

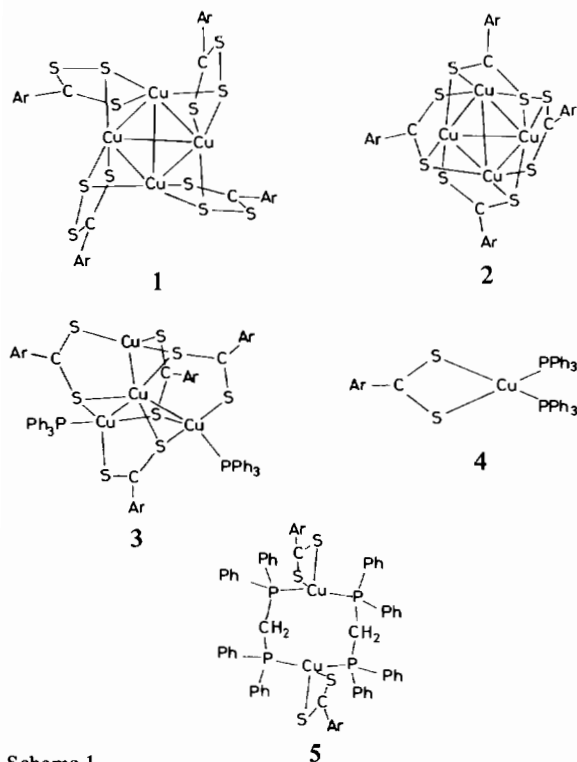
## Structural Features of Copper(I) Perthio- and Dithio-carboxylates from Carbon-13 NMR Spectra

GIORGIO PELLIZER\*, NAZARIO MARSICH  
and ANNAMARIA CAMUS

Dipartimento di Scienze Chimiche, Università di Trieste,  
Trieste, Italy

(Received August 2, 1988)

Recently we have isolated several copper(I) aryl perthio- (1) and dithio-carboxylates (2) [1, 2] and complexes of the latter with tertiary phosphines [(CuS<sub>2</sub>CAR)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (3) [3], [CuS<sub>2</sub>CAR(PPh<sub>3</sub>)<sub>2</sub>] (4) [4] and [CuS<sub>2</sub>CAR(dppm)]<sub>2</sub> (dppm = bis(diphenylphosphino)methane) (5) [5]. Their solid state structures have been determined by X-ray diffraction and are sketched in Scheme 1. In compounds 1, 2



Scheme 1.

and 3 the CS<sub>3</sub> and CS<sub>2</sub> groups behave as μ<sub>2</sub> and μ<sub>3</sub> ligands, while in compounds 4 and 5 the CS<sub>2</sub> groups are chelating. In the *o*-tolyl derivatives the aromatic ring bearing the dithio- or perthio-carboxylate

is always strongly bent with respect to the SCS plane.

As reported in this letter, <sup>13</sup>C NMR spectra are useful to distinguish between dithio- and perthio-carboxylates and to unravel the bonding mode of the ligand in these complexes. They also make available further structural information and hints on the kinetic behaviour of the phosphine complexes.

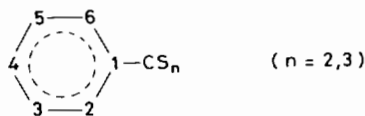
## Experimental

Preparation of the above compounds has been previously reported [1–3].

FT NMR spectra were run from 10 mm samples with a Bruker WP80 equipped with a BNC28 computer with 8K data points. Carbon spectra were obtained at 20.1 MHz with a flip angle of 40°, broad band <sup>1</sup>H decoupling and digital resolution of 1.5 Hz, from saturated solutions containing TMS as internal reference. Reported data are for room temperature spectra.

## Results and Discussion

<sup>13</sup>C δ values for aryl perthio and dithio moieties are reported in Table 1. Numbering of the aryl carbon atoms is shown in Scheme 2. The data marked ? are tentative, owing to overlap with larger peaks or to the low solubility of the compounds which, even after 100 000 scans, implies resonances of weak intensity for the CS<sub>3</sub> and CS<sub>2</sub> carbons.



Scheme 2.

The spectra of ArCS<sub>n</sub> moieties show four aromatic carbon peaks for phenyl and *p*-tolyl derivatives and six for *o*-tolyl derivatives. The above resonances are very close in corresponding PPh<sub>3</sub> and dppm derivatives.

Cu<sub>3</sub>C and CuS<sub>2</sub>C groups have strong deshielding substituent effects at the *ipso*-carbon. The effects on C-1 and C-3 are different enough (Table 1) to be useful in recognizing the functional group.

The most relevant result is, however, the strong dependence of the CS<sub>2</sub> carbon shielding on the mode of binding with copper atoms. As compounds of corresponding formulae and presumably very

\* Author to whom correspondence should be addressed.

TABLE 1.  $^{13}\text{C}$  Chemical Shifts of Perthio- and Dithio-carboxylate Moieties ( $\delta$  Values in ppm from TMS)

Compound	Solvent	Aromatic carbons						CS <sub>2-3</sub>	CH <sub>3</sub>
		C-1	C-2	C-3	C-4	C-5	C-6		
[CuS <sub>3</sub> CPh] <sub>n</sub>	d <sub>5</sub> -py	?144	127.9	129.1	131.5	129.1	127.9	?227.8	
[CuS <sub>2</sub> CPh] <sub>n</sub>	d <sub>5</sub> -py	ob.	127.9	127.9	131.9	127.9	127.9	234.1	
[(CuS <sub>2</sub> CPh) <sub>4</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	d <sub>5</sub> -py <sup>a</sup>	n.d.	127.5	127.8	131.0	127.8	127.5	238.2	
	CDCl <sub>3</sub>	147.9	127.6	127.8	131.6	127.8	127.6		
[CuS <sub>2</sub> CPh(PPh <sub>3</sub> ) <sub>2</sub> ]	CDCl <sub>3</sub>	147.5	125.8	127.6	131.1	127.6	125.8	248.5	
[CuS <sub>2</sub> CPh(dppm)] <sub>2</sub>	CDCl <sub>3</sub>	147.8	126.3	127.6	131.0	127.6	126.3	247.5	
[CuS <sub>3</sub> C- <i>p</i> -T] <sub>n</sub>	d <sub>5</sub> -py	n.d.	127.9	129.7	142.0	129.7	127.9	n.d.	21.2
[CuS <sub>2</sub> C- <i>p</i> -T] <sub>4</sub>	d <sub>5</sub> -py	146.6	128.3	128.8	141.8	128.8	128.3	234.0	21.2
[(CuS <sub>2</sub> C- <i>p</i> -T) <sub>4</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	d <sub>5</sub> -py <sup>a</sup>	?145.9	ob.	ob.	141.6	ob.	ob.	238.4	21.3
	CDCl <sub>3</sub>	145.5	128.1	ob.	142.8	ob.	128.1	n.d.	21.5
[CuS <sub>2</sub> C- <i>p</i> -T(PPh <sub>3</sub> ) <sub>2</sub> ]	d <sub>5</sub> -py	145.4	126.5	?129	142.4	?129	126.5	248.8	21.3
	CDCl <sub>3</sub>	145.2	125.9	128.3	141.6	128.3	125.9	248.0	21.5
[CuS <sub>2</sub> C- <i>p</i> -T(dppm)] <sub>2</sub>	CDCl <sub>3</sub>	?145.5	126.4	128.3	141.3	128.3	126.4	246.8	21.5
[CuS <sub>3</sub> C- <i>o</i> -T] <sub>4</sub>	<sup>b</sup>	140.5	135.3	<sup>c</sup>		126.3		231.1	20.2
[CuS <sub>2</sub> C- <i>o</i> -T] <sub>n</sub>	d <sub>5</sub> -py	?151.5	132.5	<sup>c</sup>		125.6		n.d.	20.2
[(CuS <sub>2</sub> C- <i>o</i> -T) <sub>4</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	d <sub>5</sub> -py <sup>a</sup>	?153.4	132.1	<sup>c</sup>		125.4		n.d.	20.3
[CuS <sub>2</sub> C- <i>o</i> -T(PPh <sub>3</sub> ) <sub>2</sub> ]	d <sub>5</sub> -py	153.7	132.5	<sup>c</sup>		125.7		256.0	20.6
	CDCl <sub>3</sub>	153.0	132.5			125.4		255.5	20.3
[CuS <sub>2</sub> C- <i>o</i> -T(dppm)] <sub>2</sub>	CDCl <sub>3</sub>	153.1	132.4	<sup>c</sup>		125.4		?256	20.3

ob. = obscured; n.d. = non-detectable.

<sup>a</sup>If not perfectly deaerated the sample changes slowly while recording the spectrum. <sup>b</sup>CS<sub>2</sub>/d<sub>6</sub>-acetone 2:1 v/v mixture. <sup>c</sup>Resonances at 131.6, 131.1, 128.8 ppm in [CuS<sub>3</sub>C-*o*-T]<sub>4</sub>; 130.6, 127.5, 126.7 ppm in [(CuS<sub>2</sub>C-*o*-T)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>]; 130.6, 127.9, 126.8 ppm in [CuS<sub>2</sub>C-*o*-T(PPh<sub>3</sub>)<sub>2</sub>]; 127.7, 130.5 and 126.7 ppm in [CuS<sub>2</sub>C-*o*-T(dppm)]<sub>2</sub> due to C-3; C-4 and C-6 carbons could not be assigned unambiguously. Only two resonances at 130.75 and 127.9 ppm were detected for [CuS<sub>2</sub>C-*o*-T]<sub>4</sub>.

close structures\* exhibit almost identical CS<sub>2</sub> chemical shifts, it is possible to recognize the kind of arrangement of the functional group through these  $\delta$  values.

In the complexes the CS<sub>2</sub> group is shielded with respect to the corresponding anions ArCS<sub>2</sub><sup>-</sup> [7] and deshielded with respect to the corresponding acids [7] and esters (see Supplementary Material). Chelating CS<sub>2</sub> (e.g. [CuS<sub>2</sub>CAr(PPh<sub>3</sub>)<sub>2</sub>] (4), [CuS<sub>2</sub>CAr(dppm)]<sub>2</sub> (5)) groups resonate close to the anions and are at least 10 ppm less shielded than bridging CS<sub>2</sub> groups (e.g. [CuS<sub>2</sub>CAr]<sub>n</sub> (2), [(CuS<sub>2</sub>CAr)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (3)), which resonate near to acids and esters.

\*Under inert atmosphere, all the compounds could be recovered unchanged from pyridine and chloroform solutions, suggesting that the original solid structures are retained also in these solvents. For some perthiocarboxylates, e.g. the [Cu- $\alpha$ -perthionaphthoato]<sub>4</sub> compound not considered in this letter, pyridine interferes, acting itself as a ligand and giving complexes of dimeric structure [CuS<sub>3</sub>C- $\alpha$ -C<sub>10</sub>H<sub>7</sub>(py)]<sub>2</sub>; but even then the binding mode of CS<sub>3</sub> does not change [6].

X-ray structures show that in the chelates [4, 5b] the two C-S distances are almost equal. Equal C-S bond lengths are expected for the anions. In the bridges [2, 3] the above distances are different, monodentate sulphur being nearer to carbon and therefore with a higher degree of double bonding; this difference is expected to be even more marked in acids and esters. Thus it can be concluded that the decrease of delocalization of  $\pi$ -bonding within the CS<sub>2</sub> moiety is the main factor responsible for the increase of the carbon shielding.

Both for copper complexes and for esters in the *ortho*-compounds the CS<sub>2</sub> group is remarkably more deshielded than in the corresponding phenyl and *p*-tolyl derivatives; this reflects the relevant twisting of the CS<sub>2</sub> group with respect to the aromatic ring. The same behaviour is observed moving from PhS<sub>2</sub>CPh to the non-conjugated PhS<sub>2</sub>CR [8]. A similar effect was reported also in  $\alpha$ -acetylnaphthalene,  $\gamma$ -acetylanthracene and in the methyl ester of 2,6-dimethylbenzoic acid and was attributed to a decrease of conjugation, owing to loss of coplanarity between the carbonyl group and the

TABLE 2. Phosphine  $^{13}\text{C}$  NMR Parameters<sup>a</sup>

Compound	Solvent	PPh <sub>3</sub>				CH <sub>2</sub>
		<i>ipso</i>	<i>ortho</i>	<i>meta</i>	<i>para</i>	
PPh <sub>3</sub>	d <sub>5</sub> -py	138.2d (12)	134.4d (21)	129.25d (7)	129.4	
	CDCl <sub>3</sub>	137.5d (10)	133.6d (21)	128.7d (7)	128.9	
dppm	CDCl <sub>3</sub>	139.1m	133.0m	128.6m	128.9	28.1t (23)
[(CuS <sub>2</sub> CPh) <sub>4</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	d <sub>5</sub> -py	ob.	134.2d	129.1d (9)	130.2	
	CDCl <sub>3</sub>		134.2d (15)	128.8d (9)	130.0	
[CuS <sub>2</sub> CPh(PPh <sub>3</sub> ) <sub>2</sub> ]	CDCl <sub>3</sub>	ob.	133.8 w <sub>H</sub> 9	128.7 w <sub>H</sub> 6	129.8	
[CuS <sub>2</sub> CPh(dppm)] <sub>2</sub>	CDCl <sub>3</sub>	?135.3 w <sub>H</sub> 30	133.1 w <sub>H</sub> 15	128.6 w <sub>H</sub> 8	129.6 w <sub>H</sub> 5	29.2 w <sub>H</sub> 12
[(CuS <sub>2</sub> C- <i>p</i> -T) <sub>4</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	d <sub>5</sub> -py	ob.	134.3d (14)	129.2d (9)	130.3	
[CuS <sub>2</sub> C- <i>p</i> -T(PPh <sub>3</sub> ) <sub>2</sub> ]	d <sub>5</sub> -py		134d (14)	129.3d (9)	130.3	
	CDCl <sub>3</sub>		134.0s w <sub>H</sub> 11	128.6s w <sub>H</sub> 5	129.7	
[CuS <sub>2</sub> C- <i>p</i> -T(dppm)] <sub>2</sub>	CDCl <sub>3</sub>	?135.5 w <sub>H</sub> 24	133.0 w <sub>H</sub> 10	128.6 w <sub>H</sub> 8	129.5 w <sub>H</sub> 5	29.2 w <sub>H</sub> 13
[(CuS <sub>2</sub> C- <i>o</i> -T) <sub>4</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	d <sub>5</sub> -py		134.2d (16)	129.3d (9)	?130	
[CuS <sub>2</sub> C- <i>o</i> -T(PPh <sub>3</sub> ) <sub>2</sub> ]	d <sub>5</sub> -py	?135	133.3 w <sub>H</sub> 16	129.2 w <sub>H</sub> 9	130.3	
	CDCl <sub>3</sub>	ob.	134.05 w <sub>H</sub> 12	128.8 w <sub>H</sub> 6	129.9	
[CuS <sub>2</sub> C- <i>o</i> -T(dppm)] <sub>2</sub>	CDCl <sub>3</sub>	?135.3	133.1 w <sub>H</sub> 12	128.6 w <sub>H</sub> 6	129.7 w <sub>H</sub> 5	29.3

d = doublet; m = multiplet; t = triplet.

<sup>a</sup> Values in ppm from TMS; splittings due to carbon-phosphorus coupling in parentheses in Hz; w<sub>H</sub> = half-height width of the peak, in Hz.

aryl ring [9]. Comparison of the effects observed for dithiobenzoic and benzoic esters [9] confirms that the former are more sterically hindered.

The phosphine  $^{13}\text{C}$  parameters are reported in Table 2. The *ipso*-carbon, expected to give a low intensity peak at about 134 ppm, is masked by the stronger resonances of the phosphine *ortho*-carbons. The complexation causes changes of shift negligible for *meta*- and not significant for *ortho*-carbons, while, as usual, deshields the *para*-carbons of the triphenylphosphine, which implies electron donation by the phosphine phenyls. It also decreases  $^2J_{\text{C-P}}$ , but, at our level of accuracy, does not affect  $^3J_{\text{P-C}}$ , again in agreement with the literature [10].

In compounds [(CuS<sub>2</sub>CAr)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>], where a copper atom is bonded at most to one phosphine,

the *ortho*- and *meta*-carbons of this ligand give doublets due to coupling with phosphorus, the magnitude of which are in excellent agreement with those observed for similar molecules [10]. In the [CuS<sub>2</sub>C-*p*-T(PPh<sub>3</sub>)<sub>2</sub>] compound, where in the solid state each copper is bonded to two phosphines, the spectrum shows for the same *ortho*- and *meta*-carbons broad singlets in CDCl<sub>3</sub>, but doublets in d<sub>5</sub>-pyridine.  $^{31}\text{P}$  spectra always consist of a single broad resonance. This suggests that in CDCl<sub>3</sub> the dominant form is [CuS<sub>2</sub>C-*p*-T(PPh<sub>3</sub>)<sub>2</sub>], the phosphine exchange being fast enough to cause a collapse of the carbon multiplets, while in d<sub>5</sub>-pyridine the main form has just one phosphine and the doublets observed for *ortho*- and *meta*-carbons are averages, due to fast exchange of phosphine between bonded and free situations. The complexes

with aliphatic dithiocarboxylates show this behaviour also in chloroform [10].

### Supplementary Material

Details on spectral assignment and  $^{13}\text{C}$  spectra of the mentioned methyldithiocarboxylato esters are available from the authors.

### Acknowledgements

We are grateful to the Italian MPI for support of this work. We thank Mr L. Stoppari for assistance in recording the NMR spectra.

### References

- 1 A. M. Manotti-Lanfredi, A. Tiripicchio, A. Camus and N. Marsich, *Inorg. Chim. Acta*, **142** (1988) 269.
- 2 A. Camus, N. Marsich and A. Manotti-Lanfredi, *20th Italian Meeting Inorganic Chemistry*, Pavia, Sept., 1987, p. 213.
- 3 A. M. Manotti-Lanfredi, A. Tiripicchio, A. Camus and N. Marsich, *J. Chem. Soc., Dalton Trans.*, in press.
- 4 A. Camus, N. Marsich and G. Nardin, *J. Organomet. Chem.*, **188** (1980) 839.
- 5 (a) A. Camus, N. Marsich and G. Pellizer, *J. Organomet. Chem.*, **259** (1983) 367; (b) A. M. Manotti-Lanfredi, F. Ugozzoli, A. Camus and N. Marsich, *Inorg. Chim. Acta*, **99** (1985) 111.
- 6 Jin Xiang-Lin, Jin Yi-Tan and Tang You-Qi, *Acta Chim. Sin.*, **44** (1986) 580.
- 7 T. Roberie, N. S. Baccha, D. Lankin and J. Selbin, *Can. J. Chem.*, **58** (1980) 2314; J. Selbin, *Inorg. Chim. Acta*, **71** (1983) 2.
- 8 P. Beslin, A. Dlubala and G. Levesque, *Synthesis*, (1987) 835.
- 9 J. B. Stothers, *Carbon-13 NMR Spectroscopy*, Academic Press, New York, 1972, Ch. 8.
- 10 F. Cariati, M. L. Ganadau, L. Naldini and S. Seneci, *Gazz. Chim. Ital.*, **109** (1979) 181.