

data available also support small difference in Pt(II)-Cl and Pt(IV)-Cl distances.⁷

The strong absorption of light in this compound occurs with the electric vector along the Br-Pt(IV)-Br · · · Pt(II) · · · Br-Pt(IV)-Br · · · chains. This absorption is, then, related to the many other known compounds where a halogen bridge links two different oxidation states of the same element.⁸

(7) L. Sutton, *et al.*, "Interatomic Distances," The Chemical Society, London, 1958, pp. 100-101.

(8) See, for example, N. Elliot and L. Pauling, *J. Am. Chem. Soc.*,

Presumably this is a charge transfer spectrum of the type first described by Mulliken,⁹ and the strong polarization is evidence that the transfer is through the bridging halogen from Pt(II) to Pt(IV) and is accompanied by a greater contribution of bridge halogen bonding to Pt(II) in the excited state.

60, 1846 (1938); A. J. Cohen and N. Davidson, *ibid.*, **73**, 1955 (1951), and S. Yamada and R. Tsuchida, *Bull. Chem. Soc. (Japan)*, **29**, 894 (1956).

(9) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950) and **74**, 801, 811 (1952).

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Magnetic Compounds of Hexavalent Rhenium with the Perovskite-type Structure

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Phases of composition $A^{II}(B^I_n B^{VI}_n)O_3$ have been prepared by interaction of metal oxides under controlled conditions. When A^{II} is barium and B^{VI} represents the divalent cations Ca, Mg, Mn, Fe, Co, Zn and Cd, the compounds are all of the cubic ordered perovskite type. The compounds with manganese and iron are magnetic. Substitution of strontium and calcium in the A position when B^{VI} is iron leads to distorted structures apparently related to the cubic perovskite type. The approximate Curie temperatures for the magnetic phases have been determined.

The relationship of the structure of compounds such as $Ba_3TaO_{5.5}$,¹ Ba_2ZnWO_6 ² and Ba_2NaReO_6 ³ to the perovskite structure has been described in previous publications. The structure is indicated by the formula $A^{II}(B^I_n B^{VIII-n}_n)O_3$. The B cations are arranged in a simple cubic lattice joined through oxygens. The A cations are at the centers of the cubes. When $n = 1$ or 2, the different B cations assume alternate positions in the cubic lattice as indicated in Fig. 1. The length of the unit cell edge is twice that of the simple perovskite. The ordering of the B cations apparently depends on the charge difference between the two different B ions for in the compound $Ba(Fe_n Ta_{3-n})O_3$ (where $n = 3$) there is no evidence for the larger unit cell. The size factor also plays a part, however, for the compound $Ba(La_n Ta_{3-n})O_3$ ⁴ has the ordered perovskite structure. The system is rendered somewhat more flexible by the possibility of oxygen deficiencies.¹

It is interesting to note that of all of the compounds with this structure hitherto reported none contained more than one paramagnetic cation. In view of the current interest in magnetic interaction of cations in mixed oxides, it seemed to us that the ordered perovskite structure should provide some interesting phases if both B cations could be paramagnetic. The importance of having a large charge difference pointed to the use of such ions as Mo^{+3} , Re^{+6} , Os^{+6} in combination with suitable paramagnetic divalent cations of the first transition period. Some indications have been found that osmium and molybdenum are capable of forming such phases but the greatest success has been with hexavalent rhenium. This paper describes the preparation and characterization of some of these compounds.

(1) F. Galasso, L. Katz and R. Ward, *J. Am. Chem. Soc.*, **81**, 820 (1959).

(2) E. J. Fresia, L. Katz and R. Ward, *ibid.*, **81**, 4783 (1959).

(3) A. W. Sleight and R. Ward, *ibid.*, **83**, 1088 (1961).

(4) L. H. Brixner, *ibid.*, **80**, 3214 (1958).

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR $Ba(Co_n Re_{3-n})O_3$ INDEXED ON THE BASIS OF THE ORDERED PEROVSKITE STRUCTURE ($a = 8.086 \text{ \AA}$) AND A COMPARISON OF OBSERVED AND CALCULATED INTENSITIES

hkl	$\sin^2 \theta$, obsd.	$\sin^2 \theta$, calcd.	I , obsd.	I , calcd.
111	0.0270	0.0272	11.9	13.1
220	.0723	.0726	96.3	100.0
311	.0997	.0999	8.8	8.9
222	.1088	.1090	3.2	2.3
400	.1452	.1453	32.0	30.5
331	.1725	.1725	3.8	4.1
422	.2178	.2179	39.7	41.8
333	.2455	.2452	3.6	3.2
511				
440	.2906	.2906	19.4	18.2
531	.3179	.3178	3.7	3.1
620	.3632	.3632	17.6	18.2
444	.4356	.4358	5.2	6.2
711	.4634	.4631	2.1	1.8
551				
642	.5096	.5085	21.2	23.3
731	.5361	.5357	2.4	2.3
553				
800	.5812	.5811	3.8	3.4
822	.6536	.6538	13.2	15.1
660				
840	.7262	.7264	11.6	13.8
664	.7988	.7990	10.0	11.7
844	.8716	.8717	15.4	19.2
10,20	.9439	.9443	50.0	66.9
862				

Experimental

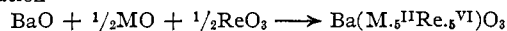
The barium oxide used was prepared by heating the peroxide (92.78%) at 950° in vacuum for 24 hrs. while the strontium oxide was prepared by heating the carbonate in a stream of hydrogen at 1150° for 48 hr. Nickelous oxide was prepared by heating the carbonate in air at 1250°, cobaltous oxide by heating the carbonate in a carbon dioxide atmosphere, manganese oxide by heating manganese dioxide in a stream of hydrogen at 900° for 36 hr. The calcium oxide, magnesium oxide, cadmium oxide, zinc oxide,

metallic iron and ferric oxide were C.P. chemicals or better. Rhenium metal (99.99%) was obtained from the Chase Brass and Copper Company.

The rhenium metal was converted to the heptoxide which in turn was converted to rhenium trioxide as described by Nechamkin and Hiskey.⁵

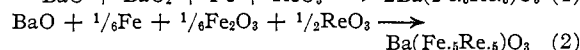
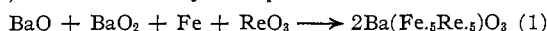
X-Ray diffraction data were obtained on a General Electric XRD-5 Diffractometer and a Philips X-ray camera of radius 57.3 mm. Six hour exposures were made using copper K_{α} radiation.

The reagents were mixed in proportions according to the equation



where M = Mg, Ca, Sr, Cd, Zn, Mn, Ni and Co.

The finely ground mixtures were heated in evacuated silica capsules at 900–1000° for about 24 hr. The products containing strontium and calcium gave X-ray patterns exhibiting only the lines of the ordered perovskite phase, while all the others showed the presence of barium mesoperhenate in varying amounts. None of the products containing nickel was free from nickel oxide. The introduction of iron (II) was carried out by these procedures



The latter method gave the better products.

Although the manganese compounds could be made from barium oxide and various proportions of manganese dioxide and rhenium metal in vacuum, pure phases could not be prepared in this way. The impurities present were manganous oxide and barium manganese oxide.

Phases giving a clean, ordered perovskite diffraction pattern were obtained from mixtures of potassium permanganate, barium oxide or peroxide and rhenium metal. The lattice parameter for this preparation was somewhat larger than those prepared by use of the oxides of manganese. It seems reasonable to suppose that the potassium ion replaces part of the barium in these preparations. By using strontium and calcium oxides in place of barium oxide, products were obtained which gave patterns closely resembling those of $\text{Sr}(\text{Fe}_{.5}\text{Re}_{.5})\text{O}_3$ and $\text{Ca}(\text{Fe}_{.5}\text{Re}_{.5})\text{O}_3$ except that the interplanar spacings were larger.

The preparation of ordered perovskite phases also was achieved from mixtures of barium oxide, sodium perhenate, manganese (II) oxide and manganese metal. This procedure was successful also using nickel (II) oxide and nickel metal in place of the manganese. The lattice parameter for the nickel preparation was larger than that of the product obtained by the procedure outlined above.

A very clean diffraction pattern was obtained from the cobalt compound. It has been indexed on the basis of a face centered cubic cell as shown in Table I. The observed intensities were obtained from the diffractometer tracing by weighing the areas under the peaks. The calculated intensities are derived from the ordered perovskite structure. An analysis of the cobalt compound $\text{Ba}(\text{Co}_{.5}\text{Re}_{.5})\text{O}_3$ gave barium (by precipitation as sulfate) 44.45%, rhenium (by colorimetric analysis as a thiocyanate complex) 29.44%, cobalt (by electrodeposition along with rhenium) 9.56%. The theoretical values are barium 44.60%; rhenium 30.25% and cobalt 9.56%.

The lattice constants for the entire series are given in Table II. They were calculated from the last five back reflections. The barium compounds all appear to be cubic, $\text{Sr}(\text{Fe}_{.5}\text{Re}_{.5})\text{O}_3$ appears to be tetragonal and $\text{Ca}(\text{Fe}_{.5}\text{Re}_{.5})\text{O}_3$ has been indexed as orthorhombic.

All of the products are black to dark blue, but the product containing nickel was a dirty green. They are not immediately attacked by water or concentrated hydrochloric acid but are slowly dissolved by concentrated nitric acid. They are taken up readily in an acidic solution of 30% hydrogen peroxide.

The iron and manganese substituted perovskites were ferromagnetic. The Curie temperatures are given in Table II. All of the compounds were very poor conductors with the exception of the iron compounds. The magnetic properties were determined using samples of approximately 0.2 gram. With the apparatus available it was possible to determine only the ferromagnetic transition temperature.

(5) H. Nechamkin and C. F. Hiskey, "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1960, p. 186.

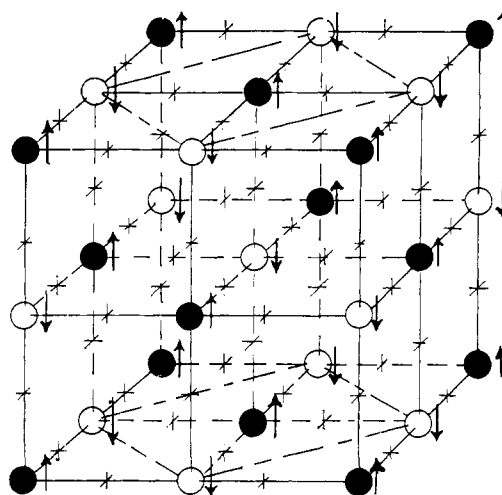


Fig. 1.—The ordered perovskite structure showing the positions of the B cations and oxide ions. The eight A cations which lie at the centers of the small cubes are omitted from the diagram. The relationship of the cubic to the orthorhombic cells is indicated: ●, Re^{VI} ; ○ B^{II} ; ×, oxygen.

The samples of $\text{Sr}(\text{Fe}_{.5}\text{Re}_{.5})\text{O}_3$ and $\text{Ca}(\text{Fe}_{.5}\text{Re}_{.5})\text{O}_3$ which were used to determine the Curie temperatures were contaminated with small amounts of Fe_3O_4 which could barely be detected from the diffraction patterns. A weak magnetic transition in these samples between 570 and 575°, however, established its presence.

TABLE II

LATTICE CONSTANTS OF $\text{Ba}(\text{M}_{.5}\text{Re}_{.5})\text{O}_3$ COMPOUNDS. CELL EDGES, Å.

Compounds		a	b	c	Curie Temp., °C.
$\text{Ba}(\text{Ni}_{.5}\text{Re}_{.5})\text{O}_3$	Cubic	8.04			
$\text{Ba}(\text{Fe}_{.5}\text{Re}_{.5})\text{O}_3$	Cubic	8.05			43
$\text{Ba}(\text{Mg}_{.5}\text{Re}_{.5})\text{O}_3$	Cubic	8.082			
$\text{Ba}(\text{Co}_{.5}\text{Re}_{.5})\text{O}_3$	Cubic	8.086			
$\text{Ba}(\text{Zn}_{.5}\text{Re}_{.5})\text{O}_3$	Cubic	8.106			
$\text{Ba}(\text{Mn}_{.5}\text{Re}_{.5})\text{O}_3$	Cubic	8.18			
$(\text{Ba K})(\text{Mn}_{.5}\text{Re}_{.5})\text{O}_3$	Cubic	8.23			-137
$\text{Ba}(\text{Cd}_{.5}\text{Re}_{.5})\text{O}_3$	Cubic	8.322			
$\text{Ba}(\text{Ca}_{.5}\text{Re}_{.5})\text{O}_3$	Cubic	8.356			
$\text{Ba}(\text{Sr}_{.5}\text{Re}_{.5})\text{O}_3$	Tetragonal	6.36		8.29	
$\text{Ba}(\text{Fe}_{.5}\text{Re}_{.5})\text{O}_3$	Tetragonal	5.70		8.05	43
$\text{Sr}(\text{Fe}_{.5}\text{Re}_{.5})\text{O}_3$	Tetragonal	5.57		7.89	128
$\text{Ca}(\text{Fe}_{.5}\text{Re}_{.5})\text{O}_3$	Orthorhombic	5.41	5.53	7.69	265

Discussion

The ordered arrangement of the two B cations is shown in Fig. 1. The large face-centered cubic cell is composed of eight small cubes in which the different B cations occupy alternate corners. The A cations, which are omitted from this figure, lie at the centers of the small cubes. The position of the oxygens is indicated by crosses. It can be seen that a smaller tetragonal cell can be used to describe this structure, and it is convenient to use this cell for the series $\text{M}^{\text{II}}(\text{Fe}_{.5}\text{Re}_{.5})\text{O}_3$ where $\text{M}^{\text{II}} = \text{Ba}, \text{Sr}, \text{Ca}$. The barium compound is apparently cubic, the strontium tetragonal and the calcium orthorhombic, but the relationship among them can best be seen by reference to the smaller cell. The c axis of the tetragonal cell corresponds to the edge of the large cubic cell. This is also taken as the long axis of the orthorhombic cell. No single crystals of any of these phases have been

obtained and the true symmetry remains a matter of conjecture.

The positions of the oxygens are not known but for lack of any evidence to the contrary (3) are assumed to be the same as in the ideal perovskite structure. The angle $\text{Re}^{\text{VI}}\text{-O-Fe}^{\text{II}}$ would be 180° . If the orthorhombic distortion found in the calcium compound should be analogous to that found in GdFeO_3 ,⁶ this angle would be somewhat smaller. In either case, this juxtaposition of the paramagnetic cations with oxygen would appear to be most favorable for the superexchange phenomenon. A qualitative explanation of the magnetic properties of the manganese and iron compounds can be given in terms of the spin moment orientation suggested in Fig. 1. The progressive rise in the magnetic transition temperature in the iron compounds from barium through strontium to calcium suggests a stronger coupling due to the closer approach of the B cations to the oxygens. The comparatively low transition temperature for the manganese compound may also be attributable to the greater separation of the B cations due in this case to the difference in the ionic radii of the manganese (II) and iron (II) cations.

The absence of any ferromagnetic properties

(6) S. Geller, *Acta Cryst.*, **9**, 563 (1956).

in the case of the cobalt compound might be rationalized by assuming that the d-orbital splitting led in this case to a wider energy gap between the three lowest levels and the others. This would lead to one unpaired electron in the Co^{2+} ion which with the Re^{6+} ion might give an antiferromagnetic system. Such an explanation does not seem to be compatible with other oxide systems containing cobalt (II), but perhaps the close proximity of hexavalent rhenium ions might have some influence on the nature of the splitting brought about by the oxide ions.

Attempts to prepare compounds containing cadmium in the A-position with rhenium (VI) and iron (II) in the B-position led to the formation of a strongly magnetic phase but with an unknown structure. A similar phase containing zinc in place of the cadmium has been prepared. The investigation of these phases is being continued.

Acknowledgments.—We are indebted to Dr. Lewis Katz for his assistance in the interpretation of the X-ray data and to Dr. T. Swoboda of the Central Research Department of the du Pont Company for making the magnetic measurements. Support for this research came from the National Science Foundation as a grant for undergraduate research participation.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS]

Molecular Association and Electronic Structures of Nickel(II) Chelates. I. Complexes of Pentane-2,4-dione and Some 1,5-Di-substituted Derivatives

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A new phenomenon which can, under certain circumstances, account for anomalous magnetic and spectral behavior of planar nickel(II) complexes has been discovered. This is molecular association of the solute molecules in solvents of low coordinating power. It is shown that the magnetic moment and spectrum of bis-(2,6-dimethyl-3,5-heptanedione)-nickel(II), $\text{Ni}(\text{DIBM})_2$, dissolved in toluene, are dependent upon both temperature and concentration. Spectral and magnetic data over a temperature range of $0\text{--}50^\circ$ and a concentration range of 0.24 to 0.010 *M* are reported and association constants and thermodynamic parameters of the association process evaluated therefrom. It is also shown that the more highly hindered, bis-(2,2,6,6-tetramethyl-3,5-heptanedione)-nickel(II), $\text{Ni}(\text{DPM})_2$, remains diamagnetic under all conditions. Preliminary results show that bis-(2,4-pentanedione)-nickel(II) is associated in non-coordinating solvents at ordinary temperatures, with significant concentrations of red monomer occurring only at temperatures near 200° and above. Possible structures for the polymeric species are considered.

Introduction

Nickel acetylacetonate (for which we shall henceforth write $\text{Ni}(\text{AA})_2$) has been the subject of considerable study over many years. The anhydrous solid has long been known to be paramagnetic (Asmussen¹ reported an effective moment of 3.04 B.M. at 20° ; Holm² has recently obtained a value of 3.27 B.M. at 27°). In benzene, chloroform and methanol solutions, the moments at 27° are 3.24, 3.12 and 3.11 B.M., respectively.² It is also well known that the anhydrous compound readily forms a dihydrate which has a moment of 3.15 B.M. at 26° .² Although the eye distinguishes easily between the emerald green of the anhydrous compound and the aqua color of the dihydrate,

there is actually little difference between the visible spectra of the two compounds.³ On comparing these spectra (considering both band energies and extinction coefficients) and the magnetic moments cited above with spectral and magnetic data⁴ for compounds known or reliably assumed to contain tetrahedrally coordinated nickel, it is clear that the latter does not occur in $\text{Ni}(\text{AA})_2$ under any known conditions.

Regarding the structure of $\text{Ni}(\text{AA})_2$ and its dihydrate there is the following information in the literature. Bullen⁵ has recently shown that $\text{Co}(\text{AA})_2 \cdot 2\text{H}_2\text{O}$ has a structure in which planar $\text{Co}(\text{AA})_2$ units with Co-O distances of 2.05 Å. bind

(3) G. Maki, *J. Chem. Phys.*, **29**, 162 (1958).

(4) F. A. Cotton and D. M. L. Goodgame, *J. Am. Chem. Soc.*, **82**, 2967 (1960), and references cited there.

(5) G. J. Bullen, *Acta Cryst.*, **12**, 703 (1959).

(1) R. W. Asmussen, Thesis, Copenhagen, 1944.

(2) R. H. Holm, Ph.D. Thesis, Massachusetts Institute of Technology, 1959.