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Zinc(II) and cadmium(II) halide complexes with 2,6-dimethyl-4*H*-pyran-4-thione

Giuseppina Faraglia*, Rodolfo Graziani, Zijian Guo**
Dipartimento di Chimica Inorganica, Metallorganica ed Analitica dell'Università, via Loredan 4, 35131 Padua (Italy)

Umberto Casellato and Sergio Sitran
Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., corso Stati Uniti, 35020 Padua (Italy)

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Abstract

The thiocarbonyl donor 2,6-dimethyl-4*H*-pyran-4-thione (DMTP) forms with zinc(II) and cadmium(II) halides complexes of general formulae $[M(DMTP)_2X_2]$ and $[M(DMTP)X_2]_n$ (M = Cd or Zn; X = halide). The compounds have been characterized by IR and proton NMR spectroscopy. The crystal structure of $[Zn(DMTP)_2Cl_2]$ was determined by X-ray crystallography and refined to the final *R* of 0.060, based on 2073 observed reflections. The crystal is triclinic, $P\bar{1}$, with $a = 7.955(6)$, $b = 8.599(6)$, $c = 14.098(5)$ Å, $\alpha = 92.12(3)$, $\beta = 110.96(3)$ and $\gamma = 108.60(3)°$. Zn is tetrahedrally coordinated by two Cl and two S(ligand) atoms. Bond distances (mean values) are Zn–Cl 2.25, Zn–S 2.37, S–C 1.69 Å. The IR absorptions due to metal–halide bond vibrations support a distorted tetrahedral structure for all 1:2 complexes. The $[Cd(DMTP)Cl_2]_n$ adduct has probably a polymeric structure by bridging halides, with the cadmium atom in an octahedral environment, whereas the $[M(DMTP)X_2]_n$ (M = Zn, X = Br or I; M = Cd, X = I) complexes are dimers by halide bridges. Proton NMR spectra in various deuterated solvents are discussed.

Introduction

Zinc and cadmium dihalide complexes with thiocarbonyl donors have not been reported extensively, especially as regards crystal structure data. Zinc–sulfur interactions are of interest in biochemical systems, owing to the presence of sulfur at the active sites of several enzymes, vitamins and proteins. The ability to coordinate sulfur is enhanced for cadmium, whose toxic and carcinogenic properties could be related to strong Cd–S bonds. Moreover chelating sulfur donors are actually under study as antidotes in cadmium poisoning [1, 2]. Zinc and cadmium dihalides form generally 1:2 adducts with monodentate thiocarbonyl donors, as imidazolethiones [3–5], benzoxazole-2-thione [6], thiazoles [7, 8], pyridinethiones [9], dithizone or dithiobiuret derivatives [10, 11]. With *N,N*-diethylbenzenecarbothioamide (L) the complexes $[ML_2X_2]$ have been isolated, in which M = Cd or Zn and X = Br or I. Zinc and cadmium chlorides gave with the same ligand lower stoichiometry species such as $[ZnLCl_2]_2$ and $[Cd_2LCl_4]_2$, whose polymeric nature was inferred on the basis of IR spectra [12]. With either *N,N*-dimethylbenzenecarbothioamide or thiophene-2-thiocarboxamide zinc halides formed 1:2 adducts, whereas a 1:1 stoichiometry was preferred in cadmium halide complexes [13, 14]. Cadmium iodide yielded either 1:1 or 1:2 adducts with benzenecarbothioamide. The crystal structure of the 1:2 complex showed a distorted tetrahedral arrangement around the cadmium atom, as for the $[Cd(ethylenetrithiocarbonate)_2I_2]$ complex [15, 16], whereas the cadmium dichloride–thioacetamide (TA) 1:1 complex consisted of infinite chains of $[Cd_2(TA)_2Cl_4]$ units linked by chlorine bridges so that each cadmium atom presented an octahedral environment [17]. Proton NMR data in dimethyl sulfoxide supported total decomposition of the zinc and cadmium trithiocarbonate adducts, whereas the analogous thioamide complexes were stable in this solvent.

Recently we have reported platinum(II), palladium(II) and mercury(II) halide complexes with 2,6-dimethyl-4*H*-pyran-4-thione (DMTP), a ligand in which the aromatic character of the ring influences the donor ability of the thiocarbonyl group. Complexes of general formula $[M(DMTP)_2X_2]$ (M = Pd, Pt or Hg; X = halide) were isolated, in which the ligand acts as a strong sulfur donor [18, 19]. Only with mercury salts were 1:1 species

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*Author to whom correspondence should be addressed.

**On leave from the Department of Basic Courses, Agricultural University of Hebei, Baoding, China.

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obtained, whose IR spectra suggested a dimeric structure through halide bridges [19]. It was then worthwhile examining the behaviour of zinc(II) and cadmium(II) halides towards such a ligand.

This paper reports the synthesis and characterization of the complexes $[M(DMTP)_2X_2]$ and $[M(DMTP)X_2]_n$ (M = Cd or Zn; X = halide) along with the X-ray structure data of $[Zn(DMTP)_2Cl_2]$.

Experimental

DMTP (C_7H_8OS, 2,6-dimethyl-4*H*-pyran-4-thione) was prepared by adding P_2S_5 to a solution of 2,6-dimethyl-4*H*-pyran-4-one in anhydrous benzene (molar ratio 1:1). The reaction went on slowly (12 h) at room temperature, yielding an orange solution. By operating in benzene under reflux, as suggested in ref. 20, the yield lowered owing to the formation of brown sticky products. The benzene solution was stirred with water, then it was separated, dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude product was recrystallized from i-PrOH (yield 50%). Anhydrous zinc and cadmium dihalides were Janssen products. $CdBr_2 \cdot 4H_2O$ (Fluka) was dehydrated by heating at *c.* 60 °C under reduced pressure. The thermograms of the hydrated salt indicated that water is evolved in the 30–130 °C temperature interval, the related endothermic peak being observed at 46 °C.

Preparation of $[M(DMTP)_2X_2]$ (M = Cd or Zn; X = halide)

The zinc adducts were prepared by adding DMTP (1.8 mmol) to a solution of the appropriate zinc halide in acetone (0.7 mmol in *c.* 3 cm^3; reaction time, 2 h). The pink solids were filtered, washed with acetone and n-pentane and dried *in vacuo*. Yield 80–90%. The $[Cd(DMTP)_2X_2]$ (X = Br or I) complexes were isolated by reaction of cadmium halide and ligand (molar ratio 1:2.2) either in acetone or in ethanol, whereas $[Cd(DMTP)_2Cl_2]$ was prepared by adding solid $CdCl_2$ (0.6 mmol) to an acetone solution of DMTP (3.5 mmol in 4 cm^3) with stirring overnight. The pink yellowish solids were filtered, washed with n-pentane and dried *in vacuo*.

Preparation of $[M(DMTP)X_2]_n$ (M = Zn or Cd; X = halide)

The pink complexes $[Zn(DMTP)X_2]_n$ (X = Br or I) were prepared by adding dropwise a 1,2-dichloroethane solution of DMTP (1mmol in 2 cm^3) to a ZnX_2 suspension in the same solvent (1 mmol in 4 cm^3). After stirring overnight the product was filtered, washed with dichloroethane and n-pentane and dried *in vacuo*. The reaction of $ZnCl_2$ and ligand (molar ratio 1:1) in acetone, ethanol, methylene chloride or dichloroethane always yielded a mixture of low stoichiometry unidentified species and the 1:2 adduct. The complexes $[Cd(DMTP)X_2]_n$ (X = Cl or I) were obtained by prolonged stirring (18 h) of cadmium salt and ligand (molar ratio 1:1) in dichloroethane. In the same conditions cadmium bromide reacted with ligand to give mixture of 1:1 and 1:2 species, whereas in acetone or methanol the pure 1:2 complexes separated.

The prepared complexes are listed in Table 1.

Measurement

IR spectra were registered by using either a Perkin-Elmer 580B spectrophotometer (4000–400 cm^{-1}) or a Bruker FT-IR instrument (500–100 cm^{-1}) as nujol mulls between KBr and polyethylene discs. ^{1}H NMR spectra were obtained with a Jeol FX 90Q spectrometer. Melting points (uncorrected) were determined by a Buchi apparatus.

X-ray data

A crystal of maximum dimension 0.2 mm was used for the analysis. Data collection was made with Mo Kα radiation on a Philips PW 1100 diffractometer. Cell dimensions were determined by least-squares refinement of 25 medium angle settings. Crystal and intensity data are reported in Table 2. The crystals are stable under irradiation. Solution of the structure was achieved by Patterson and Fourier methods, alternated with cycles of full-matrix least-squares refinement of the atomic parameters. The H atoms were introduced in calculated positions with fixed C–H distances and temperature factors (C–H = 0.96; $U_{iso} = 0.082$ A^2). Anisotropy was introduced for all non-hydrogen atoms. Refinement of scale factor, positional and thermal parameters was proceeded by minimizing the function $\Sigma w(\Delta F)^2$ with $w = 1$. At convergence the largest shift on the refined parameters was 0.1 times the standard deviation. No significant residuals of electronic density were observed in the final electron density map. Form factors for the atoms were supplied internally by the SHELX program system [22].

Final atomic parameters are listed in Table 3; bond distances and angles are reported in Table 4.

Results and discussion

The complexes $[M(DMTP)_2X_2]$ (M = Zn or Cd; X = halide; Table 1) were generally prepared by reaction of the appropriate metal salt with DMTP in acetone at molar ratio 1:2.2. Conversely the synthesis of $[Cd(DMTP)_2Cl_2]$ required a large ligand excess (*c.* 1:6), otherwise mixtures of 1:1 and 1:2 species were isolated. The 1:1 adducts were obtained by prolonged stirring

TABLE 1. Analyses[a] and selected IR absorptions

Compound	m.p.[b]	C (%)	H (%)	Wavenumbers (cm^{-1})		
$[Zn(DMTP)_2Cl_2]$[c]	225–226	40.08 (40.35)	3.96 (3.87)	1638s, 1625s	1545m	1105m
$[Zn(DMTP)_2Br_2]$[c]	220–221	33.14 (33.26)	3.24 (3.19)	1640sh,1628sbr	1544m	1105m
$[Zn(DMTP)_2I_2]$[c]	207–209	27.88 (28.04)	2.70 (2.69)	1640sh,1626sbr	1543m	1104m
$[Zn(DMTP)Br_2]_n$[d]	182–183	23.28 (23.01)	2.30 (2.21)	1630s	1542m	1103m
$[Zn(DMTP)I_2]_n$[d]	184–185	17.98 (18.30)	1.77 (1.76)	1622s	1539m	1005m
$[Cd(DMTP)_2Cl_2]$[e]	[f]	36.09 (36.26)	3.54 (3.48)	1638s,1627sh	1546m	1008m
$[Cd(DMTP)_2Br_2]$[e]	219–220	30.64 (30.43)	3.06 (2.94)	1640s,1630sh	1546m	1004m
$[Cd(DMTP)_2I_2]$[e]	193–194	26.09 (26.00)	2.58 (2.51)	1643sh,1633s	1546m	1003m
$[Cd(DMTP)Cl_2]_n$[g]	[f]	25.95 (25.99)	2.60 (2.49)	1646s	1563m 1546sh	1105m
$[Cd(DMTP)I_2]_n$[g]	144–145	16.55 (16.60)	1.60 (1.59)	1642s	1548m	1103m

[a]Calculated values in parentheses. [b]With decomposition. [c]General formula $C_{14}H_{16}X_2O_2S_2Zn$ (X = halide). [d]General formula $C_7H_8X_2OSZn$. [e]General formula $C_{14}H_{16}CdX_2O_2S_2$. [f]Long decomposition interval around 200 °C. [g]General formula $C_7H_8CdX_2OS$.

TABLE 2. Crystal and intensity data

Formula	$C_{14}H_{16}Cl_2O_2S_2Zn$
Formula weight	416.7
a (Å)	7.955(6)
b (Å)	8.599(6)
c (Å)	14.098(5)
α (°)	92.12(3)
β (°)	110.96(3)
γ (°)	108.60(3)
V (Å^3)	897.3(2)
D_c (g/cm^3)	1.54
Molecules/cell	2
Space group	$P\bar{1}$
Crystal system	triclinic
F(000)	436
μ(Mo Kα) (cm^{-1})	18
Scan method	$\theta/2\theta$
θ_{max} (°)	50
Scan speed (°/min)	2
Recorded intensities	5392
Observed intensities	2073
Wavelength (Mo Kα) (Å)	0.7107
Corrections	Lp, absorption [21]
w ($\sigma^2(F)+0.003116\ F^2$)	1.2524
Final R factor	0.060
Final R_w factor	0.065

TABLE 3. Atomic coordinates and temperature factors (×100)

Atom	x/a	y/b	z/c	U_{eq}[a]
Zn1	0.0972(1)	0.1892(1)	0.2727(1)	4.25(4)
Cl1	−0.2068(2)	0.0996(3)	0.2980(1)	5.46(8)
Cl2	0.2300(3)	0.4249(2)	0.1860(2)	5.33(7)
S1	0.1608(3)	0.1793(3)	0.4283(2)	6.05(9)
S2	0.1631(3)	−0.0448(3)	0.2004(2)	5.36(8)
C1	0.3829(10)	0.2652(10)	0.4313(6)	4.4(3)
C2	0.4527(11)	0.2188(10)	0.5066(6)	4.9(3)
C3	0.6303(12)	0.2929(12)	0.5130(6)	5.2(3)
O1	0.7401(7)	0.4079(7)	0.4491(4)	5.4(2)
C4	0.6788(10)	0.4557(10)	0.3758(6)	5.1(3)
C5	0.5057(10)	0.3861(9)	0.3648(6)	4.4(3)
C6	0.7168(15)	0.2525(16)	0.5886(7)	7.6(5)
C7	0.8238(11)	0.5808(13)	0.3134(7)	6.8(4)
C8	0.3852(9)	−0.0015(9)	0.1536(5)	4.1(3)
C9	0.5052(9)	0.1577(9)	0.1300(5)	3.9(2)
C10	0.6783(10)	0.1794(10)	0.0874(5)	4.4(3)
O2	0.7439(7)	0.0528(7)	0.0682(4)	4.6(2)
C11	0.6355(11)	−0.1004(10)	0.0924(5)	4.5(3)
C12	0.4607(11)	−0.1314(10)	0.1329(6)	4.7(3)
C13	0.8213(10)	0.3366(11)	0.0579(7)	6.2(4)
C14	0.7306(13)	−0.2238(13)	0.0664(7)	6.5(4)

[a]U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

of metal halide suspensions in 1,2-dichloroethane solutions of ligand (molar ratio 1:1). In most cases 1:2 species were formed at first, which successively reacted with the residual salt to give the 1:1 complexes, whose purity was tested by IR spectra. When the metal salt was either zinc chloride or cadmium bromide, the formation of the 1:1 adduct was evident, but samples were always impure for metal salt or 1:2 species.

The IR spectrum of DMTP contains a strong absorption at 1641 cm^{-1}, assigned to ν(C=C) [23]. The bands at 1559, 1440, 1377, 1277 and 934 cm^{-1} are due to ring vibrations whereas the ν(C=S) absorption falls

TABLE 4. Bond distances (Å) and angles (°)

Zn–Cl(1)	2.253(2)	Zn–S(1)	2.352(2)
Zn–Cl(2)	2.247(2)	Zn–S(2)	2.383(2)
S(1)–C(1)	1.692(8)	S(2)–C(8)	1.689(7)
C(1)–C(2)	1.41(1)	C(8)–C(9)	1.41(1)
C(2)–C(3)	1.37(1)	C(9)–C(10)	1.35(1)
C(3)–O(1)	1.33(1)	C(10)–O(2)	1.35(1)
C(3)–C(6)	1.48(1)	C(10)–C(13)	1.48(1)
O(1)–C(4)	1.35(1)	O(2)–C(11)	1.34(1)
C(4)–C(7)	1.47(1)	C(11)–C(14)	1.49(1)
C(4)–C(5)	1.35(1)	C(11)–C(12)	1.34(1)
C(5)–C(1)	1.41(1)	C(12)–C(8)	1.42(1)
Cl(1)–Zn–Cl(2)	115.3(1)	S(1)–Zn–S(2)	102.2(1)
Cl(1)–Zn–S(1)	103.3(1)	Cl(2)–Zn–S(1)	117.8(1)
Cl(1)–Zn–S(2)	100.8(1)	Cl(2)–Zn–S(2)	115.2(1)
Zn–S(1)–C(1)	112.5(3)	Zn–S(2)–C(8)	111.6(3)
C(1)–C(2)–C(3)	119.8(8)	C(8)–C(9)–C(10)	120.0(7)
C(2)–C(3)–O(1)	121.5(7)	C(9)–C(10)–O(2)	122.3(7)
C(3)–O(1)–C(4)	120.6(6)	C(10)–O(2)–C(11)	119.5(6)
O(1)–C(4)–C(5)	120.8(8)	O(2)–C(11)–C(12)	121.4(7)
C(4)–C(5)–C(1)	120.9(7)	C(11)–C(12)–C(8)	121.0(7)
C(5)–C(1)–C(2)	116.4(7)	C(12)–C(8)–C(9)	115.7(6)

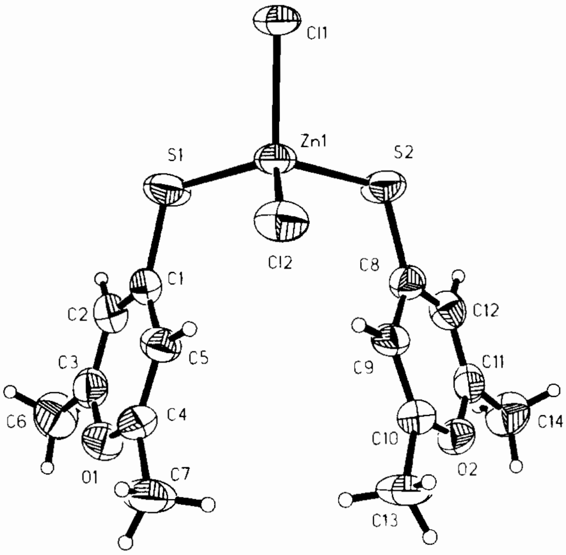

Fig. 1. The molecular structure of [Zn(DMTP)$_2$Cl$_2$].

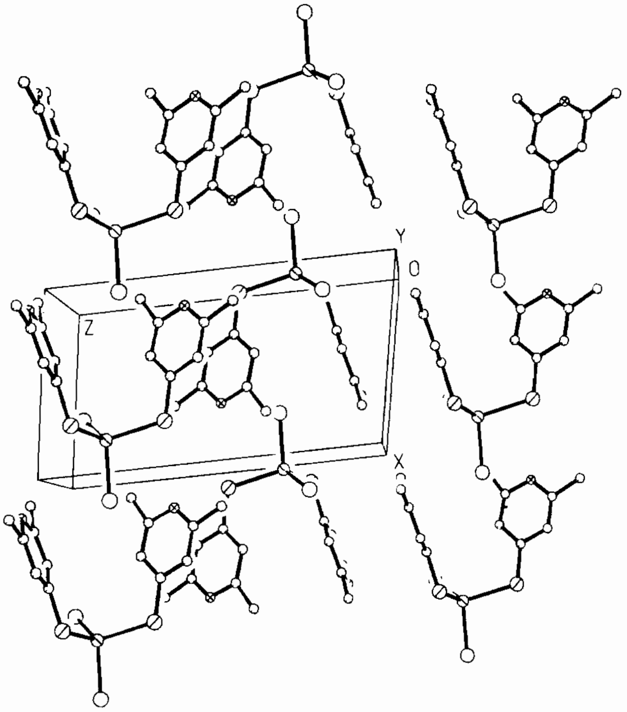

Fig. 2. View of the crystal packing showing ring to ring interactions.

at 1095 cm^{-1}. The ν(C=C) absorption is nearly unchanged in the cadmium 1:1 adducts and it shifts to low energy in the zinc analogues (Table 1), as observed for platinum, palladium and mercury complexes [18, 19]. The fact that the 1:2 complex spectra contain two close ν(C=C) absorptions could suggest a different situation in the coordinated DMTP molecules. The ν(C=S) absorption undergoes a small high energy shift, of the order of 10 cm^{-1}, whereas an opposite shift is observed for the ring absorption at 1559 cm^{-1}. The X-ray crystal structure data indicate that [Zn(DMTP)$_2$Cl$_2$] is a molecular complex in which the metal ion is four-coordinate in a rather distorted tetrahedral environment. The two neutral ligands make with the ZnCl$_2$ plane angles of 28 and 37°, respectively, and are roughly symmetric with respect to this plane, which can therefore be considered as a pseudo mirror, as shown in Fig. 1. In this way the ring H atoms bonded to C(5) and C(9) make with Cl(2) two contacts of 2.7 and 2.6 Å, respectively, which are shorter than the van der Waals approach of 3.0 Å, suggesting that some sort of weak hydrogen bond could exist between H and Cl. The Cl–Zn–Cl angle (115.3°) involving the highly electronegative Cl atoms is significantly larger than S–Zn–S (102.2°), which is likely due to stronger repulsion between the Cl than between the S atoms. Moreover, probably as a consequence of the asymmetry of the organic ligands, the Cl(1)–Zn–S angles (103.3 and 100.8°) are smaller than the corresponding Cl(2)–Zn–S ones (117.8 and 115.2°). The Zn–Cl bond lengths are normal being only slightly shorter than normally found in a series of [ZnCl$_4$]$^{2-}$ ions (2.26–2.27 Å) [24], while the Zn–S bond lengths are of the same order as found in [Zn(thiourea)$_2$Cl$_2$] (2.35(2) Å) [25]. Corresponding structural details of the rings compare very favourably and confirm the strong aromaticity of these heterocycles. The C=S bonds are essentially double in character, their lengths (mean 1.69 Å) being comparable with those found in thiourea and thioacetamide (1.71(1) Å). As shown in Figs. 2 and 3 both rings of each molecule are parallel to rings of adjacent molecules with whom they have graphite-like contacts at distances of 3.54

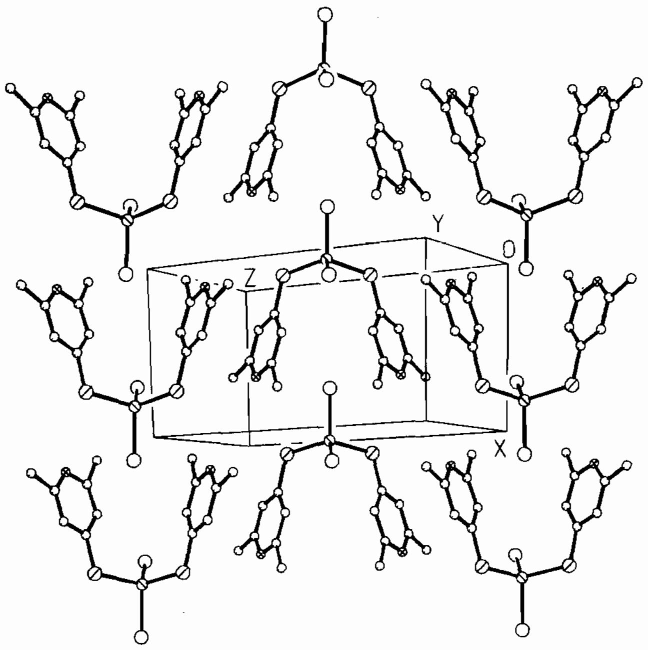

Fig. 3. Another view of crystal packing.

and 3.47 Å. This provides compactness and stability to the compound and seems to be the only relevant van der Waals interaction present in the crystal packing.

The IR spectra of the 1:2 zinc complexes (Table 5; Fig. 4) contain two bands which can be assigned to metal halide bond vibrations. The related wavenumbers have been selected by comparison with the spectra of the $[M(DMTP)_2X_2]$ (M = Pd or Pt) complexes, whose square plane geometry clearly originates different metal halide absorptions, whereas the coordinated ligand bands at *c.* 470, 430, 340, 280, 200 and 160 cm^{-1} are almost unchanged. In accordance with the structural data, the $[Zn(DMTP)_2Cl_2]$ spectrum shows the zinc–chlorine bands at 300 and 276 cm^{-1}, due to the symmetric and asymmetric vibration modes in a distorted tetrahedral arrangement. The IR data support a similar geometry in the $[Zn(DMTP)X_2]_n$ (X = Br or I) complexes, the zinc–halide band separation being in the range of 30 cm^{-1}, as observed for a number of thiocarbonyl analogues [3, 4, 6–8, 10–13]. A similar behaviour was found for the distorted tetrahedral $[Zn(L)X_2]$ complexes, in which L is a bidentate ligand such as 2,2-dimethylpropane-1,3-diamine (X = Cl, 320 and 276 cm^{-1}; X = Br, 226 and 213 cm^{-1}) [26], dimethyldithiooxamide (X = Cl, 307 and 289 cm^{-1}; X = Br, 242 and 233 cm^{-1}) [27, 28] or dithiomalonamide [29]. As a general trend, cadmium is octahedrally coordinated in 1:2 chloride or bromide complexes through halide bridges [26, 27, 30, 31], whereas the iodo analogues have a tetrahedral configuration [15, 16]. In the 2,2-dimethylpropane-1,3-diamine (L) complexes $[Cd(L)X_2]$ (X = Cl or Br) the cadmium atom is octahedrally coordinated by four halide atoms, the related terminal and bridging halide bands being observed at 257 and 170 cm^{-1} (Cl) and at 186 and 146 cm^{-1} (Br) [26]. In the parent dithiooxamide adducts these bands fall at 203 and 160 cm^{-1} (Cl) and 149 and 117 cm^{-1} (Br) [30], in both cases well below the frequencies observed for $[Cd(DMTP)_2X_2]$ (Cl, 272 and 257 cm^{-1}; Br, 194 and 177 cm^{-1}; Table 5). Moreover the DMTP complexes present the highest frequency values for cadmium–halide vibrations among the 1:2 cadmium halide adducts with thiocarbonyl donors [4, 6–8, 10, 12]. All these facts support a tetrahedral arrangement for the $[Cd(DMTP)_2X_2]$ complexes, assisted probably by the ligand intrinsic properties, which could prevent the formation of halide bridges through ring hydrogen contacts with halides. The zinc–halide absorption values in the zinc–DMTP 1:1 adducts are in favour of a dimeric structure by halide bridges, like those in the tri-*tert*-butylphosphine analogues [32]. Accordingly the higher frequency Zn–Br absorption in the spectrum of $[Zn(DMTP)Br_2]_n$ (238 cm^{-1}), due to stretching of terminal bonds, is comparable with the high energy band in the tetrahedral $[Zn(DMTP)_2Br_2]$ complex, whereas the lower energy absorption at 184 cm^{-1} can be assigned

TABLE 5. IR absorptions (470–100 cm^{-1})[a]

Compound	Wavenumbers (cm^{-1})										
$[Zn(DMTP)_2Cl_2]$	466w	422m	307sh	*300*s	*276*s			207mw		170mw	151vvw	123sbr
$[Zn(DMTP)_2Br_2]$	466w	420m	305w	295w	276w	*229*ms		208sh	*201*m	170mw		
$[Zn(DMTP)_2I_2]$	476w	419m	306w	296w	277w			200mw	*189*m	*173*mw[b]	141vvw	
$[Zn(DMTP)Br_2]_n$	466vw	422m	326mw		277w	*238*m	228w	202w	*184*ms	176sh	157w	
$[Zn(DMTP)I_2]_n$	466w	419m	322m		277w			208ms		*172*ms	160w	121m
$[Cd(DMTP)_2Cl_2]$	464w	420m	290sh	283sh	*272*vs	*257*m	216vw	208vw			143vvw	
$[Cd(DMTP)_2Br_2]$	464w	420m	286m		275w			203w	*194*s	*177*m[b]	158vw	
$[Cd(DMTP)_2I_2]$	464w	419m	287shbr		277w			203w	197w	*169*m[b]	150sh	*134*m
$[Cd(DMTP)Cl_2]_n$	465w	426w	293w	281w			218sh		*191*mbr		*156*sbr	132w
$[Cd(DMTP)I_2]_n$	464w	417m	296w	283w				208w		170m	*164*m	130w

[a] Metal–halide frequencies in italics. [b] Tentative assignement.

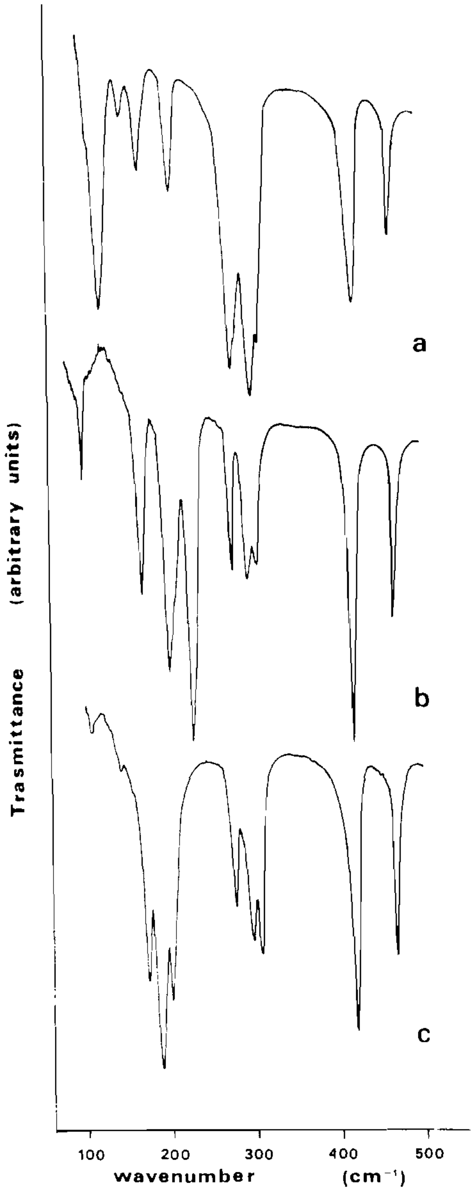

Fig. 4. IR spectra of $[Zn(DMTP)_2X_2]$: (a) X=Cl; (b) X=Br; (c) X=I.

to bridge bond stretchings. Conversely the $[Cd(DMTP)Cl_2]_n$ complex should have a polymeric octahedral configuration, in which all chlorines are bridging atoms, as in the thioacetamide [17], imidazole [33] or pyridine [34] analogues. A dramatic low energy shift of the Cd–Cl absorptions with respect to $[Cd(DMTP)_2Cl_2]$ is in fact observed, in the order of 80–100 cm^{-1}. The $[Cd(DMTP)I_2]_n$ complex, whose spectrum contains one band assignable to Cd–I stretching modes (164 cm^{-1}), close to the high energy corresponding absorption for $[Cd(DMTP)_2I_2]$ (169 cm^{-1}), should be a dimer by iodine bridges.

TABLE 6. ^{1}H NMR data (ppm; *T*, *c*. 27 °C)[a]

Compound	Solvent	CH[b]	CH_3[b]
$[Zn(DMTP)_2Cl_2]$	$(CD_3)_2CO$	7.19	2.33
$[Zn(DMTP)_2Br_2]$	$(CD_3)_2CO$	7.24	2.35
$[Zn(DMTP)_2I_2]$	$(CD_3)_2CO$	7.32	2.38
$[Cd(DMTP)_2Cl_2]$	$(CD_3)_2CO$	7.12	2.31
$[Cd(DMTP)_2Br_2]$	$(CD_3)_2CO$	7.42	2.42
$[Cd(DMTP)_2I_2]$	$(CD_3)_2CO$	7.52	2.46
$[Zn(DMTP)_2Cl_2]$	$CDCl_3$	7.58	2.41
$[Zn(DMTP)_2Br_2]$	$CDCl_3$	7.63	2.46
$[Zn(DMTP)_2I_2]$	$CDCl_3$	7.64	2.43
$[Cd(DMTP)_2Cl_2]$	$CDCl_3$	7.07	2.26
$[Cd(DMTP)_2Br_2]$	$CDCl_3$	7.44	2.37
$[Cd(DMTP)_2I_2]$	$CDCl_3$	7.56	2.43
$[Zn(DMTP)_2Cl_2]$	$(CD_3)_2SO$	6.96	2.23
$[Cd(DMTP)_2Br_2]$	$(CD_3)_2SO$	6.96	2.23
$[Cd(DMTP)_2I_2]$	$(CD_3)_2SO$	6.96	2.23
$[Zn(DMTP)_2Br_2]$	CD_3OD	7.01	2.27
$[Cd(DMTP)_2Br_2]$	CD_3OD	7.01	2.27
$[Cd(DMTP)_2I_2]$	CD_3OD	7.05	2.28
DMTP	$CDCl_3$	6.93	2.18

[a] The complexes are slightly soluble in the reported solvents. In most cases the values refer to saturated solutions. [b] Singlet.

The proton NMR data for the 1:2 complexes in various deuterated solvents are reported in Table 6. The DMTP spectra contain the singlets due to the methyl ($CDCl_3$, 2.18 ppm; $(CD_3)_2SO$, 2.23 ppm) and ring CH ($CDCl_3$, 6.93 ppm; $(CD_3)_2SO$, 6.96) protons. On coordination both signals undergo a downfield shift, the effect being larger for the CH resonance (Δppm, 0.4–0.8 in palladium, platinum and mercury dihalide adducts). The $[M(DMTP)_2X_2]$ complexes (M=Zn or Cd) show an identical behaviour in choloroform, except for $[Cd(DMTP)_2Cl_2]$, whose CH resonance (7.07 ppm), close to that of the free ligand, supports abundant ligand release to form the insoluble 1:1 complex. The complexes decompose immediately in dimethyl sulfoxide, a solvent which removes DMTP totally from the metal coordination sphere. In methanol the complexes release one ligand molecule, the pink solid residue being the corresponding 1:1 complex. A similar slow process occurs in acetone, the effect being more evident for the chloro derivatives. As a general trend, the 1:2 complexes exist in chlorinated hydrocarbons whereas they tend to decompose in donor solvents, showing a lower metal to sulfur bond strength than for mercury analogues.

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