

Co-ordinative Abilities of Ligands which favour S,S Chelation: Copper(I) Halide Complexes of *N,N'*-Diphenyldithiomalonamide. The Crystal and Molecular Structure of Bis(*N,N'*-diphenyldithiomalonamide)copper(I) Iodide–Methanol (2/1)†

Luigi P. Battaglia and Anna Bonamartini Corradi*

Istituto di Chimica Generale e Inorganica, Centro di Studio per la Strutturistica Diffraattometrica del C.N.R., University of Parma, Viale delle Scienze, 43100 Parma, Italy

Armando Marzotto

Dipartimento di Chimica Inorganica, Metallorganica e Analitica, University of Padova, Via Loredan 4, 35100 Padova, Italy

Ledi Menabue and Gian Carlo Pellacani

Dipartimento di Chimica, University of Modena, Via Campi 183, 41100 Modena, Italy

The spectroscopic (i.r. and n.m.r.) properties of $[\text{Cu}(\text{Hdpdma})_2]\text{X}$ (Hdpdma = *N,N'*-diphenyldithiomalonamide; X = Cl, Br, or I) are discussed in the light of the structural results obtained for $[\text{Cu}(\text{Hdpdma})_2]\cdot 0.5\text{MeOH}$. The compound crystallizes in the space group $P\bar{1}$ of the triclinic system. In the unit cell two crystallographically independent $[\text{Cu}(\text{Hdpdma})_2]^+$ cations, two iodine anions, and one methanol solvate molecule are present. The co-ordination around each copper atom is slightly distorted tetrahedral and involves four sulphur atoms belonging to two Hdpdma molecules, which act as bidentate neutral ligands and form two six-membered chelate rings. The i.r. study and the structural results, compared with those for other transition-metal complexes, permits some reasonable conclusions on the co-ordinative abilities of dithiomalonamides. The ^1H and ^{13}C n.m.r. results suggest that the same structural arrangement is maintained in solution.

Among sulphur ligands, dithiomalonamides are the most versatile and unique, since they can behave in the following three ways: (i) as 'simple sulphur ligands' (such as R_2S , RSH , H_2S , RS^- , and HS^- (R = alkyl group)); (ii) as ligands in which the bonding of the sulphur donor atom is affected by conjugation and other factors, which modify its capacity for bonding such as thioureas, thio- and dithio-ketonates, dithiolates, and other chelating and unidentate sulphur ligands (SCN^- , SO_3^{2-} , etc.); (iii) and/or as counter ions, readily oxidized to dithiolylium cations. Extensive and exhaustive studies have been made of their behaviour as unsaturated chelating ligands (ii)¹⁻⁵ and as counter ions (iii);^{1,6-8} their co-ordinative capability, as simple ligands (i) toward transition-metal ions, still remains an open problem, since the majority of reports, based only on spectroscopic evidence, are conflicting as regards the donor atom set.^{2-6,8} Only one recent structural report makes the co-ordination of dithiomalonamides, toward selected covalent metal halides, less ambiguous.⁹

As a contribution towards clarifying the co-ordinative behaviour of these ligands toward transition-metal ions and to enable some of us to reconsider previous statements, in this paper we report the spectroscopic (i.r. and n.m.r.) and structural results on (*N,N'*-diphenyldithiomalonamide)copper(I) halide complexes.

Experimental

The complexes $[\text{Cu}(\text{Hdpdma})_2]\text{X}$ (X = Cl, Br, or I) were prepared as reported in ref. 10. Their analytical data were in accord with calculated values within the experimental errors.

Physical Measurements.—Proton and ^{13}C n.m.r. spectra of the free ligand and its copper(I) complexes were recorded with a

model FX 90Q JEOL Fourier-transform spectrometer at 23 or 27 °C in $(\text{CD}_3)_2\text{SO}$. Chemical shifts ($\delta/\text{p.p.m.}$) are quoted downfield from tetramethylsilane. Infrared spectra were recorded with a Perkin-Elmer 180 spectrophotometer (4 000–250 cm^{-1}) in KBr pellets.

Crystallography.—A sample of $[\text{Cu}(\text{Hdpdma})_2]\text{I}$ of dimensions $0.46 \times 0.50 \times 0.76$ mm was mounted in a random orientation on a Siemens AED four-circle diffractometer. Cell dimensions were refined by least squares using 20 values of 15 accurately measured reflections using nickel-filtered Cu-K_α radiation.

Crystal data. $\text{C}_{61}\text{H}_{60}\text{Cu}_2\text{I}_2\text{OS}_8$, $M = 1\,558.6$, triclinic, $a = 20.215(5)$, $b = 14.079(1)$, $c = 12.699(2)$ Å, $\alpha = 98.36(1)$, $\beta = 78.72(5)$, $\gamma = 104.23(1)^\circ$, $U = 3\,417(1)$ Å³, $D_m = 1.53$ g cm^{-3} , $Z = 2$, $D_c = 1.51$ g cm^{-3} , $F(000) = 1\,564$, $\lambda = 1.541\,78$ Å, $\mu(\text{Cu-K}_\alpha) = 105.36$ cm^{-1} , space group $P\bar{1}$ (from structural analysis).

Intensity data were collected by the ω – 2θ scan method with individual profile analysis.¹¹ One reflection was measured every 50 reflections as a check of the alignment and instrument stability; a total of 9 990 reflections were measured and 6 050 of these, having $I > 3\sigma(I)$, were considered as observed. The structure amplitudes were obtained after usual Lorentz and polarization reduction and put on absolute scale by least squares. An empirical absorption correction was also applied.¹²

The structure was solved, locating the copper and iodine atoms by combined Patterson and direct methods; the full structure was determined by standard Fourier methods. One molecule of methanol solvate was identified, with the oxygen atom distributed in two positions each with occupancy 0.5. Refinements were carried out by block-diagonal least squares, isotropically for phenyl rings and methanol, anisotropically for other atoms.

Forty reflections were excluded from the final refinement as

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii–xx.

Table 1. Fractional atomic co-ordinates ($\times 10^4$) for $[\text{Cu}(\text{Hdpdma})_2]\text{I}$

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
I(1)	2 406(0)	545(1)	4 682(1)	C(23)	944(7)	2 003(9)	4 508(10)
I(2)	-2 086(0)	6 369(1)	3 604(1)	C(24)	1 424(7)	2 645(9)	3 669(9)
Cu(1)	-13(1)	2 986(2)	3 427(2)	C(25)	2 545(7)	2 741(10)	2 410(11)
Cu(2)	4 565(1)	1 406(2)	-2 542(2)	C(26)	2 772(8)	2 019(11)	1 706(13)
S(1)	-808(2)	3 366(3)	4 895(3)	C(27)	3 286(10)	2 322(15)	788(16)
S(2)	-361(2)	3 467(3)	1 983(3)	C(28)	3 520(10)	3 330(16)	664(16)
S(3)	-171(2)	1 294(3)	3 402(4)	C(29)	3 293(11)	4 028(16)	1 386(18)
S(4)	1 164(2)	3 538(3)	3 249(3)	C(30)	2 764(8)	3 745(12)	2 337(13)
S(5)	4 604(2)	3 118(3)	-2 087(3)	C(31)	3 788(7)	4 904(9)	-1 622(10)
S(6)	3 391(2)	770(3)	-2 217(3)	C(32)	4 468(9)	5 318(12)	-1 415(14)
S(7)	5 156(2)	1 444(3)	-4 286(2)	C(33)	4 538(9)	6 215(13)	-672(14)
S(8)	5 251(2)	941(3)	-1 591(3)	C(34)	4 001(9)	6 626(12)	-244(13)
N(1)	-1 730(5)	4 440(7)	4 838(8)	C(35)	3 345(9)	6 202(13)	-454(14)
N(2)	-1 022(5)	4 923(7)	2 011(7)	C(36)	3 227(7)	5 319(10)	-1 136(11)
N(3)	674(5)	276(7)	3 856(8)	C(37)	3 923(6)	3 258(9)	-2 561(9)
N(4)	2 016(5)	2 379(7)	3 307(8)	C(38)	3 558(6)	2 420(9)	-3 311(9)
N(5)	3 633(5)	4 020(7)	-2 338(8)	C(39)	3 094(6)	1 653(9)	-2 602(8)
N(6)	2 437(5)	1 753(7)	-2 296(8)	C(40)	1 926(7)	1 181(10)	-1 528(11)
N(7)	6 364(5)	910(7)	-5 067(7)	C(41)	1 741(9)	1 673(13)	-512(14)
N(8)	6 439(5)	347(7)	-2 380(7)	C(42)	1 197(11)	1 051(16)	201(17)
C(1)	-2 300(6)	3 991(9)	5 595(10)	C(43)	926(10)	128(16)	-150(17)
C(2)	-2 228(8)	3 438(11)	6 379(12)	C(44)	1 077(10)	-321(15)	-1 074(17)
C(3)	-2 845(9)	3 098(12)	7 138(13)	C(45)	1 633(8)	215(12)	-1 883(13)
C(4)	-3 476(8)	3 234(12)	7 057(13)	C(46)	6 656(7)	1 589(10)	-5 838(10)
C(5)	-3 524(8)	3 786(12)	6 248(13)	C(47)	7 398(7)	1 749(10)	-6 129(12)
C(6)	-2 928(8)	4 156(11)	5 510(12)	C(48)	7 707(8)	2 420(12)	-6 894(13)
C(7)	-1 094(7)	4 248(9)	4 479(10)	C(49)	7 351(8)	2 892(12)	-7 350(13)
C(8)	-650(6)	4 894(10)	3 670(9)	C(50)	6 631(9)	2 751(13)	-7 042(14)
C(9)	-698(6)	4 446(9)	2 499(9)	C(51)	6 259(8)	2 046(11)	-6 299(12)
C(10)	-1 138(6)	4 781(9)	920(10)	C(52)	5 753(6)	791(8)	-4 378(9)
C(11)	-1 219(7)	5 612(10)	542(11)	C(53)	5 649(6)	-10(9)	-3 640(9)
C(12)	-1 385(8)	5 575(12)	-509(13)	C(54)	5 823(6)	415(9)	-2 530(10)
C(13)	-1 487(8)	4 653(11)	-1 143(12)	C(55)	6 770(6)	640(9)	-1 444(10)
C(14)	-1 418(9)	3 812(13)	-747(14)	C(56)	7 479(7)	834(10)	-1 645(12)
C(15)	-1 246(7)	3 877(10)	300(11)	C(57)	7 877(8)	1 116(11)	-824(13)
C(16)	449(6)	-679(9)	3 304(10)	C(58)	7 522(9)	1 156(12)	238(13)
C(17)	-50(8)	-842(11)	2 598(13)	C(59)	6 817(9)	968(12)	469(13)
C(18)	-202(9)	-1 825(13)	2 077(14)	C(60)	6 404(7)	680(10)	-383(12)
C(19)	95(8)	-2 581(12)	2 192(13)	C(61)	5 876(28)	6 246(40)	5 857(42)
C(20)	562(7)	-2 371(11)	2 920(12)	O(2)	5 595(27)	7 134(40)	6 479(41)
C(21)	732(6)	-1 419(9)	3 483(10)	O(1)	5 229(35)	6 092(47)	5 373(52)
C(22)	490(6)	1 105(10)	3 897(10)				

they were probably affected by counting error or extinction; hydrogen atoms were not located. The final indices were $R = 0.068$ and $R' = 0.073$. The atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 13. The function minimized was $\sum w|\Delta F^2|$ where $w = k/[\sigma^2(F_o) + gF_o^2]$ ($k = 1.30$, $g = 3.06 \times 10^{-3}$).

Final atomic co-ordinates are given in Table 1. The major calculations were performed on the CRAY X/MP computer of the Centro di Calcolo dell'Italia Nord-Orientale, Bologna, and on the GOULD-SEL 77/22 computer of the Centro di Studio per la Strutturistica Diffraattometrica del C.N.R. (Parma) using the SHELX 76 program¹⁴ for solution and refinement of the structure, PARST for the geometrical description of the structure,¹⁵ and ORTEP¹⁶ for the structure drawings.

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

Results and Discussion

Structure.—In the unit cell two crystallographically independent $[\text{Cu}(\text{Hdpdma})_2]^+$ cations, two iodine anions, and one

methanol solvate molecule are present. The co-ordination around each copper atom is distorted tetrahedral and involves four sulphur atoms belonging to two Hdpdma molecules, which are bidentate and form two six-membered chelate rings (see Figures 1 and 2).

Selected bond distances and angles are given in Table 2. Distortion of the co-ordination polyhedra from the regular tetrahedral geometry is very small and can be measured by using dihedral angles between the planes $\text{S}(1)\text{—Cu}(1)\text{—S}(4)$ and $\text{S}(3)\text{—Cu}(1)\text{—S}(2)$, $90.8(2)^\circ$ for molecule (I), $\text{S}(5)\text{—Cu}(2)\text{—S}(7)$ and $\text{S}(6)\text{—Cu}(2)\text{—S}(8)$, $97.7(1)^\circ$ for molecule (II). The Cu—S distances range from 2.291(4) Å to 2.327(5) Å for (I) and from 2.268(6) to 2.381(5) Å for (II) and are comparable with those found in other similar four-co-ordinate copper(I) complexes.^{17,18} The ligand bite $[\text{S}(1) \cdots \text{S}(2)$ 3.646(5), $\text{S}(3) \cdots \text{S}(4)$ 3.617(5), $\text{S}(5) \cdots \text{S}(6)$ 3.613(5), $\text{S}(7) \cdots \text{S}(8)$ 3.644(5) Å], much larger than the sum of the van der Waals radii for sulphur (3.52 Å),¹⁹ is comparable with the value of 3.63 Å found in $[\text{Zn}\{\text{SC}(\text{OEt})\text{CHC}(\text{S})\text{Me}\}_2]$, where the Zn atom exhibits tetrahedral co-ordination.^{20,21} In the recently investigated $[\text{Ni}(\text{dpdma})_2]\cdot 2\text{dmf}$ (dmf = dimethylformamide) the bite of the ligand, $\text{S} \cdots \text{S}$ 3.213(2) Å [$\text{S} \cdots \text{S}$ interligand distance 2.903(3) Å], can be justified for the square-planar co-ordination around the metal.

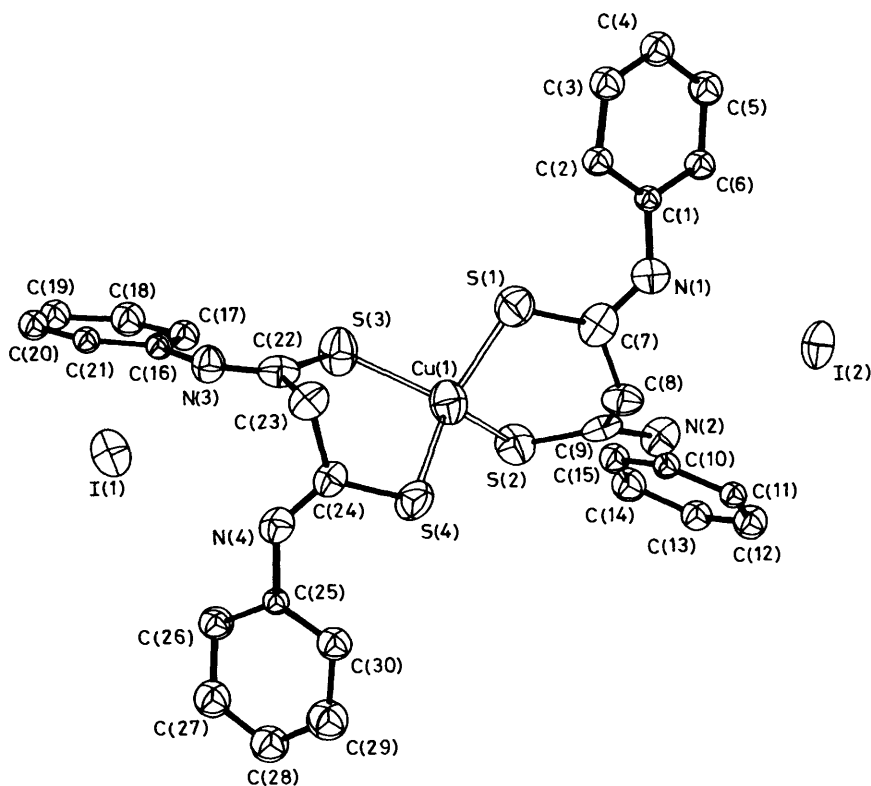


Figure 1. ORTEP view of molecule (I)

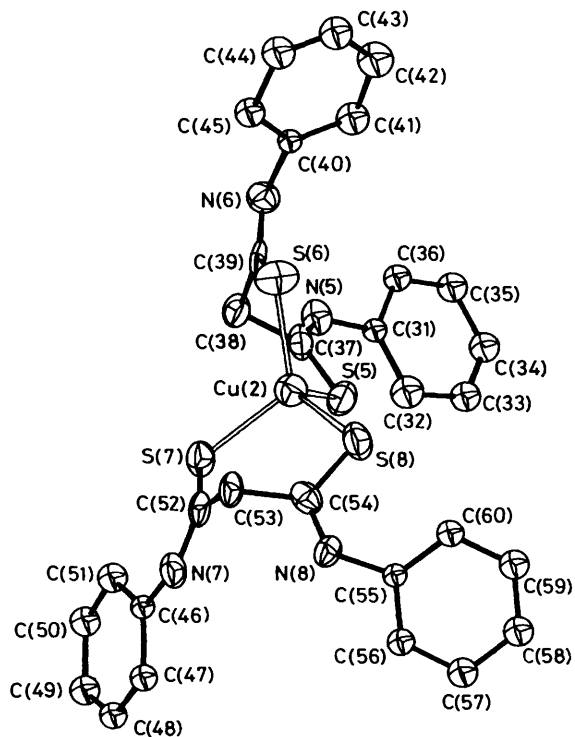


Figure 2. ORTEP view of molecule (II)

By comparing the co-ordination behaviour of the dithio-malonamides with the dithio-oxamides, it appears that the latter are more flexible ligands. Dithiomalonamides, like dithioacetyl-

acetones,^{1,22} have always been found to act as bidentate,^{1,7,9} while dithio-oxamides can act as uni-²³ or bi-dentate²⁴ ligands.

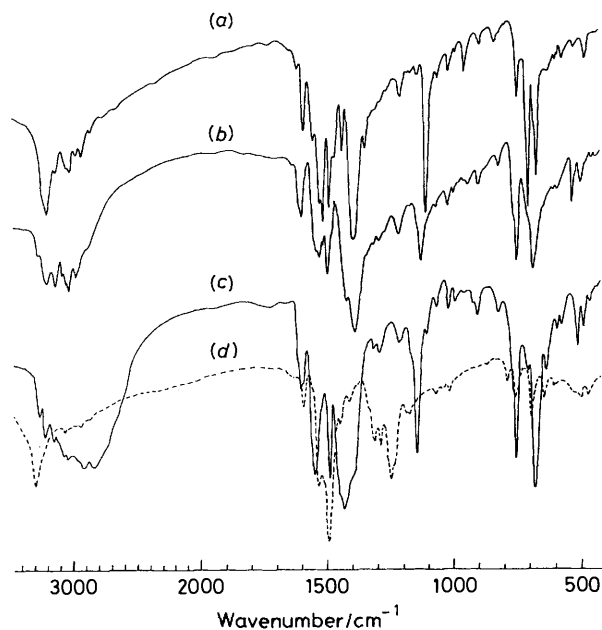
In the present structure each chelate ring exhibits a boat conformation, with copper and tetrahedral carbon atoms out of the mean plane through sulphur and adjacent carbons. The S-C-N-C systems in each ligand are planar and quite orthogonal, and the S-C and N-C bond lengths indicate a π -delocalization similar to that found in dithio-oxamide complexes.²⁴ The nitrogen atoms, exhibiting a sp^2 hybridization, are involved in N...I contacts which can be considered as hydrogen bonds. The shortest of these contacts involves N(2) and I(2): N(2)-H...I(2) 3.48(1) Å, N(2)-H...I(2) 159(2)° (the hydrogen atom is in the calculated position). The packing is determined by these contacts, by ring-stacking interactions involving C(1)-C(6) and C(46')-C(51') (I $x-1, y, z+1$) phenyl rings, the shortest contact being C(1)...C(47') 3.56(2) Å, and by an O...O contact between two symmetry-related disordered methanol molecules [O(1)...O(1^h) (II $1-x, 1-y, 1-z$) 3.05(9) Å].

I.r. Spectra.—The i.r. spectra of the complexes (Figure 3) are slightly perturbed in shape, number, and position of the bands with respect to that of the free ligand, strictly paralleling the behaviour of the ¹H and ¹³C n.m.r. spectra (see below). The bands involving the NH group appear split in the complexes owing to a different involvement of this group in hydrogen bonding with the counter anion in the packing of the molecules.

By comparing the i.r. spectra of the present complexes with those of [Ni(Hdpdma)₂]X₂ and [Ni(Hdpdma)₃]X₂ (X = Cl, Br, I, or ClO₄),² [Pd(Hdpdma)X₂] (X = Cl, Br, or I) and [Pd(Hdma)₂]X₂ (Hdma = dithiomalonamide; X = Cl, Br, I, or ClO₄),⁴ [Zn(Hdpdma)X₂] and [Zn(Hdpdma)₂][ClO₄]₂²⁵ one can observe (Figure 3) that they are practically identical. Therefore in the light of the present structural results, previous statements of S,N ligand co-ordination, based on spectroscopic

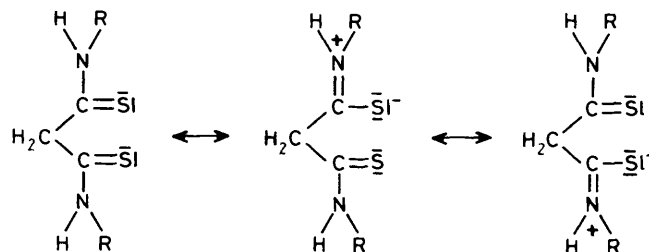
Table 2. Selected bond distances (Å) and angles (°)

(I)		(II)		(I)		(II)	
Cu(1)-S(1)	2.303(4)	Cu(2)-S(5)	2.381(5)	S(1)-Cu(1)-S(2)	103.9(2)	S(5)-Cu(2)-S(6)	100.7(2)
Cu(1)-S(2)	2.327(5)	Cu(2)-S(6)	2.298(4)	S(1)-Cu(1)-S(3)	102.7(2)	S(5)-Cu(2)-S(7)	99.4(2)
Cu(1)-S(3)	2.321(5)	Cu(2)-S(7)	2.303(4)	S(1)-Cu(1)-S(4)	125.9(2)	S(5)-Cu(2)-S(8)	109.1(2)
Cu(1)-S(4)	2.291(4)	Cu(2)-S(8)	2.268(6)	S(2)-Cu(1)-S(3)	114.1(2)	S(6)-Cu(2)-S(7)	120.3(2)
				S(2)-Cu(1)-S(4)	107.3(2)	S(6)-Cu(2)-S(8)	119.1(2)
				S(3)-Cu(1)-S(4)	103.3(2)	S(7)-Cu(2)-S(8)	105.7(2)
S(1)-C(7)	1.68(2)	S(5)-C(37)	1.67(1)	Cu(1)-S(1)-C(7)	102.5(5)	Cu(2)-S(5)-C(37)	102.5(5)
S(2)-C(9)	1.68(1)	S(6)-C(39)	1.67(1)	Cu(1)-S(2)-C(9)	105.1(4)	Cu(2)-S(6)-C(39)	101.1(5)
S(3)-C(22)	1.67(1)	S(7)-C(52)	1.67(1)	Cu(1)-S(3)-C(22)	106.7(5)	Cu(2)-S(7)-C(52)	106.2(5)
S(4)-C(24)	1.66(2)	S(8)-C(54)	1.71(1)	Cu(1)-S(4)-C(24)	103.8(5)	Cu(2)-S(8)-C(54)	105.7(5)
N(1)-C(7)	1.36(2)	N(5)-C(37)	1.32(2)	S(1)-C(7)-N(1)	124.5(9)	S(5)-C(37)-N(5)	126.9(9)
N(1)-C(1)	1.43(1)	N(5)-C(31)	1.44(1)	N(1)-C(7)-C(8)	114(1)	N(5)-C(37)-C(38)	114(1)
N(2)-C(9)	1.33(2)	N(6)-C(39)	1.35(2)	S(1)-C(7)-C(8)	121(1)	S(5)-C(37)-C(38)	119.4(9)
N(2)-C(10)	1.43(2)	N(6)-C(40)	1.44(2)	C(7)-N(1)-C(1)	132(1)	C(37)-N(5)-C(31)	130(1)
N(3)-C(22)	1.30(2)	N(7)-C(52)	1.36(1)	C(7)-C(8)-C(9)	113(1)	C(37)-C(38)-C(39)	107.2(9)
N(3)-C(16)	1.43(1)	N(7)-C(46)	1.41(2)	S(2)-C(9)-N(2)	127.6(9)	S(6)-C(39)-N(6)	123.1(9)
N(4)-C(24)	1.32(2)	N(8)-C(54)	1.32(2)	N(2)-C(9)-C(8)	112(1)	N(6)-C(39)-C(38)	115(1)
N(4)-C(25)	1.46(2)	N(8)-C(55)	1.44(2)	S(2)-C(9)-C(8)	120.4(1)	S(6)-C(39)-C(38)	122.0(9)
C(7)-C(8)	1.48(2)	C(37)-C(38)	1.54(2)	C(10)-N(2)-C(9)	130(1)	C(40)-N(6)-C(39)	125(1)
C(8)-C(9)	1.54(2)	C(38)-C(39)	1.52(2)	S(3)-C(22)-N(3)	127(1)	S(7)-C(52)-N(7)	125.8(9)
C(22)-C(23)	1.57(2)	C(52)-C(53)	1.52(2)	N(3)-C(22)-C(23)	114(1)	N(7)-C(52)-C(53)	113(1)
C(23)-C(24)	1.53(2)	C(53)-C(54)	1.52(2)	S(3)-C(22)-C(23)	118(1)	S(7)-C(52)-C(53)	120.7(9)
				C(16)-N(3)-C(22)	132(1)	C(46)-N(7)-C(52)	130(1)
				C(22)-C(23)-C(24)	108(1)	C(52)-C(53)-C(54)	112(1)
				S(4)-C(24)-N(4)	126.2(9)	S(8)-C(54)-N(8)	124.8(9)
				N(4)-C(24)-C(23)	113(1)	N(8)-C(54)-C(53)	114(1)
				S(4)-C(24)-C(23)	120(1)	S(8)-C(54)-C(53)	120.7(9)
				C(25)-N(4)-C(24)	127(1)	C(55)-N(8)-C(54)	130(1)

**Figure 3.** Comparison of the i.r. spectra of Hdpma (a) and of its complexes $[\text{Cu}(\text{Hdpma})_2]\text{I}_2$ (b), $[\text{Ni}(\text{Hdpma})_2]\text{I}_2$ (c), and $[\text{Ni}(\text{dpdma})_2]\text{I}_2$

evidence, must be corrected; for all the above mentioned complexes there is reasonable evidence for S,S ligand co-ordination.

Proton and ^{13}C N.M.R. Spectra.—The data for the free ligand (Table 3) and, in particular, the two multiplets with relative intensity ratio 2:3 (*o*-, *m*- and *p*-H, respectively), due to magnetically non-equivalent phenyl protons (^1H n.m.r.), and



the resonance assignable to C_6H_5 carbons (^{13}C n.m.r.), may be interpreted by considering the effect on the nature of the phenyl substituent by the contribution from the canonical structures shown above.

The n.m.r. spectra of the copper(I) complexes are slightly perturbed with respect to that of the free ligand. In the ^1H n.m.r. spectrum the singlets of the NH and CH_2 protons are shifted downfield by about 0.2 and 0.1 p.p.m., respectively, and the two multiplets due to the C_6H_5 protons, again in the intensity ratio 2:3, are still separated, although the distance between their peaks is diminished.

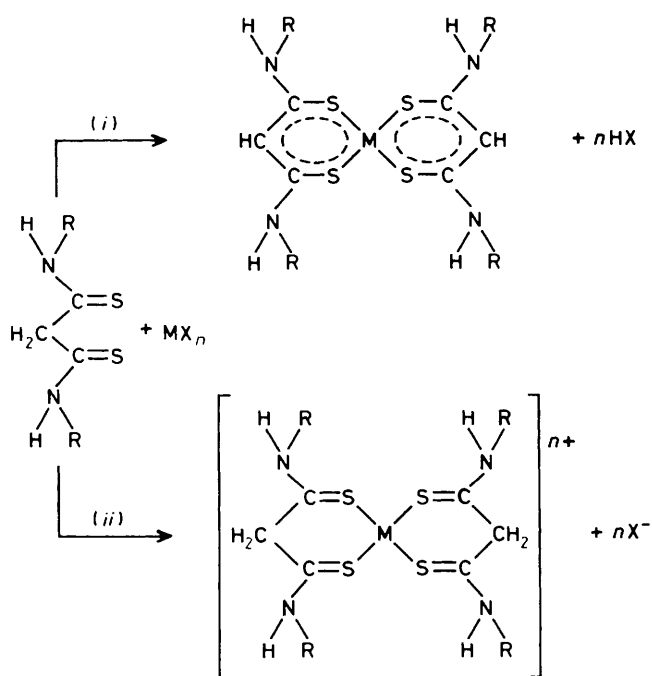
The addition of free Hdpdma to the complexes in solution causes a progressive broadening and a shift of the averaged signals towards the position of the free ligand. At ligand/complex molar ratios higher than 2:1 the pattern becomes indistinguishable from that of the free ligand. This strongly suggests that a fast exchange of the complex with the ligand occurs and the dissociation equilibrium in such a solution is more rapid than the n.m.r. time-scale.

The ^{13}C n.m.r. spectrum of $[\text{Cu}(\text{Hdpdma})_2]\text{I}_2 \cdot 0.5\text{MeOH}$ exhibits only a single C=S resonance shifted by 1.3 p.p.m. upfield with respect to that of the free ligand, excluding a S,N ligand co-ordination, and the whole set of data is consistent with S,S ligand co-ordination, in accord with the structural results.

Table 3. Proton and ^{13}C n.m.r. chemical shifts ($\delta/\text{p.p.m.}$) of Hdpdma and its metal complexes in $(\text{CD}_3)_2\text{SO}$ at 23 and 27 °C respectively

Compound	^1H			^{13}C		
	NH	C_6H_5	CH_2	C=S	C_6H_5	CH_2
Hdpdma	11.86 (s, 2 H)	7.85 (m, } 10 H) 7.45 (m, }	4.30 (s, 2 H)	195.41	139.40 128.51 126.12 123.04	62.85
$[\text{Cu}(\text{Hdpdma})_2]\text{Cl}$	12.08 (s, 4 H)	7.74 (m, } 20 H) 7.48 (m, }	4.39 (s, 4 H)			
$[\text{Cu}(\text{Hdpdma})_2]\text{Br}$	12.08 (s, 4 H)	7.74 (m, } 20 H) 7.49 (m, }	4.39 (s, 4 H)			
$[\text{Cu}(\text{Hdpdma})_2]\text{I}$	12.05 (s, 4 H)	7.73 (m, } 20 H) 7.48 (m, }	4.40 (s, 4 H)	194.11	138.42 128.78 127.04 123.47	61.39
$[\text{Ni}(\text{dpdma})_2]^*$	9.81 (s, 4 H)	7.19 (m, 20 H)		173.80	139.40 128.67 123.80	

* CH: ^1H , 6.15 (s, 2 H); ^{13}C , 99.32 p.p.m.



Scheme. (i) Neutral media, $\text{M} = \text{Ni}^{\text{II}}$, Pd^{II} , or Pt^{II} , $n = 2$; (ii) acidic media, $\text{M} = \text{Ni}^{\text{II}}$, Zn^{II} , Cu^{I} , or Pd^{II}

Because of the contribution of the canonical structures of the ligand, which acts in its neutral form (and not in the deprotonated form, as in $[\text{Ni}(\text{dpdma})_2] \cdot 2\text{dmf}$ ⁵), see Scheme, the six-membered ring formed upon co-ordination does not assume aromatic character; thus the separation between the two multiplets, due to the phenyl protons, is still maintained upon complexation.

For comparison Table 3 reports ^1H and ^{13}C n.m.r. data for $[\text{Ni}(\text{dpdma})_2] \cdot 2\text{dmf}$, in which the ligand co-ordination through sulphur involves the removal of a proton from the CH_2 group and formation of a six-membered aromatic ring (as in acetylacetonates and dithioacetylacetonates²²) as demonstrated by structural data.^{1,5} Although S,S ligand co-ordination occurs in both types of complexes, the chemical shift changes are very large in the neutral complex, as expected in view of the differences in the ligand behaviour when neutral or anionic.

These differences are also reflected in cationic copper(I) complexes where N-C (non-aromatic carbon) and C=S linkages have a more pronounced double-bond character than in neutral ML_2 ($\text{M} = \text{Ni}^{\text{II}}$ or Pd^{II}) complexes.

Conclusions

The accumulation of more recent data (this work and refs. 1, 3, 5, and 8) enables some rather more specific observations on the co-ordinative abilities of dithiomalonamides, which are found to act as anionic or neutral ligands. First they invariably function as bidentate chelates *via* the sulphur atoms, forming complexes with substantial electron delocalization in the six-membered chelate ring, stabilizing the planar form of monomeric complexes, particularly those of Ni^{II} , Pd^{II} , and Pt^{II} (obtained in neutral media).^{1,3,5,8}

When dithiomalonamides act as neutral ligands they are still found to give S,S chelation, but leading to saturated six-membered MS_2C_3 ring systems. This situation has been found in complexes such as $[\text{SbCl}_3\{\text{C}_2\text{H}_5\text{NHC}(\text{S})\text{CH}_2\text{C}(\text{S})\text{NHC}_2\text{H}_5\}]$, prepared in a neutral medium,⁹ and in the copper(I) complexes, prepared in strong acidic media (present work). Furthermore, since in acidic media dithiomalonamides form complexes of the type $[\text{Ni}(\text{HL})_3]\text{X}_2$, $[\text{M}(\text{HL})_2]\text{X}_2$ ($\text{M} = \text{Ni}^{\text{II}}$, Zn^{II} , or Pd^{II} ; $\text{X} = \text{Cl}$, Br , I , or ClO_4), and $[\text{M}(\text{HL})\text{X}_2]$ ($\text{M} = \text{Zn}^{\text{II}}$ or Pd^{II} ; $\text{X} = \text{Cl}$, Br , or I), which present i.r. spectra nearly identical to those observed for the complexes discussed in the present work, the hypothesis of S,S ligand chelation can also be reasonably extended to all those compounds.

The above conclusions are reinforced by the structural results. 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 peptide groups, the nitrogen atoms of which have never been found to bear both a proton and a metal ion simultaneously.²⁶ Therefore the co-ordination of a nitrogen bearing a hydrogen atom in dithiomalonamides, in agreement with what has been suggested for dithio-oxamides,²⁴ may be considered highly improbable.

Acknowledgements

The authors are grateful to the Centro di Calcolo of the University of Parma for computing facilities and to the Ministero of the Pubblica Istruzione of Italy for financial support.

References

- 1 T. N. Lockyer and R. L. Martin, *Prog. Inorg. Chem.*, 1980, **27**, 223.
- 2 G. Peyronel, G. C. Pellacani, G. Benetti, and G. Pollacci, *J. Chem. Soc., Dalton Trans.*, 1973, 879.
- 3 R. L. Martin and A. F. Masters, *Inorg. Chem.*, 1975, **14**, 885.
- 4 G. C. Pellacani, *Can. J. Chem.*, 1974, **20**, 52.
- 5 L. P. Battaglia, A. Bonamartini Corradi, A. Marzotto, L. Menabue, and G. C. Pellacani, *J. Crystallogr. Spectrosc. Res.*, in the press.
- 6 L. Menabue and G. C. Pellacani, *J. Chem. Soc., Dalton Trans.*, 1976, 455.
- 7 M. G. B. Drew, J. M. Kisenyi, and G. R. Willey, *J. Chem. Soc., Dalton Trans.*, 1984, 1727.
- 8 J. M. Bret, P. Castan, and J. P. Laurent, *J. Chem. Soc., Dalton Trans.*, 1984, 1975.
- 9 J. M. Kisenyi, G. R. Willey, and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1985, 1073.
- 10 G. C. Pellacani, G. Peyronel, T. Feltri, and L. Menabue, *Spectrochim. Acta, Part A*, 1976, **32**, 285.
- 11 M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A*, 1974, **30**, 580.
- 12 F. Uguzzoli, ASSORB, A program for Walker and Stuart's absorption correction, University of Parma, 1983.
- 13 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
- 14 G. M. Sheldrick, SHELX 76 program for crystal structure determination, University Chemical Laboratory, Cambridge, 1976.
- 15 M. Nardelli, *Comput. Chem.*, 1983, **7**, 95.
- 16 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, 1965.
- 17 J. T. Gill, J. J. Mayerle, P. S. Welcker, D. F. Lewis, D. A. Ucko, D. J. Barton, D. Stowens, and S. J. Lippard, *Inorg. Chem.*, 1976, **15**, 1155.
- 18 B. E. Green, C. H. L. Kennard, G. Smith, B. D. James, and A. H. White, *Acta Crystallogr., Sect. C*, 1984, **40**, 426.
- 19 L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, 1960.
- 20 R. Beckett and B. F. Hoskins, *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 679.
- 21 R. Beckett and B. F. Hoskins, *J. Chem. Soc., Dalton Trans.*, 1975, 908.
- 22 R. Beckett and B. F. Hoskins, *J. Chem. Soc., Dalton Trans.*, 1974, 622.
- 23 M. Belicchi Ferrari, G. Gasparri Fava, C. Pelizzi, and P. Tarasconi, *Inorg. Chim. Acta*, 1985, **98**, L49.
- 24 L. Antolini, A. C. Fabretti, G. Franchini, L. Menabue, G. C. Pellacani, H. O. Desseyn, R. Dommissie, and H. C. Hofmans, *J. Chem. Soc., Dalton Trans.*, 1987, 1921.
- 25 G. C. Pellacani, G. Peyronel, G. Pollacci, and R. Coronati, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1619.
- 26 H. Sigel and R. B. Martin, *Chem. Rev.*, 1982, **82**, 385.

Received 8th April 1987; Paper 7/623