in the primary hydration sphere due to the reduced net positive charge on the nickel ion. Similarly they found that the diglycinato complex loses water 3.3 times faster than the mono complex. The acetate ion could function in much the same way as the glycinate ion and thus increase the rate of reaction between nickel and Cu-EDTA. Thus $NiOAc^+$ should react 13 times faster than Ni^{+2} with CuL^{-2}. This factor is necessarily decreased by similar statistical and electrostatic effects as described for the forward rate. As before, quantitative calculations cannot be made but if the ratio of k_{Cu}/k_{CuOAc}, 2.9, is taken as a measure of these effects, the predicted ratio of k_{NiOAc}/k_{Ni} is 13/2.9, or 4.5. This is in good agreement with the observed value of 3.6. An analogous calculation for the ratio $k_{Ni(OAc)_2}/k_{NiOAc}$ gives a value of 3.3/2.1, or 1.6, which is in agreement with the observed value of 1.0.

Recently, however, Margerum and Eigen[12] have investigated the rate of replacement of a water molecule by an ammonia molecule in a number of nickel chelate complexes, including Ni-EDTA, and could not correlate these rates with the charge on the complexes. They suggest that the amine nitrogen groups influence the rate of water loss and that chelate rings may also have an effect. On this basis the effect of acetate appears anomalous.

Margerum and Zabin[13] have observed that, when the attacking metal ion is less labile than the metal ion originally bound to EDTA, hydroxide ion greatly accelerates the rate of exchange. They attributed this to an increased rate of water loss from the monohydroxo metal ion. The behavior of the acetate ion in this study parallels this behavior of hydroxide ion, increasing the rate of the less labile nickel ion. The magnitude of its effect is not as great, however.

The opposite effect of the acetate ion, *i.e.*, decreasing the rate of the more labile metal ion, may be indicative that the rate-determining step involves the breaking of original metal–EDTA bonds as in the reactions between copper(II) and the ethylenediaminetetraacetatozincate-(II),[14] -cadmate(II),[4,6] -plumbate(II),[15] and -cobaltate-(II)[16] ions. By analogy to the copper reaction with Ni-EDTA, it can be reasoned that the rate-determining step in these reactions involves the breaking of Zn–, Cd–, Pb–, and Co–EDTA bonds rather than Cu bond formation. Any further designation in rate-determining step in these systems is not possible since sufficient data are not available.

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Rhenium-Containing Complex Metal Oxides of the Formula Type $A^{II}_4Re^{VII}_2M^{II}O_{12}$

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The complex oxides of rhenium provide two new examples of layer structures based on the close packing of AO_3 layers. The composition of these oxides is $A_4Re_2MO_{12}$. The Re and the M cations occupy octahedral sites. A 12-layer stacking sequence is adopted for large A and relatively small M cations. For A = Ba, these include M = Mg, Ca, Co, Zn, Cd, and In; for A = Sr, M = Mg, Co, Ni, and Zn. When M is large, particularly relative to A, a 24-layer structure is assumed, which, however, is related to a simpler structure with an 8-layer stacking scheme. Compounds with this structure are $Ba_6Re_2O_{12}$, $Sr_5Re_2O_{12}$, $Sr_4Re_2CaO_{12}$, and $Ca_5Re_2O_{12}$. In both cases face sharing of filled octahedra is avoided by a systematic arrangement of empty octahedra.

Introduction

For complex metal oxides containing large cations in the ratio of one large cation to three oxygens, the structures are often conveniently described on the basis of close-packed AO_3 layers, where A is the large cation. Close-packed stacking of these layers leads to the formation of one octahedron of oxygens for each AO_3 unit. These octahedral sites may be occupied by metal ions or, in some cases, left vacant. A number of known examples and some new possibilities are discussed in a paper by Katz and Ward.[1] Reference was made in this paper to a series of compounds of general formula $A^{II}_4Re^{VII}_2M^{II}O_{12}$, for which early evidence indicated a 12-layer stacking sequence. In the present paper

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[1] L. Katz and R. Ward, *Inorg. Chem.*, **3**, 205 (1964).

the results of chemical and structural investigations on these and related compounds are reported.

Twelve-Layer Compounds

Preparation.—The source and purity of most of the reagents used have been described previously.[2] All other reagents were C.P. or better except for indium sesquioxide, which was prepared by dissolving the metal in nitric acid, evaporating to dryness, and then heating to decompose the nitrate.

The compounds of this series may be prepared by one or both of the following methods: the heating in air of an already prepared ordered perovskite with the general formula A_2ReMO_6[3] or the heating in air of the appropriate oxides with rhenium metal. In the first method the powdered perovskite is heated at 1000° in a zirconium silicate combustion boat. Within 15 to 30 min. the perovskite is changed to the new phase. Longer heating at this temperature does not change the product, although the compounds do volatilize at higher temperatures on prolonged heating. The compounds formed by this method are: $Ba_4Re_2MO_{12}$ with M = Mg, Cd, Co, Zn, or In and $Sr_4Re_2MO_{12}$ with M = Mg, Co, Zn, or Ni. The ordered perovskites which did not form these compounds when treated as described above are: $Ca_2Re^{VI}M^{II}O_6$ with M = Ca or Co; $A_2Re^{V}M^{III}O_6$ with A = Ba, Sr and M = Cr, Sc, or La; $Sr_2Re^{VI}M^{II}O_6$ with M = Ca or Sr; and $Ba_2Re^{VI}M^{II}O_6$ with M = Sr or Ba.

The compound Sr_2ReCaO_6 could not be oxidized under the given conditions and remained a black perovskite. The remaining perovskites formed products which were not identified.

The procedure for the second method of preparation consisted of mixing stoichiometric amounts of reactants by thorough grinding in an agate mortar. The powder was placed in a combustion boat and heated in air at 1000° in an electric muffle furnace. The sample was reground and reheated several times during the course of the preparation. The general equation is

$$4AO + 2Re + MO + 3.5O_2 \longrightarrow A_4Re_2MO_{12}$$

when A = Ba, M = Cd, Mg, Co, Zn, or Ca
when A = Sr, M = Co, Mg, Zn, or Ni

The compound $Ba_4Re_2InO_{12}$ was prepared as follows.

$$4BaO + 2Re + 0.5In_2O_3 + 3.25O_2 \longrightarrow Ba_4Re_2InO_{12}$$

Substitution of Tl_2O_3 for In_2O_3 did not yield a similar product. Attempts to prepare other 12-layer $A_4Re_2MO_{12}$ compounds were unsuccessful with the following combination of cations: A = Ba and M = Ba, Cu, Cr, Ni, Fe, Be, Sr; A = Sr and M = Sr, Cd, Fe, or Ca; A = Ca and M = Ca.

A number of the compounds with A = Ba could also be prepared by using barium peroxide as the source of barium. The use of the barium peroxide caused the reaction to proceed more rapidly and usually yielded a purer product. As an example, $Ba_4Re_2CoO_{12}$ prepared with barium oxide was contaminated with the perovskite Ba_2ReCoO_6 and with barium mesoperrhenate. However, when the preparation was made with barium peroxide, the desired product was obtained with no perovskite phase impurity and only a trace of barium mesoperrhenate.

The color of most of the compounds prepared having the 12-layer structure was red to deep orange when hot but yellow to yellow-green when cool. This color change is very characteristic of rhenium(VII) in octahedral coordination. The colors of $Ba_4Re_2CoO_{12}$, $Sr_4Re_2CoO_{12}$ (both black), and $Sr_4Re_2NiO_{12}$ (red-brown) were exceptions. This can be attributed to the cobalt or nickel in the octahedral position.

$Ba_4Re_2CoO_{12}$ dissolved readily in hydrochloric acid. The solution was analyzed for barium, by precipitation as the sulfate; for rhenium, by precipitation as nitron perrhenate; and for cobalt, by precipitation as the α-nitroso-β-naphthol complex.

Anal. Calcd. for $Ba_4Re_2CoO_{12}$: Ba, 46.8; Re, 31.8; Co, 5.0. Found: Ba, 46.5; Re, 32.0; Co, 4.8. The other compounds were not analyzed chemically but were identified by their X-ray powder diffraction patterns. The products appeared homogeneous under the microscope.

Structure Analysis.—The X-ray patterns were taken with a G.E. XRD-5 diffractometer, using Cu Kα radiation and a proportional counter. Lattice constants derived from powder data for the 12-layer compounds are listed in Table I. Intensities were measured by cutting out and weighing tracings of the peaks.

TABLE I

COMPOUNDS WITH A TWELVE-LAYER STRUCTURE

Compound	Lattice parameters, Å. a	c
$Ba_4Re_2MgO_{12}$	5.71	27.7
$Ba_4Re_2CaO_{12}$	5.82	28.3
$Ba_4Re_2CoO_{12}$	5.71	27.7
$Ba_4Re_2ZnO_{12}$	5.73	27.7
$Ba_4Re_2CdO_{12}$	5.80	28.1
$Ba_4Re_2InO_{12}$	5.78	27.9
$Sr_4Re_2MgO_{12}$	5.55	26.7
$Sr_4Re_2CoO_{12}$	5.55	26.8
$Sr_4Re_2NiO_{12}$	5.54	26.7
$Sr_4Re_2ZnO_{12}$	5.56	26.8

The most detailed X-ray analysis was done on $Ba_4Re_2CoO_{12}$. Its powder pattern could be indexed entirely on the basis of a hexagonal unit cell with $a = 5.71$ Å. and $c = 27.7$ Å. With three formula units of $Ba_4Re_2CoO_{12}$ per unit cell the theoretical density is 7.44 g./cc.; found: 7.30 g./cc. All reflections observed were consistent with the rhombohedral absence rule, $-h + k + l = 3n$. The a axis corresponds very well with the a axis of many close-packed BaO_3 layer structures. The c axis corresponds to a close-packed stacking of twelve such layers. In closest packing, only one stacking sequence for twelve layers has a rhombohedral lattice.[4] Using h to stand for a "hexagonal" layer (the two neighboring layers the same) and c to stand for a

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[2] J. Longo and R. Ward, *J. Am. Chem. Soc.*, **83**, 2816 (1961).

[3] A. W. Sleight, J. Longo, and R. Ward, *Inorg. Chem.*, **1**, 245 (1962).

[4] "International Tables for X-Ray Crystallography," Vol. II, Kynoch Press, Birmingham, England, 1959, pp. 342–354.

"cubic" layer (the two neighboring layers different), the sequence is hhcc—*i.e.*, hhcchhcchhcc for twelve layers. This sequence leads to a structure repetition in twelve layers. The octahedra of oxygens in this structure can be described as strings of three face-sharing octahedra (the middle octahedron of the three shares two faces) linked together by octahedra which share only corners. Thus a single octahedron which shares only corners links two strings of face-sharing octahedra.

In the trial structure, the three cobalt ions of the unit cell were placed in the octahedra which share corners only. The six rhenium ions were placed in the octahedra on both sides of the cobalt-containing octahedra. The octahedra which share pairs of faces were left vacant. The arrangement and occupancy of the octahedral sites are shown in Figure 1.

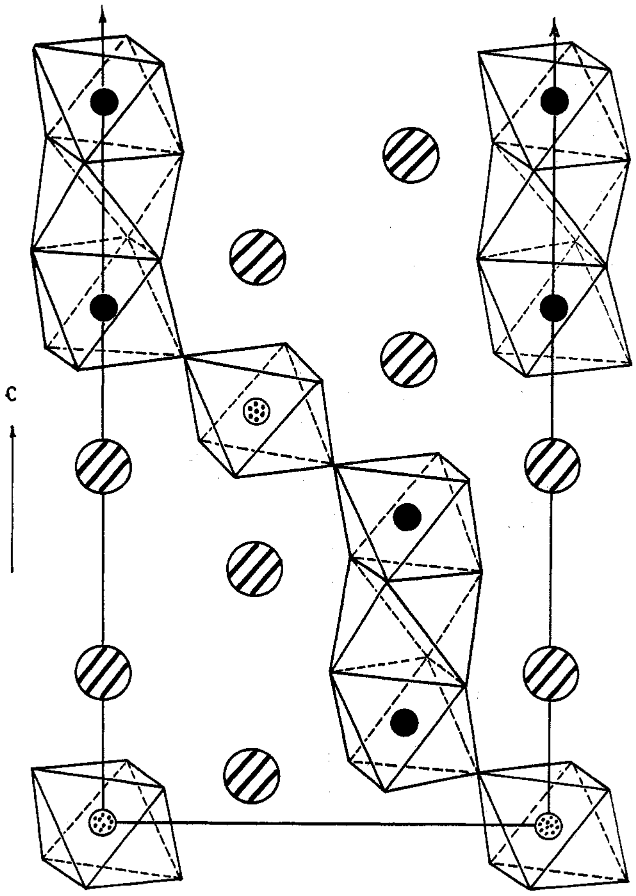

Figure 1.—Twelve-layer $A_4Re_2MO_{12}$ structure. Large striped circles are A cations, small solid circles are Re, small dotted circles are M cations. Ions shown lie in the (11·0) plane. The coordination scheme is shown for eight layers only; repetition occurs after twelve layers.

The space group for all close-packed arrangements with rhombohedral lattices is $R\bar{3}m$ and is the space group used for this structure. The theoretical intensities were calculated on an IBM 1620 computer with a program written specifically for the postulated structure. The two-dimensional electron density projection down the *b* axis, the 110 section of the three dimensional electron density, and the difference Fourier for this section were calculated on the 1620 in an effort to refine the atomic positions. In order to arrive at values for observed structure factors, for unresolved reflections, the observed intensities for these peaks were divided up in the same ratios as the calculated intensities. Perhaps partly because of this system for dividing up the unresolved intensities, the parameters determined from the electron density maps were not very different from those of the originally postulated positions. The values for position parameters are listed in Table II. The oxygens were not resolved on the Fourier maps, so no refinement of their positions was obtained. Agreement between observed and calculated intensities, Table III, was good: R', defined as $(\Sigma|I_{\text{obsd}} - I_{\text{calcd}}|)/\Sigma I_{\text{obsd}}$, = 0.18. There is thus good evidence for the general correctness of the structure proposed.

TABLE II

ATOMIC POSITIONS FOR $Ba_{12}Re_6Co_3O_{36}$

HEXAGONAL AXES

$(0, 0, 0;\ ^1/_3, ^2/_3, ^2/_3;\ ^2/_3, ^1/_3, ^1/_3) +$

		Initial	New[a]
6Ba	$0, 0, Z;\ 0, 0, \bar{Z}$	$Z = {}^7/_{24}$	0.293
6Ba	$0, 0, Z;\ 0, 0, \bar{Z}$	$Z = {}^3/_{24}$	0.126
6Re	$0, 0, Z;\ 0, 0, \bar{Z}$	$Z = {}^5/_{12}$	0.417 (unchanged)
3Co	0, 0, 0		
18O	$X, \bar{X}, Z;\ X, 2X, Z;\ 2\bar{X}, \bar{X}, Z$	$X = {}^1/_6$	
	$\bar{X}, X, \bar{Z};\ \bar{X}, 2\bar{X}, \bar{Z};\ 2X, X, \bar{Z}$	$Z = {}^{15}/_{24}$	
18O	$X, \bar{X}, Z;\ X, 2X, Z;\ 2\bar{X}, \bar{X}, Z$	$X = {}^1/_6$	
	$\bar{X}, X, \bar{Z};\ \bar{X}, 2\bar{X}, \bar{Z};\ 2X, X, \bar{Z}$	$Z = {}^{11}/_{24}$	

[a] The parameters, obtained from a Fourier section using powder data, were estimated in the third decimal place. Oxygen atoms were not resolved.

Intensity calculations were also made for Ba_4ReCdO_{12}, $Ba_4Re_2MgO_{12}$, and $Sr_4Re_2CoO_{12}$. Using the initial parameters of the cobalt compound, R' values for these three compounds are 0.26, 0.15, and 0.20. A rough test of the effect of shifting the Re z parameter in $Ba_4Re_2CdO_{12}$ was made by calculating R' for the case in which this parameter was increased by 0.003 and for the case in which it was decreased by 0.003. When z was increased, to 0.4197, R' dropped to 0.22; at z = 0.4167, R' = 0.26; at z = 0.4137, R' = 0.33. Increasing z_{Re} thus improves intensity agreement, though no systematic search for the best value for this change was made. The effect of increasing z_{Re} is to bring the pairs of rhenium atoms closer to the vacant octahedron (and further from the one occupied by the cadmium ion).

Attempts at growing single crystals of these 12-layer compounds using barium chloride as a flux were not successful. Very small single crystals of $Ba_4Re_2ZnO_{12}$ were obtained by heating the powder for 1 month at 1100°. The crystals were thin plates, light yellow in color. Precession photographs of the *hk*0 and *h*0*l* nets, using Mo Kα radiation, were obtained from one of these crystals. Due to the small size of the crystal, exposures of 6 days yielded only a few reflections (six *hk*0 and three *h*0*l*). These reflections were, however, consistent with the rhombohedral unit cell chosen.

Pseudo-Eight-Layer Compounds

Preparation.—During the study of the 12-layer compounds, a new series of complex oxides of rhenium was

Table III

X-Ray Data for the Twelve-Layer Compound, $Ba_4Re_2CoO_{12}$

HKL	I_{obs}	I_{cal}	d_{obs}	d_{cal}
101	9.5	8.6	4.870	4.870
012	9.4	11.8	4.667	4.643
006			4.619	4.619
104	15.3	15.6	3.864	3.864
107	101.6	90.0	3.087*	3.087
009				3.076
110	108.3	100.0	2.846	2.855
021	1.0	0.7	2.460	2.460
202				2.434
116	16.2	30.4	2.415*	2.427
1010**				2.415
024	8.0	8.7	2.325	2.319
0012			2.307	2.307
205	11.6	12.0	2.257	2.257
0111			2.241	2.241
027	53.7	50.7	2.092*	2.092
119				2.092
1013	2.8	5.8	1.955	1.955
211	1.9	1.7	1.857	1.857
122				1.850
0015				1.843
0210	19.0	18.0	1.836*	1.843
0114				1.836
214	2.8	4.2	1.802	1.802
1112			1.796	1.792
125	5.1	5.4	1.763*	1.770
2011				1.763
217	35.5	33.2	1.685	1.688
030	18.6	20.8	1.646	1.648
0213	2.8	4.0	1.614	1.611
036				1.552
1115				1.550
2110	21.6	30.8	1.545*	1.548
0117				1.545
2014				1.543
1211	7.1	5.1	1.500	1.500
220	17.1	18.7	1.426	1.426
213	3.1	4.1	1.403	1.403
312				1.363
226				1.362
2017	27.5	22.5	1.356*	1.358
1214				1.356
1118				1.353
137	17.0	14.0	1.287*	1.295
229				1.287
1310	8.8	15.8	1.226	1.228
1217				1.226
2212			1.214	1.212
2020			1.207	1.207
045	9.1	4.6	1.206	1.206
3111			1.203	1.203
1121			1.196	1.196
407	7.8	7.2	1.179	1.179
0024	4.1	5.4	1.153	1.153
1313				1.153
4010			1.126	1.126
3114			1.124	1.123
0318	13.0	7.7		1.123
0222			1.119*	1.121
324				1.119
1220			1.112	1.112
235	2.2	2.2	1.109*	1.111
0411				1.109
327	10.2	8.7	1.089	1.089
2023				1.082
1025	12.6	6.0	1.078*	1.080
140				1.078
1124	10.7	12.7	1.069*	1.069
4013				1.068
146				1.050
3210				1.049
3117	12.4	16.4	1.048*	1.048
0414				1.047
2218				1.045
0417	7.1	7.5	.9842	.9839
2314			.9828	.9832
1028			.9689	.9689
2221	1.7	0.4	.9657*	.9678
1127				.9644
057	3.8	3.7	.9527	.9526
330	5.6	5.1	.9506	.9509
0324	7.6	10.4	.9431	.9432
336			.9365	.9369
1415				.9365
0510	5.7	10.0	.9302*	.9308
2317				.9302
247	10.0	10.2	.9083	.9087
2224	11.0	15.1	.8964*	.8965
0513				.8964
2410			.8832	.8847
5014				.8838
1418				.8826
4022				.8811
514				.8802
3312	21.9	17.6		.8790
1031			.8768*	.8782
1130				.8774
2320				.8767
155			.8760*	.8762
4211				.8754
2128				.8736
517	9.8	8.5	.8656	.8659
5110				.8451
5017	10.8	11.7	.8441*	.8447
4214				.8443
0231				.8388
0033	10.3	8.6	.8393	.8384
1511				.8368
1421	5.6	0.2	.8337	.8344
2227				.8322
060	10.5	9.7	.8234	.8235
4217				.8098
1514				.8095
3318				.8086
434	40.0	38.9	.8088*	.8067
0426				.8062
2131				.8052
437	15.9	15.2	.7954	.7956
250	16.0	11.3	.7912	.7912
1424	43.3	49.6	.7872	.7874
256				.7798
4310	34.1	40.5	.7796*	.7793
1517				.7791

* Peak is broad.

** HKL with four numbers have L index greater than 9.

found which had the same general formula, $A_4Re_2MO_{12}$, but a different structure. The methods used for their syntheses were very similar to those for the 12-layer compounds. $Sr_4Re_2SrO_{12}$ and $Ca_4Re_2CaO_{12}$ could be formed by oxidizing the corresponding perovskites A_2ReAO_6. When the ordered perovskite Sr_2ReCdO_6 was oxidized, a compound with this new structure was obtained but with unexpectedly large cell dimensions. This suggested that some strontium was going into octahedral sites. Sr_2ReCaO_6 could not be oxidized under the conditions used. Ba_2ReBaO_6 could be oxidized, but the products were heterogeneous with large amounts of barium mesoperrhenate present.

The new phases $Ba_4Re_2BaO_{12}$, $Sr_4Re_2CaO_{12}$, $Sr_4Re_2SrO_{12}$, and $Ca_4Re_2CaO_{12}$ could all be prepared by heating stoichiometric mixtures of the appropriate reactants in air at 1000°. The general preparation techniques were the same as for the syntheses of the 12-layer compounds.

$Ba_4Re_2BaO_{12}$ was not obtained pure, but contained large amounts of barium mesoperrhenate. Using barium peroxide instead of barium oxide did not improve the purity. The use of strontium peroxide instead of strontium oxide in the preparation of $Sr_4Re_2SrO_{12}$ did yield a pure product and shortened the reaction time. With strontium carbonate the desired product was obtained, but it was not pure.

All members of this series are light yellow when prepared at temperatures below 1200°. Preparations at higher temperatures resulted in reduced products ranging in color from dark yellow to dark green. However, the powder patterns were the same as those of the oxidized products.

The compounds of this series are attacked by both acid and water. They do not appear to be affected by absolute ethyl alcohol or carbon tetrachloride.

Structure Analysis.—$Sr_4Re_2SrO_{12}$ was chosen for more detailed characterization since it could be prepared free from impurities. Except for a few weak low angle reflections, the powder pattern could be indexed using a hexagonal cell with a = 5.75 Å., c = 18.96 Å. The c axis length corresponds well to a close-packed stacking of eight close-packed SrO_3 layers. There were no systematic absences; the lattice type is therefore primitive.

By heating to 1350° for 1 day, some single crystals of $Sr_4Re_2SrO_{12}$ were obtained. The crystals were transparent, dark green, and in the shape of thin hexagonal plates. Reoxidation to the yellow color could be accomplished by heating in air for several days at temperatures between 700 and 900°. The crystals retained their shape during transformation.

A single crystal of $Sr_4Re_2SrO_{12}$ was examined using a precession camera and Mo Kα radiation. The $hk0$ and $h0l$ nets could be indexed on the basis of the hexagonal cell with a = 5.75 Å. and c = 19.0 Å. However, the hhl net could not be indexed completely; some weak additional reflections appeared which corresponded to the weak unindexed lines on the powder pattern. The additional reflections required a new a axis $\sqrt{3}$ times as long as the old and a new c axis 3 times the old, so that the new cell dimensions were a = 9.96 Å. and c = 56.9 Å. The reflections for the larger cell are consistent with the rhombohedral absence rule. Table IV gives the new cell dimensions for the compounds of this series.

TABLE IV

COMPOUNDS WITH A PSEUDO-EIGHT-LAYER STRUCTURE

Compounds	Cell dimensions, Å. a	c
$Ba_4Re_2BaO_{12}$	10.4	58.4
$Sr_4Re_2SrO_{12}$	9.96	56.9
$Sr_4Re_2CaO_{12}$	9.87	55.8
$Ca_4Re_2CaO_{12}$	9.56	54.8

Chemical analysis was carried out from the solution in hydrochloric acid by precipitating strontium as the sulfate and rhenium as nitron perrhenate.

Anal. Calcd. for $Sr_4Re_2SrO_{12}$: Sr, 43.7; Re, 37.2. Found: Sr, 42.7; Re, 37.4.

The density was determined pycnometrically using carbon tetrachloride as the displacement liquid. The theoretical density based on the above composition and the eight-layer hexagonal cell was 6.12 g./cc.; found: 6.14 g./cc.

Since the few reflections which required the larger cell were relatively weak, it is likely that the actual structure can be considered a superstructure of an 8-layer arrangement. There are six possible close-packed stacking sequences for ieght close-packed layers.[4] The only one of these which requires two, and only two, octahedra to be vacant in order to avoid face sharing of filled octahedra is ccchccch. This sequence, space group P6$_3$/mmc, was the one tested. However, in order to place the octahedral cations, the symmetry was reduced to space group P6$_3$mc. The arrangement and occupancy of the octahedral positions are shown in Figure 2. Intensity calculations were made with an IBM 7040 computer using a program written specifically for this structure. The observed and calculated intensities are compared in Table V, out to 2θ = 65°. The discrepancy factor based on intensities, R', for this set of data is 0.32 (based on structure factors it would be about one-half as large). The value of R' does indicate that the tested sequence is closely related to the actual (super) structure of this compound.

Discussion

The complex oxides of rhenium of the general formula $A_4Re_2MO_{12}$ whose preparation is described in this paper have been found to exhibit two different structure types, both apparently new examples of layer structures based upon the close packing of AO_3 layers. In both cases, face sharing of filled octahedra is avoided by systematic distribution of empty octahedra. One arrangement leads to a repetition in 12 layers; the other requires a repetition in 24 layers, although, except for a few weak reflections, the X-ray data can be interpreted quite well by an 8-layer sequence.

In the 12-layer compounds, the formation of $Ba_4Re_2InO_{12}$ is interesting since it is the only example in

Table V

X-Ray Data for Pseudo-Eight-Layer Compound, $Sr_5Re_2O_{12}$

HKL[a]	I_{obs}	I_{cal}	d_{obs}	d_{cal}
101	36.0	24.1	4.870	4.818
004			4.741	4.741
102	43.8	37.8	4.308	4.227
104	7.5	14.9	3.437	3.437
105	70.7	84.6	3.015	3.015
110	81.4	100.0	2.882	2.873
112	2.6	4.1	2.753	2.753
106	26.7	37.6	2.665	2.665
201	23.2	20.2	2.460	2.466
114				2.460
202	13.8	13.0	2.409	2.409
107			2.384	2.378
008			2.372	2.372
204	8.1	8.6	2.204	2.204
108	13.4	1.8	2.140	2.140
205	32.5	16.7	2.079	2.083
206	19.5	23.1	1.955	1.955
109			1.939	1.939
0010*	9.4	2.6	1.894	1.894
210			1.886	1.883
211			1.872	1.872
212	19.6	14.4	1.843	1.847
207			1.829	1.833
118			1.829	1.829
123			1.802	1.802
1010	24.5	18.4	1.770	1.770
214			1.745	1.745
208	0.9	1.3	1.714	1.714
215	25.4	34.0	1.685	1.685
300	18.8	21.7	1.660	1.660
1011	17.8	28.1	1.627	1.627
216			1.617	1.617
1110	24.0	10.1	1.581	1.581
0012			1.579	1.579
304			1.566	1.566
217			1.542	1.542
2010	10.4	13.3	1.506*	1.509
1012				1.504
218	2.4	1.2	1.472	1.474
306	3.0	0.0	1.470	1.470
220	11.1	18.6	1.436	1.438

[a] Indices correspond to the small, pseudo-cell.

* HKL with four numbers have L index greater than 9.

which the M cation is, presumably, not in a +2 oxidation state. It is possible that the indium is present in equal amounts of indium(I) and indium(III). This situation is not uncommon among indium compounds.

Each empty octahedron shares two faces with octahedra containing rhenium(VII). The empty octahedron is the center one of three face-sharing octahedra. The high charge on the rhenium ions makes the center octahedron an unlikely site for a cation. The compound $Ba_5Ta_4O_{15}$[5] provides a related example of a structure in which a vacant octahedron occurs between two face-sharing octahedra containing tantalum(V).

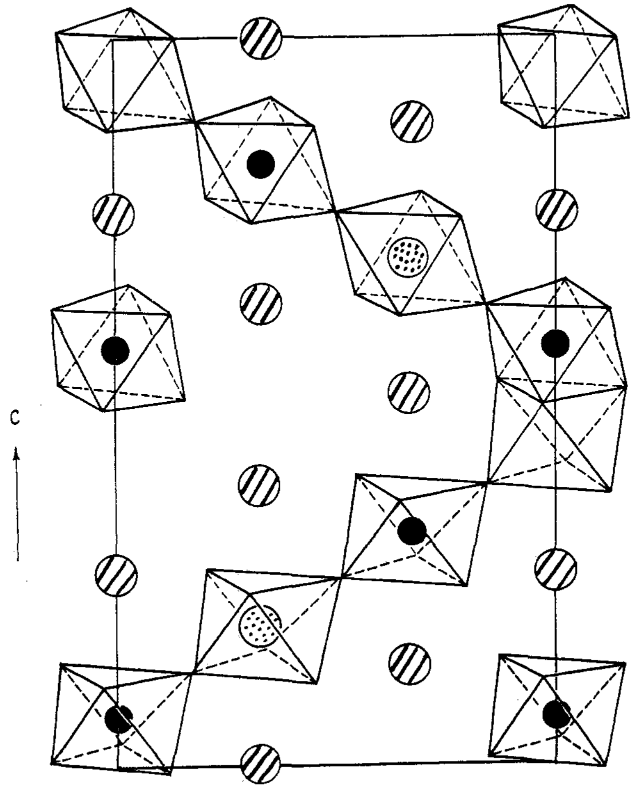

Figure 2.—Suggested 8-layer pseudo-cell for 24-layer $A_4Re_2MO_{12}$ structures. Striped circles are A cations; dotted circles are M cations (may be chemically the same as A); small solid circles are Re. Ions shown lie in (11·0) plane.

Which of the two structures is adopted by a particular compound $A_4Re_2MO_{12}$ depends on the relative sizes of the A and M cations. Thus, for example, $Ba_4Re_2CaO_{12}$ forms a 12-layer compound whereas $Sr_4Re_2CaO_{12}$ forms a pseudo 8-layer compound.

It is not yet known what changes in the 8-layer model are needed to account for the large (24-layer) cell observed. It is possible that distortion alone is responsible. Another possible explanation for the superlattice is based on the assumption that the large size of the cation taking up the octahedral sites causes strain which may be relieved by placing a rhenium atom in a tetrahedral site. The stacking of AO_3 layers, however, does not produce tetrahedral sites. By replacing one-third of the A cations by oxygen in one layer in a systematic way, an AO_5 layer is formed. Such a layer would provide an *a* axis of the required length. An AO_5 layer next to an AO_3 layer provides tetrahedral sites for a Re(VII) ion.

A third possibility to account for the superlattice involves filling one-third of the vacant octahedral sites with A cations. These A cations would come from an adjacent AO_3 layer, leaving an A_2O_9 layer (A_3O_9 less one A). Such a layer would again account for the *a* axial length. The pattern of filling octahedral sites would be repeated in 12 layers. This together with the

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(5) F. Galasso and L. Katz, *Acta Cryst.*, **14**, 647 (1961).

8-layer repetition scheme would lead to a 24-layer cell.

Other hypotheses to account for the superlattice can be advanced. These hypotheses are being examined.

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Some New Derivatives of the Octa-μ_3-chlorohexamolybdate(II), $[Mo_6Cl_8]^{4+}$, Ion[1]

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Attempts to prepare new compounds in which the six centrifugally directed Mo orbitals of $[Mo_6C_8]^{4+}$ are occupied by various ligands are described. Only in relatively few cases were stoichiometrically well-defined products obtained. These products were: $[Mo_6Cl_8L_6](ClO_4)_4$, $[Mo_6Cl_8L_2(CH_3SO_3)_4]$, and $[Mo_6Cl_{12}L_2]$, where L, in each type of compound, is either $(CH_3)_2SO$ or $HCON(CH_3)_2$. The infrared spectra of these compounds have been studied and the assignments show that the ClO_4^- ions do not become coordinated while all $(CH_3)_2SO$ and $HCON(CH_3)_2$ molecules and the $CH_3SO_3^-$ ions are coordinated to Mo atoms through their oxygen atoms. From the composition and infrared evidence regarding coordination, it appears that in all cases the Mo_6Cl_8 group binds just six additional ligands.

Introduction

The preparation of compounds containing molybdenum and tungsten in the formal oxidation state of II was first reported by K. Lindner and co-workers in the early 1920's.[2] The X-ray work of Brosset[3] established the presence of the unit $[Mo_6Cl_8]^{4+}$ in these compounds. More recent chemical studies by Sheldon[4] have shown that this $[Mo_6Cl_8]^{4+}$ ion is a persisting species which binds up to six additional donors (halide ions, water or amine molecules, etc.), presumably by means of the six centrifugally directed orbitals of the molybdenum atoms. The electronic structure of the $[Mo_6Cl_8]^{4+}$ ion has been treated on a molecular orbital basis by Crossman, Olsen, and Duffey[5] and by Cotton and Haas.[6] The presence of an empty, centrifugally directed, σ-orbital on each molybdenum atom is indicated by these MO treatments.

The related questions of the ability of these orbitals to bind electron pair donors, and the types of donors which might be preferred, naturally arise. While previous work[3,4] has shown that binding of additional ligands in these positions does occur, it seemed of interest to extend this line of enquiry using other ligands, especially those which can indicate by their infrared spectra the manner and strength of their attachment. This paper reports some results of such a study.

Experimental

Hexamolybdenum dodecachloride, Mo_6Cl_{12}, was prepared by a method which was essentially that of Sheldon.[4] The yield, based on molybdenum, was improved by having excess molybdenum in the long Vycor tube and passing the $MoCl_4$ over red hot molybdenum in a stream of nitrogen. The excess molybdenum was conveniently recovered when the Mo_6Cl_{12} was dissolved in hydrochloric acid.

Analyses for molybdenum were carried out by decomposing samples in ammoniacal peroxide solution and precipitating as lead molybdate. Other analytical results were obtained by S. M. Nagy, M.I.T.

$Mo_6Cl_{12}(DMF)_2$.[7]—Mo_6Cl_{12} was dissolved in a small volume of warm DMF. The solution was filtered and the product precipitated by slow addition of 2-propanol. Alternatively, the Mo_6Cl_{12} was dissolved in absolute ethanol, the solution filtered, and the product caused to precipitate by addition of a slight excess of DMF. The product was filtered, washed well with ethanol, then ether, and dried under vacuum.

Anal. Calcd. for $C_6H_{14}Cl_{12}Mo_6N_2$: C, 6.46; H, 1.27; N, 2.51; Mo, 51.61. Found: C, 6.20; H, 1.37; N, 2.26; Mo, 49.7.

$Mo_6Cl_{12}(DMSO)_2$.[7]—This was prepared in the same way as the DMF compound, using DMSO in place of DMF.

Anal. Calcd. for $C_4H_{12}Cl_{12}Mo_6O_2S_2$: C, 4.15; H, 1.05; Mo, 49.74. Found: C, 4.15; H, 1.12; Mo, 50.0.

$[Mo_6Cl_8(DMF)_6](ClO_4)_4$.—$Mo_6Cl_{12}$ (1 g.) was dissolved in 10 ml. of methanol and the solution added to a solution of 0.82 g. of $AgClO_4$ in 10 ml. of methanol. The mixture was stirred well and left to stand in the dark with intermittent agitation for 30 min. The precipitated AgCl was filtered off and washed several times with 1-ml. portions of methanol. DMF (1 ml.) was added to the combined liquors, and the precipitated product was filtered

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[1] This work has been supported by the U. S. Atomic Energy Commission.

[2] *Cf.* N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, 1950, Vol. II, pp. 1061–1066, for a summary of the literature up to 1946.

[3] C. Brosset, *Arkiv. Kem. Min. Geol.*, **20A**, No. 7 (1945); **22A**, No. 11 (1946).

[4] J. C. Sheldon, *J. Chem. Soc.*, 1007, 3106 (1960); 4183 (1963); 1287 (1964).

[5] L. D. Crossman, D. P. Olsen, and G. H. Duffey, *J. Chem. Phys.*, **38**, 73 (1963).

[6] F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 10 (1964).

[7] In this paper DMF represents dimethylformamide and DMSO represents dimethyl sulfoxide.