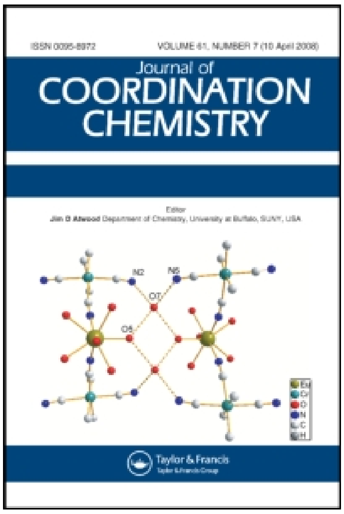

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STRUCTURAL AND SPECTROSCOPIC CHARACTERIZATION OF COPPER(I) HALOGEN COMPLEXES WITH ω-THIOCAPROLACTAM AND TRIPHENYLPHOSPHINE

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STRUCTURAL AND SPECTROSCOPIC CHARACTERIZATION OF COPPER(I) HALOGEN COMPLEXES WITH ω-THIOCAPROLACTAM AND TRIPHENYLPHOSPHINE

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A series of mixed ligand copper(I) halogeno complexes with ω-thiocaprolactam, (tclH) and triphenylphosphine (PPh_3) of general formula $Cu(tclH)_n(PPh_3)_{3-n}X$ where n = 1, 2 and X = Cl, Br, I has been studied. The crystal structure of $Cu(tclH)(PPH_3)_2Br$ is reported and discussed with respect to those of other members of the series. Solution ^{13}C and ^{31}P NMR spectra of the compounds are related to structural characteristics. $Cu(tclH)(PPH_3)_2Br$ crystallizes in the monoclinic system, space group $P2_1/c$, with a = 16.11(2), b = 9.749(2), c = 26.46(3)Å, β = 91.03(5)° and Z = 4. The local copper environment is irregular tetrahedral with Cu-P equal to 2.289(4) and 2.277(4)Å, while Cu-S and Cu-Br are 2.344(4) and 2.522(2)Å, respectively.

KEYWORDS: copper, halogen, thiocaprolactam, phosphine, X-ray structure

INTRODUCTION

Understanding of the stereochemical preferences and reactivity of copper(I) compounds, especially towards sulfur donor ligands, is among the major goals of coordination chemistry in view of Cu(I) participation in several bioprocesses.[1] Along this line of research we have focused our interest on monitoring structural changes in the coordination sphere of copper(I) with respect to stereoelectronic effects induced by the coordinated ligands. Heterocyclic thiones with α-nitrogen

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heteroatoms are studied as models for thioamide groups, or other sulfur-containing functional groups, while tertiary phosphines[2] or arsines[3] have been used to complete the coordination sphere. Among the thiones studied, the seven-membered heterocyclic ring of ω-thiocaprolactam has been extensively investigated, since it presents a considerable bulk and a non-conjugated thioketo group, thus reducing the role of ligand electronic effects with respect to coordination sphere geometry. The ligand is known to form, with copper(I) halides, monomeric three-coordinate compounds of formula $Cu(tclH)_2X$.[4] It was therefore interesting to investigate the concerted effects of this ligand and several phosphines, of which triphenylphosphine is used as the starting point. The present study is devoted to a study of compounds with general formula $Cu(tclH)_n(PPH_3)_{3-n}X$, where X denotes a halogen atom and $n = 1$ or 2. The crystal and molecular structure of $Cu(tclH)(PPh_3)_2Br$ is reported and discussed in connection with previously reported copper(I) complexes with tclH and triphenylphosphine or triphenylarsine.

EXPERIMENTAL

Analytical grade solvents were used throughout. Thiocaprolactam (Aldrich) was recrystallized from hot ethanol and triphenylphosphine (BDH) from chloroform prior to use. Copper(I) halides (Merk) were used without further purification.

The syntheses of the complexes were carried out by stirring, under moderate heating, copper halide and thiocaprolactam in the appropriate mol ratio (1:1 or 1:2) in acetonitrile. To the white suspensions formed was added the desired amount (2 or 1 equivalents, respectively) of triphenylphosphine and the reaction continued as previously reported.[5] Product stoichiometry was confirmed by elemental analysis for C, H and N on a Perkin-Elmer 240 B instrument.

^{13}C and ^{31}P NMR specta were recorded on a Varian VXR 300 spectrometer in deuterated chloroform solutions. ^{13}C chemical shifts are reported in ppm relative to $CDCl_3$ and ^{31}P relative to external $(NPCl_2)_3$ standard. ^1H spectra were recorded on a Varian VXR 300 spectrometer relative to $CDCl_3$, or on a Bruker AW 80 spectrometer using internal TMS standard. During the study precipitation of the title compound occurred in the NMR tube. This observation prompted us to prepare a substantial amount of the complex which was subsequently dissolved in a 1:1 mixture of chloroform:ethanol and the solution allowed to evaporate at room temperature. The crystals thus obtained were subjected to X-ray analysis, the results of which are presently reported.

Solution of the structure

Table 1 contains details of data collection and refinement. Data reduction was performed by the Enraf-Nonius SDP/VAX package;[6] Lorentz and polarization effects were taken into account. Reference reflections showed a gain of intensity of about 23.8% during data collection.

The structure was solved by direct methods using SHELX86.[7] Copper scattering factors and anomalous dispersion values were taken from the International Tables for X-ray Crytallography, Vol. IV.[8] For the other atoms, scattering factors

Table 1 Crystal Data and Details of the Structure Determination.

a) Crystal Data	
Molecular formula	$CuBrSP_2NC_{42}H_{43}O$
M_r	815.27
a [Å]	16.11(2)
b [Å]	9.749(2)
c [Å]	26.46(3)
β [°]	91.03(5)
V [Å^3]	4155.04(3)
D_x [g cm^{-3}]	1.30(1)
Z	4
Crystal system	monoclinic
Space group	$P2_1/c$
Crystal size [mm]	0.1 × 0.2 × 0.2
Linear absorption coefficient (cm^{-1}]	16.32
F(000)	1680
b) Data Collection	
Diffractometer	Enraf-Nonius-CAD4F
Radiation	MoKα (λ = 0.71073 Å) graphite-monochromator
Temperature [K]	295(3)
θ_{min}, θ_{max} [°] for cell det.	8, 17
No. of reflections used for cell det.	25
θ_{min}, θ_{max}	2, 25
$\omega/2\theta$ scan [°]	$\Delta\omega = 0.8 + 0.35 \tan\theta$
hkl limits	(0,19; 0,11; -31,31)
Reflections measured	7470
c) Refinement	
Independent reflections observed with $I > 2.5\sigma(I)$	2584
No. of parameters	373
Quantity minimized, $\Sigma w \| \|F_o\| - \|F_c\| \|^2$	$w^{-1} = (\sigma^2(F_o) + 0.0012\, F_o^2)/k$
R, R_w	0.070, 0.067
Max. final parameter shift, $(\Delta/\sigma)_{max}$	0.36 (C20, z)
Residual electron density, $(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ [eÅ^{-3}]	0.73, -0.49

were those implemented in the SHELX77 program.[9] Disorder was observed in the location of the crystal water oxygen atom; therefore, two such positions were located assuming an identical population factor for both. The phenyl rings were assumed to be regular hexagons with bond lengths equal to 1.395 Å and were subsequently refined as rigid groups. The hydrogen atom positions were calculated on stereochemical grounds, except that on the heterocyclic nitrogen atom, which was not located. The structure was solved by full-matrix least-squares methods on F values,[9] non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. The phenyl ring hydrogen atoms were treated as part of the rigid group while tclH protons were treated in accordance with their pivot atom geometry. Thermal parameters for all hydrogen atoms were kept fixed.

Interatomic distance and bond angle calculations, and the packing diagram drawings were carried out by the EUCLID package of programs[10] and the molecular plot was performed using ORTEP.[11] Calculations were run on the micro VAXII computer in the X-ray Laboratory of the Rudjer Boskovic Institute in Zagreb.

RESULTS AND DISCUSSIONS

The coordination of copper(I) to soft ligands, especially those bearing sulfur and phosphorus donor atoms like thiones and phosphines is versatile, though in the present case the bulk of thiocaprolactam limits the possible local copper environment to being monomeric three- or four-coordinate.

The fractional atomic coordinates of the non-hydrogen atoms are listed in Table 2. It is worth comparing the structural data of the title compound to its triphenylarsino counterpart, $Cu(tclH)(AsPh_3)_2Br$,[3a] hereafter refered to as complex **1**, as well as the closely related species $Cu(tclH)_2(AsPh_3)Br$ (**2**)[3b] and $Cu(tclH)_2(PPh_3)Cl$ (**3**).[5] Relevant structural parameters are presented in Table 3.

Coordination around copper is distorted tetrahedral, with one sulfur, two phosphorus and one bromine atoms completing the chromophore (Fig. 1). The two Cu-P bond distances are both longer than was observed in **3** (see Table 3) lying towards the upper extremity of the range between 2.23 and 2.31 Å defined in analogous compounds. Such an observation was made in the case of the Cu-As bonds in **1**.

The Cu-S distance is the longest among the compounds of the series studied, but still less than the sum of the covalent radii of the constituent atoms (2.39 Å). It may therefore be assumed that the coordinated thione ligand retains much of the double bond character of the thioketo group although some delocalization towards the adjacent C-N bond is evident. Indeed, the C-S distance is 1.66(1) Å, close to 1.67 (2) Å observed in **1** and the average value of 1.66 Å in **3**, and certainly shorter than

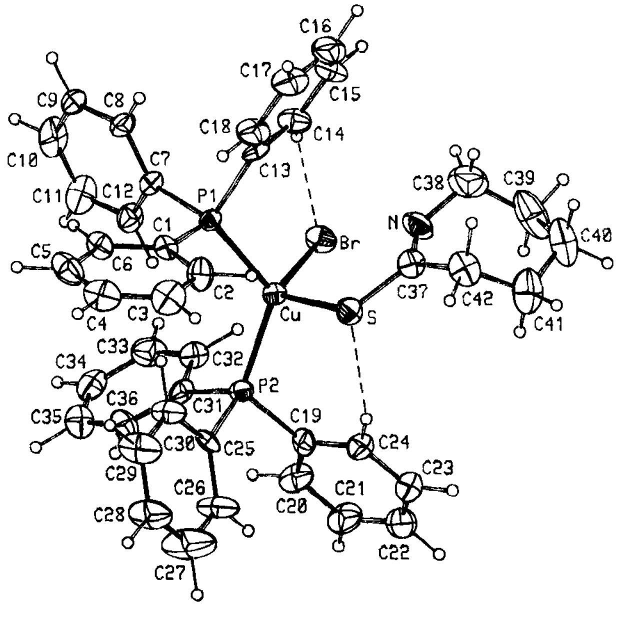

Figure 1 An ORTEP plot of the molecule along with the atom numbering. Dashed lines denote intermolecular hydrogen bonds. Thermal ellipsoids are scaled at 30%.

Table 2 Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen atoms for the complex.

Atom	*x/a*	y/b	z/c	U(eq) (Å^2)*
Br	0.10840(9)	0.56611(17)	0.10181(6)	0.0592(6)
Cu	0.23753(10)	0.69037(18)	0.13172(6)	0.0424(6)
S	0.2237(2)	0.9295(4)	0.12791(15)	0.0563(16)
P(1)	0.2423(2)	0.6545(3)	0.21721(13)	0.0366(12)
P(2)	0.3396(2)	0.6315(4)	0.07740(14)	0.0423(12)
N	0.0642(8)	0.8888(14)	0.1241(6)	0.076(6)
C(1)	0.3342(7)	0.7248(10)	0.2491(4)	0.037(5)
C(2)	0.3504(7)	0.8645(10)	0.2432(4)	0.065(7)
C(3)	0.4212(7)	0.9224(10)	0.2656(4)	0.081(8)
C(4)	0.4759(7)	0.8407(10)	0.2939(4)	0.081(8)
C(5)	0.4597(7)	0.7010(10)	0.2998(4)	0.079(8)
C(6)	0.3889(7)	0.6431(10)	0.2774(4)	0.052(6)
C(7)	0.2380(6)	0.4806(11)	0.2394(3)	0.037(5)
C(8)	0.2146(6)	0.4435(11)	0.2881(3)	0.056(6)
C(9)	0.2191(6)	0.3067(11)	0.3033(3)	0.073(7)
C(10)	0.2470(6)	0.2069(11)	0.2698(3)	0.085(9)
C(11)	0.2704(6)	0.2439(11)	0.2212(3)	0.085(8)
C(12)	0.2660(6)	0.3808(11)	0.2060(3)	0.059(6)
C(13)	0.1546(7)	0.7353(11)	0.2500(3)	0.041(5)
C(14)	0.0751(7)	0.6997(11)	0.2329(3)	0.062(6)
C(15)	0.0057(7)	0.7588(11)	0.2549(3)	0.096(9)
C(16)	0.0158(7)	0.8534(11)	0.2941(3)	0.096(10)
C(17)	0.0953(7)	0.8889(11)	0.3113(3)	0.082(8)
C(18)	0.1647(7)	0.8299(11)	0.2892(3)	0.070(7)
C(19)	0.3192(6)	0.6756(10)	0.0108(5)	0.049(6)
C(20)	0.3350(6)	0.5873(10)	-0.0294(5)	0.068(7)
C(21)	0.3218(6)	0.6315(10)	-0.0790(5)	0.080(8)
C(22)	0.2928(6)	0.7641(10)	-0.0885(5)	0.084(9)
C(23)	0.2771(6)	0.8524(10)	-0.0483(5)	0.079(8)
C(24)	0.2903(6)	0.8082(10)	0.0014(5)	0.066(7)
C(25)	0.4397(6)	0.7134(13)	0.0904(3)	0.037(5)
C(26)	0.4917(6)	0.7581(13)	0.0522(3)	0.089(8)
C(27)	0.5687(6)	0.8160(13)	0.0644(3)	0.142(13)
C(28)	0.5936(6)	0.8292(13)	0.1150(3)	0.097(9)
C(29)	0.5416(6)	0.7844(13)	0.1532(3)	0.092(8)
C(30)	0.4647(6)	0.7265(13)	0.1409(3)	0.067(7)
C(31)	0.3650(5)	0.4494(11)	0.0734(4)	0.045(5)
C(32)	0.2990(5)	0.3593(11)	0.0649(4)	0.054(6)
C(33)	0.3134(5)	0.2183(11)	0.0630(4)	0.076(8)
C(34)	0.3938(5)	0.1674(11)	0.0695(4)	0.071(7)
C(35)	0.4599(5)	0.2576(11)	0.0779(4)	0.068(7)
C(36)	0.4455(5)	0.3986(11)	0.0799(4)	0.062(7)
C(37)	0.1247(10)	0.9756(15)	0.1264(5)	0.054(6)
C(38)	-0.0221(12)	0.920(2)	0.1249(9)	0.114(10)
C(39)	-0.0525(12)	0.988(2)	0.0749(10)	0.126(12)
C(40)	-0.0291(12)	1.138(2)	0.0724(9)	0.115(10)
C(41)	0.0619(12)	1.1753(19)	0.0756(8)	0.101(9)
C(42)	0.1045(11)	1.1268(17)	0.1236(7)	0.076(8)
O(1)	0.17820	0.18660	0.4412	0.161(17)
O(2)	0.1164	0.01690	0.4583	0.166(16)

* *U(eq)* = 1/3 of the trace of the orthogonalized *U*.

Table 3 Relevant Structural Parameters for Mixed Ligand Copper(I) Complexes with tclH; E Denotes P or As, X stands for Cl or Br. The Labelling of the Sulfur and P or As Atoms is in Accord with the Labelling in the Original Structure.

Parameter	$Cu(tclH)(PPh_3)_2Br$	1	2	3
Cu-S(1)	2.344(4)	2.313(4)	2.310(1)	2.330(3)
Cu-S(2)			2.315(1)	2.339(3)
Cu-E(1)	2.289(4)	2.411(2)	2.370(1)	2.234(2)
Cu-E(2)	2.277(4)	2.372(2)		
Cu-X	2.522(2)	2.456(3)	2.605(1)	2.394(2)
S(1)-Cu-S(2)			103.2(1)	96.5(1)
S(1)-Cu-E(1)	107.0(2)	106.3(1)	111.1(2)	115.9(1)
S(1)-Cu-E(2)	101.3(2)	104.4(1)		
S(2)-Cu-E(1)			121.4(1)	117.3(1)
E(1)-Cu-E(2)	125.0(1)	116.1(1)		
S(1)-Cu-X	112.8(1)	114.7(1)	112.7(1)	110.6(1)
S(2)-Cu-X			104.6(1)	107.9(1)
E(1)-Cu-X	104.5(1)	105.9(1)	103.9(0)	108.1(1)
E(2)-Cu-X	106.4(1)	109.7(1)		

the average value in **2**. The adjacent C-N bond (1.29(2) Å) is indicative of the abovementioned delocalization.

The Cu-Br distance lies between those observed in **1** and **2** and longer than 2.462(0) Å observed in $Cu(PPh_3)_2$(pyridine-2-thione)Br.[12] Its elongation relative to that in **1** may be attributed partly to the extensive participation of the bromine atom in hydrogen bonding in the present complex.

A general remark about the structurally characterized species of this group of compounds is that hydrogen bonding is present in all cases and possibly plays an important role in the stabilization of the observed molecular arrangements. In the title compound, two close intramolecular contacts are observed, namely C14-H141...Br [C14...Br 3.753(9) Å, H141...Br 2.822(8) Å, C-H-Br angle 144.5(9)°] and C24-H241...S [C24...S 3.73(1) Å, H241...S 2.7(1) Å, C-H-S angle 152(1)°]. In the crystal packing, interaction between C-H and Br is also present; molecules are related by the x, y, z, and x, $y \pm 1$, z symmetry operations [C41-H411...Br, C41...Br 3.94(2) Å, H411...Br 2.90(2) Å, C-H-Br angle 161(2)°]. In this way, infinite chains are produced along b. It is worth noting that the disordered water molecule does not appear to participate in the hydrogen bond network (Fig. 2).

The chromophore is distorted tetrahedral, the bond angles lying between 101.3(1)° for S-Cu-P(1) to 125(1)° for P(1)-Cu-P(2). The P1-Cu-P2 and S-Cu-Br planes form an angle of 88.6°. A characteristic feature of the cycle is its chair conformation[13] ($Q(2) = 0.43$ Å, $Q(3) = 0.63$Å, $\varphi_2 = 307°$ and $\varphi_3 = 285°$) and the intraligand bond distances are normal compared to mean values observed in structures reported in the literature for the thione molecule. The well-documented asymmetry around the tetrahedral phosphorus atom is also evident in the phosphine ligands, both in the P-C bond distances, which vary from 1.80 to 1.85 Å as well as in the C-P-C angles, which range from 102.4 to 104.1°.

Solution ^{31}P NMR spectra of the compounds present a single signal. A sample of pure triphenylphosphine was run independently and was found to resonate at −5.48 ppm; signals of the phosphorus atoms in the complexes are found to lie closely around this value, indicating small changes in the phosphorus electronic environment upon coordination. In two of the compounds, namely $Cu(tclH)(PPh_3)_2Cl$ and

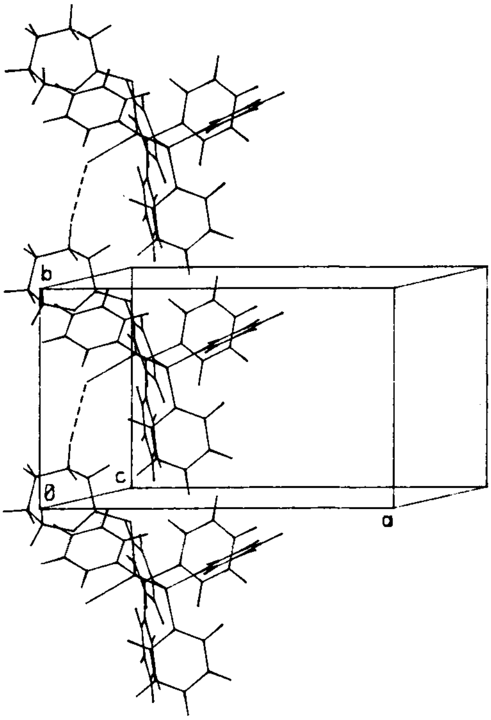

Figure 2 Molecular packing within the unit cell. Dashed lines denote intermolecular hydrogen bonds.

its bromo counterpart, traces of triphenylphosphine oxide were detected at 43.23 ppm. This was apparent from the pattern of ^{13}C NMR shifts of the phenyl ring carbon atoms, which was more complicated in the above cases. The presence of phosphine oxide was not observed in other studies and may be due to the preparation scheme adopted, in which no precautions were taken for exclusion of air and moisture from the reaction medium.

The compounds may be classified into two closely related groups, namely those bearing one tclH and two triphenylphosphine ligands and those with two lactam and one phosphine ligand, respectively. In both classes, a progressive change of the phosphorus chemical shift to higher fields is observed on passing from the chloro to the iodo compound, an observation in accord with the deshielding effect of the halogens. Differences observed between members within each group, though small in absolute value, are more pronounced where two thione ligands are present in the molecule. The more pronounced hydrogen bonding occurring in this case probably affects more drastically the more polarizable of the halogen atoms, therefore increasing shielding provided by copper to its neighbouring phosphorus atom.

A ^{31}P NMR measurement was attempted at -70°C, ($CDCl_3$ glass) which revealed a split and broadening of the room temperature signal. The signal consisted of a doublet, bearing at both extremes shoulders, resembling the expected quartet due to coupling of the phosphorus (^{31}P, nuclear spin $I = 1/2$) with the copper nucleus

Table 4 ^{13}C and ^{31}P NMR Data for the Complexes.

	^{13}C shifts							
Compound	Thione						Phosphine	^{31}P shift
tclH	24.5	28.1	30.4	45.1	47.1	210.5		
PPh_3							128.0 - 134.5	-5.48
$Cu(tclH)(PPh_3)_2Cl$	24.1	27.4	30.2	43.6	46.7	204.3	128.1 - 134.4	-4.77
$Cu(tclH)(PPh_3)_2Br$	24.1	27.4	30.2	43.5	46.6	203.9	128.1 - 134.3	-5.55
$Cu(tclH)(PPh_3)_2I$	24.1	27.4	30.2	43.4	46.6	203.4	128.1 - 134.3	-7.06
$Cu(tclH)_2(PPh_3)Cl$	24.1	27.3	30.2	43.0	47.1	205.1	128.3 - 133.9	-4.11
$Cu(tclH)_2(PPh_3)Br$	24.2	27.5	30.2	43.4	46.9	205.0	128.2 - 134.2	-6.51
$Cu(tclH)_2(PPh_3)I$	24.2	27.5	30.2	43.4	46.8	204.3	128.2 - 134.1	-7.48

(^{63}Cu, ^{65}Cu, nuclear spin $I = 3/2$)[14] which is encountered in solid state MAS measurements.

The shifts of the thione carbon atoms in the ^{13}C NMR spectra are indicative of ligand complexation by comparison to the free ligand[15] (see Table 4) and of analogous coordination compounds.[4a] Of special interest is the high field shift of the thioketo group carbon atom by *ca* 5 ppm, relative to the resonance observed in the ligand; this shielding is parallelled by a deshielding, of less pronounced magnitude of the carbon atoms adjacent to the heterocyclic nitrogen and the thioketo carbon atoms. The same phenomenon was observed in *N*-alkylated thiolactams relative to their unsubstituted analogues and was rationalized in terms of reduced polarity of the amido group brought about by steric crowding around the C-N bond in the former case. Indeed, in all the structures of $Cu(tclH)_2X$ or $Cu(tclH)_n(EPh_3)_{3-n}X$ compounds, the C-S bond seems to retain partly its double bond character, its length varying between 1.66 and 1.71Å. The adjacent C-N distance lies between 1.29 and 1.31Å, implying partial delocalization. The shielding of the planar carbon atom, though not prominent in magnitude, follows that observed for the phosphorus one, *i.e.* it is enhanced on passing from the chloro to the iodo compound, regardless of the number of phosphine and thione ligands present in the molecule. It seems that the presence of two competing thione molecules minimizes this effect (Table 4).

Supplementary Material

Full lists of H atom coordinates and associates isotropic thermal parameters, anisotropic parameters for non-hydrogen atoms, bond lengths and angles, and observed and calculated structure factors are available from the authors upon request.

References

1. K.B. Karlin and J. Zubieta (eds), *Copper Coordination Chemistry, Biochemical and Inorganic Perspectives* (Adenine, New York, 1983).
2. (a) S.K. Hadjikakou, P. Aslanidis, P. Karagiannidis, D. Mentzafos and A. Terzis, *Polyhedron*, **10**, 935 (1991); (b) S.K. Hadjikakou, P. Aslanidis, P.D. Akrivos, P. Karagiannidis, B. Kojic-Prodic and M Luic, *Inorg. Chim. Acta*, **197**, 31 (1992); (c) P.D. Akrivos, G. Kapsomenos, P. Karagiannidis, S. Skoulika and A. Aubry, *Inorg. Chim. Acta*, **202**, 73 (1992).

3. (a) P. Karagiannidis, P.D. Akrivos, D. Mentzafos and A. Terzis, *Inorg. Chim. Acta,* **181**, 263 (1991); (b) P. Karagiannidis, P.D. Akrivos, S. Skoulika and A. Aubry, *Inorg. Chim. Acta,* **188**, 79 (1991).
4. (a) P. Castan, *Trans. Metal Chem.,* **6**, 14 (1981); (b) P. Karagiannidis, P.D. Akrivos, B. Kojic-Prodic and M. Luic, *J. Coord. Chem.,* **26**, 215 (1992); (c) P. Karagiannidis, P.D. Akrivos, D. Mentzafos and A. Hountas, *Inorg. Chim. Acta,* **180**, 93 (1991).
5. B. Kojic-Prodic, M. Luic, P. Karagiannidis, P.D. Akrivos and S. Stoyanov, *J. Coord. Chem.,* **25**, 21 (1991).
6. B.A. Frenz, The Enraf-Nonius CAD4-SDP, in *Computing in Crystallography*, Eds. H. Schenk, R. Olthof-Hazenkamp, H. van Koningveld and G.C. Bassi, (University Press, Delft, Holland 1978), pp. 64-71.
7. G.T.M. Sheldrick, SHELX86, in *Crystallography Computing 3*, Eds. G.T.M. Sheldrick, C. Krueger and R. Goddard (Oxford University Press, Oxford, 1986).
8. International Tabels for X-ray Crystallography Vol. IV, Eds. J.A. Ibers and W.C. Hamilton, (Kynoch Press, Birmingham, 1973).
9. G.T.M. Sheldrick, *SHELX-77, Program for Structure Determination*, (University of Cambridge, Cambridge 1983).
10. A.L. Spek, *The EUCLID Package in Computational Crystallography*, Ed. D. Sayre, (Clarendon Press, Oxford, 1982), p. 528.
11. C.K. Johnson, *ORTEPII*, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, U.S.A. (1976).
12. P. Karagiannidis, P. Aslanidis, D.P. Kessissoglou, B. Krebs and M. Dartman, *Inorg. Chim. Acta,* **156**, 47 (1989).
13. (a) K.I. Boessenkool and J.C.A. Boeyens, *J. Cryst Mol. Struct.,* **10**, 11 (1980); (b) D. Cremer and J.A. Pople, *J.Am. Chem. Soc.,* **97**, 1354 (1975).
14. (a) G.A. Bowmaker, J.D. Cotton, P.C. Healy, J.D. Kildea, S.B. Silong, B.W. Skelton and A.H. White, *Inorg. Chem.,* **28**, 1462 (1989); (b) J.V. Hanna, M.E. Smith, S.N. Stuart and P.C. Healy, *J. Phys. Chem.,* **96**, 7560 (1992).
15. I.D. Rae, *Aust. J. Chem.,* **32**, 567 (1979).