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Synthesis and characterization of the complexes $[Cu(II)(Et_4todit)X_2]_n \cdot n$THF ($Et_4$todit = 4,5,6,7-tetrathiocino[1,2-*b*:3,4-*b'*]-diimidazolyl-1,3,8,10-tetraethyl-2,9-dithione; X = Cl, Br). Crystal and molecular structure of $[Cu(II)(Et_4todit)Cl_2]_n \cdot n$THF

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Abstract

By reacting CuX_2 (X = Cl or Br) with Et_4todit (Et_4todit = the title ligand) in THF, the new ligand-bridged polynuclear complexes $[Cu(II)(Et_4todit)X_2]_n \cdot n$THF have been obtained. The X-ray crystallographic studies on the Cl derivative show that the compound crystallizes in the orthorhombic space group *Fdd*2, with $a = 32.674(6)$, $b = 34.547(6)$, $c = 10.162(3)$ Å, $Z = 16$. The coordination around the metal involves two Cl^- ions and two S-thioamide atoms of two ligand molecules related by a screw axis, and is nearer to a square planar than to a tetrahedral arrangement. The bridging ligands form helical chains running parallel to *c*. The copper–copper distances in and between the chains are 7.601(4) and 9.185(5) Å, respectively. ESR measurements on this polymer give *g* values in accordance with a strongly distorted rhombic structure. The magnetic susceptibility data within the temperature range 5–150 K exhibit a Curie behaviour for both complexes ($\mu = 1.82$ and 1.72 BM for Cl and Br complexes, respectively). Electronic spectroscopic results show that: (i) the environment around the copper(II) is the same in the solid state and in THF solution; (ii) reagents and products exist in THF at supersaturation conditions; (iii) S-(thioamide)copper(II) LMCT bands are observed at 555 and 620 nm for Cl and Br complexes, respectively. IR spectra agree with the X-ray structural results.

Introduction

We are interested in the coordinating properties of ligands containing one or more N–C=S groups in the same molecule, towards diiodine [1–3] and transition metals [4–7]. Despite the presence in the ligand of other donor sites, the thiocarbonyl sulfur is always involved in the coordination in the investigated cases. However the reactivity and the coordination mode strongly depend on the relative position of the C=S groups in the molecule.

In the case of the new title ligand Et_4todit (Fig. 1) recently prepared by us [8], the two thiocarbonyl sulfurs are located in mutually distant positions (8.405 Å). This makes the molecule potentially suitable as a ligand in polynuclear metal complexes including one-dimensional systems. Also the involvement of halide ions in terminal or bridging environments plays a role in determining the final product.

We have recently synthesized the new ligand-bridged polymeric complexes $[M(Et_4todit)X_2]_n$ (M = Zn, Cd, Hg; X = Cl, Br) [9]. The X-ray structure of $[Cd(Et_4todit)Cl_2]_n$ shows that the coordination around the metal is trigonal-bipyramidal, that apical sites are occupied by Cl atoms, and that a polymeric three-dimensional structure is formed through the bridging of the Et_4todit ligand and of one of the Cl^- ions. In the other complexes IR results are consistent with a tetrahedral stereochemistry.

We describe in this report some aspects of the copper(II) coordination chemistry of the Et_4todit

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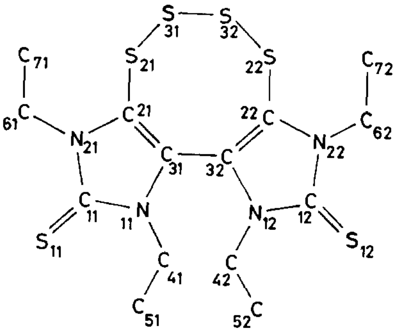

Fig. 1. Non-hydrogen atoms numbering scheme in Et_4todit.

ligand and the X-ray structure of the $[Cu(Et_4todit)Cl_2]_n \cdot n$THF complex.

Experimental

Materials

The ligand was synthesized as described in ref. 8. $CuCl_2$ and $CuBr_2$ were Merck reagents. THF was purchased from Carlo Erba (RPE reagent), it was distilled before use. The complex $[Cu(Et_4todit)Cl_2]_n \cdot n$THF was obtained as dark red–brown crystals suitable for X-ray analysis by slow evaporation of a THF solution containing anhydrous $CuCl_2$ and Et_4todit in equimolecular amounts. On varying the reagent ratio between 2:1 and 1:2, the same compounds were always obtained.

$[Cu(Et_4todit)Cl_2]_n \cdot n$THF: IR bands (KBr pellets, cm^{-1}): 2968m, 2925m, 2860m, 1529wbr, 1442s, 1410vs, 1393s, 1378s, 1335s, 1262s, 1195m, 1151s, 1102s, 1090m, 1081sh, 1058s, 981m, 961m, 908mbr, 815mw, 801ms, 771m, 698w, 608wbr, 540vw, 452vw, 432w, 402w, 333s, 323m, 298s, 245s. *Anal.* Found: C, 33,3; H, 4.4; N, 8.3. Calc. for $C_{18}H_{28}N_4OS_6CuCl_2$: C, 33.6; H, 4.4; N, 8.7%.

The dark-green $[Cu(Et_4todit)Br_2]_n \cdot n$THF complex was obtained analogously, starting from $CuBr_2$. IR bands (KBr pellets, cm^{-1}): 2969m, 2929m, 2864m, 1522m, 1444s, 1408vs, 1394vs, 1378s, 1336s, 1264s, 1195m, 1151s, 1103s, 1089m, 1059s, 983m, 963m, 907mbr, 803ms, 773m, 718w, 694w, 640vw, 609vw, 540vw, 480vw, 452vw, 435w, 400w, 359m, 300br, 245mbr. *Anal.* Found: C, 29.2; H, 3.5; N, 7.5. Calc. for $C_{18}H_{28}N_4OS_6CuBr_2$: C, 29.5; H, 3.8; N, 7.7%.

Elemental analyses were performed by the Istituto di Chimica Farmaceutica dell'Università di Cagliari. IR spectra were recorded on a Perkin-Elmer model 983 spectrophotometer. UV–Vis spectra were recorded on a Cary 2300 spectrophotometer. Magnetic susceptibilities were measured with a fully automated AZTEC DSM5 susceptometer, equipped with an Oxford continuous flow cryostat CF 12005, using $Gd_2(SO_4)_3 \cdot 8H_2O$ as calibrant, at the Dipartimento di Chimica dell'Università di Firenze. Diamagnetic corrections were estimated from Pascal constants. ESR spectra were recorded on a Varian E9 spectrometer (X band) at the Dipartimento di Chimica dell'Università di Sassari. DPPH was used as standard field marker.

X-ray crystallography

Crystal structure determination

$C_{18}H_{28}CuN_4OCl_2S_6$, $M = 643.258$, orthorhombic, $a = 32.674(6)$, $b = 34.547(6)$, $c = 10.162(3)$ Å (by least-squares refinements from the θ values of 27 reflections accurately measured), $U = 11471(4)$ $Å^3$, space group $Fdd2$ (unambiguously defined from the systematic absences), $Z = 16$, $D_c = 1.490$ Mg m^{-3}, $F(000) = 5296$, crystal dimensions $0.10 \times 0.13 \times 0.28$ mm, μ(Cu Kα) = 70.23 cm^{-1}.

Data collection and processing

Siemens AED diffractometer, Ni-filtered Cu Kα radiation ($\lambda = 1.541838$ Å), θ–2θ scan mode, scan speed 3–6° min^{-1}, scan width $1.20 + 0.142$ tgθ; all the reflections in the 3–60° range were measured for $h = 0$–38, $k = 0$–42, $l = 0$–11. A total of 1169 reflections (of 2482 measured), having $I \geqslant 2\sigma(I)$, was considered observed and used in the analysis. The recorded intensities were corrected for Lorentz and polarization factors, for absorption (maximum and minimum values 1.29652 and 0.82132) and extinction (maximum and minimum values 1.05183 and 0.67512) following the empirical method of Walker and Stuart [10].

Structure analysis and refinement

Patterson and Fourier methods were used. Full-matrix least-squares refinement was carried out, initially with isotropic thermal parameters for all atoms, followed by anisotropic thermal parameters only for copper, chlorine and sulfur atoms (because of the small number of reflections). The tetrahydrofuran molecule was found to be disordered and the corresponding atoms were inserted in two positions with site occupancy factors of 0.60 and 0.40, respectively, as found from the refinement, and with the constraints: C–O 1.47; C–C 1.53 Å. Hydrogen atoms were placed in their calculated positions and their coordinates were fixed in the final refinement as well as their thermal parameters ($U = 0.1205$ $Å^2$). The weighting scheme used in the final cycles was $w = 0.5811/[\sigma^2(F_o) + 0.004573F_o^2]$. Final R and R_w values were 0.0617 and 0.0762, respectively; the maximum shift/e.s.d. was 0.13 and the minimum and maximum heights in the final difference map were -0.35 and 0.36 e/Å^3, respectively. Scattering factors and corrections for anomalous dispersion effects were those from ref. 11. Calculations were carried out on the GOULD-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma). The SHELX 76 system of computer programs [12] and the programs ASSORB [13], PARST [14], PLUTO [15] and ORTEP[16] were used. Final atomic coordinates are reported in Table 1, bond distances and angles in Table 2. See also 'Supplementary material'.

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

	x/a	*y/b*	*z/c*	U_{eq}/U[a]
Cu	304(1)	3266(1)	752	656(10)
Cl(1)	561(2)	3276(2)	2751(6)	837(22)
Cl(2)	133(2)	3443(2)	−1291(6)	873(21)
S(11)	828(2)	2904(2)	−223(6)	721(19)
S(21)	1919(2)	2390(2)	3487(6)	901(24)
S(31)	2205(2)	1918(2)	2590(8)	1125(31)
S(12)	345(2)	1639(2)	6669(6)	787(21)
S(22)	1446(2)	1309(2)	2728(7)	1035(28)
S(32)	2007(2)	1441(2)	3545(7)	850(24)
N(11)	852(4)	2371(4)	1785(15)	554(38)
N(21)	1419(4)	2691(4)	1558(15)	612(41)
N(12)	737(4)	2017(4)	4713(16)	626(41)
N(22)	916(5)	1426(5)	4877(17)	677(44)
C(11)	1040(5)	2654(5)	1074(19)	616(51)
C(21)	1475(5)	2424(5)	2574(20)	630(51)
C(31)	1128(6)	2238(5)	2749(19)	614(51)
C(41)	430(6)	2216(5)	1514(20)	650(55)
C(51)	450(7)	1911(7)	450(28)	1079(81)
C(61)	1727(7)	2968(6)	1116(26)	944(71)
C(71)	1715(8)	3324(8)	1876(28)	1132(89)
C(12)	661(6)	1690(6)	5391(21)	680(55)
C(22)	1121(6)	1575(6)	3797(20)	677(53)
C(32)	1003(5)	1948(5)	3696(18)	533(45)
C(42)	530(6)	2389(6)	4974(21)	678(53)
C(52)	765(8)	2612(8)	5998(28)	1244(94)
C(62)	941(7)	1029(7)	5255(28)	1016(76)
C(72)	699(8)	787(8)	4568(28)	1164(89)
O(1s)[b]	1806(15)	2199(13)	−834(47)	1929(179)
C(1s)[b]	1448(15)	1953(17)	−1106(66)	1698(241)
C(2s)[b]	1658(24)	1685(17)	−2101(71)	1959(324)
C(3s)[b]	1953(22)	1941(21)	−2884(70)	1778(270)
C(4s)[b]	2162(17)	2121(27)	−1681(76)	1992(307)
O(1s1)[c]	2075(23)	1944(25)	−1223(78)	2340(376)
C(1s1)[c]	1952(25)	2159(27)	−2418(84)	1618(372)
C(2s1)[c]	1605(21)	1947(20)	−3134(63)	1089(216)
C(3s1)[c]	1462(24)	1716(24)	−1928(54)	1249(280)
C(4s1)[c]	1691(20)	1800(17)	−643(54)	955(189)

[a] $U_{eq} = 1/3$ trace $\tilde{U}$. [b] s.o.f. = 0.60. [c] s.o.f. = 0.40.

TABLE 2. Bond distances (Å) and angles (°) with e.s.d.s in parentheses[a]

Coordination around metal			
Cu–Cl(1)	2.198(6)	Cl(1)–Cu–S(11)	96.9(2)
Cu–Cl(2)	2.235(6)	Cl(1)–Cu–(S12′)	88.6(2)
Cu–S(11)	2.340(7)	Cl(2)–Cu–S(11)	86.3(2)
Cu–S(12′)	2.339(7)	Cl(2)–Cu–S(12′)	96.0(2)
Cl(1)–Cu–Cl(2)	161.7(3)	S(11)–Cu–S(12′)	155.1(3)
Ligand molecule			
	i = 1, *j* = 2	*i* = 2, *j* = 1	
S(2*i*)–S(3*i*)	2.089(10)	2.063(9)	
S(31)–S(32)	2.019(10)		
S(1*i*)–Cl(*i*)	1.72(2)	1.67(2)	
S(2*i*)–C(2*i*)	1.73(2)	1.78(2)	
N(1*i*)–C(1*i*)	1.36(2)	1.35(3)	
N(1*i*)–C(3*i*)	1.41(2)	1.37(2)	
N(1*i*)–C(4*i*)	1.50(2)	1.48(2)	
N(2*i*)–C(1*i*)	1.34(2)	1.34(3)	
N(2*i*)–C(2*i*)	1.40(2)	1.39(3)	
N(2*i*)–C(6*i*)	1.46(3)	1.43(3)	
C(2*i*)–C(3*i*)	1.32(3)	1.35(3)	
C(31)–C(32)	1.45(3)		
Cu–S(1*i*)–C(1*i*)	103.8(7)	103.7(8)	
S(3*i*)–S(2*i*)–C(2*i*)	101.2(7)	99.8(8)	
S(2*i*)–S(3*i*)–S(3*j*)	106.5(4)	105.8(4)	
C(1*i*)–N(1*i*)–C(3*i*)	108.3(1.4)	110.9(1.5)	
C(1*i*)–N(1*i*)–C(4*i*)	124.9(1.5)	123.6(1.6)	
C(3*i*)–N(1*i*)–C(4*i*)	126.7(1.5)	125.3(1.5)	
C(1*i*)–N(2*i*)–C(2*i*)	109.3(1.4)	110.9(1.7)	
C(1*i*)–N(2*i*)–C(6*i*)	126.0(1.6)	125.8(1.8)	
C(2*i*)–N(2*i*)–C(6*i*)	124.8(1.5)	122.9(1.8)	
N(1*i*)–C(1*i*)–S(1*i*)	125.8(1.3)	127.0(1.6)	
N(1*i*)–C(1*i*)–N(2*i*)	106.9(1.5)	104.9(1.7)	
N(2*i*)–C(1*i*)–S(1*i*)	127.3(1.4)	128.0(1.6)	
S(2*i*)–C(2*i*)–N(2*i*)	123.5(1.2)	125.6(1.5)	
S(2*i*)–C(2*i*)–C(3*i*)	128.2(1.5)	128.2(1.6)	
N(2*i*)–C(2*i*)–C(3*j*)	108.0(1.6)	106.1(1.7)	
N(1*i*)–C(3*i*)–C(2*i*)	107.4(1.6)	106.9(1.6)	
N(1*i*)–C(3*i*)–C(3*j*)	120.5(1.6)	124.0(1.5)	
C(2*i*)–C(3*i*)–C(3*j*)	132.2(1.8)	129.1(1.7)	

[a] Key to symmetry operations (′): $-x$, $\frac{1}{2}-y$, $z-\frac{1}{2}$.

Results and discussion

Crystal structure

The packing of $[Cu(Et_4todit)Cl_2]_n \cdot n$THF is shown in Fig. 2. The coordination around the metal involves two Cl$^-$ ions and two S-thioamide atoms of two different ligand molecules related by a screw axis and it is nearer to a square planar than to a tetrahedral arrangement. In fact the angle between the CuCl(2)S(11) and CuCl(1)S(12) ($-x$, $\frac{1}{2}-y$, $z-\frac{1}{2}$) planes is only 31.8(2)°. Both the metal and the ligand are bridging and polymeric chains running parallel to *c* are formed, as shown in Fig. 3, where the ethyl groups of the ligand are deleted for reasons of clarity. The structural data show that the geometry of the

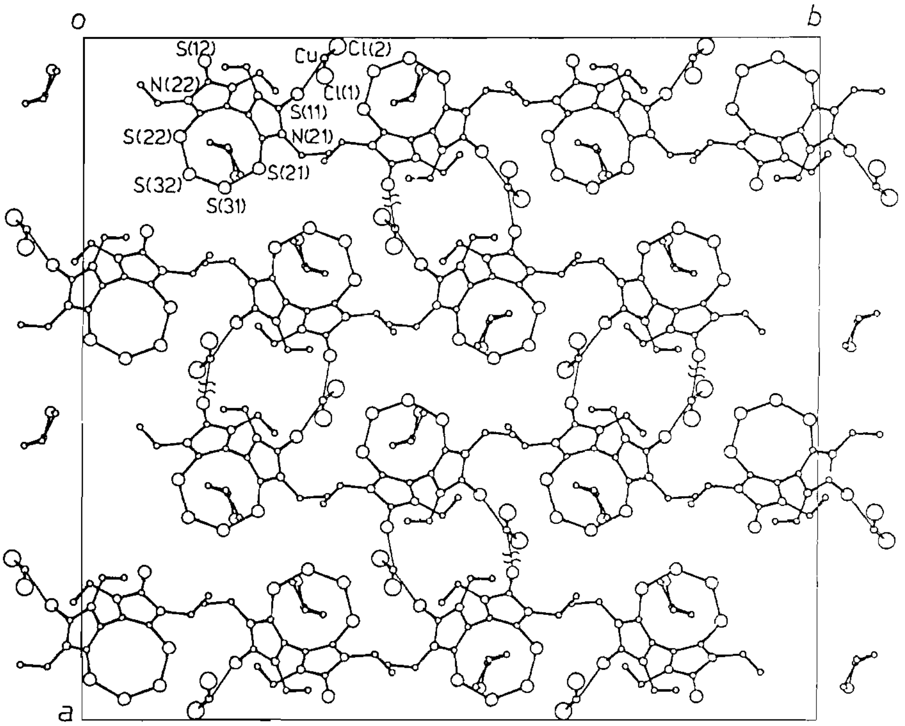

Fig. 2. Projection of the structure along [001].

ligand molecule is similar to that observed in the uncomplexed molecule [8], in its bis-diiodine adduct [17] and in its complex with $CdCl_2$ [9]. In fact the following features are maintained: (i) the chair conformation of the eight-membered ring; (ii) the presence of a pseudo two-fold axis; (iii) the value ($-72(2)°$) of the torsion angle N(11)–C(31)–C(32)–N(12) indicating the mutual orientation of the imidazoline rings; (iv) the disposition of the ethyl groups with respect to the corresponding ring plane. The packing is determined by contacts of the type: Cl...S, $S...CH_{3ethyl}$, $S...CH_{2solv}$, $CH_{3ethyl}...CH_{2solv}$, $CH_{3ethyl}...O_{solv}$.

Visible spectroscopy

The $[Cu(Et_4todit)X_2]_n \cdot n$THF compounds are very sparingly soluble in THF. This is in accordance with their polymeric nature, and can explain why no satisfactory equilibrium constants could be obtained by spectrophotometric measurements in THF solution. The existence of equilibria between reagents and products is suggested by the increase in the intensities of the characteristic bands of the complexes as a consequence of the addition of increasing amounts of the ligand to a constant amount of copper halogenides (see as an example Fig. 4). The spectrophotometric data have been analyzed by using the computer program described in ref. 3. Different equilibrium models have been invoked in order to fit the experimental data, however no satisfactory equilibrium constants could be obtained for the investigated wavelength and temperature range. Due to the low solubility of the polymers, it is likely that these complexes exist in solution at supersaturation conditions. An approximate estimation of the extinction coefficients of the bands at 555 and 620 nm for the Cl and Br complexes, gave $\epsilon > 3000$ and 2000 $mol^{-1}\ dm^3\ cm^{-1}$, respectively. The intensity of these bands suggest that they are of the charge-transfer type. We attribute these bands to the S-thioamide–> copper(II) LMCT transitions. The electronic spectra of copper(II) in sulfur environments have been extensively studied by many groups mainly in order to understand the optical properties of blue-copper proteins [18]. It is now well established that the intense absorption in the 500–600 nm range is due to a $S \rightarrow Cu(II)$ LMCT transition [19], and a shift of this band to lower energies as the ligand field becomes weaker has previously been observed by Veit *et al.* [19] for copper(II) dithiooxamides, where the absorption at 525 nm in the Cl derivative is shifted to 560 nm in the Br one. We observe a similar trend. Moreover, we attribute the band near 850 nm to the d–d transition for a copper(II) in an almost planar environment. This band is expected to fall in the near infrared region in distorted te-

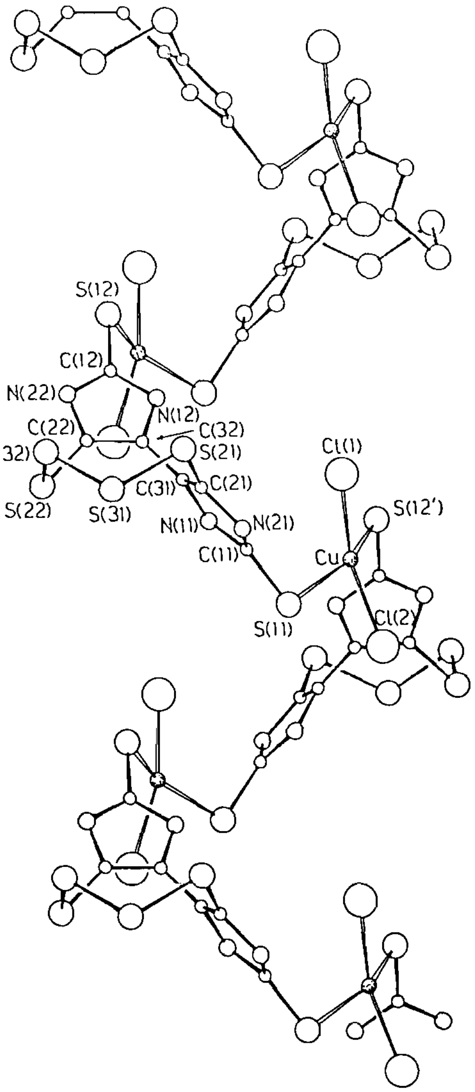

Fig. 3. Perspective view of the chain running parallel to *c*.

trahedral Cu(II) complexes, and to move towards higher energy as the distortion towards a square planar coordination continues [20]. The reflectance spectra of $[Cu(Et_4todit)Cl_2]_n \cdot n$THF and of $[Cu(Et_4todit)Br_2]_n \cdot n$THF are reported in Fig. 5. The features of the spectra in solution are maintained in the solid state, indicating that the environment around the copper(II) is the same in both phases.

IR spectroscopy

The most significant bands are reported with their assignments in Table 3. A simultaneous shift of the bands mainly associated to ν(CN) and ν(CS) to higher and lower wavenumbers, respectively as a consequence of coordination, is consistent with S-thioamide coordination [21]. The observed, modest shift is in accordance with X-ray results showing that the bond distances of the ligand are slightly modified as a consequence of coordination to the metal. The new bands appearing upon coordination in the low-frequency region, attributed to ν(MS) and ν(MX) fall in the usual range [21, 22]. The presence of THF is indicated by the appearance of the characteristic absorption at 908 cm^{-1}.

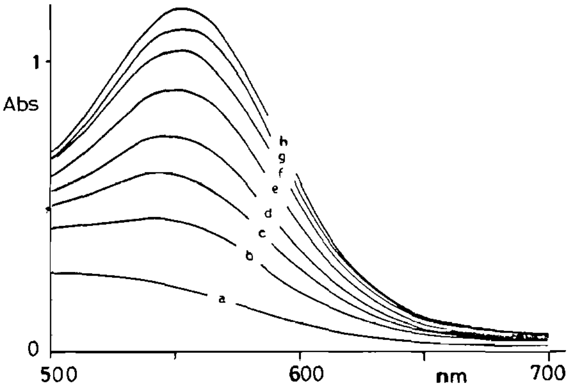

Fig. 4. Visible spectra at 288 K in a 1 cm cell of THF solutions containing constant amounts of $CuCl_2$ (2.7×10^{-4} mol dm^{-3}) and variable amounts of Et_4todit in the ratios (Et_4todit/Cu): a = 2; b = 5; c = 7; d = 10; e = 15; f = 20; g = 30; h = 40.

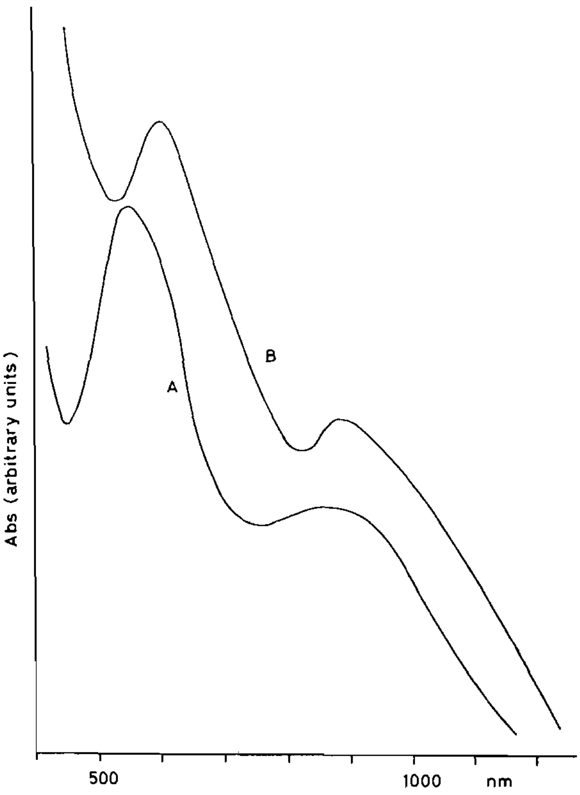

Fig. 5. Reflectance spectra in the range 1200–440 nm for: A, $[Cu(II)(Et_4todit)Cl_2]_n \cdot n$THF; B, $[(Cu(II)(Et_4todit)Br_2]_n \cdot n$THF.

TABLE 3. Selected IR absorptions of ligand and complexes in KBr[a] or polyethylene[b] pellets, ν(cm^{-1}); X = Cl or Br

Compound	ν(CN)[a]	ν(CS)[a]	ν(MX)[b]	ν(MS)[b]
Et_4todit	1435s	821m 810s		
$[(Cu(II)(Et_4todit)Cl_2]_n \cdot n$THF	1442s	801m	333s, 323m	298s, 245s
$[(Cu(II)(Et_4todit)Br_2]_n \cdot n$THF	1444s	803m	covered	300m, 245br

ESR and magnetic results

X-band powders ESR spectrum of $[Cu(II)Et_4todit)Cl_2]_n \cdot n$THF complex is shown in Fig. 6. The g values ($g_1 = 2.16$, $g_2 = 2.07$, $g_3 = 2.03$) indicate a strongly distorted rhombic structure [23]. The spectrum does not change with temperature in the explored 125–300 K range or when taken in a frozen CH_2Cl_2 solution. Moreover the linewidth is quite sharp, indicating that some exchange coupling among copper centers may be operating [24].

Plots of the temperature dependence of the reciprocal magnetic susceptibility are shown in Fig. 7. The plots $1/\chi_M$ versus temperature are linear. The slopes obtained by the least-squares method correspond to a Curie constant of 0.42 emu mol^{-1} K, $\mu = 1.82$ BM (Cl complex) and 0.37 emu mol^{-1} K, $\mu = 1.72$ BM (Br complex). This Curie behaviour seems to rule out that magnetic interactions are operating in the polymer. However an exchange interaction with very low coupling constant $|J| < \sim 0.3$ cm^{-1} cannot be excluded, since it cannot be detected in magnetic measurements taken to a temperature of 5 K. In fact, in this case, the expression calculated on the basis of the Ising model [24] for a one-dimensional infinite chain structure, coincides with the Curie law. A similar behaviour has recently been reported in ref. 25.

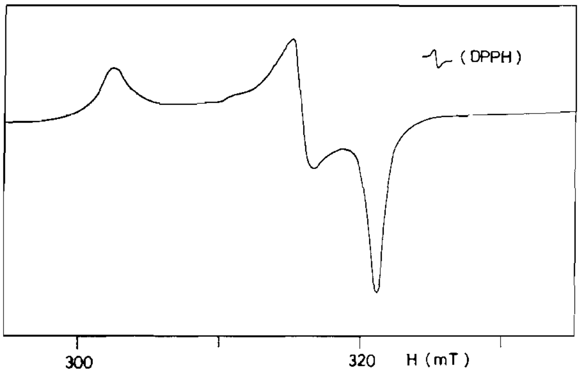

Fig. 6. ESR spectra for $[Cu(II)(Et_4todit)Cl_2]_n \cdot n$THF powders.

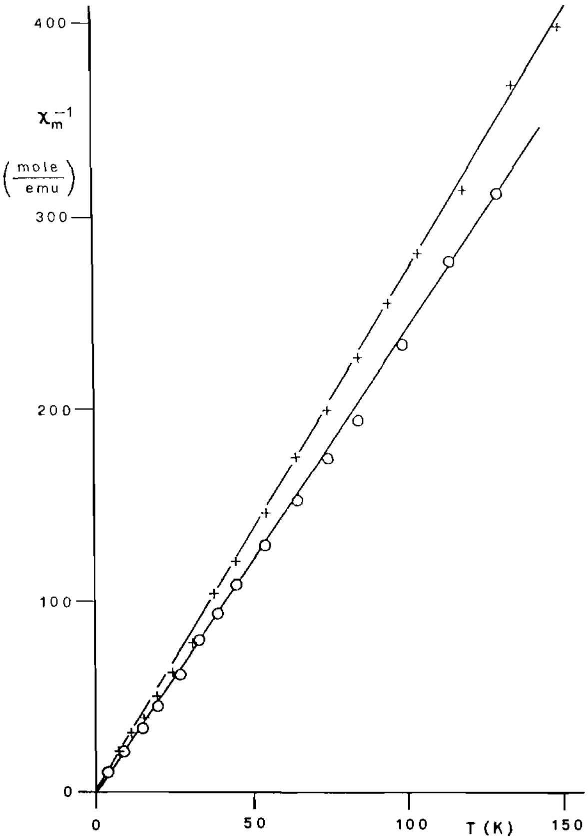

Fig. 7. Plot of reciprocal magnetic susceptibility against T (K) for $[(Cu(II)(Et_4todit)Cl_2]_n \cdot n$THF (○) and $[(Cu(II)(Et_4todit)Br_2]_n \cdot n$THF (+).

Supplementary material

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

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