1-Methyl-3-alkyl-2(3*H*)imidazolethione Complexes of Metal Halides: A Thematic-Ligand Approach to Involve Undergraduates in Research Projects

Daniel J. Williams,* Segmia K. Tata, Marina C. Koether, Vicky L. H. Bevilacqua, Benjamin E. Huck, and Richard E. Hart

Department of Chemistry and Biochemistry, Kennesaw State University, Kennesaw, GA 30144, dwilliam@kennesaw.edu

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Abstract: A method that we have used to attract undergraduates into research projects incorporates a thematic-ligand approach using a class of thiourea-type ligands known as 1-methyl-3-alkyl-2(3*H*)-imidazolethiones (*mait*) to make new metal and nonmetal halide addition products never before reported in the literature. A related selenium analog and a bidentate thione are also employed in the process, which to date has produced 24 new compounds. Twenty-one student co-authors, 10 female and 11 male, have been involved in the presentation of these results in a total of 15 published in peer-reviewed journals and in 13 presentations at regional, national, or international symposia. The students start the work as a team research project in an intermediate inorganic synthesis laboratory course by first making the ligand and then its addition product which is characterized by standard methods during the course. Many of the attempts are failures, but teams that produce new compounds often go on to research projects that result in further structural characterization through collaborative efforts with the Georgia Institute of Technology or with Clemson University. A case study involving the synthesis and characterization of 1-methyl-3-(2-propyl)-imidazole-2(3*H*)-thione (*mipit*) and its bismuth trichloride adduct, $BiCl_3$ (*mipit*)$_2$ is presented in this report.

Introduction

Getting more students involved in undergraduate research has been the focus of many chemical educators, and some successful approaches have been recently reported in the literature [1, 2]. A recent symposium at the 53rd Southeast Meeting of the American Chemical Society (SERMACS 2001) included a few presenters giving ideas that have successfully attracted undergraduates into real-life hands-on research experiences [3]. Many, though not all, of these proposed models come from institutions with graduate programs that already have vigorous on-going research activities in place. It is perhaps most challenging to get undergraduates involved in research where undergraduate instruction is the sole mission of the institution. Instructors at small undergraduate colleges or even larger regional universities without graduate programs often have to struggle to get viable research programs going in the face of heavier teaching loads, less funding, and in some cases, smaller student pools from which to draw. We have used a thematic ligand approach similar to that of Professor Cassandra Eagle of Appalachian State University as a starting point to involve undergraduates in research [3–5]. Our inorganic synthesis laboratory, started in 1981, evolved by 1988 into a team research approach to involve students in the synthesis and characterization of compounds never before reported in the literature. In the second half of the semester, the team starts a synthetic design project to make a new compound focused around the thematic ligand class of compounds, 1-methyl-3-alkyl-2(3*H*)-imidazolethione (*mait*). The goal of the research is to make a new metal halide complex with the *mait*-type ligand. (Figure 1). Both ligand and complex syntheses are normally simple, and there are a variety of compounds that have yet to be made because of the ability to vary the alkyl group and/or the metal halide. Additional variations on this approach have included incorporating 1,3-dimethyl-2(3*H*)-imidazoleselone (*dmise*) for a few select student teams or using a related bidentate thione ligand as part of the synthetic scheme.

The general schematic for the ligand synthesis is shown in Figure 1. It is an adaptation of the method reported by Benac, Burgess, and Arduengo [6], who used this method for the synthesis of 1,3-dimethy-2(3*H*)-imidazolethione (*dmit*). We further adapted this method for the synthesis of the selenium analog [7] where R = methyl and gray selenium is substituted for sulfur in the scheme. In addition, we have made the bidentate ligand mentioned above [8, 9] by using methylene iodide as the alkyl halide in a stoichiometric ratio of two equivalents of 1-methylimidazole to one of the halide. Figure 2 shows the product, 1,1'-methylenebis(3-methyl-2*H*-imidazole-2-thione) or *mbit*, for short. There have been a few new complexes made with *mbit* which acts either as a bridging ligand between two metal centers (Figure 2a) [8] or as a bidentate ligand to form an eight-member ring with the acceptor (Figure 2b) [9].

The purpose of this paper is twofold. First, we wish to present a detailed example case study of the synthesis and characterization for a specific ligand, namely, 1-methyl-3-(2-propyl)-2(3*H*)-imidazolethione (*mipit*) and a new bismuth trichloride adduct of this ligand. We have included enough experimental detail and subsequent interpretation so the reader will be able to duplicate these or similar procedures if they so desire. Secondly, we have recounted some other shorter case

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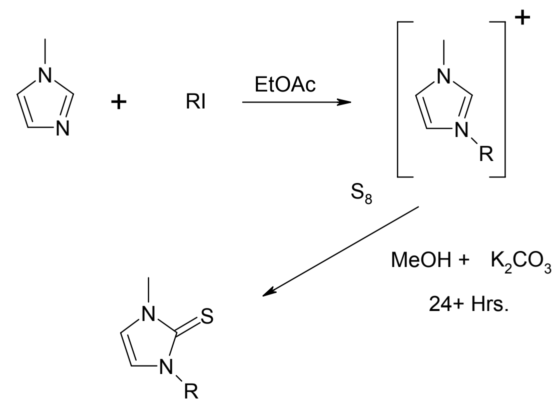

Figure 1. General schematic for the synthesis of *mait.*

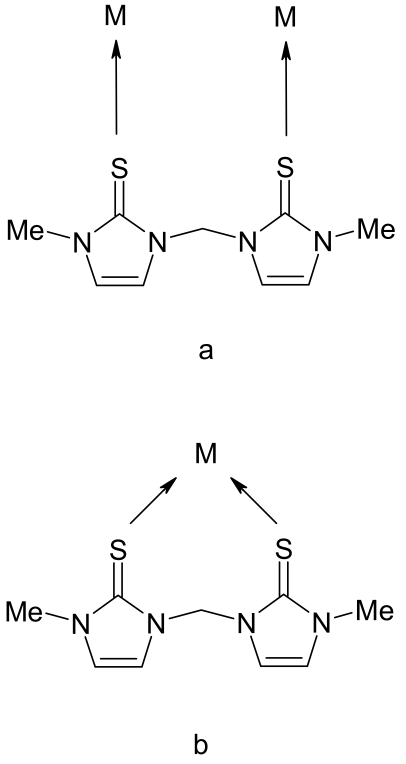

Figure 2. 1,1'-methylenebis(3-methyl-2H-imidazole-2-thione) (*mbit*).

studies and the overall results we've experienced from using this thematic ligand approach over the past fifteen years.

Experimental

All chemicals used were reagent grade and used as obtained from the supplier without further purification. Carbon, hydrogen, and nitrogen analyses were done by Atlantic Microlabs, Inc. Bismuth composition was measured *via* FAAS using a Varian SpectrAA 220 Fast Sequential Spectrophotometer at manufacturer's recommended settings for bismuth and employing an air/acetylene flame. Commercial (Fisher) bismuth standards prepared to concentrations of 5, 10, and 20 ppm were used for calibration. A 61.5 mg sample of $BiCl_3$(*mipit*)$_2$ rendered in 5% (v/v) HNO_3 was used for the determination. Melting points (uncorrected) were taken in open capillary tubes on a Mel-Temp II melting point apparatus.

Gas chromatographic mass spectroscopy (GC/MS) analysis was performed using a Shimadzu GC-17 Gas Chromatograph in tandem with a Shimadzu QP5000 Mass Spectrometer. Fourier transform infrared spectra (FTIR) were collected on powdered solids using a Perkin-Elmer Spectrum One FTIR instrument fitted with a diamond attenuated reflectance stage. Spectra for the ligand and the complex are shown in Figures 3 and 4 respectively. Results are reported in cm^{-1} (±2.0). A Fourier transform proton nuclear magnetic resonance (FT-NMR) spectrum was collected in spectroscopic grade $CDCl_3$ for the ligand only. The spectrum is shown in Figure 5. Proton shifts are reported in ppm (δ) relative to internal TMS.

1-Methyl-3-(2-propyl)-2(3*H*)-imidazolethione (mipit). Two three-hour laboratory periods are required for this part of the procedure. It is recommended that the procedure be done under a fume hood. Generally the ligand may be used in crude form for synthesizing the complex. Proton NMR, GC/MS, and FTIR spectra can be collected on the crude ligand product to help verify its identity. The procedure below adds a recrystallization step.

Into a three-necked 500-mL round bottom flask equipped with dropping funnel and heating mantle sitting on top of a magnetic stirrer, 25 mL (25 g; 0.31 mol) of 1-methylimidazole (Aldrich) and 85 mL of ethyl acetate (Baker) were placed along with a football-shaped stir bar. Into the dropping funnel was added 35 mL (60 g; 0.35 mol) of 2-iodopropane (Aldrich). The iodopropane was added with stirring to the solution in the flask over a period of about 45 minutes with low heat applied through the heating mantle. The heat was removed, and yellow oil was observed settling to the bottom of the flask. The flask was allowed to cool, and the ethyl acetate was decanted off. To the yellow oil in the flask were added 300 mL of methanol (Baker), 11.2 g of sulfur (Baker), and 41.4 g of K_2CO_3 (Baker) with continual stirring. The reaction flask was left to stir for 7 days until the next class period.

A Celite 545 (Fisher) filter was prepared by placing four heaping standard scoopulas full of Celite into 150-mL beaker containing 30 mL of methanol (Baker). The slurry was stirred and vacuum filtered into a 9-cm Bűchner funnel fitted with premoistened qualitative-grade filter paper. The reaction solution was filtered through the Celite pad, and the solid was discarded into a proper waste container. The filtrate was washed with 100 mL of warm methanol. Three milliliters of the filtrate was saved for GC/MS injection. The methanol extract was reduced in volume with a rotary evaporator, which left a residual red oil and solid. The oil was brought up in 100 mL of methylene chloride (Baker), gravity filtered, and rotary evaporated once again. The white crystalline mass was brought up in hot water, hot filtered, and cooled in an ice bath. The white crystals were dried and weighed. The mass of the recrystallized product was 5.8g (12% yield) and the mp was 86 to 89°C. The GC/MS spectrum for the methanol extract revealed the major component to be the expected thione with parent peak of 156 amu.

Trichlorobis[1-methyl-3-(2-propyl)-2(3*H*)-imidazolethione]-bismuth(III) [$BiCl_3(mipit)_2$]. This procedure requires two three-hour periods. It can generally be done on the bench top unless particularly hazardous solvents or metal halides are used.

In a 250-mL Erlenmeyer flask were placed ca. 100 mL of acetonitrile (Baker) and 2.94 g (18.8 mmol) of *mipit*. The solution was heated to 40 °C, and 3.12 g (9.36 mmol) of $BiCl_3{\cdot}H_2O$ was added to the ligand solution. A bright-orange precipitate formed immediately. The acetonitrile was boiled off to about half volume in a hood, and the solution was cooled. The crystals were suctioned filtered and allowed to dry until the next period. A total of 5.63 g (96% yield) of product with mp 167 to 168 °C was isolated. A 100-mg sample was sent off to Atlantic Microlabs, Inc. for carbon, hydrogen, and nitrogen analysis, and %Bi was determined by FAAS (Anal. Calcd for $C_{14}H_{24}BiCl_3N_4S_2$: C, 26.78%; H, 3.86%; N, 8.93%, Bi, 33.3%. Found: C, 26.80%; H, 3.90%, N, 8.86%, Bi, 33.6%). The FTIR spectrum is shown in Figure 4.

Results and Discussion

Much of the above and following discussion entails experimental analysis and shorter case studies based on our experience to aid the reader in reproducing these projects or in

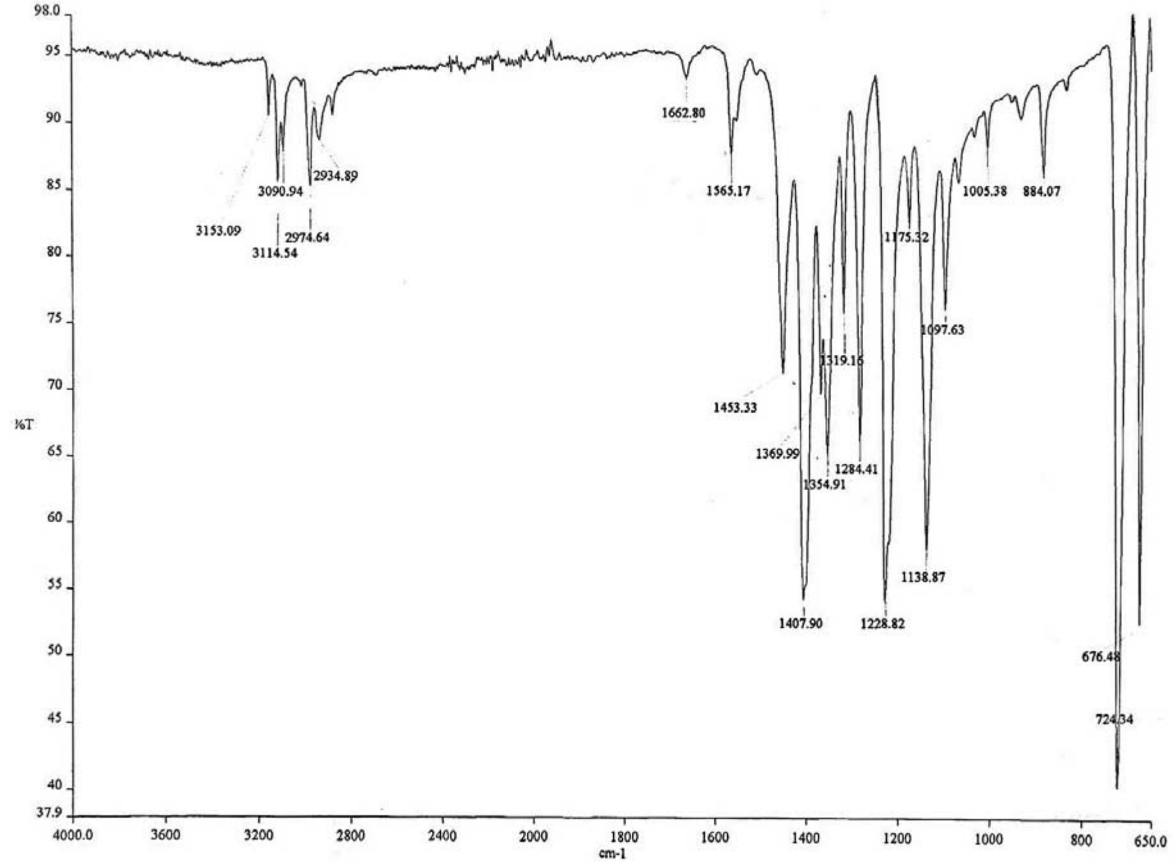

Figure 3. FTIR spectrum of 1-methyl-3-(2-propyl)-2(3H)-imidazolethione (*mipit*).

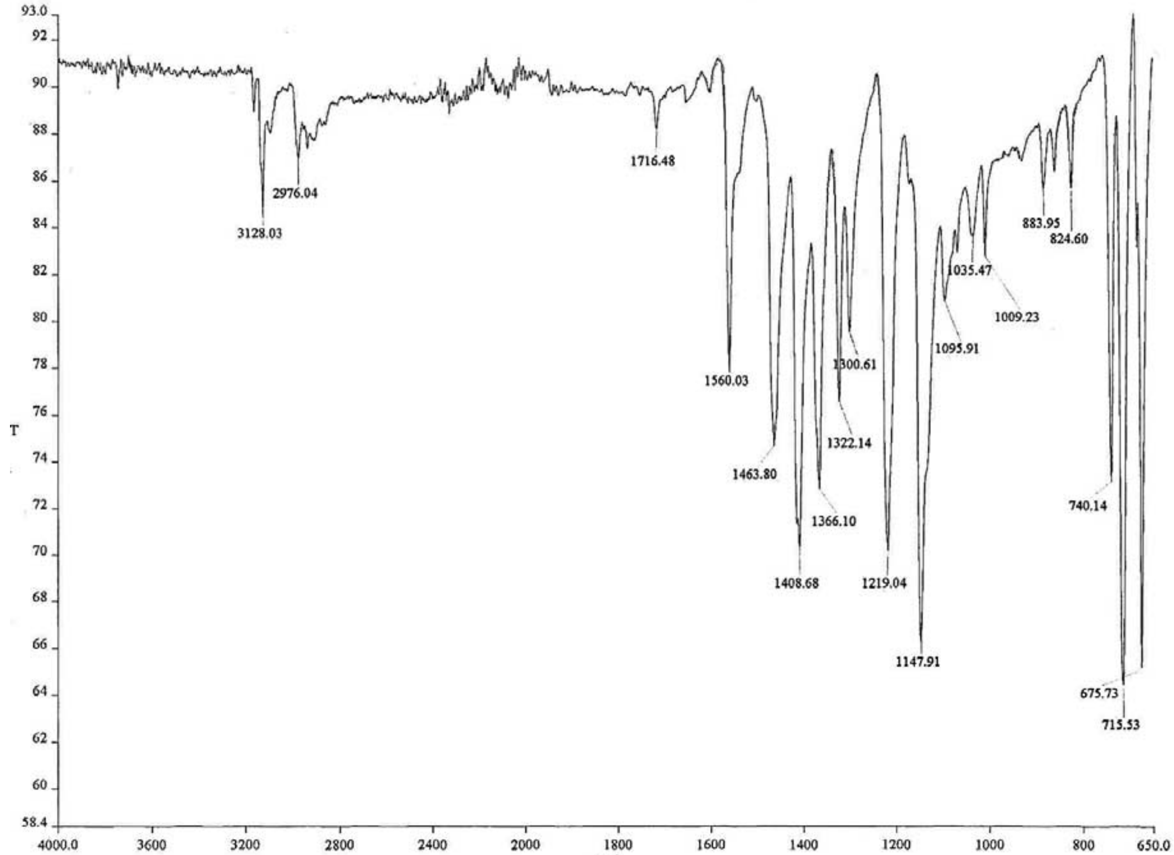

Figure 4. FTIR spectrum of trichlorobis[1-methyl-3-(2-propyl)-2(3H)-imidazolethione]bismuth(III)-$BiCl_3$ (*mipit*)$_2$.

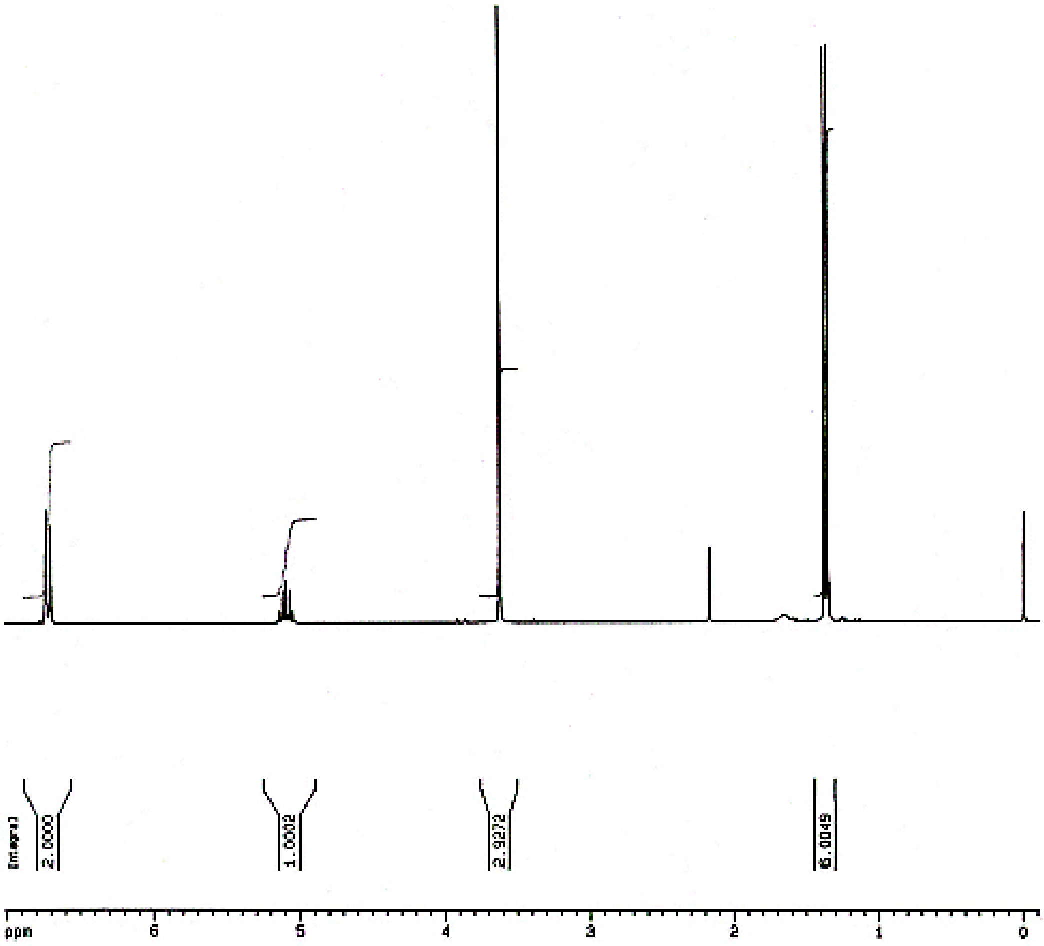

Figure 5. Proton FT-NMR of *mipit* in $CDCl_3$.

designing similar projects that they and their students may wish to try. Certainly there are enough variations possible to allow different avenues of pursuit. For example, one may wish to look at making the oxygen-based analogs or to pursue the *N*-methyl-*N*-alkylbenzimidazole analogs and their metal halide complexes. The synthesis of a heterocyclic thione ligand (*mipit*) and its $BiCl_3$ complex reported above is an actual case study of a project started by a student team in our inorganic laboratory course using a thematic ligand approach. In our intermediate-level inorganic synthesis laboratory course, the first half of the semester consists of basic preliminary laboratory procedures which introduce standard methods like specific conductivity, molar susceptibility, synthesis in liquid ammonia, spectroscopic characterizations using Fourier transform infrared spectroscopy (FTIR) and flame atomic absorption spectrophotometry (FAAS), and a brief review of basic organic synthetic techniques. During this time, each member of the student team writes an individual laboratory report for each procedure in the form of a journal article. Template articles are given as examples of the format to be used. The reports are graded and returned, and substandard reports may be rewritten for resubmission and regrading. The goal is to help the students refine their technical writing skills. The team then launches into the thematic ligand-based research project by investigating possible ligands and target metal halide complexes that have never been made before. The team makes the ligand and new complex and writes a jointly authored paper describing their results. In the case of a failed experiment, literature-based speculation is to be made as to why they believe their target complex was not obtained.

To date, the student research teams have produced 24 new compounds never before reported in the literature. Twenty-one student co-authors, ten female and eleven male, have been involved in the presentation of these results in a total of fifteen papers published in main-line peer-reviewed chemical journals and in thirteen presentations at regional, national, or international symposia. It should be emphasized, however, that there are many more failures than there are successes. This points out to the learner that real research embodies both success and failure, and oftentimes, more of the latter than the former. In our experience with the students, however, this has not been a negative situation because, as in the case of Vallarino's model [1], they are required to critically evaluate their results in a "broader scientific context" and come up with a reasonable speculation as to why they did not produce a complex. Thus, failure is not viewed as negative, but rather accepted, as it should be, as being part of the total educational experience regarding research.

Since the laboratory is taught in conjunction with a lecture section, some of the class time is used to help guide students in the general direction of possible target compounds. We discuss the precepts of Pearson's Hard–Soft Acid–Base (HSAB) model [10], and point out that the ligands they will be synthesizing would probably fall in the soft category; therefore, soft–hard combinations may not work (e.g., a complex between *mait* and $AlCl_3$), but they may wish to test this hypothesis by attempting hard–soft combinations. The experimental framework is limited by the heterocyclic thione and metal halides available. The *mait* ligands that have been used are the following: dimethylimidazolethione (*dmit*), ethyl-methylimidazolethione (*emit*), methyl-*n*-propylimidazolethione (*mnpit*), methyl-*iso*-propylimidazolethione (*mipit*), methyl-2-propenylimidazolethione (*mpit*), and methyl-*n*-butylimidazolethione (*mnbit*) as well as the *mbit* and *dmise* ligands mentioned above [11]. Because there have been so many compounds of the *dmit* analog already reported in the literature, we normally try to guide the research team in the direction of the one of the asymmetric analogs. If the researchers find a metal halide complex with the *dmit* derivative yet to be made, however, they are certainly encouraged to pursue the project. We have not employed the asymmetric selenium analogs simply because many of the thione asymmetric compounds come out as oils prior to purification, and the oils have a strong odor. One can only imagine what an oily, volatile selone would be like, and we do not wish to subject the research team, indeed the entire science building, to such an experience. On the other hand, the dimethylimidazoleselone (*dmise*) is a stable white crystalline solid, and it is virtually odorless. A few teams selected on the basis of synthesis skill have been encouraged to make *dmise*, and two new compounds have been made and reported [12, 13].

For metal halides, we generally let the student peruse the stockroom to see what we have on hand. We also sometimes encourage thinking about pseudohalides such as cyanate or thiocyanate. We strongly discourage the use of cyanide. If the target metal halide is not available, the student team may have to synthesize it.

Spectral data collected for both ligand and halide complex are part of the normal characterization routine. Generally GC/MS is used to verify the presence of the targeted ligand in the reaction mixture. As stated earlier, crude ligand generally suffices for complex synthesis, so spectral data collected on the crude material helps establish its identity. The proton NMR spectrum shown in Figure 5 is typical where the methyl protons are generally seen as a singlet around 3.6 δ and the ethylene protons around 6.7 δ as two sets of doublets. The other spitting patterns are generally recognizable as in the case of this study where the isopropyl protons are easily assigned. From our experience, most metal halide complexes with *mait*-type ligands are very insoluble in most common solvents, so solution state spectra are not pursued except in occasional instances where a suitable solvent can be found.

Once the complex is made and isolated, traditional characterization, such as solubilities, FTIR, and melting point is employed. If the melting point range is sufficiently narrow, a small sample is immediately collected and sent off for C, H, and N analysis. The turnover time for analyses at a local commercial supplier (Atlantic Microlabs, Inc.) is fast enough to get results normally returned to us by FAX within a week or two, and the cost, generally less than $40.00, is also quite reasonable per sample. In the meanwhile, the team is attempting to grow crystallographic-grade crystals, finishing up spectral collection, and determining the metal percent composition to add to the analytical information. If crystallographic-grade crystals are isolated, then the student team is encouraged to pursue a crystallographic research project with our collaborators either at Georgia Tech or Clemson University.

FTIR spectra in Figures 3 and 4 show typical results observed for these types of compounds. It should be emphasized that only powdered sample or mulls should be used for data collection. A very common mistake made by researchers is to press KBr pellets. This technique should be avoided altogether for solid-state inorganic spectra due to the possibility of coordination-sphere substitution of bromide under the vigorous conditions inherent in pellet formation. While it is not as critical for these types of compounds because the rock-salt region would tend not to show any such aberration, it is still a habit that should be avoided.

In examining the FTIR spectra, it will be noted that there is very little difference between the ligand spectrum and the complex spectrum in the region scanned. This is to be expected because several crystallographic studies have shown virtually no structural alteration for the ligand in going from the free to the complexed state [14]. Thus, only minor shifts (±10 to 15 cm^{-1}) are observed for the alkyl modes, ring modes and C=S stretch (ca. 1170 to 1180 cm^{-1}). The infrared spectra and structural correlations for these types of compounds have been thoroughly investigated and discussed in a separate report [14].

The detailed case study shown above also went on to be completed by one of the two team members in a separate research project done in conjunction with Georgia Tech, and the results of an completed x-ray crystallographic study will be reported in a separate communication to a peer-reviewed chemical research journal. Three additional case studies are presented below to illustrate what may be done to garner undergraduate research involvement using this thematic ligand approach.

The first case involved a team attempting to make a *dmit* complex with $SiBr_4$. In the process of making the adduct, trace amounts of water had apparently gotten into the reaction mixture resulting in the hydrolysis of silicon tetrabromide. The net result was a 1:2 addition product between HBr and *dmit* as verified by x-ray crystallography [15]. This is a good example of an HSAB interaction of preference where the softer bromide became attached to the sulfur donor, and the harder oxygen chose its normal silicon association. It also pointed out that failure in some cases can still have a successful outcome, and that serendipity is very much a part of research.

Another case produced one of the few structural studies ever reported for bismuth (III) thiocyanate [16] isolated as a *tris*-complex of *dmit*. Lewis base stabilization of normally unstable halides has literature precedence [17], and this is yet another example. The subsequent directed-study project showed an interesting structure of a distorted octahedral-site symmetry about the bismuth atom with no strong evidence of a stereoactive lone pair. Additionally, it demonstrated the ambidentate nature of the thiocyanate ligand with two ligands N-bonded and one S-bonded. The three thione ligands assumed a meridional configuration.

The third and most recent example is the *bis-dmise* adduct of $ZnCl_2$ which in thermal decomposition studies was demonstrated to be a synthon for zinc selenide, an optically significant material with many industrial applications [13, 18]. An additional perk for the student researcher in this study was that she had the opportunity to present her results at the international Pacifichem2000 symposium in Honolulu.

In conclusion, the simple metal halide addition products from the *mait*-type ligand and its analogs have been a successful method that we have used to generate interest in undergraduate research in the absence of graduate programs. We have used this approach to teach some of the more typical inorganic synthesis and characterization methodology and to give students the satisfaction of participating in real-life hands-on research that contributes to the body of chemical knowledge.

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