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SPECTROSCOPIC STUDIES OF METAL-PYRIMIDINE COMPLEXES. CRYSTAL STRUCTURES OF 4,6-DIMETHYL-2-THIOPYRIMIDINE COMPLEXES WITH Zn(II) AND Cd(II)

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SPECTROSCOPIC STUDIES OF METAL-PYRIMIDINE COMPLEXES. CRYSTAL STRUCTURES OF 4,6-DIMETHYL-2-THIOPYRIMIDINE COMPLEXES WITH Zn(II) AND Cd(II)

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The structures of $\text{Zn}(\text{DMTP})_2\text{Cl}_2$ and $\text{Cd}(\text{DMTP})_2\text{Cl}_2$ (DMTP = 4,6-dimethyl-2-thio-pyrimidine), have been obtained by X-ray diffraction methods. Both compounds crystallize in the monoclinic system. $\text{Zn}(\text{DMTP})_2\text{Cl}_2$ crystals are of the $P2_1$ space group, with $a = 7.133(2)$, $b = 16.315(8)$, $c = 7.403(2)$ and $\beta = 92.48(2)$, $V = 860.7 \text{ \AA}^3$, $Z = 2$, $F(000) = 420$ and $Dm = 1.60 \text{ g cm}^{-3}$. $\text{Cd}(\text{DMTP})_2\text{Cl}_2$ crystals are of the $P2_1/c$ space group, with $a = 13.197(3)$, $b = 8.438(3)$, $c = 15.862(5)$ and $\beta = 97.30(2)$, $V = 1752.0 \text{ \AA}^3$, $Z = 4$, $F(000) = 912$ and $Dm = 1.75 \text{ g cm}^{-3}$. The structures were refined anisotropically to $R = 0.028$ and $R_w = 0.027$ on the basis of 2178 observed reflections ($\text{Zn}(\text{DMTP})_2\text{Cl}_2$ complex) and to $R = 0.038$ $R_w = 0.035$ on the basis of 2687 observed reflections ($\text{Cd}(\text{DMTP})_2\text{Cl}_2$ complex). The structures contain individual $\text{Zn}(\text{DMTP})_2\text{Cl}_2$ and $\text{Cd}(\text{DMTP})_2\text{Cl}_2$ distorted tetrahedral units in which DMTP molecules are *S*-bonded as monodentates to the corresponding metal ions; chloride ions are also coordinated. On the basis of the crystallographic data of the above complexes, different coordination patterns of DMTP with several metal ions were established in a set of DMTP complexes ($\text{Hg}(\text{DMTP})\text{Cl}_2$, $\text{Pd}(\text{DMTP})_2\text{Cl}_2$, $\text{Pt}(\text{DMTP})_2\text{Cl}_2$ and $\text{Au}(\text{DMTP})\text{Cl}_3$) by a study of their ir, ^1H and ^{13}C NMR spectra.

KEYWORDS: Pyrimidines, Zn(II), Cd(II), X-ray structures

INTRODUCTION

Among heterocyclic derivatives containing sulphur thiopyrimidine derivatives are very important because of their biological activity. Some of these can act as inhibitors,¹⁻² and antimetabolites.^{3,4} 2-Thiopyrimidine shows a strong *in vitro* bacteriostatic activity against *Escherichia coli*,⁵ and 6-amino-2-thiouracil is well known because of its antiviral and chemotherapeutic activities.⁶⁻⁸ In many cases it

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seems probable that complex formation is implicated in the biological action of these pyrimidine derivatives.⁹

Over the last few years we have focussed attention on a study of metal complex formation with several 2-methylthiopyrimidine¹⁰⁻¹⁹ and 2-thiopyrimidine derivatives.²⁰⁻²⁴ As part of this work, in the present paper we report the synthesis and properties of some new metal complexes of neutral 4,6-dimethyl-2-thiopyrimidine (DMTP). Although DMTP would be expected to coordinate, in the neutral molecular form, through sulphur or nitrogen atoms as a monodentate, or as an N, S-chelate, this has only been established through infrared studies of the complexes.²⁵⁻²⁸ Concerning the ligand in the anionic form, bonding as an N,S-chelate has been found in several complexes by X-ray diffraction techniques,^{29,30} whereas monodentate S or N-bonding has not been demonstrated structurally.

In the present paper we report the synthesis and characterization of the following metal complexes of neutral 4,6-dimethyl-2-thiopyrimidine: Zn(DMTP)₂Cl₂, Cd(DMTP)₂Cl₂, Hg(DMTP)Cl₂, Pd(DMTP)₂Cl₂, Pt(DMTP)₂Cl₂ and Au(DMTP)Cl₃. The compounds Zn(DMTP)₂Cl₂ and Cd(DMTP)₂Cl₂ have previously been synthesized by a different method from that used in this work and on the basis of ir data, N, S-chelation was proposed for the ligand DMTP in an octahedral arrangement of six donor atoms around the metal ions.^{28,31} We now report the structural characterization, by X-ray diffraction, of the compounds Zn(DMTP)₂Cl₂ and Cd(DMTP)₂Cl₂, from which it has been established that the complexes have tetrahedral structures in which neutral molecules of DMTP as monodentates are linked to the Zn(II) and Cd(II) ions through the S atom of the thione Ir, ¹H-NMR and ¹³C-NMR spectra of the complexes have been interpreted in view of the molecular structures of Zn(II) and Cd(II) complexes.

EXPERIMENTAL

Preparation of the complexes

Zn(DMTP)₂Cl₂ and Cd(DMTP)₂Cl₂ were prepared by dissolving DMTP and the corresponding metal salt (ZnCl₂ and CdCl₂) in a 1:3 molar ratio, in the minimum amount of water. The solutions were then evaporated on a water bath at 60°C. Pale yellow crystals of the complexes precipitated after two days.

The remaining complexes were obtained by mixing, in water, the ligand DMTP and the corresponding metallic salt (HgCl₂, K₂PdCl₄, K₂PtCl₄ and HAuCl₄) in a molar ratio DMTP:metal equal to 1:2 in the case of Hg(II), and 1:1 in the other cases.

X-ray investigations

Crystal data, collection and refinement parameters are summarized in Table 1. The crystals were mounted on a glass fibre and placed on a SYNTEX R3 diffractometer using graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). Unit cell parameters were determined by the automatic indexing of 29(Cd)/23(Zn) centred reflections. Intensity data were corrected for Lorentz, polarisation and absorption effects (ψ scans of 7 reflections in the range of 10(Cd)/5(Zn) $< 2\theta < 47$ (Cd)/46(Zn)). Equivalent reflections were merged. The structures were solved by conventional Patterson and difference Fourier methods using the SHELXTPLUS program

Table 1 Crystal data, data collection and refinement parameters.

	Compound	
	Zn(DMTP) ₂ Cl ₂	Cd(DMTP) ₂ Cl ₂
Crystal size (mm)	0.25 × 0.30 × 0.70	0.05 × 0.15 × 0.65
Empirical Formula	ZnC ₁₂ H ₁₆ N ₄ S ₂ Cl ₂	CdC ₁₂ H ₁₆ N ₄ S ₂ Cl ₂
<i>M</i>	414.7	461.7
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>
Unit cell	<i>a</i> = 7.133; <i>b</i> = 16.315; <i>c</i> = 7.403 Å; <i>β</i> = 92.48°	<i>a</i> = 13.197; <i>b</i> = 8.438; <i>c</i> = 15.862 Å, <i>β</i> = 97.30°
Volume (Å ³)	860.7	1752.0
<i>Z</i>	2	4
Density (g cm ⁻³)	1.60	1.75
Radiation	MoKα, λ = 0.71073 Å	MoKα, λ = 0.71073 Å
F(000)	420	912
θ-range (deg)	1.5→27.5	1.5→26.0
<i>h</i> range	0→10	0→17
<i>k</i> range	0→22	0→11
<i>l</i> range	-10→10	-20→20
Observed reflections	2200	3699
Reflections with <i>I</i> > 2.0σ(<i>I</i>)	2178	2687
Reflections with <i>I</i> > 2.5σ(<i>I</i>)	1917	2754
<i>R</i>	0.028	0.038
<i>R</i> _w	0.027	0.035

package.³² The function minimized during full-matrix least-squares refinement was $\sum w^{1/2} (|F_o| - |F_c|)^2$ with weights, $w = 1/\sigma^2(F)$. Neutral-atom scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from the literature.³³ The positions of the hydrogen atoms were placed at calculated positions. Final atomic coordinates and equivalent isotropic displacement parameters of the Zn(II) and Cd(II) complexes for non-hydrogen atoms appear in Table 2.

Other measurements

Microanalyses were performed by the Technical Services of the University of Granada (STUGRA). Infrared spectra were obtained using a Perkin-Elmer 983G spectrophotometer in KBr pellets in the 4000-250 cm⁻¹ range, and polyethylene pellets in the 600-180 cm⁻¹ range. ¹³C-NMR spectra of DMTP and the metal complexes were recorded using a Bruker AM-300 spectrometer, using DMSO-*d*₆ as solvent and TMS as internal standard. Magnetic susceptibilities of the ligand DMTP and Pt(II), Pd(II) and Au(III) complexes at room temperature were measured using a Bruker B-E15 Faraday balance.

RESULTS AND DISCUSSION

Analytical data for the complexes are summarized in Table 3. All of the complexes are poorly soluble in water and in most common solvents. The magnetic suscepti-

Table 2 Fractional atomic coordinates and equivalent isotropic displacement parameters (e.s.d.s in parentheses).

Zn(DMTP) ₂ Cl ₂					Cd(DMTP) ₂ Cl ₂				
Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{eq} (Å ²) ^a	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{eq} (Å ²) ^a
Zn(1)	9353(1)	10000	8430(1)	38(1)	Cd(1)	2466(1)	1580(1)	745(1)	42(1)
Cl(1)	8896(2)	11270(1)	7119(2)	55(1)	Cl(1)	3654(1)	-723(2)	1163(1)	51(1)
Cl(2)	7877(2)	9976(1)	11139(2)	51(1)	Cl(2)	1268(1)	1504(2)	1896(1)	51(1)
S(1)	12582(1)	10016(1)	9130(1)	41(1)	S(1)	1371(1)	184(2)	-471(1)	51(1)
S(2)	7985(2)	8975(1)	6615(2)	42(1)	S(2)	3237(1)	4288(2)	1219(1)	49(1)
N(1)	14679(5)	8723(2)	9986(5)	39(1)	N(1)	1092(3)	3290(5)	-556(3)	42(1)
N(2)	11743(5)	8437(2)	8613(5)	38(1)	N(2)	-137(3)	1748(5)	-1384(2)	40(1)
N(3)	4677(5)	8807(3)	4949(5)	42(1)	N(3)	374(3)	6133(5)	-22(3)	39(1)
N(4)	5644(5)	10171(2)	5403(5)	38(1)	N(4)	3529(3)	3429(5)	-333(3)	40(1)
C(1)	13013(6)	8983(3)	9245(5)	36(1)	C(1)	749(4)	1860(6)	-820(3)	39(2)
C(2)	17007(7)	7726(3)	11063(8)	60(2)	C(2)	1052(4)	6125(6)	-594(4)	55(2)
C(3)	15156(7)	7925(3)	10169(7)	44(2)	C(3)	599(4)	4572(6)	-891(3)	42(2)
C(4)	13865(7)	7364(3)	9509(7)	47(2)	C(4)	-278(4)	4488(6)	-1478(3)	44(2)
C(5)	12178(7)	7639(3)	8710(6)	43(2)	C(5)	-655(4)	3027(6)	-1720(3)	41(2)
C(6)	10758(8)	7059(3)	7939(7)	62(2)	C(6)	-1611(4)	2747(7)	-2314(3)	55(2)
C(7)	5970(7)	9341(3)	5600(6)	37(1)	C(7)	3525(3)	4631(6)	225(3)	39(2)
C(8)	1645(7)	8483(3)	3532(7)	55(2)	C(8)	4105(4)	8166(6)	-1029(4)	61(2)
C(9)	3074(7)	9101(3)	4202(6)	44(2)	C(9)	3917(3)	6493(7)	-824(3)	44(2)
C(10)	2703(6)	9941(4)	4055(5)	49(2)	C(10)	3881(4)	5275(7)	-1399(3)	49(2)
C(11)	4035(7)	10480(3)	4669(6)	45(2)	C(11)	3696(4)	3754(6)	-1131(3)	44(2)
C(12)	3870(8)	11400(3)	4634(8)	68(2)	C(12)	3692(5)	2374(7)	-1725(3)	63(2)

$${}^a B_{eq} = 8\pi(2/3)\sum_i \sum_j U_{ij} a_{ij} a_i^* a_j^*$$

Table 3 Analytical data (theoretical values in parentheses).

Compound	Colour	C	H	N
Zn(DMTP) ₂ Cl ₂	Pale yellow	34.46 (34.58)	3.84 (3.84)	13.62 (13.45)
Cd(DMTP) ₂ Cl ₂	Pale yellow	30.79 (31.07)	3.44 (3.45)	12.22 (12.08)
Hg(DMTP)Cl ₂	White	18.53 (17.49)	1.80 (1.94)	7.34 (6.80)
Pd(DMTP) ₂ Cl ₂	Dark brown	29.50 (31.48)	2.90 (3.50)	11.33 (12.24)
Pt(DMTP) ₂ Cl ₂	Orange	25.07 (26.36)	2.24 (2.93)	9.77 (10.25)
Au(DMTP)Cl ₃	Dark Brown	16.07 (16.23)	1.71 (1.80)	6.27 (6.31)

bilities of Pd(DMTP)₂Cl₂, Pt(DMTP)₂Cl₂ and Au(DMTP)Cl₃ show that these compounds are diamagnetic at room temperature.

X-ray structures of Zn(DMTP)₂Cl₂ and Cd(DMTP)₂Cl₂

The crystals contain individual, M(DMTP)₂Cl₂ (M = Zn or Cd) neutral molecules. Perspective drawings of them, together with the atom labelling schemes are shown in Figure 1. Diagrams of the contents of the corresponding unit cells are shown in Figure 2.

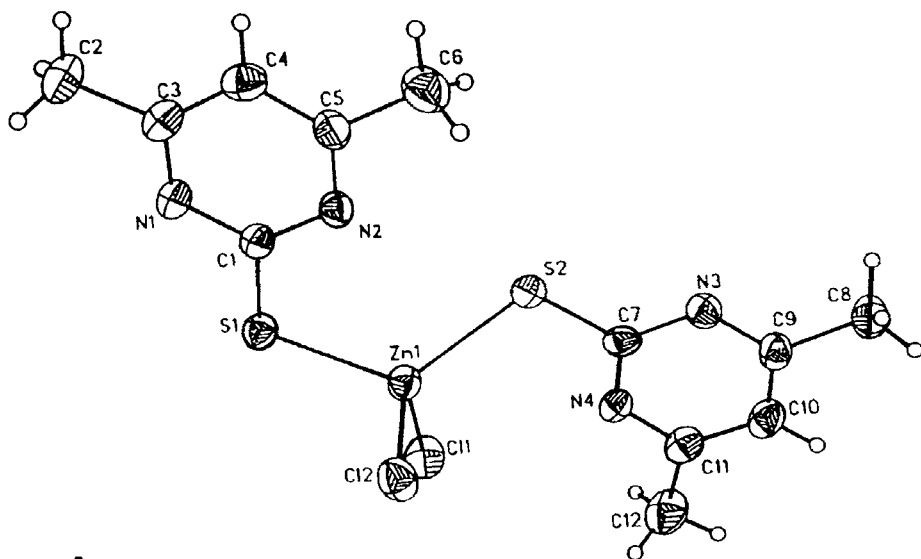
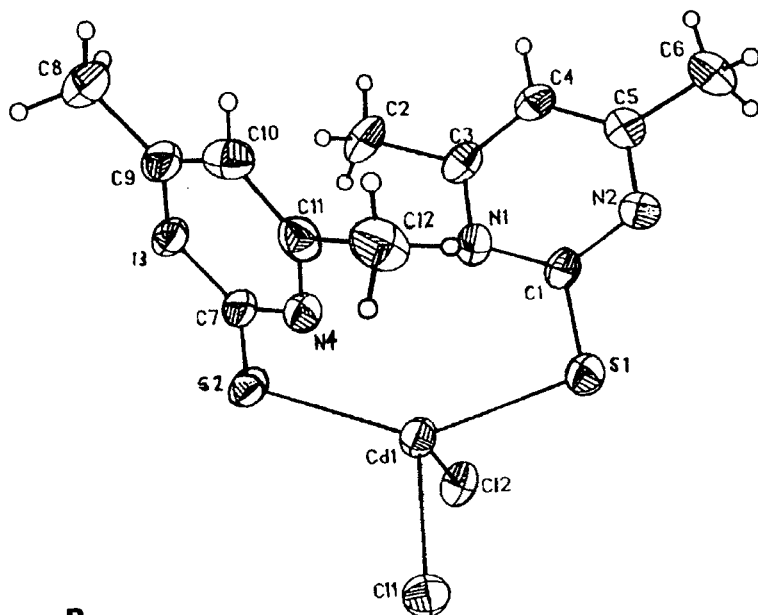
**A****B**

Figure 1 Perspective view of a) Zn(DMTP)₂Cl₂ and b) Cd(DMTP)₂Cl₂.

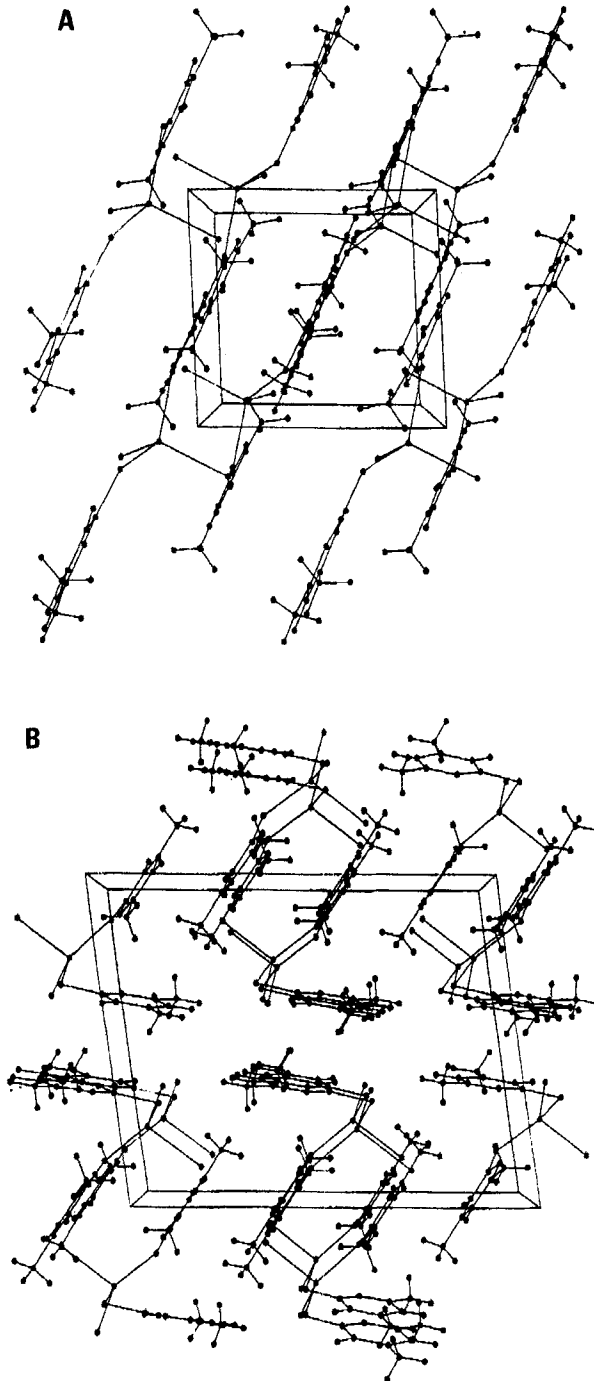


Figure 2 Packing of the molecules in the unit cell; a) $\text{Zn}(\text{DMTP})_2\text{Cl}_2$ and b) $\text{Cd}(\text{DMTP})_2\text{Cl}_2$.

Although for thiopyrimidine complexes a strong preference for S,N bonding has been observed,^{20,34-39} S coordination with a secondary intramolecular interaction to an N atom,^{40,41} and single S coordination,(in the complex bis[tetrahydro-1-H-pyrimidine-2-thione]copper(I)⁴²) have been proved. In the case of the DMTP anion there is crystallographic evidence of N,S coordination and it would be expected that neutral DMTP would act either as an N, S chelate or as a monodentate S or N ligand. Zn(DMTP)₂Cl₂ and Cd(DMTP)₂Cl₂ complexes constitute the first crystallographic evidence for DMTP being S bonded. The preference for S atoms (softer donor than the N) is not surprising in the case of the soft Zn(II) and Cd(II) acids.

In both Zn(II) and Cd(II) complexes, each metal atom is tetraordinated and surrounded by two DMTP molecules acting as monodentate ligands through the S atoms, and two terminal chlorine atoms. This design yields a strongly distorted tetrahedral environment around each metal ion (Table 4). The general stereochemistry for tetrahedral molecules containing one pair of ligands different from the other pair (MA₂B₂ with A and B as unidentate ligands) would be those having a twofold axis bisecting the angle between each pair of ligands. On the other hand, distortion in angles would depend on the ratio between MA and MB distances, in such a way that when MA/MB = 1 the tetrahedral angles would be that of a regular tetrahedron (109.47°).⁴³ In the complexes under study, Zn-S and Zn-Cl distances are almost equal; likewise, in the Cd(II) complex, Cd-Cl and Cd-S distances are similar. Thus the strong distortion in the tetrahedral environment of the four donor atoms in the complexes is explained on the basis of strong steric interactions between the two DMTP molecules of each complex.

Strong steric hindrance would be expected for a hypothetical *cis** conformation in the Zn(II) complex in view of the short Zn-S distances found. This probably is the reason why the most symmetrical *cis* conformation is not possible in the Zn(II) complex (in which the molecule has the *trans** conformation), but does exist in the Cd(II) complex. In fact, the N2-S2 length (see Fig 1a), 3.130Å, is shorter than the sum of the Van der Waals radius of S and N atoms (3.350Å), in accordance with the above suggestion.

Only a few complexes of Zn(II) and Cd(II) ions with pyrimidine and purine base have been crystallographically described.⁴⁵ Most of the Cd(II) complexes with pyrimidines, purines and nucleic acid constituents recorded to date have geometries other than those exhibited by the Cd(II) complexes studied here, whereas the tetrahedral environment is the most common in Zn(II) complexes with the said bases.⁴⁴⁻⁴⁶

The Zn-S and Cd-S distances (see Table 4) in the complexes are in the range of those found for metal-S terminal bonds in other complexes of Zn(II) and Cd(II), which range between 2.29-2.60Å in the case of Zn(II) complexes, and between 2.52-2.79Å in that of Cd(II) complexes; they are shorter than those found in Zn(II) and Cd(II) complexes in which the metal ions are S,N bonded.^{44,47} Zn-Cl and Cd-Cl distances are also in the range of those found in other Zn(II) and Cd(II) chloro complexes with terminal M-Cl bonds and are shorter than corresponding M-Cl distances in complexes with bridging chlorine ligands.^{44,45} The lengthening in the C-S bond distances in both complexes is as expected for a C-S double bond (1.61Å),⁴⁸ and reflects the effect of coordination of the ligand through the S atom.

The bond lengths between the ring atoms (Table 4) vary between 1.338 and 1.392Å, in the Zn(II) complex, and from 1.337 to 1.392Å in the Cd(II) complex; these values indicate large delocalization of the double bonds and are fairly similar

Table 4 Bond lengths (Å) and angles (°) for non-hydrogen atoms.

Zn(DMTP) ₂ Cl ₂				Cd(DMTP) ₂ Cl ₂			
Atoms	Length	Atoms	Angle	Atoms	Length	Atoms	Angle
Zn1-Cl1	2.306(2)	Cl1-Zn1-Cl2	108.6(1)	Cd1-Cl1	2.531(2)	Cl1-Cd1-Cl2	102.2(1)
Zn1-Cl2	2.305(2)	Cl1-Zn1-S1	101.7(1)	Cd1-Cl2	2.564(2)	Cl1-Cd1-S1	96.6(1)
Zn1-S1	2.339(2)	Cl2-Zn1-S1	106.9(1)	Cd1-S1	2.547(2)	Cl2-Cd1-S1	100.7(1)
Zn1-S2	2.333(2)	Cl1-Zn1-S2	110.7(1)	Cd1-S2	2.574(2)	Cl1-Cd1-S2	113.4(1)
S1-Cl1	1.714(5)	Cl2-Zn1-S2	107.1(1)	S1-Cl1	1.694(5)	Cl2-Cd1-S2	94.0(1)
S2-C7	1.702(5)	Zn1-S1-Cl1	121.2(1)	S2-C7	1.694(5)	S1-Cd1-S2	142.8(1)
N1-Cl1	1.355(5)	S1-Zn1-S2	100.0(2)	N1-Cl1	1.337(6)	Cd1-S1-Cl1	93.8(2)
N1-C3	1.352(6)	Zn1-S2-C7	109.1(2)	N1-C3	1.337(6)	Cd1-S2-C7	90.4(2)
N2-Cl1	1.340(6)	Cl-N1-C3	123.6(4)	N2-Cl1	1.381(6)	Cl-N1-C3	118.5(4)
N2-C5	1.341(6)	Cl-N2-C5	118.4(4)	N2-C5	1.350(6)	Cl-N2-C5	123.0(4)
N3-C7	1.343(6)	C7-N3-C9	118.5(4)	N3-C7	1.367(6)	C7-N3-C9	122.8(4)
N3-C9	1.338(6)	C7-N4-C11	123.2(4)	N3-C9	1.357(7)	C7-N4-C11	118.8(4)
N4-C7	1.380(6)	S1-Cl-N1	118.7(3)	N4-C7	1.346(7)	S1-Cl-N1	121.3(3)
N4-Cl1	1.347(6)	S1-Cl-N2	121.2(3)	N4-Cl1	1.340(7)	S1-Cl-N2	119.3(4)
C2-C3	1.487(7)	N1-Cl-N2	120.1(4)	C2-C3	1.492(7)	N1-Cl-N2	119.3(4)
C3-C4	1.373(7)	N1-C3-C2	118.0(4)	C3-C4	1.392(7)	N1-C3-C2	115.5(4)
C4-C5	1.392(7)	N1-C3-C4	116.4(4)	C4-C5	1.366(7)	N1-C3-C4	123.1(5)
C5-C6	1.481(7)	C2-C3-C4	125.6(5)	C5-C6	1.495(7)	C2-C3-C4	121.5(5)
C8-C9	1.502(7)	C3-C4-C5	119.4(5)	C8-C9	1.476(8)	C3-C4-C5	118.4(5)
C9-Cl0	1.398(9)	N2-C5-C4	121.9(4)	C9-Cl0	1.371(8)	N2-C5-C4	117.6(4)
Cl0-Cl1	1.359(7)	N2-C5-C6	116.6(4)	Cl0-Cl1	1.384(8)	N2-C5-C6	117.9(5)
Cl1-Cl2	1.506(8)	C4-C5-C6	121.5(4)	Cl1-Cl2	1.498(8)	C4-C5-C6	124.6(5)
		S2-C7-N3	118.9(3)			S2-C7-N3	120.3(4)
		S2-C7-N4	121.8(3)			S2-C7-N4	120.2(4)
		N3-C7-N4	119.2(4)			N3-C7-N4	119.5(5)
		N3-C9-C8	116.8(5)			N3-C9-C8	118.2(5)
		N3-C9-Cl0	122.6(4)			N3-C9-Cl0	117.5(5)
		C8-C9-Cl0	120.6(4)			C8-C9-Cl0	124.3(5)
		C9-Cl0-Cl1	118.8(4)			C9-Cl0-Cl1	118.9(5)
		N4-Cl1-Cl0	117.5(5)			N4-Cl1-Cl0	122.5(5)
		N4-Cl1-Cl2	116.5(4)			N4-Cl1-Cl2	116.6(5)
		Cl0-Cl1-Cl2	126.0(5)			Cl0-Cl1-Cl2	120.9(5)

to lengths found in other pyrimidine derivatives. Likewise, bond angles show little modification in relation to those obtained by other X-ray studies.^{48,55} The lack of strain in the pyrimidine ring angles is in accordance with the S-M interactions observed.

Significant hydrogen bond lengths are collected in Table 5. The existence of intramolecular N1.....Cl2ⁱ (i = 1 + x, y, z) and N4.....Cl1ⁱⁱ (ii = x, y, z) hydrogen bonds seems to play an important role in the stability of the “*trans*” conformation of the

Table 5 Intra- and intermolecular hydrogen bondlengths (Å).

Compound	DH.....A	Distance
Zn(DMTP) ₂ Cl ₂	N1.....Cl2 ⁱ	3.153
	N4.....Cl1 ⁱⁱ	3.156
Cd(DMTP) ₂ Cl ₂	N3.....Cl1 ⁱⁱⁱ	3.261
	N2.....Cl2 ^{iv}	3.180

Equivalent positions: i = 1 + x, y, z, ii = x, y, z, iii = x, 1 + y, z, iv = -x, -y, -z.

molecule. Lack of intermolecular hydrogen bonds indicates Van der Waals interactions between molecules in the crystal. Intermolecular $N3 \dots Cl1^{iii}$ ($iii = x, 1 + y, z$) and $N2 \dots Cl2^{iv}$ ($iv = -x, -y, -z$) hydrogen bonds between vicinal molecules of $Cd(DMTP)_2Cl_2$ determine the packing of molecules in the crystal.

Spectroscopic study of the complexes

Assignment of some of the ir bands of DMTP and its complexes in Table 6, has been carried out on the basis of literature data concerning $DMTP^{25-28,31}$ and other analogous compounds.⁵⁶⁻⁶¹ A very broad band in the ir spectrum of DMTP at *ca* 2500 cm^{-1} is assigned to the $\nu(NH-S)$ mode, due probably to the existence of intramolecular hydrogen bonding.⁶² The existence of dimeric species of the type shown in Figure 3 has been proven in $DMSO-d_6$ solutions of DMTP using NMR methods. None of the ir spectra of the complexes exhibits the $\nu(NH-S)$ mode, a fact which suggests breaking of intramolecular hydrogen bonds upon complexation of DMTP. The presence in the ir spectra of DMTP and its metal complexes of strong bands assignable to $\nu(NH)$, thioamide I (with $\nu(N-C=S)$ contribution), and thioamide III (with strong $\nu(C=S)$ contribution), suggests that the ligand may be formulated in the thione form.

Although the ir spectra of $Zn(II)$ and $Cd(II)$ complexes of DMTP have been previously discussed concerning the low frequency range,^{28,31} some aspects of the data need be reviewed at the light of the X-ray structure. An important feature concerns those bands assigned to $\nu(C=C)$ and $\nu(C=N)$ stretching vibrations; these are practically unaffected upon coordination of DMTP, thus confirming the unexistence of $M-N_{cy}$ interactions (see Table 6). On the other hand the strong band at 1221 cm^{-1} corresponding to the thioamide III band (strong $\nu(C=S)$ contribution) decreases in intensity and shifts to lower wavenumber upon coordination. All data are consistent with the X-ray diffraction data for these two complexes.

The ir spectrum of $AuDMTPCl_3$ shows the same features as do the $Zn(DMTP)_2Cl_2$ and $Cd(DMTP)_2Cl_2$ complexes, which indicates that DMTP is also S-coordinated to the Au(III) ion. A broad, medium intensity band at 345 cm^{-1} confirms the existence of chloride ions coordinated to the Au(III) ion (see Table 6). Ir spectra of $Pd(DMTP)_2Cl_2$ and $Pt(DMTP)_2Cl_2$ complexes are very similar. In

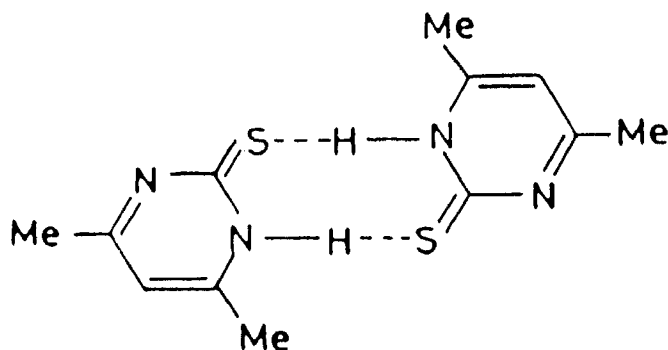


Figure 3 Dimeric structure of DMTP.

Table 6 IR data for the ligand and complexes.

Compound	$\nu(\text{NH})$	$\nu(\text{NH} \dots \text{S})$	$\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$	Thioamide I	Thioamide III	$\nu(\text{MS})$	$\nu(\text{MN})$	$\nu(\text{MC})$
DMTP	2912m	2500vbr	1624s, 1568s	1498m	1221s, 1187m	193m		250v
Zn(DMTP) ₂ Cl ₂	2918s		1620s, 1566s	1488w	1200m, 1168w			269v
Cd(DMTP) ₂ Cl ₂	2919s		1619s, 1564s	1476w	1193m, 1177m	a		206v
Hg(DMTP)Cl ₂	2917w		1579s, 1528s	1425m	1190sh, 1176mw	190w	364m	235ss
Pd(DMTP) ₂ Cl ₂	2912w		1586s, 1521s	1430s	1249s, 1190m			2958s
Pt(DMTP) ₂ Cl ₂	2916w		1591s, 1529s	1434s	1245s, 1181w			311s
Au(DMTP)Cl ₃	2858m		1632s, 1599s	1423m	1187s, 1148sh	a		304s
								322s
								303s
								320s
								345m

^a Concealed.

contrast to the ir spectra of $\text{Zn}(\text{DMTP})_2\text{Cl}_2$ and $\text{Cd}(\text{DMTP})_2\text{Cl}_2$, the abovementioned spectra show strong decreases in the frequency of the $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ bands; the thioamide III bands appear to be practically unaffected. These observations indicate that, in the Pd(II) and Pt(II) complexes, DMTP is coordinated as a neutral molecule *via* N1 or N3. The existence of two bands assignable to (M-Cl) in the low frequency range in these two complexes suggests that the two chloride ions are probably *cis*-coordinated.⁶³ The ir spectrum of $\text{Hg}(\text{DMTP})\text{Cl}_2$ shows strong decrease in the frequencies of the $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ bands relative to DMTP. Furthermore, the thioamide III bands show a strong decrease in intensity and frequency. These facts taken together suggest a different pattern of coordination of DMTP to the metal ion. DMTP is probably S, N bonded to the metal ion. Hg-Cl bands corresponding to the coordinated chloride ions appear at 295 and 311 cm^{-1} (Table 6).

¹³C NMR data for DMTP and $\text{Zn}(\text{DMTP})_2\text{Cl}_2$, $\text{Cd}(\text{DMTP})_2\text{Cl}_2$, $\text{Hg}(\text{DMTP})\text{Cl}_2$ and $\text{Pt}(\text{DMTP})_2\text{Cl}_2$ are summarized in Table 7; these were obtained from spectra recorded in $\text{DMSO}-d_6$. NMR spectra of other complexes could not be obtained because of their insolubility.

Two signals at 18.4 and 24.0 ppm in the ¹³C NMR spectrum of DMTP, assignable to the two methyl groups, confirms their inequivalence in accordance with the existence of the hydrogen bonded dimer shown in Figure 3 (in the ¹³C NMR spectrum of DMTP in CDCl_3 at 304 K, only a very broad signal at 22 ppm is detected⁶⁴). A very broad signal at 157.2 ppm, assignable to C4 and C6 is detected. C2 and C5 signals appear as two singlets at similar field values as in CDCl_3 solutions.

¹³C NMR spectra of $\text{Zn}(\text{DMTP})_2\text{Cl}_2$ and $\text{Cd}(\text{DMTP})_2\text{Cl}_2$ are very similar, in accordance with the similar coordination patterns of DMTP in both complexes. Bonding of DMTP to the metal ions cause a decrease in electron density of the ring, deshielding the C atoms. In the case of the C2 atom (directly linked to the S atom), the breaking of the hydrogen bond (in which the S atom is directly implicated) upon coordination probably causes some shielding. This probably explains the fact that C2 signals are practically unshifted in $\text{Zn}(\text{DMTP})_2\text{Cl}_2$ and $\text{Cd}(\text{DMTP})_2\text{Cl}_2$, but shift towards higher field values in $\text{Hg}(\text{DMTP})\text{Cl}_2$ (in which there is probably a weak Hg-S interaction), and in $\text{Pt}(\text{DMTP})_2\text{Cl}_2$ (in which there is no Pt-S interaction). Decrease in electron density of the pyrimidine ring also causes deshielding of the hydrogen atom linked to C5, thus explaining the shift of the corresponding signal in the ¹H NMR spectra of the complexes. This also explains the increasing

Table 7 NMR data (δ in ppm).

Compound	¹ H NMR			¹³ C NMR			
	CH ₃	C5-H	NH	C2	C5	C4 and C6	Me
DMTP	2.23	6.60	13.46	180.90(s)	109.60(s)	157 vb	18.40b 24.00b
$\text{Zn}(\text{DMTP})_2\text{Cl}_2$	2.25	6.65	a	180.20(s)	110.10(s)	164.40(s)	21.10(s)
$\text{Cd}(\text{DMTP})_2\text{Cl}_2$	2.32	6.84	a	178.40(s)	111.60(s)	164.20(s)	21.10(s)
$\text{Hg}(\text{DMTP})\text{Cl}_2$	2.53	6.96	a	173.40(s)	115.30(s)	166.50(s)	22.90(s)
$\text{Pt}(\text{DMTP})_2\text{Cl}_2$	2.36	6.99	a	168.80(s)	116.10(s)	166.10(s)	21.20(s)
	2.48						23.60(s)

S-singlet; b = broad; vb = very broad; *Not detected.

lability of the N_{cyclic}-H bond, for which the corresponding signals were not detected in the said NMR spectra of the complexes.

In accordance with the above data, the probable structure for Pd(II) and Pt(II) complexes is defined by the square-planar arrangement of two Cl⁻ ions and N atoms of the two DMTP molecules. Likewise, the four donor atoms in AuDMTPCl₃ complex (three Cl⁻ ions and the S atom of the C2-thio substituent of DMTP), are probably arranged in square-planar form. Finally, a probable tetrahedral arrangement of the two chloride ions and the S and N atoms of a DMTP molecule around the Hg(II) ion would be expected in Hg(DMTP)Cl₂.

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Supplementary data

Full lists of H atom coordinates, thermal parameters and observed and calculated structure factors are available from the authors.

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