TABLE IX

THERMODYNAMIC PROPERTIES OF EQUILIBRIUM SOLID II OF CARBONYL CHLORIDE IN GIBBS MOLE^{-1}

T, °K.	$C_{p\text{meas}}$	$C_{p\text{corr.}}$	S	$-(F - H_0^0)/T$	$(H - H_0^0)/T$
15	1.674	1.674	0.600	0.156	0.444
20	3.446	3.446	1.339	.354	0.985
25	4.844	4.844	2.264	.642	1.622
30	6.059	6.059	3.256	.994	2.262
35	7.173	7.173	4.276	1.390	2.886
40	8.028	8.028	5.292	1.814	3.478
45	8.718	8.718	6.278	2.255	4.023
50	9.344	9.345	7.229	2.705	4.524
55	9.907	9.910	8.146	3.158	4.988
60	10.389	10.386	9.030	3.610	5.420
70	11.228	11.253	10.698	4.504	6.194
80	11.931	11.994	12.251	5.376	6.875
90	12.567	12.695	13.704	6.221	7.483
100	13.191	13.408	15.078	7.038	8.040
110	13.763	14.094	16.389	7.829	8.560
120	14.273	14.730	17.642	8.594	9.048
130	14.755	15.349	18.846	9.387	9.459
139.19	15.177	15.898	19.910	9.999	9.911
140	15.213	15.947	20.005	10.057	9.948
142.09	15.308	16.070	20.243	10.203	10.040

The fact that the liquid comes to equilibrium with all solid phases enables the calculation of their free energies of transition.

Solid I = Solid III
ΔF = 57.1 cal. mole^{-1} at 139.19°K.
ΔH = 182 cal. mole^{-1}
ΔS = 0.90 gbs. mole^{-1}
$T_{(\text{transition})}$? = 202°K.

Since this temperature is far above the melting points it is evident that solid III is always metastable with respect to solid I at one atmosphere.

Solid II = Solid III
ΔH = 177 cal. mole^{-1}
ΔS = 1.08 gbs. mole^{-1}
$T_{(\text{transition})}$? = 164°K.

Since 164° K. is also far above the melting region, it is evident that no transition point exists between solids II and III at one atmosphere.

Solid I = Solid II
ΔF = 30.6 cal. mole^{-1}
ΔH = 5.4 cal. mole^{-1}
ΔS = −0.18 gbs. mole^{-1}

all at 142.09° K.

From Tables VII and IX, and the above data, $\Delta H_0^0 = -5.9$ cal. mole^{-1} and ΔF may be calculated for the above transition as a function of temperature. Since ΔH_0^0 is negative, it is evident that solid II would be stable at the absolute zero, where $\Delta F = \Delta H_0^0$, and that ΔF must pass through zero at some low temperature. Calculation gives $\Delta F = 0$ at about 40° K. This calculation is not very accurate because ΔH_0^0 happens to be such a small negative quantity, derived as a difference of large quantities involved in combining data on solids I and II. The estimated heat of transition at 40° K. is about 10 cal. mole^{-1}.

We thank L. E. Murch for assistance with the experimental measurements, D. S. Thompson for some of the calculations and R. H. Valentine for much assistance during the entire research.

[CONTRIBUTION FROM THE U. S. ARMY SIGNAL RESEARCH AND DEVELOPMENT LABORATORY, FORT MONMOUTH, NEW JERSEY]

Preparation and X-Ray Diffraction Data[1] for Some Rare Earth Stannates

BY CHARLES G. WHINFREY, DONALD W. ECKART AND ARTHUR TAUBER

RECEIVED OCTOBER 9, 1959

A series of eight rare earth stannates and yttrium stannate isostructural with pyrochlore have been prepared by solid state reaction at elevated temperatures. The general formula for these compounds is $A_2Sn_2O_7$ where A is Nd, Sm, Pr, La, Gd, Er, Eu, Yb or Y. Lattice constants calculated from X-ray powder diffraction data are given. The lanthanide contraction is demonstrated. A linear relationship is developed between lattice constant and ionic radius.

Oxide compounds isostructural with cubic pyrochlore have been the subject of recent investigations. Bystrom[2] first showed by X-ray diffraction powder diagrams that the paraelectric form of cadmium niobate has this structure. Interest in this compound and other isostructural oxides was stimulated as a result of the discovery by Cook and Jaffe[3a,3b] that it is ferroelectric below room temperature. Jona, Shirane and Pepinsky[4] have refined the structure reported by Bystrom with data collected on single crystals. Its space group is Fd3m with 8 formula weights per unit cell. The structure of $Cd_2Nb_2O_7$ is viewed as a three dimensional network of corner-sharing (NbO_6) octahedra. The Cd ions and the seventh oxygen ion occupy large open spaces in the network. The network of linked octahedra results in an Nb:O ratio of 2:6.

Investigations of systems yielding $A_2B_2O_7$ compounds isostructural with pyrochlore have been made by Roth[5] and Aleshin and Roy.[6]

Roth has prepared $La_2Sn_2O_7$, showing these to be cubic pyrochlores. Padurow and Schusterius[7] have referred to pyrochlore phases in the system La_2O_3–SnO_2–TiO_2. Dielectric measurements as a function of temperature have been made by Marzullo and Bunting[8] on several compositions studied

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[1] Data supplementary to this paper have been deposited as Document No. 6096 with the ADI Auxiliary Publications Project. Photoduplication Service, Library of Congress, Washington 25, D. C.

[2] A. Bystrom, *Arkiv Kemi, Mineral. Geol.*, **18A**, 21 (1944).

[3] (a) W. R. Cook, Jr., and H. Jaffe, *Phys. Rev.*, **88**, 1426 (1952) (b) W. R. Cook, Jr., and H. Jaffe, *ibid.*, **89**, 1297 (1953).

[4] F. Jona, G. Shirane and R. Pepinsky, *ibid.*, **98**, 903 (1955).

[5] S. Roth, *J. Research Natl. Bur. Standards*, **56**, 17 (1956).

[6] E. Aleshin and R. Roy, unpublished report, June. 1958.

[7] N. N. Padurow and C. Schusterius, *Ber. deut. Keram. Ges.*, **31**, 391 (1954).

[8] S. Marzullo and E. N. Bunting, *J. Amer. Cer. Soc.*, **41**, 40 (1958).

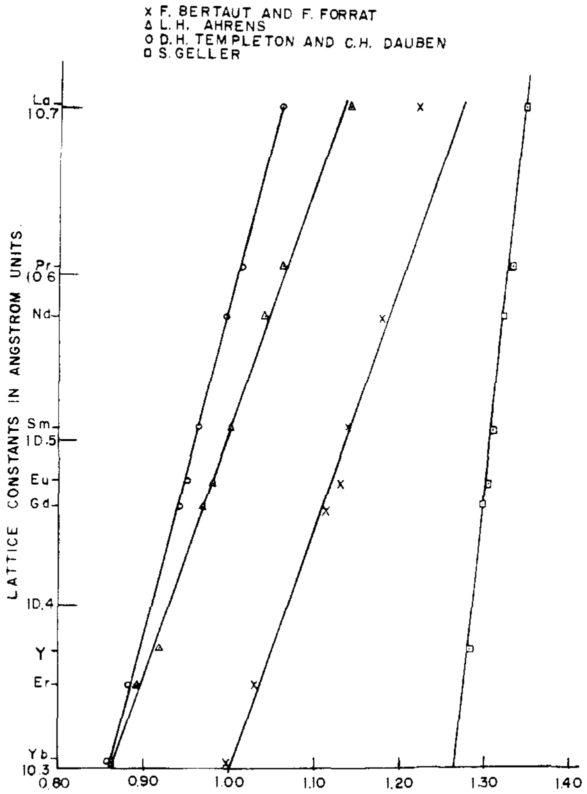

Fig. 1.

by Roth. They found a rather small change (±180 p.p.m./°C.) in the temperature coefficient of capacitance between −40 and 200°. The (±) refers to the change in sign of the coefficient as a function of composition. Thus it seems possible that rare earth stannates might offer a range of ceramic capacitors with a variety of temperature coefficients of capacitance.

Experimental

The constituent oxides used to prepare samples were SnO_2 obtained from Fisher Scientific Co., New York, and designated Certified Reagent, and rare earth oxides from Rare Earths Inc., Pompton Plains, New Jersey, specified 99.9% pure. The SnO_2 was dried at 600° overnight and kept in a desiccator until used. X-Ray diffraction powder patterns indicated that the rare earths as received were not well crystallized and were sometimes hydrated. These were heated in air for 5 hr. at 1000°. After cooling they were stored in a desiccator until used. No corrections were made for the presence of impurities. Sample weights ranged from 0.5 to 2.0 g. depending upon the availability of the rare earth oxide. After weighing out the calculated quantity of each constituent, the oxide powders were mixed together with a few drops of ethyl acetate in an agate mortar. The mixed oxides were pressed into $^1/_4$ inch diameter pellets at 20,000 psi.

Solid state reactions were carried out by heating the pellets on platinum foil in a platinum wound furnace. The temperature was measured with a Pt *versus* Pt–10% Rh thermocouple mounted with its tip just above the sample center. Firing temperatures ranged between 1450 and 1550°. Samples were held at the firing temperature for 5 to 20 hr. Subsequently, they were removed from the furnace and allowed to cool to room temperature. The product was ground to a fine powder and Debye–Scherrer powder diagrams were prepared. These were overexposed so that small amounts of unreacted SnO_2 could be detected. When incomplete reactions were detected, the samples were reground, repressed and fired for longer times at higher temperatures. Recycling procedures were similar to original firing schedules. In no instance was a sample fired at temperatures higher than 1550° nor for more than 20 hr.

When the X-ray film indicated no second phase and the sample was well crystallized, as defined by the sharpness of the X-ray diffraction lines, a diffractometer trace was made. Filtered CuK radiation was used. The scanning rate was $^1/_4$ deg./min. Traces for $Eu_2Sn_2O_7$ and $Yb_2Sn_2O_7$ were not prepared because of an insufficient quantity of sample. X-Ray data reported for these compounds were obtained from Debye–Scherrer diagrams made with a 114.6 mm. diameter camera.

Analysis for Sn was made using X-ray fluorescence analysis. The results were in satisfactory agreement with theoretical values based on the synthesis from SnO_2.

Eight different rare earth stannates and yttrium stannate were prepared. The general formula is $A_2Sn_2O_7$ where A is La, Pr, Nd, Sm, Eu, Gd, Er, Yb or Y. All of these compounds were found to be isostructural with pyrochlore. Lattice constants were obtained by plotting the lattice constant as determined from the last ten lines against $^1/_2[(\cos^2\theta/\sin\theta) + (\cos^2\theta/\theta)]$ and extrapolating to 90°. The probable error in lattice constants, including those obtained from powder film, was less than ± 0.003 Å. Agreement between the values of lattice constant for $La_2Sn_2O_7$ and $Nd_2Sn_2O_7$ obtained in this work and that of Roth[5] is excellent. However, the value obtained by Padurow and Schusterius[7] for $La_2Sn_2O_7$ is in poor agreement, see Table I.

TABLE I

Source	Lattice const. $La_2Sn_2O_7$ (Å.)	Lattice const. $Nd_2Sn_2O_7$ (Å.)
Padurow and Schusterius[7]	10.640	....
Roth[5]	10.702	10.568
This work	10.702	10.573

The lanthanide contraction is demonstrated when the lattice constants of the rare earth stannates are plotted as a function of rare earth trivalent radii, Fig. 1. The experimental lattice constants are plotted against the ionic radii of Bertaut and Forrat,[9] Ahrens,[10] Templeton[11] and Geller.[12] All adequately demonstrate the phenomenon. The relative linearity of the curves suggests that a Vegard's law relationship should exist between the end-member stannates.

A linear equation of the type

$$a_0 = x + ya + zb$$

similar to that employed by Bertaut and Forrat[9] was fitted to the data in the four curves, where

x = an arbitrary constant
a = ionic radius of the rare-earth trivalent ion
b = ionic radius of tetravalent tin (taken as 0.65 Å. for all eq.)

The four equations are:

Templeton and Dauben	eq. 1	$a_0 = 1.920a + 8.658$
Geller	eq. 2	$a_0 = 4.719a + 4.238$
Ahrens	eq. 3	$a_0 = 1.468a + 9.028$
Bertaut and Forrat	eq. 4	$a_0 = 1.802a + 8.471$

The radii used in the four equations differ considerably in absolute values since they are based on cations in several different coördinations: the radii of Templeton and Dauben[11]

TABLE II

Compound	Lattice const. exp., Å.	Limits deviation calcd. lattice const., Å.	
$La_2Sn_2O_7$	10.702	+0.009	−0.033
$Pr_2Sn_2O_7$	10.604	+ .006	− .011
$Nd_2Sn_2O_7$	10.573	− .011	+ .024
$Sm_2Sn_2O_7$	10.507	− .001	+ .018
$Eu_2Sn_2O_7$	10.474	.000	+ .033
$Gd_2Sn_2O_7$	10.460	.000	+ .011
$Y_2Sn_2O_7$	10.371	− .001	+ .017
$Er_2Sn_2O_7$	10.350	.000	− .023
$Yb_2Sn_2O_7$	10.304	+ .002	− .031

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(9) F. Bertaut and F. Forrat, *Compt. rend.*, **244**, 96 (1957).

(10) L. H. Ahrens, *Geochimica Cosochimica Acta*, **2**, 115 (1954).

(11) D. H. Templeton and C. H. Dauben, THIS JOURNAL, **76**, 5237 (1954).

(12) S. Geller, *Acta Cryst.*, **10**, 248 (1957).

and Ahrens[10] are for cations in 6-fold coördination while those of Bertaut and Forrat[9] are for 8-fold, and those of Geller[12] are for 12-fold coördination. No corrections in the above mentioned radii have been made for coördination.

The lattice constants found experimentally in this work and the deviations from constants calculated from referenced atomic radii are listed in Table II.

The data obtained with rare earth radii according to Templeton and Dauben[11] gives the closest agreement with experimentally determined lattice constants. Calculations based on the radii of Geller[12] and Ahrens[10] give fairly good agreement with experimental results. The radii of Bertaut and Forrat[9] give the poorest agreement.

The lattice constants calculated from equations 1 through 3 for each particular rare earth stannate are quite close, indicating that the ratios of analogous radii in each set are comparable. Thus the data support the conclusion that radius ratios for trivalent lanthanide ions are essentially unchanged by the particular coördination in the isostructural series used for radii determinations.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY, WORCESTER, MASSACHUSETTS]

Dipole Moments of Metal Chelate Compounds. IV. Metal Chelates of Analogs and Polar Substituted Analogs of Bisacetylacetoneethylenediimine[1,2]

BY RICHARD J. HOVEY AND ARTHUR E. MARTELL

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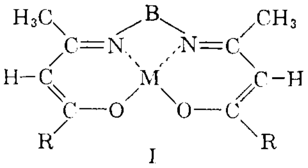
The dipole moments of some copper(II) and nickel(II) chelates of the tetradentate Schiff base ligands, bis-*p*-bromobenzoylacetonepropylenediimine, bis-*m*-nitrobenzoylacetonepropylenediimine, bistrifluoroacetylacetonepropylenediimine, bisbenzoylacetonetramethylenediimine and bisbenzoylacetone-1,3-diimino-2-propanol and of the vanadyl complexes of dibenzoylmethane and bisbenzoylacetonepropylenediimine have been measured. The observed dipole moments of the metal chelates which contain highly polar substituents such as trifluoromethyl and *p*-bromophenyl groups agree approximately with the values calculated for the theoretical structures in which these groups occupy terminal positions. Differences between the observed and theoretical values have been interpreted as due to resonance interaction between the polar groups and the conjugated metal chelate rings. The large dipole moment value of bisdibenzoylmethano-oxovanadium(IV) is indicative of the ionic character of the vanadium–oxygen bond perpendicular to the plane of the chelate rings. This is further reflected in the dipole moment of bisbenzoylacetonepropylenediimino-oxovanadium(IV) which is approximately one and a half to two Debye units higher than the dipole moments of the other metal chelates of this ligand.

In an earlier paper[3] the electric dipole moments of metal chelates prepared from bisacetylacetoneethylenediimine and some of its analogs were reported. The purpose of the present investigation was primarily to observe the changes in dipole moments resulting from the introduction of polar groups such as *p*-C_6H_4Br, *m*-$C_6H_4NO_2$, OH and CH_3 into the chelate molecules. For this purpose the metal chelates represented by I and listed in Table I were synthesized[4] and their dipole moments were measured. In chelates containing (a) a benzoylacetone residue, R = C_6H_5, (b) a *p*-bromobenzoylacetone residue, R = *p*-C_6H_4Br, (c) a *m*-nitrobenzoylacetone residue, R = *m*-$C_6H_4NO_2$ and (d) a trifluoroacetylacetone residue, R = CF_3. Where the bridge is (a) propylenediimine, B = $CH(CH_3)$-CH_2, (b) tetramethylenediimine, B = $(CH_2)_4$ and (c) 1,3-diimino-2-propanol, B = $CH_2CH(OH)CH_2$.



I

The dipole moments of the ligands, from which the metal chelates reported here were derived, have been reported in previous publications.[5,6]

Experimental

Procedure.—A description of the superheterodyne-beat apparatus and the procedure employed in measuring the dielectric constants of benzene solutions of the metal chelates have been given earlier.[5] The densities of these solutions were measured with a 25-ml. Rieschauer pycnometer. All measurements were carried out in a constant temperature oil-bath at 25°; for the determination of an individual dipole moment the temperature remained within ± 0.01°. The method of calculating the dipole moments from the experimental data and the significance of the parameters listed in Table I have also been given before.[5,7]

Induced Polarization.—Since all of the metal chelates reported here are highly colored, the molar refraction of each was taken as the sum of the individual bond refractions obtained from Vogel's table.[8] The molar refractions so calculated are considered to be quite reliable and differ from observed values usually by less than 1%.[9]

The atomic refractions used for four-coördinated copper (II) and nickel(II) are the same as those used by McCarthy and Martell[3] and are 14.5 ± 2 and 10.0 ± 2 cc., respectively. A value of 12 cc. has been allowed for both copper(II) and nickel(II) in similar four-coördinated complexes by Macqueen and Smith.[10] This represented the average difference between the observed molar refraction of several organic parent compounds and their corresponding metal chelates for which the measurements did not seem to be vitiated by anomalous dispersion.

No literature values are available on the atomic refraction of six-coördinated vanadium. However, the atomic refractions for four-coördinated Co, Ni, Cu and Pd range between 10 and 16 cc., with a general tendency for the

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[1] Abstracted from a dissertation submitted by Richard J. Hovey to the Faculty of Clark University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1958.

[2] This work was sponsored by the Office of Ordnance Research under Contract No. DA-19-020-ORD-3243.

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