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Studies on Pyrimidine Derivative Complexes: Spectroscopy, Thermal Behaviour and Crystal Structure of μ-Dichloro-μ-sulphur-chloro(4,6-diamino-1,2-dihydro-2-thiopyrimidine-N^3,S^2)cadmium(II) Monohydrate

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Abstract

The crystal structure of Cd(DATP)$Cl_2 \cdot H_2O$ has been determined by X-ray diffraction methods. It crystallizes in the tetragonal space group $I4_1cd$ with $a = 24.296(7)$, $c = 7.108(9)$ Å, $V = 4196(4)$ Å^3, and $Z = 16$. The structure has been solved by Patterson and Fourier syntheses and refined by full-matrix least-squares procedure to $R = 0.049$ for 1688 observed reflections. The crystal does not contain individual Cd(DATP)$Cl_2 \cdot H_2O$ neutral molecules. Cadmium atoms show a coordination number of six.

On the basis of the molecular structure of the Cd(DATP)$Cl_2 \cdot H_2O$ complex the most significant IR bands have been assigned in the 4000–600 cm^{-1} range. Likewise, the ν(Cd–N), ν(Cd–S) and ν(Cd–X) bands were assigned by comparing the IR spectra of the Cd(DATP)$Cl_2 \cdot H_2O$ and Cd$(DATP)_2Br_2$ complexes in the 600–180 cm^{-1} range.

Finally, by using an IR technique for the identification of intermediates, a thermal decomposition mechanism for the Cd(DATP)$Cl_2 \cdot H_2O$ complex has been proposed.

Introduction

Cadmium, as well as other metals of the first transition series, has been found to be an environmental pollutant and to inhibit RNA polymerase activity *in vivo* [1], and it is one of the most potent agents in diminishing the fidelity of DNA [2] and RNA [3] syntheses *in vitro*. Soft metal ions will bind tightly to a range of biological sites, particularly those with sulphur ligands. They will often displace native metal ions and inhibit metalloenzymes [4]. Several general reviews of the biochemical toxicity of these cations are available [5–7]. The toxicity is reflected in behavioural disturbances, anaemia, alterations in membrane permeability, and inhibition of oxidative phosphorylation and protein synthesis. There is also much evidence of the carcinogenic effects of a wide range of metals, including Cd, and their compounds, all of which are associated with cancer in humans [8]. Cadmium is also notorious for its toxic effect on bone, as in 'itai-itai byo' disease [9, 10]. In spite of this, only relatively few data have been recorded about reactions of cadmium with nucleic acid constituents [11–13].

The present paper reports the spectroscopic characterization, thermal behaviour and crystal structure of the octahedral complex formed between Cd and 4,6-diamino-1,2-dihydro-2-thiopyrimidine in aqueous medium.

Experimental

Preparation of the Complexes

Cd(DATP)$Cl_2 \cdot H_2O$

This complex was prepared by dissolving $CdCl_2 \cdot 2H_2O$ and DATP (3:1 molar ratio) in a minimum amount of hot water, and slowly evaporating at room temperature. Pale yellow prismatic crystals precipitated over several days and were found suitable for X-ray work. *Anal.* Calc. for $C_4H_8CdCl_2N_4OS$: C, 14.02; H, 2.34; N, 16.36; Cd, 32.83. Found: C, 14.34; H, 2.29; N, 16.27; Cd, 33.85%.

Cd$(DATP)_2Br_2$

This complex was obtained by the same method as the above complex, using as solvent a $CdCl_2$/DATP/KBr aqueous solution in which $CdCl_2$ and KBr were in a 1:10 molar ratio.

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X-ray Study

The diffraction data were obtained from a single crystal of dimensions 0.083 × 0.083 × 0.092 mm. Crystal data: $M = 343.5$, tetragonal, $a = 24.296(7)$, $c = 7.108(9)$ Å, $V = 4196(4)$ Å^3, $Z = 16$, $D_m = 2.23(2)$, $D_c = 2.17$ g cm^{-3}, $F(000) = 2656$, Mo Kα radiation, $\lambda = 0.7107$ Å, μ(Mo Kα) = 27.99 cm^{-1}. Space group $I4_1cd$.

Unit-cell parameters were obtained from least-squares analyses of 25 reflections ($9 \leqslant \theta \leqslant 11°$) on a Philips PW1100 computer-controlled diffractometer. Intensity data were recorded on the same instrument using Mo Kα radiation ($\lambda = 0.7107$ Å, monochromatized graphite), in the $\theta/2$ scan mode with a θ range of 1.5 to 30°.

The stability of the measurements was checked periodically using three standard reflections; no significant variation could be observed during the experiment. Collected intensities were corrected for Lorentz-polarization and absorption effects ($\mu = 27.99$ cm^{-1}). The absorption correction was calculated by the Gaussian integration method; the absorption correction varied between 1.551 and 1.491.

The program system X-ray 70 [14] was used for the reduction of the data and the solution of the structure. Atomic scattering factors, calculated by Cromer and Mann, were assigned to Cd^{2+}, Cl^{1-}, N, C, and O. Anomalous scattering coefficients for Cd and Cl atoms [15] have been included in the structure factor calculations.

After averaging equivalent reflections, a set of 1987 independent reflections was obtained, of which 1688 reflections with $I \geqslant 3\sigma(I)$ were classified as observed.

The positions of Cd atoms were determined from a three-dimensional Patterson synthesis. After some cycles of block least-squares refinement with Cd atom and 1509 of the strongest reflections, the R-value was reduced to 0.296. The positions of the two Cl atoms, of the S atoms and C, N, O atoms were obtained by successive Fourier-synthesis and least-squares refinements with all observed reflections, including all non-H atoms and isotropic temperature factors; the R-value was reduced to 0.068. Using anisotropic thermal parameters, the structure was refined to the final R-value of $R = 0.049$ and $R_w = 0.053$ for all observed reflections. The final atomic coordinates and the equivalent isotropic temperature factors for non-H atoms appear in Table I.

IR Spectra

The IR spectra of the complexes were obtained using a Perkin-Elmer 983G spectrophotometer, from KBr pellets in the range between 4000–600 cm^{-1}, and polyethylene pellets in the 600–180 cm^{-1} range.

TABLE I. Fractional Atomic Coordinates (×10^4, Cd × 10^5) and Equivalent Isotropic Thermal Parameters for the Non-hydrogen Atoms (e.s.d.s. in Parentheses)

Atom	x	y	z	B_{eq} (Å^2)^a
Cd	34314(4)	3643(4)	75000(0)	1.894(10)
Cl1	3699(2)	1367(1)	7683(8)	3.076(12)
Cl2	4116(2)	−167(2)	9620(6)	2.738(7)
S	2834(2)	−508(2)	6092(6)	2.305(3)
C2	2378(5)	36(6)	5684(22)	1.622(7)
C4	2173(6)	961(6)	5722(21)	2.308(8)
C5	1639(6)	876(6)	4986(31)	2.763(9)
C6	1485(6)	326(6)	4612(18)	2.152(9)
N1	1860(4)	−90(4)	4985(24)	2.033(7)
N3	2533(5)	542(4)	6072(19)	1.810(7)
N4	2348(6)	1475(5)	6087(28)	3.627(22)
N6	989(6)	159(6)	3882(24)	3.216(12)
O	2581(6)	1885(6)	1359(29)	4.936(21)

$^a B_{eq} = 8\pi(2/3)\Sigma_i\Sigma_j U_{ij} a_i a_j a_i^* a_j^*$.

Thermal Studies

The thermal measurements were made in a Mettler TA 3000 equipment. TG curves were obtained by heating samples of the corresponding complex in a pure air atmosphere (100 ml min^{-1}) and a heating rate of 10 °C min^{-1}; likewise DSC plots were carried out at the same pure air flux and 10 °C min^{-1}.

Discussion

General Description of the Structure

The crystal does not contain individual Cd(DATP)-Cl$_2$·H$_2$O neutral molecules. The coordination sphere of cadmium (excluding hydrogen atoms) is depicted in Fig. 1. A diagram of the contents of the unit cell is shown in Fig. 2. The observed value for the Cd–Cd distance, 3.970(4) Å, strongly suggests that no direct cadmium–cadmium bond interaction is present in this structure.

For metal–thiopyrimidine complexes a strong preference for metal bidentate binding (S, N) over S

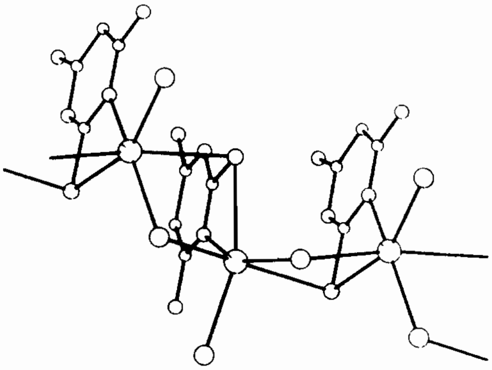

Fig. 1. Perspective view of Cd(DATP)Cl$_2$.

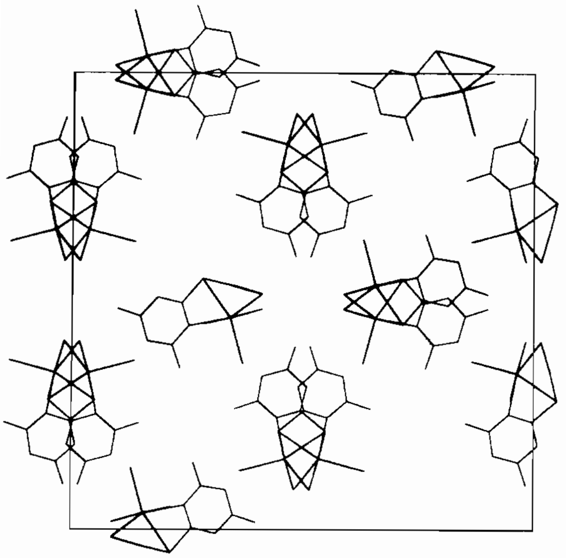

Fig. 2. Packing of the molecules in the unit cell.

TABLE II. Bond Lengths (Å) and Bond Angles (deg) (e.s.ds. in parentheses)

Atoms	Distance	Atoms	Angles
Coordination sphere		Angles about Cd	
Cd–Cl1	2.525(4)	Cl1–Cd–Cl2	106.6(1)
Cd–Cl2	2.589(4)	Cl1–Cd–N3	94.6(3)
Cd–Cl2	2.681(5)	Cl2–Cd–S	99.6(1)
Cd–N3	2.446(12)	S–Cd–N3	61.0(3)
Cd–S	2.758(4)	Cl2–Cd–Cl2^{ii}	87.5(2)
Cd–S^{i}	2.958(5)	S–Cd–Cl2	85.0(1)
		Cl1–Cd–S	153.6(1)
		N3–Cd–Cl2^{ii}	105.6(4)
		Cl2–Cd–N3	154.5(2)
		Cl1–Cd–Cl2^{ii}	93.0(1)
		Cd–Cl2–Cd^{i}	97.8(1)
		Cl2–Cd–S^{i}	82.7(1)
		Cl1–Cd–S^{i}	88.2(1)
Equivalent positions:		$i = x, \bar{y}, z + 1/2$ $ii = x, \bar{y}, z - 1/2$	

has been observed. This is confirmed by the crystal structures of the known molybdenum, tungsten, cobalt, iron and platinum complexes: [MoL$_4$]·CH$_2$Cl$_2$ [16], [Mo$_2$L'$_4$]·2CH$_2$Cl$_2$ [17], [WL$_4$] [18], [CoL'$_3$] [19], [WMe$_4$][FeL$_3$] [16] and diiodotetrakis(μ-pyrimidine-2-thionato-N^1,S^2)diplatinum(III) [20] (L = pyrimidine-2-thiolate, L' = 4,6-dimethylpyrimidine-2-thiolate) in which the coordination takes place through the S,N atoms. However, studies carried out on the interaction between methylmercury(II) ion (soft acid) and several thiopyrimidines showed that the coordination of the pyrimidine derivatives occurs through the S atom with a secondary intramolecular interaction to a N atom [21, 22]. On the other hand, in the chlorobis[tetrahydro-1*H*-pyrimidine-2-thione]copper(I), the Cu(I) is only bonded to the S atom [23]. In the present cadmium complex the thiopyrimidine acts as an S,N chelate.

Environment of Cadmium

The cadmium atom is hexa-coordinated and is surrounded by one 4,6-diaminopyrimidine-2-thione acting as a bidentate ligand through the S2 atom, which acts as a bridge between two Cd atoms and the N3 atom (Fig. 1), two bridging chlorine atoms and one non-bridging chlorine atom. The coordination geometry can be described as a distorted octahedron (Table II).

Although a large number of crystallographic results for the complexes of metals with nucleic acid constituents have been recorded to date [11–13, 24] only a few complexes of cadmium have been reported. In Table III, the metal binding sites, distances and geometry of the present complex, Cd(DATP)Cl$_2$·H$_2$O, and those found in the metal–pyrimidine and purine derivatives are compared [25–38]. The present structural analysis reveals that hexa-coordination is relatively common in analogous cadmium complexes and that the coordination to the bases through N3 is the preferable site of binding to metal.

The Cd–N bond length, 2.446(12) Å, in this complex is in the normal range observed with a variety of similar ligands (Table III). The Cd–S bond lengths (2.753(4) and 2.958(5) Å) are very similar to that found by Griffith and Amma [29], 2.790(3) Å for the di-μ-chlorodichloro-bis(6-mercaptopurine)diaquadicadmium(II) complex.

Crystal structures are known for a number of cadmium–chloro complexes [39], most of them having bridged-chlorine, as observed in the complex under study. The Cd–Cl terminal distance has an intermediate value between those corresponding to most of the tetra- and hexa-coordinated Cd chloro complexes, but comparable to those found in chloro complexes of Cd with pyrimidines and purines.

Most of the complexes shown in Table III have one or more water molecules attached to the Cd atom. The longest Cd–O(water) distance found is 2.67 Å [29]. Nevertheless, in the Cd(DATP)Cl$_2$·H$_2$O complex such a distance is 5.04(2) Å, greatly larger than the sum of the admitted Van der Waals radii of Cd and O atoms [40, 41]; therefore there is not any type of interaction between the Cd atom and water molecules.

Geometry of 4,6-Diaminopyrimidine-2-thione

On the other hand, bond lengths appearing in Fig. 3 show large delocalization of the double bonds and do not differ appreciably from the analogous lengths determined in 2-thiopyrimidine derivatives [17–23, 42].

TABLE III. Comparison of Metal Coordination Site Distances (Å) and Molecular Conformations of the Cd–Pyrimidine and Purine Derivatives[a]

Compounds	Coordination geometry	Coordinate site	Distance		References
			M–L	M–Cl	
$[Cd(UR)_2(H_2O)_3]$	trigonal bipyramidal	N3	2.211(4)		25
$Cd(AMNU)_2$	dodecahedral	N5	2.341(2)		26
		O4	2.478(2)		
		N1	2.302(2)		
		O2	2.773(2)		
$Cd(DATP)Cl_2 \cdot H_2O$	octahedral	N3	2.446(12)	2.589(4); 2.681(5)b	
		S	2.758(4)	2.525(4)t	
			2.958(5)		
$Cd(MC)_2Cl$	4 + 2	N3	2.281(4)	2.497(1)	27
		O2	2.296(4)	2.485(2)	
$[Cd(AD)(NO_3)_2H_2O]_2{}^{2+}$	octahedral	N3	2.413(7)		28
		N9	2.349(6)		
$[Cd(MP)Cl_2H_2O]$	octahedral	N7	2.32(6)	2.615(3)b	29
		S	2.79(3)	2.49(3)t	
$[Cd(AHX^-)_2(H_2O)_4]$	octahedral	N7	2.333(8)		30
$[Cd(5'\text{-}CMP)(H_2O)]_n$ monoclinic	pentagonal–bipyramidal	N3	2.32(2); 2.34(2)		31
		O2	2.87(2); 2.58(2)		
		O(phos)	2.36		
$[Cd(5'\text{-}CMP)(H_2O)]_n$ orthorhombic	square–pyramidal	N3	2.36		32
		O2	2.92		
		O(phos)	2.24		
$[Cd(5'\text{-}CMP)H_2O] \cdot H_2O$ orthorhombic	square–pyramidal	N3	2.327		33
		O2	(b)		
		O(phos)	2.250		
$[Cd(5'\text{-}dCMP)_2(H_2O)_2]$	octahedral	N3	2.29(1)		34
		O2	2.64(1)		
		O(phos)	2.225		
$[Cd_2(5'\text{-}dCMP)_2(H_2O)_2] \cdot 3H_2O$	pentagonal–bipyramidal	N3	2.47(4); 2.22(3)		34
		O2	2.89(3); 2.56(2)		
		O(phos)	2.42		
$[Cd(5'\text{-}UMP)(H_2O)_2] \cdot 2H_2O$	octahedral	O(phos)	2.29		35
$[Cd(5'\text{-}dUMP)_2(H_2O)_6]$	octahedral	O(phos)	2.24		35
$[Cd(5'\text{-}UMP)(dpa)(H_2O)_2]$	octahedral	O(phos)	2.253		36
$[Cd(5'\text{-}GMP)(H_2O)_5] \cdot 3H_2O$	octahedral	N7	2.37(1)		37
$[Cd(5'\text{-}IMP)_3] \cdot 12H_2O$	octahedral	N7	2.36		38
		O(phos)	2.23		
		O(2′)	2.42		
		O(3′)	2.32		

[a] Abbreviations: b = bridge; t = terminal; UR = uracil; AMNU = 6-amino-3-methyl-5-nitrosouracil; MC = 1-methylcytosine; AD = adenine; MP = 6-mercaptopurine; AHX = 8-azahypoxanthine; 5′-CMP = 5′-cytidine monophosphate; 5′-dCMP = deoxycytidine 5′-monophosphate; 5′-UMP = uridine 5′-monophosphate; 5′-dUMP = 2′-deoxyuridine 5′-monophosphate 2,2′-dipyridylamine; 5′-GMP = guanosine 5′-monophosphate; 5′-IMP = inosine 5′-monophosphate.

Bond angles show little modification in relation to those obtained in the X-ray study of 4-amino-6-oxo-2-thiopyrimidine [42]. The greatest displacement of these values has been found in the angles adjacent to C2 and N3, probably due to the strain produced by the metal–ligand bonds. This fact has also been observed on solving the crystal structures of (4-amino-5-methyl-2-pyrimidinethiolato)methylmercury(II) and (4-amino-2-mercapto-6-pyrimidinato)methylmercury(II) monohydrate [2].

Hydrogen Bonding and Packing

Water molecules play an important role in the crystal packing, and significant hydrogen bond lengths are collected in Table IV. These bond lengths are in the range of values found in other complexes having the same hydrogen bonds as those of the complex studied here [41].

Spectroscopic and Thermal Studies

IR spectra of $Cd(DATP)Cl_2 \cdot H_2O$ show as the most significant bands those at 3550 cm^{-1} ν(OH),

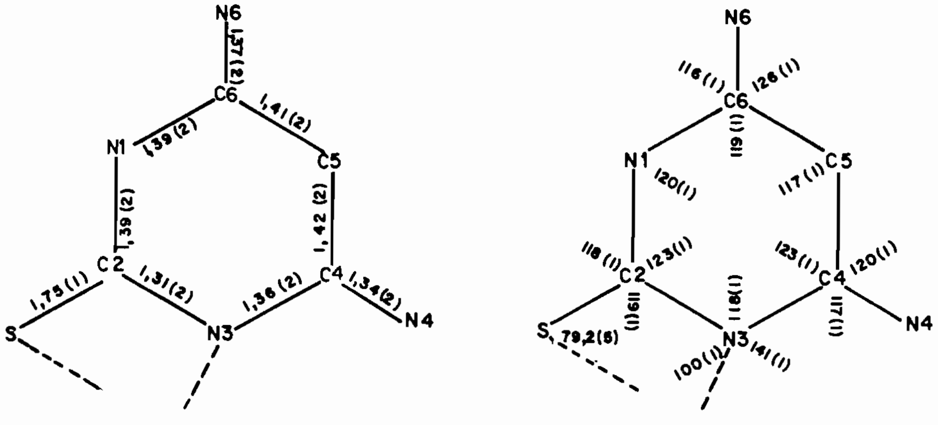

Fig. 3. Interatomic distances and bond angles of the coordinated ligand.

TABLE IV. Hydrogen Bonds

D–H···A	Distance (Å)	r(D) + r(A)
$O\cdots O^{iii}$	2.78(2)	3.0
$N4\cdots O^{iv}$	3.01(2)	3.05
$O^{v}\cdots Cl1$	3.38(2)	3.2–3.4

Equivalent positions: $iii = \bar{y} + 1/2, x, z - 1/4$
$iv = y, 1/2 - x, z + 1/4$
$v = 1/2 - y, x, z + 3/4$

3450–2800 cm^{-1} ν(N–H) + ν(C–H), 1660 cm^{-1} δ(OH), 1549 and 1464 cm^{-1} ν(C=C) + ν(C=N) + ν(NCS), and 1343, 1267, 1235 ν(CN) + ν(NCS) + ν(CS), 282 cm^{-1} ν(Cd–N), 242 cm^{-1} ν(Cd–S), 221 cm^{-1} ν(Cd–Cl1), and 200 cm^{-1} ν(Cd–Cl2). These assignments are in accordance with the tautomeric form of the ligand corresponding to the 4,6-diaminopyrimidine-2-thione. The bands at 3550 cm^{-1} and 1660 cm^{-1} are lost in the IR spectrum of a sample of Cd(DATP)Cl_2·H_2O heated up to 220 °C.

On the other hand, the assignments carried out in the 600–180 cm^{-1} range have been made by comparison with the spectra of Cd(DATP)Cl_2·H_2O, DATP and the Cd(DATP)$_2$$Br_2$ complex which was previously isolated, as described in the experimental section. The Cd(DATP)$_2$$Br_2$ complex shows three bands at 276, 231 and 198 cm^{-1}. In accordance with the literature [43], the last one can be assigned as ν(Cd–Br) stretching vibrations, and the remaining two are assigned as ν(Cd–N) (276 cm^{-1}) and ν(Cd–S) (231 cm^{-1}). The lower frequency values of these two bands can be explained on the basis of stronger steric interactions between the ligand molcules in the last complex.

Furthermore, the assignment of the bands at 221 cm^{-1} and 200 cm^{-1} in the IR spectrum of Cd(DATP)Cl_2·H_2O as ν(Cd–Cl) stretching vibrations was confirmed by the fact that such bands disappear in the IR spectrum of a sample of the complex after heating at 320 °C. On the other hand, this spectrum showed a new band at 246 cm^{-1} which can be assigned to $CdCl_2$ formed in the process:

$$2\mathrm{Cd(DATP)Cl_2} \longrightarrow \mathrm{Cd(DATP^-)_2} + \mathrm{CdCl_2} + 2\mathrm{HCl}$$

as we will see below.

The thermogravimetric curve of Cd(DATP)Cl_2·H_2O shows a first weight loss in the 50–200 °C temperature range, where 5.2% of the initial weight is eliminated. This value is in agreement with the theoretical value calculated for the dehydration process (5.24%). The expected endothermic effect was observed in the DSC curve at 84 °C. From the

TABLE V. Thermoanalytical Data

Process	T (°C)	ΔH (kJ mol^{-1})	Weight loss	
			Found	Calculated
$\mathrm{Cd(DATP)Cl_2{\cdot}H_2O} \longrightarrow \mathrm{Cd(DATP)Cl_2} + \mathrm{H_2O}$	84.0	32.2	5.2	5.24
$\mathrm{Cd(DATP)Cl_{2(s)}} \longrightarrow \mathrm{Cd(DATP)Cl_{2(l)}}$	218.9	21.4		
$2\mathrm{Cd(DATP)Cl_2} \longrightarrow \mathrm{Cd(DATP)_2} + \mathrm{CdCl_2} + 2\mathrm{HCl}$	280–350	21.6	15.0	15.89
$\mathrm{Cd(DATP^-)_2} \longrightarrow \mathrm{CdO}$ $\mathrm{CdCl_{2(s)}} \longrightarrow$ sublimates	350–750	exo	74.6	81.31

area of this effect, the dehydration enthalpy, 32.2 kJ mol^{-1}, was calculated.

At 218.9 °C, the DSC plot shows a sharp endothermic effect, which is assigned to the fusion of the anhydrous complex ($\Delta H = 21.4$ kJ mol^{-1}). The fused complex is stable up to 280 °C; at this temperature a dehalogenation process starts, steadily followed by pyrolysis of the ligand.

From both DSC and TG data, the thermal decomposition scheme shown in Table V has been obtained.

Supplementary Material

A list of the observed and calculated structure factors and anisotropic thermal parameters are available from the Editor-in-Chief.

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