Reinvestigation of the Synthesis of Tris[benzoyl(thiobenzoyl)-methanato-*S*]arsenic(III): Synthesis and *X*-Ray Structure of 3,3′-Thiodi-(1,3-diphenylprop-2-en-1-one)†

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Tris[benzoyl(thiobenzoyl)methanato-*S*]arsenic(III), prepared by the reaction of arsenic trichloride with benzoyl(thiobenzoyl)methane, appears to be essentially tetrahedral, involving only sulphur-bonded ligands. Under reflux, the *Z*,*Z* isomer of 3,3′-thiodi(1,3-diphenylprop-2-en-1-one) is obtained exclusively as confirmed by a single-crystal *X*-ray analysis.

We are currently interested in the chemistry and structural aspects of monothio-β-diketonates of main group elements.[1–4] Our recent report[5] describes the reaction of indium trichloride with monothio-β-diketones and the *X*-ray structure determination of tris[benzoyl(thiobenzoyl)methanato-*O*,*S*]indium(III). The solid-state structure of this compound shows remarkable similarities with tris[benzoyl(thiobenzoyl)methanato-*O*,*S*]-iron(III).[6]

Due to difficulties encountered in obtaining suitable single crystals of monothio-β-diketonates of Group 3 elements, we diverted our attention to Group 5 elements in oxidation state III which are 'class b' soft acids and for which enhanced reactivity is expected. In this report, we describe our results on the reactions of arsenic trichloride with benzoyl(thiobenzoyl)methane.

Experimental

All experimental manipulations were performed under strictly anhydrous conditions. Solvents were purified and stored under dinitrogen. Commercial arsenic trichloride (B.D.H.) was distilled before use. Benzoyl(thiobenzoyl)methane was prepared by a literature procedure.[7] For analysis of arsenic,[8] the compound was decomposed by refluxing (*ca.* 5 h) with fuming sulphuric and nitric acids. The resulting solution was saturated with sulphur dioxide and allowed to stand for *ca.* 16 h. Excess sulphur dioxide was removed by boiling. After complete removal of sulphur dioxide, the solution was cooled to room temperature, made alkaline by sodium bicarbonate, and titrated with standard iodine solution using starch as an indicator. Sulphur was analyzed by Messenger's method.

Molecular weights were determined cryoscopically in benzene. I.r. spectra were recorded on a Perkin-Elmer-621 spectrometer in the range 4 000—200 cm^{-1} as Nujol mulls. Proton and ^{13}C n.m.r. spectra were recorded on a JEOL-FX-90 Q spectrometer using tetramethylsilane as an internal reference.

Preparation of Tris[*benzoyl*(*thiobenzoyl*)*methanato*-S]-*arsenic*(III), As(PhCSCHCOPh)$_3$ (**1**).—To a stirred solution of arsenic trichloride (0.6 g, 3.3 mmol) in methanol (*ca.* 20 cm^3) was added a solution of benzoyl(thiobenzoyl)methane (2.3 g, 9.5 mmol) and sodium acetate (0.78 g, 9.5 mmol) in methanol (*ca.* 45 cm^3). After complete addition, stirring was continued for *ca.* 4 h. Volatiles were removed and the residue extracted with dichloromethane. Removal of solvent and crystallization from chloroform–methanol (1:3) furnished a yellow crystalline material. Yield: 2.4 g, 95%, m.p. 150 °C (Found: C, 68.4; H, 4.9; As, 10.0; S, 12.3. Calc. for $C_{45}H_{33}AsO_3S_3$: C, 68.1; H, 4.5; As, 9.4; S, 12.1%). ^{13}C N.m.r. (p.p.m.): 188.2, 156.5, 140.6, 132.7, 131.2, 128.9, 128.6, 128.5, 128.3, 122.1, and 110.7. I.r. (cm^{-1}): 1 640s $\nu(C\overset{\cdots}{-}O)$, 1 540s $\nu(C\overset{\cdots}{-}C)$, and 345s ν(As–S).

Reaction of Arsenic Trichloride with Benzoyl(*thiobenzoyl*)-*methane*.—A solution of arsenic trichloride (0.18 g, 0.99 mmol) and benzoyl(thiobenzoyl)methane (2.3 g, 9.50 mmol) in benzene (60 cm^3) was refluxed for *ca.* 7 h. The precipitated solid, AsS(PhCSCHCOPh) (**2**), was filtered off, washed with benzene, and purified by precipitation with benzene from its solution in dimethyl sulphoxide. Yield: 0.3 g, 88% (based on $AsCl_3$), m.p. 125—127 °C (Found: As, 21.7; S, 18.3. Calc. for $C_{15}H_{11}AsOS_2$: As, 21.6; S, 18.6%). I.r. (cm^{-1}): 1 595s $\nu(C\overset{\cdots}{-}O)$, 1 512s $\nu(C\overset{\cdots}{-}C)$, 1 245s $\nu(C\overset{\cdots}{-}S)$, 570s ν(As–O), and 320s ν(As–S). Removal of solvent from the filtrate and crystallization from dichloromethane–methanol (1:3) furnished crystals of 3,3′-thiodi(1,3-diphenylprop-2-en-1-one), S(PhC=CHCOPh)$_2$ (**3**). Yield: 1.5 g, 76% (based on PhCSCH$_2$COPh), m.p. 179—180 °C (Found: C, 80.9; H, 5.0; S, 7.1. Calc. for $C_{30}H_{22}O_2S$: C, 80.7; H, 4.9; S, 7.1%). ^1H N.m.r. (p.p.m.): 8.0, 7.5, and 6.9; ^{13}C n.m.r. (p.p.m.): 188.5, 155.5, 140.6, 138.1, 132.7, 128.5, 128.3, 127.9, and 124.7. I.r. (cm^{-1}): 1 640s $\nu(C\overset{\cdots}{-}O)$ and 1 538s $\nu(C\overset{\cdots}{-}C)$.

Reaction of H_2S *with the Product formed from the Equimolar Reaction of* $AsCl_3$ *with* PhCSCH$_2$COPh (*in the Presence of One Mole of Sodium Acetate*).—Arsenic trichloride (0.46 g, 2.5 mmol) dissolved in methanol (15 cm^3) was added to a methanolic solution (*ca.* 40 cm^3) of benzoyl(thiobenzoyl)-methane (0.6 g, 2.4 mmol) and sodium acetate (0.2 g, 2.4 mmol) at −10 °C. The reaction mixture was stirred for *ca.* 4 h. Methanol was removed and the residue treated with dichloromethane to separate sodium chloride which was removed by filtration. H_2S gas was passed into the filtrate for 0.5 h. The precipitated light yellow paste was separated off by decantation, washed, and dissolved in dimethyl sulphoxide. The light yellow solid product was obtained by the addition of benzene. Yield: 0.73 g, 84% (based on $AsCl_3$), m.p. 127 °C (Found: As, 21.3; S, 18.9. Calc. for $C_{15}H_{11}AsOS_2$: As, 21.6; S, 18.6%). I.r. (cm^{-1}): 1 595s $\nu(C\overset{\cdots}{-}O)$, 1 512s $\nu(C\overset{\cdots}{-}C)$, 1 245s $\nu(C\overset{\cdots}{-}S)$, 570s ν(As–O), and 320s ν(As–S).

X-*Ray Analyses of* S(PhC=CHCOPh)$_2$ (**3**).—*Crystal data.* $C_{30}H_{22}O_2S$, *M* = 446.57, monoclinic, space group $P2_1/n$ (no.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

14), $a = 11.5159(36)$, $b = 17.3292(91)$, $c = 11.7350(37)$ Å, $\beta = 90.350(25)°$, $U = 2\,341.8(16)$ Å^3, $Z = 4$, $D_c = 1.266$ g cm^{-3}, $F(000) = 936$, and $\mu(\text{Mo-}K_\alpha) = 1.55$ cm^{-1}.

Transparent yellow-orange crystals of elongated rectangular prism habit were obtained from dichloromethane–methanol (1:3). A crystal of approximate dimensions 0.24 × 0.26 × 0.76 mm was selected and mounted in a glass capillary. It was optically aligned on the goniometer of a Syntex P3/F automated four-circle diffractometer and the setting angles of 25 automatically centred reflections were used to determine the orientation matrix and the dimensions of the unit cell. The latter were checked by axial photographs. Graphite monochromated Mo-K_α radiation was used ($\lambda = 0.710\,69$ Å).

The intensities of 12 054 reflections in 2θ limits $2 < h, k \neq l < 55°$ including Friedel related reflections were measured; three check reflections (400, 080, 004) were recorded after every 141 reflections. Lorentz and polarization corrections were applied and an empirical absorption correction based on a ψ scan was made. Intensities were converted to structure factors by standard procedures. 5 401 Reflections were space group allowed and 3 102 reflections had $F > 4\sigma(F)$.

The structure was solved by direct methods using SHELXTL.[9] All the non-hydrogen atoms were found in the Fourier map. Refinement with individual anisotropic thermal parameters converged to $R = 0.093$. At this stage, the hydrogens were calculated in fixed positions (riding model). Final refinement with anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms led to the final $R = 0.0675$ and $R' = 0.0480$ [$R = \Sigma|\Delta F|/\Sigma|F_o|$ and $R' = \Sigma(|\Delta F|w^{\frac{1}{2}}/\Sigma w^{\frac{1}{2}}|F_o|)$]. The weighting scheme applied was $w = 1/[\sigma^2(F)]$. 298 Parameters were refined in the last cycles using blocked cascade calculations. Fractional atomic co-ordinates are given in Table 1. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters, H-atom co-ordinates, and remaining bond lengths and angles.

Table 1. Fractional atomic co-ordinates of the non-hydrogen atoms of S(PhC=CHCOPh)$_2$ (**3**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
S(1)	0.260 20(7)	0.702 01(4)	0.293 61(6)
O(1)	0.483 82(16)	0.733 98(9)	0.208 05(16)
O(2)	0.063 89(17)	0.799 29(10)	0.298 67(16)
C(1)	0.503 0(2)	0.666 8(1)	0.178 6(2)
C(2)	0.414 8(2)	0.607 5(1)	0.185 8(2)
C(3)	0.312 0(2)	0.613 7(1)	0.240 1(2)
C(4)	0.017 4(2)	0.764 3(1)	0.375 8(2)
C(5)	0.079 1(2)	0.705 5(1)	0.442 0(2)
C(6)	0.178 9(2)	0.671 3(1)	0.412 1(2)
C(11)	0.621 0(2)	0.645 4(1)	0.135 7(2)
C(12)	0.712 7(2)	0.694 8(2)	0.161 5(2)
C(13)	0.823 5(3)	0.679 1(2)	0.122 4(3)
C(14)	0.842 1(3)	0.614 5(2)	0.056 8(2)
C(15)	0.753 4(3)	0.566 0(2)	0.031 0(2)
C(16)	0.642 0(2)	0.581 7(1)	0.069 9(2)
C(21)	0.232 5(2)	0.546 4(1)	0.244 9(2)
C(22)	0.275 6(2)	0.473 2(1)	0.271 8(2)
C(23)	0.202 3(3)	0.410 0(2)	0.274 7(2)
C(24)	0.087 3(3)	0.418 7(2)	0.250 7(2)
C(25)	0.043 9(3)	0.490 7(2)	0.222 5(2)
C(26)	0.114 9(2)	0.553 4(1)	0.219 7(2)
C(31)	−0.108 2(2)	0.779 1(1)	0.403 3(2)
C(32)	−0.174 5(3)	0.729 8(2)	0.466 8(2)
C(33)	−0.291 5(3)	0.745 8(3)	0.485 3(3)
C(34)	−0.339 4(3)	0.810 5(2)	0.438 8(3)
C(35)	−0.274 6(3)	0.860 6(2)	0.377 2(3)
C(36)	−0.158 8(3)	0.845 0(2)	0.358 4(3)
C(41)	0.231 6(2)	0.611 0(1)	0.485 4(2)
C(42)	0.164 3(3)	0.553 4(2)	0.531 1(2)
C(43)	0.213 8(5)	0.495 5(2)	0.597 8(3)
C(44)	0.332 0(5)	0.497 6(3)	0.618 8(4)
C(45)	0.398 4(4)	0.555 2(3)	0.574 6(3)
C(46)	0.350 9(3)	0.611 3(2)	0.508 0(2)

Results and Discussion

The synthesis of As(PhCSCHCOPh)$_3$ (**1**) was first reported by Uhlemann and Thomas[10] in 1967. Following their procedure, we examined the reaction of arsenic trichloride with benzoyl(thiobenzoyl)methane in refluxing benzene. Instead of (**1**), this reaction, in our hands, furnished S(PhC=CHCOPh)$_2$ (**3**), together with [benzoyl(thiobenzoyl)methanato-*O*,*S*]arsenic(III) sulphide, AsS(PhCSCHCOPh) (**2**). The formation of (**3**) is an AsCl$_3$ (Lewis acid)-catalyzed reaction since reaction with a large excess of ligand (1:10 molar ratio) in refluxing benzene converts most of the ligand into (**3**) while a small quantity of it, proportional to arsenic trichloride, is converted into (**2**). The reaction can be represented by equation (1). Thiols are known to convert into sulphides in refluxing solvent with evolution of H$_2$S under the catalytic influence of aluminium trichloride.[11,12]

$$\mathrm{2PhCSCH_2COPh} \xrightarrow[\text{heat, benzene}]{\mathrm{AsCl_3}} \underset{(\mathbf{3})}{\mathrm{S(PhC{=}CHCOPh)_2}} + \mathrm{H_2S} \quad (1)$$

The formation of (**2**) may occur by the reaction of H$_2$S with AsCl$_2$(PhCSCHCOPh) which could not be isolated. The reaction of AsCl$_2$(PhCSCHCOPh) (formed *in situ* from an equimolar mixture of arsenic trichloride and PhCSCH$_2$COPh in the presence of one mole of sodium acetate) with H$_2$S produces (**2**) quantitatively [equation (2)].

$$\begin{aligned} &\mathrm{AsCl_3 + PhCSCH_2COPh + NaO_2CMe} \longrightarrow \\ &\qquad \mathrm{AsCl_2(PhCSCHCOPh) + NaCl + MeCO_2H} \quad (2) \\ &\qquad {\scriptstyle\mathrm{H_2S}}\Big\downarrow \\ &\qquad \underset{(\mathbf{2})}{\mathrm{AsS(PhCSCHCOPh)}} + \mathrm{2HCl} \end{aligned}$$

Compound (**1**) can be conveniently prepared by an alternative procedure involving the reaction of arsenic trichloride with benzoyl(thiobenzoyl)methane in the presence of sodium acetate in methanol at room temperature. The product is isolated as a yellow crystalline solid [equation (3)].

$$\begin{aligned} &\mathrm{AsCl_3 + 3PhCSCH_2COPh + 3NaO_2CMe} \longrightarrow \\ &\qquad \underset{(\mathbf{1})}{\mathrm{As(PhCSCHCOPh)_3}} + \mathrm{3NaCl + 3MeCO_2H} \quad (3) \end{aligned}$$

The i.r. spectrum of (**1**) exhibits a strong band at 1 640 cm^{-1} which is assignable to unco-ordinated $\nu(\mathrm{C\overset{\cdots}{-}O})$. Its position is almost the same as the $\nu(\mathrm{C\overset{\cdots}{-}O})$ vibration for (**3**) which suggests that the ligands are bonded to arsenic through sulphur only. Only one absorption (below 600 cm^{-1}) at 345 cm^{-1} due to ν(As–S) further substantiates the above bonding mode. ^{1}H N.m.r. data do not provide definitive structural information for (**1**). ^{13}C N.m.r. data, on the other hand, provide additional evidence for the unidentate behaviour of the ligands. The carbonyl carbon resonance appears at 156.5 p.p.m., at a much higher field than the corresponding absorption (186.2 p.p.m.) in tris[benzoyl(thiobenzoyl)methanato-*O*,*S*]indium(III),[5] and is very close to the shift for S(PhC=CHCOPh)$_2$ (155.5 p.p.m.). The thiocarbonyl shows a chemical shift at 188.2 p.p.m. which

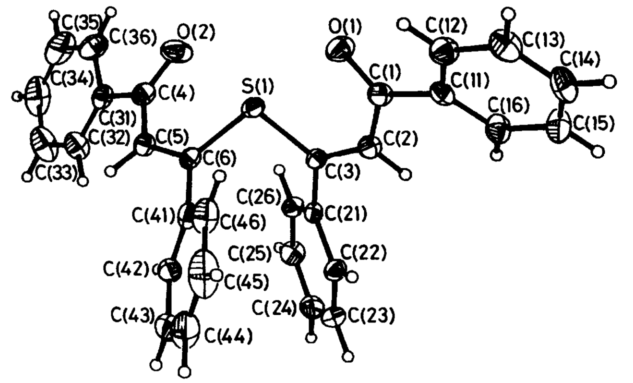

Figure. ORTEP plot and atomic numbering scheme for S(PhC=CHCOPh)$_2$ (**3**). Thermal ellipsoids represent the 50% probability level

Table 2. Selected bond lengths (Å) and angles (°) for S(PhC=CHCOPh)$_2$ (**3**) with estimated standard deviations in parentheses

S(1)–C(3)	1.759(2)	C(1)–C(2)	1.448(3)
S(1)–C(6)	1.763(2)	C(4)–C(5)	1.462(3)
O(1)–C(1)	1.235(3)	C(2)–C(3)	1.352(3)
O(2)–C(4)	1.216(3)	C(5)–C(6)	1.343(3)
C(1)–C(11)	1.498(4)	C(3)–C(21)	1.484(3)
C(4)–C(31)	1.506(4)	C(6)–C(41)	1.481(3)
C(3)–S(1)–C(6)	101.6(1)	O(1)–C(1)–C(11)	119.4(2)
O(1)–C(1)–C(2)	121.7(2)	O(2)–C(4)–C(31)	120.1(2)
O(2)–C(4)–C(5)	121.9(2)	C(2)–C(1)–C(11)	118.9(2)
C(1)–C(2)–C(3)	126.0(2)	C(5)–C(4)–C(31)	117.9(2)
C(4)–C(5)–C(6)	125.7(2)	C(2)–C(3)–C(21)	119.8(2)
S(1)–C(3)–C(2)	122.5(2)	C(5)–C(6)–C(41)	120.5(2)
S(1)–C(6)–C(5)	122.2(2)	S(1)–C(3)–C(21)	117.4(2)
		S(1)–C(6)–C(41)	117.0(2)

is very close to the resonance (191.5 p.p.m.) reported for In(PhCSCHCOPh)$_3$.[5] These two ^{13}C chemical shifts can be regarded as being diagnostic for distinguishing a sulphur-bonded unidentate ligand from its bidentate bonding mode.

From the spectroscopic data compound (**1**) can be considered to contain pyramidal or tetrahedral arsenic depending on the stereochemically active nature of the lone pair. This is unusually different from the xanthate, As(S$_2$COR)$_3$,[13] or dithiocarbamate, As(S$_2$CNR$_2$)$_3$,[14] where single-crystal *X*-ray structure determinations show pseudo-trigonally distorted octahedral geometry. An *X*-ray structure determination could have unequivocally provided the structural details of (**1**), however, efforts to grow suitable single crystals were not successful.

The insoluble nature of compound (**2**) prevented us from obtaining substantial spectroscopic data. The i.r. spectrum is consistent with a bidentate bonding mode for the ligand. The bands at 1 595 and 1 512 cm^{-1} assigned to $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ vibrations respectively are consistent with the conjugated chelate ring structure having a high degree of π delocalization in the ligand. A band at 1 245 cm^{-1} due to $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ and two bands at 570 and 320 cm^{-1} due to ν(As–O)[15] and ν(As–S)[16] respectively are also observed. The insoluble nature of (**2**) suggests an oligomeric or polymeric structure.

The i.r. spectrum of compound (**3**) exhibits strong bands at 1 640 cm^{-1} due to $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ and at 1 538 cm^{-1} due to $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$. The ^{1}H n.m.r. spectrum shows three multiplets centred at 8.0, 7.5, and 6.9 p.p.m. These chemical shifts are due to the *ortho* (8.0 p.p.m.) and *para* and *meta* (7.5 p.p.m.) protons of the phenyl attached to the carbonyl carbon. The multiplet at 6.9 p.p.m. is due to the phenyl protons attached to the thio carbon. The ^{13}C n.m.r. spectrum shows the carbonyl carbon at 155.5 p.p.m. and the thio carbon at 188.5 p.p.m. Low-temperature ^{13}C n.m.r. data were not helpful in determining whether (**3**) was an *E,E*, *E,Z*, or *Z,Z* isomer. This compound has also been synthesized by different routes[17–19] *e.g.*, by reacting acetylenic ketones with NH$_4$SC(S)NH$_2$ or hydrogen sulphide in the presence of pyridine or thiobenzamide. In all cases, a mixture of *Z,Z* and *E,Z* isomers is obtained. However, the present reaction of arsenic trichloride with PhCSCH$_2$COPh in refluxing benzene furnished exclusively the *Z,Z* isomer as established by a single-crystal *X*-ray structure analysis.

An ORTEP plot of S(PhC=CHCOPh)$_2$ (**3**) is shown in the Figure. Selected bond lengths and angles are given in Table 2. The average C–C bond distance for the phenyl groups is 1.377 Å, and the average C–S bond distance is 1.761 Å. There is a significant difference of 0.019 Å between the two C=O carbonyl group bond distances. Although all the equivalent bond angles are comparable (Table 2), the pair of bond angles C(2)–C(1)–C(11) [118.9(2)°] and C(5)–C(4)–C(31) [117.9(2)°] differ noticeably from one another. The observed C(3)–S(1)–C(6) bond angle of 101.6(1)° is very close to the reported values of organic sulphides, R$_2$S (dimethyl sulphide, 99.0;[20] di-*o*-tosyl sulphide, 103.0°[21]). With a sterically bulky organo group, *e.g.* in bis(triphenylmethyl) sulphide,[22] the corresponding angle opens up to 119.8°.

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References

1 M. Cox and J. Darken, *Coord. Chem. Rev.*, 1971, **7**, 29.
2 S. E. Livingstone *Coord. Chem. Rev.*, 1971, **7**, 59.
3 R. C. Mehrotra, R. Bohra, and D. P. Gaur, 'Metal β-diketonates and allied Derivatives,' Academic Press, New York, 1978, p. 215.
4 T. N. Lockyer and R. L. Martin, *Prog. Inorg. Chem.*, 1980, **27**, 223.
5 Ch. Sreelatha, V. D. Gupta, C. K. Narula, and H. Nöth, *J. Chem. Soc., Dalton Trans.*, 1985, 2623.
6 B. F. Hoskins and C. D. Pannon, *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 409.
7 E. Uhlemann and H. Müller, *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 154.
8 G. C. W. Foulk, H. V. Moyer, and W. M. MacNevin, 'Quantitative Chemical Analysis,' McGraw-Hill, New York, 1972, p. 371.
9 G. M. Sheldrick, SHEXLTL, program for structure determination, revision 4, University of Göttingen, 1983.
10 E. Uhlemann and P. Thomas, *Z. Anorg. Allg. Chem.*, 1967, **356**, 71.
11 J. R. Meadow, U.S.P. 2 336 453/1945.
12 E. E. Reid, 'Organic Chemistry of Bivalent Sulphur,' Chemical Publishing Co., New York, 1960, p. 16.
13 G. Carrai and G. Gottardi, *Z. Kristallogr.*, 1960, **113**, 373.
14 C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1975, 2425.
15 J. Kaufmann and F. Fober, *J. Organomet. Chem.*, 1974, **81**, 59.
16 P. H. Jarora, E. A. Meyer, and R. A. Zingaro, *Inorg. Chem.*, 1976, **15**, 2525.
17 F. G. Baddar, F. H. Al-Hajjar, and N. R. El-Rayyes, *J. Heterocycl. Chem.*, 1976, **13**, 691.
18 M. N. Basyouni and M. T. Omar, *Aust. J. Chem.*, 1974, **27**, 1585.
19 M. N. Basyouni, M. T. Omar, and E. A. Ghali, *Indian J. Chem., Sect. B*, 1980, **18**, 266.
20 T. Tijima, S. Tsuchiya, and M. Kimura, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2564.
21 M. Sacerdoti, V. Bertolasi, and G. Gills, *Cryst. Struct. Commun.*, 1976, **5**, 477.
22 G. A. Jeffrey and A. Robbins, *Acta Crystallogr., Sect. B*, 1980, **38**, 1820.

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