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Crystal Structure and Vibrational Spectra of Pyridine-2,6-dithio-carbomethylamide

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The crystal structure of Pyridine-2,6-dithio-carbomethylamide (*PDTA*) is described: $C_9H_{11}N_3S_2$, monoclinic, $P2_1/c$, $Z = 4$, $a = 6.000\ (1)$ Å, $b = 8.840\ (1)$ Å, $c = 21.452\ (1)$ Å, $\beta = 105.47\ (1)^\circ$, $d_x = 1.47$ gcm^{-3}. The structure was solved with direct methods and refined to a conventional R-factor of 0.047. The molecule is nearly planar in the crystal. There are possibly weak intramolecular H-bonds between the two amide nitrogens and the pyridine nitrogen and intermolecular H-bonds between two amide nitrogens and one thioamide sulfur atom. The IR and *Raman* spectra of *PDTA* and deuterated *PDTA* are discussed.

(Keywords: Crystal structure analysis; Pyridine-2,6-dithiocarbomethylamide; Vibrational spectra)

Kristallstruktur und Schwingungsspektren von Pyridin-2,6-dithiocarbomethylamid

Die Kristallstruktur von Pyridin-2,6-dithiocarbomethylamid (*PDTA*) wurde bestimmt: $C_9H_{11}N_3S_2$, monoklin, $P2_1/c$, $Z = 4$, $a = 6{,}000\ (1)$ Å, $b = 8{,}840\ (1)$ Å, $c = 21{,}452\ (1)$ Å, $\beta = 105{,}47\ (1)^\circ$, $d_x = 1{,}47$ gcm^{-3}. Das Phasenproblem wurde mittels direkter Methoden gelöst und die Struktur bis zu einem R-Faktor von $R = 0{,}047$ verfeinert. Das Molekül ist im Kristall nahezu planar. Das Vorliegen schwacher intramolekularer Wasserstoffbrücken zwischen den beiden Thioamid-Stickstoffatomen und dem Pyridinstickstoff sowie intermolekularer Wasserstoffbrücken zwischen Thioamid-Stickstoff- und Thioamid-Schwefelatomen wird postuliert. IR- und *Raman*-Spektren von *PDTA* und deuteriertem *PDTA* werden diskutiert.

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Introduction

The title compound (henceforth abbreviated *PDTA*) readily forms stable complexes with a large number of metal atoms[1]. Its versatility as a complex former is largely due to the fact that it can coordinate to a metal atom either through its soft thioamide sulfur or through its harder amide nitrogen. In addition, metal-*PDTA* complexes are stabilized by the chelate effect of 2 fivemembered rings. Although a large number of structural and analytical investigations were reported on the closely related 2,6-Pyridine dicarboxylic acid[2,3], we know of no crystal structure investigation on one of its derivatives or on a derivative of the corresponding thioacid.

In this communication, we report the crystal structure of the free *PDTA* ligand, which is to be compared with its nickel complex in the following paper[4]. Of particular interest will be a correlation of structural changes upon metal complexation with changes in the IR absorption of the thioamide system[5–7].

Experimental

Crystals were prepared as described previously[1]; they grow in the form of yellow prisms. A fragment of the dimensions 0.2 × 0.25 × 0.35 mm was chosen and approximate cell dimensions, the *Laue* class (2/m) and systematic extinctions ($h0l$, $l = 2n$; $0k0$, $k = 2n$) were obtained from a set of precession photographs. The crystal was subsequently transferred to a *Stoe* 4-circle diffractometer, where accurate cell dimensions and the orientation matrix were determined by least-squares from the setting angles of 8 carefully centered reflections.

Intensity measurements were carried out in the $\omega/2\theta$-scan mode, with graphite-monochromated MoK_α-radiation ($\lambda = 0.71069$ Å). The intensity was integrated over an ω-range of 0.6°, with fixed scan speed. All symmetry-independent reflections within $2\theta < 46°$ ($\sin\theta/\lambda < 0.55$) were recorded, yielding a total of 1529 reflections (including 125 systematically extinct ones). Data reduction involved Lp-correction, but no absorption correction ($\mu = 4.4\ \mathrm{cm}^{-1}$). Of the 1404 non-extinct reflections, 1079 had $|F_0| > 3\sigma(|F_0|)$. The structure was solved with direct methods and refined by conventional full-matrix least-squares techniques. Anisotropic refinement for all non-hydrogen atoms with fixed contribution for hydrogen atoms (at calculated positions) converged at $R = 0.052$.

Hydrogen atoms were subsequently included into the refinement at calculated positions and allowed to refine subject to the following constraints: both N—H distances and the pyridine C—H distances were constrained to the value 1.05 Å, whereas the two methyl groups were refined as rigid groups. With 159 parameters and 1367 reflections, the refinement converged at $R = 0.047$ (weighting system: $W_i = 1/[\sigma^2\{F_{0i}\} + K\{F_{0i}\}^2]$, $K = 0.0134$). A final difference *Fourier* synthesis did not show any peaks higher than $0.25\ \mathrm{e}\text{Å}^{-3}$. Refined coordinates and temperature factors are listed in Table 1 (non-hydrogen atoms) and Table 2 (hydrogen atoms)[8].

Table 1. *Fractional atomic coordinates and vibrational tensor components* ($\times 10^4$, *U values in* Å^2) *for the non-hydrogen atoms of pyridine-2,6-dithio-carbomethylamide*. The temperature factor is of the form $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)]$ E.s.d.'s (in parentheses) are in units of the last significant figure

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S (1)	1757 (2)	2064 (2)	5268 (1)	631 (8)	731 (8)	457 (7)	—18 (4)	—93 (5)	—104 (5)
S (2)	—2928 (2)	—1466 (1)	1829 (1)	584 (8)	712 (8)	575 (8)	—196 (5)	48 (5)	11 (5)
N (1)	—2134 (5)	2623 (4)	4390 (1)	552 (18)	565 (18)	441 (17)	—15 (14)	48 (14)	2 (15)
N (2)	—4744 (5)	691 (4)	2387 (1)	442 (16)	650 (19)	379 (16)	—24 (13)	—20 (13)	80 (14)
N (3)	—1378 (4)	811 (3)	3479 (1)	374 (14)	431 (15)	406 (15)	25 (12)	37 (12)	—33 (11)
C (1)	—115 (6)	1924 (4)	4547 (2)	468 (19)	464 (17)	426 (19)	104 (14)	43 (15)	—127 (15)
C (2)	—3004 (6)	—224 (4)	2412 (2)	466 (20)	508 (19)	410 (18)	38 (15)	76 (15)	—30 (16)
C (3)	340 (5)	950 (4)	4023 (1)	408 (18)	471 (18)	388 (18)	69 (14)	14 (15)	—86 (15)
C (4)	—1037 (5)	—84 (4)	3012 (2)	406 (18)	446 (18)	443 (17)	44 (14)	70 (14)	—31 (13)
C (5)	2444 (6)	227 (4)	4107 (2)	422 (19)	686 (24)	478 (20)	120 (18)	—48 (15)	0 (16)
C (6)	991 (6)	—879 (4)	3068 (2)	475 (20)	566 (22)	639 (23)	57 (18)	123 (17)	95 (17)
C (7)	2783 (6)	—697 (5)	3621 (2)	423 (20)	703 (24)	677 (26)	147 (21)	50 (18)	112 (18)
C (8)	—2983 (7)	3596 (5)	4817 (2)	672 (27)	720 (27)	577 (25)	—135 (20)	150 (21)	—25 (20)
C (9)	—6832 (7)	770 (6)	1845 (2)	541 (23)	949 (33)	506 (23)	—26 (21)	—100 (18)	166 (21)

Infrared spectra were obtained from KBr pellets, Nujol mulls and $CDCl_3$ solutions on a Perkin-Elmer 580 B spectrometer. The *Raman* spectra were measured on a Spex 1301 double spectrometer equipped with a photocounting detection system and a cooled RCA C31031 PM-tube. The 514.5 nm line from a Spectra Physics argon ion laser was used as excitation source. The rotating sample technique was applied to avoid thermal decomposition.

Deuterated *PDTA* was prepared through isotropic exchange by dissolving in a mixture of dioxane and D_2O.

Table 2. *Fractional atomic coordinates and vibrational tensor components* ($\times 10^3$, *U values in* $Å^2$) *for the hydrogen atoms of pyridine-2,6-dithio-carbomethylamide.* The temperature factor is of the form $T = \exp[-(8\pi^2 U_{iso} \sin^2\theta/\lambda^2)]$

	x/a	y/b	z/c	U_{iso}
H (N 1)	—318 (6)	220 (5)	396 (1)	93 (15)
H (N2)	—466 (7)	145 (4)	276 (1)	76 (13)
H (C5)	376 (5)	45 (5)	453 (1)	72 (12)
H (C6)	114 (9)	—168 (4)	272 (2)	105 (18)
H (C7)	450 (3)	—104 (5)	368 (2)	95 (15)
H 1 (C8)	—474 (1)	392 (1)	458 (0)	90 (14)
H 2 (C8)	—191 (1)	459 (1)	492 (0)	79 (13)
H 3 (C8)	—294 (1)	302 (1)	526 (0)	146 (26)
H 1 (C9)	—795 (1)	159 (1)	198 (0)	102 (17)
H 2 (C9)	—774 (1)	—29 (1)	173 (0)	248 (45)
H 3 (C9)	—633 (1)	117 (1)	143 (0)	109 (18)

Results and Discussion

Crystal Structure

A projection of the *PDTA* molecule into the plane of the pyridine ring is shown in Fig. 1. Fig. 2 shows a stereo-picture of the packing in the crystal. Within the respective standard deviations (for non-hydrogen atoms: bond length: $\sigma \sim 0.005$ Å, bond angles: $\sigma \sim 0.5°$) the distribution of bond lengths and angles (Fig. 2) is in keeping with the accepted chemical constitution, with the exception of the thioamide C—S bond. In the few available structure determinations of thioamides[5–7], values between 1.63 Å[7] and 1.72 Å[5] are reported for this parameter. The available structural evidence is insufficient to give a definite reason for this reported spread, but it appears that long C = S bonds are found whenever the sulfur is involved in strong hydrogen bonding. The values found in the present structure (1.655 and 1.673 Å) are consistent with this picture in so far, as only very weak hydrogen bonds exist in the crystal (vide infra).

A comparison of the IR spectra of the crystalline *PDTA* with *PDTA* in solution ($CDCl_3$; Table 3) reveals a splitting of the N—H stretching mode and a shift towards higher frequency by about 70 cm^{-1}. Smaller shifts are also observed for some of the thioamide modes. The most obvious explanation would be the existence of hydrogen bonds in the solid state, which are broken in solution.

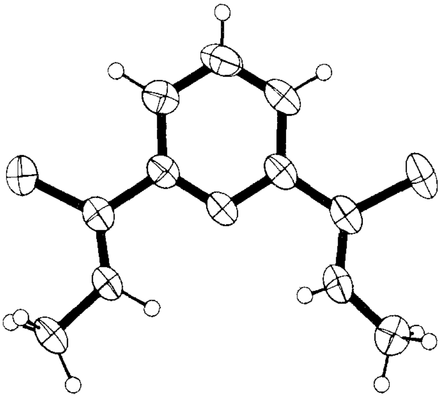

Fig. 1. Projection of the pyridine-2,6-dithiocarbomethylamide molecule into the plane of the pyridine ring. Ellipsoids are drawn at the 50% level with the exception of hydrogen atoms, which are drawn artificially small

There is, indeed, some evidence for the existence of *intra* molecular H-bonding between the amide-nitrogens and the pyridine nitrogen (Fig. 3). However, the corresponding proton-acceptor distances and the angles around H(N1) and H(N2) suggest rather weak interaction. Hydrogen bonds also appear to exist between N1 and N2 and the thioamide sulfur S2 of a symmetry equivalent molecule (at $-1-x$, $1/2+y$, $1/2-z$). Compared to H-bonds between N and S in related structures, these H-bonds are rather long and show appreciable deviations from linearity. Fig. 3 shows that the amide proton H(N1) mainly interacts with the pyridine nitrogen, whereas the other amide proton H(N2) is predominantly involved in intermolecular H-bonding. Although both types of H-bonds are rather weak, they do offer an explanation for the difference in the IR-spectra of solid and solute *PDTA*. This picture is quite consistent with thioacetamide, where much shorter N...S hydrogen bonds are observed in the crystal structure (N...S: 3.396 Å)[5] and where the shift in the N—H stretching mode is about twice as large[9].

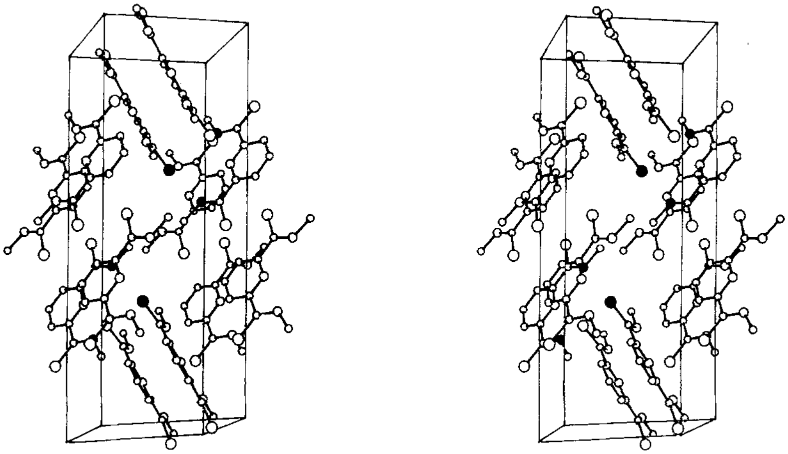

Fig. 2. Packing diagram for the crystal structure of pyridine-2,6-dithiocarbomethylamide. Atoms involved in intermolecular hydrogens bonds are represented as full circles

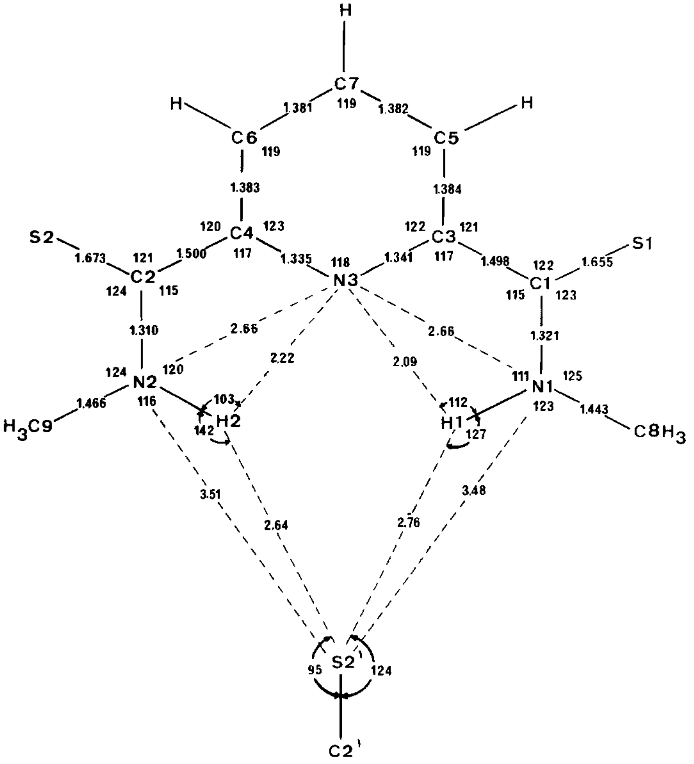

Fig. 3. Bondlengths, bondangles and some interatomic contact distances

The distances from the pyridine α-carbon atoms to the thioamide carbon atoms do not suggest much bond-shortening as a result of conjugation. Nevertheless, the pyridine ring is nearly coplanar with the two thioamide groups (torsion angles: N1-C1-C3-N3: —4°; N2-C2-C4-N3: 7°). This agrees with the situation in related structures (e.g. dipicolinic acid[10]).

IR- and Raman-Spectra

The observed mutual exclusion of IR and *Raman* frequencies in the solid state is in keeping with the centrosymmetric space group. Table 3 lists observed IR and *Raman* frequencies. The assignment is based on the isotopic exchange (to identify modes with NH contribution) and on an analogy with literature data[9,10] and is therefore only tentative, since no normal coordinate analysis was carried out.

The νNH, δNH and o.o.p. NH are assigned to the IR bands at 3331/3290, 1342 and 720 cm^{-1}. On deuteration, their frequencies decrease to 2475/2450/2435, 880 and 485 cm^{-1}. The band at 1526 cm^{-1} has mainly νCN character, but the frequency lowering upon deuteration suggests considerable contribution from δNH.

Assignment of bands with strong νCS character, on the other hand, is much more problematical for the thioamide group: force-field calculations[9,10] have shown, that several bands of this strongly coupled system show νCS character. However, no more than 50% νCS contribution was found for any of these bands. Since they should appear fairly intensely in the *Raman* spectrum, we assign them to the *Raman* bands at 1276, 941 and 679 cm^{-1}.

The splitting of the NH stretching mode in the solid state is most probably due to the difference in H-bonding between two crystallographically independent NH-protons, possibly in combination with a factor group splitting. In solution, the shoulder at 3300 cm^{-1} can be unequivocally interpreted as arising from intermolecular H-bonding, since it disappears at very low concentrations. The two remaining modes (3440 and 3357 cm^{-1}) are both strongly dependent on the polarity of the solvent; in acetonitrile, they coalesce into one broader band at 3318 cm^{-1}. The available experimental evidence does not support an unambiguous assignment of each of the two N—H modes to a well defined species; in solution, the *PDTA* molecule can, in principle, exist in a large number of conformations by rotation around C1-C3 and C2-C4 and, possibly, by rotation around the two thioamide C—N bonds (to form *Z*- or *E*-isomers[11]). It is, however, plausible to assign the strong band at 3357 cm^{-1} to an N—H mode shifted by a weak intramolecular hydrogen bond to the pyridine nitrogen, similar to the situation found

Table 3. *Observed IR and Raman frequencies (in* cm^{-1}*)*. Solid IR spectra were measured as nujol mulls, with the exception of frequencies marked with a cross (+), which were observed from a KBr disc. The assignment (last column) refers to frequencies in *italic*

undeuterated			deuterated		
I.R. solid	I.R. $CDCl_3$	Raman solid	Raman solid	I.R. solid	Assignments
3331 s	*3440 w*			*3438 m*	
3290 vs	*3357 vs*			*3325 w*	νNH
3269 sh	*3300 sh*			*3295 w*	
3208 vw	3090 w		3048 (10)	*3250 w*	
3089 vw+	3082 w		3013 (10)	3012 w+	
3016 w+	3010 w		3000 (5)	2960 m+	
2963 m+	2965 w		2962 (5)	2938 m+	
2930 m+	2935 w		2932 (10)		
2850 m+			*2480 (15)*	*2475 m*	
			2457 (10)	*2450 s*	νND
				2435 m	
				1742 m	
1590 w	1600 w	1604 (10)	1592 (25)	1587 m	
1542 m			1570 (10)		
1526 vs	*1536 vs*	*1528 (25)*			νCN + δNH
1505 vw	1505 vw		*1502 (15)*	*1503 vs*	
1440 m	1442 m	1446 (25)	1442 (15)	1445 s+	
	1433 m		1418 (30)		
1409 m	1413 w	1410 (10)	1400 (15)	1400 s+	
1342 s	*1356 s*	*1330 (10)*		1310 w	δNH + νCN
1285 vw				1286 m	
1272 w	1265 w	*1276(100)*	*1278(100)*	1273 w	νCS + ν CN
		1258 (15)	1258 (25)	*1238 vs*	
1210 m	*1212 m*	1210 (10)	1198 (5)	1189 m	
1172 m	1177 m	1170 (5)	1161 (10)	1170 vw	
1156 vw			1149 (10)	1142 w	
1085 m	1080 m	1071 (10)	1085 (5)	1077 s	
1063 s	1068 s	1061 (5)			
	1048 m		1054 (5)	1050 w	
1038 s		1037 (5)	1046 (5)	1021 w	
1000 w	1001 w	1002 (80)	1003 (60)	998 m	
			953 (10)	945 w	
938 s	*942 m*	*941 (70)*	*940 (13)*	*938 m*	νCS + νCC
			885 (25)	*880 s*	δND
828 s	*828 m*		*830 (5)*	*826 s*	νCS ?
750 m	-		748 (20)	780 w	
735 s	-		740 (5)	736 s	
720 m	-	*720 (20)*	718 (5)	720 m	o.o.p.NH
673 s	-	*679 (70)*	*678 (45)*	*665 m*	δNCS + ν CC
607 m	610 w		609 (20)	610 m	o.o.p.NCS
591 w	592 m			601 m	
550 w	-		474 (5)	*485 s(b)*	o.o.p.ND
501 w	-			478 s(b)	
445 w	-			440 w(b)	
436 w				425 w	
413 w			413 (10)	410 w	
380 w		290 (10)	295 (10)	372 m	
290 vw		221 (20)	278 (10)	340 m	
268 vw		153 (30)	250 (2)		
240 vw		88(150)	224 (5)		
200 s		75(150)	200 (5)		
		49(200)	153 (6)		
		35(100)	89 (30)		
		30(100)	78 (30)		
			48 (13)		
			34 (45)		

in the crystal. The other N—H mode would then arise from a species with an unassociated thioamide proton, possibly formed by rotation of one of the thioamide groups around its bond to the pyridine ring.

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