4,6-Dimethylpyrimidine-2-thionato ($dmpymt^-$) Complexes of Nickel(II) and Cadmium(II). Crystal Structure of $[Cd(dmpymt)_2]$: a Compound with a Calixarene-like Structure†

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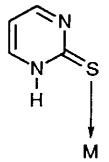
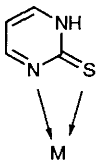
Nickel and cadmium complexes of the anionic form of 4,6-dimethylpyrimidine-2-thione (Hdmpymt) and their adducts with neutral ligands (1,10-phenanthroline or 2,2'-bipyridine) have been prepared by an electrochemical procedure and characterized by spectroscopic (IR, UV, ^1H and ^{13}C NMR) methods, and for the $[\{Cd(dmpymt)_2\}_6]$ complex by X-ray crystallographic techniques. This compound is hexanuclear with an array of six cadmium atoms bridged by twelve sulfur atoms. Each cadmium atom has a distorted-octahedral *cis*-CdS_4N_2 environment with each ligand acting in a N,S bidentate S-bridging mode. The hexamer has a calixarene-like structure with cavities large enough to accommodate molecules such as acetonitrile, carbon monoxide and molecular iodine.

It is well known that metal thiolate complexes adopt various nuclearities and great structural complexities. These features are the result of the tendency of thiolate ligands to bridge metal centres to yield oligo- or poly-meric species. These aggregation phenomena may be limited by providing steric constraints by appropriate ligand design or introducing coligands to block a number of co-ordination sites. Thus, for example, the 4,6-dimethylpyrimidine-2-thione (Hdmpymt) copper(I) complex is hexanuclear, $[\{Cu(dmpymt)\}_6]$, with all coppers in a distorted-octahedral geometry;[1] the pyridine-2-thione (Hpyt) complex $[Cd(pyt)_2]$ is polymeric[2] and that with 3-trimethylsilylpyridine-2-thione (Hspyt) is dimeric,[3] $[\{Cd(spyt)_2\}_2]$. An analogous situation has been found previously in $[Ni(spyt)_2]$,[4] $[\{Cu(spyt)\}_6]$[5] and $[\{Zn(spyt)_2\}_2]$.[6]

In this paper we report the electrochemical synthesis and characterization of a series of complexes of nickel(II) and cadmium(II) with 4,6-dimethylpyrimidine-2-thione, a compound which, besides having methyl groups that might modify the degree of aggregation as a result of steric constraints, is one of the most versatile sulfur donors since it can act, as in the case of pyrimidine-2-thione, as (*a*) a neutral monodentate ligand co-ordinated *via* the sulfur atom[7] (**A**) or as a chelate[8] (**B**), and (*b*) as an anionic ligand, in which case it can be monodentate through the sulfur atom[9] (**C**), chelating[10] (**D**) or bridging between two (**E**)[9,11] and (**F**) or three[1] (**G**) metal atoms co-ordinated by both nitrogen and sulfur atoms. The complex $[\{Cd(dmpymt)_2\}_6]$ is the first reported in which pyrimidine-2-thione links two metal atoms in the form **F**.



A



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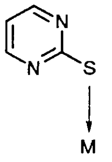

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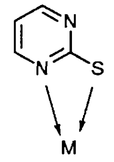

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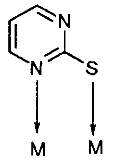
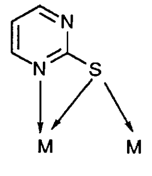
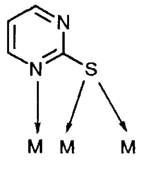


E



F



G

Experimental

Acetonitrile, 4,6-dimethylpyrimidine-2-thione, 1,10-phenanthroline and 2,2'-bipyridine were used as supplied (Aldrich). The metals (Ega Chemie) were used as plates (*ca.* 2 × 2 cm).

Electrochemical Syntheses.—The electrochemical method used in the synthesis of the metal complexes is similar to that described by Tuck and co-workers.[12] The cell consists of a tall-form beaker ($100\ cm^3$) containing an acetonitrile ($50\ cm^3$) solution of 4,6-dimethylpyrimidine-2-thione and a small amount of tetraethylammonium perchlorate (*ca.* 10 mg) as the supporting electrolyte; a platinum cathode and the sacrificial anode (nickel or cadmium), attached to a platinum wire, served as the electrodes and were connected to a d.c. power supply. For the synthesis of mixed-ligand complexes, either 1,10-phenan-

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† *Supplementary data available:* The atomic positions, full lists of bond lengths and angles and other crystallographic data have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlichtechnische Informationen, 76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference number CSD 57468.

throline or 2,2′-bipyridine was added to the electrolyte phase. In all cases, hydrogen evolved at the cathode. These cells can be summarized as Pt(−)|MeCN + Hdmpymt|M(+) and Pt(−)| MeCN + Hdmpymt + L|M(+) where M is nickel or cadmium and L represents 1,10-phenanthroline or 2,2′-bipyridine. When neither 1,10-phenanthroline nor 2,2′-bipyridine was present, precipitation took place within *ca.* 15 min of the start of the electrolysis and continued throughout the experiment. The solid was collected, washed with acetonitrile and diethyl ether and dried *in vacuo*. When 1,10-phenanthroline or 2,2′-bipyridine was present, as the electrolysis proceeded, the colour of the solution changed from pale brown to red-brown for nickel and to orange for cadmium. A black product was formed on the cathode but no effort was made to identify it. After the electrolysis the solution was filtered to remove any solid impurities and the solvent evaporated in a Rotavapor to give an oil, which was treated with diethyl ether to produce a solid. The solution compositions and experimental conditions are given in Table 1.

Physical Measurements.—Microanalyses were performed using a Carlo-Erba EA1108 microanalyser. The analytical data are given in Table 2. The IR spectra were recorded in KBr mulls on a Perkin Elmer 180 spectrophotometer, solid reflectance spectra on a Perkin Elmer Lambda 9 spectrophotometer. Magnetic measurements were taken using a SQUID magnetometer. Proton NMR spectra were recorded on a Bruker WM 250 MHz spectrometer using $(CD_3)_2SO$ as solvent; chemical shifts were determined against $SiMe_4$ as internal standard.

Crystal Structure Determination of [{Cd(dmpymt)$_2$}$_6$].—*Crystal data.* $C_{90}H_{84}Cd_6N_{33}S_{12}$, M = 2687.05, rhombohedral (hexagonal axes), space group $R\bar{3}(h)$ (no. 148), a = 18.784(6), c = 32.13(1) Å, U = 9819(6) Å^3, Z = 3, D_c = 1.363 g cm^{-3}, F(000) = 4005, λ(Mo-Kα) = 0.710 69 Å, μ = 11.86 cm^{-1}.

Data collection and processing. A colourless trapezoid of approximate dimensions 0.20 × 0.15 × 0.05 mm was mounted in a Lindeman glass tube in the presence of mother-liquor. All measurements were made on a Rigaku AFC65 diffractometer with graphite-monochromated Mo-Kα radiation. Cell constants and an orientation matrix for data collection (obtained from a least-squares refinement using the setting angles of 19 carefully centred reflections in the range 6.76 < 2θ < 14.86°) corresponded to a rhombohedral (hexagonal axes) cell.

The data were collected at room temperature using the ω–2θ scanning technique to a maximum 2θ value of 50.1°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.39° with a take-off angle of 6.0°. Scans of (1.31 + 0.30 tan θ)° were made at a speed of 4.0° min^{-1} (in ω).

Of the 3685 reflections collected, 3423 were unique (R_{int} = 0.0391). An empirical absorption correction applied using the program DIFABS[13] resulted in transmission factors ranging from 0.77 to 1.33 The data were corrected for Lorentz and polarization effects.

Structure solution and refinement. The structure was solved by direct methods.[14] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure-factor calculation in idealized positions. The final cycle of full-matrix least-squares refinement was based on 923 observed reflections [$I > 2\sigma(I)$] and 205 variable parameters and converged to $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.073$, and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.074$. The standard deviation of an observation of unit weight was 2.10. The weighting scheme was based on counting statistics and included a factor (p = 0.03) to downweight the intense reflections. Plots of $\Sigma(|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, (sin ω)/λ, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final Fourier difference map were to 0.55 and −0.67 e Å^{-3}, respectively.

Neutral atom scattering factors were those of Cromer and Waber;[15] corrections for anomalous dispersion effects were those of Cromer.[16] All calculations were performed using the TEXSAN[17] crystallographic software package.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The thiolate complexes, [M(dmpymt)$_2$] (M = Ni or Cd), and their adducts with 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy), [M(dmpymt)$_2$(phen)] or [M(dmpymt)$_2$(bipy)], are easily prepared in good yield by the simple one-step electrochemical method described, in keeping with previous work on related systems.[1,3,18,19]

The electrochemical efficiency, defined as moles of metal dissolved per Faraday of charge, was found to have an average of 0.5 ± 0.02 mol F^{-1} for nickel and cadmium, irrespective of the presence or absence of neutral ligand. These results, together with the evolution of hydrogen at the cathode, are compatible with the occurrence of the following electrode reactions (1)–(3) where M = Ni or Cd and L = bipy or phen.

$$\text{Cathode: } 2\ \text{Hdmpymt} + 2\ e^- \longrightarrow H_2 + 2\ \text{dmpymt}^- \quad (1)$$

$$\text{Anode: } 2\ \text{dmpymt}^- + M \longrightarrow [M(\text{dmpymt})_2] + 2\ e^- \quad (2)$$

$$2\ \text{dmpymt}^- + M + L \longrightarrow [M(\text{dmpymt})_2L] + 2\ e^- \quad (3)$$

In the case of [Cd(dmpymt)$_2$], crystals suitable for X-ray diffraction studies could be isolated. However, these deteriorated in a short time, and had to be prepared immediately prior to being mounted for data collection.

Structure of [{Cd(dmpymt)$_2$}$_6$].—The molecular structure of [{Cd(dmpymt)$_2$}$_6$] is shown in Fig. 1, together with the atomic numbering scheme adopted. For clarity, a view of the coordination sphere of the metals is shown in Fig. 2. Final atomic coordinates, selected bond distances and angles are listed in Tables 3 and 4. The structure contains discrete molecules having a crystallographically imposed symmetry with three molecules in the unit cell.

The structure consists of a regular non-planar hexagon of six

Table 1 Experimental conditions for the electrochemical syntheses[a]

Compound	Amount of bipy or phen (g)	Initial voltage (V)[b]	Metal dissolved (mg)	E_f/ mol F^{-1}
[Ni(dmpymt)$_2$]·2.75H$_2$O		31	66.9	0.51
[Ni(dmpymt)$_2$(bipy)]·1.5H$_2$O	0.18	30	63.5	0.48
[Ni(dmpymt)$_2$(phen)]·1.5H$_2$O	0.22	22	66.2	0.50
[Cd(dmpymt)$_2$]		15	130.0	0.52
[Cd(dmpymt)$_2$(bipy)]·0.5H$_2$O	0.18	16	125.3	0.50
[Cd(dmpymt)$_2$(phen)]·H$_2$O	0.23	17	130.0	0.52

[a] 0.31 g Hdmpymt + *ca.* 20 mg NEt$_4$ClO$_4$. [b] Voltage required to produce a current of 20 mA.

Table 2 Analytical data * for the complexes

		Analysis (%)		
Compound	Colour	C	N	H
[Ni(dmpymt)$_2$]·2.75H$_2$O	Green	37.1 (37.3)	14.0 (14.5)	4.7 (5.0)
[Ni(dmpymt)$_2$(bipy)]·1.5H$_2$O	Green	50.5 (50.8)	15.8 (16.2)	4.5 (4.8)
[Ni(dmpymt)$_2$(phen)]·1.5H$_2$O	Brown	52.8 (52.9)	15.4 (15.4)	4.5 (4.5)
[Cd(dmpymt)$_2$]	White	37.4 (36.9)	14.0 (14.3)	4.0 (3.6)
[Cd(dmpymt)$_2$(bipy)]·0.5H$_2$O	Yellow	47.7 (47.5)	14.6 (15.1)	4.6 (4.4)
[Cd(dmpymt)$_2$(phen)]·H$_2$O	Yellow	49.0 (48.9)	14.0 (14.3)	4.0 (4.1)

* Calculated values given in parentheses.

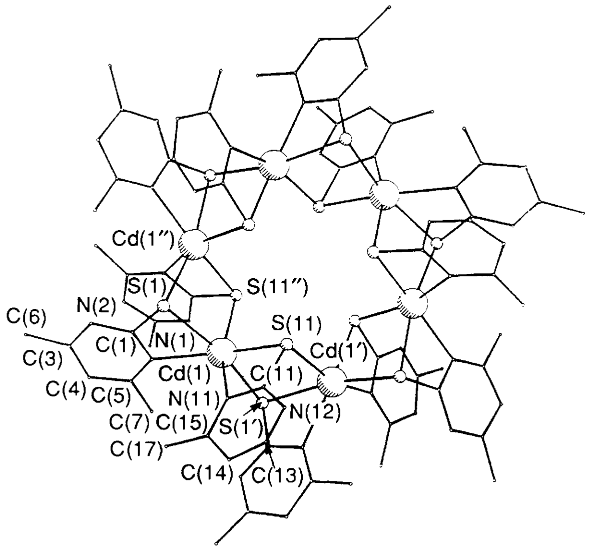


Fig. 1 Perspective view of the structure of [{Cd(dmpymt)$_2$}$_6$]

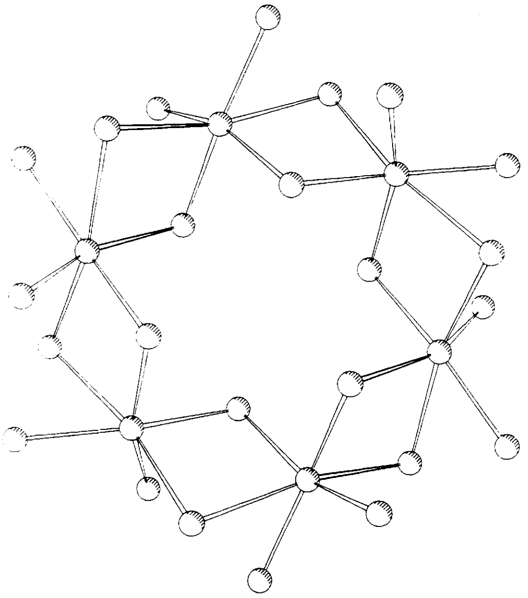


Fig. 2 Perspective view of the co-ordination sphere of the metals in [{Cd(dmpymt)$_2$}$_6$]

Table 3 Final fractional atomic coordinates for [{Cd(dmpymt)$_2$}$_6$] with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Cd(1)	0.169 3(1)	0.447 4(1)	0.669 71(7)
S(1)	0.059 1(4)	0.478 3(5)	0.711 5(2)
S(11)	0.300 3(4)	0.529 3(4)	0.718 6(3)
N(1)	0.028(1)	0.366(2)	0.656(1)
N(2)	−0.089(2)	0.375(2)	0.681(1)
N(11)	0.184(2)	0.380(2)	0.729 3(7)
N(12)	0.295(2)	0.425(2)	0.777(1)
C(1)	−0.007(2)	0.399(2)	0.683(1)
C(3)	−0.137(2)	0.310(2)	0.653(1)
C(4)	−0.104(3)	0.268(2)	0.628(1)
C(5)	−0.019(2)	0.303(2)	0.632(1)
C(6)	−0.225(2)	0.287(2)	0.654(1)
C(7)	0.018(2)	0.264(2)	0.606(1)
C(11)	0.255(2)	0.435(2)	0.746(1)
C(13)	0.260(3)	0.352(4)	0.793(1)
C(14)	0.189(3)	0.288(3)	0.783(1)
C(15)	0.146(2)	0.301(2)	0.749(2)
C(16)	0.299(2)	0.335(2)	0.827(1)
C(17)	0.063(2)	0.241(2)	0.728(1)
N(3)	−0.190(3)	0.519(3)	0.880(2)
C(31)	−0.174(5)	0.503(4)	0.887(2)
C(32)	−0.047(4)	0.500(4)	0.879(2)
N(4)	0.262(6)	0.62(1)	0.837(4)
C(41)	0.193(5)	0.594(5)	0.852(3)
C(42)	0.112(6)	0.547(5)	0.862(3)
N(5)	0.182(5)	0.564(5)	0.811(3)
C(51)	0.131(6)	0.550(6)	0.815(4)
C(52)	0.043 8	0.519 5	0.845 6

cadmium atoms bridged above and below by the sulfur atoms of twelve thiolate anions. These sulfur atoms belong to two sets of six, each (see Fig. 2) being approximately planar, with three atoms above the best least-squares plane (+0.114 Å) and the other three below it (−0.114 Å). These planes are parallel to each other and also to the best least-squares plane defined by the six cadmium atoms (maximum deviation 0.098 Å) which lies in the middle of the sulfur atom planes, with a dihedral angle between them of 0°. The Cd • • • Cd distances in the hexameric rings are all *ca.* 3.716 Å, showing that no significant cadmium–cadmium interactions exist in the compound.

Each cadmium atom is co-ordinated to one nitrogen atom and the bridging sulfur atom of two 4,6-dimethylpyrimidine-2-thionate ligands, and to other two bridging sulfur atoms from two ligands bound to other cadmium atoms. Therefore, each ligand acts as a bridging [N,(μ-S)$_2$] five-electron donor ligand.

Each cadmium atom is in a distorted-octahedral environment, CdS$_4$N$_2$, with the two nitrogens in *cis* position; the angles defined by two *trans* atoms and the cadmium atom, S(1)–Cd–S(1′), S(11)–Cd–N(1) and S(11′)–Cd–N(11) have values of 168.0(2), 154.7(8) and 161.3(7)°, respectively, instead of the required 180°. The bond angles between cadmium and the adjacent atoms of the chelate rings have values lower than 90°, 60.4(8) and 61.0(7)°, whereas the angles involving the other *cis* atoms of different ligands have values larger than 90°, in the range 102(1)–90.5(2)°. These values deviate greatly from the theoretical and result in distortion of the octahedral geometry.

The Cd–S distances are also slightly different. Thus, in the ring Cd$_2$S$_2$ defined by cadmium and bridging sulfur atoms there are three Cd–S bond distances in the range 2.638(8)–2.666(8) Å and one at 2.761(8) Å, as in other six-co-ordinated compounds with Cd$_2$S$_2$ units; for example, in polymeric bis(pyridine-2-thionato)cadmium(II)[2] and bis(benzothiazole-2-thionato)cadmium(II)[2] the distances between cadmium atoms and sulfur bridge atoms lie in two groups, but contrary to [{Cd(dmpymt)$_2$}$_6$], there are two Cd–S bonds in each group. In [{Cd(dmpymt)$_2$}$_6$] the shorter bond lengths are close to those found in the above complexes, 2.543(5) and 2.649(4) Å for [Cd(pyt)$_2$] and 2.547(4) and 2.606(4) Å for [Cd(bztt)$_2$]. However, in this compound the longer Cd–S bond lengths are much shorter than those found in [Cd(pyt)$_2$], 2.809(4) and 3.038(4) and in [Cd(bztt)$_2$], 3.061(5) and 3.129(4) Å. Moreover,

Table 4 Selected interatomic distances (Å) and angles (°) for [{Cd(dmpymt)$_2$}$_6$]

Cd(1)–S(1)	2.761(8)	N(11)–C(11)	1.33(3)
Cd(1)–S(1′)	2.666(8)	N(11)–C(15)	1.42(4)
Cd(1)–S(11)	2.665(8)	N(12)–C(11)	1.35(4)
Cd(1)–S(11″)	2.638(8)	N(12)–C(13)	1.29(4)
Cd(1)–N(1)	2.36(2)	C(3)–C(4)	1.47(4)
Cd(1)–N(11)	2.38(2)	C(3)–C(6)	1.49(4)
S(1)–C(1)	1.66(3)	C(4)–C(5)	1.40(4)
S(11)–C(11)	1.76(3)	C(5)–C(7)	1.49(4)
N(1)–C(1)	1.39(3)	C(13)–C(14)	1.31(4)
N(1)–C(5)	1.31(3)	C(13)–C(16)	1.44(4)
N(2)–C(1)	1.37(3)	C(14)–C(15)	1.46(5)
N(2)–C(3)	1.41(4)	C(15)–C(17)	1.55(4)
S(1)–Cd(1)–S(1′)	168.0(2)	Cd(1)–N(11)–C(11)	104(3)
S(1)–Cd(1)–S(11)	99.5(2)	Cd(1)–N(11)–C(15)	141(3)
S(1)–Cd(1)–S(11″)	90.5(2)	C(11)–N(11)–C(15)	115(3)
S(1)–Cd(1)–N(1)	60.4(8)	C(11)–N(12)–C(13)	115(3)
S(1)–Cd(1)–N(11)	90.9(6)	S(1)–C(1)–N(1)	116(3)
S(1′)–Cd(1)–S(11)	92.1(2)	S(1)–C(1)–N(2)	122(3)
S(1′)–Cd(1)–S(11″)	90.8(2)	N(1)–C(1)–N(2)	122(3)
S(1′)–Cd(1)–N(1)	107.6(8)	N(2)–C(3)–C(4)	123(3)
S(1′)–Cd(1)–N(11)	91.6(6)	N(2)–C(3)–C(6)	113(4)
S(11)–Cd(1)–S(11″)	100.4(3)	C(4)–C(3)–C(6)	124(4)
S(11)–Cd(1)–N(1)	154.7(8)	C(3)–C(4)–C(5)	113(3)
S(11)–Cd(1)–N(11)	61.0(7)	N(1)–C(5)–C(4)	124(3)
S(11″)–Cd(1)–N(1)	95.3(7)	N(1)–C(5)–C(7)	121(3)
S(11″)–Cd(1)–N(11)	161.3(7)	C(4)–C(5)–C(7)	115(4)
N(1)–Cd(1)–N(11)	102(1)	S(11)–C(11)–N(11)	112(3)
Cd(1)–S(1)–Cd(1″)	86.4(2)	S(11)–C(11)–N(12)	120(3)
Cd(1)–S(1)–C(1)	81(1)	N(11)–C(11)–N(12)	128(3)
Cd(1″)–S(1)–C(1)	106(1)	N(12)–C(13)–C(14)	129(4)
Cd(1)–S(11)–Cd(1′)	88.9(2)	N(12)–C(13)–C(16)	119(5)
Cd(1)–S(11)–C(11)	82(1)	C(14)–C(13)–C(16)	112(5)
Cd(1′)–S(11)–C(11)	100(1)	C(13)–C(14)–C(15)	115(3)
Cd(1)–N(1)–C(1)	103(2)	N(11)–C(15)–C(14)	119(3)
Cd(1)–N(1)–C(5)	136(2)	N(11)–C(15)–C(17)	112(4)
C(1)–N(1)–C(5)	121(3)	C(14)–C(15)–C(17)	130(4)
C(1)–N(2)–C(3)	116(3)		

(′) Denotes $\frac{2}{3} + x - y, \frac{1}{3} + x, \frac{4}{3} - z$ and (″) $y - \frac{1}{3}, \frac{1}{3} - x + y, \frac{4}{3} - z$.

both lengths in the complex are longer than those found in [Cd(pymt)$_2$(phen)],[19] 2.588(3) and 2.549(3) Å, but are similar to those found for terminal Cd–S bonds in other octahedral cadmium(II) complexes, 2.647–2.777 Å.[20–22]

The Cd–N bond distances, 2.36(2) and 2.38(2) Å, are slightly shorter than those found in octahedral cadmium(II) compounds containing the pyrimidine-2-thionate moiety, [Cd(pymt)$_2$(phen)],[19] 2.42(2) and 2.53(2) Å, but they are very close to those observed in other octahedral cadmium(II) complexes involving other heterocyclic nitrogen-donor ligands, for example 2.343(4) Å in [Cd(pyt)$_2$],[2] 2.306(4) Å in [Cd(bztt)$_2$],[2] 2.376(3) Å in diaquadiformatobis(nicotinamide)cadmium(II)[23] and 2.35 Å in CdCl$_2$·2py (py = pyridine).[24]

Each of the pyrimidine rings is planar, but the sulfur atoms lie out of the plane of pyrimidine to which they are bound [by 0.031 Å for S(1) and 0.104 Å for S(11)]. The interplanar angle between the pyrimidine ring of ligands bound to the same metal is only 9° whereas the rings of ligands bonded to adjacent cadmium have interplanar angles in the range 73–82°. The solvent acetonitrile molecules do not interact with the cadmium complex in any significant manner and there are no noteworthy intermolecular contacts.

Comparison of this structure with those of cadmium with pyridine-2-thione[2] and 3-trimethylsilylpyridine-2-thione[3] shows that an increase of the steric constraint produced by the substituents on the ligand modifies drastically the structure of the isolated complex. So, the cadmium complex with pyridine-2-thione has a polymeric structure with a cadmium bonded to four bridging sulfur and two nitrogen atoms. In this case the ligands act as double bridges, type **F**, and the pyridine rings bonded to the adjacent cadmium atoms are almost perpendicular to each other. The increased steric constraint introduced by the methyl groups in the case of 4,6-dimethylpyrimidine-2-thione reduces the polymerization and the compound is a hexamer. When the case of 3-trimethylsilylpyridine-2-thione, which has a more voluminous substituent, is considered, it is found that the complex is a dimer, where each cadmium atom has a five-co-ordinate environment, being bonded to a terminal three-electron-donor ligand (**D**) and to two bridging sulfur atoms and one nitrogen of two five-electron-donor bridging ligands (**F**). This steric property shows well that the extent of aggregation can be tuned by careful control of the steric demand imposed on the thiolate ligands. Naturally, other factors, such as reaction conditions, solvent nature, *etc*., can also play a role.

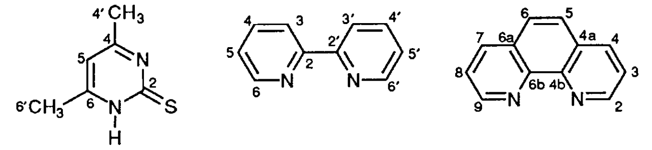
Fig. 3 Space-filling representation of the crystal structure of [{Cd(dmpymt)$_2$}$_6$]

It is noteworthy that the hexamer is positioned on a crystallographic 3 site, which generates a triangular, sulfur-rich calixarene-like well on either side of the molecule. Disordered acetonitrile guest molecules are clearly associated with the above cavities (see Fig. 3), which are also sufficiently large to accommodate alternative guest molecules such as acetylene, carbon monoxide and molecular iodine.

Vibrational Spectra.—The IR spectrum of Hdmpymt exhibits a band in the range 3200–3060 cm^{-1}, attributed to ν(N–H).[25] This band is absent in the spectra of the nickel and cadmium complexes, indicating that the ligand is in the thiolate form. A very strong band around 1620 cm^{-1} for the ligands, assigned to ν(C=C) and ν(C=N) of a non-aromatic ring, is shifted to lower wavenumbers, in the range 1570–1580 cm^{-1}, for the complexes; this is further confirmation of the thiolate form of the ligands. Besides these bands, the mixed-ligand complexes show bands typical of co-ordinated 2,2′-bipyridine (*ca*. 770 and 740 cm^{-1})[26] and 1,10-phenanthroline[26,27] (*ca*. 1510, 850 and 725 cm^{-1}).

NMR Spectra.—The ^{1}H NMR spectrum of 4,6-dimethylpyrimidine-2-thione in (CD$_3$)$_2$SO shows a broad singlet at δ 13.49 assignable to NH. This signal is absent in the NMR spectra of the cadmium compounds, further conformation of deprotonation of the ligand during the electrolysis process. The spectra of the complexes (Table 5) show a singlet at δ 6.60 due to the H^5 proton and a singlet at δ 2.21–2.10 due to the methyl group; this shows that at room temperature both methyl groups are chemically equivalent. This equivalency is observed

Table 5 Proton and carbon-13 NMR data for cadmium(II) complexes *



	^1H		^{13}C	
Compound	dmpymt$^-$	phen(bipy)	dmpymt$^-$	phen(bipy)
Hdmpymt	6.62 (s) H^5		181.2 C^2	
	2.24 (s) $N^{4',6'}$		109.8 C^5	
[Cd(dmpymt)$_2$]	6.60 (s) H^5		181.6 C^2	
	2.14 (s) $H^{4',6'}$		165.4 $C^{4,6}$	
			112.5 C^5	
			22.6 $C^{4',6'}$	
[Cd(dmpymt)$_2$(bipy)]	6.60 (s) H^5	8.72 (d) $H^{6,6'}$	181.8 C^2	153.2 C^2
	2.11 (s) $H^{4',6'}$	8.43 (d) $H^{3,3'}$	165.5 $C^{4,6}$	149.2 C^6
		8.00 (m) $H^{4,4'}$	112.6 C^5	138.5 C^5
		7.52 (m) $H^{5,5'}$	22.6 $C^{4',6'}$	125.0 C^3
				121.2 C^4
[Cd(dmpymt)$_2$(phen)]	6.60 (s) H^5	9.16 (d) $H^{2,9}$	165.5 $C^{4,6}$	149.8 C^2
	2.20 (s) $H^{4',6'}$	8.79 (d) $H^{4,7}$	112.7 C^5	139.1 C^{4b}
		8.20 (s) $H^{5,6}$	22.6 $C^{4',6'}$	139.1 C^4
		8.03 (m) $H^{3,8}$		129.0 C^{4a}
				127.2 C^5
				125.2 C^3

* Relative to tetramethylsilane.

Table 6 Electronic spectroscopic and magnetic data for nickel(II) complexes

Compound	$\tilde{\nu}$/cm^{-1}	μ/μ_B
[Ni(dmpymt)$_2$]·2.75H$_2$O	9950, 11 100, 16 130	3.6
[Ni(dmpymt)$_2$(bipy)]·1.5H$_2$O	10 000, 11 360 (sh), 16 950	3.8
[Ni(dmpymt)$_2$(phen)]·1.5H$_2$O	10 530, 11 500 (sh), 16 130	3.1

in the ^{13}C NMR spectra where only a signal assigned to both methyl groups is seen around δ 22.5.

However, the structure of [{Cd(dmpymt)$_2$}$_6$] shows that the methyl groups should be non-equivalent. It is tentatively proposed that the observed equivalency at room temperature is due to a fluxional behaviour. Such behaviour could be demonstrated by using variable-temperature NMR experiments in the case of complexes of pyrimidine-2-thione.[19] Unfortunately, the poor solubility of our complexes in chloroform and similar solvents precludes such studies.

The NMR spectra of the mixed-ligand complexes [Cd(dmpymt)$_2$L] show additional signals due to co-ordinated 2,2′-bipyridine and 1,10-phenanthroline.[28] Consequently an octahedral monomeric structure can be suggested for them. Similar structures have been found by X-ray diffraction analysis for [Zn(pyt)$_2$(phen)][29] or [Cd(pymt)$_2$(phen)].[19]

Magnetic Moments and Electronic Spectra.—The diffuse reflectance spectra of the nickel complexes (Table 6) show bands in the ranges 9900–10 550 (ν_1) and 16 100–16 950 cm^{-1} (ν_2). These are very similar to the ranges found for other nickel complexes with similar ligands, the structures of which have been shown to be octahedral by X-ray diffraction analysis.[18] Consequently, these bands can be attributed to $^3T_{2g} \longleftarrow {}^3A_{2g}$ (ν_1) and $^3T_{1g}(F) \longleftarrow {}^3A_{2g}$ (ν_2) transitions in an octahedral field.[30] The clearly discernible shoulder observed for ν_1, at 11 000–11 500 cm^{-1}, reflects the distorted-octahedral geometry of these complexes. No band attributable to the $^3T_{1g}(P) \longleftarrow {}^3A_{2g}$ (ν_3) transition is observed, probably because it is very weak and obscured by a strong charge-transfer band in the region 25 000–32 000 cm^{-1}.

The magnetic moments of the nickel complexes lie in the range 3.1–3.8 μ_B at room temperature. Some of these values are unusual for octahedral or pseudo-octahedral nickel(II) complexes which in general have room-temperature magnetic moments of the order of 3.1–3.3 μ_B.[31] We cannot offer any explanation for our values.*

These data support an octahedral environment for nickel. Consequently, it is suggested that [Ni(dmpymt)$_2$] is a polymer with a structure similar to that found for [Cd(pyt)$_2$]. For the mixed-ligand complexes a monomeric octahedral NiN$_4$S$_2$ structure is suggested.

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