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Journal of Organometallic Chemistry 517 (1996) 19–23

Journal
of Organometallic
Chemistry

Organometallic alkylthiolate-bridged manganese cubanes

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Received 14 June 1995; in revised form 8 December 1995

Abstract

The thermal reaction of tricarbonyl- η^5 -pentadienylmanganese **1**, with mercaptans RSH leads to the corresponding tetramers $[\text{MnSR}(\text{CO})_3]_4$ (R = phenyl **2**, furfuryl **3**, and phenethyl **4**). Synthetic and spectroscopic aspects, as well as the single crystal X-ray structure of **3**, are discussed.

Keywords: Manganese; Thiolates; Cubanes; Pentadienyl complexes

1. Introduction

The alkylthiolate-bridged manganese heterocubanes $[\text{MnSR}(\text{CO})_3]_4$ were first synthesized by Abel et al. in 1965. The synthetic method consisted in the reaction of bromopentacarbonylmanganese with bis(thioalkyl)dialkyltin or monofunctional $\text{R}_3\text{SnSR}'$ at temperatures above 70°C [1]. Since then a number of synthetic routes for these manganese tetramers have appeared in the literature. For example, the reaction of bromopentacarbonylmanganese with benzenethiol in boiling cyclohexane for 3 h was found to give the corresponding tetramer in 22% yield [2]. Decacarbonyldimanganese and alkyl thiocyanates were reacted under toluene reflux to give manganese tetramers in low yield [3]. The interaction of bromopentacarbonylmanganese with an excess of methyl- or phenylthiotrimethylsilane at 50°C for 30 min and then above 70°C leads to the tetrameric species in 70% and 55% yield respectively [4]. Abel and coworkers described the following two additional synthetic methods for the manganese tetramers: (1) reaction between bromotricarbonyl-2,5-dithiahexanemanganese and an excess of methylthiotrimethyltin under 1,2-dimethoxyethane reflux for 3 h to give the methylthiolate-manganese heterocubane in 60% yield [5]; (2) reaction of benzenethiol with the trimeric species $[\text{MnOEt}(\text{CO})_3]_3$ at 20°C in hexane for 4 h, to give the tetramer,

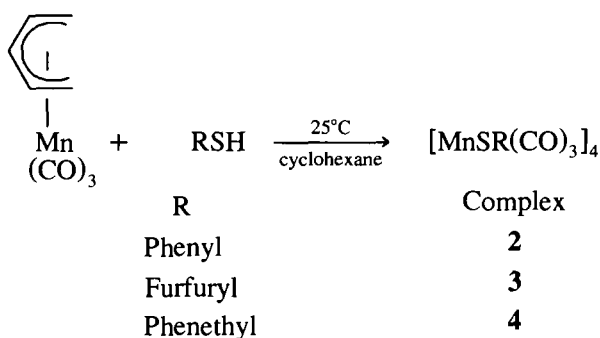
$[\text{MnSPh}(\text{CO})_3]_4$ in 10% yield [6]; this tetramer has also been synthesized photochemically from $\text{Mn}_2(\text{CO})_{10}$ and S_2Ph_2 in equimolar amounts irradiating 12 h at 25°C in pentane [7]. These tetrameric manganese complexes were originally formulated as trimeric. However, electron impact mass spectrometry [8] and IR spectra studies [9] established their tetrameric nature in vapor phase and in solution respectively. To our knowledge no crystal structure of the alkylthiotricarbonylmanganese tetramers has previously been reported [10].

2. Results and discussion

In an effort to extend our studies on the reactivity of the tricarbonylpentadienylmanganese complex **1**, $\text{Mn}(\eta^5\text{-C}_5\text{H}_7)(\text{CO})_3$, towards neutral Lewis bases [11], we turned our attention to electron donor sulfur compounds. The reaction of complex **1** in equimolar amounts with phenyl, furfuryl, and phenethyl mercaptan, at 25°C in cyclohexane produced the tetrameric species $[\text{MnSR}(\text{CO})_3]_4$ as shown in Scheme 1.

The isolated complexes are air-stable for long periods of time in the solid state. Solutions of these complexes change color from yellow-orange to deep green in about 72 h at 25°C . Dialkylsulfides do not react with complex **1** under the same reaction conditions. No reaction took place even in boiling cyclohexane. This suggests that the SH function plays a key role in the tetramer formation (vide infra). Either the addition of an

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Scheme 1.

excess of mercaptan or an increase in temperature were found to result in a slight increase in reaction yield and generation of new unidentified species. The crude products could be purified by crystallization. The stability of the reported tetramers is indicated by their reluctance to react with tertiary phosphines at cyclohexane reflux temperature.

IR monitoring of the reaction mixtures showed the gradual formation of the tetramers and the consumption of complex **1** through change in ratio of the $\nu(\text{CO})$ bands for complex **1** (2025, 1958, 1938 cm^{-1} , cyclohexane). The reactions were stopped when no further changes in the spectra were observed (3.5 h in all cases). IR monitoring was not helpful in detecting any intermediate species. We have reported that a detailed proton NMR study of the reaction of complex **1** with benzyl mercaptan in C_6D_6 revealed formation of 1,3-pentadiene immediately after addition of the mercaptan and formation of the corresponding tetramer. After 6 h at 33°C the consumption of **1** was complete [11c]. On the basis of these observations, and without evidence for the formation of any transient intermediates in these reactions, we presume that the sulfhydryl group adds the metal center across the S–H bond to generate an $[\text{MnSR}(\eta^3\text{-C}_5\text{H}_7)(\text{H})(\text{CO})_3]$ species, in which the hydride saturates an η^3 -pentadienyl ligand to form 1,3-pentadiene leaving the terminal SR group free to interact (as a formal five-electron donor) with three $-\text{Mn}(\text{CO})_3$ groups after loss of 1,3-pentadiene. This results in the formation of tetrameric species in which there are 18 electrons around each metal center. This contrasts with the behavior of primary and secondary amines as well as secondary phosphines where the LH function ($\text{L} = \text{N}, \text{P}$) leads to the formation of an L–C covalent bond giving amino- and phosphinopentenylyl adducts respectively [11].

Positive FAB mass spectra of all the complexes show that the primary fragmentation pattern involves the loss of 12 carbonyl groups; the molecular ion M^+ fragment appears with low intensity and the base peak corresponds to the fragment $\text{M}^+ - 3\text{CO}$.

Proton NMR spectroscopy indicates the hydrogen

loss of the SH group. In the case of complex **2**, coordination to the metal center is reflected in the downfield shift of the phenyl protons with respect to the free ligand (see Experimental section) whereas for the other complexes such a shift is not to be seen, with the alkyl or aryl protons appearing at the same frequency as in the free ligands. Sulfur coordination to the manganese was observed in carbon-13 NMR spectra by the chemical shift of the methylene groups. In the case of complex **3**, the methylene group shifts downfield ($\delta\Delta = 14.9$ ppm), whereas the methylene group attached to the sulfur atom of complex **4** shifts 11.2 ppm downfield with respect to the free ligand. The methylene group adjacent to the phenyl substituent exhibits a slight upfield shift ($\delta\Delta = 1.5$ ppm). The methylene groups assignments in complex **4** were made based on NOE DIF experiments; the metal carbonyl groups appear as a broad signal (linewidth, 16.5 Hz) around 220 ppm, indicating free rotation of the three carbonyl groups at 25°C. This dynamic behavior is still observed at -50°C in the carbon-13 NMR spectrum, in which the carbonyl groups' signal sharpens (linewidth, 2.4 Hz).

The IR spectra of the dodecacarbonyl complexes **2**, **3**, and **4** exhibit two active carbonyl stretching modes (see Experimental section). In the case of complex **2** the reported bands [2,7] match well with those of the present work. It has been proposed that the tetrameric structures in the solid state and in solution are the same [9c]. This has been established for the rhenium complex $[\text{ReSCH}_3(\text{CO})_3]_4$ which has been studied by X-ray crystallography [12]. There are two examples of crystallographically characterized tetranuclear manganese carbonyls: (1) the complex $\text{Mn}_4(\text{CO})_{15}\text{S}_4$ in which two disulphide ligands link the four manganese atoms where each achieves an approximate octahedral ligand arrangement [13a]; (2) a cubane-type tetranuclear complex with $\text{Mn}(\text{CO})_3$ units at one set of vertices and fluoro or hydroxy groups at the other set [13b].

In our hands, suitable crystals for X-ray analysis of complex **3** were grown from a dichloromethane–cyclohexane solution (4:1). The molecular structure is shown in Fig. 1. The fractional atomic coordinates for all non-hydrogen atoms are given in Table 1, whereas selected bond distances and angles are given in Table 2.

The structure predicted in solution is the same as that shown in Fig. 1 for the solid state. Each sulfur atom is equidistant from three manganese atoms resulting in μ_3 -bridges. All of the Mn–S bond distances are equal within experimental error (average 2.366(4) Å). This, along with the S–Mn–S ($77.8(1)^\circ$) and the Mn–S–Mn ($101.0(1)^\circ$) average bond angles, indicates a distorted cubane-like structure in which there are two sets of atoms arranged tetrahedrally; one set consists of four manganese atoms and the other of four sulfur atoms. The Mn–Mn distances (3.625–3.676 Å) are longer than the corresponding average Mn–Mn bond distance in

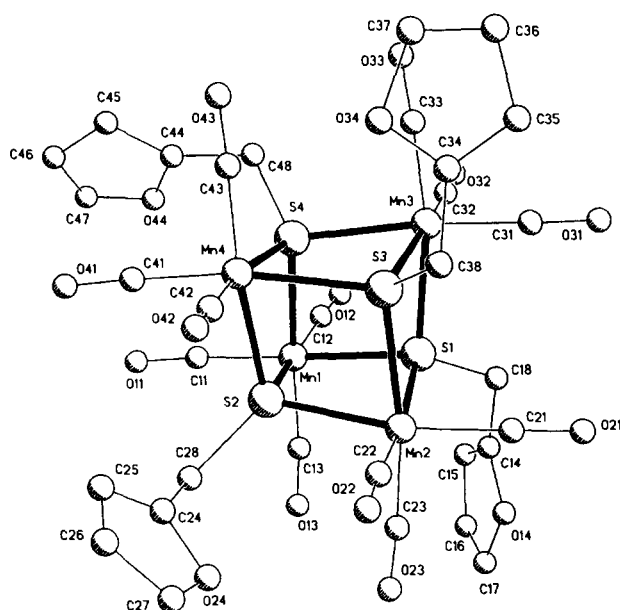


Fig. 1. Molecular structure and atom numbering scheme for complex 3. Hydrogen atoms omitted for clarity.

$[\text{Mn}(\mu_2\text{-H})(\text{CO})_4]_3$, 3.111(2) Å, in which the hydrogen atoms bridge two manganese atoms [14]. This confirms the prediction of the lack of interaction among the manganese atoms in the $[\text{MnSR}(\text{CO})_3]_4$ species. Each $\text{S}_3\text{-Mn}(\text{CO})_3$ unit can be regarded as a distorted octahedron. The angles around each sulfur atom suggest sp^3 -hybridization.

3. Experimental section

All manipulations were carried out under an atmosphere of nitrogen by Schlenk tube techniques. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. IR spectra were recorded on a Nicolet FT-IR 55X spectrometer. NMR experiments were performed on a Varian VXR 300S spectrometer, ^1H (300 MHz) and ^{13}C (75.4 MHz). The chemical shifts are reported in ppm relative to tetramethylsilane. FAB(+) mass spectra were recorded on a JEOL SX-102A instrument. Melting points were determined in capillary tubes in a Büchi apparatus and are uncorrected.

Cyclohexane, hexane, dichloromethane, tetrahydrofuran, and diethyl ether were purified and dried prior to use by standard methods [15]. Tricarbonylpentadienylmanganese was synthesized according to the literature [16]. The mercaptans were purchased from Aldrich and were used without further purification.

3.1. General procedure for preparation of the $[\text{MnSR}(\text{CO})_3]_4$ tetramers

Tricarbonylpentadienylmanganese **1**, (0.5 g, 2.54 mmol), was dissolved in 60 cm^3 of deoxygenated cyclo-

hexane. An equimolar amount of mercaptan was added (phenyl mercaptan, 0.34 g; furfuryl mercaptan, 0.28 g and phenethyl mercaptan, 0.34 g). The reaction mixture

Table 1
Positional parameters ($\times 10^4$) with their estimated standard deviations and temperature factors ($\text{Å}^2 \times 10^3$) for complex 3

	x	y	z	U
Mn(1)	2350(1)	1278(2)	6293(1)	75(1)
C(11)	2140(9)	2611(11)	6410(10)	99(7)
O(11)	1974(6)	3461(8)	6468(7)	125(5)
C(12)	3033(8)	1496(11)	5531(9)	91(6)
O(12)	3454(6)	1591(9)	5045(7)	127(6)
C(13)	1572(8)	1209(12)	5626(10)	93(7)
O(13)	1056(6)	1223(9)	5222(7)	119(5)
O(14)	1458(10)	-1634(9)	4959(8)	138(7)
O(14)	2119(9)	-1146(14)	4886(12)	91(8)
C(15)	2128(10)	-558(13)	4295(13)	96(8)
C(16)	1446(21)	-678(19)	3913(14)	176(18)
C(17)	1036(14)	-1261(21)	4322(17)	161(14)
C(18)	2713(8)	-1266(10)	5466(8)	92(6)
S(1)	2578(2)	-520(3)	6361(2)	75(1)
Mn(2)	1608(1)	-1009(2)	7248(1)	76(1)
C(21)	1808(7)	-2363(11)	7106(9)	88(6)
O(21)	1949(6)	-3209(8)	6998(7)	126(5)
C(22)	982(9)	-1292(11)	8026(10)	98(7)
O(22)	566(6)	-1527(8)	8515(8)	127(6)
C(23)	805(8)	-978(12)	6579(9)	95(7)
O(23)	283(6)	-896(9)	6193(7)	130(6)
O(24)	-230(7)	490(9)	8043(7)	119(6)
C(24)	251(8)	1278(13)	8108(11)	87(7)
C(25)	227(10)	1686(13)	8791(13)	110(8)
C(26)	-288(13)	1113(19)	9225(13)	135(11)
C(27)	-564(10)	412(18)	8747(16)	136(11)
C(28)	718(7)	1508(10)	7416(9)	88(6)
S(2)	1615(2)	802(2)	7389(2)	71(1)
Mn(3)	3657(1)	-574(2)	7171(1)	72(1)
C(31)	3840(8)	-1941(11)	7089(9)	95(7)
O(31)	3971(6)	-2785(8)	7053(7)	120(5)
C(32)	4292(8)	-301(11)	6375(10)	96(7)
O(32)	4692(6)	-98(10)	5888(7)	134(6)
C(33)	4385(7)	-429(11)	7908(9)	82(6)
O(33)	4855(5)	-277(8)	8345(7)	114(5)
O(34)	3580(10)	-1120(11)	9833(11)	159(8)
C(34)	3442(11)	-1773(18)	9279(13)	106(9)
C(35)	4013(13)	-2399(15)	9176(10)	108(8)
C(36)	4570(13)	-2128(13)	9712(14)	149(13)
C(37)	4284(16)	-1367(19)	10123(14)	154(13)
C(38)	2732(8)	-1754(11)	8826(8)	94(6)
S(3)	2663(2)	-747(2)	8073(2)	71(1)
Mn(4)	2493(1)	1016(2)	8422(1)	75(1)
C(41)	2247(7)	2346(12)	8522(9)	92(7)
O(41)	2058(6)	3196(8)	8586(7)	127(5)
C(42)	1896(9)	697(14)	9207(10)	112(8)
O(42)	1560(7)	440(10)	9741(7)	141(6)
C(43)	3284(8)	1126(12)	9064(9)	90(6)
O(43)	3787(6)	1233(9)	9464(7)	124(5)
O(44)	3603(8)	3638(13)	6910(14)	185(10)
C(44)	3890(10)	3128(14)	7478(14)	106(9)
C(45)	3905(13)	3732(22)	8134(13)	170(13)
C(46)	3594(16)	4633(24)	7807(27)	264(32)
C(47)	3475(23)	4574(40)	7047(32)	353(43)
C(48)	4074(6)	2052(10)	7326(9)	87(6)
S(4)	3266(2)	1151(2)	7303(2)	70(1)

was stirred at 25°C until monitoring of the reaction showed no further change in the IR $\nu(\text{CO})$ pattern (3.5 h). A precipitate appeared after 1 h and was filtered off at the end of the reaction period. The solvent was removed under reduced pressure to give a solid residue. The crude products were purified by crystallization.

Complex **2** was crystallized from hexane (0.13 g, yield 21%); m.p. 226 °C (dec). IR (hexane), $\nu(\text{CO})$: 2025s, 1952s cm^{-1} . ^1H NMR (CDCl_3): 7.4–7.6m ($\text{H}_{\text{m,p}}$); 8.1d ($^1J = 7.5$ Hz), (H_0). ^{13}C NMR (CDCl_3): 129.7 C_0 ; 131.0 C_m ; 128.7 C_p ; 132.7 C_i ; 220 (CO). MS (m/e): 992, 908, 852, 824, 796, 768, 740, 712, 684, 656, 579, 524, 501, 492, 469, 425, 393, 348, 55.

Complex **3** was crystallized from a 4:1 dichloromethane–cyclohexane mixture (0.14 g, yield 23%); m.p. 115–118°C. Anal. Found: C, 38.3; H, 1.73. $\text{C}_{32}\text{H}_{20}\text{Mn}_4\text{O}_{16}\text{S}_4$. Calc. C, 38.1; H, 2.0%. IR (hexane), $\nu(\text{CO})$: 2021s, 1950s cm^{-1} . ^1H NMR (CDCl_3): 3.7s (CH_2); 6.3m [$-\text{CH}_2-(\text{C}=\text{CH}-\text{CH}=\text{CH}-\text{O})$]; 7.3m [$-\text{CH}_2-(\text{C}=\text{CH}-\text{CH}=\text{CH}-\text{O})$]. ^{13}C NMR (CDCl_3): 55.5 [$-\text{CH}_2-(\text{C}=\text{CH}-\text{CH}=\text{CH}-\text{O})$]; 109.3 [$-\text{CH}_2-(\text{C}=\text{CH}-\text{CH}=\text{CH}-\text{O})$]; 110.7 [$-\text{CH}_2-(\text{C}=\text{CH}-\text{CH}=\text{CH}-\text{O})$]; 142.5 [$-\text{CH}_2-(\text{C}=\text{CH}-\text{CH}=\text{CH}-\text{O})$]; 152.5 [$\text{CH}_2-(\text{C}=\text{CH}-\text{CH}=\text{CH}-\text{O})$]; 220 (CO). MS (m/e): 1008, 924, 812, 784, 756, 728, 700, 672, 591, 504, 429, 397, 348, 81, 55. Suitable crystals for X-ray analysis were obtained from a saturated solution in a 4:1 dichloromethane–cyclohexane mixture by leaving the crystals grow at about 4°C for a period of approximately 2 months.

Complex **4** was crystallized from acetone (0.16 g, yield, 24%); m.p. 182–186°C. Anal. Found: C, 48.1; H, 2.9. $\text{C}_{44}\text{H}_{36}\text{Mn}_4\text{O}_{12}\text{S}_4$. Calc. C, 47.8; H, 3.3%. IR (hexane), $\nu(\text{CO})$: 2016s, 1945s cm^{-1} . ^1H NMR (CDCl_3): 2.87–2.93m ($\text{CH}_2\text{CH}_2\text{Ph}$), 3.15–3.21m ($-\text{CH}_2\text{CH}_2\text{Ph}$); 7.3–7.4m (Ph). ^{13}C NMR (CDCl_3): 37.2 $\text{CH}_2\text{CH}_2\text{Ph}$; 38.7 $\text{CH}_2\text{CH}_2\text{Ph}$; 128.6 C_0 ; 129.1 C_m ; 127.2 C_p ; 138.4 C_i ; 119.8 (CO). MS (m/e): 1103, 1020, 908, 880, 852, 824, 796, 768, 691, 663, 608, 576, 487, 455, 404, 348, 105, 55.

3.2. Single-crystal X-ray diffraction studies

Crystal data $\text{C}_{32}\text{H}_{20}\text{Mn}_4\text{O}_{16}\text{S}_4$; $M = 1008.5$; monoclinic; $a = 17.671(7)$ Å; $b = 12.959(4)$ Å; $c = 17.163(7)$ Å; $\beta = 90.33(3)^\circ$; $V = 3930(3)$ Å³; $Z = 4$; $D_c = 1.704$ g cm^{-3} ; $F(000) = 2016$; space group $P2_1/c$; Cu K α radiation, $\lambda = 1.54178$ Å; $\mu(\text{Cu K}\alpha) = 12.83$ mm^{-1} ; crystal size $0.42 \times 0.22 \times 0.08$ mm³; crystal color, yellow-orange; habit, plates.

The X-ray data collection was carried out on a Nicolet P3/F four-cycle diffractometer with a Ni-filter for 4684 reflections in the ω - 2θ mode, of which 4490 were independent ($R_{\text{int.}} = 3.28\%$) and 2579 observed reflections ($F > 4.0\sigma(F)$) were used in the full-matrix least squares refinement [17]. Intensity data were corrected for Lorentz and polarization effects and an absorption correction based on a face indexed crystal was also applied. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropi-

Table 2

Selected bond distances (Å) and bond angles (deg) with their estimated standard deviations for complex **3**

Bond distances					
Mn(1)–S(1)	2.367(4)	Mn(2)–S(1)	2.385(4)	Mn(3)–S(1)	2.353(4)
Mn(1)–S(2)	2.374(4)	Mn(2)–S(2)	2.360(4)	Mn(3)–S(3)	2.358(4)
Mn(1)–S(4)	2.370(4)	Mn(2)–S(3)	2.359(4)	Mn(3)–S(4)	2.351(4)
		Mn(4)–S(2)	2.366(4)		
		Mn(4)–S(3)	2.382(4)		
		Mn(4)–S(4)	2.366(4)		
Bond angles					
S(1)–Mn(1)–S(2)	78.4(4)	S(1)–Mn(3)–S(3)	77.7(1)		
S(1)–Mn(1)–S(4)	77.3(1)	S(1)–Mn(3)–S(4)	78.0(1)		
S(2)–Mn(1)–S(4)	77.1(1)	S(3)–Mn(3)–S(4)	78.9(1)		
S(1)–Mn(2)–S(2)	78.3(1)	S(2)–Mn(4)–S(3)	77.4(1)		
S(1)–Mn(2)–S(3)	77.0(1)	S(2)–Mn(4)–S(4)	77.3(1)		
S(2)–Mn(2)–S(3)	78.0(1)	S(3)–Mn(4)–S(4)	78.0(1)		
Mn(1)–S(1)–Mn(2)	99.8(1)	Mn(2)–S(3)–Mn(3)	102.0(2)		
Mn(1)–S(1)–Mn(3)	101.3(1)	Mn(2)–S(3)–Mn(4)	100.9(1)		
Mn(2)–S(1)–Mn(3)	101.4(1)	Mn(3)–S(3)–Mn(4)	99.7(1)		
Mn(1)–S(2)–Mn(2)	100.3(1)	Mn(1)–S(4)–Mn(3)	101.3(1)		
Mn(1)–S(2)–Mn(4)	101.7(1)	Mn(1)–S(4)–Mn(4)	101.7(1)		
Mn(2)–S(2)–Mn(4)	101.3(1)	Mn(3)–S(4)–Mn(4)	100.3(1)		
Mn(1)–S(1)–C(18)	120.0(4)	Mn(2)–S(3)–C(38)	111.6(5)		
Mn(2)–S(1)–C(18)	119.5(5)	Mn(3)–S(3)–C(38)	118.8(5)		
Mn(3)–S(1)–C(18)	111.8(5)	Mn(4)–S(3)–C(38)	120.8(5)		
Mn(1)–S(2)–C(28)	111.6(5)	Mn(1)–S(4)–C(48)	119.8(5)		
Mn(2)–S(2)–C(28)	119.7(4)	Mn(3)–S(4)–C(48)	112.1(4)		
Mn(4)–S(2)–C(28)	119.1(5)	Mn(4)–S(4)–C(48)	118.6(5)		

cally. Hydrogen atoms were placed at idealized positions and included in the structure factor calculation with fixed isotropic thermal parameters ($U = 0.08 \text{ \AA}^2$). The final R values are $R = \sum |F_o - F_c| / \sum |F_o| = 7.22\%$ and $R_w = [\sum w(|F_o - F_c|)^2 / \sum w|F_o|^2]^{1/2} = 8.62\%$ ($R = 11.49\%$ and $R_w = 10.25\%$ for all data) with weights $w^{-1} = \sigma^2(F) + 0.0024F^2$; goodness-of-fit, 1.30. The residual electron density from a final difference Fourier synthesis was in the range of $0.53, -0.55 \text{ e \AA}^{-3}$.

Acknowledgements

N.Z.-V. wishes to acknowledge Dr. M. Angeles Paz-Sandoval (CINVESTAV) for helpful discussions and Dr. Cecilio Alvarez for providing the facilities to do this work.

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