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Alkahest for V_2VI_3 Chalcogenides: Dissolution of Nine Bulk Semiconductors in a Diamine-Dithiol Solvent Mixture

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Supporting Information

ABSTRACT: The ability to solution deposit semiconductor films has received a great deal of recent attention as a way to potentially lower costs for many optoelectronic applications; however, most bulk semiconductors are insoluble in common solvents. Here we describe a novel and relatively nonhazardous binary solvent mixture comprised of 1,2-ethanedithiol and 1,2-ethylenediamine that possesses the remarkable ability to rapidly dissolve a series of nine bulk V_2VI_3 chalcogenides (V = As, Sb, Bi; VI = S, Se, Te) at room temperature and atmospheric pressure. After solution deposition and low-temperature annealing, the chalcogenides can be fully recovered as good quality, highly crystalline thin films with negligible organic content, as demonstrated for Sb_2Se_3 and Bi_2S_3.

Solution processing of semiconductor thin films holds great promise for various optoelectronic applications, such as photovoltatics,[1] thin-film transistors,[2] nonlinear optics,[3] and nonvolatile phase-change memory.[4] Liquid inks comprised of true molecular solutions are an especially promising medium for semiconductor deposition because they can lead to very homogeneous films; however, most metal chalcogenide semiconductors are totally insoluble in "normal" solvents. As exceptions to this statement, it is known that *N*,*N*-dimethylformamide will dissolve (K,Rb)PSe_6 and (K,Rb,Cs)-$ZrPS_6$,[3,5] methanol will dissolve (Li,Na)$AsSe_2$,[6] and primary amines will dissolve As_2S_3.[7] While the dissolution of other metal chalcogenides is generally much more difficult, a number of these materials (e.g., SnS_2, In_2Se_3, Cu_2S, etc.) can be dissolved with hydrazine in the presence of stoichiometric elemental chalcogen via "dimensional reduction".[8] In this process, soluble chalcogenometallate anions are formed by reaction of M_xE_y metal chalcogenides with E^{2-} ($E^{2-} = S^{2-}$, Se^{2-}, Te^{2-}; formed by the *in situ* reduction of the chalcogen with hydrazine). The dissolution of metal chalcogenides by the hydrazine/chalcogen route allows for the solution deposition of high-quality metal chalcogenide thin films, but the explosive, highly toxic, and carcinogenic properties of hydrazine make scale up difficult. Alternatively, colloidal dispersions of semiconductor nanocrystals can be used as inks,[9] but this also presents serious scalability challenges as compared with using molecular solutions.[10] Thus, new alkahests (or "universal" solvents) for the solution processing of bulk metal chalcogenide semiconductors are required.

Both crystalline and amorphous V_2VI_3 chalcogenides possess considerable importance in areas as diverse as thermoelectrics ($Bi_{2-x}Sb_xTe_{3-y}Se_y$),[11a] photovoltaics (Sb_2S_3,[11b,c] Sb_2Se_3,[11d] Bi_2S_3[11e]), photodetection (Bi_2S_3),[11f] and infrared optics.[11g] Herein, we present a novel binary solvent mixture comprised of 1,2-ethylenediamine (en) and 1,2-ethanedithiol ($edtH_2$) that possesses the remarkable ability to rapidly dissolve nine bulk V_2VI_3 semiconductors (V = As, Sb, Bi; VI = S, Se, Te) at room temperature and ambient pressure. We describe the dissolution and subsequent solution redeposition of these V_2VI_3 chalcogenides, with specific focus placed on the facile solution processing of Sb_2Se_3 and Bi_2S_3 thin films from bulk material.

A 1:10 vol/vol mixture of chelating $edtH_2$/en was found to possess marked solvent ability for all nine V_2VI_3 chalcogenides. Metal chalcogenide solubilities, expressed as wt% solute in the saturated solution (at 25 °C, 1 atm), are extraordinarily high for As_2S_3, As_2Se_3, As_2Te_3, Sb_2S_3, Sb_2Se_3, and Sb_2Te_3 (21−32 wt %), moderate for Bi_2S_3 (9.8 wt %), and lower but still significant for Bi_2Se_3 and Bi_2Te_3 (0.75 and 1.5 wt %, respectively) (see Supporting Information, Table S1). Significantly, the V_2VI_3 chalcogenides can be dissolved very rapidly under these conditions (e.g., on the order of minutes for the As_2E_3 and Sb_2E_3 chalcogenides), as compared to substantially slower dissolution sometimes required with the hydrazine/chalcogen route.[1a] Dilute solutions of As_2S_3 and Sb_2S_3 are both nearly colorless, while As_2Se_3, Sb_2Se_3, Bi_2S_3, and Bi_2Se_3 give golden yellow solutions, and the tellurides all give dark brown solutions (Figure 1). All nine V_2VI_3 chalcogenide solutions in $edtH_2$/en were optically transparent and free of visible scattering at all concentrations. For the detailed investigation described below, solutions of Sb_2Se_3 were prepared under nitrogen by the complete dissolution of 125 mg of the chalcogenide in an empirically chosen solvent mixture of 1.0 mL en and 0.1 mL $edtH_2$; however this volume ratio of $edtH_2$/en can be deviated from and dissolution still occurs. The same quantities were used for Bi_2S_3 dissolution, but in this instance there remained undissolved solid, so the saturated solution was filtered prior to use. Moreover, the dissolution procedure was generally scalable; this was demonstrated on the 4× and 20× scales with Bi_2S_3 and Sb_2Se_3, respectively.

Recovery of the dissolved chalcogenide as a solid is critically important for practical applications; therefore, thermogravimetric analysis (TGA) was employed to determine appropriate temperatures for recovery of the solid inorganic phase. Solutions were evaporated to dryness *in situ* (200 mL min^{-1}

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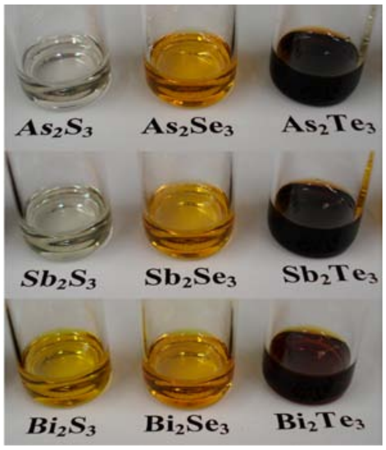

Figure 1. Photograph of dilute (0.75 wt %) solutions of all nine V_2VI_3 semiconductors in a 1:10 v/v 1,2-ethanedithiol/1,2-ethylenediamine solvent mixture.

flowing nitrogen, 5 °C min^{-1} to 125 °C, 20 min isothermal) and then cooled to 30 °C before commencing analysis (60 mL min^{-1} flowing nitrogen, 10 °C min^{-1} to a sample-specific maximum temperature; see Figures S1−S3). The solids recovered via evaporation from the V_2VI_3 chalcogenide solutions all showed negligible mass loss above 300−350 °C, indicating end-point of decomposition. The solid recovered via evaporation of the dissolved Sb_2Se_3 solution shows a multistep mass loss of 24% from 30−350 °C (Figure 2a). Similarly, the solid recovered via evaporation of the dissolved Bi_2S_3 solution shows a multistep mass loss of 31% from 30−325 °C (Figure 2a). These mass loss events very likely correspond with elimination and/or decomposition of organic species from the dried solid. To test this hypothesis, dissolved solutions of Sb_2Se_3 and Bi_2S_3 were drop-cast on an IR-transparent disc and dried at 100 °C, a temperature at which no thermal decomposition is observed by TGA. FT-IR spectra of the films displayed strong ν(C−H) and ν(N−H) stretches at 3300−2800 cm^{-1} along with other bands corresponding to organics; however, heat treatment to 350 °C resulted in elimination of the organic species as evidenced by complete loss of the ν(C−H) and ν(N−H) stretches (Figure 2b,c), in accordance with TGA data. The temperatures corresponding to organic mass loss for all these systems are comparable with literature precedent set by the hydrazine/chalcogen route, where a temperature of 350 °C is typically employed to volatize excess chalcogen that must be added in order to dissolve the metal chalcogenide.[8a]

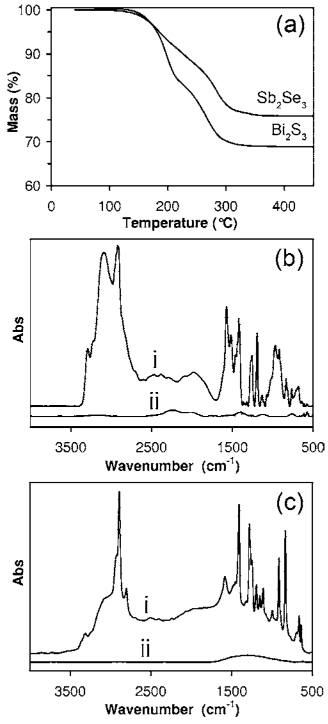

Figure 2. (a) TGA traces of the solid precursors obtained by predrying Sb_2Se_3 and Bi_2S_3 solutions in 1,2-ethanedithiol/1,2-ethylenediamine at 125 °C. FT-IR spectra of dried (b) Sb_2Se_3 and (c) Bi_2S_3 films drop-cast from solution and subsequently heat-treated at (i) 100 °C and (ii) 350 °C.

Solutions of all nine V_2VI_3 chalcogenides investigated here were dried and heat-treated under nitrogen, with sulfur vapor being used in the case of Bi_2S_3 to remove the small amount of elemental Bi present as an impurity in the as-bought material. Powder X-ray diffraction (XRD) revealed that As_2S_3, As_2Se_3, Sb_2S_3, Sb_2Se_3, Bi_2S_3, and Bi_2Se_3 can be recovered as phase pure material after deposition and annealing to temperatures ranging from 270−350 °C (see Figures S4−S10). In the case of Sb_2Se_3 and Bi_2S_3, which share identical orthorhombic stibnite (or bismuthinite) crystal structures, they were recovered from solution as crystalline and completely phase pure materials after annealing to 350 °C (Figures 3a,b). The elemental composition (at %) of the recovered chalcogenides was also compared against that of the as-bought materials by energy dispersive X-ray spectroscopy (EDX). For example, EDX analysis revealed a high degree of compositional agreement between the as-bought material and that recovered from solution for Sb_2Se_3 (41% Sb, 59% Se as bought; 39% Sb, 59% Se, 2% S recovered from solution); however, significant Bi and S peak overlap in the EDX spectrum precluded quantitative elemental analysis for Bi_2S_3.

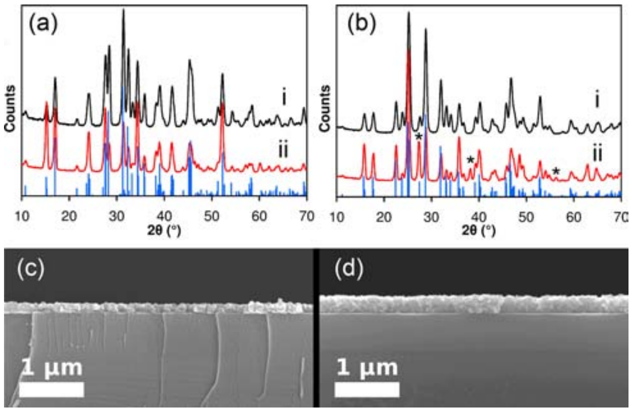

Figure 3. Powder XRD patterns of (i) material deposited from solution and subsequently annealed to 350 °C and (ii) as-bought material for (a) Sb_2Se_3 and (b) Bi_2S_3. Stick patterns correspond to orthorhombic Sb_2Se_3 (PDF no. 03-065-2433) and Bi_2S_3 (PDF no. 01-074-9437), and the diffraction peaks marked by asterisks indicate the presence of elemental Bi in the as-bought Bi_2S_3. Cross-sectional SEM micrographs of (c) Sb_2Se_3 and (d) Bi_2S_3 thin films spin-cast on silicon.

To demonstrate the utility of this approach for solution processing V_2VI_3 chalcogenides, thin films of Sb_2Se_3 and Bi_2S_3 were produced by spin coating the dissolved species, followed by rapid annealing to 350 °C. For example, a dilute Sb_2Se_3 solution (~4 wt %) proved very easy to spin-coat onto glass or silicon substrates. Subsequent heat treatment to 350 °C (under nitrogen) produced a dark gray, specularly reflective film, shown to be dense and polycrystalline by scanning electron microscopy (SEM). Cross-sectional and plane view SEM of the resulting thin film revealed it to be ~150 nm in thickness and composed of grains ranging from ~50−200 nm in width (Figures 3c and S11a). Similarly, spin coating a saturated Bi_2S_3 solution (~9.8 wt %) followed by rapid annealing to 350 °C (under nitrogen) produced a ~270 nm thick film comprised of ~30−100 nm grains (Figures 3d and S11b). The optical properties of the resulting Sb_2Se_3 and Bi_2S_3 thin films were characterized by transmission UV−vis NIR spectroscopy using an integrating sphere. The direct optical band gap transitions were estimated from Tauc plots (i.e., $(\alpha h\nu)^2$ vs $h\nu$), giving values of $E_{g,dir}$ = 1.7 and 1.5 eV for Sb_2Se_3 and Bi_2S_3, respectively (see Figures S12 and S13). These values agree well with the direct band gaps previously reported for Sb_2Se_3 and Bi_2S_3 ($E_{g,dir}$ = 1.7−1.9 and 1.4−1.7 eV, respectively).[12]

To investigate why this $edtH_2$/en binary solvent mixture possesses high solvent power for the V_2VI_3 chalcogenides, a number of informative control experiments were performed by qualitatively gauging the solubility of the metal chalcogenides in various solvent mixtures over the course of several minutes. Generally, the V_2VI_3 chalcogenides were insoluble in the absence of $edtH_2$, with the exception of As_2S_3 and As_2Se_3, which were soluble in neat en. This demonstrates the need for a thiol component in the solvent mixture. Experiments with mixtures of 2,3-butanedithiol with en, or mixtures of $edtH_2$ with diethylenetriamine, showed good solvent ability for Bi_2S_3. This is consistent with the observed solvent power of $edtH_2$/en, since all these binary solvent mixtures possess 1,2-dithiol/1,2-diamine functionality. On the other hand, mixtures of $edtH_2$ with *n*-butylamine possessed much poorer solvent ability for Bi_2S_3, as did mixtures of 1,3-propanedithiol or *n*-propanethiol with en. Moreover, it was found that mixtures of *n*-propanethiol and *n*-butylamine, or using $edtH_2$ alone without amine, did not possess any appreciable solvent power for Bi_2S_3. It therefore appears that a 1,2-chelating dithiol and 1,2-chelating diamine are both essential for maximum solvent power for these materials.

It was found that the addition of $edtH_2$ to en (1:10 vol/vol) resulted in a ~15 000× increase in electrolytic conductivity (i.e., the observed solution resistance fell from 2.04 MΩ to 136 Ω), suggesting that extensive ion formation occurs in this binary solvent mixture. The formation of ionic species upon mixing $edtH_2$ and en is supported by the crystal structure of their addition product. It was found that the addition of $edtH_2$ to en can produce a colorless crystalline solid; however, the solid easily redissolved on gentle warming, and the liquid remained supercooled at room temperature for hours. The solid-state structure was solved using high-quality crystals, and the N-bonded hydrogen positions were positively identified from the electron density map. The data showed a stoichiometry of $(enH^+)_2(edt^{2-})(en)$, with a crystal lattice evidently stabilized by extensive N−H···S hydrogen bonding (see Figures S14 and S15). The complete deprotonation of $edtH_2$ in excess en is not expected based on pK_a values ($edtH_2$, ~9.1; $edtH^+$, ~10.6; enH^+, 9.9; enH_2^{2+}, 6.8; all in aqueous solution at 25 °C);[13] however, the actual pK_a values in a given system are highly dependent on solvation energetics, of which H-bonding can be a major component. It therefore seems possible that stabilization of thiolate anions in this binary solvent mixture is an important contributor to the observed solvent power. Consistent with this hypothesis, replacement of the en by *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, which is a comparable base ($pK_a \approx 9.1, 5.7$)[13b] but a less effective H-bond donor, resulted in a solvent mixture of negligible solvent power for the V_2VI_3 chalcogenides.

As mentioned previously, the observed lack of visible scattering in the V_2VI_3 solutions suggests that the solute may be a molecular rather than nanoparticulate species. Dynamic light scattering was performed on concentrated Sb_2Se_3 and Bi_2S_3 solutions, confirming the complete absence of clusters or particles with diameters above the detection limit of 1 nm. Moreover, solid obtained by drying Sb_2Se_3 and Bi_2S_3 solutions under mild conditions (100 °C, flowing nitrogen) revealed only weak reflections by XRD that do not match known materials (Figure S16), likely resulting from mostly amorphous precursor complexes. Importantly, XRD did not reveal any crystalline Sb_2Se_3 or Bi_2S_3 at temperatures ≤100 °C. In the absence of more complete data, we cannot state with certainty the nature of the dissolved V_2VI_3 chalcogenides; however, the formation of en-ligated thiolatochalcogenometallate anions counterbalanced by enH^+ cations appears to be a reasonable working hypothesis. The dissolution mechanism would then be expected to increase the overall concentration of ions in solution, which is consistent with electrolytic conductivity data. Resistances of 94 and 86 Ω were observed for solutions of Sb_2Se_3 and Bi_2S_3, respectively, which are lower than the 136 Ω measured for an identical volume of the 10:1 vol/vol en/$edtH_2$ solvent mixture (i.e., conductivity increased by a factor of ~1.4−1.6 upon V_2VI_3 dissolution). Thiolatothiometallate anions are well established in the literature,[14] and the formation of analogous species in V_2VI_3/en/$edtH_2$ systems is plausible, but further work is required to confirm this hypothesis.

In summary, this work describes a simple and general method for the solution processing of bulk V_2VI_3 chalcogenides using a relatively nonhazardous binary solvent mixture. Specifically, we have discovered an ionic solvent mixture resulting from 1,2-ethylenediamine and 1,2-ethanedithiol that can be used to dissolve and redeposit nine bulk V_2VI_3 semiconductors. Among the nine semiconductors that can be dissolved with this solvent mixture, As_2S_3, As_2Se_3, Sb_2S_3, Sb_2Se_3, Bi_2S_3, and Bi_2Se_3 can be recovered as phase pure material after deposition and annealing. The V_2VI_3 solutions hold promise for thin-film deposition via spin coating, which was demonstrated for the deposition of Sb_2Se_3 and Bi_2S_3 thin films. We believe these initial results indicate that the chemistry can be further extended to other families of chalcogenide materials and may hold promise for applications that would benefit from the solution deposition of semiconductor thin films.

■ ASSOCIATED CONTENT

S Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Mitzi, D. B.; Yuan, M.; Liu, W.; Kellock, A. J.; Chey, S. J.; Deline, V.; Schrott, A. G. *Adv. Mater.* **2008**, *20*, 3657. (b) Bob, B.; Lei, B.; Chung, C.-H.; Yang, W.; Hsu, W.-C.; Duan, H.-S.; Hou, W. W.-J.; Li, S.-H.; Yang, Y. *Adv. Energy Mater.* **2012**, *2*, 504.

(2) (a) Kim, D.; Jeong, Y.; Song, K.; Park, S.-K.; Cao, G.; Moon, J. *Langmuir* **2009**, *25*, 11149. (b) Meyers, S. T.; Anderson, J. T.; Hung, C. M.; Thompson, J.; Wagner, J. F.; Keszler, D. A. *J. Am. Chem. Soc.* **2008**, *130*, 17603. (c) Mitzi, D. B.; Kosbar, L. L.; Murray, C. E.; Copel, M.; Afaili, A. *Nature* **2004**, *428*, 299.

(3) Chung, I.; Kim, M.-G.; Jang, J. I.; He, J.; Ketterson, J. B.; Kanatzidis, M. G. *Angew. Chem., Int. Ed.* **2011**, *123*, 11059.

(4) (a) Wang, R. Y.; Caldwell, M. A.; Jeyasingh, R. G. D.; Aloni, S.; Shelby, R. M.; Wong, H.-S. P.; Milliron, D. J. *J. Appl. Phys.* **2011**, *109*, 113506. (b) Milliron, D. J.; Raoux, S.; Shelby, R. M.; Jordan-Sweet, J. *Nat. Mater.* **2007**, *6*, 352.

(5) Banerjee, S.; Szarko, J. M.; Yuhas, B. D.; Malliakas, C. D.; Chen, L. X.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2010**, *132*, 5348.

(6) Bera, T. K.; Jang, J. I.; Song, J.-H.; Malliakas, C. D.; Freedman, A. J.; Ketterson, J. B.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2010**, *132*, 3484.

(7) Norian, K. H.; Chern, G. C.; Lauks, I. *J. Appl. Phys.* **1984**, *55*, 3795.

(8) (a) Mitzi, D. B. *Adv. Mater.* **2009**, *21*, 3141. (b) Yuan, M.; Mitzi, D. B. *Dalton Trans.* **2009**, 6078.

(9) (a) Guo, Q.; Ford, G. M.; Yang, W.-C.; Walker, B. C.; Stach, E. A.; Hillhouse, H. W.; Agrawal, R. *J. Am. Chem. Soc.* **2010**, *132*, 17384. (b) Panthani, M. G.; Akhavan, V.; Goodfellow, B.; Schmidtke, J. P.; Dunn, L.; Dodabalapur, A.; Barbara, P. F.; Korgel, B. A. *J. Am. Chem. Soc.* **2008**, *130*, 16770. (c) Cao, Y.; Denney, M. S.; Caspar, J. V.; Farneth, W. E.; Guo, Q.; Ionkin, A. S.; Johnson, L. K.; Lu, M.; Malajovich, I.; Radu, D.; Rosenfeld, H. D.; Choudhury, K. R.; Wu, W. *J. Am. Chem. Soc.* **2012**, *134*, 15644.

(10) Sun, Y.; Zhang, Y.; Wang, H.; Xie, M.; Zong, K.; Zheng, H.; Shu, Y.; Liu, J.; Yan, H.; Zhu, M.; Lau, W.-M. *J. Mater. Chem. A* **2013**, *1*, 6880.

(11) (a) Tritt, T. M. *Annu. Rev. Mater. Res.* **2011**, *41*, 433. (b) Im, S. H.; Lim, C.-S.; Chang, J. A.; Lee, Y. H.; Maiti, N.; Kim, H.-J.; Nazeeruddin, M. K.; Grätzel, M.; Seok, S. I. *Nano Lett.* **2011**, *11*, 4789. (c) Christians, J. A.; Kamat, P. V. *ACS Nano* **2013**, *7*, 7967. (d) Guijarro, N.; Lutz, T.; Lana-Villarreal, T.; O'Mahoney, F.; Gómez, R.; Haque, S. A. *J. Phys. Chem. Lett.* **2012**, *3*, 1351. (e) Rath, A. K.; Bernechea, M.; Martinez, L.; Konstantatos, G. *Adv. Mater.* **2011**, *23*, 3712. (f) Konstantatos, G.; Levina, L.; Tang, J.; Sargent, E. H. *Nano Lett.* **2008**, *8*, 4002. (g) Popescu, M. A. *Non-Crystalline Chalcogenides*; Kluwer Academic Publishers: Dordrecht, 2000.

(12) (a) Vadapoo, R.; Krishnan, S.; Yilmaz, H.; Marin, C. *Phys. Status Solidi B* **2011**, *248*, 700. (b) Rajpure, K. Y.; Lokhande, C. D.; Bhosale, C. H. *Mater. Res. Bull.* **1999**, *34*, 1079. (c) Gildart, L.; Kline, J. M.; Mattox, D. M. *J. Phys. Chem. Solids* **1961**, *18*, 286. (d) Medles, M.; Benramdane, N.; Bouzidi, A.; Nakrela, A.; Tabet-Derraz, H.; Kebbab, Z.; Mathieu, C.; Khelifa, B.; Desfeux, R. *Thin Solid Films* **2006**, *497*, 58.

(13) (a) Sergeant, E. P.; Dempsey, B. *Ionization Constants of Organic Acids in Aqueous Solution*, (IUPAC Chemical Data Series No. 23); Pergamon Press: Oxford, 1979, p 22. (b) Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution*, (IUPAC); Butterworths: London, 1965, pp 25–27.

(14) Dance, I. G. *Polyhedron* **1986**, *5*, 1037.