

ducted in benzene and at ambient temperature for 24–72 hr.; benzene-insoluble crystalline products were obtained. Gas evolution was between 0.9 and 1.0 mole per mole of decaborane utilized.

Bis(N-methylformamide)decaborane (III) was an off-white solid which neither melted nor decomposed up to 250°. The infrared spectrum of III displayed an NH stretch at 3300 cm.⁻¹, a B—H stretching frequency at 2488 cm.⁻¹, and a C=O stretch at 1669 cm.⁻¹. Once again the B—H—B absorption was not present. (*Caution!*—The product stored in a vial, presumably under nitrogen, detonated spontaneously while awaiting elemental analysis.)

Bis(N-methylacetamide)decaborane (IV) was a white solid which decomposed at about 200° with no liquefaction to 305°. *Anal.* Calcd. for B₁₀H₁₂·2CH₃C(=O)NH(CH₃): B, 40.60. Found: B, 40.90. The infrared spectrum of IV displayed stretching frequencies at 3333 cm.⁻¹ (—NH), 2488 cm.⁻¹ (B—H), 1005 cm.⁻¹ (B—H deformation), and 1634 cm.⁻¹ (C=O); no B—H—B bridge absorption was evident. The rate of reaction of N-methylacetamide with decaborane was slower than the interaction of decaborane with N,N-dimethylformamide.

The proposed reaction for the above two materials is essentially the same as that shown previously.

In contrast to the previous products the interaction of 2-pyrrolidone with decaborane produced a 3:1 product with the evolution of 1 mole of gas per mole of decaborane utilized. The third mole of 2-pyrrolidone may be present as a mole of solvation, *i.e.*, (Pyr)₂·B₁₀H₁₂·Pyr, or of the form PyrH⁺[B₁₀H₁₁·Pyr₂]. The product, bis(2-pyrrolidone)decaborane pyrolydonate (V) starts to decompose at 200°; no liquefaction occurs to 305°. *Anal.* Calcd. for B₁₀H₁₂·3C₄H₇NO: B, 28.8. Found: B, 28.7. The infrared spectrum of V displays the NH stretch at 3356 cm.⁻¹, the B—H absorption at 2500 cm.⁻¹, and the C=O stretching frequency at 1656 and 1653 cm.⁻¹; no B—H—B bridge absorption was displayed.

In marked contrast to the tertiary and secondary amides, the primary amides (formamide, acetamide, adipamide, and acrylamide) underwent little or no reaction at ambient temperatures. At 40° acetamide interacted with decaborane to produce 2 moles of hydrogen per mole of decaborane consumed. A white solid product was isolated (VI) which did not melt to 250° but which did change color from white to orange as it was heated. The product was soluble in alcohol (with decomposition), ethyl acetate, dimethylformamide, pyridine (with formation of a yellow color), and diglyme (formation of a transitory blue color). The infrared spectrum of VI contains an —NH stretch at 3367 cm.⁻¹, a B—H stretch at 2513 cm.⁻¹, a B—H deformation at 1010 cm.⁻¹, and a C=O doublet at 1672 and 1650 cm.⁻¹. These data are consistent with the formation of a covalent compound; the B₁₀H₁₀²⁻ compound would be expected to show absorption peaks⁶ at about 2450 and 1034 cm.⁻¹. When the reaction was conducted at benzene reflux an orange product was isolated with

respective absorptions at 3356, 2525, and 1656 cm.⁻¹. The latter spectrum lacked definition about 1429 cm.⁻¹ and the C=O absorption was diminished.

Acknowledgment.—We wish to acknowledge the support of the United States Air Force in this research under Contract AF 33(616)5867 and the invaluable assistance of L. Adlum, R. Storey, and B. Lichstein.

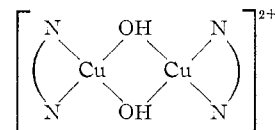
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Copper(II) Complexes of Secondary and Tertiary N-Substituted Ethylenediamines

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Received October 2, 1964

Several investigators^{2–4} have reported that secondary and tertiary ethylenediamines such as N-methyl-N,N'-diethyl-, N,N,N'-triethyl-, and N,N'-diisopropylethylenediamine form hydroxy-bridged dinuclear complexes of the type



in aqueous solutions instead of the normal bis and tris amine complexes. Measurements^{5–7} of the formation constants between Cu(II) and N-alkyl-substituted ethylenediamines demonstrate that the first and, especially, the second formation constant is lower than for ethylenediamine. Steric requirements of the ligands have been invoked to explain both the lower formation constants and formation of the dinuclear complexes, but since the majority of the work was done in aqueous solutions, the equilibria and complex formation are affected by solvation terms, ion-pair association, and entropy effects.^{8–10}

In order to resolve the apparent paradox between the instability of secondary and tertiary amine-metal complexes and amine basicity toward the proton, we^{11,12} have studied transition metal coordination complexes of N-substituted ethylenediamines. This paper re-

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TABLE I
 PROPERTIES AND ANALYSES OF THE Cu(II) COMPLEXES^a

Complex	Color	Molar conductance, mho ^b		Analyses ^d							
		CH ₃ NO ₂	CH ₃ OH	C, %		H, %		N, %		Br, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
[Cu(CH ₃ NHCH ₂ CH ₂ NHCH ₃)Br ₂]	Dark green	<12°	102	15.41	15.80	3.85	4.03	8.96	8.93		
[Cu{(CH ₃) ₂ NCH ₂ CH ₂ NHCH ₃ }Br ₂]	Very dark green	<50°	100	18.44	18.67	4.30	4.24	49.12	49.23
[Cu{(CH ₃) ₂ NCH ₂ CH ₂ N(CH ₃) ₂ }Br ₂]	Greenish black	<15°	96.5	21.21	21.48	4.71	4.99	8.25	8.49		
[Cu(C ₆ H ₅ NHCH ₂ CH ₂ NHC ₆ H ₅)Br ₂]	Brown		110.5	38.55	38.44	3.67	3.69	6.43	6.21		
[Cu(CH ₃ NHCH ₂ CH ₂ NHCH ₃) ₂ Br ₂]	Blue	78.3	108	24.00	24.31	6.00	6.07	14.02	14.33		
[Cu{(CH ₃) ₂ NCH ₂ CH ₂ NHCH ₃ } ₂ Br ₂]	Blue-green	85.2		28.08	28.05	6.55	6.52	37.39	37.20
[Cu(CH ₃ NHCH ₂ CH ₂ NHCH ₃) ₂](ClO ₄) ₂	Violet	168	181	21.89	21.98	5.48	5.54	12.78	12.74		
[Cu{(CH ₃) ₂ NCH ₂ CH ₂ NHCH ₃ } ₂ -(ClO ₄) ₂]	Violet	208		25.72	25.63	6.00	6.08	12.00	11.88		
[Cu(C ₆ H ₅ NHCH ₂ CH ₂ NHC ₆ H ₅) ₂ -(ClO ₄) ₂]	Brown		210	48.90	48.17	4.66	4.84	8.15	8.35		
[Cu ₂ {(CH ₃) ₂ NCH ₂ CH ₂ N(CH ₃) ₂ } ₂ -(OH) ₂](ClO ₄) ₂	Blue-violet	193	186	24.37	24.66	5.75	5.75	9.48	9.47		

^a All yields were approximately 70–90%. ^b The conductance measurements were made on $1 \times 10^{-3} M$ solutions in nitromethane and/or methanol. ^c The conductance values reported were measured 10 min. after mixing. The values increase with time, but very rapid measurements of the conductance in nitromethane demonstrate that the monoamine complexes originally are nonelectrolytes. ^d Microanalyses for C, H, and Br were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., whereas the N analyses were obtained in this laboratory with a Coleman Model 29 nitrogen analyzer.

ports the preparation, characterization, and spectra of several such complexes of Cu(II).

Experimental

Materials.—The N,N'-dialkylethylenediamines were dried over barium oxide, decanted, and then distilled two or more times from fresh barium oxide until the boiling points corresponded to literature values. N,N,N'-Trimethyl- and N,N,N',N'-tetramethylethylenediamine were distilled from sodium metal. Reagent grade methanol was refluxed over magnesium and then fractionated (b.p. 64.5°). Reagent grade N,N-dimethylformamide was dried for 24 hr. over barium oxide and then fractionated [b.p. 55° (20 mm.)]. The nitromethane was washed with 5% aqueous NaHCO₃, dried over anhydrous Na₂SO₄, and then distilled (b.p. 100–101°). Acetonitrile was purified according to the literature procedure.¹³ Other reagent grade materials were used without further purification.

Conductivity Measurements.—Conductivity determinations were performed at 24.6° using an Industrial Instruments, Inc., Model RC-16B conductivity bridge. The measurements were obtained in approximately $10^{-3} M$ solutions of nitromethane or methanol.

Spectral Measurements.—Spectra of finely ground solid samples were obtained with a Beckman DU spectrophotometer equipped with a standard Beckman reflectance attachment using U.S.P. MgCO₃ as a blank. Readings were taken at 10- μ intervals except in the regions of absorption maxima where readings were taken every 5 μ . Absorption spectra of the complexes in solution were obtained with a Cary Model 14 recording spectrophotometer in matched sets of 1- and 5-cm. quartz cells.

The infrared spectra were obtained with a Perkin-Elmer Model 21 spectrophotometer with the samples mounted as KBr disks and in Nujol mulls. The polystyrene spectrum was used for calibration.

General Preparation of the Complexes. (1) **Monoamine Complexes of CuBr₂.**—To a filtered solution of 0.02 mole (4.47 g.) of anhydrous CuBr₂ in 40 ml. of absolute ethanol was added slowly 0.02 mole of each of the ethylenediamines. Dark green precipitates usually formed immediately on complete mixing. The compounds were collected on a filter, washed with ether, and recrystallized from either a methanol-ether mixture or a dimethylformamide-ether mixture.

(2) **Bis-Amine Complexes of CuBr₂.**—Anhydrous cupric bromide (4.47 g., 0.02 mole) was dissolved in 50 ml. of absolute ethanol. The solution was filtered and then added to 0.04 mole of the appropriate ethylenediamine. The compounds, which crystallized on complete mixing, were collected on a filter and dried in a moisture-free air stream. The N,N'-dimethylen complex was recrystallized from a methanol-ether mixture whereas the N,N,N'-trimethylen complex decomposed in methanol. The latter complex was recrystallized from a DMF-ether mixture.

(3) **Bis-Amine Complexes of Cu(ClO₄)₂.**—Cu(ClO₄)₂·6H₂O (3.71 g., 0.01 mole) was dehydrated with 12 ml. of 2,2-dimethoxypropane while stirring for 45–60 min. The resulting solution was filtered to remove any undissolved impurities, diluted with 10 ml. of methanol, and added slowly to 0.02 mole of the appropriate ethylenediamine. Usually the complex precipitated immediately, but in some cases ether was added to promote crystallization. The compounds were recrystallized from hot methanol.

(4) **Attempted Syntheses of [Cu(N,N,N',N'-tetramethylen)₂](ClO₄)₂:** **Synthesis of Di- μ -hydroxo-bis(N,N,N',N'-tetramethylethylenediamine)dicopper(II) Perchlorate.**—Cu(ClO₄)₂·6H₂O (3.71 g., 0.01 mole) was dehydrated with 12 ml. of 2,2-dimethoxypropane. The solution was filtered, diluted with 10 ml. of absolute ethanol, and added to 0.02 mole (2.90 ml.) of N,N,N',N'-tetramethylen while stirring. The resulting blue-violet precipitate was collected and recrystallized from methanol or dichloromethane.

Anal. Calcd. for C₁₂H₃₄N₄Cl₂Cu₂O₁₀: C, 24.37; H, 5.75; N, 9.48. Found: C, 24.46; H, 5.75; N, 9.47.

A second preparation used [Cu(DMSO)₆](ClO₄)₂¹⁴ as the source of cupric perchlorate in an attempt to exclude water. The DMSO complex (2.5 mmoles) was dissolved in methanol and added to 12.5 mmoles of N,N,N',N'-tetramethylen. The resulting blue-violet compound was protected from moisture and recrystallized from methanol. Both the infrared spectrum and the nitrogen analysis (9.47% N) were identical with those of the above dinuclear complex.

Other preparative efforts using freshly distilled N,N,N',N'-tetramethylen and amine to copper(II) molar ratios of up to 25:1 always yielded the dinuclear complex.

Discussion

The compounds listed in Table I illustrate that cupric bromide forms both monoamine and bis-amine com-

(13) W. S. Muney and J. F. Coetzee, *J. Phys. Chem.*, **66**, 89 (1962).

(14) DMSO = dimethyl sulfoxide, (CH₃)₂SO.

plexes with all the N-substituted ethylenediamines¹⁵ investigated except N,N,N',N'-tetramethylen and N,N'-diphenylen.¹⁶ The copper(II) complexes were isolated from nonaqueous solutions, filtered in a closed system, and dried with air which had been passed through a P₄O₁₀ column. The dry compounds were not especially sensitive to atmospheric moisture, but they were decomposed in water, dimethyl sulfoxide, and acetonitrile.

The colors of the monoamine complexes of cupric bromide change progressively from a very bright green for the ethylenediamine complex to a greenish black for the N,N,N',N'-tetramethylen compound. The reflectance spectra of these complexes are given in Figure 1. The two absorption maxima shift systematically to

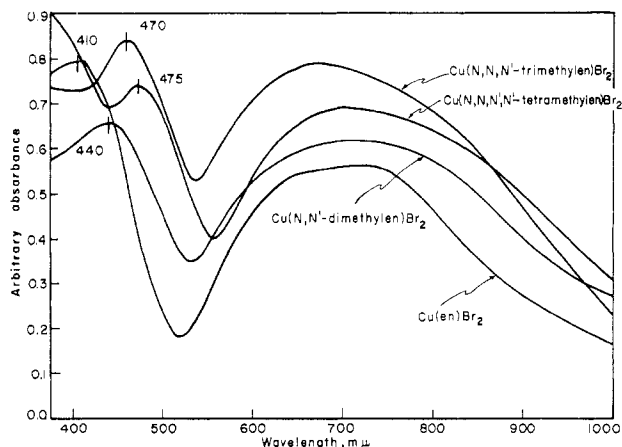


Figure 1.—Reflectance spectra of monoamine cupric bromide complexes.

lower energies as the number of N-methyl groups increases. Since the N-substituted ethylenediamines are somewhat more basic than ethylenediamine itself, the shifts to lower energies must result from the increased steric requirement of the N-substituted ligands. The absorption spectra indicate that the complexes assume six-coordinate structures in the solid state *via* bridging bromides between adjacent copper ions. Such tetragonal complexes should exhibit three or four¹⁷ electronic absorption bands, consistent with the observed spectra. The absorption spectra of the compounds dissolved in dichloromethane correspond very closely to the reflectance spectra, whereas extensive solvation occurs in methanol. The latter observation is confirmed by the high molar conductance values of the methanol solutions. In addition, the conductivity of the compounds increased with time in nitromethane.

The spectrum of Cu(N,N,N'-trimethylen)₂Br₂ differs markedly from those of Cu(en)₂Br₂ and Cu(N,N'-

(15) Although we did not attempt preparation of the N-methylen complexes of CuBr₂, the analogous complexes of Ni(II) have been prepared and there is no reason to suspect that the Cu(II) complexes could not be prepared also [S. F. Pavkovic, Ph.D. Thesis, The Ohio State University, 1964].

(16) The suffix en refers to ethylenediamine; *i.e.*, N,N,N',N'-tetramethylen = N,N,N',N'-tetramethylethylenediamine. This type of abbreviation will be used throughout this paper to designate the N-substituted ethylenediamines.

(17) The first definitive example of four bands was reported in 1962 [G. Basu, R. L. Belford, and R. E. Dickerson, *Inorg. Chem.*, **1**, 438 (1962)]. However, one must use very low temperatures to resolve the spectrum clearly into four bands. Two or three transitions are possible under the broad band at 600–800 mμ in our complexes.

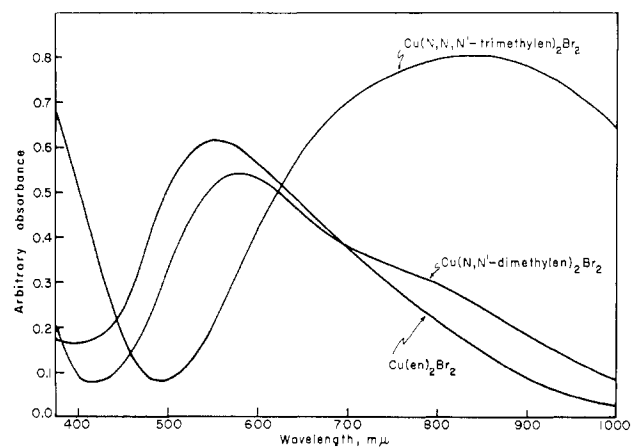
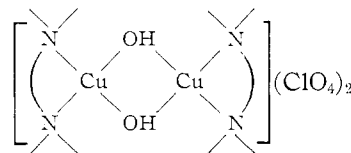


Figure 2.—Reflectance spectra of bis-amine cupric bromide complexes.

dimethylen)₂Br₂ (Figure 2). The one very broad peak at much lower energy suggests a different structure from the square-planar structure of the two other complexes. In the analogous Ni(N,N,N'-trimethylen)₂Cl₂ complex¹⁸ each amine molecule is coordinated through only one nitrogen atom (presumably the secondary amino group). The X-ray powder patterns of both the Cu(II) and Ni(II) complexes are similar. This suggests that the amines function as monodentate ligands in the Cu(II) complex also. In this connection, it is significant that no bis-amine complex of N,N,N',N'-tetramethylen could be prepared, even with rigorous exclusion of water and large molar ratios of amine. Thus, both N,N,N'-trimethylen and N,N,N',N'-tetramethylen form different types of complexes than the simpler N-substituted ethylenediamines.

Ethylenediamine, N,N'-dimethylen, and N,N,N'-trimethylen all form stable, square-planar cupric perchlorate complexes of the type [Cu(amine)₂](ClO₄)₂. However, the bis-amine complex of N,N,N',N'-tetramethylen could not be prepared. Instead, the dinuclear complex



is obtained. An extra very sharp infrared peak at 3530 cm.⁻¹ has been assigned as the O–H stretching frequency of the hydroxo bridge.

Formation of the dinuclear complex prevails over chelation of two bulky N,N,N',N'-tetramethylen molecules around the small Cu(II) ion. In contrast to the dinuclear complex formation behavior of Cu(II) and also of Ni(II),¹⁸ the larger Pd(II) ion forms the chelated bis-amine complex with N,N,N',N'-tetramethylen.¹²

The contours of the electronic spectra (Figure 3) of the bis-amine complexes of cupric perchlorate are all very similar, but the λ_{max} are shifted progressively to lower energies as the number of methyl groups on the ethylenediamine moiety increases. This again demon-

(18) S. F. Pavkovic, Ph.D. Thesis, The Ohio State University, 1964.

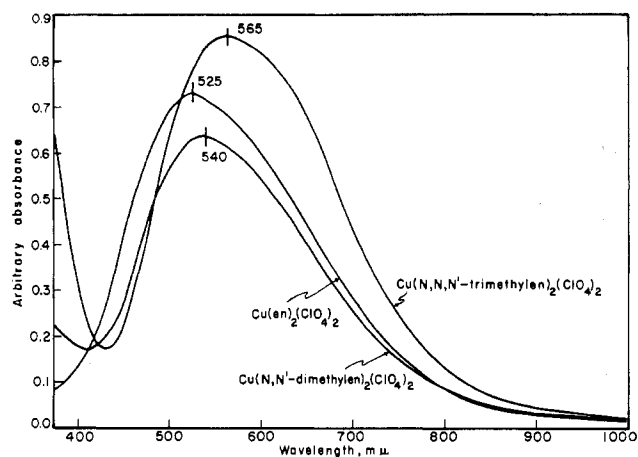


Figure 3.—Reflectance spectra of cupric perchlorate complexes.

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

CONTRIBUTION FROM PENNSALT CHEMICALS CORPORATION,
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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 BiS₂Se and BiSe₂ have been synthesized by high pressure, high temperature techniques. Another member of this series, BiS₂, 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 apparatus² and procedure³ 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 BiSe₂, a 1:2.2 atomic ratio of Bi:Se was subjected to 45 kbars at 1280° for 5–10 min. For BiS₂Se, 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 CS₂, followed by an ether rinse and suction filtration.

(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).

TABLE I
X-RAY DIFFRACTION POWDER PATTERNS

BiS ₂		BiS ₂ Se		BiSe ₂	
<i>d</i> , Å. ^a	<i>I</i> ^b	<i>d</i> , Å.	<i>I</i>	<i>d</i> , Å.	<i>I</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 K_α 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 BiSe₂: Bi, 57.0; Se, 43.0. Found: Bi, 55.4, 55.4; Se, 42.2, 42.4. The weight loss of a BiSe₂ product on oxidation in pure oxygen supported this analytical result: loss calculated for BiSe₂ converted to Bi₂O₃, 36.5; found, 37.8. A small amount of spattering was probably responsible for the difference. *Anal.* Calcd. for BiS₂Se: 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 HNO₃. Density determinations on both crude and purified milligram samples using a Berman density balance ranged from 7.23 to 7.79 g./cc. for BiSe₂, 6.35 to 6.72 g./cc. for BiS₂Se, and 6.02 to 6.08 g./cc. for BiS₂. The increase in density with increasing selenium content may indicate structural similarities for these compounds. As was the case with BiS₂, these materials when heated at 5°/min. in either O₂ or N₂ decompose, in an initial step, primarily to the corresponding trivalent bismuth compound. With BiSe₂, conversion to Bi₂Se₃ occurred at 275°, as indicated by the X-ray diffraction powder pattern of the residue. BiS₂Se decomposed above 240° to a material whose X-ray diffraction powder pattern was in agreement with that of the mineral guanajuatite, Bi₂(S,Se)₃.

The X-ray diffraction powder patterns obtained for BiSe₂ and BiS₂Se each contained over 60 lines; the strongest are listed in Table I. For comparison, the pattern obtained for BiS₂ is also included. Although these materials are not isomorphs, general agreements