Dedicated to Prof. P.T. Frangopol on the occasion of his 75th anniversary

A Dinuclear Adduct of bis (di-*sec*-butyl dithiophosphato) Cadmium(II) Built around the Hexamethylenetetramine Cage as Coordination Center

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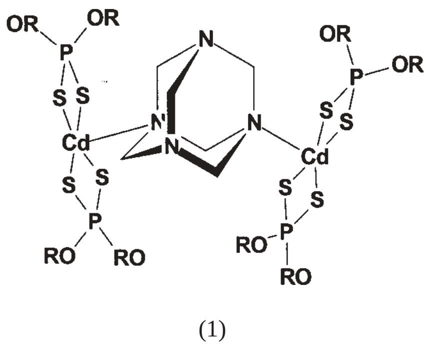
Bis(di-sec-butyldithiophosphato)cadmium(II) forms a 2:1 adduct with hexamethylenetetramine (urotropine), which was characterized by FT-IR and NMR spectroscopy. The compound is a dinuclear complex with the cadmium atoms coordinated at two nitrogen atoms of hexamethylenetetramine cage which is the actual coordination center. The X-ray diffraction analysis of the complex reveals a distorted square pyramidal coordination of the five-coordinate cadmium atoms. At each cadmium, one dithiophosphato group behaves as slightly anisobidentate whereas the other one is an isobidentate chelating ligand.

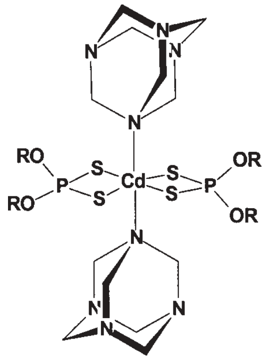
Keywords: Crystal structure, dinuclear complex, hexamethylenetetramine, coordination center.

Dithiophosphato ligands display a variety of coordinations patterns leading to a remarkable structural diversity [1]. Their metal complexes have been intensively investigated due to their applications as vulcanization agents [2], extraction and analytical reagents [3, 4], lubricant additives [5, 6], insecticides [7] among others.

We report a dinuclear bis(di-*sec*-butyldithiophosphato)cadmium adduct **(1)** built around the hexamethylenetetramine (urotropine) cage as coordination center This can be described as an inverse coordination compound, in which the center is a neutral molecule, with two regular complexes attached to it in a second coordination sphere. So far only one other cadmium dithiophosphate-hexamethylenetetramine complex has been previously reported in the literature. This is a 1:2 adduct $Cd[S_2P(OEt)_2]_2.2(CH_2)_6N_4$ **(2)** which possesses an octahedral coordination geometry of the six-coordinate metal atom with the two amine molecules in *trans* positions [8]. We intended to use more than one nitrogen coordination sites of the nitrogen base. Although the tetramine has four potential nitrogen donor sites only two coordinate to cadmium atoms. Probably steric factors prevent addition of more than two metal complex units.



(1)



(2)

Results and discussion

The reaction of potassium di-*sec*-butyldithiophosphate with cadmium(II) acetate and hexamethylenetetramine (2:1:1) in methanol yields a cadmium(II) complex identified as a 2:1 adduct. The complex is air and light stable and is soluble in methanol and $CDCl_3$.

The FT-IR spectra of di-*sec*-butyldithiophosphato potassium salt and the corresponding cadmium(II) complex were recorded in 4000-400cm^{-1} and bands associated with PS_2, (P)-O-C and P-O-(C) stretching vibrations have been identified by comparison, in accordance with literature values [9]. The compound shows the symmetric and antisymmetric stretching modes for the PS_2 group ($\upsilon_{as}(PS_2)$ 659m, $\upsilon_s(PS_2)$ 586s, 526s). The ^1H, ^{13}C and ^{31}P NMR data confirm the identity of the products; they show no unusual features (see experimental part).

The X-ray diffraction analysis of **(1)** reveals a dinuclear complex, illustrated in figure 1. The structure is centered around the hexamethylenetetramine cage, with cadmium atoms coordinated at two nitrogen sites. Additionally, the cadmium atoms are coordinated by two dithiophosphato ligands, in a distorted square pyramidal geometry of the five-coordinate metal atoms. Selected interatomic distances and bond angles are listed in tables 1 and 2 respectively. Details of crystallographic determination are given in table 3. The coordination mode of the P(1) and

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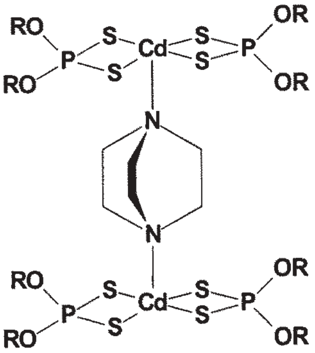
P(4) dithiophosphoric ligands are basically isobidentate because the P-S bonds lengths are not significantly different [*e.g.* P(1)-S(1) 1.955(6) Å; P(1)-S(2) 1.957(7) Å and P(4)-S(7) 1.986(4) Å; P(4)-S(8) 1.980(3) Å], but they are different at P(2) [with P(2)-S(3) 1.976(3) Å and P(2)-S(4) 1.948(4) Å] and P(3) [with P(3)-S(5) 1.947(5) Å and P(3)-S(6) 2.000(4) Å].

It is interesting to compare the bond parameters in the cadmium dithiophosphate-hexamethylenetetramine complexes **(1)** and **(2)**. In the *trans* octahedral complex **(2)** the Cd-N bonds are longer 2.596(1) Å, compared to the square pyramidal complex **(1)** 2.345(5) and 2.354(5) Å[8]. These latter two values are comparable to Cd-N distances observed in a dinuclear cadmium dithiophosphato complex of diazabicyclooctane, $2Cd[S_2P(OCy)_2]_2N(CH_2CH_2)_3N$ **(3,** R = Cy**),** in which the Cd-N distance is 2.318(7)Å [10]. The Cd-S distances in the later are also unsymmetrical as in **1**, *i.e.* short [2.530(3) and 2.521(2) Å] and long [2.769(3) and 2.818(3) Å].



(3)

Similarly, in the related dinuclear compound, $2Cd[S_2P(OPr^i)_2]_2.N(CH_2CH_2)_3N$ **(3,** *R* = *iso*-Pr) the Cd-N distances are 2.331(2) Å, and the Cd-S distances are also unsymmetrical, *i.e.* short [2.532-2.536(2) Å] and long [2.708-2.767(2)Å] [11].

Experimental part

Cadmium(II) acetate, potassium di-*sec*-butyldithiophosphate and hexamethylenetetramine were commercial products. IR spectra were recorded on a FT-IR JASCO 615 apparatus in potassium bromide pellets. The NMR spectra were recorded on a Bruker instrument in saturated $CDCl_3$ solutions at room temperature. All chemicals were used without further purification.

Table 1

SELECTED INTERATOMIC DISTANCES [Å] FOR **(1)**

Cd(1)-N(1)	2.344(6)
Cd(1)-S(2)	2.601(3)
Cd(1)-S(3)	2.605(2)
Cd(1)-S(1)	2.618(3)
Cd(1)-S(4)	2.637(4)
Cd(2)-N(2)	2.355(5)
Cd(2)-S(7)	2.570(3)
Cd(2)-S(6)	2.576(3)
Cd(2)-S(5)	2.660(3)
Cd(2)-S(8)	2.716(2)
S(1)-P(1)	1.955(6)
S(2)-P(1)	1.957(7)
S(3)-P(2)	1.976(3)
S(4)-P(2)	1.948(4)
S(5)-P(3)	1.947(5)
S(6)-P(3)	2.000(4)
S(7)-P(4)	1.986(4)
S(8)-P(4)	1.980(3)
P(1)-O(2)	1.561(10)
P(1)-O(1)	1.570(18)
P(1)-O(1A)	1.889(18)
P(2)-O(3)	1.536(8)
P(2)-O(4)	1.562(12)
P(3)-O(6)	1.564(9)
P(3)-O(5)	1.576(9)
P(4)-O(8)	1.568(7)
P(4)-O(7)	1.568(6)

Table 2

BOND ANGLES [DEG] FOR **(1)**

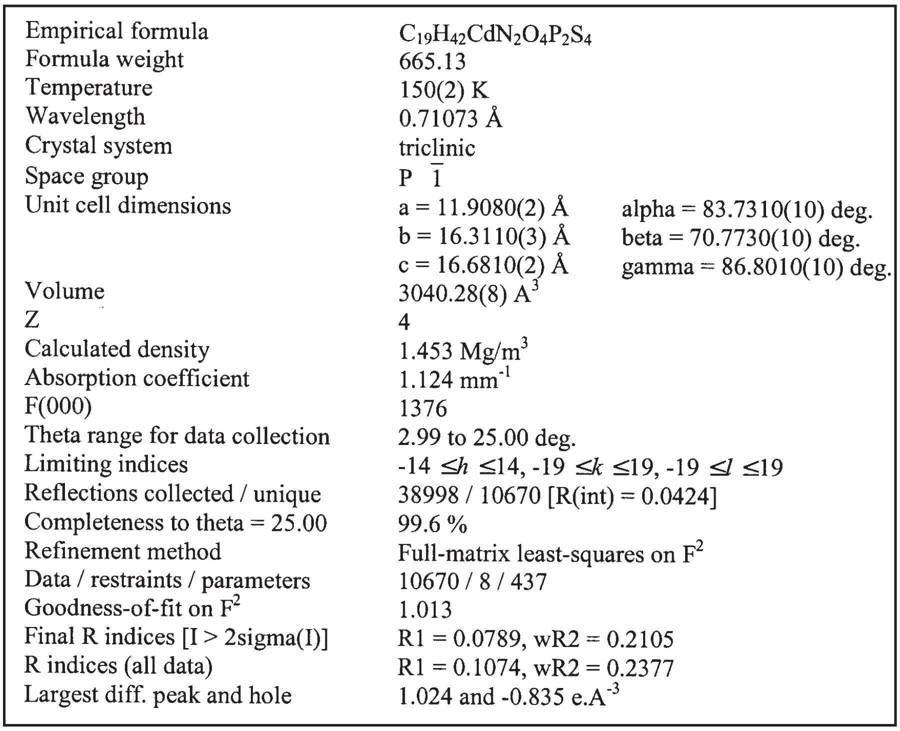
N(1)-Cd(1)-S(2)	100.92(17)
N(1)-Cd(1)-S(3)	102.68(15)
S(2)-Cd(1)-S(3)	156.40(11)
N(1)-Cd(1)-S(1)	101.45(19)
S(2)-Cd(1)-S(1)	77.38(15)
S(3)-Cd(1)-S(1)	97.67(11)
N(1)-Cd(1)-S(4)	100.85(19)
S(2)-Cd(1)-S(4)	98.14(17)
S(3)-Cd(1)-S(4)	77.59(9)
S(1)-Cd(1)-S(4)	157.70(14)
N(2)-Cd(2)-S(7)	104.08(17)
N(2)-Cd(2)-S(6)	106.78(17)
S(7)-Cd(2)-S(6)	148.73(10)
N(2)-Cd(2)-S(5)	97.77(15)
S(7)-Cd(2)-S(5)	102.73(10)
S(6)-Cd(2)-S(5)	78.07(10)
N(2)-Cd(2)-S(8)	94.44(15)
S(7)-Cd(2)-S(8)	77.30(8)
S(6)-Cd(2)-S(8)	95.30(8)
S(5)-Cd(2)-S(8)	167.36(9)
P(1)-S(1)-Cd(1)	84.51(19)
P(1)-S(2)-Cd(1)	84.92(15)
P(2)-S(3)-Cd(1)	84.14(11)
P(2)-S(4)-Cd(1)	83.80(14)
P(3)-S(5)-Cd(2)	83.22(12)
P(3)-S(6)-Cd(2)	84.50(14)
P(4)-S(7)-Cd(2)	86.81(12)
P(4)-S(8)-Cd(2)	82.98(11)
O(2)-P(1)-O(1)	101.6(8)
O(2)-P(1)-O(1A)	91.9(8)
O(1)-P(1)-O(1A)	47.0(7)
O(2)-P(1)-S(1)	111.0(6)
O(1)-P(1)-S(1)	126.1(7)
O(1A)-P(1)-S(1)	89.2(6)
O(2)-P(1)-S(2)	114.8(6)
O(1)-P(1)-S(2)	88.7(5)
O(1A)-P(1)-S(2)	133.2(6)
S(1)-P(1)-S(2)	113.0(2)
O(3)-P(2)-O(4)	95.1(7)
O(3)-P(2)-S(4)	107.3(4)
O(4)-P(2)-S(4)	113.9(6)
O(3)-P(2)-S(3)	113.9(3)
O(4)-P(2)-S(3)	111.7(5)
S(4)-P(2)-S(3)	113.61(18)
O(6)-P(3)-O(5)	101.2(7)
O(6)-P(3)-S(5)	114.3(5)
O(5)-P(3)-S(5)	105.0(4)
O(6)-P(3)-S(6)	109.6(5)
O(5)-P(3)-S(6)	112.7(4)
S(5)-P(3)-S(6)	113.39(19)
O(8)-P(4)-O(7)	100.1(4)
O(8)-P(4)-S(8)	111.6(4)
O(7)-P(4)-S(8)	112.6(3)
O(8)-P(4)-S(7)	112.5(4)
O(7)-P(4)-S(7)	106.6(3)
S(8)-P(4)-S(7)	112.78(16)

Experimental details relating to the single-crystal X-ray crystallographic studies are summarized in table 3. For all structures, data were collected on a Nonius Kappa CCD diffractrometer at 150(2) K using Mo-Kα.radiation (λ = 0.71073 Å). The structures were refined using full-matrix least-squares on F2. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at calculated positions. Due to a very poor dataset most of the carbon atoms had to be refined isotropically. One of the sec-butyl groups showed disorder in the ratio 1:1 and two others had to be restrained during refinement.

Synthesis of bis(di-sec-buthyl)dithiophosphato cadmium (II) hexamethylenetetramine adduct **(1)**

Cadmium(II) acetate (0.13g, 0.56 mmol) was dissolved in methanol (10 mL) and stirred for ½ h with potassium

Table 3
CRYSTAL DATA FOR COMPOUND **(1)**



Empirical formula	$C_{19}H_{42}CdN_2O_4P_2S_4$	
Formula weight	665.13	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	$P\ \bar{1}$	
Unit cell dimensions	a = 11.9080(2) Å	alpha = 83.7310(10) deg.
	b = 16.3110(3) Å	beta = 70.7730(10) deg.
	c = 16.6810(2) Å	gamma = 86.8010(10) deg.
Volume	3040.28(8) A^3	
Z	4	
Calculated density	1.453 Mg/m^3	
Absorption coefficient	1.124 mm^{-1}	
F(000)	1376	
Theta range for data collection	2.99 to 25.00 deg.	
Limiting indices	$-14 \leq h \leq 14, -19 \leq k \leq 19, -19 \leq l \leq 19$	
Reflections collected / unique	38998 / 10670 [R(int) = 0.0424]	
Completeness to theta = 25.00	99.6 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10670 / 8 / 437	
Goodness-of-fit on F^2	1.013	
Final R indices [I > 2sigma(I)]	R1 = 0.0789, wR2 = 0.2105	
R indices (all data)	R1 = 0.1074, wR2 = 0.2377	
Largest diff. peak and hole	1.024 and -0.835 $e.A^{-3}$	

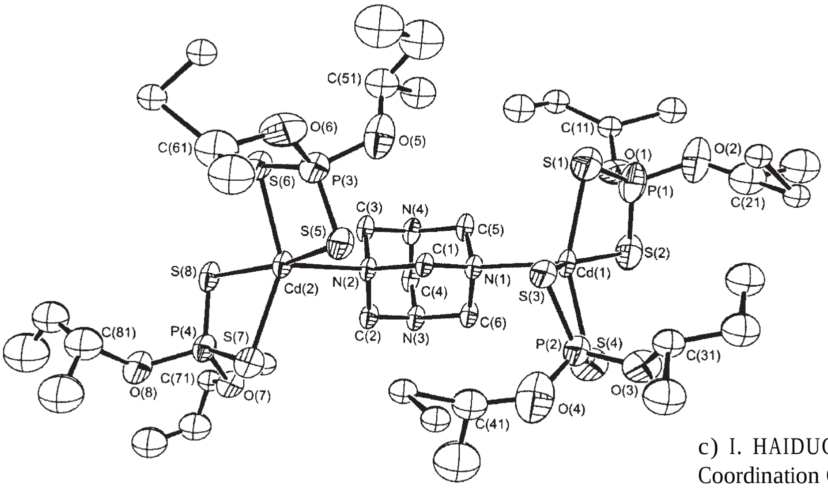


Fig.1.The crystal structure of $2Cd[S_2P(OCHMeEt)_2]_2.(CH_2)_6N_4$ (Hydrogen atoms and the minor component of the disorder are omitted for clarity; thermal ellipsoids are at the 20% level)

di-*sec*-butyldithiophosphate (0.24g, 0.85 mmol); after another 2 h a solution of hexamethylenetetramine (0.07g, 0.49 mmol) in methanol (10 mL) was added at room temperature. The solution was concentrated to give colorless crystals, yield 60%. M.p. 80^0C.

FT-IR (cm^{-1}): $\nu_{as}(PS_2)$ 659m, $\nu_s(PS_2)$ 586s, 526s, ν(P-OC) 954w, 997w, ν(PO-C) 1172s

NMR data (ppm):

^{1}H: 0.93 (6H, t CH_3), 1.43 (6H, d CH_2) 1.61 (4H, m, $CHCH_3$), 4.69, (2H, m $CHCH_3$); 4.95 (6H, s, NCH_2);

^{13}C: 9.67 (CH_3), 30.3 (CH_2), 20.82 ($CHCH_3$), 78.69 ($CHCH_3$), 74.55 (NCH_2);

^{31}P: 101.93 (1P,d, PS_2), J_{P-H} = 8.39 MHz .

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