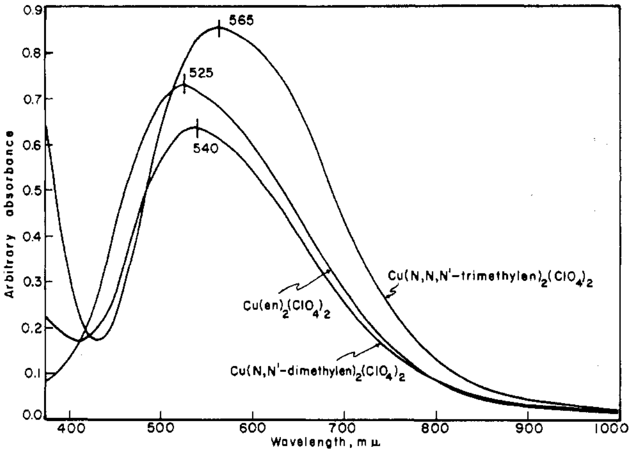

Figure 3.—Reflectance spectra of cupric perchlorate complexes.

strates that steric considerations predominate over inductive factors in the coordinating tendency of N-substituted ethylenediamines.[11,12]

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High Pressure Synthesis of New Compounds—Bismuth Diselenide and Bismuth Monosulfide Monoselenide

BY MEYER S. SILVERMAN

Received October 23, 1964

Two new compounds with empirical formulas BiSSe and $BiSe_2$ have been synthesized by high pressure, high temperature techniques. Another member of this series, BiS_2, was reported earlier.[1] Apparently, the highest Se:Bi or (S + Se):Bi ratio heretofore reported for either natural or synthetic materials is 3:2. The tetrahedral anvil apparatus[2] and procedure[3] used to synthesize the new materials have been described previously. The only change made was the addition of a boron nitride insulating sleeve between the compressed pellet and the graphite heater.

To obtain an essentially quantitative yield of $BiSe_2$, a 1:2.2 atomic ratio of Bi:Se was subjected to 45 kbars at 1280° for 5–10 min. For BiSSe, a mixture of Bi:S:Se in a 1:1.1:1.1 atomic ratio was held at 47 kbars and 1000° for 5–10 min. All of the starting materials were greater than 97% pure. The lustrous black crystals from each product mixture were purified by washing out the excess sulfur and selenium with CS_2, followed by an ether rinse and suction filtration.

TABLE I
X-RAY DIFFRACTION POWDER PATTERNS

BiS_2		BiSSe		$BiSe_2$	
d, Å.[a]	*I*[b]	*d*, Å.	*I*	*d*, Å.	*I*
4.13	40	4.18	40	4.7	65
				3.88	60
3.11	100	3.15	100	3.20	95
2.91	60	2.96	35	3.00	60
2.62	65	2.65	50		
2.53	35			2.58	60
2.49	35			2.49	60
2.43	35				
2.37	55			2.38	80
2.27	60	2.31	35[c]	2.34	70
		2.21	25		
2.01	55	2.04	40	2.06	100
1.96	50	1.97	40	1.99	70
1.93	50	1.92	30	1.97	90
1.88	70	1.85	25	1.89	70
				1.88	70
1.81	70	1.84	30	1.82	80

[a] Copper Kα radiation taken as 1.5418 Å. [b] The intensities of the diffraction lines were measured as peak heights above background using a densitometer. They are expressed as percentages of the intensity of the strongest line. [c] Broad line.

Anal. Calcd. for $BiSe_2$: Bi, 57.0; Se, 43.0. Found: Bi, 55.4, 55.4; Se, 42.2, 42.4. The weight loss of a $BiSe_2$ product on oxidation in pure oxygen supported this analytical result: loss calculated for $BiSe_2$ converted to Bi_2O_3, 36.5; found, 37.8. A small amount of spattering was probably responsible for the difference. *Anal.* Calcd. for BiSSe: Bi, 65.3; S, 24.7; Se, 10.0. Found: Bi, 64.6; S, 23.6; Se, 10.4. Considering limitations by the small product weight and difficulties in the analyses for these particular elements, the results are considered satisfactory. Also, there is a possibility that the actual stoichiometry can vary somewhat from the proposed formulas. Further, in the ternary compound it is likely that a range of $Bi(S,Se)_2$ compositions can be prepared.

Both products are stable in water, aqueous ammonia, and concentrated HCl at room temperature, but react rapidly and vigorously with concentrated HNO_3. Density determinations on both crude and purified milligram samples using a Berman density balance ranged from 7.23 to 7.79 g./cc. for $BiSe_2$, 6.35 to 6.72 g./cc. for BiSSe, and 6.02 to 6.08 g./cc. for BiS_2. The increase in density with increasing selenium content may indicate structural similarities for these compounds. As was the case with BiS_2, these materials when heated at 5°/min. in either O_2 or N_2 decompose, in an initial step, primarily to the corresponding trivalent bismuth compound. With $BiSe_2$, conversion to Bi_2Se_3 occurred at 275°, as indicated by the X-ray diffraction powder pattern of the residue. BiSSe decomposed above 240° to a material whose X-ray diffraction powder pattern was in agreement with that of the mineral guanajuatite, $Bi_2(S,Se)_3$.

The X-ray diffraction powder patterns obtained for $BiSe_2$ and BiSSe each contained over 60 lines; the strongest are listed in Table I. For comparison, the pattern obtained for BiS_2 is also included. Although these materials are not isomorphs, general agreements

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(1) M. S. Silverman, *Inorg. Chem.*, **3**, 1041 (1964).
(2) E. C. Lloyd, U. O. Hutton, and D. P. Johnson, *J. Res. Natl. Bur. Std.*, **63C**, 59 (1959).
(3) J. R. Soulen and M. S. Silverman, *J. Polymer Sci.*, **1**, 823 (1963).

apparent in the patterns may indicate structural similarities. Single crystal studies are now in progress on BiS_2 elsewhere,[4] and studies of the structures of the related compounds are planned.

Acknowledgments.—The author thanks Dr. J. R. Soulen for many useful discussions, Mr. E. A. Bruce for experimental assistance, Dr. W. Clavan and Mr. R. Hamilton for obtaining the X-ray patterns, and the analytical and shop groups for their help. This work was supported in part by the Office of Naval Research.

(4) Robert A. Jacobson, to be published.

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The Reduction of Potentiometric Hydrolysis Data[1]

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Received October 26, 1964

Potentiometric measurement of acidity is perhaps the most widely used method of investigating cation hydrolysis in aqueous solutions. Such measurements, usually employing the glass electrode, have become quite precise ($< \pm 0.1$ mv. or $< \pm 0.002$ pH unit) owing to the sensitive electrometers now in use. Variations in ionic activity coefficients are reduced to low values[2a] by maintenance of a relatively high and constant ionic strength compared with the changes in the concentration of acid and in the concentration of the metal ion being studied. Provided the salt bridge or the reference electrode used contains a solution similar in composition to the solutions being measured, the effect of liquid junction potentials, while appreciable, can be estimated with sufficient accuracy.[2b] Often the largest errors which can appear in such studies are introduced by unsuspected errors in the compositions of the solutions used or by the manner in which the experimental data are reduced to yield the amount of hydrolysis as a function of acidity and metal ion concentration.

It is the purpose of this note to describe briefly the method of hydrolysis data reduction which we have developed in the attempt to do justice to the precision which now appears attainable in such potentiometric measurements. This method was usually used to treat data from runs (titrations) well on the acid side of neutrality, as is usually true in the study of cation hydrolysis, and hence the concentration of OH^- could be neglected in the hydrolyzing solution. With obvious modifications, the same general procedure can be used in dealing with pH data from more basic media (*cf.* footnote *d*, Table I) or with potentiometric data wherein the concentration of some ion other than H^+ is being measured.

The conversion of the data for each point in a potentiometric titration to a value of the hydroxyl number ($\bar{n}$), the average number of OH^- ions per hydrolyzing metal ion M^{z+} in solution, and the corresponding acid concentration is simple in principle but involved and laborious in practice. The basic steps used (*cf.* Table I) are: (1) to compute, from the volumes and compositions of the initial cell solution and titrant solution, the acidity (m_H) which is expected in the absence of hydrolysis, (2) to compute from the measured e.m.f. the actual acidity (h), and (3) to compute from these two quantities and the concentration of the hydrolyzing cation the hydroxyl number ($\bar{n}$).

To obtain $\bar{n}$ and h values, it is desirable in addition to compute the concentrations of all ionic species in the solution since they affect the liquid junction potential which can in turn appreciably affect the measured e.m.f. values. The inclusion of liquid junction terms in the equation relating the cell e.m.f. to the acidity requires an iterative solution for the acidity (h). Finally, the completed computation often shows that systematic errors are present which significantly affect $\bar{n}$ in the important initial stages of hydrolysis; in this region the differences $h - m_H$ on which $\bar{n}$ depends are small and quite sensitive functions of the assigned values of the initial acidity ($m_{H,0}$), the reference acidity (h_r), and a liquid junction parameter (D_H). This necessitates corrections of these quantities and a recalculation of the data. In our hydrolysis studies, data reduction has, to an increasing extent, been performed with the aid of the 7090 computer.[3]

As the equation in Table I (2) indicates, the *changes* in observed cell potential are related to the *changes* in acidity and the *changes* in liquid junction potential which occur during a titration. The reference point, at which $\Delta E = 0$, is usually the point in the titration, at the beginning or the end, at which the acidity is highest. If hydrolysis of the cation being studied is negligible here, h_r may be taken as equal to m_H, otherwise h_r is determined indirectly (*vide infra*). The form in which the liquid junction potential is represented was derived from the Henderson equation[2c] when applied to titrations in which the ionic strength is held constant and the concentrations that vary are low compared with the inert electrolyte concentration. The coefficients, D_i, can be estimated from the equivalent conductance, λ_i, and charge (with sign), Z_i, of each ion

$$D_i = RT\lambda_i/(Z_iF\Sigma\, m_i\lambda_i) \qquad (1)$$

or they can be measured experimentally in titrations not involving hydrolysis. Strictly, the last term in the equation for ΔE should be of the form $\Sigma D_i(i_r - i)$, in which the actual concentration of each ion other than H^+ appears. Such usage would require a fore-knowledge of the hydrolysis reactions being investigated.

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(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

(2) C. F. Baes, Jr., and N. J. Meyer, *Inorg. Chem.*, **1**, 780 (1962): (a) footnote 16, p. 786; (b) Table I; (c) footnote 12, p. 783.

(3) The computer programs employed were written by R. J. McNamee of the Operations Analysis Division, Oak Ridge Gaseous Diffusion Plant.