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Polymeric and Monomeric Forms of Metalphosphinates

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Abstract

Diphenylphosphinic acid reacts with Mn^{2+} in the presence of dimethylformamide and two kinds of compounds are formed. Compound **1**, $\{Mn[O_2P(C_6H_5)_2]_2(DMF)\}\cdot DMF$, consists of one-dimensional, infinite centrosymmetric chains of Mn(II) atoms connected by double phosphinate bridges. Each manganese atom is coordinated to four phosphinate oxygen atoms and one DMF molecule in a trigonal bipyramidal geometry with three equatorial angles of 123.7(6), 116.8(5) and 117.4(6)° and an axial–metal–axial angle of 173.3(7)°. The M...M separation is 4.583 Å.

Compound **2**, $\{Mn[O_2P(C_6H_5)_2]_2[HO_2P(C_6H_5)_2]_2(DMF)_2\}$ cocrystallizes with **1** under the same conditions. The manganese atom is coordinated to two phosphinate ions, to two phosphinic acid molecules and to two DMF molecules in an octahedral geometry. Two very strong, intramolecular hydrogen bonds are formed between the P–OH group of one ligand and the $P-O^-$ group of another ligand with O...O separation of 2.444(3) Å.

Compound **3** is the Co(II) analogue of **2**, $\{Co[O_2P(C_6H_5)_2]_2[HO_2P(C_6H_5)_2]_2(DMF)_2\}$. The O...O separation in the intramolecular hydrogen bond in **3** is 2.422(4) Å.

Compound **1**: triclinic, space group $P\bar{1}$ with $a = 13.174(2)$, $b = 13.364(2)$, $c = 9.995(1)$ Å, $\alpha = 96.05(3)$, $\beta = 110.23(3)$, $\gamma = 104.54(2)°$, $V = 1562(1)$ Å^3 and $Z = 2$. Compound **2**: triclinic, space group $P\bar{1}$ with $a = 12.019(1)$, $b = 12.390(1)$, $c = 9.479(1)$ Å, $\alpha = 94.90(3)$, $\beta = 101.71(2)$, $\gamma = 102.65(3)°$, $V = 1336(1)$ Å^3 and $Z = 1$. Compound **3**: monoclinic, space group $P2_1/c$ with $a = 12.552(2)$, $b = 9.921(1)$, $c = 21.558(3)$ Å, $\beta = 101.88(3)°$, $V = 2627(1)$ Å^3 and $Z = 2$.

Introduction

The profound tendency of phosphinic acid derivatives to form inorganic coordination polymers with metal ions was demonstrated by the preparation of a series of poly(metalphosphinates) of various metal ions. Several polymers with dialkylphosphinates were structurally characterized and their magnetic and spectroscopic properties were elucidated [1]. The preparation and structure of polymers of diphenylphosphinates of Pb^{2+} and Cu^{2+} were reported recently. The metal atoms in both compounds are doubly bridged by OPO bridges. In $Pb[O_2P(C_6H_5)_2]_2$, the geometry of the tetracoordinated lead atom is described as a distorted trigonal bipyramid in which a lone pair of electrons occupies an equatorial position [2]. The geometry of the copper atom in $Cu[O_2P(C_6H_5)_2]_2$ however is square planar [3]. The magnetic properties and structure of a manganese(II) polymer with dimethylphosphinate were reported by Thompson *et al.* [1h]. The octahedral manganese atoms in $Mn(H_2O)_2[O_2P(CH_3)_2]_2$ are connected in the chains by double phosphinate bridges with four oxygen atoms forming a square planar array around the metal atom and with two coordinated H_2O ligands. The intrachain distance between manganese atoms is 4.8652(2) Å. The anhydrous compound shows relatively strong antiferromagnetic behaviour.

We report here the preparation and the results of an X-ray structural analysis of two compounds which resulted from the reaction between Mn^{2+} and diphenylphosphinic acid. Compound **1**, $\{Mn[O_2P(C_6H_5)_2]_2(DMF)\}\cdot DMF$, is a polymer in which the manganese atom is pentacoordinated with a trigonal bipyramidal geometry. Compound **2**, $\{Mn[O_2P(C_6H_5)_2]_2[HO_2P(C_6H_5)_2]_2(DMF)_2\}$ is an octahedral monomeric complex in which two phosphinates and two phosphinic acid molecules are coordinated to the metal atom through one of the PO oxygen atoms. We also report the structure of the Co^{2+} analogue of **2**, namely $\{Co[O_2P(C_6H_5)_2]_2[HO_2P(C_6H_5)_2]_2(DMF)_2\}$, compound **3**.

Experimental

Preparation of $\{Mn[O_2P(C_6H_5)_2]_2(DMF)\}\cdot DMF$ *(1) and* $\{Mn[O_2P(C_6H_5)_2]_2[HO_2P(C_6H_5)_2]_2(DMF)_2\}$ *(2)*

$Mn(ClO_4)_2\cdot 6H_2O$ (0.18 g) and diphenylphosphinic acid (0.055 g) were dissolved in a solution containing

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TABLE I. Crystallographic Data

Compound	1	2	3
Formula	$C_{30}H_{34}MnN_2O_6P_2$	$C_{54}H_{56}MnN_2O_{10}P_4$	$C_{54}H_{56}CoN_2O_{10}P_4$
Formula weight	635.49	1071.87	1075.87
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	13.174(2)	12.019(1)	12.552(2)
b (Å)	13.364(2)	12.390(1)	9.921(1)
c (Å)	9.995(1)	9.479(1)	21.558(3)
α (°)	96.05(3)	94.90(3)	
β (°)	110.23(3)	101.71(2)	101.88(3)
γ (°)	104.54(2)	102.65(3)	
V (Å^3)	1562(1)	1336(1)	2627(1)
Z	2	1	2
D_{calc} (g cm^{-3})	1.354	1.332	1.360
μ (cm^{-1})	5.15	3.75	4.56
Crystal size (mm)	0.1 × 0.2 × 0.2	0.3 × 0.3 × 0.4	0.2 × 0.3 × 0.4
Range of 2θ (°)	4–45	4–55	4–55
No. unique data	4082	6142	5912
Data with $F_o^2 > 3\sigma(F_o^2)$	1773	5201	4531
No. parameters	206	327	327
R	0.099	0.040	0.047
R_w	0.111	0.041	0.049

2 ml of DMSO, 5 ml of DMF, 5 ml of acetone and 0.014 g of $NaOCH_3$. The solution was placed in an open beaker at room temperature. Large colorless prisms of **2** and a few long colorless needles of **1** were obtained from the reaction mixture after several days. Pure samples of **2** were obtained when 0.045 g of $Mn(ClO_4)_2 \cdot 6H_2O$ and 0.11 g of diphenylphosphinic acid were used.

Preparation of $\{Co[O_2P(C_6H_5)_2]_2[HO_2P(C_6H_5)_2]_2(DMF)_2\}$ *(3)*

Pink prisms of **3** were obtained using $Co(ClO_4)_2 \cdot 6H_2O$ (0.045 g) and diphenylphosphinic acid (0.11 g) with the same solution composition as for **1** and **2**.

X-ray Crystallography

A crystal of **1** was mounted inside a glass capillary tube above a column of the solution from which it was grown. Crystals of compounds **2** and **3** were sealed with epoxy cement to the end of a glass fiber.

Data were collected at 20 ± 2 °C on a Philips PW 1100 four circle diffractometer. Mo Kα ($\lambda = 0.71069$ Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 20 reflections in the range $12° < \theta < 16°$. Data were measured by using ω–2θ motion. Crystallographic data and other pertinent information are given in Table I. For each crystal Lorentz and polarization corrections were applied. The heavy atom positions in all structures were obtained by using the results of SHELXS-86 direct method analysis. Structure **1** was refined* in space group $P\bar{1}$ to convergence by using anisotropic thermal parameters for all manganese, phosphorous and oxygen atoms and isotropic ones for all nitrogen and carbon atoms. All the hydrogen atoms of the diphenylphosphinate ligands were introduced in calculated positions with $U = 0.05$.

Structures **2** and **3** were refined in space groups $P\bar{1}$ and $P2_1/c$ respectively using anisotropic thermal parameters for all non-hydrogen atoms and isotropic ones for the OH hydrogen atom, H(1). All hydrogen atoms were located from the difference maps and were introduced in fixed positions except H(1) whose positional and thermal parameters were refined.

The discrepancy indices $R = \Sigma|F_o| - |F_c|/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ are listed in Table I.

Results

$\{Mn[O_2P(C_6H_5)_2]_2(DMF)\} \cdot DMF$ *(1)*

The atomic positional parameters are listed in Table II. Table III presents important bond lengths and angles. Figure 1 shows the structure and numbering scheme in the complex. Figure 2 shows a stereoscopic view of a section of the polymeric chain. The chains consist of fused centrosymmetric eight-membered rings formed by two manganese atoms

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*All crystallographic computing was done on a CYBER 855 computer at the Hebrew University of Jerusalem, using the SHELX 1977 structure determination package.

TABLE II. Positional Parameters[a] for 1

Atom	x	y	z	Atom	x	y	z
Mn	0.0215(2)	0.0081(2)	0.2388(3)	C(14)	0.229(2)	0.332(2)	0.282(2)
P(1)	0.1809(4)	0.0071(4)	0.6060(5)	C(15)	0.340(2)	0.408(2)	0.354(3)
P(2)	0.0473(4)	0.1988(4)	0.0441(5)	C(16)	0.403(2)	0.430(2)	0.273(3)
O(1)	0.123(1)	0.014(1)	0.452(1)	C(17)	0.370(2)	0.392(2)	0.129(3)
O(2)	0.124(1)	0.0035(9)	0.714(1)	C(18)	0.253(2)	0.317(2)	0.059(2)
O(3)	0.013(1)	0.1423(9)	0.151(1)	C(19)	−0.039(1)	0.285(1)	−0.006(2)
O(4)	0.039(1)	0.1360(9)	−0.094(1)	C(20)	−0.048(2)	0.325(2)	−0.133(2)
O(5)	0.190(1)	0.039(1)	0.207(2)	C(21)	−0.113(2)	0.396(2)	−0.172(2)
C(1)	0.313(2)	0.120(1)	0.688(2)	C(22)	−0.159(2)	0.425(2)	−0.084(2)
C(2)	0.361(2)	0.157(1)	0.837(2)	C(23)	−0.152(2)	0.391(2)	0.040(3)
C(3)	0.463(2)	0.243(2)	0.895(3)	C(24)	−0.086(2)	0.320(2)	0.083(2)
C(4)	0.504(2)	0.289(2)	0.801(2)	C(25)	0.235(2)	−0.010(2)	0.156(2)
C(5)	0.458(2)	0.255(2)	0.654(3)	N(1)	0.339(2)	0.009(1)	0.175(2)
C(6)	0.354(2)	0.168(2)	0.591(2)	C(26)	0.393(4)	−0.062(3)	0.135(5)
C(7)	0.234(2)	−0.108(1)	0.601(2)	C(27)	0.419(3)	0.120(3)	0.249(4)
C(8)	0.262(2)	−0.137(2)	0.488(3)	O(6)	0.312(2)	0.490(2)	0.744(2)
C(9)	0.302(2)	−0.227(2)	0.488(3)	C(28)	0.255(2)	0.395(2)	0.703(3)
C(10)	0.308(2)	−0.280(2)	0.593(3)	N(2)	0.145(2)	0.361(1)	0.617(2)
C(11)	0.284(2)	−0.255(2)	0.704(3)	C(29)	0.081(3)	0.430(2)	0.546(3)
C(12)	0.239(2)	−0.163(2)	0.715(3)	C(30)	0.082(2)	0.247(2)	0.578(3)
C(13)	0.191(1)	0.286(1)	0.138(2)				

[a] e.s.d.s in the least significant digits are shown in parentheses.

TABLE III. Important Bond Lengths (Å) and Angles (°) for 1

Mn–O(1)	2.07(1)	P(1)–O(2)	1.51(2)
Mn–O(2)′	2.11(2)	P(1)–C(1)	1.85(2)
Mn–O(3)	2.09(1)	P(1)–C(7)	1.85(2)
Mn–O(4)′	2.07(1)	P(2)–O(3)	1.50(1)
Mn–O(5)	2.29(2)	P(2)–O(4)	1.49(1)
P(1)–O(1)	1.49(1)		
O(1)–Mn–O(2)′	93.4(6)	O(1)–Mn–O(4)′	116.8(5)
O(1)–Mn–O(5)	83.1(7)	O(3)–Mn–O(4)′	117.4(6)
O(2)′–Mn(O(3)	93.8(5)	O(2)′–Mn–O(5)	173.3(7)
O(2)′–Mn–O(4)′	97.4(6)	N–O(1)–P(1)	172(1)
O(3)–Mn–O(5)	83.5(5)	N–O(3)–P(2)	140.9(7)
O(4)′–Mn–O(5)	89.3(6)	N–O(5)–C(25)	137(2)
O(1)–Mn–O(3)	123.7(6)	O(1)–P(1)–O(2)	123.0(9)

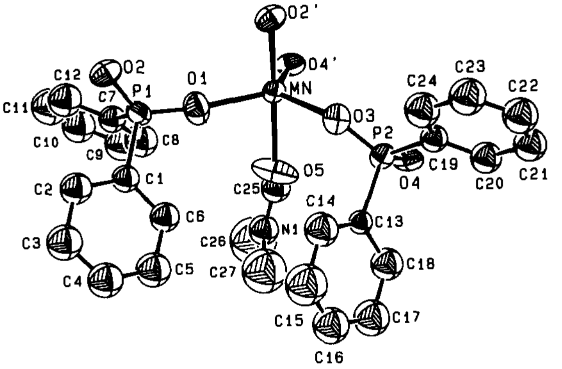

Fig. 1. View of $Mn[O_2P(C_6H_5)_2]_2(DMF)$ showing the atom numbering scheme and the coordination around the Mn atom.

bridged by two phosphinato groups. Each manganese atom is coordinated to four oxygen atoms of different phosphinate groups with an average Mn–O distance of 2.08(1) Å and to one DMF oxygen atom with a Mn–O(DMF) distance of 2.29(2) Å. The geometry around the metal atom is nearly that of a trigonal bipyramid (TBP). From Table II it can be seen that the trigonal bipyramidal coordination is slightly distorted from the ideal TBP geometry. Thus the axial–metal–axial angle is 173.3(7)°, while the three equatorial angles are 123.7(6), 116.8(5) and 117.4(6)°. The six axial–metal–equatorial angles are within the range of 83°–97°.

$\{Mn[O_2P(C_6H_5)_2]_2[HO_2P(C_6H_5)_2]_2(DMF)_2\}$ (2)

The atomic positional parameters are listed in Table IV and Table V presents important bond lengths and angles. Figure 3 shows the structure and numbering scheme in the complex. With one molecule in the cell of space group $P\bar{1}$ there is only half a $MnL_2(HL)_2(DMF)_2$ unit in the asymmetric unit, with the other half related to it by a crystallographic center of symmetry at ½, ½, ½. Each manganese atom is coordinated to two phosphinate and two phosphinic acid groups through the P=O oxygen atom in a square planar geometry. Dimethylformamide molecules are coordinated to the metal atom above and

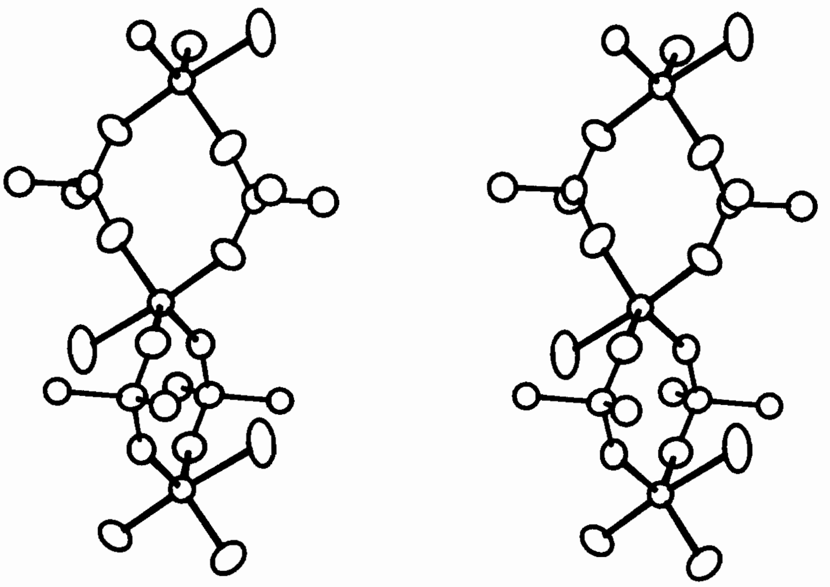

Fig. 2. Stereoview of a section of $Mn[O_2P(C_6H_5)_2]_2(DMF)$. Only α carbon atoms of the phenyl groups and oxygen atoms of coordinated DMF molecules are shown.

TABLE IV. Positional Parameters[a] for **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mn	0.500	0.500	0.500	C(11)	0.0899(4)	0.1392(3)	0.1082(4)
P(1)	0.28031(5)	0.26947(4)	0.52075(6)	C(12)	0.1207(3)	0.1877(2)	0.2550(3)
P(2)	0.24752(5)	0.59359(5)	0.52908(6)	C(13)	0.2075(2)	0.7021(2)	0.4294(2)
O(1)	0.3976(1)	0.3485(1)	0.5490(2)	C(14)	0.2963(2)	0.7937(2)	0.4209(3)
O(2)	0.1793(2)	0.3137(1)	0.5576(2)	C(15)	0.2684(3)	0.8829(2)	0.3548(3)
H(1)	0.168(3)	0.395(4)	0.511(4)	C(16)	0.1535(3)	0.8815(2)	0.2982(3)
O(3)	0.3682(1)	0.5866(1)	0.5205(2)	C(17)	0.0646(3)	0.7922(3)	0.3063(3)
O(4)	0.1489(1)	0.4878(1)	0.4717(2)	C(18)	0.0917(2)	0.7014(2)	0.3717(3)
O(5)	0.5753(2)	0.5455(1)	0.7431(2)	C(19)	0.2457(2)	0.6388(2)	0.7150(2)
C(1)	0.2913(2)	0.1527(2)	0.6205(2)	C(20)	0.3497(3)	0.6657(2)	0.8211(3)
C(2)	0.3997(3)	0.1421(2)	0.6919(3)	C(21)	0.3477(3)	0.7034(3)	0.9642(3)
C(3)	0.4100(3)	0.0493(3)	0.7632(4)	C(22)	0.2464(4)	0.7151(3)	0.9994(3)
C(4)	0.3112(4)	−0.0327(3)	0.7608(4)	C(23)	0.1435(4)	0.6892(3)	0.8948(4)
C(5)	0.2032(4)	−0.0231(2)	0.6899(4)	C(24)	0.1421(3)	0.6498(3)	0.7519(3)
C(6)	0.1916(3)	0.0694(2)	0.6197(3)	N	0.7176(2)	0.5788(2)	0.9502(2)
C(7)	0.2369(2)	0.2083(2)	0.3314(2)	C(25)	0.6744(2)	0.5476(2)	0.8078(3)
C(8)	0.3216(3)	0.1806(2)	0.2627(3)	C(26)	0.6465(4)	0.6132(3)	1.0445(3)
C(9)	0.2868(4)	0.1310(3)	0.1165(4)	C(27)	0.8382(3)	0.5832(3)	1.0163(4)
C(10)	0.1723(5)	0.1111(3)	0.0426(3)				

[a] e.s.d.s in the least significant digits are shown in parentheses.

below the plane with a Mn–O(DMF) distance of 2.279(1) Å.

Two intramolecular hydrogen bonds between the phosphinic acid P–OH group and the phosphinate $P–O^-$ group, exist in the complex. The O...O separation of 2.444(3) Å indicates a very strong hydrogen bond which creates an eight-membered ring chelating to the metal atom as can be seen from Fig. 2.

$\{Co[O_2P(C_6H_5)_2]_2[HO_2P(C_6H_5)_2]_2(DMF)_2\}$ (*3*)

The structure and the dimensions of the complex are essentially identical with those of **2** (see 'Supplementary Material'). Unlike **2**, compound **3** crystallizes in space group $P2_1/c$ but in both cases the complex resides on a crystallographic center of symmetry. The $Co–O(\Phi_2PO_2^-)$ and $Co–O(\Phi_2PO_2H)$ distances are 2.059(2) and 2.113(2) Å respectively. The Co–O-

TABLE V. Important Bond Lengths (Å) and Angles (°) for **2**

Mn–O(1)	2.150(2)	P(2)–O(3)	1.490(2)
Mn–O(3)	2.129(2)	P(2)–O(4)	1.535(2)
Mn–O(5)	2.270(1)	O(2)–O(4)	2.444(3)
P(1)–O(1)	1.488(2)	O(2)–H(1)	1.15(5)
P(1)–O(2)	1.526(2)	O(4)–H(1)	1.29(5)
O(1)–Mn–O(3)	91.87(6)	Mn–O(3)–P(2)	154.0(1)
O(1)–Mn–O(3)′	88.13(6)	Mn–O(5)–C(25)	126.6(2)
O(1)–Mn–O(5)	86.93(7)	O(2)–H(1)–O(4)	173(4)
O(1)–Mn–O(5)′	93.07(7)	P(1)–O(2)–H(1)	115(2)
O(3)–Mn–O(5)	88.97(7)	P(2)–O(4)–H(1)	117(2)
O(3)–Mn–O(5)′	91.03(7)	O(1)–P(1)–O(2)	118.0(1)
Mn–O(1)–P(1)	146.5(1)		

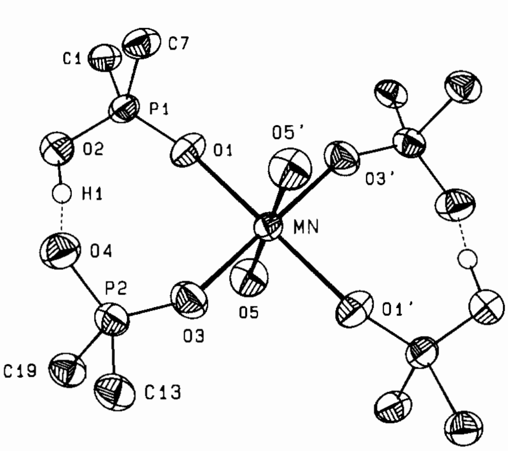

Fig. 3. The structure of $Mn[O_2P(C_6H_5)_2]_2[HO_2P(C_6H_5)_2]_2(DMF)_2$. Only α carbon atoms of phenyl groups and oxygen atoms of the DMF ligands are shown.

(DMF) distance is 2.115(2) Å. The O...O separation in the intramolecular hydrogen bond is 2.422(4) Å.

Discussion

Compound **1** is one of the few examples of TBP geometry for a manganese(II) complex with five monodentate ligands. Another example is dichlorotris(2-methylimidazole)manganese(II) in which large deviations from the ideal TBP geometry were observed [4]. It should be noted that the metal ion in **1** is not entirely free to adopt the ideal geometry since the complex is, in fact, a section of an infinite framework. The M...M separation in **1** (4.583 Å) is shorter by *ca.* 0.4 Å than those found in other related polymers [1–3]. Such a decrease in the M...M distance may cause a change in the magnetic interactions within the chain.

Some changes in the product distribution of **1** and **2** were observed when the ligand to metal ratio and the amount of CH_3ONa were varied but unfortunately, attempts to obtain pure samples of **1** were unsuccessful and crystals of **2** were present in all batches. The fact that both **1** and **2** cocrystallize under the same condition implies that several species coexist in solution, differing by ligand/metal ratio and degree of protonation.

The formation of the polymeric chain of TBP Mn(II) in **1** led us to attempt to synthesize the Co(II) analogue of **1** but all the experiments invariably yielded crystals of the monomeric species of **3**.

The existence of the two very strong hydrogen bonds in **2** and **3** and the formation of the eight-membered rings in the complexes contribute to the stability of these species. This stability is probably the cause of the shift in the monomer–polymer equilibrium towards the formation of a monomeric system rather than polymeric chains.

Acknowledgement

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Supplementary Material

Tables of structure factors, thermal parameters, non-essential bond distance and angles and positional parameters of hydrogen atoms for **1** and **2** and all crystallographic material for **3** (84 pages) are available from the authors.

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