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Synthesis, Properties and Structure of Bis(dialkyldithiophosphinato)manganese(II) Complexes

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Abstract

Reaction of $Mn_2(CO)_{10}$ or powdered manganese with bis(diorganothiophosphoryl)disulfanes, $R_2P(S)S_2P(S)R_2$ (R = Et, *n*-Pr) gives tetrahedral Mn(II)-dithiophosphinates, $(R_2PS_2)_2Mn$, which are dimerized in solution and in the solid state via ligand bridges. The crystal structure of the ethylcomplex is reported. Crystals are orthorhombic, space group *Pbca* with cell dimensions $a = 20.164(4)$, $b = 13.837(3)$ and $c = 11.960(2)$ Å.

Introduction

Our attempts to prepare dialkyldithiophosphinates of Mn(II) by common procedures [1] have failed as yet. Only a few compounds of type $(R_2PS_2)_2Mn$ (R = aryl, CH_3, CF_3) [2, 3] have been reported in the literature. They are either insoluble or sparingly soluble solids for which complete data or X-ray structure determinations are lacking. Recently we described a convenient method for the synthesis of metal dithiophosphinates by reaction of metals or metal carbonyls with bis(diorganothiophosphoryl)-disulfanes, $R_2P(S)S_2P(S)R_2$ (**1**) [4–6], which proved to be successful also in the case of Mn(II)-dithiophosphinates $(R_2PS_2)_2Mn(II)$ (**2**) (**a**: R = Et; **b**: R = *n*-Pr).

Experimental

All operations were performed under argon and with degassed and anhydrous solvents. Mass spectra (MS): Varian MAT 311 A; UV–Vis: Perkin-Elmer Lambda 5; molecular weight: Knauer Cryoscope; magnetic studies (Faraday method): Bruker magnet B-E 10 in combination with a Sartorius microbalance 4170.

Preparation of $(R_2PS_2)_2Mn(II)$ (2)

$Mn_2(CO)_{10}$ (3.9 g, 0.01 mol) and 0.02 mol of the corresponding disulfane **1** [7] in 25 ml 1,2,4-trimethylbenzene were stirred at 125 °C for 1.5 h. After filtration at 80 °C nearly colorless crystals separated from the solution on cooling, which were recrystallized from toluene.

2a (R = Et): Yield 5.4 g (79%); m.p. 173–175 °C; *Anal.* Calc. for $C_8H_{20}P_2S_4Mn$ (361.4): C, 26.6; H, 5.6; P, 17.1; S, 35.5; Mn, 15.2. Found: C, 26.6; H, 5.5; P, 17.1; S, 35.7; Mn, 15.3%. Electron-impact induced MS (70 eV): *m/z* 361 (100% rel. int.) $[M]^{+\bullet}$, *m/z* 208 (96%) $[MnEt_2PS_2]^+$.

2b (R = *n*-Pr): Yield 6.1 g (73%); m.p. 155–158 °C; *Anal.* Calc. for $C_{12}H_{28}P_2S_4Mn$ (417.5): C, 34.5; H, 6.8; P, 14.8; S, 30.7; Mn, 13.2. Found: C, 34.4; H, 6.9; P, 14.6; S, 30.7; Mn, 13.0%. Electron-impact induced MS (70 eV): *m/z* 417 (100%) $[M]^{+\bullet}$, *m/z* 236 (69%) $[MnPr_2PS_2]^+$, molecular weight (cryoscopic in benzene): 740 (0.015 mol/kg), 755 (0.034 mol/kg), 772 (0.073 mol/kg).

X-ray Data Collection

For the X-ray investigations needle-shaped colorless crystals of **2a** were sealed into capillaries at normal atmosphere. Photographs showed orthorhombic symmetry and the systematic absences of the unique group *Pbca*. The needle axis was identified as [011]. The experimental determination of the density failed with respect to the high solubility of the crystals in many liquids. A comparison of the volume per molecule with that of an analogous Zn [8] and Cd complex [9] yielded 8 molecules per unit cell. A crystal of approximately 0.35 × 0.6 × 0.9 mm on a Siemens AED2 diffractometer (crystal monochromator, Mo Kα) was used for the determination of the lattice parameters (24 reflections, $41 < 2\theta < 43°$) and for the data collection. For the latter a variable $\omega:\theta$ scan with variable scan speeds was used, three standard reflections were monitored every two hours and did not show any significant variations. The indices ranged from 0 to $h = 28$, $k = 19$, and $l = 16$, all 5390 reflections within $4 < 2\theta < 60°$ were measured. After elimination of systematic absences and reflections with zero or negative intensities the final set of data contained 4194 unique reflections of which 2881 were classified observed ($F > 4\sigma_F$). For an empirical absorption correction a ψ-scan

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TABLE I. Crystallographic Data and Data Collection Parameters for $(Et_2PS_2)_2Mn(II)$ (**2a**)

Formula	$C_8H_{20}MnP_2S_4$
Molecular weight	361.4
Crystal system	orthorhombic
Space group	*Pbca*
a (Å)	20.164(4)
b (Å)	13.837(3)
c (Å)	11.960(2)
V (Å^3), Z	3336(1), 8
D_{calc} (g cm^{-3})	1.439
Diffractometer	Siemens AED2
Radiation, λ (Å)	Mo Kα, 0.71073
Linear absorption coefficient (mm^{-1})	1.37
Scan technique	$\omega:\theta$
Scan speed (deg. min^{-1})	0.7–4.2
Scan width 2θ (deg)	1.4 (plus separation α_1/α_2)
2θ min., max. (deg)	4, 60
Reflections for ψ-scan	10
Total no. of reflections	4194
Observed reflections ($F > 4\sigma_F$)	2881
$R(F)$ obs. (all) data	0.050 (0.080)
$Rw(F)$ obs. (all) data	0.067 (0.072)

every 10° for selected reflections was performed. Crystallographic and experimental details are summarized in Table I.

Crystal Structure Determination

From direct methods the atomic coordinates of all Mn, S, and P atoms were found. The structure was completed and refined in the usual way. Unexpectedly high values of U_{ii} for the atoms S(4), C(6) and C(8) (up to $U = 0.35$ Å^2) pointed to a disorder of these. However, all atempts to describe this disorder by split atom positions did not improve the quality of the model. Finally, the high displacement parameters had to be accepted. All H atoms were constructed and added as fixed atom contributions with fixed geometry. The refinement of 136 parameters converged at $\Sigma w \| F_o | - | F_c \|^2 = 1.7$ with all $\Delta/\sigma < 0.02$. Residual electron densities ranged from -0.56 to 0.49 e Å^{-3}. Weights were derived from counting statistics by $1/w = \sigma_F{}^2 + 0.00078F^2$. All calculations were performed with the program system SHELXTL using atomic scattering factors, including corrections for anomalous dispersions as implemented. Final atomic parameters of the non-H atoms are given in Table II.

Results and Discussion

Synthesis and Properties of $(R_2PS_2)_2Mn(II)$ (2)

Reaction of $Mn_2(CO)_{10}$ with bis(diorganothiophosphoryl)disulfanes (**1**) in 1,2,4-trimethylbenzene according to

TABLE II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameter U_{eq} (×10^3 Å^2) with e.s.d.s in Parentheses for **2a**[a]

	x	y	z	U_{eq}
Mn	4103(1)	4622(1)	178(1)	51(1)
S(1)	5146(1)	5446(1)	1477(1)	49(1)
S(2)	3814(1)	6373(1)	207(1)	61(1)
S(3)	4026(1)	3363(1)	1622(1)	66(1)
S(4)	3011(1)	3863(1)	−433(1)	97(1)
P(1)	4542(1)	6615(1)	1326(1)	49(1)
P(2)	3171(1)	2990(1)	863(1)	63(1)
C(1)	5013(2)	7666(3)	948(4)	64(1)
C(2)	4196(2)	6846(4)	2688(4)	71(2)
C(3)	4630(3)	8613(4)	1001(5)	98(2)
C(4)	3770(3)	6056(5)	3157(4)	99(3)
C(5)	2499(3)	3010(5)	1839(5)	92(2)
C(6)	3198(4)	1753(6)	393(10)	152(4)
C(7)	2375(4)	3939(7)	2423(7)	128(4)
C(8)	3531(6)	1062(6)	830(14)	216(7)

[a] U_{eq} is defined by $\frac{1}{3}(U_{11}a^{*2}a^2 + U_{12}a^*b^*ab\cos\gamma + \ldots)$.

$$\underset{}{Mn_2(CO)_{10}} + \underset{\mathbf{1}}{2R_2P(S)S_2P(S)R_2} \longrightarrow \underset{\mathbf{2}}{2(R_2PS_2)_2Mn(II)} + 10CO$$

1, 2	**a**	**b**
R	Et	*n*-Pr

leads to the Mn(II)-dithiophosphinates **2**. They were also obtained by reacting **1** with powdered manganese according to

$$Mn + \mathbf{1} \longrightarrow \mathbf{2}$$

However, the latter reaction afforded much longer reaction times (15 h) and gave considerably lower yields. Compounds **2** are colorless crystals, larger samples of which show a slightly yellow–greenish colour. They are easily soluble in CH_2Cl_2 but less soluble in benzene and alcohols. While the solid compounds **2** are rather stable in dry air, their solutions decompose rapidly in contact with moist air, forming brown precipitates.

Electron-impact induced (EI) mass spectra show abundant signals for the molecular ions which are the base peaks in the spectra of both compounds **2** [10]. Another intensive signal is that for $[Mn(R_2PS_2)]^+$. Remarkably, nearly all ions observed are metal-containing species, whereas ligand ions and their fragments are of less abundance.

Compound **2b**, which proved to be sufficiently soluble in benzene for cryoscopic molecular weight determinations, was found to be dimeric in this solvent. We assume that the complexes **2** are tetra-

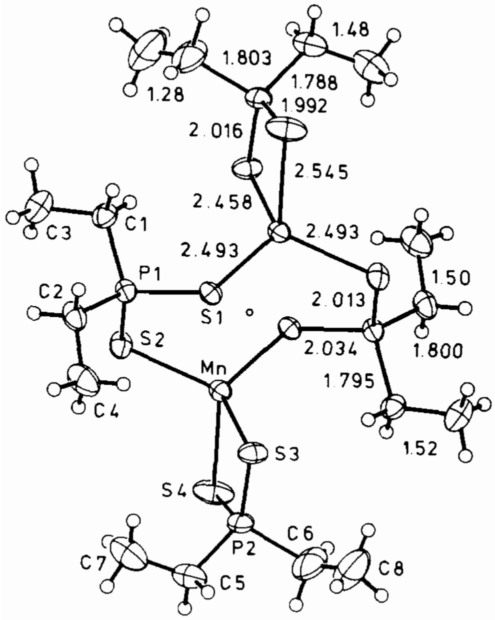

Fig. 1. One dimer of $(Et_2PS_2)_2Mn(II)$ (**2a**) with bond lengths (Å). The e.s.d.s are: Mn–S 0.001, P–S 0.001–0.002, P–C 0.004–0.009, and C–C 0.01 Å. The point symmetry of the dimer is $\bar{1}$. The non-H atoms are represented by displacement ellipsoids of 25% probability (SHELXTL), the radius of the constructed H atoms was set to 0.15 Å.

hedral and dimerize via ligand bridges, e.g. tetrahedral dithiophosphinates of Zn(II) and Cd(II) [1, 8, 9, 11]. This assumption was confirmed in the case of **2a** by the results of an X-ray structure analysis (*vide infra*).

The effective magnetic moments at 295 K of 5.85 BM (**2a**) and 5.82 BM (**2b**) correspond with the spin-only value of five unpaired electrons (5.92 BM). These values compare favorably well with those reported for similar Mn(II) complexes [2, 3].

The electron spectra of **2** are dominated by a strong CT-band tailing into the visible region and thus probably superposing possible d–d-transitions for which only weak intensities are to be expected.

Description of the Crystal Structure of 2a

Figure 1 shows two molecules of the Mn complex **2a** with main bond lengths. Bond angles at the atoms Mn, S and P are listed in Table III. Within the crystals the complex forms discrete dimers via crystallographic centers of symmetry. The puckered eight-membered ring formed by this dimerization reveals a distorted chair conformation, the atoms Mn, S(1), S(2), and P(1) are planar within 0.11 Å, while the four atoms of the 'seat' are exactly planar by symmetry. The angle between the 'back' and 'seat' is 104.2°. The torsion angles within the ring are Mn–[–95.3]–S(2)–[11.7]–P1–[76.3]–S(1)–156.3]–Mn^{a} while the remaining angles are generated by inversion at the center of symmetry. The non-bonding distance Mn–S(1) of 2.854(1) Å is remarkably short. The four-membered ring Mn–S(3)–P(2)–S(4) appears to be planar within 0.002 Å, which is in contrast to many other chelating alkyldithiophosphinato complexes (e.g. bis(ethylmethyldithiophosphinato)nickel(II) [12]). However, the anisotropic displacement parameters of the atoms S(4), C(6) and C(8) (see Fig. 1) point very strongly to a disorder of these atoms; *i.e.* their coordinates listed in Table II and their geometry have to be interpreted as those of an average of several positions varying from unit cell to unit cell.

TABLE III. Main Bond Angles (°) of **2a**. The e.s.d.s at Atoms Mn and S are 0.1°, and at Atoms P 0.1–0.3°

S(1)^a–Mn–S(2)	100.9	S(2)–Mn–S(3)	131.6
S(1)^a–Mn–S(3)	124.7	S(2)–Mn–S(4)	101.7
S(1)^a–Mn–S(4)	106.4	S(3)–Mn–S(4)	81.7
S(1)–P(1)–S(2)	111.3	S(2)–P(1)–C(1)	110.7
S(1)–P(1)–C(1)	110.5	S(2)–P(1)–C(2)	110.4
S(1)–P(1)–C(2)	107.0	C(1)–P(1)–C(2)	106.8
S(3)–P(2)–S(4)	109.5	S(4)–P(2)–C(5)	112.1
S(3)–P(2)–C(5)	110.5	S(4)–P(2)–C(6)	109.7
S(3)–P(2)–C(6)	110.9	C(5)–P(2)–C(6)	103.9
Mn^a–S(1)–P(1)	108.9	Mn–S(3)–P(2)	85.3
Mn–S(2)–P(1)	90.1	Mn–S(4)–P(2)	83.5

^{a}Symmetry code $1 - x, 1 - y, -z$.

Supplementary Material

Tables of anisotropic displacement parameters, calculated hydrogen atom positions, and structure factors (F_o, σ_F) are available from the Editor-in-Chief.

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