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COMPARISON OF THE MOLECULAR STRUCTURES OF MONOVALENT CATION SALTS OF N,N-DIMETHYLDITHIOCARBAMATE. NOVEL SYNTHESIS AND CRYSTAL STRUCTURE OF $(P\phi_4)(S_2CN(CH_3)_2)2H_2O$

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ABSTRACT

Crystals of the tetraphenylphosphonium N,N-dimethyldithiocarbamate dihydrate ($C_{27}H_{30}NO_2PS_2$; F.W. = 495.6) are monoclinic; $P2_1/n$; $a = 13.349(6)$, $b = 20.968(6)$, $c = 9.800(4)$ Å, $\beta = 109.01(3)^\circ$; $Z = 4$; $V = 2593.4(16)$ Å³; $D_x = 1.269$ gcm⁻³. Data were collected at ambient temperature using MoK α radiation ($\lambda = 0.71069$ Å). $F(000) = 1048$, linear absorption coefficient, $\mu = 2.80$ cm⁻¹. The structure was solved by direct methods and subsequently refined by full matrix least squares techniques. Final R value = 0.064 for 1610 reflections and 298 varied parameters. Due to the nature of the cation, interactions between the tetraphenylphosphonium group and the sulfur atoms of the anion are absent, unlike previous dimethyldithiocarbamate structures (Na^+ , Cs^+ , Tl^+). Intermolecular interactions between the waters of hydration and the anion are present.

INTRODUCTION

Attempts to prepare the tetraphenylphosphonium ($P\phi_4^+$) salt of $Ni(CS_2)_2^{2-}$ (Fackler and Coucouvanis, 1966) led to the isolation of low yields of $(P\phi_4)_2S_2CN(CH_3)_2$ as a reaction by-product. The dithiocarbamate was characterized by X-ray diffraction techniques. This report describes a novel synthesis and structural comparisons to monovalent cation salts of dimethyldithiocarbamate.

MATERIALS AND METHODS

Crystals of tetraphenylphosphonium dimethyldithiocarbamate, I, were obtained by the slow evaporation of the filtrate from the reaction of ethanolic nickel acetate, a dimethylformamide solution of KOH and CS_2 , and aqueous $P\phi_4Cl$ (Fackler and Coucouvanis, 1966). The pale yellow crystal was cleaved to give $0.3 \times 0.3 \times 0.4$ mm dimensions. Intensity data were collected on a Syntex P3 automated diffractometer. Unit cell dimensions were determined by least squares refinement of the best angular positions for 15 independent reflections ($2\theta > 15^\circ$) during normal alignment procedures. Data (3411 points) were collected using a variable scan rate, $\theta - 2\theta$ scan mode and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ (h , -14 to +13; k , 0 to +8; l , 0 to +10). Maximum 2θ value was 45.0° . Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. Corrections were applied for Lorentz, polarization and background effects. No absorption correction was applied. The intensities of three standard reflections (remeasured after every 97 reflections) showed crystal stability. Data reduction ($I < 3.0 \sigma(I)$) gave 1610 reflections used in the solution and refinement of the structure.

The structure was solved by direct methods for positions of nonhydrogen atoms. Least squares refinement using the X-Ray System program (1980 version) converged with anisotropic thermal parameters. A difference Fourier synthesis allowed location of all hydrogen positions and these were included in the final refinement with isotropic thermal parameters ($U_{11} = 3.97$) but all hydrogen parameters were held invariant. Maximum least squares shift to error ratio = 0.4. $\Delta\rho_{max} = 0.34$ and $\Delta\rho_{min} = -0.30$ eÅ⁻³ on the final difference map. The final cycle of refinement - function minimized ($\sum(|F_o| - |F_c|)^2$), led to final agreement factor, $R = 6.4\%$, $R = (\sum(|F_o| - |F_c|)/\sum|F_o|) \times 100$. A weight equal to $1/\sigma F$ was introduced in the final cycles of refinement: $R_w = 8.1\%$. $S = 0.30$, with 298 parameters refined.

Scattering factors were taken from the tables of Cromer and Mann (1968). Anomalous dispersion factors, f' and f'' were applied for P and S (Ibers and Hamilton, 1974).

RESULTS

Crystal data are given in Table 1. The structure of $(P\phi_4)_2S_2CN(CH_3)_2 \cdot 2H_2O$, I, is seen in Fig. 1. Atomic positional and thermal parameters are given in Table 2. Selected bond distances and angles can be seen in Table 3.

Table 1. Crystal Data for $(P\phi_4)_2S_2CN(CH_3)_2 \cdot 2H_2O$

Formula	$C_{27}H_{30}NO_2PS_2$
MWT	495.6
Space group	monoclinic $P2_1/n$
a	13.349(6)Å
b	20.968(6)Å
c	9.800(4)Å
β	109.01(3)°
V	2593.4(16)Å ³
F(000)	1048
μ_{MoK}	2.80 cm ⁻¹
MoK	0.71069Å
D_{calc}	1.269 gcm ⁻³
Z	4
Observed reflections	1610
R/R _w	6.4/8.1%

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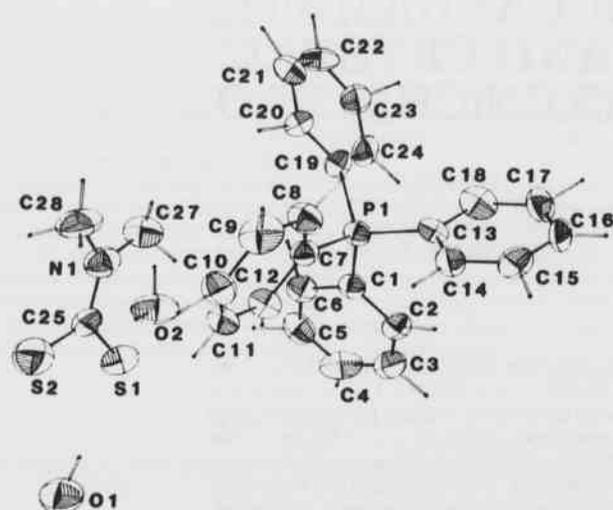


Figure 1. The asymmetric unit of $(P\phi)_2(S_2CN(CH_3)_2) \cdot 2H_2O$. Thermal ellipsoids drawn at 50% probability level.

Table 2. Positional Parameters of Nonhydrogen Atoms for $(\phi)_2P$ (dimethyldithiocarbamate) (H_2O).

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))	Eqv $\times 10^3$
P1	0.6719(2)	0.0386(1)	0.2830(2)	33
S1	0.7375(2)	0.2377(1)	-0.1244(3)	40
S2	0.5842(3)	0.3441(2)	-0.1442(3)	79
O1	0.1785(6)	0.2336(4)	0.0249(7)	81
O2	0.5821(5)	0.1815(4)	0.0147(8)	86
N1	0.6964(6)	0.2892(4)	0.0981(9)	98
C1	0.7363(6)	0.0121(4)	0.1609(8)	35
C2	0.7087(6)	-0.0456(4)	0.0845(9)	41
C3	0.7593(8)	-0.0643(5)	-0.0129(10)	54
C4	0.8332(7)	-0.0250(6)	-0.0386(10)	64
C5	0.8602(8)	0.0311(5)	0.0353(10)	39
C6	0.8151(7)	0.0510(5)	0.1340(9)	44
C7	0.5851(7)	0.1041(4)	0.2056(8)	38
C8	0.5184(7)	0.1271(5)	0.2766(9)	30
C9	0.4512(8)	0.1766(5)	0.2159(12)	65
C10	0.4464(8)	0.2028(5)	0.0811(11)	51
C11	0.5125(8)	0.1784(5)	0.0158(10)	48
C12	0.5810(6)	0.1296(5)	0.0733(9)	43
C13	0.5934(6)	-0.0245(4)	0.3183(8)	37
C14	0.4888(7)	-0.0261(5)	0.2467(9)	43
C15	0.4263(8)	-0.0781(6)	0.2679(10)	37
C16	0.4749(9)	-0.1287(5)	0.3549(11)	65
C17	0.5806(8)	0.1261(5)	0.4274(10)	58
C18	0.6407(7)	-0.0743(5)	0.4101(10)	59
C19	0.7737(6)	0.0613(4)	0.4481(9)	35
C20	0.7645(7)	0.1181(4)	0.5174(9)	44
C21	0.8406(8)	0.1318(5)	0.6487(10)	51
C22	0.9229(7)	0.0887(6)	0.7031(9)	51
C23	0.9321(8)	0.0334(5)	0.6375(11)	53
C24	0.8563(7)	0.0189(5)	0.5055(10)	47
C25	0.6748(8)	0.2904(5)	-0.0472(10)	30
C27	0.7761(8)	0.2463(5)	0.1910(11)	63
C28	0.6449(9)	0.3286(6)	0.1735(11)	84

Eqv = 1/3 the trace of the diagonalized matrix

Table 3. Bond Angles ($^\circ$) and Distances (\AA) for $(\phi)_2P$ (Dimethyldithiocarbamate) (H_2O).

P1 - C1	1.775(10)	C1 - P1 - C7	109.9(4)
P1 - C7	1.798(8)	C1 - P1 - C13	110.0(4)
P1 - C13	1.790(10)	C1 - P1 - C19	107.3(4)
P1 - C19	1.805(8)	C7 - P1 - C13	108.0(4)
C25 - S1	1.704(11)	C7 - P1 - C19	111.7(4)
C25 - S2	1.700(10)	C13 - P1 - C19	109.8(4)
C25 - N1	1.36(1)	S1 - C25 - S2	123.0(6)
N1 - C27	1.46(1)	S1 - C25 - N1	119.1(7)
N1 - C28	1.42(2)	S2 - C25 - N1	117.9(8)
C1 - C2	1.41(1)	C25 - N1 - C27	121.8(9)

Table 3 (cont.)

C2 - C3	1.39(2)	C25 - N1 - C28	124.0(8)
C3 - C4	1.37(2)	C27 - N1 - C28	114.2(8)
C4 - C5	1.36(2)	P1 - C1 - C2	121.8(7)
C5 - C6	1.36(2)	P1 - C1 - C6	119.8(7)
C6 - C1	1.42(1)	C2 - C1 - C6	118.4(9)
C7 - C8	1.38(1)	C1 - C2 - C3	120.3(9)
C8 - C9	1.37(1)	C2 - C3 - C4	119.7(9)
C9 - C10	1.40(2)	C3 - C4 - C5	120.1(10)
C10 - C11	1.36(2)	C4 - C5 - C6	122.6(10)
C11 - C12	1.36(1)	C5 - C6 - C1	118.8(8)
C12 - C7	1.39(1)	P1 - C7 - C8	119.1(7)
C13 - C14	1.39(1)	P1 - C7 - C12	120.9(7)
C14 - C15	1.40(2)	C7 - C8 - C9	118.8(9)
C15 - C16	1.38(1)	C8 - C9 - C10	121.8(11)
C16 - C17	1.36(1)	C9 - C10 - C11	117.6(9)
C17 - C18	1.39(2)	C10 - C11 - C12	122.3(9)
C18 - C13	1.39(1)	C11 - C12 - C7	119.5(9)
C19 - C20	1.40(1)	C12 - C7 - C8	119.9(8)
C20 - C21	1.38(1)	P1 - C13 - C14	120.0(6)
C21 - C22	1.39(1)	P1 - C13 - C18	120.6(6)
C22 - C23	1.38(2)	C13 - C14 - C15	119.0(8)
C23 - C24	1.39(1)	C14 - C15 - C16	121.2(9)
C24 - C19	1.37(1)	C15 - C16 - C17	119.4(10)
		C16 - C17 - C18	120.5(9)
		C17 - C18 - C13	120.4(8)
		P1 - C19 - C20	120.1(6)
		P1 - C19 - C24	118.1(7)
		C19 - C20 - C21	118.3(8)
		C20 - C21 - C22	119.6(9)
		C21 - C22 - C23	121.5(8)
		C22 - C23 - C24	118.8(9)
		C23 - C24 - C19	120.0(9)
		C24 - C19 - C20	121.7(7)

DISCUSSION

The synthesis of dithiocarbamates directly from dimethylformamide, DMF, is novel. This can be explained by the base (OH^-) hydrolysis of DMF followed by the nucleophilic attack of the $[N(CH_3)_2]^-$ generated during the reaction, on CS_2 . The $(P\phi)_2S_2CN(CH_3)_2$ can be prepared directly by the metathesis of $NaS_2CN(CH_3)_2$ and $P\phi_2Cl$, and compares well with the product obtained from DMF.

The use of $P\phi_2^+$ as counterion prohibits interaction of the cation with the dithiocarbamate anion. In the molecular structures of the Na^+ (Ymen, 1981; Oskarsson and Ymen, 1983), Tl^+ (Jennische and Hesse, 1973), Cs^+ (Wahlberg, 1976) and $NH_2(CH_3)_2^+$ (Wahlberg, 1978) salts, there is direct interaction between cation and anion (see Table 4).

The structure of the Na^+ (Ymen, 1981; Oskarsson and Ymen, 1983) complex indicates that the Na^+ ion is attached to the S atoms of the dithiocarbamate and four O atoms from waters of hydration, forming a distorted octahedral arrangement. Na-S distances are 2.992(1) and 3.015(a) \AA . This structure correlates well with the structure of the $NaS_2CN(CH_3)_2$ complex (Albertsson *et al.*, 1980). The Tl^+ reaction yields dimetallic species which are interconnected to one another through long Tl-S interactions, giving rise to layers of these dimers parallel to

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the a,b plane (Jennische and Hesse, 1973). The Tl atoms are seven coordinate with the Tl-S distances ranging from 3.0 to 3.7 Å. For Cs⁺, a coordination number of 8 is found for the cation in the structure of Cs₂CN(CH₃)₂ (Wahlberg, 1976). Cs-S distances range from 3.636(1) to 4.099(a) Å. The NH₂(CH₃)₂⁺ complex gives a one-dimensional arrangement with the ammonium hydrogens interacting with the sulfurs on the dithiocarbamate. Each dithiocarbamate hydrogen bonds to two

Table 4. Comparisons of Selected Bond Distances (Å) and Angles (°) for Complexes of Dimethyldithiocarbamate

M' =	(PØ ₄) ⁺	(H ₂ N(CH ₃) ₂) ⁺	Cs ⁺	Tl ⁺	NaS ₂ CN(CH ₂) ₄
C-S	1.70	1.71	1.71	1.72	1.72
C-N	1.36	1.34	1.34	1.36	1.32
N-CH ₃	1.44	1.46	1.46	1.44	-
N-CH ₂	-	-	-	-	1.48
S-M'	-	2.66, 2.61 2.46, 2.73	3.64 3.71 4.10	2.99, 3.03 3.28, 3.44 3.46, 3.52 3.74	3.00 2.95
S-C-S	123.0	119.7	121.2	121	122.3
S-C-N	118.5	120.2	119.4	120	118.9
C-N-CH ₃₍₂₎	122.9	122.7	121.2	123	124.6
CH ₃ -N-CH ₃	114.2	114.7	117.5	114	-
CH ₂ -N-CH ₂	-	-	-	-	110.8

NH₂(CH₃)₂⁺ forming a zig-zag chain (Wahlberg, 1978).

The Li⁺ complex shows an interaction between the waters of hydration and the dithiocarbamate anion (Ymen, 1984). The Li⁺ ion is coordinated to four H₂O molecules forming a distorted tetrahedral arrangement. The electron density on the S atom is distributed to the coordinated waters through hydrogen bonds. This is similar to the structure found for PØ₄(S₂CN(CH₃)₂), in which the waters of hydration are hydrogen bonded to the dithiocarbamate anion. Unlike the Li⁺ example, the waters do not interact with the PØ₄⁺ moiety. Thus, the structure reported within is the first example of a monovalent cationic species that does not bind to the dimethyldithiocarbamate ion.

SUPPLEMENTAL MATERIAL

Anisotropic Thermal Parameters, Positional Parameters for the Hydrogen Atoms, and Structure Factor Tables (31 pages) are available from the authors upon request.

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