

Main group metal halide complexes with sterically hindered thioureas

XIV. A reinvestigation of coordination sensitive modes in the solid state vibrational spectrum of 1,3-dimethyl-2(3*H*)-imidazolethione and related compounds

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(Received July 26, 1993; revised December 13, 1993)

Abstract

The assignment of the carbon–sulfur stretch in the infrared spectrum for 1,3-dimethyl-2(3*H*)-imidazolethione (dmit) reported in an earlier paper was reinvestigated in light of new compounds reported and an X-ray structure of 1,3-dimethyl-2-(*S*-methylthio)-2(3*H*)-imidazolium iodide (tmii). Conflicting literature values and assignments were also investigated. It was concluded that for dmit, the carbon–sulfur stretch was found in the 1170–1180 cm^{-1} region, and that three of the four thioamide peaks reported by other researchers as coordination sensitive modes for thiourea-type compounds did not have significant carbon–sulfur contribution based on the compounds studied in this paper. Crystallographic data for tmii: $\text{C}_6\text{H}_{11}\text{N}_2\text{SI}$, $M=207.04$, space group $P2_1/n$, $Z=4$, $\lambda(\text{Mo K}\alpha)=0.71073 \text{ \AA}$, $\mu(\text{Mo K}\alpha)=3.13 \text{ mm}^{-1}$, $D_c=1.699 \text{ g/cm}^3$, $D_o=1.66 \text{ g/cm}^3$, $a=7.846(2)$, $b=11.754(2)$, $c=12.578(2) \text{ \AA}$, $\beta=95.51(2)^\circ$, $R=0.034$, $R_w=0.042$. Additionally, a new sterically hindered thiourea, 1-methyl-3-(2-propenyl)-2(3*H*)-imidazolethione (mpit), and a new complex, $\text{ZnCl}_2(\text{mpit})_2$, are reported and characterized.

Key words: Crystal structures; Spectroscopic study; Thiourea compounds; Zinc complexes; Thione complexes

Introduction

In an earlier paper, we had reported several new main group metal complexes with 1,3-dimethyl-2(3*H*)-imidazolethione (dmit, Fig. 1(a)) [1]. In that same study, we also reported some characteristic infrared (IR) stretching frequencies that appeared sensitive to coordination for both dmit and 1,1,3,3-tetramethylthiourea (tmtu). One the modes investigated was $\nu(\text{C}=\text{S})$, which for dmit was assigned to peaks appearing between 1170 and 1180 cm^{-1} agreeing with those noted in the literature for dmit [2] and transition metal dmit complexes [3]. It later came to our attention, however, that there existed some disparity in the literature for the assignment of the carbon–sulfur stretch in heterocyclic imidazole-

type thioureas such as dmit, ethylene thiourea (etu) and related compounds [4–9]. For example, reported values of $\nu(\text{C}=\text{S})$ for etu ranged from as low as 516 cm^{-1} [8] to as high as 1208 cm^{-1} [10]. Other authors chose four so-called ‘thioamide’ modes as indicators of complexation since some of these peaks were also noted to shift upon coordination [4–7]. Although these thioamide modes were mixed in character, at least three of the four were reported to have significant carbon–sulfur stretching contribution [4]. Interestingly, at least in the case of dmit derivatives, peaks in the 1170–1180 region were apparently not observed by these researchers [4, 5]. Our choice of the $\nu(\text{C}=\text{S})$ frequency came principally from Mille *et al.* [2] who assigned $\nu(\text{C}=\text{S})$ on the basis of its apparent disappearance from the spectrum of the methyl iodide addition product,

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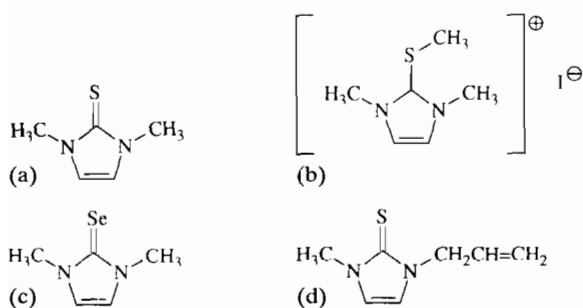


Fig. 1 (a) 1,3-Dimethyl-2(3*H*)-imidazolethione (dmit), (b) 1,3-dimethyl-2-(*S*-methylthio)-2(3*H*)-imidazolium iodide (tmii); (c) 1,3-dimethyl-2(3*H*)-imidazoleselone (dmise); (d) 1-methyl-3-(2-propenyl)-2(3*H*)-imidazolethione (mpit).

1,3-dimethyl-2-(*S*-methylthio)-2(3*H*)-imidazolium iodide (Fig. 1(b), tmii).

In order to resolve this discrepancy, we recently determined the X-ray crystallographic structure of tmii and reinvestigated the IR spectrum. Additionally, since the time of our first study noted above, we have reported the synthesis, characterization and X-ray crystal structure of the selenium analog of dmit, 1,3-dimethyl-2(3*H*)-imidazoleselone (Fig. 1(c), dmise) [11] and have also synthesized and characterized a new sterically hindered thiourea, 1-methyl-3-(2-propenyl)-2(3*H*)-imidazolethione (mpit, Fig. 1(d)), and a new complex thereof, $\text{ZnCl}_2(\text{mpit})_2$. This paper looks at the FTIR spectra of tmii, dmit, dmise, mpit and $\text{ZnCl}_2(\text{mpit})_2$ with respect to the suggested assignments for $\nu(\text{C}=\text{S})$ and reports the results of the X-ray study for tmii to support our conclusions. Furthermore, the details of the synthesis and characterization of the new thiourea and its ZnCl_2 complex are included, as well as the detailed synthesis and characterization for tmii.

Experimental

Chemicals

All chemicals were reagent grade and used as commercially obtained without further purification. Spectroscopic grade CD_3CN and perdeuterated dimethyl sulfoxide (DMSO-d_6) (Aldrich) were used as solvents to obtain the proton and ^{13}C NMR data. Dmise [11] and dmit [12] were prepared using methods reported in the literature.

Analytical

Carbon, hydrogen and nitrogen analyses were done by Atlantic Microlabs, Inc. The Zn analysis was done on a Varian model 1475 atomic absorption spectrophotometer (AAS).

Solution studies

Specific conductivity for tmii was measured in deionized H_2O using methods previously reported [1]. Proton and proton decoupled ^{13}C NMR spectra were recorded with a 300 MHz GE model QE-300 FT-NMR spectrometer. Chemical shifts are reported in ppm (δ) relative to tetramethylsilane. Key: s = singlet, d = doublet, m = multiplet.

Solid state spectra

IR spectra of tmii, dmit and dmise were collected as KBr pellets from 4000 to 400 cm^{-1} using a Mattson Galaxy 2020 Fourier transform infrared spectrophotometer (FTIR). The spectrum of mpit was collected as a neat film between AgCl plates. $\text{ZnCl}_2(\text{mpit})_2$ data were collected as a powder from evaporation out of a petroleum ether slurry on a background subtracted polyethylene film (3M 'IR card'). Only the peaks within the range of primary interest (viz. up to 1600 cm^{-1}) are reported below. All values are in cm^{-1} (± 4). The spectral results with assignments are reported in Table 1.

Synthesis

Melting points (uncorrected) were obtained on a Fisher-Johns stage-type apparatus and reported in degrees Celsius. Crystallographic grade crystals of tmii were obtained directly from the reaction mixture.

1-Methyl-3-(2-propenyl)-2(3H)-imidazolethione (mpit)

Equal molar quantities of 1-methylimidazole (0.31 mol, 25.0 ml, Fisher) and 3-bromo-1-propene (allyl bromide, 29.5 ml, Eastman) were mixed with 85 ml of ethyl acetate in a 250 ml round bottomed flask. An exothermic reaction produced a dark brown oil within a few minutes. The reaction was allowed to stir for 20 min after which the oil was separated and mixed with 11.2 g sulfur, 38.2 g of K_2CO_3 and 300 ml of methanol in a 500 ml round bottomed flask fitted with heating mantle, reflux condenser and magnetic stirrer. The mixture was stirred and refluxed for *c.* 24 h after which it was mixed with 800 ml of water and extracted in a large separatory funnel with three 100 ml aliquots of CH_2Cl_2 . The methylene chloride layer was dried with anhydrous MgSO_4 and the solvent was stripped off on a rotary evaporator. The remaining oil was vacuum distilled yielding 14.5 g (30% yield) of an amber yellow oil. B.p. $64\text{ }^\circ\text{C}$ (54 torr). *Anal.* Calc. for $\text{C}_7\text{H}_{10}\text{N}_2\text{S}$: C, 54.51; H, 6.54; N, 18.16; S, 20.79. Found: C, 53.52; H, 6.62; N, 17.81; S, 20.51%. Proton NMR (δ): 3.50 (s, 3H, methyl), 4.60 (d, 2H, terminal vinyl, $J_{\text{AB}}=5\text{ Hz}$), 5.11 (d, 1H, allylic, $J_{\text{AB}}=17\text{ Hz}$), 5.21 (d, 1H, allylic, $J_{\text{AB}}=10\text{ Hz}$), 5.93 (m, 1H, vinyl), 6.84 (d, 2H, ring olefinic, $J_{\text{AB}}=13\text{ Hz}$).

TABLE 1. IR spectra of dmit, mpit, $\text{ZnCl}_2(\text{mpit})_2$, dmise and tmii with selected tentative assignments

| dmit | mpit | $\text{ZnCl}_2(\text{mpit})_2$ | dmise | tmii | Assignment |
|-----------|--------------|--------------------------------|--------|-----------|--------------------------------------------------------------------------------------------------------|
| 1572m | 1567m | 1562m | 1570m | 1572m | $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})^a$ or $\nu_{\text{as}}(\text{N}-\text{C}-\text{N})^b$ |
| 1493s | | | | 1500vs | thioamide I ^c |
| 1466s | 1467s | 1472s | 1466s | 1462m, sh | |
| 1442s | | | 1435m | 1433s | |
| 1388vs | 1407s, br | 1412s, br | 1381vs | | $\nu(\text{N}-\text{Me})^a$ |
| 1346m, sh | 1347m | | | 1362m | |
| | | 1316w | 1319m | 1316m | $\delta(\text{CH}_3\text{S})^c$ (tmii) |
| 1238s | 1246s | 1235s | 1235s | 1248vs | thioamide II ^a |
| | 1212s | 1213s | | | |
| 1180s | | | | 1186m | $\nu(\text{C}=\text{S})^{b,c}$ δCH^c or $\nu(\text{C}=\text{S})$ (see text) |
| | 1158m | 1152m 1135m, sh | | | |
| 1146m, sh | | | 1144s | | δCH^c |
| 1084m | 1090m | 1086m | 1084m | 1101m | thioamide III ^d |
| 985w | 994m 935s | 993m 941s | | 978s | $r(\text{CH}_3\text{S})^c$ (tmii) or πCH^d (vinyl, mpit) |
| | 777m | | 885w | | |
| 752m, sh | | 752s | | 790vs | πCH^c thioamide IV ^a or πCH (see text) |
| 732s | | | 739vs | 744w | |
| | 727s | | | | |
| | | 706w | | 719w | |
| | | 697s | | | |
| | | 677w | | | |
| 663m | 668s | | | 669s | $\delta(\text{C}-\text{S})^a$ |
| | | | 650m | | |
| | | | | 623w | |
| | 589w | | | | |
| | | 579w | | | |
| 513m | 510w | | | | |
| 496m, sh | 482w | 496w | | | $\pi(\text{C}-\text{S})^a$ |
| | | | 470mw | 480m | |

^aRef. 4. 'Thioamide'-type modes are described as follows: thioamide I = $\nu(\text{C}-\text{N}) + \delta\text{CH}$; thioamide II = $\nu(\text{C}-\text{N}) + \delta\text{CH} + \nu(\text{C}=\text{S})$; thioamide III = $\nu(\text{C}-\text{N}) + \nu(\text{C}=\text{S})$; thioamide IV = $\nu_s(\text{C}=\text{S}) + \nu_{\text{as}}(\text{C}=\text{S})$. ^bRef. 1. ^cRef. 2. ^dRef. 13. Key: v = very, w = weak, m = medium, s = strong, br = broad, sh = shoulder, ν = stretching, δ = bending, π = out-of-plane bending, r = rocking, s = symmetric, as = asymmetric (or antisymmetric)

Bis-[1-Methyl-3-(2-propenyl)-2(3H)-imidazolethione]-dichlorozinc(II)

A mixture of 12.8 g (94 mmol) ZnCl_2 (Fisher) and 14.0 g (91 mmol) of mpit were mixed in 100 ml of boiling water. Upon cooling, light tan crystals were obtained in c. 30% yield. M.p. 122–124 °C. *Anal.* Calc. for $\text{C}_{14}\text{H}_{20}\text{Cl}_2\text{N}_4\text{S}_2\text{Zn}$: C, 37.81; H, 4.53; Cl, 15.94; N, 12.60; Zn, 14.70. Found: C, 37.92; H, 4.54; Cl, 15.87; N, 12.65; Zn, 14.7%. Proton NMR (δ): 3.66 (s, 3H, methyl), 4.70 (d, 2H, terminal vinyl, $J_{\text{AB}} = 6$ Hz), 5.21 (d, 1H, allylic, $J_{\text{AB}} = 18$ Hz), 5.26 (d, 1H, allylic, $J_{\text{AB}} = 10$ Hz), 5.97 (m, 1H, vinyl), 7.06 (d, 2H, ring olefinic, $J_{\text{AB}} = 13$ Hz).

1,3-Dimethyl-2-(S-methylthio)-2(3H)-imidazoylium iodide (tmii)

In 100 ml of ethanol were placed 9.3 g (73 mmol) dmit and 10.3 g (73 mmol) iodomethane (Aldrich). The mixture was warmed to c. 40 °C for 1 h and the ethanol was removed by rotary evaporation. The oily mother liquor was refrigerated at c. 10 °C for 24 h, and from it was obtained 10.7 g of a pale yellow crystalline solid (55% yield). M.p. 182–183 °C. *Anal.* Calc. for $\text{C}_6\text{H}_{11}\text{N}_2\text{SI}$: C, 26.68; H, 4.10; N, 10.37; I, 46.98. Found: C, 26.70; H, 4.06; N, 10.29; I, 47.06%. Λ_{M} (c. 10^{-3} M) = 105 mho cm^2/mol . Proton NMR (δ):

2.50 (s, 3H, S-methyl), 3.92 (s, 6H, N-methyl), 7.63 (s, 2H, olefinic). ^{13}C NMR (δ): 17.31, 36.20, 124.46, 140.66.

X-ray crystallographic data

Crystallographic data collection as well as structural solution and refinement for tmii were performed as previously described [11]. Absorption corrections were not applied. Final calculated values for R and R_w as well as other crystallographic data for tmii are summarized in Table 2. Table 3 lists selected interatomic angles and distances, and Fig. 2 shows an ORTEP drawing at the 50% probability level. See also 'Supplementary material'.

TABLE 2. Data collection and processing parameters

| | |
|-----------------------------------------------|------------------------------------------------------------------|
| Molecular formula | $\text{C}_6\text{H}_{11}\text{N}_2\text{S}$ |
| Molecular weight | 207.04 |
| Unit cell parameters | |
| a (Å) | 7.846(2) |
| b (Å) | 11 754(2) |
| c (Å) | 12.578(2) |
| β (°) | 95.51(2) |
| V (Å ³) | 1056.38 |
| Z | 4 |
| $F(000)$ | 520 |
| $\lambda(\text{Mo K}\alpha)$ (Å) | 0.71073 |
| $\mu(\text{Mo K}\alpha)$ (mm^{-1}) | 3.13 mm^{-1} |
| Temperature (K) | 294 |
| Density (calc.) (g/cm^3) | 1.699 |
| Density (obs) (g/cm^3) | 1.66 (floatation $\text{CCl}_4/\text{CH}_3\text{CH}_2\text{I}$) |
| Space group | $P2_1/n$ |
| Crystal size (mm) | $0.37 \times 0.37 \times 0.20$ |
| Unique data measured | 3071 |
| Observed data with $ F_o > 2.5\sigma F_o $ | 2229 |
| Conventional R | 0.034 |
| Weighted R | 0.042 |
| Goodness of fit | 1.362 |
| Residual electron density ($e/\text{Å}^3$) | $-0.530/+0.530$ |
| Max. shift/error ratio final cycle | 0.015 |

TABLE 3. Selected interatomic distances (Å) and angles (°) for tmii with e.s.d.s in parentheses (see Fig. 2 for the atomic designators)

| | | | |
|----------|----------|----------|----------|
| S-C1 | 1.731(4) | N2-C2 | 1.370(5) |
| S-C6 | 1.805(5) | N1-C3 | 1.353(6) |
| C1-N1 | 1.338(5) | N2-C4 | 1.462(6) |
| C1-N2 | 1.342(5) | N1-C5 | 1.466(6) |
| C2-C3 | 1.337(7) | | |
| C1-S-C6 | 99.6(2) | S-C1-N1 | 127.2(3) |
| S-C1-N2 | 126.1(3) | N1-C1-N2 | 106.6(3) |
| C1-N1-C3 | 109.4(2) | C1-N2-C2 | 109.3(4) |
| C1-N1-C5 | 124.6(4) | C1-N2-C4 | 126.5(4) |
| C3-N1-C5 | 125.8(4) | C2-N2-C4 | 123.8(4) |
| C3-C2-N2 | 106.6(4) | C2-C3-N1 | 108.1(4) |

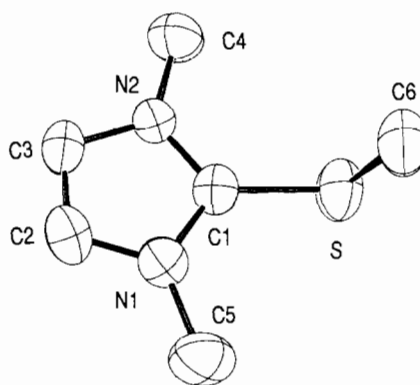


Fig. 2. ORTEP drawing of tmii. Thermal ellipsoids drawn at 50% probability level. (Iodide ion omitted.)

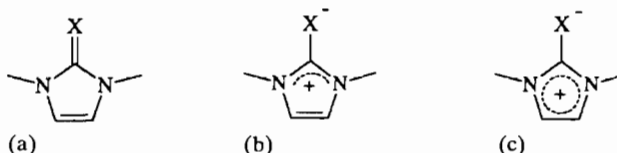


Fig. 3. Possible electronic structural configuration for 2(3H)-imidazolechalcones. X = S, Se.

Results and discussion

The recorded IR spectra of tmii, dmit and dmise shown in Table 1 compare reasonably well to literature values [2, 4, 12]. The most notable result from this comparison, however, is the fact that the assigned 'thioamide' modes for dmit have almost identical corresponding peaks in the IR spectrum of dmise. The two spectra are virtually superimposable except for the region between 1170 and 1180 cm^{-1} . Furthermore, the IR spectrum reported by Campbell *et al.* [14] of the oxygen analog, 1,3-dimethyl-2(3H)-imidazolone, also shows corresponding peaks (viz. 1487s, 1239s, 1094m, 761m). This, of course, casts serious doubt on the significance of carbon-sulfur contribution to the thioamide peaks II-IV. The peak assigned as $\nu(\text{C}=\text{S})$ for dmit by Mille *et al.* at 1177 cm^{-1} corresponds to our peak seen at 1180 cm^{-1} , and as we had previously demonstrated in a number of metal halide complexes, was not very sensitive to coordination [1]. The rationale for this was the fact that the C-S bond length did not change to a large extent upon coordination (from 1.69 Å in the unbonded ligand to an average of 1.72 Å in the observed complexes [1]).

The bond distances in tmii (Table 3) show two values for carbon-sulfur bonds which help to demonstrate the degree of delocalization for the thionyl C=S. Figure 3 shows three possible resonance contributors corresponding to increased degrees of involvement for the p orbitals of the thionyl sulfur with the ring π -system. Based on the length of the C=S bond in dmit (1.695 Å), and the relative shortness of the ethylenic carbon

double bond distance (1.31 Å), Ansell *et al.* [15] concluded that Fig. 3(b) was the best representation for the degree of delocalization. The carbon–sulfur bond distance lay almost halfway between that of a double bond estimated at 1.61 Å and a single bond of 1.81 Å [15]. As can be seen in Table 3, the S–methyl distance (S–C6, Fig. 2) of 1.805 Å is as expected for a carbon–sulfur single bond, but the thionyl carbon–sulfur distance of 1.731 Å (S–C1) is only slightly longer than that noted for the average distance of 1.72 Å parenthetically noted above. A large shift in stretching frequency again would not be expected based on these relatively small differences in thionyl carbon–sulfur bond distances, yet, as mentioned earlier, Mille *et al.* interpreted their spectra for tmii as showing the disappearance of the C=S stretch [2], but did report a weaker peak at 1186 cm⁻¹. Upon examining our spectrum of tmii, however, and considering the carbon–sulfur bond distance, the peak noted at 1186 cm⁻¹ should perhaps be reassigned as $\nu(\text{C}=\text{S})$ rather than the out-of-plane CH deformation mode as assigned by Mille *et al.* [2].

Another notable point in the structure of tmii is the greater uniformity in ring bond distances. The elongation of the olefinic double bond and the trend toward greater uniformity of the other ring interatomic distances suggests a more aromatic-type delocalization as demonstrated by Fig. 3(c). Increase in aromaticity of the ring is further substantiated by both ¹³C and proton NMR spectra. The olefinic carbons are shifted downfield from δ 117.94 for dmit [16] to δ 124.46 for tmii. Likewise, there is a downfield shift for the olefinic protons in tmii (δ 7.63) relative to dmit (δ 6.69 [17]). Arduengo *et al.* have already noted the sensitivity of these protons to increased aromatic ring character [18]. A similar type of increased delocalization is noted in the crystal structures of dmise [11] and (dmise)Br₂ [19], a molecular complex with a linear Br–Se–Br moiety attached perpendicularly to the planar imidazole ring. Again, ¹³C NMR shows the expected downfield shift for the olefinic protons from 120.13 ppm in dmise to 124.24 ppm for (dmise)Br₂ [16]. Several crystal structures of dmit metal halide complexes or other dmit derivatives show changes in ring bond distances upon coordination, although not all necessarily show a clear trend toward increased aromaticity [1, 3, 9, 20, 21]. The thiocarbonyl group at δ 140.66 in tmii shows the expected increased shielding upon S-methylation relative to dmit (δ 161.63 [16]). This same trend is observed in the spectra for the alpha form of the I₂ charge transfer complex of dmit (δ 165.78 to 154.77), and is accompanied by a similar degree of elongation of the C–S bond noted above (1.695 to 1.724 Å) [9].

A new complex added for comparison purposes is the 1:2 adduct of ZnCl₂ and mpit. Given the relatively

low melting point and ease of solubility of this compound in most non-polar or slightly polar solvents, it is likely to be a discrete molecular complex similar to CoBr₂(dmit)₂ reported by Kheddar *et al.* [3]. Looking at the indicator modes noted in our earlier study, the $\nu_{\text{as}}(\text{N}-\text{C}-\text{N})$ stretch is shifted to lower wave numbers upon coordination (1568 to 1562 cm⁻¹) as is the carbon–sulfur stretch which we assign to the peak at 1158 cm⁻¹ in mpit and to the peak at 1152 cm⁻¹ in the complex. These peaks follow a similar trend regarding direction and magnitude of shift noted for several dmit complexes cited in our earlier study [1]. The classical allylic CH deformation mode pattern of two peaks in the 900–1000 cm⁻¹ region are observed [13], and appear to be insensitive to coordination. In the solution studies for mpit and ZnCl₂(mpit)₂, there is shift downfield in the ring olefinic proton signal for the ZnCl₂ complex relative to the uncoordinated ligand similar to that noted above for the other compounds in this study (δ 6.89 for mpit and δ 7.06 for the complex).

In seeking an alternate explanation for the assignments of the thioamide modes noted above, it seems likely that these are all associated with vibrations that are relatively independent of the exocyclic heteroatom and can perhaps be attributed to either ring vibrations or CH modes of various types. For example, the peaks between 700–800 cm⁻¹ may better be assigned as out-of-plane CH deformations characteristic of *cis*-olefinic protons [2]. Shifts in the thioamide modes may better be attributed to changes in ring bond character as evidenced by changes in distances which in some cases is the result of increased aromaticity of the ring when the exocyclic heteroatom is coordinated to an acceptor site. Based on the evidence above, it seems unlikely, however, that carbon–sulfur stretching modes contribute to thioamide II, III or IV.

Supplementary material

Final positional parameters for the non-hydrogen atoms, calculated hydrogen positions, thermal parameters, and a list of calculated and observed structure factor tables are available from the Cambridge Crystallographic Data Center.

Acknowledgements

D.J.W. thanks the Kennesaw State College Faculty Development Fund and the Wilcom Foundation of Marietta, GA (USA) for partial support of this research. We are also grateful to the National Science Foundation (CSI-8851864) who provided funds for the atomic absorption spectrophotometer. We wish to express our

gratitude also to Dr Al Panu of Kennesaw State College for the ChemDraw® structures presented in this report. Our thanks also to Dr Alex Kitaygorodskiy of Emory University for the ¹³C NMR spectra reported in this paper. Part of this work represents the results of directed team research completed in fulfillment of the laboratory requirements of Intermediate Inorganic Chemistry (CHEM 310) at KSC.

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