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Complexes of 4,5,6,7-Tetrathiocino[1,2-*b*:3,4-*b*′]diimidazolyl-1,3,8,10-tetraethyl-2,9-dithione (Et_4todit) with Group IIb Metal Halides. Crystal and Molecular Structure of $(Cd(II)Et_4toditCl_2)_n$

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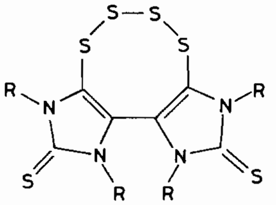
Abstract

The capability of Et_4todit (title ligand) to coordinate through the two C=S groups forced at very distant positions has been used to prepare some new ligand-bridged polymeric complexes, having stoichiometry $M(II)Et_4toditX_2$ (M(II) = Zn, Cd, Hg; X = Cl, Br). IR spectral results show that the ligand binds via thionic sulphur in all isolated compounds, and the low frequency spectrum of $(CdEt_4toditX_2)_n$ gives a different pattern from the rest, which all are very similar and consistent with a tetrahedral stereochemistry.

The X-ray structure of $(CdEt_4toditCl_2)_n$ shows that the crystals are orthorhombic, space group $P2_12_12$, $a = 14.199(4)$, $b = 15.550(4)$, $c = 10.575(3)$ Å, $Z = 4$. Solution and refinement of the structure gave final residuals $R = 0.0461$ and $R_w = 0.0615$ using 1402 observed reflections. Coordination around the metal is trigonal-bipyramidal. Apical sites are occupied by Cl atoms (Cl(1) and Cl(2)). Both bidentate ligand and Cl(2) are bridging to form a polymeric tridimensional structure.

Introduction

We have recently synthesized [1] new molecules of the type



= R_4todit

and are investigating their coordinative properties. When the C=S groups are involved in coordination, their relative position makes the molecule capable of behaving as a bidentate-bridging ligand; consequently it can potentially give a variety of polymers either linear or not.

We have already characterized the $(CuEt_4toditX_2)_n \cdot n$THF (X = Cl, Br) complexes, and the crystal and molecular structure of the Cl derivative has shown that a ligand-bridged polynuclear compound with helicoid chains is formed [2]. The coordination around the metal, involving two Cl atoms and two S-thioamide atoms, is nearer to a square-planar than a tetrahedral stereochemistry. In spite of a 7.601 Å distance between the copper centers, ESR results suggest weak interactions between the metal centers.

In this paper we report the synthesis and characterization of $(M(II)Et_4toditX_2)_n$, where M(II) = Zn, Cd, Hg; X = Cl, Br, and the X-ray structure of the $(CdEt_4toditCl_2)_n$ complex.

Experimental

The Et_4todit ligand was prepared as described previously [1]. The complexes were prepared by adding a solution of the anhydrous metal halogenide in 1:1 MeOH–THF to the required stoichiometric amount of the ligand in the same solvent mixture. The complexes either precipitated immediately (Hg) or during several hours after concentration (Zn, Cd) as ivory or pale yellow microcrystals. The products were washed with 1:1 MeOH–THF and petroleum ether. Since these compounds dissolve in polar organic solvents with decomposition, they are not recrystallizable. Only in the $CdEt_4toditCl_2$ case were satisfactory crystals for crystallographic measurements isolated. Microanalyses were carried out by the Istituto di Chimica Farmaceutica, University of Cagliari. IR spectra were recorded as KBr pellets

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in the 4000–400 cm^{-1} range and polyethylene pellets (400–180 cm^{-1}) by using a Perkin-Elmer model 983 spectrophotometer.

X-ray Crystallography

Crystal structure determination

$C_{14}H_{20}CdN_4Cl_2S_6$, $M = 620.005$, orthorhombic, $a = 14.199(4)$, $b = 15.550(4)$, $c = 10.575(3)$ Å, $U = 2334.9(1.1)$ Å^3 (by least-squares refinements of 29 reflections accurately measured), space group $P2_12_12$, $Z = 4$, $D_c = 1.764$ Mg m^{-3}, $F(000) = 1240$, crystal dimensions 0.03 × 0.17 × 0.18 mm, μ(Cu Kα) = 149.16 cm^{-1}.

Data collection and processing

All diffraction measurements were made on a Siemens AED diffractometer using the Ni-filtered Cu Kα radiation ($\bar{\lambda} = 1.541838$ Å). Observations were collected by the $\theta/2\theta$ scan from $6 < 2\theta < 140°$ for $h = 0$–17, $k = 0$–18, $l = 0$–12 giving 2521 measurements of which 1402 having $I \geqslant 2\sigma(I)$ were considered observed and used in the analysis. Intensity data were corrected for the Lorentz polarization factor, for absorption (maximum and minimum values 1.43182, 0.81559) and extinction (maximum and minimum values 1.07661, 0.99117) following the empirical method of Walker and Stuart [3] using the ABSORB [4] program.

Structure analysis and refinement

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares using anisotropic thermal parameters for all the non-hydrogen atoms. The coordinates of the hydrogen atoms placed at their geometrically calculated positions were not refined, but introduced in the final structure factor calculation with fixed isotropic thermal parameters ($U = 0.0974$ Å^2). To define the absolute configuration of the atomic arrangement in the structure, a complete refinement was carried out assuming the centrosymmetric $\bar{x}\bar{y}\bar{z}$ coordinates for all the atoms [$R_w(xyz) = 0.0615$; $R_w(\bar{x}\bar{y}\bar{z}) = 0.0820$]. Applying Hamilton's significance test [5], the ratio $R_w(\bar{x}\bar{y}\bar{z})/R_w(xyz)$ was calculated as 1.3333, while the theoretical value, for 1402 independent F_o and 245 variables, at the half-percent confidence level, is $\mathcal{R}_{1,1157,0.005} = 1.0034$. So the xyz atomic coordinates of Table 1 correspond to the correct absolute configuration. The refined variables were 245 and the weighting scheme used in the final cycles was $w = 0.1797/[\sigma^2(F_o) + 0.011936F_o^2]$. Final R and R_w values were 0.0461 and 0.0615 respectively; the maximum shift/e.s.d. was 0.14 and the minimum and maximum heights in the final difference map were −0.67 and 0.83 e Å^{-3} respectively.

TABLE 1. Fractional atomic coordinates (×10^4) and thermal parameters (Å^2 × 10^4)^a of non-hydrogen atoms

	x/a	y/b	z/c	U_{eq} ^{a}
Cd	1136(1)	4326(1)	3977(1)	384(3)
Cl(1)	2863(3)	4520(3)	4311(4)	509(17)
Cl(2)	−746(3)	4145(3)	3356(5)	492(14)
S(11)	687(3)	3853(3)	6268(4)	415(14)
S(21)	3670(3)	5148(3)	8961(6)	649(18)
S(31)	3258(5)	4846(4)	10799(6)	852(25)
S(12)	6492(3)	2115(3)	7178(5)	410(13)
S(22)	3655(4)	2797(4)	10508(5)	662(20)
S(32)	4124(5)	3899(5)	11387(5)	902(29)
N(11)	2460(8)	3329(8)	6985(12)	289(42)
N(21)	2109(9)	4621(9)	7601(14)	380(45)
N(12)	4784(9)	2925(9)	7148(13)	355(47)
N(22)	5185(8)	2418(8)	8943(13)	342(40)
C(11)	1772(12)	3942(9)	6894(16)	324(49)
C(21)	3009(11)	4435(12)	8070(18)	415(55)
C(31)	3212(13)	3624(11)	7669(15)	385(54)
C(41)	2375(12)	2466(10)	6427(15)	361(50)
C(51)	1898(15)	1833(11)	7288(18)	517(67)
C(61)	1574(12)	5441(9)	7764(17)	391(53)
C(71)	1883(14)	6082(11)	6755(21)	558(71)
C(12)	5462(12)	2499(11)	7753(18)	409(50)
C(22)	4306(11)	2800(11)	9086(18)	409(53)
C(32)	4055(10)	3135(11)	7986(15)	345(52)
C(42)	4798(13)	3149(12)	5779(18)	495(67)
C(52)	5394(16)	3892(15)	5526(23)	805(92)
C(62)	5688(14)	1972(12)	9981(18)	516(71)
C(72)	5468(18)	994(15)	9903(21)	807(98)

$^aU_{eq}$ = 1/3 trace $\tilde{U}$.

Scattering factors were taken from tabulation in ref. 6. Data reduction, structure solution and refinement were carried out on a CRAY X-MP/12 computer of the Centro di Calcolo dell'Italia Nord-Orientale, Bologna and on a Gould-SEL 32/77 of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, using the SHELX-76 system of computer programs [7] and the programs PARST [8], PLUTO [9] and ORTEP [10]. Final atomic coordinates are in Table 1, bond distances and angles in Table 2. See also 'Supplementary Material'.

Results and Discussion

The complexes were obtained by reacting anhydrous metal(II) halides (Zn, Cd, Hg) with Et_4todit in THF/MeOH solutions. The elemental analyses are in accordance with a (MEt_4toditX_2) formulation (see Table 3).

Because of the properties of these compounds (low solubility, non informative visible spectra), the infrared spectroscopy has been conveniently used in order to attribute the mode of binding of the ligand and the stereochemistry of the complexes. The most significative bands, together with their attributions are reported in Table 4.

TABLE 2. Bond distances (A) and angles (°) with e.s.d.s in parentheses

Coordination around metal

Cd–Cl(1)	2.496(5)	Cl(1)–Cd–S(12″)	88.8(2)
Cd–Cl(2)	2.766(5)	Cl(2)–Cd–S(11)	87.5(2)
Cd–S(11)	2.611(5)	Cl(2)–Cd–Cl(2′)	79.8(2)
Cd–Cl(2′)	2.528(5)	Cl(2)–Cd–S(12′)	89.4(2)
Cd–S(12″)	2.602(5)	S(11)–Cd–Cl(2′)	116.9(2)
Cl(1)–Cd–Cl(2)	174.3(2)	S(11)–Cd–S(12″)	103.9(2)
Cl(1)–Cd–S(11)	98.2(2)	Cl(2′)–Cd–S(12″)	136.9(2)
Cl(1)–Cd–Cl(2′)	98.0(2)		

Ligand molecule

	$i = 1, j = 2$	$i = 2, j = 1$
S(2i)–S(3i)	2.083(9)	2.060(9)
S(31)–S(32)	2.017(10)	
S(1i)–C(1i)	1.68(2)	1.69(2)
S(2i)–C(2i)	1.73(2)	1.77(2)
N(1i)–C(1i)	1.37(2)	1.33(2)
N(1i)–C(3i)	1.37(2)	1.40(2)
N(1i)–C(4i)	1.47(2)	1.49(2)
N(2i)–C(1i)	1.38(2)	1.32(2)
N(2i)–C(2i)	1.40(2)	1.39(2)
N(2i)–C(6i)	1.49(2)	1.48(2)
C(2i)–C(3i)	1.36(3)	1.32(2)
C(31)–C(32)	1.46(2)	
C(4i)–C(5i)	1.50(2)	1.46(3)
C(6i)–C(7i)	1.52(3)	1.55(3)
S(3i)–S(2i)–C(2i)	102.2(7)	102.3(6)
S(2i)–S(3i)–S(3j)	106.3(4)	105.7(4)
C(1i)–N(1i)–C(3i)	111.1(1.3)	110.2(1.4)
C(1i)–N(1i)–C(4i)	123.3(1.2)	125.0(1.4)
C(3i)–N(1i)–C(4i)	125.6(1.3)	124.8(1.3)
C(1i)–N(2i)–C(2i)	110.5(1.4)	109.2(1.4)
C(1i)–N(2i)–C(6i)	122.6(1.3)	127.2(1.4)
C(2i)–N(2i)–C(6i)	126.8(1.4)	123.5(1.4)
S(1i)–C(1i)–N(1i)	128.6(1.2)	128.9(1.4)
S(1i)–C(1i)–N(2i)	126.4(1.2)	124.4(1.3)
N(1i)–C(1i)–N(2i)	104.3(1.3)	106.8(1.4)
S(2i)–C(2i)–N(2i)	123.7(1.4)	124.2(1.4)
S(2i)–C(2i)–C(3i)	130.4(1.4)	127.5(1.3)
N(2i)–C(2i)–C(3i)	105.9(1.4)	108.3(1.4)
N(1i)–C(3i)–C(2i)	108.1(1.5)	105.4(1.3)
N(1i)–C(3i)–C(3j)	126.0(1.5)	125.7(1.4)
C(2i)–C(3i)–C(3j)	125.9(1.5)	129.0(1.5)
N(1i)–C(4i)–C(5i)	113.1(1.3)	111.8(1.6)
N(2i)–C(6i)–C(7i)	109.3(1.4)	108.8(1.5)

Key to symmetry operations: $' = -x,\ 1 - y,\ z$; $'' = x - \frac{1}{2},\ \frac{1}{2} - y,\ 1 - z$.

TABLE 3. Analytical data for M(II)Et_4toditX_2 complexes

Complex	Analysis (%)						Colour
	Found			Calculated			
	C	H	N	C	H	N	
ZnEt_4toditCl_2	27.62	3.42	9.14	29.35	3.52	9.78	ivory
ZnEt_4toditBr_2	25.43	2.93	8.29	25.40	3.04	8.46	ivory
CdEt_4toditCl_2	27.31	3.35	8.80	27.12	3.25	9.04	pale yellow
CdEt_4toditBr_2	24.40	2.20	8.03	23.72	2.84	7.90	pale yellow
HgEt_4toditCl_2	23.22	2.47	8.18	23.74	2.85	7.91	ivory
HgEt_4toditBr_2	20.94	2.04	6.79	21.09	2.53	7.03	ivory

TABLE 4. Selected IR absorptions of ligand and complexes, ν (cm^{-1}), X = Cl or Br

Compound	ν(CN)	ν(CS)	ν(MX)	ν(MS)
Et_4todit	1435s	821m 810s		
ZnEt_4toditCl_2	1455s 1445s	818m 808s	315vs	237ms
ZnEt_4toditBr_2	1453s 1443s	815sh 808s	235vs	covered
CdEt_4toditCl_2	1446s 1439s	802s	265sh 237s	206s
CdEt_4toditBr_2	1443s	802s	202s	206s
HgEt_4toditCl_2	1455s 1443m	803s	265s	240s
HgEt_4toditBr_2	1450s	802s	190m	238br

Even though the absorptions at 1435 and 810 cm^{-1} associated with ν(CN) and ν(CS) stretching cannot be considered pure vibration modes, a simultaneous shift of ν(CN) to higher and of ν(CS) to lower wavenumbers is very likely indicative of an S-thioamide binding, in accordance with spectral studies, often supported by X-ray results, carried out by us [11–15] and others [16] on several complexes in which similar ligands are S-thioamide coordinated. The modest shift of the above discussed bands in the CdX_2 derivatives is in accordance with the X-ray results (see below) showing, *inter alia*, that the bond distances of the free ligand are slightly modified by coordination. Similar behaviour has been observed in Et_4todit·$2I_2$ [17] and $(CuEt_4toditCl_2)_n \cdot n$THF [2].

In the low frequency range new bands appear upon coordination. The ones which do not change in the corresponding Cl and Br derivatives are attributed to ν(MS), while those changing on passing from Cl to Br derivatives are attributed to the metal halogen vibrations.

Interestingly the low IR spectrum of the $CdCl_2$ complex shows a different spectral pattern from those of the other complexes studied, which are instead very similar (see as an example Fig. 1) and show metal–halogen bands in the range expected for a tetrahedral stereochemistry [18–20].

The low value observed for ν(CdCl) is not consistent with a tetrahedral stereochemistry. In fact

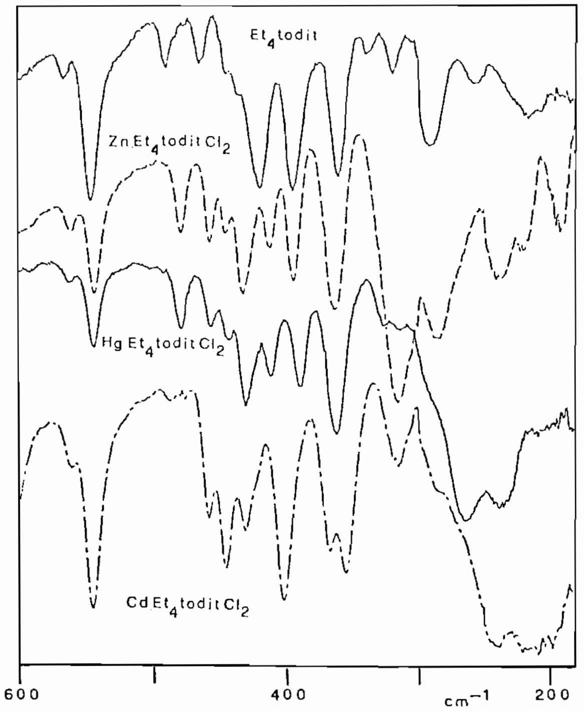

Fig. 1. Low frequency IR spectra in polyethylene pellets of Et_4todit, $ZnEt_4toditCl_2$, $CdEt_4toditCl_2$ and $HgEt_4toditCl_2$.

the X-ray results on the $(CdEt_4toditCl_2)_n$ complex (see below) show surprisingly that its stereochemistry is trigonal-bipyramidal and both ligand and one halogen atom are bridging. The whole structure (Fig. 2) consists of a three dimensional network of distorted trigonal-bipyramidal complexes held together by bridges of Cl(2) anions and organic molecules through the two C(S) groups forced in very distant positions. Coordination around the metal involves the two independent Cl atoms, which occupy the two axial positions, and in the equatorial coordination plane two S atoms of the C=S group of two ligand molecules related by a screw axis and the Cl(2) atom generated by a two-fold axis. The metal results −0.217(2) Å out of the equatorial plane toward Cl(1). The Cd–S distances [2.602(5) and 2.611(5) Å] are normal. The Cd–Cl(1) distance [2.496(5) Å] is appropriate for a Cd–Cl single bond and the chlorine bridges are asymmetric, the value for $Cd–Cl(2)_{ax}$ [2.766(5) Å] being comparable with the sum of the ionic radii [2.78 Å] and that of $Cd–Cl(2)_{eq}$ shortened by 0.2 Å [2.528(5) Å]. The geometry of the organic molecule is in good agreement with that observed in the uncomplexed molecule [1], in its bis-diiodine adduct [17] and in its complex with $CuCl_2$ [2]. In particular we observe the presence of a pseudo two-fold axis, the planarity

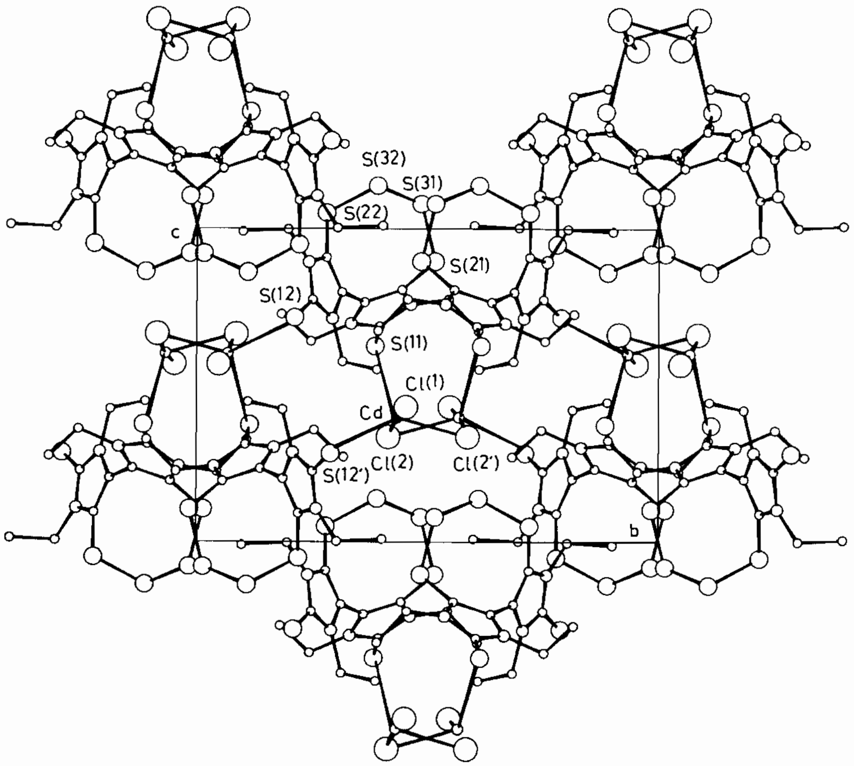

Fig. 2. Projection of the structure along |100|.

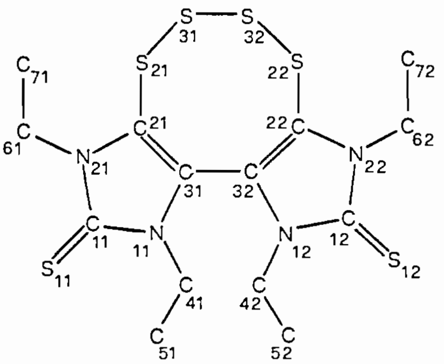

Fig. 3. Non-hydrogen atoms numbering scheme in Et$_4$todit.

of the imidazoline rings, whose orientation [N(11)–C(31)–C(32)–N(12) 74(2)°] is determined by the perpendicular and mutually opposite disposition of the ethyl groups with respect to the corresponding ring plane [C(1*i*)–N–C–C (*i* = 1 or 2) in the range −79(2)°–93(2)°] and the chair conformation for the eight-membered ring. The numbering scheme is given in Fig. 3.

Supplementary Material

Additional data available from the Cambridge Crystallographic Data Center comprises H atom coordinates, thermal parameters, and observed and calculated structure factors.

References

1 F. Bigoli, M. A. Pellinghelli, D. Atzei, P. Deplano and E. F. Trogu, *Phosphorus Sulfur, 37* (1988) 189.
2 D. Atzei, F. Bigoli, P. Deplano, M. A. Pellinghelli, A. Sabatini, E. F. Trogu and A. Vacca, *Can. J. Chem.*, (1989) submitted for publication.
3 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158.
4 F. Ugozzoli, *Comput. Chem., 11* (1987) 109.
5 W. C. Hamilton, *Acta Crystallogr., 18* (1965) 502.
6 *International Tables for X-ray Crystallography,* Vol. 4, Kynoch Press, Birmingham, 1974, pp. 99, 149.
7 G. Sheldrick, *SHELX-76,* a program for crystal structure determination, University of Cambridge, 1976.
8 M. Nardelli, *Comput. Chem., 7* (1983) 95.
9 W. D. S. Motherwell, *PLUTO*, University of Cambridge, 1976.
10 C. K. Johnson, *ORTEP, Report ORNL-3794,* revised, Oak Ridge National Laboratory, TN, 1965.
11 P. Deplano and E. F. Trogu, *Inorg. Chim. Acta, 61* (1982) 261.
12 G. Crisponi, P. Deplano and E. F. Trogu, *Inorg. Chim. Acta, 75* (1983) 135.
13 G. Crisponi, P. Deplano, V. Nurchi and E. F. Trogu, *Polyhedron, 3* (1984) 1241.
14 D. Atzei, F. Bigoli, P. Deplano, M. A. Pellinghelli, E. F. Trogu and A. Vacca, *Can. J. Chem., 66* (1988) 1483.
15 D. Atzei, P. Deplano and E. F. Trogu, *Transition Met. Chem., 14* (1989) 287.
16 E. S. Raper, *Coord. Chem. Rev., 61* (1985) 115, and refs. therein.
17 D. Atzei, F. Bigoli, P. Deplano, M. A. Pellinghelli, A. Sabatini, E. F. Trogu and A. Vacca, *Can. J. Chem., 67* (1989) 1416.
18 J. R. Ferraro, *Low Frequency Vibrations of Inorganic and Coordination Compounds,* Plenum, New York, 1971.
19 Y. Saito, M. Cordes and K. Nakamoto, *Spectrochim. Acta, Part A, 28* (1972) 1459.
20 W. L. Stefan and G. J. Palenik, *Inorg. Chem., 16* (1977) 1119.