Dithio-oxamides as Ligands: Crystal Structures and Vibrational Analyses of Bis(*N,N'*-dicyclohexyldithio-oxamidato)palladium(II), Bis(*N,N'*-dibenzyldithio-oxamide)copper(II) Diperchlorate, and Dichloro(*N,N'*-dimethyldithio-oxamide)zinc(II) and the Carbon-13 Nuclear Magnetic Resonance Spectra of Related Compounds†

Luciano Antolini, Antonio C. Fabretti, Giancarlo Franchini, Ledi Menabue, and Gian Carlo Pellacani *
Department of Chemistry, University of Modena, Via Campi 183, 41100 Modena, Italy
Herman O. Desseyn, Roger Dommisse, and Hendrik C. Hofmans
Laboratory of Inorganic Chemistry, Rijksuniversitait Centrum Antwerpen University, Groenenborgerlaan 171, B2020 Antwerp, Belgium

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Three *N,N'*-disubstituted dithio-oxamide metal complexes $[Pd(Hdcdto)_2]$, $[Cu(H_2dbzdto)_2][ClO_4]_2$, and $[Zn(H_2dmdto)Cl_2]$ (H_2dcdto, $H_2dbzdto$, and H_2dmdto = *N,N'*-dicyclohexyl-, *N,N'*-dibenzyl-, and *N,N'*-dimethyl-dithio-oxamide respectively) have been prepared and their crystal and molecular structures determined for the first time. In all cases the *N,N'*-disubstituted dithio-oxamides act as *S,S'*-chelating ligands. The Pd^{II} and Cu^{II} ions show nearly idealized square-planar S_4 co-ordination, and the Zn^{II} ion a distorted tetrahedral S_2Cl_2 co-ordination geometry. The co-ordination ability of the organic ligands and the conformations of their chelate rings are discussed. The i.r. spectra of the complexes are discussed and compared with analogous compounds. The ^{13}C n.m.r. spectra of related complexes have been recorded in the solid state and in solution. E.s.r. spectra of a series of copper(II) complexes are also discussed in the light of the covalent strength of the ligands.

Sulphur ligands are generally divided into two classes: (i) 'simple sulphur ligands,' such as R_2S, RSH, H_2S, RS^-, or HS^- (R = alkyl); or (ii) thioureas, thiocarboxylates, thioketonates, dithioketonates, dithiolates, and other chelating and unidentate sulphur ligands (SCN^-, SO_3^{2-}, *etc.*), which contrast with class (i), since the bonding of the sulphur donor atom is affected by conjugation or other factors which modify its capacity for bonding. The interactions of these ligands with metal ions give rise to a wide variety of molecules, containing different types of metal–sulphur bonds, such as polymeric insoluble compounds, as well as defined clusters,[1–3] which present multifaceted applications, ranging from pure academic syntheses to large-scale industrial productions.

The presence of sulphur-containing amino acids bound to metal ions at the active site of metalloproteins in cytochromes, iron–sulphur proteins, blue-copper proteins, molybdenum-containing enzymes, and vitamins[1–3] makes the metal–sulphur interaction interesting from a biological point of view too.

Among sulphur ligands, dithio-oxamides represent a unique type of ligand, behaving from time to time as class (i) or (ii), depending on the reaction media.

Although extensively studied and the tacit assumption of their bidentate involvement in metal-ion co-ordination, the majority of reports[4] are mainly based on spectroscopic evidence, for which their co-ordinative behaviour still remains questionable.

Only recently have some structural reports made the co-ordination profile of dithio-oxamides towards selected covalent metal halides less ambiguous.[5] Furthermore the crystal structures of one palladium(II) complex with *N,N'*-dicyclopentyl-dithio-oxamide[6] and of two copper(II) sulphate complexes with *N,N'*-di(2-hydroxyethyl)dithio-oxamide[7] have also been described. In the copper(II) complexes, which present interesting magnetic properties, *S,N*-ligand co-ordination is imposed by the hydroxy substituent on the nitrogen atoms.

Having been particularly interested in this field, in this paper we report the structural data of three dithio-oxamide complexes: bis(*N,N'*-dicyclohexyldithio-oxamidato)palladium(II), $[Pd(Hdcdto)_2]$; bis(*N,N'*-dibenzyldithio-oxamide)copper(II) diperchlorate, $[Cu(H_2dbzdto)_2][ClO_4]_2$; and dichloro(*N,N'*-dimethyldithio-oxamide)zinc(II), $[Zn(H_2dmdto)Cl_2]$, together with e.s.r. data of some copper(II) complexes, in order to clarify the co-ordinative behaviour of these ligands towards transition-metal ions.

Experimental

Preparation of the Complexes.—Bis(*N,N'*-dicyclohexyldithio-oxamidato)palladium(II) was prepared by mixing an ethanolic solution of palladium(II) nitrate with an ethanolic solution of the ligand in a 1:2 metal to ligand molar ratio. The compound was repeatedly recrystallized from ethanol. All the other complexes were prepared in strong acidic media as reported.[8,9] Suitable crystals for *X*-ray analyses were obtained by repeated recrystallization in the same preparation media. Elemental analyses are within experimental errors.

Physical Measurements.—The i.r. spectra were recorded with a Perkin-Elmer 580 spectrometer. The spectra were recorded in perfluorolube (a mixed oily solution) (4 000—1 350 cm^{-1}) and in Nujol (1 350—500 cm^{-1}) between KBr discs. The 500—180 cm^{-1} region was recorded between polyethylene pellets in Nujol. The i.r. spectra in solution were recorded from 10^{-3} mol dm^{-3} solutions in CCl_4, $CHBr_3$, or CS_2 (spectrograde quality).

All n.m.r. spectra were recorded on a JEOL FX 100 spectrometer at 25.0 MHz for carbon-13 and equipped with a Texas Instruments 980B computer for Fourier transformation.

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† *Supplementary data available* (No. SUP 56673, 4 pp.): i.r. assignments of the compounds. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. *X*-Ray experimental data

Compound	$[Pd(Hdcdto)_2]$	$[Cu(H_2dbzdto)_2][ClO_4]_2$	$[Zn(H_2dmdto)Cl_2]$
(*a*) Crystal parameters[a] at ~20 °C			
Formula	$C_{28}H_{48}N_4PdS_4$	$C_{32}H_{32}Cl_2CuN_4O_8S_4$	$C_4H_8Cl_2N_2S_2Zn$
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$ (C^5_{2h}, no. 14)	$P2_1/a$ (C^5_{2h}, no. 14)	$Pbcn$ (D^{14}_{2h}, no. 60)
a/Å	21.502(2)	16.435(3)	13.770(2)
b/Å	11.324(2)	11.126(2)	8.210(1)
c/Å	6.642(1)	10.297(2)	9.056(1)
β/°	91.70(1)	102.94(2)	
U/Å^3	1 616.5	1 835.0	1 023.8
M	675.36	863.34	284.53
Z	2	2	4
F(000)	708	886	568
D_c/g cm^{-3}	1.387	1.562	1.846
D_m/g cm^{-3}	1.40 (by flotation)	1.59 (by flotation)	1.83 (by flotation)
(*b*) Data collection			
Radiation[b]	Mo-K_α	Mo-K_α	Mo-K_α
Reflections measured	$\pm h, +k, +l$	$\pm h, +k, +l$	$+h, +k, +l$
Scan type	ω–2θ	ω–2θ	ω–2θ
θ range/°	2—24	2—24	2.5—25
Scan speed/° min^{-1}	3.0	2.4	4.8
Scan width/°	1.1	1.3	0.9
Background time/s	10	10	10
Standard reflections	1 every 50 (no changes)	1 every 50 (no changes)	3 every 120 (no changes)
Collected reflections	2 906	3 048	1 083
Observed reflections	1 664 with $I > 3\sigma(I)$[c]	849 with $I > 2\sigma(I)$	632 with $I > 2\sigma(I)$
Crystal size/mm	~0.39 × 0.34 × 0.30	~0.21 × 0.13 × 0.12	~0.28 × 0.17 × 0.07
μ(Mo-K_α)/cm^{-1}	7.7	9.5	31.4
Absorption correction	Not applied	Not applied	Applied[d] (T factor range: 0.76—0.59)
(*c*) Structure determination			
Non-H atoms	Anisotropic	Cu, S, Cl, O anisotropic N, C, isotropic	Anisotropic
H atoms	x, y, z refined, B fixed	Riding at ideal positions	Refined isotropically
Variable parameters	238	142	67
w	$0.71/[\sigma^2(F) + 0.0019F_o^2]$	$1.0/[\sigma^2(F) + 0.0028F_o^2]$	$1.08/[\sigma^2(F) + 0.0006F_o^2]$
R[e]	0.0348	0.0541	0.0292
R'[f]	0.0380	0.0583	0.0329
Peak in final electron density map/e Å^{-3}	0.95	1.00	0.36
Secondary extinction	No evidence	No evidence	No evidence

[a] Unit-cell parameters were derived from least-squares fits to the setting angles of the unresolved Mo-K_α component of 24 reflections from different regions of reciprocal space. [b] Graphite monochromated; λ = 0.710 69 Å. [c] $\sigma(I)$ = (peak counts + total background counts)$^{\frac{1}{2}}$. [d] Empirical absorption correction based on the scan. [e] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [f] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]$.

Table 2. Final positional parameters for $[Pd(Hdcdto)_2]$

Atom	x	y	z
Pd	0.5	0.5	0.5
S(1)	0.449 2(1)	0.450 1(1)	0.786 1(2)
S(2)	0.486 3(1)	0.696 8(1)	0.571 8(3)
C(1)	0.420 2(2)	0.579 8(4)	0.864 0(7)
N(1)	0.382 1(2)	0.587 1(4)	1.015 6(7)
C(2)	0.357 3(2)	0.492 3(5)	1.140 2(8)
C(3)	0.311 4(3)	0.413 9(5)	1.023 7(8)
C(4)	0.285 9(4)	0.317 9(6)	1.157 9(11)
C(5)	0.254 2(3)	0.369 1(8)	1.336 3(11)
C(6)	0.298 1(4)	0.451 7(7)	1.453 6(10)
C(7)	0.326 1(3)	0.546 5(6)	1.318 0(9)
C(8)	0.436 0(2)	0.696 2(4)	0.771 8(8)
N(2)	0.409 9(2)	0.785 4(4)	0.851 9(7)
C(9)	0.420 4(2)	0.904 5(4)	0.772 8(8)
C(10)	0.374 1(3)	0.929 9(5)	0.599 6(11)
C(11)	0.381 4(4)	1.057 2(6)	0.523 8(12)
C(12)	0.372 8(4)	1.144 6(6)	0.691 9(13)
C(13)	0.418 2(4)	1.121 5(5)	0.865 9(11)
C(14)	0.412 7(3)	0.994 3(5)	0.942 8(9)

A special cross-polarization magic-angle spinning accessory was used on the same spectrometer for solid-state n.m.r. recordings. In this case samples of the compound (100—150 mg) contained in bullet-shaped Kel-F spinning rotors were used.

E.s.r. spectra were obtained on a Varian E spectrometer on polycrystalline samples with diphenylpicrylhydrazyl (dpph, g = 2.0036) as calibrating field marker.

X-Ray Crystallography.—All diffraction data were obtained on a Philips PW 1100 automated four-circle diffractometer, at room temperature, with use of graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å). Details of data collection and processing are given in Table 1.

Systematic absences (from survey of the complete data sets) allow the space groups to be determined uniquely.

All data were corrected for Lorentz and polarization effects; the absorption correction was neglected for the Pd and Cu complexes, in view of their small absorption coefficients and small or almost isotropic crystal dimensions. Only the observed reflections were used in the structure determinations.

Table 3. Final positional parameters for $[Cu(H_2dbzdto)_2][ClO_4]_2$

Atom	x	y	z
Cu	0.0	0.0	0.0
S(1)	0.074 1(3)	0.172 6(4)	0.057 4(4)
S(2)	0.052 1(2)	−0.020 0(4)	−0.188 0(4)
C(1)	0.133 5(8)	0.172 2(13)	−0.055 1(13)
N(1)	0.206 8(7)	0.226 8(10)	−0.032 9(10)
C(2)	0.246 1(10)	0.290 0(14)	0.092 3(16)
C(3)	0.203 2(9)	0.400 0(13)	0.120 3(15)
C(4)	0.152 4(10)	0.468 2(14)	0.023 3(16)
C(5)	0.112 4(11)	0.572 2(16)	0.052 6(17)
C(6)	0.127 6(11)	0.608 3(16)	0.183 1(18)
C(7)	0,180 9(11)	0.546 7(15)	0.280 3(17)
C(8)	0.218 4(11)	0.443 1(16)	0.251 2(18)
C(9)	0.105 4(8)	0.107 1(11)	−0.184 6(13)
N(2)	0.124 3(7)	0.159 5(10)	−0.288 0(11)
C(10)	0.099 8(9)	0.113 8(13)	−0.425 0(15)
C(11)	0.043 9(10)	0.200 5(13)	−0.507 3(15)
C(12)	−0.037 2(11)	0.216 0(15)	−0.489 4(18)
C(13)	−0.089 0(12)	0.301 1(18)	−0.563 4(19)
C(14)	−0.065 6(13)	0.363 6(18)	−0.661 5(20)
C(15)	0.014 1(12)	0.351 3(16)	−0.680 1(17)
C(16)	0.066 2(10)	0.267 7(16)	−0.608 6(17)
Cl	0.220 3(3)	−0.074 5(4)	0.291 4(6)
O(1)	0.225 2(11)	0.044 6(14)	0.326 2(19)
O(2)	0.298 3(11)	−0.118 4(14)	0.286 3(18)
O(3)	0.202 7(13)	−0.134 9(21)	0.394 1(19)
O(4)	0.161 3(13)	−0.101 2(15)	0.176 1(20)

Table 4. Final positional parameters for $[Zn(H_2dmdto)Cl_2]$

Atom	x	y	z
Zn	0.0	0.134 6(1)	0.25
Cl	0.112 6(1)	−0.019 1(1)	0.138 3(2)
S	0.075 5(1)	0.336 4(1)	0.398 0(2)
C(1)	0.044 6(3)	0.502 7(5)	0.299 1(5)
N	0.093 9(3)	0.638 1(5)	0.305 5(5)
C(2)	0.180 4(4)	0.662 3(8)	0.396 3(9)
H(1)	0.074(3)	0.714(6)	0.255(6)
H(2)	0.157(5)	0.613(8)	0.499(8)
H(3)	0.195(4)	0.770(8)	0.399(7)
H(4)	0.233(5)	0.595(8)	0.372(7)

Table 5. Selected bond distances (Å) and angles (°)*

(*a*) $[Pd(Hdcdto)_2]$			
Pd–S(1)	2.291(1)	Pd–S(2)	2.300(1)
S(1)–C(1)	1.683(4)	S(2)–C(8)	1.738(4)
C(1)–N(1)	1.318(6)	C(8)–N(2)	1.279(5)
N(1)–C(2)	1.465(5)	N(2)–C(9)	1.468(5)
C(1)–C(8)	1.497(6)		
S(1)–Pd–S(2)	90.00(5)	C(1)–N(1)–C(2)	129.1(4)
Pd–S(1)–C(1)	103.3(1)	S(2)–C(8)–C(1)	118.0(3)
Pd–S(2)–C(8)	104.0(1)	S(2)–C(8)–N(2)	127.3(3)
S(1)–C(1)–N(1)	122.2(3)	C(1)–C(8)–N(2)	114.7(4)
S(1)–C(1)–C(8)	123.5(3)	C(8)–N(2)–C(9)	120.2(4)
N(1)–C(1)–C(8)	114.3(4)		
(*b*) $[Cu(H_2dbzdto)_2][ClO_4]_2$			
Cu–S(1)	2.281(4)	Cu–S(2)	2.297(3)
S(1)–C(1)	1.67(1)	S(2)–C(9)	1.66(1)
C(1)–N(1)	1.32(1)	C(9)–N(2)	1.31(1)
N(1)–C(2)	1.48(2)	N(2)–C(10)	1.47(2)
C(1)–C(9)	1.50(2)		
S(1)–Cu–S(2)	91.2(1)	C(1)–N(1)–C(2)	125(1)
Cu–S(1)–C(1)	100.3(5)	S(2)–C(9)–C(1)	119(1)
Cu–S(2)–C(9)	101.2(5)	S(2)–C(9)–N(2)	126(1)
S(1)–C(1)–N(1)	122(1)	C(1)–C(9)–N(2)	115(1)
S(1)–C(1)–C(9)	120(1)	C(9)–N(2)–C(10)	124(1)
N(1)–C(1)–C(9)	118(1)		
(*c*) $[Zn(H_2dmdto)Cl_2]$			
Zn–Cl	2.240(1)	C(1)–N	1.303(6)
Zn–S	2.371(1)	C(1)–C(1′)	1.516(8)
S–C(1)	1.688(5)	N–C(2)	1.461(7)
Cl–Zn–S	110.2(1)	S–C(1)–N	122.3(4)
Cl–Zn–Cl′	111.4(1)	S–C(1)–C(1′)	121.0(5)
Cl–Zn–S′	116.2(1)	N–C(1)–C(1′)	116.6(5)
S–Zn–S′	91.3(1)	C(1)–N–C(2)	124.5(5)
Zn–S–C(1)	98.9(2)		

* Primed atoms are related to unprimed by the symmetry transformation $-x, y, \frac{1}{2} - z$ of the reference co-ordinates.

The structures were solved by conventional Patterson and Fourier techniques, and refined by full-matrix least-squares procedures. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weighting factor.

Complex neutral-atom scattering factors[10] were used throughout. Major calculations were carried out on a CDC Cyber 7600 computer by using the SHELX 76 program package[11] and the ORTEP plotting program.[12]

Final positional parameters are given in Tables 2—4.

Results and Discussion

X-Ray Crystallography and Description of Structures.—Selected bond distances and angles are reported in Table 5.

$[Pd(Hdcdto)_2]$. As shown in Figure 1, the structure consists of discrete molecular units separated by normal van der Waals distances.

The molecule has crystallographically-imposed C_i symmetry, with the metal atom lying at the inversion centre, which requires the PdS_4 moiety to be planar, in a nearly idealized D_{4h} symmetry. The same *S,S′* metal binding by the ligand and the same co-ordination geometry about the metal ion was found in bis(*N,N′*-dicyclopentyldithio-oxamidato)palladium(II), whose crystal structure was determined at 150 K.[6] In both structures the Pd atom lies on an inversion centre, and the differences between the dimensions of the co-ordination polyhedra do not appear significant. Furthermore, in both cases the thioamidic groups are nearly coplanar with small torsional angles (0.8 and 2.7°, respectively) about the central C–C bond [see Table 6, in which some relevant structural features of *N,N′*-disubstituted dithio-oxamides and (or) of their metal complexes are also summarized]. A planar conformation of the ligand is the most suitable for an intramolecular hydrogen-bonding interaction between the amide nitrogen atoms; in the present case their separation is 2.57 Å, the N···H distance 2.08 Å, and the N–H···N angle 115.6°. The most interesting differences between the two Pd complexes involve the thioamidic C–S and C–N bonds; the two crystallographically independent values of their lengths were found equal within one standard deviation in the cyclopentyl complex, whose crystal structure was determined at 150 K in order to increase its rigidity.[6] Moreover, the unique amide proton was located at both nitrogen atoms, with half occupancy factors. Our present results clearly show that this statistical disorder involves the whole thioamide function, whose dimensions we found to differ significantly between themselves, but with mean values [C–S = 1.711(4), C–N = 1.298(6) Å] nearly coincident with those reported for the cyclopentyl derivative (Table 6). Furthermore, present results and previous structural reports (Table 6) suggest that the changes in partial double-bond character of either the C–S or

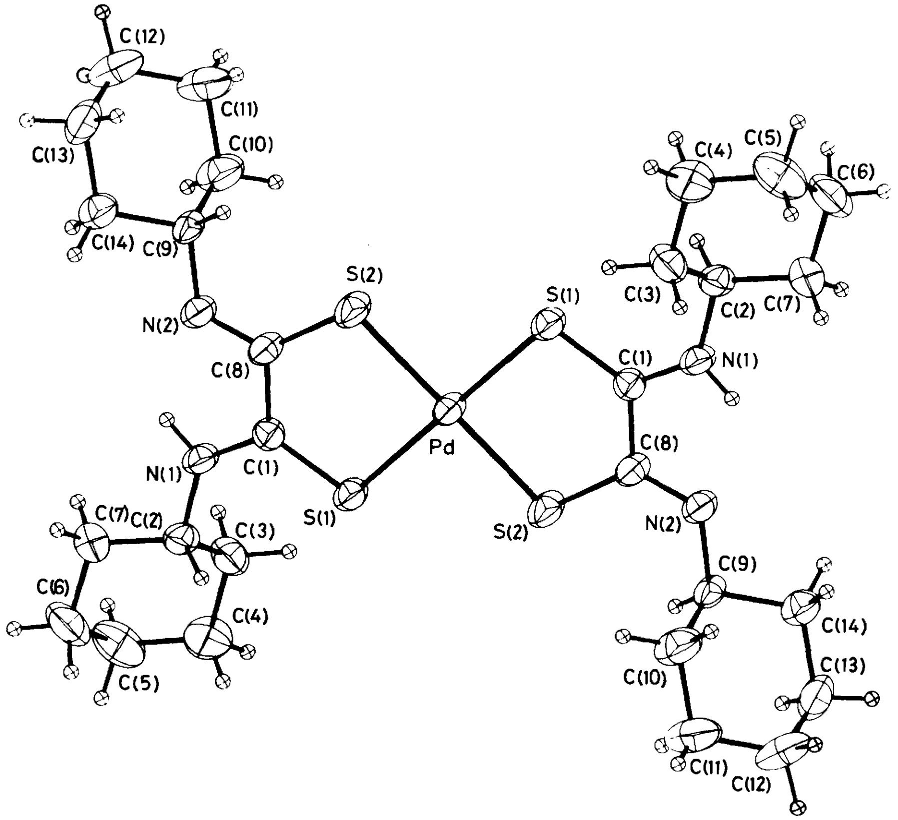


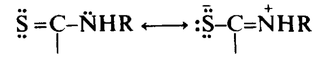
Figure 1. ORTEP view of $[Pd(Hdcdto)_2]$ showing the atom numbering and atomic vibrational ellipsoids (50%). The hydrogen atoms are represented as spheres of radius 0.08 Å

Table 6. Summary of structural data for dithio-oxamide (H_4L) and its *N,N'*-disubstituted derivatives (H_2R_2L) and complexes

Compound	R	C–S (Å)	C–N (Å)	C–C (Å)	S–C–C–S (°)	Metal binding	Ref.
H_4L		1.649(5)[a]	1.323(7)[a]	1.537(14)[a]	180		32
H_2R_2L[b]	CH_3[b]	1.666(4)[a]	1.313(6)[a]	1.518(6)	89.9		13
H_2R_2L	C_2H_5	1.664(5)	1.305(6)	1.542(6)	180		33
$[\{Sb(H_2R_2L)_{1.5}Cl_3\}_n]$	C_2H_5	1.667(9)[a]	1.302(11)[a]	1.526(13)[a]	180 −173.3	*S,S'* (bridging)	33
$[Zn(H_2R_2L)Cl_2]$	CH_3	1.688(5)	1.303(6)	1.516(8)	−38.4	*S,S'*	This work
$[Cu(H_2R_2L)_2][ClO_4]_2$	$CH_2C_6H_5$	1.666(13)[a]	1.317(13)[a]	1.496(17)	−35.0	*S,S'*	This work
$[Pd(HR_2L)_2]$	C_5H_9	1.714(8)[a]	1.298(8)[a]	1.497(10)	2.7	*S,S'*	6
$[Pd(HR_2L)_2]$	C_6H_{11}	1.683(4) 1.738(4)	1.318(6) 1.279(5)	1.497(6)	0.8	*S,S'*	This work
$[Cu_2(R_2L)(H_2O)_2]SO_4$	C_2H_4OH	1.710(4)	1.297(5)	1.499(8)	180	*S,N* (and *O*)	14
$[\{[Cu_2(R_2L)(H_2O)(SO_4)]_2(H_2O)_2\}_2]$	C_2H_4OH	1.722(4)[a]	1.294(5)[a]	1.514(5)	188.7	*S,N* (and *O*)	7

[a] Averaged bond distance. [b] *N,N*-Disubstituted (all other L derivatives are *N,N'*-disubstituted).

C–N bonds of the thioamide function, due to the resonance configurations[6,13] (see below), are strongly influenced by the



$$\ddot{S}=\underset{|}{C}-\ddot{N}HR \longleftrightarrow :\overset{-}{\ddot{S}}-\underset{|}{C}=\overset{+}{N}HR$$

deprotonation of the amide nitrogen, but weakly by the metal binding of the group. Compared to the free ligands, the lengthening of the C–S and the shortening of the C–N bond of undeprotonated thioamide functions bonded to the metal ion appear negligible. As expected, the loss of the amide proton increases the contribution of the charged resonance configuration to the thioamide function. The present C–S bond distance of 1.738(4) Å and C–N length of 1.279(5) Å are the longest and the shortest, respectively, yet reported for dithio-oxamide derivatives, but close to those observed in the copper complexes of the dianion of *N,N'*-di(2-hydroxyethyl)dithio-oxamide [from 1.710(4) to 1.723(4) Å for the C–S bond, and from 1.291(5) to 1.297(5) Å for the C–N bond].[7,14]

The central C–C bond [1.497(6) Å] between the thioamide groups of $[Pd(Hdcdto)_2]$ shows the expected shortening due to the partial sp^2 character of the carbon atoms.

$[Cu(H_2dbzdto)_2][ClO_4]_2$. The structure is shown in Figure 2 and consists of $[Cu(H_2dbzdto)_2]^{2+}$ dications and ClO_4^- anions each interacting through hydrogen bonds.

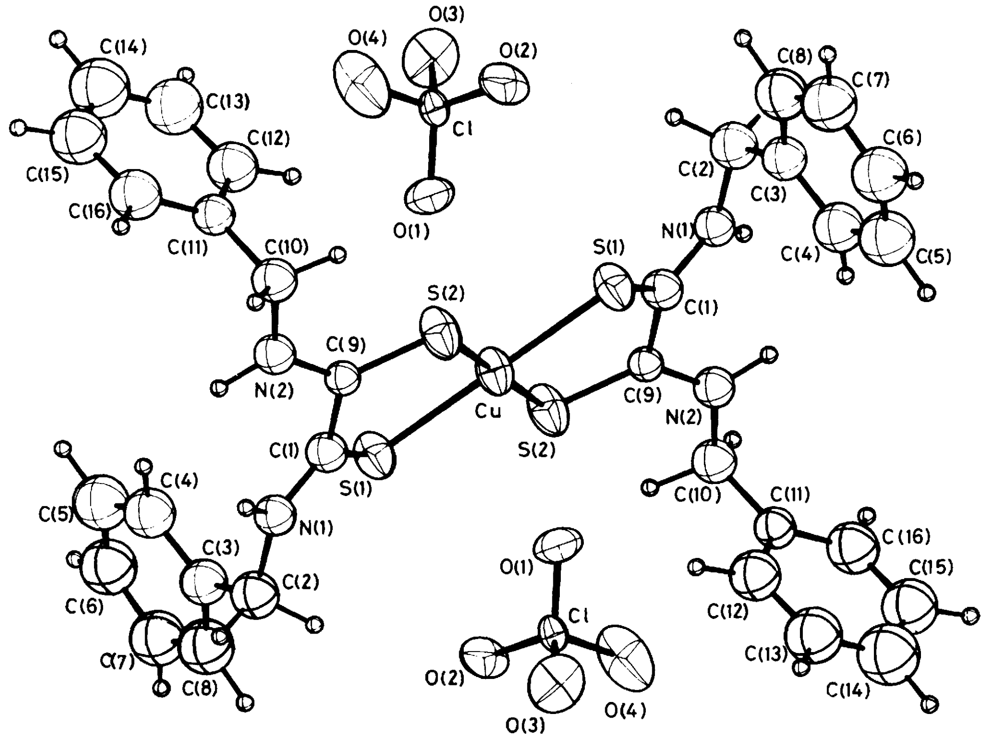


Figure 2. ORTEP view of [Cu(H$_2$dbzdto)$_2$][ClO$_4$]$_2$ showing the atom-labelling scheme and thermal motion ellipsoids at the 50% level, except for ClO$_4^-$ ions and H atoms which are drawn arbitrarily small for clarity

The co-ordination geometry is closely related to that observed in [Pd(Hdcdto)$_2$], having the same crystallographically imposed C_i and nearly idealized D_{4h} symmetry. The closest approaches to the octahedral co-ordination sites of the copper ion are by two O(4) perchlorate atoms, but at a distance (3.07 Å) too great to be involved in even weak co-ordination to the metal atom.[15]

The most interesting differences between the copper and palladium complexes involve the conformation of the substituted dithio-oxamides, in both cases acting as *S,S'*-chelating ligands. The individual (and planar) thioamide groups are nearly coplanar in the Pd complex; such a coplanarity in the neutral ligand would require a non-bonded H ··· H distance of *ca.* 1.40 Å between the amide protons. It may be emphasized that extremely short non-bonded H ··· H distances have been reported in the range 1.71—1.75 Å.[16] Hence, a *S,S'*-geometry in undeprotonated dithio-oxamides requires a torsional motion about the C–C bond between the thioamide moieties, whose planes were found to make a dihedral angle of 36.3° in the present complex [the separation between the amide protons (at calculated ideal positions) becomes 1.92 Å]. As a consequence, there is a relevant distortion of the five-membered chelate ring, whose atoms show deviations from their mean plane ranging from −0.159 to 0.173 Å. The corresponding deviations in [Pd(Hdcdto)$_2$] range from −0.044 to 0.082 Å.

Bond distances and angles within the *N,N'*-dibenzyldithio-oxamide ligand are all in the expected ranges.

The perchlorate ion, which appears slightly disordered in view of the high thermal motion parameters of its O atoms, interacts with the complex dication through a strong hydrogen bond involving one amide function (N ··· O = 2.78, H ··· O = 1.80 Å, N–H ··· O = 165°). It is rather surprising that the second amide function does not give rise to any hydrogen-bond interaction.

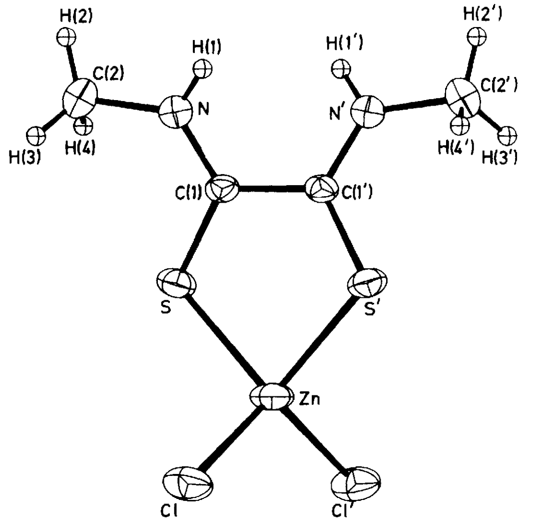


Figure 3. ORTEP view of [Zn(H$_2$dmdto)Cl$_2$] showing the atom-labelling scheme and atomic vibrational ellipsoids (50%). The hydrogen atoms are represented as spheres of radius 0.09 Å. Primed atoms are related to unprimed by a two-fold axis through the Zn atom and bisecting the S–Zn–S' angle

[Zn(H$_2$dmdto)Cl$_2$]. The structure consists of discrete molecular units (Figure 3). The molecule has crystallographically-imposed C_2 symmetry, with the metal ion lying on the two-fold axis which bisects the S–Zn–S' (and Cl–Zn–Cl') angle.

The metal atom shows distorted tetrahedral co-ordination geometry, being bonded to two Cl atoms and to one H$_2$dmdto molecule, which acts as a *S,S'*-chelating ligand. As expected, the constraints of the chelate ligand [the S–Zn–S' angle of the five-membered chelate ring, 91.3(1)°, is only slightly larger than those in the square-planar Pd and Cu complexes] enhance the distortion of the co-ordination geometry previously observed in similar tetrahedral Zn^{II} complexes.[17–19] This may also explain some lengthening in the Zn–S bond distance to 2.371(1) Å, when compared to the mean value of 2.348(2) Å observed in the parent complex dichlorobis(thioacetamide)zinc(II).[18]

The dimensions of the H$_2$dmdto ligand compare very well with those in [Cu(H$_2$dbzdto)$_2$][ClO$_4$]$_2$. In particular, the dihedral angle between the thioamide planes (36.9°) and the separation between the amide protons (observed and refined) of 2.05 Å are very close to those in the square-planar copper complex, and strongly suggest that the conformation of the five-membered chelate ring is mainly determined by the inner amide proton repulsions, and is not dependent upon the co-ordination geometry of the metal ion.

Both the amide functions of [Zn(H$_2$dmdto)Cl$_2$] are involved in intermolecular hydrogen bonds with Cl atoms [N $\cdots$ Cl = 3.206(5), H $\cdots$ Cl = 2.49(5) Å, N–H $\cdots$ Cl = 147(4)°], which link the molecules onto linear chains which parallel the *b* axis. These chains are separated by normal van der Waals distances.

I.r. Spectra.—The i.r. bands of [Pd(Hdcdto)$_2$] are assigned by comparison with those of other [Pd(HR$_2$L)$_2$] complexes (H$_2$R$_2$L = *N*,*N'*-dialkyldithio-oxamide) with planar dithio-oxamides.[20] These compounds are characterized by an intramolecular hydrogen bond between the two thioamide nitrogen atoms. The absence of the free ν(NH) vibration in the i.r. spectrum of [Pd(Hdcdto)$_2$] as a 10^{-3} mol dm^{-3} solution in CCl$_4$ demonstrates this intramolecular character: the ν(NH) band is situated at 3 190 cm^{-1} in the solid state and at 3 180 cm^{-1} in the dilute CCl$_4$ solution. As for the complex [Pd(HR$_2$L)$_2$] (R = cyclopentyl), the ν(NH) band is less intense in solution than in the solid state.

The π(NH) band is situated at 736 cm^{-1} in the solid-state spectrum and shifts to 560 cm^{-1} for the deuteriated compound. This band is shifted to 765 cm^{-1} in a dilute CS$_2$ solution. The small ν(NH) shift to a lower wavenumber in going from the solid state to the solution corresponds to a small shift of the π(NH) band to higher energy. The δ(NH) band is observed at 1 343 cm^{-1} in the solid state and shifts to 1 346 cm^{-1} in a 10^{-3} mol dm^{-3} solution in CCl$_4$. The ν(PdS) band is found at 357 cm^{-1}.

The i.r. spectrum of [Cu(H$_2$dbzdto)$_2$][ClO$_4$]$_2$ is rather complicated due to the overlap and coupling of the thioamide vibrations, the vibrations of the benzyl substituents, and the vibrations of the ClO$_4^-$ anion. This complex is strongly related to [M(H$_2$R$_2$L)$_2$]X$_2$ (M = Pt, Pd, or Ni; X = Cl, Br, or I) discussed in a previous investigation,[21,22] which are characterized by strong intermolecular $^+$N – H $\cdots$ X$^-$ associations, as suggested by the position and profile of the ν(NH) absorption band. The i.r. spectrum of [Cu(H$_2$dbzdto)$_2$][ClO$_4$]$_2$ reveals a similar ν(NH) profile, which appears as a rather strong broad band with several sub-maxima between 3 200 and 2 800 cm^{-1} due to the structurally demonstrated associations with the ClO$_4^-$ anions. The ν(CuS) vibration is found at 402 cm^{-1}.

No spectra of the compounds [M(H$_2$R$_2$L)$_2$]X$_2$ can be recorded in a dilute solution, as they behave as 1:2 electrolytes and dissociate into [M(H$_2$R$_2$L)$_2$]$^{2+}$ + 2X$^-$.

The i.r. spectrum of [Zn(H$_2$dmdto)Cl$_2$] is characterized by strong intermolecular NH $\cdots$ Cl associations, in agreement with the structural data. The ν(NH) vibration is observed as a broad band with a maximum at 3 153 cm^{-1}. The bands with π(NH) character are located at 798 and 736 cm^{-1}. These high positions also indicate strong NH associations. The ν(ZnS) vibrations are assigned to the bands at 346 and at 337 cm^{-1}.[23] Two ν(ZnCl) vibrations are expected, however only one is observed at 297 cm^{-1}.

Table 7. The ^{13}C n.m.r. spectra in solution and in the solid state of some planar dithio-oxamides and their [Pd(HR$_2$L)$_2$] complexes. Chemical shifts in p.p.m.

		Free ligand	[Pd(HR$_2$L)$_2$]	
(*a*) H$_2$R$_2$L				
In solution	N–C=S	185.46	180.65	
	CH$_3$	34.06	35.90	
In solid state	N–C=S	187.3 181.7	191.5 (N–C=S) 167.9 (N=C–S)	mean 179.7
	CH$_3$	39.0 34.2	40.8 33.9	
(*b*) H$_2$dcprdto				
In solution	N–C=S	185.38	181.23	
	CH	30.15	31.31	
	CH$_2$	7.25	8.83	
In solid state	N–C=S		193.7 (N–C=S) 167.7 (N=C–S)	mean 180.7
	CH and CH$_2$		40.8, 28.7, 9 (broad)	
(*c*) H$_2$dibudto				
In solution	N–C=S	184.63	180.41	
	CH$_3$	20.38	20.58	
	CH$_2$	54.80	56.01	
	CH	27.42	28.44	
In solid state	N–C=S		182.6 (N–C=S) 177.4 (N=C–S)	mean 180.0
	CH$_3$		21.7	
	CH$_2$		56.9	
	CH		27.9	

^{13}*C N.M.R. Spectra.*—Proton and ^{13}C n.m.r. spectra were used previously[24] to prove that the ligand is co-ordinated through both sulphur atoms in Pd^{II} and Pt^{II} *N*,*N'*-dialkyldithio-oxamides. The position of the unique hydrogen atom in each ligand of the compounds studied here can be described by a double minimum potential.

The ^{13}C n.m.r. results of some [Pd(HR$_2$L)$_2$] compounds recorded in CDCl$_3$ or dimethyl sulphoxide (dmso) are summarized in Table 7. The spectra recorded in solution show only one signal for the four thioamide C atoms, so we can assume that the rearrangement of the hydrogen atom in the fluxional complex occurs rather fast in solution.

The ^{13}C n.m.r. spectra of the [Pd(HR$_2$L)$_2$] complexes were also recorded in the solid state. For the solid-state ^{13}C n.m.r. spectra of the ligand, we are restricted to H$_2$dmdto as the melting points of the other ligands are too low, giving practical problems during the n.m.r. recording.

Table 7 summarizes the solid-state ^{13}C n.m.r. results of [Pd(Hdmdto)$_2$], [Pd(Hdcprdto)$_2$], and [Pd(Hdibudto)$_2$] (H$_2$dcprdto = *N*,*N'*-dicyclopropyldithio-oxamide, H$_2$dibudto = *N*,*N'*-di-isobutyldithio-oxamide). The spectra of the complexes show pronounced differences between the solid and solution states (Table 7). The solid-state ^{13}C n.m.r. spectra show two thioamide C peaks of equal intensity that are separated by several tens of p.p.m. This separation is too large to be explained by interaction with the nitrogen quadrupole.[25] It appears, therefore, that the hydrogen rearrangement is slow compared to the n.m.r. time-scale in the solid state. The peak near 190 p.p.m. can be assigned to the thioamide C atoms in the protonated thioamide functions with high S=C–N character, while the peak

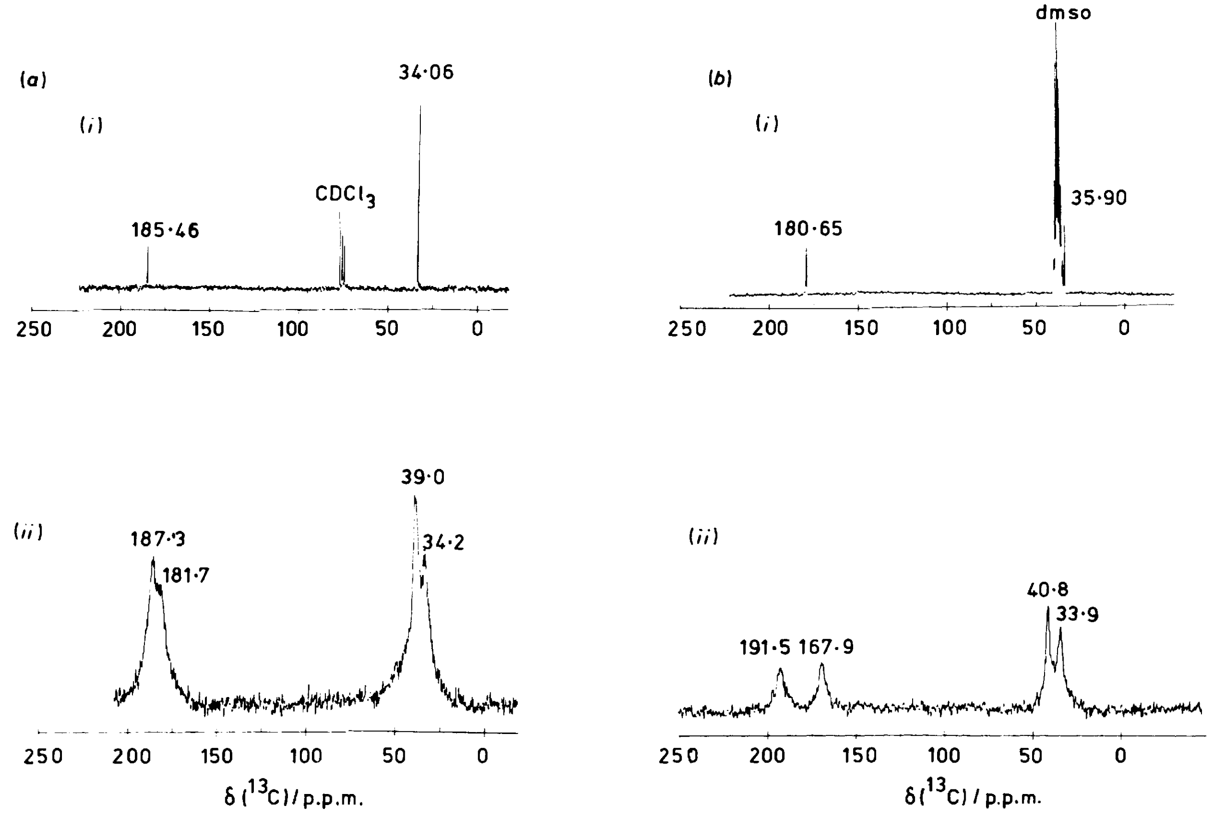


Figure 4. The ^{13}C n.m.r. spectra of (*a*) H_2dmdto and (*b*) [Pd(Hdmdto)$_2$] in solution (*i*) and in the solid state (*ii*)

in the 170 p.p.m. region corresponds to the thioamide C atoms in the deprotonated thioamide functions with S–C=N character.

The difference between the ^{13}C n.m.r. spectra of the complexes in the solid state and in solution indicates that the energy barrier between the underprotonated and deprotonated forms is lowered by solvent effects.

The spectrum of H_2dmdto is almost identical in the solid state and in solution (Figure 4). The peak at 185.46 p.p.m. in $CDCl_3$ and at 187.3 p.p.m. and 181.7 p.p.m. in the solid state is assigned to the thioamide C atoms. The small splitting observed in the solid-state ^{13}C n.m.r. spectrum can be explained by interaction with the quadrupole of the nitrogen neighbour.

The ^{13}C n.m.r. spectra of the complexes [M(H_2R_2L)$_2$]X_2 have been recorded (M = Pt, Pd, or Ni; H_2R_2L = H_2dmdto and H_2dibudto; X = Cl) in the solid state and in a saturated solution in which no dissociation occurs[22] (Table 8). Corresponding C atoms exhibit identical shifts, confirming the MS_4 co-ordination as deduced from the structural data of the similar compound [Cu(H_2dbzdto)$_2$][ClO_4]$_2$. The downfield shift for the thioamide C atom peak in comparison to the [Pd(HR_2L)$_2$] complexes can be caused by the presence of a quaternary N^+ group.

The thioamide C peak is broadened by the nitrogen quadrupole, as observed for the H_2dmdto ligand, but is not split into two separate peaks as for the [Pd(HR_2L)$_2$] compounds. This is indeed not expected as none of the four thioamide groups is deprotonated.

E.S.R. Spectra.—In order to make evident the covalent character of the dithio-oxamides we have also investigated a series of copper(II) complexes at room and liquid-nitrogen temperature (same spectra have been found) by the *X*-band e.s.r. technique (Table 9). No transitions in the $\Delta M_s = 2$ region of the spectra for any of the powdered samples have been observed.

Table 8. The ^{13}C n.m.r. spectra in a saturated $CDCl_3$ solution and in the solid state of some [M(H_2R_2L)$_2$]Cl_2 complexes. Chemical shifts in p.p.m.

(*a*) In $CDCl_3$	CH_3	CH_2	CH	CS
[Pd(H_2dibudto)$_2$]Cl_2	20.69	56.97	26.63	186.98
[Pt(H_2dibudto)$_2$]Cl_2	20.75	56.64	26.57	186.74
[Ni(H_2dibudto)$_2$]Cl_2	20.69	57.76	26.88	187.77
(*b*) In solid state				
[Pd(H_2dibudto)$_2$]Cl_2	21.1	58.3	26.6	189.6
	23.0			186.9
[Pd(H_2dmdto)$_2$]Cl_2	36.9			190.7
	35.0			187.2

Table 9. E.s.r. data of some *N,N'*-disubstituted dithio-oxamide Cu^{II} complexes*

Compound	g_1	$g_{\parallel}$	g_2	$g_{\perp}$	g_3	g_{iso}
[Cu(H_2dto)Cl_2]						2.080
[Cu(H_2dto)Br_2]						2.058
[Cu(H_2dto)$_2$][ClO_4]$_2$		2.094		2.027		
[Cu(H_2dbzdto)Cl_2]	2.102		2.075		2.032	
[Cu(H_2dbzdto)Br_2]	2.100		2.070		2.030	
[Cu(H_2dbzdto)$_2$]-[ClO_4]$_2$						2.030
[Cu(H_2dcdto)Cl_2]	2.100		2.080		2.030	
[Cu(H_2dcdto)Br_2]						2.060
[Cu(H_2dcdto)$_2$][ClO_4]$_2$						2.030
[Cu(H_2dmdto)Cl_2]		2.130		2.058		
[Cu(H_2dmdto)Br_2]						2.060
[Cu(H_2dmdto)$_2$]-[ClO_4]$_2$	2.066	2.050		2.025		

* Abbreviations: H_2dto = dithio-oxamide, for others see text.

This would seem to indicate that all the compounds are monomeric in nature.

Considering the g values a predominant $d_{x^2-y^2}$ (or less likely d_{xy}) ground state is indicated.[26] The spectra are axial or slightly non-axial types indicating that the chromophores CuS_2X_2 or CuS_4 are somewhat distorted. No hyperfine profile and in some cases no resolution of the g tensor can be observed in the spectra.

It is well known that metal–sulphur bonding is more covalent than metal–oxygen or metal–nitrogen bondings,[27,28] and that $g_{\parallel}$ values for Cu^{II} complexes are moderately sensitive to the metal–ligand covalency.[29]

The $g_{\parallel}$ values of the present complexes are indicative of strongly covalent environments due to sulphur co-ordination to the copper(II) ion. A certain lowering in the g values is expected on passing from the CuS_2X_2 to CuS_4 chromophores. A comparison of e.s.r. spectra of the present compounds with those of copper(II) heterocyclic dithiocarbamates {*e.g.* $S_2CN[(CH_2)_4CH_2]$}[30] and dithiolates[31] demonstrates a similar covalent bond order.

Conclusions

(*i*) The complexes $[Cu(H_2dbzdto)_2][ClO_4]_2$ and $[Zn(H_2dmdto)Cl_2]$ represent the first structurally-characterized examples of metal complexes of neutral dithio-oxamides. (*ii*) The present results confirm that, within the limits of experimental error, the thioamide group has a planar configuration; the amide proton was found to deviate from the plane by 0.008 Å in the Zn^{II} complex and by 0.092 Å in the Pd^{II} derivative. The partial double-bond character of the C–N bond and the fundamental sp^2 geometry at the nitrogen atom of the thioamide functions are very close to those of the peptide group,[32] and hence similar co-ordination behaviours are expected. Since 'the peptide nitrogen has never been found to bear both a proton and a metal ion in any crystal-structure determination,'[32] and 'the metal ion substitutes for the proton at the trigonal peptide nitrogen,'[33] the co-ordination of a nitrogen bearing a hydrogen atom in dithio-oxamides may be considered improbable. Confirmation is supplied by the present and previous structural determinations[3,6,14,32] on *N,N'*-disubstituted dithio-oxamide metal complexes. (*iii*) A covalent bond order of dithio-oxamides comparable to that of dithiocarbamates and dithiolates has been found. (*iv*) The i.r. spectra confirm the intramolecular character of the NH associations for the complex $[Pd(Hdcdto)_2]$ and indicate strong intermolecular $\overset{+}{N}H\cdots X^-$ associations for $[Cu(H_2dbzdto)_2][ClO_4]_2$. (*v*) For the first time ^{13}C n.m.r. spectra of complexes with planar dithio-oxamides have been recorded. These spectra indicate the presence of an energy barrier between the two equivalent positions for the thioamide H atom in the $[Pd(HR_2L)_2]$ complexes. This was not observed for the n.m.r. spectra recorded in solution.

Acknowledgements

The authors are grateful to the Centro Elettronico, University of Modena, for computing support, and the Centro Strumenti, University of Modena, for recording the e.s.r. spectra. The authors also thank the Ministero della Pubblica, Istruzione (Italy) for financial support.

References

1 D. Coucouvanis, *Prog. Inorg. Chem.*, 1979, **26**, 301 and refs. therein.
2 R. P. Burns and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1979, **22**, 303 and refs. therein.
3 C. G. Kuehn and S. S. Isied, *Prog. Inorg. Chem.*, 1980, **27**, 153 and refs. therein.
4 M. G. B. Drew, J. M. Kisenyi, G. R. Willey, and S. O. Wandinga, *J. Chem. Soc., Dalton Trans.*, 1984, 1717 and refs. therein.
5 M. G. B. Drew, J. M. Kisenyi, and G. R. Willey, *J. Chem. Soc., Dalton Trans.*, 1984, 1722 and refs. therein.
6 H. C. Hofmans, H. O. Desseyn, R. A. Dommisse, P. U. Nuffel, and A. T. H. Lenstra, *Transition Met. Chem. (Weinheim, Ger.)*, 1984, **9**, 213.
7 C. Chavvel, J. J. Girerd, Y. Jeannin, O. Kahn, and G. Lavigne, *Inorg. Chem.*, 1979, **18**, 3015 and refs. therein.
8 G. C. Pellacani, G. Peyronel, and A. Pignedoli, *Gazz. Chim. Ital.*, 1972, **102**, 835.
9 A. C. Fabretti, G. C. Pellacani, and G. Peyronel, *Gazz. Chim. Ital.*, 1973, **103**, 1259.
10 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99—101 and 149—150.
11 G. M. Sheldrick, SHELX 76 Program for Crystal Structure Determination, University Chemical Laboratory, Cambridge, 1976.
12 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.
13 A. Christensen, H. J. Geise, and B. J. Van der Veken, *Bull. Chem. Soc. Belg.*, 1975, **84**, 1173.
14 J. J. Girerd, S. Jeannin, Y. Jeannin, and O. Kahn, *Inorg. Chem.*, 1978, **17**, 3034.
15 W. Fitzgerald and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1981, 567.
16 O. Ermer and S. A. Mason, *J. Chem. Soc., Chem. Commun.*, 1983, 53.
17 M. Nardelli and I. Chierici, *Gazz. Chim. Ital.*, 1957, **87**, 1478.
18 M. Rolies and C. J. De Ranter, *Cryst. Struct. Commun.*, 1977, **6**, 275.
19 J. A. McGinnety, *Inorg. Chem.*, 1974, **13**, 1057.
20 H. Hofmans, H. O. Desseyn, A. J. Aarts, and M. A. Herman, *Bull. Soc. Chem. Belg.*, 1982, **91**, 19.
21 H. Hofmans, H. O. Desseyn, R. Dommisse, and M. A. Herman, *Bull. Soc. Chem. Belg.*, 1982, **91**, 175.
22 H. Hofmans, H. O. Desseyn, and M. A. Herman, *Spectrochim. Acta, Part A*, 1982, **38**, 1307.
23 P. Geboes and H. O. Desseyn, unpublished work.
24 R. A. Dommisse, A. J. Aarts, H. O. Desseyn, and F. C. Alderweireldt, *Bull. Soc. Chem. Belg.*, 1979, **88**, 109.
25 A. Naito, S. Ganapathy, and C. A. McDowell, *J. Magn. Reson.*, 1982, **48**, 367.
26 H. W. Richardson, J. R. Wasson, W. E. Estes, and W. E. Hatfield, *Inorg. Chim. Acta*, 1977, **23**, 205.
27 I. Tamiga and S. Fujiwara, *Spectrosc. Lett.*, 1969, **2**, 127.
28 K. I. Zamarev, *J. Struct. Chem. (Engl. Transl.)*, 1969, **10**, 32.
29 D. Kivelson and R. Neiman, *J. Chem. Phys.*, 1961, **35**, 149.
30 A. C. Fabretti, F. Forghieri, A. Giusti, C. Preti, and G. Tosi, *Inorg. Chim. Acta*, 1984, **86**, 127.
31 J. Stach, R. Kirmse, W. Dietzsch, R. M. Olk, and E. Hoyer, *Inorg. Chem.*, 1984, **23**, 4779.
32 P. J. Wheatley, *J. Chem. Soc.*, 1965, 396.
33 M. G. B. Drew, J. M. Kisenyi, and G. R. Willey, *J. Chem. Soc., Dalton Trans.*, 1982, 1729.

Received 11th July 1986; *Paper* 6/1387