

Bonding properties of thiocyanate groups in copper(II) and copper(I) complexes

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Abstract

The bonding properties of thiocyanate groups of over one hundred copper species, studied by X-ray analysis were analysed. It is shown that the bonding properties of thiocyanate groups in heterogeneous copper thiocyanate complexes depend on the size of the positive charge on the copper atom.

Keywords: Bonding properties; Thiocyanate groups; Copper (II) complexes; Copper (I) complexes

Abbreviations

actt	(1,4,7,13,16,19)-hexa-azacyclotetracosane
ae	aminoethanolate
aebg	1-(2-aminoethyl)biquanide
amal	2-(3-aminopropyl-amino)-ethanolate
amepy	2-(2-aminoethyl)pyridine

amprox	bis(3-aminopropyl)oxamide
bedo-ttf	bis(ethylenedioxy)tetrathiafulvalene
bedt-ttf	bis(ethylenedithio)tetrathiafulvalene
bidhx	1,6-bis(5-methyl-4-imidazolyl)-2,5-dithiahexane
bim	2-(2-pyridyl)benzimidazole
bimthp	1,5-bis(4-imidazolyl)-3-thiapentane
bipy	2,2'-bipyridine
bispictn	1,7-bis(2-pyridyl)-2,6-diazaheptane
dam	<i>N,N'</i> -bis(2-dimethylaminoethyl)-oxamidate
dbae	2-dibutylamine-ethanolate
dbapr	di- <i>n</i> -butylamino-1-propanolate
db-ttf	dibenzotetrathiafulvalene
deae	2-diethylamino-ethanolate
deapr	3- <i>N,N'</i> -diethylamino-1-propanolate
dec	4,7-diazadecanediamide
decane	3,3,9,9-tetramethyl-4,8-diazaundecane 2,10-dione dioximate
den	(2-aminoethyl)amine
des	<i>N</i> -(2-(diethylamino)ethyl)salicylaldiminate
detaac	4-diethylenetriaminemonoacetate
detapr	4-diethylenetriaminemono-3-propionate
dhegly	bis(2-hydroxyethyl)glycinate
dhf	(2,5-bis(2,6-diaza-hepta-1,6-diene-1,7-diyl)-di-furane
dimepyra	1,6-bis(3,5-dimethylpyrazol-1-yl)-2,5-dimethyl-2,5-diazaheptane
dma	2-dimethylaminoethanolate
dmapr	3- <i>N,N'</i> -dimethylamino-1-propanolate
dmate	2-(2-(dimethylamino)-ethylthio)-ethanolate
dmpol	1,3-diamino-2-propanolate
dmtp	5,7-dimethyl(1,2,4)triazolo(1,5- <i>a</i>) pyrimidine
dod	3,6-diazaoctane-1,8-diamine
dpae	2-dipropylaminoethanolate
dpt	bis(3-aminopropyl)amine
en	ethylenediamine
Et	ethyl
ETO	ethoxo
hlbim	2-(2-hydroxybenzyl)-benzimidazole
hxt	hexamethylenetetramine
imith	imidazolidine-2-thione
Me	methyl
Me ₂ fm	dimethylformamide
5-Metiazimid	5-methyl(1,2,4)triazolo(1,5- <i>a</i>)pyrimidine
6-Metiazimid	6-methyl(1,2,4)triazolo(1,5- <i>a</i>)pyrimidine
ml	bis(3,5-dimethyl-1-pyrazolylmethyl)aminobenzene
pcam	bis(2-pyridylcarbonyl)amininate
pcph	pyridine-2-carbaldehyde 2'-pyridylhydrazone

Ph	phenyl
phen	1,10-phenanthroline
pmsalh	<i>N'</i> -pyridylmethylene- <i>N''</i> -salicyloylhydrazinate
py	pyridine
pymetmed	<i>N,N'</i> -bis(2-pyridylmethylene)-tetramethylenediamine
quin	quinoline
sal	(salicylidene-(<i>R</i>)-phenylalaninato)-(<i>N</i> -salicylidene-(<i>S</i>)-phenylalaninate)
S-apip	(<i>S</i>)-3-aminopiperidine
tadto	(3,7,14,18-tetra-aza-23,24-dioxatricyclo(18.2.1.1*9.12)tetracosane-2,7,9,11,13,18,20,22-octaene
taec	tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane
terpy	2,2':6',2''-terpyridine
thaepy	((<i>N,N'</i> -4,7-dithiadecane-1,10-diyl)-2,6-bis(acetylimino)-pyridine
thion	1-methylimidazoline-2(3H)-thionate
thtaco	6,19,27,28-tetrathia-3,9,16,22-tetraazatricyclo(22.2.1.1,11,14)octacosane-2,9,11,13,15,22,24,26-octaene
tim	(2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene
tmthip	2,6-bis(((4 <i>S</i> ,7 <i>R</i>)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano(2H)-indazol-2-yl)methyl)pyridine
tn	1,3-diaminopropane
tnol	1,3-diamine-2-hydroxypropane
tpca	tris(2-pyrazolyethyl)-amine
tren	2,2',2''-triaminotriethylamine
triaz	1,2,4-triazole
triazimid	1,2,4-triazolo(1,5- <i>a</i>)pyrimidine
trien	triethylenetetramine
tff	tetrathiafulvalenium
xam	(1 <i>SR</i> ,4 <i>RS</i> ,7 <i>RS</i> ,8 <i>SR</i> ,11 <i>RS</i> ,14 <i>RS</i>)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane

1. Introduction

Many authors have dealt with the causes of the different coordination modes of the thiocyanate group in complexes of transition metals. They showed that in

Table 1
Theoretical coordination modes of thiocyanate groups

	NCS—	NCS=	(NCS=)
—NCS	—NCS—	—NCS=	—NCS=
=NCS	(=NCS—)	=NCS=	(=NCS=)

Thiocyanate groups in parentheses have not yet been observed.

Table 2
Coordination mode of thiocyanate groups in Cu(II) and Cu(I) complexes

Coordination mode of thiocyanate groups	Coordination number of central atom; chromophore	Interatomic distance (Å)		Reference
		Cu–N _{eq}	Cu–N _{ax} Cu–S _{ax}	
<i>Cu(II) complexes</i>				
[Cu(bipy) ₂ (NCS)](NCS) ^{x1}	–NCS 3 + 2 [Cu(N2N)(N2)]	1.950(14) 1.970(9)		[10]
[Cu(bipy) ₂ (NCS)](BF ₄)	[Cu(N2N)(N2)]	1.966(9)		[11]
[Cu(tmthip)(NCS) ₂]	[Cu(NN2)(N2)]	1.970(5) 1.971(6)		[12]
K[Cu(hxt) ₂ (NCS) ₃]·2H ₂ O	[Cu(N3)(N2)]	1.980(2) 1.982(2) 2.085(2)		[13]
[Cu(pyrimedmet)(NCS)]·(NCS)	[Cu(N2N)(N2)]	1.986(8)		[14]
[Cu(bipy) ₂ (NCS)](NO ₃)·H ₂ O	[Cu(N2N)(N2)]	2.009(3)		[15]
[Cu(dod)(NCS)](ClO ₄) ^{x1}	[Cu(N2N)(N2)]	2.115(1) 2.193(2)		[16]
[Cu(tn) ₂ (NCS)](ClO ₄)	[Cu(N2N)(N2)]	2.115(1)		[17]
α-[Cu(bispietn)(NCS)]·(NCS)	[Cu(N2N)(N2)]	2.118(12)		[18]
γ-[Cu(bispietn)(NCS)]·(NCS)	[Cu(N2N)(N2)]	2.162(14)		[18]
Cu ₂ (tadto)(ETO) ₂ (NCS) ₂	[Cu(N2O)(ON)]		1.919(23)	[19]
β-[Cu(dmtip) ₂ (NCS) ₂] ^{1/2}	[Cu(N2S)(NN)]		1.937(2)	[20]
[Cu ₂ (amprox)(H ₂ O)(NCS) ₂]	[Cu(NO2)(NN)]		1.941(1)	[21]
[Cu(tren)(NCS)] ₂ ·(BPh ₄) ₂	[Cu(N3)(NN)]		1.945(2)	[22]
Cu ₂ (tadto)(ETO) ₂ (NCS) ₂	[Cu(N2O)(ON)]		1.947(2)	[23]
[Cu(tren)(NCS)](NCS)	[Cu(N3)(NN)]		1.958(4)	[24]
[Cu(tpca)(NCS)]· ^{x1,y1}	[Cu(N3)(NN)]		1.958(4)	[25]
[Cu(NCS) ₂]				
[Cu(thaepp)(NCS)](ClO ₄)·0.5H ₂ O	–NCS 4 + 1 [Cu(N3N)(S)]	1.854(3)		[26]

[Cu(dbae)(NCS)] ₄ ^{x3}	[Cu(NO ₂ N)(O)]	1.885(2)	[27]
		1.901(1)	
		1.916(3)	
		1.930(1)	
		1.924(2)	
[Cu(pcam)(H ₂ O)(NCS)]	[Cu(N ₃ N)(O)]	1.936(7)	[28]
[Cu(dam)(NCS)(Me ₂ fm)] ₂	[Cu(N ₂ ON)(O)]	1.939(2)	[29]
[Cu(dmate)(NCS)] ₂ ^{x1}	[Cu(O ₂ SN)(N)]	1.940(5)	[30]
[Cu(bim)(NCS) ₂] ^{x1,y1}	[Cu(N ₃ N)(S)]	1.954(2)	[14]
α-[Cu(dmtfp) ₂ (NCS) ₂] ₂ ^{x1,y1}	[Cu(N ₃ N)(S)]	1.994(3)	[31]
[Cu(bimthp)(NCS) ₂]	[Cu(N ₂ N ₂ (S)]	2.003(3)	[32]
		2.000(3)	
		2.020(7)(2 _x)	
[Cu(aebg)(NCS)](NCS)	[Cu(N ₃ N)(H)]	1.944(3)	[33]
[Cu(terpy)(NCS) ₂]	[Cu(N ₂ N ₂ (N)]	1.922(2)	[34]
[Cu ₂ (actt)(NCS) ₄] ^{x1,y1}	[Cu(N ₃ N)(N)]	1.957(2)	[35]
		1.965(13)	
[Cu(dec)(NCS) ₂]	[Cu(N ₂ ON)(N)]	1.973(10)	[36]
[Cu(den)(NCS) ₂]	[Cu(N ₃ N)(N)]	1.980(10)	[37]
[Cu(3-Mepy) ₃ (NCS) ₂]	[Cu(N ₃ N)(N)]	2.037(10)	[38]
[Cu(3,4-Me ₂ py) ₃ (NCS) ₂]	[Cu(N ₃ N)(N)]	2.190(7)	[39]
[Cu(dpt)(NCS) ₂]	[Cu(N ₃ N)(N)]	2.236(8)	[40]
[Cu(taec)(NCS)] ₂ (ClO ₄) ₂ ·H ₂ O	[Cu(N ₄ (N)]	2.237(14)	[41]
[Cu(S-apip) ₂ (NCS)]·(ClO ₄)	[Cu(N ₄ (N)]	2.296(2)	[42]
[Cu(Meen) ₂ (NCS)](NCS)	[Cu(N ₄ (N)]	2.384(13)	[43]
[Cu(decane)(NCS)]·H ₂ O	[Cu(N ₄ (N)]	2.696(19)	[44]
[Cu(tim)(NCS)](PF ₆)	[Cu(N ₃ O)(N)]		[45]
[Cu ₃ (dmpol) ₄ (NCS) ₂] ^{x2,y1} ·(NCS) ₂ ^{x2,y1}			
	–NCS 4 + 2		
	[Cu(N ₂ N ₂ (S ₂)]	1.907(5)(2 _x)	[46]
	[Cu(N ₂ N ₂ (N ₂)]	1.934(6)(2 _x)	[47]
	[Cu(N ₂ N ₂ (S ₂)]	1.935(2)	[48]
		1.978(2)	
	[Cu(N ₂ N ₂ (O ₂)]	1.956(5)(2 _x)	[49]
[Cu(hbim) ₂ (NCS) ₂] ^{x1} ·(Me ₂ CO) ₂	[Cu(NO ₂ N)(N ₂)]	1.962(2)	[50]
[Cu(detaac)(NCS)]	[Cu(N ₂ SN)(SO)]	1.967(2)	[51]
[Cu(bidhx)(NCS)(NO ₃)]	[Cu(N ₂ N ₂ (N ₂)]	1.984(3)(2 _x)	[52]
[Cu(triaz) ₂ (NCS) ₂]	[Cu(N ₂ N ₂ (N ₂)]	2.013(10)(2 _x)	[53]
[Cu(phen) ₂ (NCS) ₂]			

Table 2 (continued)

Coordination mode of thiocyanate groups	Coordination number of central atom; chromophore	Interatomic distance (Å)		Reference
		Cu–N _{eq}	Cu–N _{ax}	
[Cu(dimpyra)(NCS) ₂] ^a	[Cu(N2N2)(N2)]	2.032(2)(2 _x)		[54]
[Cu(dimpyra)(NCS) ₂]	[Cu(N2N2)(N2)]	2.060(4)(2 _x)		[54]
[Cu(detapr)(NCS)]·H ₂ O	[Cu(N3O)(ON)]		2.178(2)	[50]
[Cu(Me ₂ en) ₂ (NCS) ₂]	[Cu(N4)(N2)]		2.517(7)(2 _x)	[55]
[Cu(amepy) ₂ (NCS) ₂]	[Cu(N4)(N2)]		2.592(3)(2 _x)	[56]
<i>Cu(I) complexes</i>				
(PPh ₄) ₂ [Cu ₂ (NCS) ₂ WS ₂] ^{x1}	–NCS 3 [Cu(S2N)]	1.844(1)		[57]
(PPh ₄) ₂ [Cu ₄ (NCS) ₄ WS ₄] ^{x3,y1}	[Cu(S2N)]	1.864(1)		[57]
(NEt ₄) ₂ [Cu ₃ (NCS) ₃ WS ₄] ^{x2,y1}	[Cu(S2N)]	1.860(1)		[58]
(PPh ₄) ₂ [Cu ₃ (NCS) ₃ MoOS ₃] ^{x2,y1}	[Cu(S2N)]	1.881(1)		[59]
(NEt ₄) ₃ [Cu ₄ (NCS) ₃ WS ₄] ^{x3,y1}	[Cu(S2N)]	1.864(1)		[58]
		1.865(2)		[59]
		1.873(1)		[58]
		1.871(5)		[58]
		1.876(6)		[58]
(bedt-ttf) ₂ [Cu(NCS) ₂] ^{y1}	Cu(NSN)]	1.890(5)		[60]
(bedt-ttf) ₂ [Cu(NCS) ₂] ^{y1}	[Cu(NSN)]	1.885(24)		[60]
[Cu(imth) ₂ (NCS)]	[Cu(S2N)]	1.938(7)		[61]
		1.956(4)		[61]
<i>–NCS 4</i>				
(NEt ₄) ₄ [Cu ₂ (NCS) ₈ WS ₄] ^{x1}	[Cu(S3N)]	1.841(1)(2 _x)		[62]
		1.902(2)(2 _x)		[62]
[Cu(des)(NCS)] ^{x1}	[Cu(N2ON)]	1.850(2)		[63]
[Cu(5-Mettriazimid) ₂ ·(NCS) ₂]	[Cu(N2N2)]	1.921(2)(2 _x)		[64]
[Cu(6-Mettriazimid) ₂ ·(NCS) ₂]	[Cu(N2N2)]	1.930(2)(2 _x)		[64]
(NEt ₄) ₃ [Cu ₄ (NCS) ₅ WS ₄] ^{x3,y1}	[Cu(S2N2)]	1.968(1)		[58]
		1.985(1)		[58]
<i>Cu(II) complexes</i>				
[Cu(popph)(NCS) ₂] ^{x1}	=NCS 4 + 2 [Cu(N3N)(SN)]	1.918(13)	3.054(12)	[40]
[Cu(en) ₂ (NCS)]Br	[Cu(N4)(N2)]		2.670(10)(2 _x)	[65]

[Cu(en) ₂ (NCS)](BF ₄)	[Cu(N ₄)(N ₂)]	[66]
[Cu(en) ₂ (NCS)](ClO ₄)	[Cu(N ₄)(N ₂)]	[67]
	<i>NCS</i> − 4 + <i>I</i>	
[Cu(trien)(NCS)](NCS)	[Cu(N ₄)(S)]	[68]
[Cu ₂ (actt)(NCS) ₄] ^{x1,y1}	[Cu(N ₄)(S)]	[35]
[Cu(xam)(NCS)](ClO ₄) · 2H ₂ O	[Cu(N ₄)(S)]	[69]
	<i>NCS</i> − 4 + 2	
[Cu(pcph)(NCS) ₂] ₂ ^{x1}	[Cu(N ₄)(NS)]	[70]
[Cu(tno) ₂ (NCS) ₂]	[Cu(N ₄)(S ₂)]	[71]
[Cu(NH ₃) ₄ (NCS) ₂]	[Cu(N ₄)(S ₂)]	[72]
[Cu(tn) ₂ (NCS) ₂]	[Cu(N ₄)(S ₂)]	[73]
[Cu(en)(NCS)]	[Cu(N ₄)(S ₂)]	[74]
	<i>NCS</i> − 4	
<i>Cu(I)</i> complexes	[Cu(S ₃ S)]	[75]
[{[Cu(thion) ₂ (NCS)] ₂ }]		
<i>Cu(II)</i> complexes	<i>NCS</i> = 4 + <i>I</i>	
[Cu ₃ (dmpol) ₂ (NCS) ₂] ^{x2,y1}	[Cu(N ₂ O ₂)(S)] ·	[45]
(NCS) ₂	[Cu(N ₃ O)(S)]	
	<i>NCS</i> = 4	
<i>Cu(I)</i> complexes	[Cu(N ₂ S ₂)]	[76]
[Cu ₂ (dhf)(NCS) ₂]		
	<i>NCS</i> − 3 + 2	
<i>Cu(II)</i> complexes	[Cu(NNS)(N ₂)]	[20]
β-[Cu(dmp) ₂ (NCS) ₂] ₂ ^{x1}		
	<i>NCS</i> − 4 + <i>I</i>	
[Cu(dma)(NCS)] ₂ ^{x1}	[Cu(NO ₂ N)(S)]	[77]
[Cu(dpae)(NCS)] ₂ ^{x1}	[Cu(NO ₂ N)(S)]	[78]
[Cu(pmsalh)(NCS)] ₂ ^{x1}	[Cu(N ₂ ON)(S)]	[79]
[Cu(dbapr) ₂ (NCS)] ₂ ^{x1}	[Cu(NO ₂ N)(S)]	[80]
[Cu(dmapr) ₂ (NCS)] ₂ ^{x1}	[Cu(NO ₂ N)(S)]	[80]
[Cu(deapr) ₂ (NCS)] ₂ ^{x1}	[Cu(NO ₂ N)(S)]	[80]
[Cu(deae)(NCS)] ₂ ^{x1,y1}	[Cu(NO ₂ N)(S)]	[81]
[Cu(bim)(NCS) ₂] ₂ ^{x1,y1}	[Cu(N ₃ N)(S)]	[14]

Table 2 (continued)

Coordination mode of thiocyanate groups	Coordination number of central atom; chromophore	Interatomic distance (Å)		Reference
		Cu—N _{eq}	Cu—N _{ax} Cu—S _{ax}	
[Cu(des)(NCS)] ¹	[Cu(N2ON)(S)]	1.947(3)	2.923(3)	[63]
[Cu(den)(NCS)] ₂ (ClO ₄) ₂ ¹	[Cu(N3N)(S)]	1.948(3)	2.786(4)	[82]
α -[Cu(dmp) ₂ (NCS) ₂] ^{1,2,1}	[Cu(N3N)(S)]	1.953(4)	2.885(3)	[31]
K ₂ [Cu ₂ (sal)(NCS) ₂] ¹	[Cu(NO2N)(S)]	1.971(5)	2.995(5)	[83]
[Cu(ae)(NCS)] ₂ ¹	[Cu(NO2N)(S)]	1.976(1)	2.872(1)	[84]
[Cu(dpt) ₂ (NCS)](ClO ₄) ₂ ¹	[Cu(N3N)(S)]	2.001(10)	2.792(10)	[85]
[Cu ₂ (ml)(NCS) ₃] ¹	[Cu(N3N)(N)]· [Cu(NS3)]	1.944(6)	2.172(6)	[86]
[Cu ₂ (amal) ₂] ₂ [Cu(NCS) ₄] ¹ ·(NCS)	[Cu(N2O2)(S)]· [Cu(N2N2)]	{1 _N →Cu ¹ ; 3 _S →Cu ¹ }	2.732(4)	[87]
	—NCS— 4 + 2	{2 _N →Cu ¹ }		
	[Cu(4-Mepy) ₂ (NCS) ₂] ^{2,4}	[Cu(N2N2)(S2)]	1.886(10) 1.903(10) 1.931(10) 1.936(10) 1.951(10) 1.958(10) 1.919(20) 1.949(20) 1.958(18) 2.038(20)	3.109(10) 3.005(10) 3.171(10) 2.960(10) 2.911(10) 2.927(10) 3.058(10) 3.078(10) 3.070(10) 2.911(10)
[Cu(4-Brpy) ₂ (NCS) ₂] ¹	[Cu(N2N2)(S2)]			[89]
[Cu(4-Mepy) ₂ (NCS) ₂] ^{2,2}	[Cu(N2N2)(S2)]	1.933(8) 1.938(8) 1.939(8) 1.952(8) 1.955(8) 1.972(9) 1.933(2) 1.938(10)	3.109(4) 3.124(4) 3.005(4) 2.968(4) 3.158(4) 2.977(4) 3.101(3) 3.049(6)	[90]
[Cu(dhegly)(NCS)]·H ₂ O	[Cu(NO2N)(OS)]			[91]
[Cu(4-Mepy) _{1.75}] ¹	[Cu(N2N2)(S2)]			[92]

(3-Me-py) ₃ (NCS) ₂]		1.942(10)	3.270(5)	
		1.954(10)	3.263(5)	
		1.956(10)	3.043(5)	
[Cu(py) ₂ (NCS) ₂]	[Cu(N2N2)(S2)]	1.943(20)(2 _x)	3.040(20)(2 _x)	[93]
[CuHg(NCS) ₄] ¹	[Cu(N2N2)(S2)]	1.945(20)(2 _x)	{2 _x S→Hg ^{II} }	[94]
[Cu ₂ (NH ₃) ₃ (NCS) ₃] ^{x1,y2}	[Cu(N3N)(SS)]	1.987(13)	3.286(9)	[95]
[Cu ₂ (bidhx)(NCS) ₃] ^{x1}	[Cu(N2SN)(SN)]•	2.002(4)	2.394(4)	[96]
	[Cu(NS3)]	{1 _x N→Cu ^I ; 3 _x S→Cu ^I }		
[CuHg(en) ₂ (NCS) ₄]	[Cu(N4)(N2)]•	2.58(4)		[97]
		2.81(5)		
	[Hg(S2S2)]		{2 _x S→Hg ^{II} }	
<i>Cu(I) complexes</i>	–NCS–3			
(bedt-ttf) ₂ [Cu ₂ (NCS) ₃] ^{x1}	[Cu(N2S)]•	1.888(4)	2.303(5)	[98]
	[Cu(NS2)]	1.899(5)	2.242(5)	
		1.913(5)	2.361(4)	
(bedt-ttf) ₂ [Cu(NCS) ₂] ^{y1}	[Cu(NNS)]	1.898(20)	2.231(7)	[60]
[Cu(2,6-Me ₂ py)(NCS)]	[Cu(NNS)]	1.915(4)	2.232(1)	[99]
(bedo-ttf) ₃ [Cu ₂ (NCS) ₃] ^{x1}	[Cu(NS2)]•	1.920(4)	2.273(4)	[100]
	[Cu(N2S)]	1.936(4)	2.235(5)	
		1.893(4)	2.253(5)	
(bedt-ttf) ₂ [Cu(NCS) ₂] ^{b,y1}	[Cu(NNS)]	1.964(6)	2.198(2)	[60]
	–NCS–4			
(PPH ₄) ₂ [Cu ₄ (NCS) ₄ WS ₄] ^{x3,y1}	[Cu(S2NS)]	1.886(1)	2.570(1)	[57]
		1.893(1)	2.608(1)	
(PPH ₄) ₂ [Cu ₃ (NCS) ₃ MoOS ₃] ^{2,y1}	[Cu(S2NS)]	1.893(5)	2.711(2)	[59]
[CuHg(dmtf) ₂ (NCS) ₃]	[Cu(NN3)]•	1.912(2)		[101]
		1.990(2)		
		2.001(2)		
	[Hg(NS3)]		{3 _x S→Hg ^{II} }	
[Cu(2,4-Me ₂ py) ₂ (NCS) ₂] ^{x1}	[Cu(N2NS)]	1.944(9)	2.379(4)	[99]
		1.968(9)	2.371(4)	
(ttf)[Cu(NCS) ₂]	[Cu(N2S2)]	1.983(4)	2.374(1)	[102]
		1.994(5)	2.400(1)	
[NMe ₄] ₂ [Cu ₄ (NCS) ₄ WS ₄] ^{x3}	[Cu(S2NS)]•	1.925(2)	2.662(1)	[103]
	[Cu(S2S2)]•	1.928(2)	2.427(1)	
	[Cu(S2N2)]	2.022(2)	2.333(1)	
		2.035(2)	2.341(1)	

Table 2 (continued)

Coordination mode of thiocyanate groups	Coordination number of central atom; chromophore	Interatomic distance (Å)		Reference
		Cu–N _{eq}	Cu–N _{ax} Cu–S _{ax}	
(NEt ₄) ₂ [Cu ₃ (NCS) ₃ WS ₄] ^{x2,y1}	[Cu(S2NS)]	1.936(7)	2.526(2)	[58]
		1.937(7)	2.551(2)	
[Cu(2,9-Me ₂ phen)(NCS)]	[Cu(N2NS)]	1.943(6)	2.322(2)	[104]
(NEt ₄) ₂ [Cu ₄ (NCS) ₂ WS ₄] ^{x1}	[Cu(S2NS)]	1.943(4)	2.489(2)	[58]
		2.008(6)	2.324(2)	
[Cu(4-Mepy) ₂ (NCS)]	[Cu(N2NS)]	1.944(1)	2.365(1)	[99]
(NEt ₄) ₂ [Cu ₄ (NCS) ₄ MoS ₄] ^{x1}	[Cu(S2NS)]	1.946(5)	2.506(2)	[58]
		2.011(7)	2.331(2)	
(pyH)[Cu ₂ (NCS) ₃] ^{x1,y1}	[Cu(NS2S)]· [Cu(NS2N)]	1.947(9)	2.318(3)	[105]
	[Cu(N2SN)]· [Cu(N2SS)]	1.951(11)	2.244(5)	[106]
[Cu ₂ (thtaco)(NCS)]·(ClO ₄)·MeCN	[Cu(N2NS)]	1.959(3)	2.336(2)	[99]
	[Cu(N2SS)]	1.959(5)	2.478(4)	[25]
[Cu(3-Mepy) ₂ (NCS)]	[Cu(N2S2)]	1.961(5)	2.430(5)	
[Cu(tpca)(NCS)] ^{x1,y1}		1.964(1)	2.349(2)	[99]
[Cu(NCS) ₂]	[Cu(N2NS)]	1.969(1)	2.324(1)	[96]
[Cu(2-Mepy) ₂ (NCS)]	[Cu(NS3)]· [Cu(N2SN)(SN)]	{2 _x N→Cu ^{II} }	2.367(1)	
[Cu ₂ (bidhx)(NCS) ₃] ^{x1,y1}			2.446(2)	
			2.406(3)	[107]
[Cu(PPh ₃) ₂ (NCS)] ₂	[Cu(P2NS)]	1.984(3)	2.327(2)	[86]
[Cu ₂ (ml)(NCS) ₃] ^{x1}	[Cu(NS3)]· [Cu(N3N)(N)]	1.984(6)	2.442(2)	
		{2 _x N→Cu ^{II} }	2.407(2)	
[Cu(quin) ₂ (NCS)]	[Cu(N2NS)]	1.998(1)	2.290(4)	[99]
[Cu ₂ (amal) ₂] ₂ ·x ⁴	[Cu(N4)]· [Cu(N2O2)(S)]	1.999(4)(4 _x)	{4 _S →Cu ^{II} }	[87]
[Cu(NCS) ₄](NCS)	[Cu(P2NS)]	2.016(2)	2.462(1)	[108]
[Cu(PPh ₂ Me) ₂ (NCS)] ₂ ^{x1}	–NCS = 4 + 1 [Cu(N4)(N)]· (Ag(S2S2))		{2 _x S→Ag ^I }	[109]
Cu(II) complexes				
[CuAg(en) ₂ (NCS) ₃]		2.384(10)		

$-\text{NCS} = 4 + 2$				
$[\text{CuHg}(\text{NCS})_4]$	$[\text{Cu}(\text{N}2\text{N}2)(\text{S}2)] \cdot$	$1.85(3)(2_x)$	$3.00(2)(2_x)$	[94]
	$[\text{Hg}(\text{S}2\text{S}2)]$	$\{2_x \text{S} \rightarrow \text{Hg}^{\text{II}}\}$		
$[\text{Cu}(\text{NH}_3)_2(\text{NCS})_2]$	$[\text{Cu}(\text{N}2\text{N}2)(\text{S}2)] \cdot$	$1.964(8)(2_x)$	$2.925(10)(2_x)$	[46]
	$[\text{Cu}(\text{N}4)(\text{S}2)]$		$3.108(10)(2_x)$	
$[\text{Cu}_2(\text{NH}_3)_3(\text{NCS})_3]^{x1,y2}$	$[\text{Cu}(\text{N}4)(\text{S}2)] \cdot$		$3.107(9)$	[95]
	$[\text{Cu}(\text{NSNS})]$	$\{1_x \text{N} \rightarrow \text{Cu}^{\text{I}}; 1_x \text{S} \rightarrow \text{Cu}^{\text{I}}\}$		
$[\text{Cu}(\text{en})(\text{NCS})_2]^{x1}$	$[\text{Cu}(\text{N}2\text{N}2)(\text{S}2)] \cdot$	$1.99(2)$	$3.01(2)$	[48]
	$[\text{Cu}(\text{N}4)(\text{S}2)]$	$2.01(2)$	$3.10(2)$	
			$2.99(2)$	
Cu(I) complexes			$3.10(2)$	
$[\text{Cu}(\text{quin})[\text{NCS}]]$	$-\text{NCS} = 4$			
	$[\text{Cu}(\text{NNS}2)]$	$1.904(2)$	$2.406(1)$	[110]
			$2.644(1)$	
$[\text{Cu}(2\text{-Mepy})(\text{NCS})]$	$[\text{Cu}(\text{NNS}2)]$	$1.917(2)$	$2.363(1)$	[99]
			$2.805(1)$	
$(\text{pyH})[\text{Cu}_2(\text{NCS})_3]^{x2,y1}$	$[\text{Cu}(\text{SNS}2)] \cdot$	$1.926(9)$	$2.429(3)$	[105]
	$[\text{Cu}(\text{NNS}2)]$	$1.935(9)$	$2.421(3)$	
			$2.448(3)$	
			$2.439(3)$	
$[\text{Cu}_2(\text{NH}_3)_3(\text{NCS})_3]^{x1,y2}$	$[\text{Cu}(\text{NSNS})] \cdot$	$1.996(24)$	$2.376(8)$	[95]
	$[\text{Cu}(\text{N}4)(\text{S}2)]$	$\{1_x \text{S} \rightarrow \text{Cu}^{\text{II}}\}$		
	$-\text{NCS} = 4$			
$\beta\text{-}[\text{Cu}(\text{NCS})]$	$[\text{Cu}(\text{NS}3)]$	$1.923(11)$	$2.343(2)$	[111]
			$2.343(2)$	
			$2.343(2)$	
$\alpha\text{-}[\text{Cu}(\text{NCS})]$	$[\text{Cu}(\text{NS}3)]$	$1.927(6)$	$2.344(2)$	[112]
			$2.354(2)$	
			$2.367(2)$	

^a At 140 K; ^b at 104 K; ^c at 180 K; ^d at 118 K; ^e bond $\text{Cu}-\text{S}_{\text{eq}}$.

^{x1} Crystal structure contains two symmetrically independent coordination polyhedra.

^{x2} Crystal structure contains three symmetrically independent coordination polyhedra.

^{x3} Crystal structure contains four symmetrically independent coordination polyhedra.

^{x4} Crystal structure contains five symmetrically independent coordination polyhedra.

^{y1} Crystal structure contains two coordination modes of the thiocyanate group.

^{y2} Crystal structure contains three coordination modes of the thiocyanate group.

homogeneous thiocyanates, the coordination mode is influenced by the nature of the central atom [1]. In heterogeneous thiocyanates, the coordination mode of the thiocyanate group was ascribed to the influence of steric factors [2], the polarizing activity of the central atom [3], symbiosis of “hard and soft” ligands in the coordination sphere [4], and the influence of the solvent [5,6].

The bonding properties of a thiocyanate group in heterogeneous complexes are influenced by the cooperative effects of other ligands present in the inner coordination sphere [7]. The π -bonding hypothesis [8] proposed that, through cooperative effects, only other π -bonding ligands can change the bonding mode of thiocyanate groups. However, several $M(NCS)_xL_y$ complexes (where M is the central atom of class A or B), in which the π -bonding ligand L does not change the coordination mode of the thiocyanate group, have been found [9]. This discovery reveals that the cooperative effects of ligands in heterogeneous thiocyanate complexes are not only transported but also influenced simultaneously by the properties of the central atom.

This paper concentrates on the bonding properties of thiocyanate groups in the crystal structures of copper complexes. It seeks to establish that the coordination mode of thiocyanate groups in heterogeneous copper complexes depends primarily on the size of the positive charge on the copper atom.

2. Bonding properties of thiocyanate groups in the coordination sphere of central atoms Cu(II) and Cu(I)

A linear triatomic thiocyanate group with 16 valence electrons possesses a great variety of bonding possibilities. In known crystal structures the thiocyanate group uses, at maximum, two coordination bonds by a nitrogen atom and three by a sulphur atom. Combining these five possibilities, there are 11 possible coordination modes (Table 1). Individual coordination modes of thiocyanate groups of known copper coordination compounds are given in Table 2.

Table 2 summarizes the Cu—N and Cu—S bond lengths of thiocyanate groups with regard to the different coordination modes and the “position” in various coordination polyhedra. In real crystal structures of copper complexes, seven coordination modes of thiocyanate groups have been observed, Cu—NCS and Cu—NCS—Cu coordination being the most common.

Among the complexes in which the Cu—NCS mode occurs, several trends can be seen. For Cu(II) atoms in trigonal-bipyramidal environments, the mean Cu(II)—N_{eq} bond distance of 2.038 Å (range 1.950–2.162 Å) is somewhat longer than that of Cu(II)—N_{ax}, 1.944 Å (range 1.919–1.958 Å). However, when the Cu(II) atom is in a tetragonal-pyramidal or tetragonal-bipyramidal environment, the mean Cu(II)—N_{eq} bond distances are shorter than those of Cu(II)—N_{ax}. For example 1.953 Å (range 1.854–2.037 Å) vs. 2.285 Å (range 2.140–2.696 Å) for the former, and 1.979 Å (range 1.907–2.060 Å) vs. 2.479 Å (range 2.178–2.592 Å) for the latter. The mean Cu(I)—N bond distance of 1.882 Å, found in tricoordinated Cu(I) complexes, is about 0.026 Å shorter than that found for tetrahedrally coordinated Cu(I) com-

plexes. In general, the Cu—N bonds of thiocyanate groups can occur in an arbitrary position in various coordination polyhedra.

Cu—S bond lengths of thiocyanate groups in Cu(I) and Cu(II) complexes occur in the interval 2.198–3.286 Å. Cu—S bond distances (unlike Cu—N bond distances) depend on the oxidation state of the central atom. In three-coordinated Cu(I) complexes, the Cu—S bond distances are in the range 2.198–2.361 Å; in tetrahedrally coordinated species they range from 2.244 to 2.805 Å. As can be seen (Table 2), among square-pyramidal and pseudo-octahedral coordinated Cu(II) species, Cu—SCN “contact” ranging from 2.698 to 3.286 Å is found only in the axial positions of coordination polyhedra. However, in the trigonal-bipyramidal species, thiocyanate groups with Cu—SCN contacts occur in the equatorial plane.

3. Effective charge on the central atom Cu(II) and the coordination mode of thiocyanate groups

For several crystal structures of thiocyanate copper complexes, it is possible to demonstrate mutual relations between the bonding properties of thiocyanate groups and the size of the positive charge on the central atom. The decrease in effective positive charge on a copper atom increases the tendency to S-coordination of thiocyanate groups and vice versa.

For a chosen group of heterogeneous thiocyanate copper complexes, given in Table 3, it is possible to generalize that a change in the size of the effective positive charge on the central atom can be influenced by the following: varying basicity of the N-donor atoms in ligands L as a result of differences in their π -bonding properties; varying basicity of the N-donor atoms in ligand L as a consequence of induction effects of substituents; different number of ligands L in the coordination sphere of the central atom; different number of thiocyanate groups in the coordination sphere of the central atom.

3.1. π -bonding properties of ligands L

The influence of different π -bonding properties of ligands L on the coordination mode of thiocyanate groups can be demonstrated (Table 3) by comparing complexes I to V with complexes VI and VII. In complexes I to V, where ligands L are σ -bonded to the central atom, the thiocyanate group is coordinated through the S atom. This is in agreement with the so-called π -hypothesis [8].

The influence of the different π -bonding properties of ligands L also affects the bonding properties of bridging thiocyanate groups. In complexes X to XIV, the ligands L have σ and π bonding possibilities. The thiocyanate group binds as a bifunctional bridge, using a Cu—S bond in axial and a Cu—N bond in equatorial positions of the coordination polyhedra.

In complexes XIX and XX, the ligands are without distinct π -acceptor properties and the pair of thiocyanate groups marks significant differences in the coordination mode. One of the pairs of the thiocyanate group is bonded monofunctionally by a

Table 3
Interatomic distances of Cu–N and Cu–S and coordination mode of thiocyanate groups in some thiocyanatocopper(II) complexes

Number	Complex	Coordination mode of thiocyanate groups	Interatomic distance (Å)			Reference
			Cu–N _{eq}	CuN _{ax}	Cu–S _{ax}	
I	[Cu(NH ₃) ₄](NCS) ₂]	NCS–			≈ 3.000	[72]
II	[Cu(trien)(NCS)](NCS)	NCS–			2.606(2)	[68]
III	[Cu(en) ₂](NCS) ₂]	NCS–			3.270(10)	[74]
IV	[Cu(tn) ₂](NCS) ₂]	NCS–			3.154(14)	[73]
V	[Cu(tno1) ₂](NCS) ₂]	NCS–			2.971(2)	[71]
VI	[Cu(amepy) ₂](NCS) ₂]	–NCS		2.593(3)		[56]
VII	[Cu(bispietn)(NCS)]·(NCS)	–NCS	2.118(12)			[18]
VIII	[CuMe ₂ en ₂](NCS) ₂]	–NCS		2.517(7)		[55]
IX	[Cu(tn) ₂](NCS)](ClO ₄)	–NCS	2.115(4)			[17]
X	[Cu(bim)(NCS) ₂]	–NCS–	1.946(5)		2.950(40)	[14]
XI	[Cu(pmsalh)(NCS)]	–NCS–	1.929(5)		2.707(2)	[79]
XII	[Cu(py) ₂](NCS) ₂]	–NCS–	1.943(20)		3.040(20)	[93]
XIII	[Cu(4-Mepy) ₂](NCS) ₂] ^a	–NCS–	1.939(8)		3.127(4)	[90]
			1.956(8)		3.109(4)	
		–NCS–	1.933(8)		3.005(4)	
			1.939(8)		2.968(4)	
		–NCS–	1.973(9)		3.258(4)	
			1.952(8)		2.977(4)	
		–NCS–	1.958(18)		3.058(10)	[89]
			1.949(20)		3.078(10)	
		–NCS–	1.919(20)		3.070(10)	
			2.038(20)		2.911(10)	
XIV	[Cu(4-Brpy) ₂](NCS) ₂] ^b	–NCS–				
XV	[Cu(en) ₂](NCS)](ClO ₄)	=NCS		2.730(10)		[67]
XVI	[Cu(en) ₂](NCS)](BF ₄)	=NCS		2.720(12)		[66]
XVII	[Cu(en) ₂](NCS)]Br	=NCS		2.670(10)		[65]
XVIII	[Cu(NCS)]	–NCS=	1.927(6)			[112]
					2.344(2)	
					2.354(2)	
					2.367(2)	

XIX	$[\text{Cu}(\text{NH}_3)_2(\text{NCS})_2]$	—NCS —NCS=	1.907(5) 1.964(8)		2.925(10) 3.108(10)	[46]
XX	$[\text{Cu}(\text{en})(\text{NCS})_2]^b$	—NCS —NCS=	2.01(3) 2.01(2)		3.01(2) 3.10(2)	[48]
XXI	$[\text{Cu}(\text{Meen})_2(\text{NCS})](\text{NCS})$	—NCS...				
XXII	$[\text{Cu}(3,4\text{-Me}_2\text{py})_3 \cdot (\text{NCS})_2]$	—NCS —NCS...	1.98(1)	2.237(14)	3.348(10)	[41] [38]
XXIII	$[\text{Cu}(3\text{-Mep})_3(\text{NCS})_2]$	—NCS —NCS...	1.97(1)	2.22(2)	3.62(1)	[38]
				2.19(2)	3.41(2)	

^a Crystal structure contains three symmetrically independent coordination polyhedra.

^b Crystal structure contains two symmetrically independent coordination polyhedra.

Cu—N bond in the equatorial plane of the coordination polyhedron. The remaining thiocyanate group forms a trifunctional bridge, using a Cu—N bond in the equatorial plane and a twofold axis with a sulphur atom Cu—S—Cu in axial positions of two neighbouring coordination polyhedrons.

These results seem to show that an increased tendency to S-coordination in bridging thiocyanate groups is realized by an increased number of coordination bonds on the sulphur atom. In this relation it is possible to mention complex XVIII (containing Cu(I)) in which the bridge thiocyanate group brings, on the sulphur atom, three coordinate bonds.

3.2. Induction effects of substituents in ligands *L*

A comparison of the complexes III, XXI and VIII containing en and its methyl or dimethyl derivatives proves that with an increasing number of methyl substituents a gradual change in axial S-coordination of monofunctional thiocyanate groups to axial N-coordination occurs. Complex XXI can be considered as an intermediate where the original Cu—SCN bond is markedly weakened and axial Cu—NCS coordination is beginning to be realized.

Considering the dependence of the influence of induction effects of ligand substituents, varying basicity can be reflected in quantitatively small changes in the bonding properties of thiocyanate ligands. While preserving the coordination mode, changes in strength among the Cu—S bonds are observed.

For instance, in complexes XII, XIII and XIV an identical bifunctional bridge of thiocyanate groups occurs. In complex XII only one length of Cu—S bond was found. Complex XIII contains six Cu—S bonds of different lengths. There are three bond lengths which are comparable with the Cu—S bond length in complex XII. The remaining three Cu—S bond lengths have a different degree of elongation. The elongation of Cu—S bonds can be explained in connection with the positive induction effect of the 4-methyl substituent on the pyridine ring. An opposite phenomenon was observed in complex XIV, which contains four different Cu—S bond lengths. There are three bonds which are comparable in length with the Cu—S bond length in complex XII, while the fourth is significantly shorter. The shortening of Cu—S bond distances can be correlated with the inductive effect of the 4-halogeno substituent on the pyridine ring, but in the opposite direction.

3.3. A different number of ligands *L* in the coordination sphere

Comparison of complexes X to XIV with complexes XXII and XXIII shows that an increased number of ligands with π -bonding properties practically excludes the S-coordination of thiocyanate groups from the inner coordination sphere of the central atom.

In complexes XXII and XXIII, three ligands are bonded in the equatorial planes of the tetragonal pyramidal coordination polyhedra. Thiocyanate groups are bonded terminally by their nitrogen atoms in the equatorial and axial positions of the coordination polyhedra. In both crystal structures, sulphur atoms from the axially

coordinated thiocyanate groups are oriented in the direction of the sixth coordination places of the neighbouring polyhedra. Significant differences in $\text{Cu}\cdots\text{S}$ contacts, were observed (Table 3). Because the complexes compared are isostructural, it is also possible to discuss the observed differences in $\text{Cu}\cdots\text{S}$ contacts, in connection with the additional influence of a different number of substituents in ligands L.

3.4. A different number of thiocyanate groups in the coordination sphere

A comparison of complexes XV, XVI and XVII with complex III and of complex IX with IV demonstrates another type of change in the coordination sphere. The properties of ligands L do not change. A change takes place in the substitution of one of a pair of thiocyanate groups in complexes III and IV with the anion, which does not enter into the coordination sphere of the central atom. In complexes XV, XVI, XVII and IX it was observed that after substitution a transformation to N-coordination of the thiocyanate group occurred. Such interference with the coordination sphere of the central atom can be understood as a limitation of the number of such ligands which by their reduction properties decrease the size of the effective positive charge on the central atom. In this connection then, the transformation of the coordination mode of a non-substituted thiocyanate group also supports the idea of conditioning of the bonding properties of thiocyanate groups and the size of the positive charge.

4. Concluding remarks

In this study we have analysed the bonding properties of thiocyanate groups of approximately one hundred crystal structures of solid copper thiocyanate complexes. A summary of the $\text{Cu}-\text{N}$ and $\text{Cu}-\text{S}$ bond distances of thiocyanate groups in Cu(II) and Cu(I) complexes is given in Table 4. The bonding properties of thiocyanate groups in connection with the effective charge of a copper atom can be documented as follows: by the change in bond lengths by which a thiocyanate group is bonded with a copper atom; by space orientation of thiocyanate groups in coordination polyhedra; by changes in the coordination mode of thiocyanate group in the coordination sphere Cu(II) .

Differences in the positive charge of the central atom in the thiocyanate complexes of copper influence the strength of $\text{Cu}-\text{S}$ bonds. With a decreasing positive charge of the copper atom, in general, the strength of the $\text{Cu}-\text{S}$ bonds increases. While in Cu(II) complexes the length of $\text{Cu}-\text{S}$ bonds is in the range 2.412–3.286 Å, in Cu(I) complexes it is in the range 2.198–2.805 Å.

In Cu(II) complexes, N-bonded thiocyanate groups occur in an arbitrary position of the coordination polyhedron, while S-bonded groups, have a preferential spatial orientation. The S-bonding of thiocyanate groups in tetragonal-pyramidal and pseudo-octahedral coordination polyhedra was only observed in the axial directions. On the contrary, in trigonal-bipyramidal coordination polyhedra, $\text{Cu}-\text{S}$ bonds occupy the equatorial positions.

Table 4
Summary of the Cu–N and Cu–S bond distances (Å) of thiocyanate groups in Cu(II) and Cu(I) complexes

Coordination mode of thiocyanate groups	Coordination number of central atom							
	3+2	4+1	4+2	3+2	4+1	4+2	3	4
–NCS	$Cu^{II}-N_{ax}$ 1.919–1.958 — — — —	2.149–2.696	2.178–2.592	$Cu^{II}-N_{eq}$ 1.950–2.162 — 2.205 —	1.854–2.037	1.907–2.060	Cu^I-N 1.844–1.956 — 1.888–1.964 —	1.841–1.985
=NCS		—	2.670–3.054		—	1.918		—
–NCS–		2.172	2.394–2.810		1.901–1.976	1.886–2.002		1.886–2.016
–NCS=		2.384	—		—	1.850–2.010		1.904–1.996
–NCS≡		—	—		—	—		1.923–1.927
	1.919–1.958	2.149–2.696	2.178–3.054	1.950–2.205	1.854–2.037	1.850–2.060	1.844–1.964	1.841–1.996
NCS–	$Cu^{II}-S_{ax}$ — — — — —	$Cu^{II}-S_{eq}$ 2.606–2.879 2.815–2.885 2.707–3.078 — 2.606–3.078	2.698–3.270	Cu^I-S — — 2.198–2.361 — 2.198–2.361	—	—	—	2.332
NCS=			—		—	—	—	2.372–2.386
–NCS–			2.911–3.286		—	—	—	2.318–2.662
–NCS=			2.925–3.107		—	—	—	2.363–2.805
–NCS≡			—		—	—	—	2.343–2.367
	—	—	2.698–3.286	2.412	—	—	2.198–2.361	2.318–2.805

Slight changes in the effective charge of the central Cu(II) atom can also be observed in the change in the coordination mode of the thiocyanate group. In monodentate thiocyanate groups the decreasing value of the effective charge increases the tendency to S-coordination. In bridging thiocyanate groups, although the decreasing value of effective charge of the bridging coordination mode remains, the number of coordination bonds on the sulphur atom increases. In the groups of complexes chosen in this paper, changes in the coordination mode of the thiocyanate groups can be obtained, by changing the basicity of N-donor atoms of the other ligands L, by a different number of ligands L, or by a different number of thiocyanate groups in the coordination sphere of the central Cu(II) atom.

References

- [1] S. Ahrland, *Struct. Bonding*, 1 (1966) 207; 5 (1968) 118.
- [2] F. Basolo, W.H. Braddley and K.J. Weidenbaum, *J. Am. Chem. Soc.*, 88 (1966) 1576.
- [3] M.F. Farona and A. Wojcicki, *Inorg. Chem.*, 4 (1965) 1402.
- [4] C.K. Jørgensen, *Inorg. Chem.*, 3 (1964) 1201.
- [5] J.L. Burmeister and F. Basolo, *Inorg. Chem.*, 3 (1964) 1587.
- [6] A. Sabatini and J. Bertini, *Inorg. Chem.*, 4 (1965) 1665.
- [7] A. Turco and C. Pecile, *Nature*, 191 (1961) 66.
- [8] A.H. Norbury, *Adv. Inorg. Chem. Radiochem.*, 17 (1975) 231.
- [9] M. Kabešová and J. Gažo, *Chem. Zvesti*, 34 (1980) 800.
- [10] A. Sedov, J. Kožíšek, M. Kabešová, M. Dunaj-Jurčo, J. Gažo and J. Garaj, *Inorg. Chim. Acta*, 75 (1983) 73.
- [11] S. Tyagi and B.J. Hathaway, *J. Chem. Soc., Dalton Trans.*, (1981) 2029.
- [12] A.A. Watson, D.A. House and P.J. Steel, *Inorg. Chim. Acta*, 130 (1987) 167.
- [13] J. Pickardt, *Z. Naturforsch.*, 36b (1981) 649.
- [14] L.P. Battaglia, M.B. Ferrari, A.B. Corradi, G.G. Fava, C. Pelizzi and M.E.V. Tani, *J. Chem. Soc., Dalton Trans.*, (1976) 2197.
- [15] V. Manriquez, I. Brito, C. Andrade, O. Wittke, H.G. von Schnering and K. Peters, *Acta Crystallogr. C*, 44 (1988) 1191.
- [16] G. Marongiu and M. Cannas, *J. Chem. Soc., Dalton Trans.*, (1979) 41.
- [17] M. Cannas, G. Carta and G. Marongiu, *J. Chem. Soc., Dalton Trans.*, (1974) 550.
- [18] N.A. Bailey and E.D. McKenzie, *J. Chem. Soc., Dalton Trans.*, (1972) 1566.
- [19] M. Nelson, F. Esho, A. Lavery and M.G.B. Drew, *J. Am. Chem. Soc.*, 105 (1983) 5693.
- [20] J.G. Haasnoot, W.L. Driessen and J. Reedijk, *Inorg. Chem.*, 23 (1984) 2803.
- [21] X.-K. Yao, H.-G. Wang, D.-Z. Liao, Z.-Y. Zhang, S.-Q. Hao, Z.H. Jiang and G.-L. Wang, *J. Struct. Chem.*, 10 (1991) 143.
- [22] E.J. Laskowski, D.M. Duggan and D.N. Hendrickson, *Inorg. Chem.*, 14 (1975) 2449.
- [23] M.G.B. Drew, P.C. Yates, F.S. Esho, J. Trocha-Grimshaw, A. Lavery, K.P. McKillop, S.M. Nelson and J. Nelson, *J. Chem. Soc., Dalton Trans.*, (1988) 2995.
- [24] P.C. Jain and E.C. Lingafelter, *J. Am. Chem. Soc.*, 89 (1967) 6131.
- [25] M. DiVaira and F. Mani, *J. Chem. Soc., Dalton Trans.*, (1985) 2327.
- [26] M.G.B. Drew, C. Cairns, S.M. Nelson and J. Nelson, *J. Chem. Soc., Dalton Trans.*, (1981) 942.
- [27] R. Mergehenn and W. Haase, *Acta Crystallogr. B*, 33 (1977) 2734.
- [28] G. Madariaga, F.J. Zuniga, T.R. Roio and V. Folgado, *Acta Crystallogr. C*, 47 (1991) 1632.
- [29] A. Yoshino and W. Nowacki, *Z. Kristallogr.*, 139 (1974) 337.
- [30] M. Mikuriya, H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 54 (1981) 2979.
- [31] M.B. Cingi, A.M.M. Lanfredi, A. Tiripicchio, J.G. Haasnoot and J. Reedijk, *Inorg. Chim. Acta*, 72 (1983) 81.

- [32] M. Zoeteman, E. Bouwman, R.A.G. deGraff, W.L. Driessen, J. Reedijk and P. Zanello, *Inorg. Chem.*, 29 (1990) 3487.
- [33] G.D. Andreotti, L. Coghi, M. Nardelli and P. Sgarabotto, *J. Cryst. Mol. Struct.*, 1 (1971) 147.
- [34] M.I. Arriortua, J.L. Mesa, T. Rojo, T. Debaerdemaeker, D. Beltrán-Porter, H. Stratemeier and D. Reinen, *Inorg. Chem.*, 27 (1988) 2976.
- [35] A.E. Martin and S.J. Lippard, *J. Am. Chem. Soc.*, 106 (1984) 2579.
- [36] T.-H. Lu, C.-C. Wang, Y.-L. Liou and C.-S. Chung, *Acta Crystallogr. C*, 48 (1992) 269.
- [37] M. Cannas, G. Carta and G. Marongiu, *J. Chem. Soc., Dalton Trans.*, (1974) 553.
- [38] M. Kabešová and Z. Kožíšková, *Collect. Czech. Chem. Commun.*, 54 (1989) 1800.
- [39] M. Cannas, G. Carta, A. Cristini and G. Marongiu, *J. Chem. Soc., Dalton Trans.*, (1974) 1278.
- [40] M. Mikuriya, S. Kida and J. Murase, *Bull. Chem. Soc. Jpn.*, 60 (1987) 1355.
- [41] K. Miyamura, M. Saburi, S. Tsuboyama, K. Tsuboyama and T. Sakurai, *J. Chem. Soc., Dalton Trans.*, (1988) 1543.
- [42] A. Pajunen and R. Hamalainen, *Suom. Kemistil. B*, 45 (1972) 122.
- [43] T.-J. Lee, T.-Y. Lee, C.-S. Chung and Y.-M. Wang, *Acta Crystallogr. C*, 47 (1991) 711.
- [44] A.E. Elia, E.C. Lingafelter and V. Schomaker, *Acta Crystallogr. C*, 40 (1984) 1313.
- [45] R. Kivekäs, A. Pajunen and K. Smolander, *Finn. Chem. Lett.*, (1977) 256.
- [46] J. Garaj, *Chem. Zvesti*, 21 (1967) 865.
- [47] M.B. Cingi, A.M.M. Lanfredi, A. Tiripicchio, J.P. Cornelissen, J.G. Haasnoot and J. Reedijk, *Inorg. Chim. Acta*, 129 (1987) 217.
- [48] J. Garaj, M. Dunaj-Jurčo and O. Lindgren, *Collect. Czech. Chem. Commun.*, 36 (1971) 3863.
- [49] B. Piggott, L.M. Hursthouse and R.L. Short, *Polyhedron*, 8 (1989) 769.
- [50] A.B. Ilyukhin, L.M. Shkol'nikova, A.L. Poznyak and N.M. Dyatlova, *Koord. Khim.*, 16 (1990) 811.
- [51] E. Bouwman, R. Day, W.L. Driessen, W. Tremel, B. Krebs, J.S. Wood and J. Reedijk, *Inorg. Chem.*, 27 (1988) 4614.
- [52] D.W. Engelfriet, W. den Brinker, G.C. Verschoor and S. Gorter, *Acta Crystallogr. B*, 35 (1979) 2922.
- [53] M. Kabešová and Z. Kožíšková, *Collect. Czech. Chem. Commun.*, 57 (1992) 1269.
- [54] F. Paap, W.L. Driessen, J. Reedijk, M. Dartmann and B. Krebs, *Inorg. Chim. Acta*, 121 (1986) 185.
- [55] J. Korvenranta and A. Pajunen, *Suom. Kemistil. B*, 43 (1970) 119.
- [56] D.L. Kozlowski and D.J. Hodgson, *J. Chem. Soc., Dalton Trans.*, (1975) 55.
- [57] C. Potvin, J.M. Manoli, F. Sechresse and S. Marzak, *Inorg. Chem.*, 26 (1987) 4370.
- [58] J.M. Manoli, C. Potvin, F. Sechresse and S. Marzak, *Inorg. Chim. Acta*, 150 (1988) 257.
- [59] W. Clegg, A. Beheshti and C.D. Garner, *Acta Crystallogr. C*, 44 (1988) 170.
- [60] H. Uramayama, H. Yamochi, G. Saito, S. Sato, A. Kawamoto, J. Tananka, T. Mori, Y. Maruyama and H. Inokuchi, *Chem. Lett.*, (1988) 463.
- [61] E.S. Raper, J.R. Greighton, J.D. Wilson, W. Clegg and A. Milne, *Inorg. Chim. Acta*, 155 (1989) 85.
- [62] J.-H. Wu, N.-Y. Zhu, S.-W. Du, X.-T. Wu and J.-X. Lu, *Inorg. Chim. Acta*, 185 (1991) 181.
- [63] J.R. Roper, H. Paulus and H. Elias, *Inorg. Chem.*, 28 (1989) 2323.
- [64] J.P. Cornelissen, R.A.G. de Graff, J.G. Haasnoot, R. Prins, M. Reedijk, M. Biagini-Cingi, A.M. Manotti Lanfredi and A. Tiripicchio, *Polyhedron*, 8 (1989) 2313.
- [65] N.V. Pervuchina, N.V. Podberezskaja and V.N. Kirichenko, *Zh. Strukt. Khim.*, 23 (1982) 130.
- [66] M. Koman, L. Macášková, G. Ondrejovič, B. Koreň, L. Battaglia and A. Corradi, *Acta Crystallogr. C*, 44 (1988) 245.
- [67] M. Cannas, G. Carta and G. Marongiu, *J. Chem. Soc., Dalton Trans.*, (1973) 251.
- [68] G. Marongiu, E.C. Lingafelter and P. Paoletti, *Inorg. Chem.*, 8 (1969) 2763.
- [69] T.-H. Lu, D.-T. Wu and C.-S. Chung, *J. Chem. Soc., Dalton Trans.*, (1986) 1999.
- [70] J.L. Mesa, T. Rojo, M.L. Arriortua, G. Villeneuve, J.V. Folgado, A. Beltrán-Porter and D. Beltrán-Porter, *J. Chem. Soc., Dalton Trans.*, (1989) 53.
- [71] K. Smolander, *Finn. Chem. Lett.*, (1974) 199.
- [72] M.A. Poraj-Koshitz and G.V. Tsintsadze, *Kristallochimia, Itogi Nauki*, Moscow, 1967.
- [73] G.D. Andreotti, L. Cavalca and P. Sgarabotto, *Gazz. Chim. Ital.*, 101 (1971) 483.
- [74] B.W. Brown and E.C. Lingafelter, *Acta Crystallogr.*, 17 (1964) 254.
- [75] E.S. Raper and W. Clegg, *Inorg. Chim. Acta*, 180 (1991) 239.
- [76] S.M. Nelson, F.S. Esho and M.G.B. Drew, *J. Chem. Soc., Chem. Commun.*, (1981) 388.

- [77] W. Haase, R. Mergehenn and W. Krell, *Z. Naturforsch.*, 31b (1976) 85.
- [78] M. Mikuriya, Y. Nishida, S. Kida, T. Uechi and I. Ueda, *Acta Crystallogr. B*, 33 (1977) 538.
- [79] P. Domiano, A. Musatti, M. Nardelli, C. Pelizzi and G. Predieri, *J. Chem. Soc., Dalton Trans.*, (1975) 2357.
- [80] L. Walz and W. Haase, *J. Chem. Soc., Dalton Trans.*, (1985) 1243.
- [81] A. Pajunen and K. Smolander, *Finn. Chem. Lett.*, (1974) 99.
- [82] M. Cannas, G. Carta and G. Marongiu, *J. Chem. Soc., Dalton Trans.*, (1974) 556.
- [83] J. Sívý, F. Pavelčík, J. Krátsmar-Šmogrovič, M. Žemlička and V. Seressová, *Collect. Czech. Chem. Commun.*, 55 (1990) 2924.
- [84] M.B. Hursthouse, K.J. Izod, M.A. Mazid and P. Thornton, *Polyhedron*, 9 (1990) 535.
- [85] M. Cannas, G. Carta and G. Marongiu, *Gazz. Chim. Ital.*, 104 (1974) 581.
- [86] W.L. Driessen, H.L. Blonk, W. Hinrichs and J. Reedijk, *Acta Crystallogr. C*, 43 (1987) 1885.
- [87] K. Nieminen, *Acta Chem. Scand., Ser. A*, 35 (1981) 753.
- [88] M. Kabešová, Z. Kožíšková and M. Dunaj-Jurčo, *Collect. Czech. Chem. Commun.*, 55 (1990) 1184.
- [89] M. Kabešová, M. Dunaj-Jurčo and J. Soldánová, *Inorg. Chim. Acta*, 130 (1987) 105.
- [90] Z. Kožíšková, J. Kožíšek and M. Kabešová, *Polyhedron*, 9 (1990) 1029.
- [91] H. Yamaguchi, Y. Inomata and T. Takeuchi, *Inorg. Chim. Acta*, 172 (1990) 105.
- [92] A.S. Antsyshkina, M.A. Porai-Koshits, G.G. Sadikov, M. Kabešová and J. Gažo, *Koord. Khim.*, 7 (1981) 1018.
- [93] J. Soldánová, M. Kabešová and J. Gažo, *Inorg. Chim. Acta*, 76 (1983) L203.
- [94] A. Korczynski, *Rocz. Chem.*, 36 (1962) 1539.
- [95] J. Garaj, *Inorg. Chem.*, 8 (1969) 304.
- [96] E. Bouwman, W.L. Driessen and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, (1988) 1337.
- [97] H. Scouloudi, *Acta Crystallogr.*, 6 (1953) 651.
- [98] O. Geiser, M.A. Beno, A.M. Kini, H. Wang Hau, A.J. Schultz, B.D. Gates, C.S. Cariss, K.D. Carlson and J.M. Williams, *Synth. Met.*, 27 (1988) A235.
- [99] P.C. Healy, C. Pakawatchai, R.I. Papasergio, V.A. Patrick and A.H. White, *Inorg. Chem.*, 23 (1984) 3769.
- [100] M.A. Beno, H.H. Wang, A.M. Kini, K.D. Carlson, W. Geiser, W.K. Kwok, J.E. Thompson, J.W. Williams, J.-G. Ren and M.-H. Whangbo, *Inorg. Chem.*, 29 (1990) 1599.
- [101] M.B. Cingi, A.M.M. Lanfredi, A. Tiripicchio, J. Reedijk and J. Haasnoot, *Acta Crystallogr. C*, 42 (1986) 427.
- [102] G.J. Pyrka, M.R. Fernando, M.R. Inoue and M. Inoue, *Inorg. Chim. Acta*, 156 (1989) 257.
- [103] J.M. Manoli, C. Potvin, F. Secheresse and S. Marzak, *J. Chem. Soc., Chem. Commun.*, (1986) 1557.
- [104] G.O. Morpurgo, G. Dessy and V. Fares, *J. Chem. Soc., Dalton Trans.*, (1984) 785.
- [105] C.L. Raston, B. Walter and A.H. White, *Aust. J. Chem.*, 32 (1979) 2757.
- [106] A. Lavery, S.M. Nelson and M.G.B. Drew, *J. Chem. Soc., Dalton Trans.*, (1987) 2975.
- [107] N.K. Homsy, M. Noltmeyer, H.W. Roesky, H.G. Schmidt and G.M. Sheldrick, *Inorg. Chim. Acta*, 90 (1984) L59.
- [108] A.P. Gaughan, R.F. Ziolo and Z. Dori, *Inorg. Chim. Acta*, 4 (1970) 640.
- [109] J.-L. Huang, J.-X. Lu, D.-B. Huang and S.-X. Liu, *Sci. Sin., Ser. B*, 26 (1983) 19.
- [110] P.C. Healy, B.W. Skelto, A.F. Waters and A.H. White, *Aust. J. Chem.*, 44 (1991) 1049.
- [111] L.D. Smith and V.J. Saunders, *Acta Crystallogr. B*, 37 (1981) 1807.
- [112] M. Kabešová, M. Dunaj-Jurčo, M. Serátor, J. Gažo and J. Garaj, *Inorg. Chim. Acta*, 17 (1976) 161.