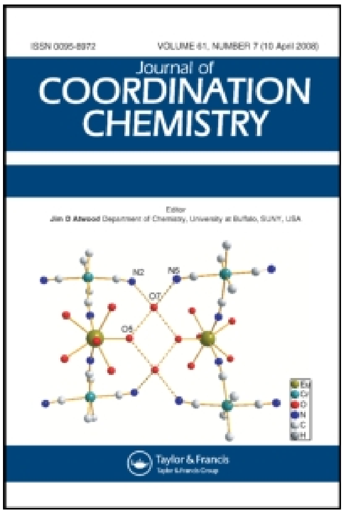

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SYNTHESES AND PROPERTIES OF SOME FIVE-AND SIX-COORDINATE COPPER(II) COMPLEXES WITH ACETYLACETONATE AND THE STRUCTURAL CHARACTERISATION OF A BIGUANIDE-ACETYLACETONATE DOUBLE SALT

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SYNTHESES AND PROPERTIES OF SOME FIVE-AND SIX-COORDINATE COPPER(II) COMPLEXES WITH ACETYLACETONATE AND THE STRUCTURAL CHARACTERISATION OF A BIGUANIDE-ACETYLACETONATE DOUBLE SALT

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Compounds of formulae $[M(Hbg)_2][Cu(acac)_2X]_2$ (*1*) and $[Ni(Rbg)_2][Cu(acac)_2Cl_2]$ (*2*) (acac = acetylacetonate, X = Cl, Br, I; M = Cu, Ni; Hbg = biguanide, Rbg = *N*-alkylbiguanide, R = CH_3, C_2H_5) have been prepared by the interaction of the respective chelates in methanol. The presence of five and six coordinate copper(II) in the anions of (*1*) and (*2*) respectively is suggested from their conductance data, electronic and vibrational spectra, magnetic moments and thermal analyses. Compound (*1*), where M = Cu and X = Cl has been characterized by single crystal X-ray crystallography. Crystals are orthorhombic, space group *Pbca* with $Z = 4$ with $a = 15.218(2)$, $b = 15.986(3)$, $c = 14.565(3)$Å. The structure was solved by Patterson and Fourier methods and refined by least-squares methods to $R = 0.052$ and $R_W = 0.052$ for 4267 reflexions and $R = 0.065$ for all 5206 reflexions. The structure consists of square-planar $[Cu(Hbg)_2]^{2+}$ cations and square-pyramidal $[Cu(acac)_2Cl]^-$ anions. The nonhydrogen atoms of the cation lie within 0.02Å of the plane of best fit defined by the two chelate rings. The copper atom in the anion lies 0.2Å above the plane of best fit of four oxygen atoms of the coordinated acetylacetonate and is directed towards the chlorine atom. The ions are linked by very weak hydrogen bonds between the oxygen atoms of the anion and the –NH groups of the cation. The Cu–Cl distance is much longer than those in $CuCl_2$.

INTRODUCTION

It is well known that copper(II) complexes can display a variety of coordination polyhedra with usual coordination numbers varying from four to six.[1] A wealth of X-ray crystallographic data has established the existence of five-coordinate square-based pyramidal[2-5] and trigonal-bipyramidal[6-8] stereochemistries for copper(II) in its complexes. Six coordinate copper(II) complexes are common and these generally attain a tetragonally distorted octahedral configuration.[9,11] Reports of simple five and six coordinate complexes containing the $[Cu(acac)_2]$ species are unknown to the authors though mixed ligand penta-coordinate copper(II) species containing β-diketonate ligands[3,5] have been isolated. This paper describes the isolation and characterization of some penta- and hexa-coordinate copper(II) complexes derived from square-planar $[Cu(acac)_2]$ species.

EXPERIMENTAL

Reagents and solvents were distilled before use. The ligands and the known complexes were prepared according to the literature.[13] Vibration (in KBr disc) and electronic spectral studies, magnetic and conductance measurements and thermal studies were carried out using Beckman IR-12 and Cary-17D spectrophotometers, a Gouy balance, a Philips conductivity bridge and a Derivatograph (Paulik, Paulik and Erdey), respectively.

Preparation of the complexes

$[Cu(Hbg)_2][Cu(acac)_2X]_2$; (X = Cl, Br, I).

The compounds were prepared from $[Cu(acac)_2]$ and $[Cu(Hbg)_2X_2]$ in dry methanol as follows. A light blue solution was obtained on mixing a solution of $[Cu(Hbg)_2X_2]$ (0.015 mol in 30 cm^3) with that of $[Cu(acac)_2]$ (0.03 mol in 20 cm^3), by the dropwise addition of the ligand acetylacetone in solution (0.04 mol in 20 cm^3) to a well stirred solution of $[Cu(Hbg)_2X_2]$ (0.03 mol in 30 cm^3) or by the addition of a biguanide halide solution (0.02 mol in 25 cm^3) to a well-stirred solution of $[Cu(acac)_2]$ (0.03 mol in 30 cm^3).

In each case the mixture was refluxed on a water bath for 2 h by which time the blue colour of the solution changed to blue-green and blue-green crystals of the desired compound separated out slowly. These were filtered, washed several times with hot chloroform to remove any unreacted metal acetylacetonate and then with methanol to dissolve any remaining metal biguanide. The crystals were dried in vacuum over fused $CaCl_2$.

$[Ni(Hbg)_2][Cu(acac)_2X]_2$; (X = Cl, Br, I)

The light blue solution obtained by mixing a methanolic solution of $[Cu(acac)_2]$ (0.04 mol in 50 cm^3) with that of the appropriate $[Ni(Hbg)_2X_2]$ complex (0.02 mol in 40 cm^3) was refluxed on water bath. The colour of the solution changed to deep green and shining green crystals of each product separated out almost quantitatively from the solution within 3h. Each mixture was filtered hot and the crystals were successively washed several times with chloroform and methanol.

$[Ni(Rbg)_2][Cu(acac)_2Cl_2]$

Pale green crystals of $[Ni(Rbg)_2][Cu(acac)_2Cl_2]$ ($R = CH_3, C_2H_5$) were obtained in high yields on refluxing a methanolic solution (50 cm^3) of $[Cu(acac)_2]$ (0.01 mol) and $[Ni(Rbg)_2]Cl_2$ (0.01 mol) for 3h on a water bath. These were washed and dried as above.

X-ray structural studies

Single crystals of $[Cu(Hbg)_2][Cu(acac)_2Cl]_2$ were obtained after 40 days from a methanolic solution (150 cm^3) containing $[Cu(acac)_2]$ (0.01 mol) and $[Cu(Hbg)_2Cl_2]$ (0.005 mol) kept over fused $CaCl_2$.

Crystal data

$C_{24}H_{42}Cl_2Cu_3N_{10}O_8$, $M = 860.19$, orthorhombic, $a = 15.218(2)$, $b = 15.986(3)$, $c = 14.565(3)$Å, $U = 3543.3$Å^3, $Z = 4, D_c = 1.612$ g cm^{-3}, $D_m = 1.60$ g cm^{-3}, μ(Mo-$K\alpha$) = 19.98 cm^{-1}, space group *Pbca* (No 61), from systematic absences $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0, h = 2n + 1$.

Cell constants were obtained from precession photographs and refined with the indexed lines of a Guinier photograph. 5206 unique reflexions of the layers $hk0$ to $hk20$ up to $\theta = 30°$ were measured on a Weissenberg diffractometer (STOE – Stadi 2, Mo – $K\alpha$ radiation, graphite monochromator, ω-scan) yielding 4267 observed reflexions with intensities I greater than $\sigma_I(\sigma_I = [Z + (U_1 + U_2)^2 \cdot q^2 + (0.03 \cdot I)^2]^{1/2}$ where Z is the peak count, U_1 and U_2 are background counts, q is the ratio of the peak scan time to the time for both background measurements). Lorentz-polarisation and absorption corrections were applied. The structure was solved by Patterson and Fourier methods and refined by least-squares methods. After refinement of the non-hydrogen atoms with anisotropic temperature factors all hydrogen atoms other than those of the methyl groups could be located and were refined with individual isotropic temperature factors. The methyl groups were refined as rigid groups. The refinement converged to $R = 0.052$ and $R_W = 0.052$ (w was set equal to σ_F^{-2}) for 4267 observed reflexions and $R = 0.065$ for all 5206 reflexions. The maximum shift to error ratio in the last cycle of least-squares was less than 0.15. The final difference Fourier map showed no peaks greater than 0.5 $e\text{Å}^{-3}$. Atomic scattering factors were taken from the paper of Cromer and Mann.[14] The anomalous dispersion correction for Cu was included.[15] The program system SHELX-76 was used.[16] The final atomic parameters are given in Table V, the distances and angles in Table VI. Lists of thermal parameters and structure factors have been deposited with the editor and are available on request.

RESULTS AND DISCUSSION

The compounds were prepared in methanol and crystallized from it without decomposition. They have low solubilities in most solvents including benzene, acetone, chloroform, dichloromethane and ethanol. Dissolved in water or DMF the complexes undergo decomposition slowly at 0° and rapidly at elevated temperatures to produce $[Cu(acac)_2]$ and the corresponding metal biguanide halides. The compounds are unstable towards acid or base.

Uni-bi and bi-bivalent electrolytic behaviour was observed for $[M(Hbg)_2]\,[Cu(acac)_2X]_2$ [M = Cu, Ni, X = Cl, Br, I) and $[Ni(Rbg)_2]\,[Cu(acac)_2Cl_2]$ (R = CH_3, C_2H_5) respectively (Table I). Methanolic $AgNO_3$ precipitates only the corresponding metal biguanide nitrates and not the silver halide from these solutions. Similar precipitations also occur if $LiNO_3$ or Li_2SO_4 are used. Electronic spectra of the filtrates from these reactions demonstrate the loss of absorption due to metal biguanide ions with the other band positions remaining unaltered. Thus it may be concluded that the Cu-X bonds are not cleaved under these conditions.

During the preparation of the compounds use of the reacting material in different stoichiometries always led to the isolation of the described compounds but with contamination from the excess unreacted component. The magnetic moments of those compounds containing the Cu-Cu system lie in the range 1.71 to 1.74 BM. Those of the Cu-Ni system are in accord with the presence of a square-planar diamagnetic nickel(II) species. The size and charge of both cation and anion appear to be important determinants for the isolation of these complexes. Attempts to isolate complexes of general formulae $[ML_2]\,[Cu(acac)_2X]_2$ or $[M'L'_2]\,[Cu(acac)_2X'_2]$ (M = Cu, Ni; L = Rbg, ½ endbg; X = F and M′ = Ni; L′ = Hbg, ½ endbg; X′ = F, Cl, Br, I; endbg = ethylenedibiguanide) were unsuccessful. Similarly, attempts to convert square-planar copper(II) or nickel(II) biguanide into the corresponding five- or six-coordinate complexes using halide ion salts alone were unsuccessful. This may be due to π-electronic delocalization in these species preventing further coordination.

The solid state (nujol mull) and solution spectra of the complexes were recorded and the data are presented in Table II. A good correspondence between the solid state and the solution spectra was observed. The spectra of the $[Cu(acac)_2X]^-$ ions are independent of the nature of $[M(Hbg)_2]^{2+}$ (M = Cu, Ni) and show three absorption bands relative to only two in $[Cu(acac)_2]$. The peak positions, however, depend on the nature

TABLE I
Analytical, conductance and magnetic data for the complexes.

Compounds	Colour	Cu(%)	Ni(%)	N(%)	C(%)	X(%)	H(%)	μ_{eff}^{b} at 300 K (B.M.)	Λ^{c} ($cm^2\ mol^{-1}$)
$[Cu(acac)_2Cl]_2[Cu(Hbg)_2]$	Green-Blue	22.12 (22.26)[a]		16.21 (16.36)	33.48 (33.66)	8.16 (8.30)	4.62 (4.76)	1.64	152
$[Cu(acac)_2Br]_2[Cu(Hbg)_2]2H_2O$	Green-Blue	19.22 (19.35)		14.18 (14.22)	29.11 (29.25)	16.18 (16.25)	4.12 (4.47)	1.68	148
$[Cu(acac)_2I]_2[Cu(Hbg)_2]$	Green-Blue	18.26 (18.34)		13.78 (13.85)	27.75 (27.73)	24.38 (24.73)	3.92 (3.85)	1.66	152
$[Cu(acac)_2Cl]_2[Ni(Hbg)_2]$	Green	14.78 (14.92)	6.82 (6.93)	16.41 (16.45)	33.71 (33.84)	8.22 (8.34)	4.52 (4.70)	1.70	156
$[Cu(acac)_2Br]_2[Ni(Hbg)_2].2H_2O$	Green	12.86 (12.96)	5.96 (6.02)	14.18 (14.29)	29.16 (29.38)	16.26 (16.32)	4.61 (4.69)	1.72	152
$[Cu(acac)_2I]_2[Ni(Hbg)_2]$	Green	12.12 (12.23)	5.62 (5.70)	13.38 (13.45)	27.72 (27.85)	24.26 (24.56)	3.65 (3.87)	1.72	154
$[Cu(acac)_2Cl_2][Ni(Mebg)_2].H_2O$	Pale Green	9.86 (9.93)	9.16 (9.22)	21.82 (21.89)	29.88 (30.02)	10.92 (11.10)	5.26 (5.31)	1.72	146
$[Cu(acac)_2Cl_2][Ni(Etbg)_2].H_2O$	Pale Green	9.46 (9.51)	8.71 (8.84)	20.86 (20.97)	32.18 (32.36)	10.56 (10.63)	5.58 (5.69)	1.73	156

[a] Figures in parentheses are calculated values [b] Per copper atom. [c] In methanol.

TABLE II
Electronic spectral data for the complexes (cm ;1)

Compound	Medium	Absorption maxima (cm^{-1})				
[Cu(acac)$_2$Cl]$_2$ [Cu(Hbg)$_2$]	Nujol	10,990sh[a]	13,330sh	16,000	18,870sh	
	Methanol	11,110sh(35.5)	13,160sh(47.2)[b]	15,750(66.5)	18,870sh(58.2)	
[Cu(acac)$_2$Br]$_2$ [Cu(Hbg)$_2$]	Nujol	10,810sh	13,330sh	16,130	18,870	
	Methanol	10,990sh(32.6)	13,250sh(46.5)	15,870(61.7)	18,870sh(54.6)	
[Cu(acac)$_2$I]$_2$ [Cu(Hbg)$_2$]	Nujol	11,110sh	13,330sh	16,260	18,870	
	Methanol	11,110sh(36.8)	13,330sh(43.5)	16,130(70.5)	18,870sh(51.2)	
[Cu(acac)$_2$Cl]$_2$ [Ni(Hbg)$_2$]	Nujol	10,990sh	13,340sh	16,000		21,739
	Methanol	11,111sh(32.6)	13,160sh(41.2)	15,870(52.5)		21,739(18.5)
[Cu(acac)$_2$Br]$_2$ [Ni(Hbg)$_2$]	Nujol	10,810sh	13,330sh	16,130		21,739
	Methanol	11,050sh(34.6)	13,330sh(37.5)	15,870(51.2)		21,739(15.8)
[Cu(acac)$_2$I]$_2$ [Ni(Hbg)$_2$]	Nujol	11,110sh	13,330sh	16,260		21,739
	Methanol	11,110sh(32.6)	13,330sh(41.2)	16,260(52.5)		21,739(18.5)
[Cu(acac)$_2$Cl$_2$] [Ni(Mbg)$_2$]	Nujol	10,000sh	12,820sh	15,040		21,505
	Methanol	10,000sh(28.2)	12,820sh(38.6)	15,040(54.2)		21,505(18.6)
[Cu(acac)$_2$Cl$_2$] [Ni(Etbg)$_2$]	Methanol	10,152sh(34.5)	12,820sh(42.5)			
Cu(Hbg)$_2$Cl$_2$	Methanol				18,870(43.1)	
Cu(acac)$_2$	Methanol			15,260	18,150	
Ni(Hbg)$_2$Cl$_2$	Methanol					21,645(19.4)

[a]Sh = shoulder [b]Figures in parentheses indicate molar absorbance (cm^{-1} mol^{-1}).

TABLE III

Selected infrared spectral data for some of the complexes.

$[Cu(acac)_2Cl]_2$ $[Cu(Hbg)_2]$	$[Cu(acac)_2Br]_2$ $[Cu(Hbg)_2]$	$[Cu(acac)_2Cl]_2$ $[Ni(Hbg)_2]$	$[Cu(acac)_2Cl_2]$ $[Ni(Mbg)_2]$	$[Cu(acac)_2]$	Assignments
3460s, 3360vs, 3255w, 3160s,	3450s, 3340s, 3160s	3460w, 3350m, 3150ms	3350s, 3250w, 3145w		νN-H
3060w, 2920w	3040w, 2920w	3040w, 2910w	3020w, 2920w	3072w, 2987w, 2969w, 2920w	ν_{CH}, ν_{CH_3}
1660s,	1660ms,	1660s,	1650s, 1640sh,	–	ν_{N-C-N}
1620w	1620w	1615w	1630sh	–	δ_{NH_2}
1575vs,	1575s	1570w	1560ms	1577ms	ν_{C-C-O}
1530s	1530s	1530s	1525s	–	ν_{N-C-N}
1505ms	1505w	1505m	1505m	1529m	ν_{C-C-O}
1430sh	1430sh	1430sh	1420sh	1461sh	$\delta_{(C-H)} + \nu_{C-O}$
1390vs	1390s	1390vs	1390s	1413s	$\delta_{d(CH_3)}$
1270vs	1270s	1270s	1260vs	1274vs	$\nu_{C-CH_3} + \nu_{C-C}$
1020vs	1015s	1020vs	1010ms, 990w	1019ms	$\nu_{(CH_3)}$
930vs	930vs	930vs	920(s)	936ms	$\nu_{C-C} + \nu_{C-O}$
840vs, 810s	820bw	835ms, 815ms,	830w; 800ms		$-NH_2$ wagging
780s	770ms	780w	780w		NH-bending
680s	680s	680m	680w	684	ν_{C-CH_3} + M-O + ring def.
650ms	650ms	640ms	640mb	653	π
605ms	605w	610ms	610m	612	ring def. + ν_{M-O}
520ms	520ms	540w, 520s	540w, 495s		ν_{M-N}
435ms	435ms	430ms	420ms	451	ν_{M-O}
290w	290w	290w	290w	290	
240w		245w	240mb		ν_{M-Cl}

TABLE IV
Thermal analytical data for selected complexes.

Compound	Temperature range (°)	Nature of decomposition	Weight loss[a]	Volatile products
$[Cu(Hbg)_2][Cu(acac)_2Cl]_2$	270–310	Endothermic + Exothermic	47.7% (48.1%)	4acacH + $2NH_3$
$[Cu(Hbg)_2][Cu(acac)_2Br]\cdot 2H_2O$	70–110	Endothermic	3.2% (3.6%)	$2H_2O$
	260–300	Endothermic + Exothermic	41.6% (43.6%)	4acacH + $2NH_3$
$[Ni(Hbg)_2][Cu(acac)_2Cl]_2$	240–300	Endothermic + Exothermic	46.4% (48.4%)	4acacH + $2NH_3$
$[Ni(Mebg)_2][Cu(acac)_2Cl_2]\cdot H_2O$	70–110	Endothermic	2.4% (2.8%)	H_2O
	240–300	Endothermic + Exothermic	38.2% (39.2%)	4acacH + $2CH_3NH_2$

[a] Figures in parentheses indicate calculated weight losses.

of the halogen atoms indicating halogen coordination. The band positions of the solid state and the solution spectra are slightly different and this may well be accounted for by weak methanol coordination. The spectral pattern accords well with the presence of five-coordinate square-pyramidal copper(II) atoms.[3,4,6] The six-coordinate $[Cu(acac)_2Cl_2]^{2-}$ species exhibits three absorption bands both in the solid state and in solution. All these bands are slightly shifted to lower frequency compared to those of the $[Cu(acac)_2X]^-$ species. The reflectance spectra of $[Ni(Rbg)_2][Cu(acac)_2Cl_2]$ ($R = CH_3$, C_2H_5) are not markedly different from those in solution, thus implying similar structures in both states. The bands at 18,870 and 21,739 cm^{-1} in the spectra of $[Cu(Hbg)_2][Cu(acac)_2X]_2$ and $[Ni(Hbg)_2][Cu(acac)_2X]_2$ respectively are attributable to the corresponding metal biguanide cations only.

The vibrational spectral data of the complexes, together with those of related complexes, are listed in Table III. Band assignments have been made according to the literature.[17-19] The band at 1529 cm^{-1} due to $\nu C\overset{-}{-}C\overset{-}{-}\bar{O}$ of $[Cu(acac)_2]$ is considerably shifted to lower frequencies in the present complexes. Similarly the band due to $-NH_2$ wagging in metal biguanide complexes is shifted to higher frequencies and undergoes splitting (from 712 cm^{-1} to 810 cm^{-1}). This may be attributed to hydrogen bonding between the $-NH_2$ group and the oxygen atom of the acetylacetone (N-H –O = 3.03-3.26Å). The peaks appearing at 240 cm^{-1} in the chloro-complexes are assigned to νM-Cl.[18] The positions of νM-X (X = Br, I) were not located.

Thermal analysis results are shown in Table IV. Lattice water molecules are lost in temperature range 70-110°. Sharp decreases in weight corresponding to loss of 4(acacH) and $2(NH_3/CH_3NH_2)$ mol per mol of the compound were observed for the complexes. This step is a combination of both endo- and exothermic processes and occurs in the temperature range 240 to 300°. White crystalline sublimates were obtained over this

TABLE V
Atomic coordinates for $[Cu(Hbg)_2][Cu(acac)_2Cl]_2$.

Atom	*x/a*	*y/b*	*z/c*
Cu1	0.5	0.5	0.5
Cu2	0.44537(3)	0.36709(2)	0.02082(2)
Cl	0.40292(6)	0.23595(5)	0.12107(5)
N1	0.4524(2)	0.4004(2)	0.4426(1)
C2	0.4363(2)	0.3833(2)	0.3577(2)
N3	0.4523(2)	0.4423(2)	0.2899(1)
C4	0.4850(2)	0.5206(2)	0.3007(2)
N5	0.5044(2)	0.5509(2)	0.3797(1)
N6	0.4027(2)	0.3120(2)	0.3270(2)
N7	0.4931(3)	0.5631(2)	0.2214(2)
O8	0.5390(2)	0.4032(2)	0.0995(1)
C9	0.6188(2)	0.3781(2)	0.0943(2)
C10	0.6518(2)	0.3274(2)	0.0256(2)
C11	0.6038(2)	0.2964(2)	−0.0488(2)
O12	0.5227(1)	0.3098(1)	−0.0624(1)
C13	0.6770(3)	0.4068(3)	0.1705(2)
C14	0.6481(3)	0.2433(3)	−0.1202(2)
O15	0.3733(2)	0.4454(1)	0.0883(1)
C16	0.2954(2)	0.4655(2)	0.0666(2)
C17	0.2497(3)	0.4361(2)	−0.0090(2)
C18	0.2817(2)	0.3798(2)	−0.0739(2)
O19	0.3578(2)	0.3485(1)	−0.0725(1)
C20	0.2520(3)	0.5269(3)	0.1303(3)
C21	0.2247(3)	0.3545(3)	−0.1535(3)

temperature range. These are suggested to be the condensation product of acetylacetone and ammonia or the corresponding alkylamines. No sublimation or decomposition of the compounds below 240° was observed although such observations have been reported for $[\mathrm{Cu(acac)_2}]$ at 70° by earlier workers.[11] The residues left were found to be the corresponding metal oxides in all cases.

The structure of the compound prepared from $[\mathrm{Cu(acac)_2}]$ and $[\mathrm{Cu(Hbg)_2Cl_2}]$ consists of discrete $[\mathrm{Cu(acac)_2Cl}]^-$ anions and $[\mathrm{Cu(Hbg)_2}]^{2+}$ cations. The ions are linked by weak hydrogen bonds forming sheets perpendicular to the *a* axis (Figure 1). There are no shorter distances between these sheets, which is consistent with a facile cleavage of the crystals perpendicular to this axis.

TABLE VI

Distances (Å) and Angles (°) in the structure of $[\mathrm{Cu(Hbg)_2}][\mathrm{Cu(acac)_2Cl}]_2$[a].

Cation					
Cu1-N1	1.939(3)	N1-Cu-N5	88.2(1)		
Cu1-N5	1.933(2)	Cu1-N1-C2	131.1(2)	Cu1-N5-C4	130.3(2)
C2-N1	1.290(3)	N1-C2-N3	120.4(3)	N3-C4-N5	122.5(2)
C2-N3	1.387(3)	N1-C2-N6	125.3(3)	N5-C4-N7	123.9(3)
C2-N6	1.327(4)	N3-C2-N6	114.3(2)	N3-C4-N7	113.6(2)
C4-N3	1.358(4)	C2-N3-C4	127.5(2)		
C4-N5	1.282(3)				
C4-N7	1.346(4)				
Anion					
Cu2-Cl	2.635(1)	Cl-Cu2-O8	95.2(1)	O15-Cu2-O19	93.8(1)
Cu2-O8	1.918(2)	Cl-Cu2-O12	96.9(1)	O8-Cu2-O15	85.6(1)
Cu2-O12	1.922(2)	Cl-Cu2-O15	95.4(1)	O8-Cu2-O19	169.1(1)
Cu2-O15	1.933(2)	Cl-Cu2-O19	95.7(1)	O12-Cu2-O19	84.6(1)
Cu2-O19	1.926(2)	O8-Cu2-O12	93.7(1)	O12-Cu2-O15	167.7(1)
C9-O8	1.281(4)	Cu2-O8-C9	125.1(2)	Cu2-O12-C11	125.3(2)
C9-C10	1.382(5)	C10-C9-O8	124.8(3)	C10-C11-O12	124.7(3)
C9-C13	1.493(5)	C13-C9-O8	115.0(3)	C14-C11-O12	115.1(3)
C11-O12	1.267(4)	C10-C9-C13	120.2(3)	C10-C11-C14	120.2(3)
C11-C10	1.398(4)	C9-C10-C11	125.4(3)		
C11-C14	1.502(5)				
C16-O15	1.267(4)	Cu2-O15-C16	124.6(2)	Cu2-O19-C18	125.9(2)
C16-C17	1.386(5)	C17-C16-O15	125.6(3)	C17-C18-O19	124.5(3)
C16-C20	1.503(5)	C20-C16-O15	115.0(3)	C21-C18-O19	115.8(3)
C18-O19	1.262(4)	C17-C16-C20	119.4(3)	C17-C18-C21	119.7(3)
C18-C17	1.393(5)	C16-C17-C18	125.7(4)		
C18-C21	1.503(5)				
Hydrogen bonds					
N3-O15	3.173(6)	N3-H3-O15	162(3)		
N3-H3	0.70(5)				
O15-H3	2.50(11)				
N6-O19'	3.032(6)	N6-H61-O19'	167(3)		
N6-H61	0.96(4)				
O19'-H61	2.09(10)				
N6-Cl	3.236(4)	N6-H62-Cl	168(3)		
N6-H62	0.70(6)				
Cl-H62	2.56(8)				
N5-Cl"	3.277(4)	N5-H5-Cl"	178(3)		
N5-H5	0.75(5)				
Cl"-H5	2.54(8)				

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[a] Relative to the atoms at *x, y, z*, primed and double primed atoms are at *x*, ½ − *y*, ½ + *z* and 1 − *x*, ½ + *y*, ½ − *z*, respectively.

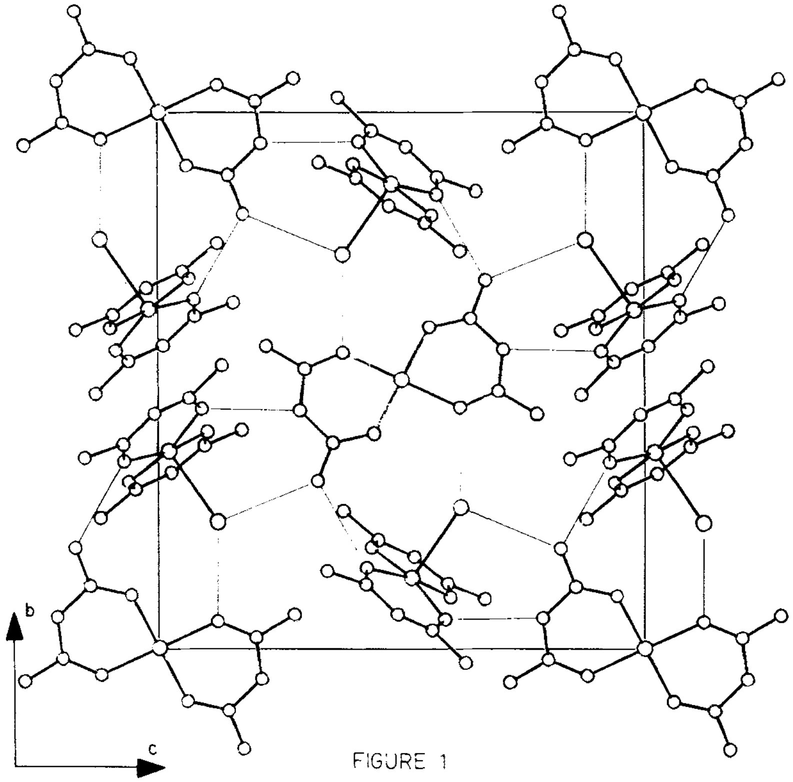

FIGURE 1 Projection of a segment of the structure along the a-axis ($0.225 \leqslant x \leqslant 0.775$). Only the molecules of one sheet are shown. Hydrogen bonds are indicated by light lines.

The copper atom in the cation (Cul) has a square-planar coordination of four nitrogen atoms of the two biguanide ligands (Figure 2). All distances around Cul to non-hydrogen atoms of neighbouring ions are greater than 3.5Å. The non-hydrogen atoms of the cation

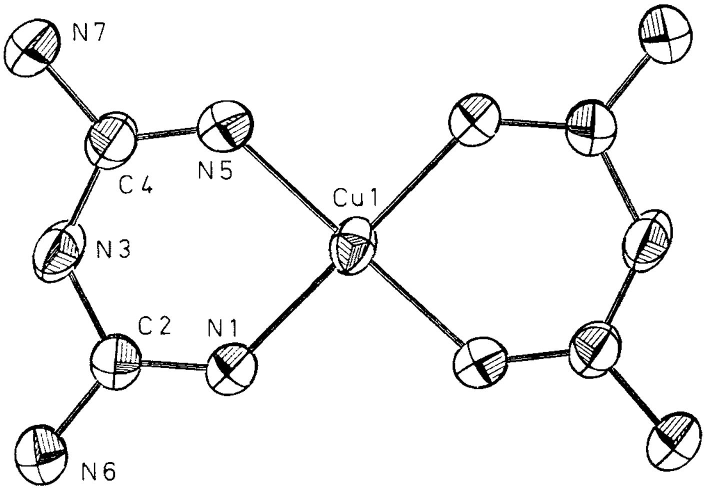

FIGURE 2 ORTEP plot of the $[Cu(Hbg)_2]^{2+}$ cation (thermal ellipsoids with 50% probability).

TABLE VII

Least-squares planes. Deviations (Å) of atoms from the plane are given in brackets.

Plane: Cu1, N1-N7

$14.1274\,x + 5.6444\,y + 1.6939\,z = 0.0$

Cu1(0.0);	N1(–0.013);	C2(0.000);	N3(0.008);
C4(0.009);	N5(–0.022);	N6(–0.020);	N7(0.018).

Plane: Plane: O8, O12, O15, O19

$3.6564\,x + 12.8422\,y - 7.9364\,z = 6.3716$

O8(–0.013);	O12(0.013);	O15(0.012);	O19(–0.013);
Cu2(–0.194);	Cl(–2.829).		

lie within 0.02Å of the plane of best fit defined by the two chelate rings (Table VII). Distances and angles are in good agreement with those found in $[Cu(Hbg)_2]CO_3 \cdot H_2O$[20] and $[Cu(C_3H_8N_4)_2](ClO_4)_2$.

In the anion, Cu2 has a square-pyramidal coordination with the four oxygen atoms of the two acetylacetonates forming the base and the chlorine atom the apex (Figure 3). Cu2 lies 0.2Å above the plane of best fit defined by the four oxygen atoms and is directed toward the chlorine atom (Table VII). Apart from this distortion the structure of the anion is very similar to other *bis*(β-dicarbonyl) copper(II) complexes.[22] The Cu-Cl distance is much longer than those in $CuCl_2$ or related compounds[23] (about 2.29Å). This elongation of the apical bond is found in other square-pyramidal copper(II) complexes.[24]

Some of the shorter distances between the NH or NH_2 groups of the cation and the chlorine or oxygen atoms of the anion may be described as hydrogen bonds. While the N – Cl distances differ hardly from the mean value of 3.23Å found for N-H – Cl bonds, the N – O distances (3.03-3.26Å) are much greater than the mean N-H – O distance of 2.89Å.[25] Only those N – O contacts, where the N-H bond is directed towards the oxy-

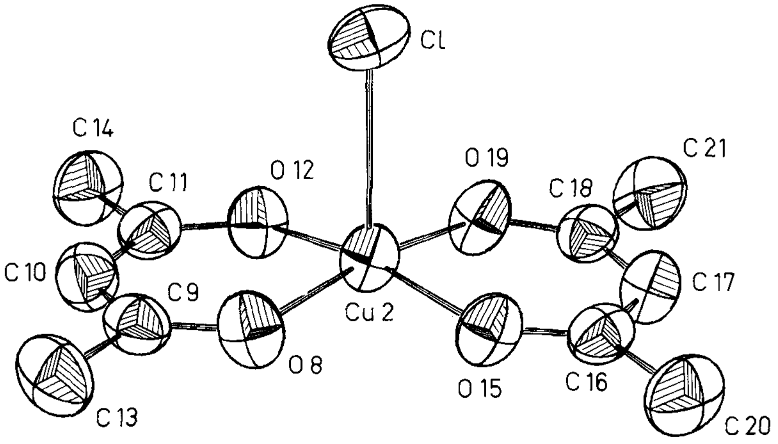

FIGURE 3 ORTEP plot of the $[Cu(acac)_2Cl]^-$ anion (thermal ellipsoids with 50% probability).

gen atom are considered to be weak hydrogen bonds (Table VI). Figure 1 shows the hydrogen bonding within one sheet. Distances between atoms of neighbouring sheets are too long for hydrogen bonding.

On the basis of the properties detailed above, the structures of the analogous pentacoordinate copper(II) complexes of the form $[M(Hbg)_2][Cu(acac)_2X]_2$ (M = Cu; X = Br, I; M = Ni; X = Cl, Br, I) are suggested to be similar to that of $[Cu(Hbg)_2][Cu(acac)_2Cl]_2$. The structures of $[Ni(Rbg)_2][Cu(acac)_2Cl_2]$ ($R = CH_3, C_2H_5$) probably contain the discrete square-planar $[Ni(Rbg)_2]^{2+}$ ion and the tetragonally distorted *trans*-octahedral $[Cu(acac)_2Cl_2]^{2-}$ anion.

The presence of π-electronic delocalization in the chelates $[M(Hbg)_2]^{2+}$ (M = Cu, Ni) and $[Cu(acac)_2]$ have been proved experimentally.[26,27,12] In the present case, coordination of the halide ions occur with copper in the neutral $[Cu(acac)_2]$ molecule in preference to the metal ions in the cation $[ML_2]^{2+}$ (M = Cu, L = Hbg; M = Ni, L = Hbg, Rbg). This suggests a stronger involvement of the metal pz or dz^2 orbital in the chelate ring current in metal biguanides than is the case in metal acetylacetonates.

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