Porphyrin-like Macrocyclic Complexes: Molecular and Electronic Structure of (5,14-Dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecinato)copper(II)†

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Reaction of equimolar amounts of Li_2(tmtaa) (H_2tmtaa = 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine) with $Cu(O_2CMe)_2$ afforded the [Cu(tmtaa)] complex in >98% yield. Single-crystal X-ray diffraction studies have shown that the structure of [Cu(tmtaa)] is monoclinic, space group $P2_1/c$, with a = 14.332(1), b = 16.443(2), c = 16.313(2) Å, β = 100.03(1)° and Z = 8. The complex exhibits the usual saddle-shaped geometry reported for this ligand. The average Cu–N distance is 1.929 Å and the displacement of the copper centre out of the N_4 plane is only 0.070 Å. The electronic structure of the complex has been established by combined ultraviolet photoelectron spectroscopy and density functional calculations. The relevant features of the metal–ligand interaction are typical of porphyrin-like copper tetraazamacrocycles.

The H_2tmtaa ligand (H_2tmtaa = 'tetramethyltetraazaannulene' = 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*]-[1,4,8,11]tetraazacyclotetradecine} shares many common characteristics with other tetraazamacrocyles, such as porphyrins and phthalocyanines. It features, however, important differences that include its modest core size (1.902 Å) and the unusual saddle-shaped geometry resulting from steric interactions within the macrocyclic ligand.[1] These distinctive features confer unusual reactivity patterns and co-ordination geometries for both transition-metal and main-group complexes. Thus, while similarities to porphyrins make the tmtaa macrocycle of bioinorganic interest, its peculiarities make it of fundamental interest in its own right.[1–5] Transition-metal tmtaa complexes have been quite extensively studied,[1] and, very recently, also main-group element co-ordination compounds of this ligand have been synthesized and structurally characterized.[2d]

Among the first-row late-transition metal complexes of tmtaa, [Cu(tmtaa)] has received considerable interest owing to its excellent ability to mimic the active site of superoxide dismutase[3a,c] and its versatility to act as a molecular building block for electroactive polymeric films.[3a,c,e] In spite of such attraction, the molecular structure of this complex still remains unknown, most likely because of the difficulties in growing crystals suitable for X-ray studies. Similarly no theoretical studies are available on [Cu(tmtaa)] and its most relevant spectroscopic features are simply interpreted by analogy with porphyrin analogues.

Knowledge of the molecular and electronic structure would be needed, however, in order to provide a more reliable interpretation of the remarkable chemical and physical properties of [Cu(tmtaa)], and to open new perspectives in the study of the condensed-phase behaviour of this compound.

To this purpose we have undertaken a structural, spectroscopic and theoretical investigation of [Cu(tmtaa)] which has been prepared using a new efficient synthetic route and its molecular structure has been determined by single-crystal X-ray diffractometry. The electronic structure has been studied by ultraviolet photoelectron spectroscopy (UPS) and by density functional calculations. Since this is, to our knowledge, the first detailed investigation of the electronic structure of a complex of the tmtaa ligand, similarities and differences with unmethylated congeners and other porphyrin-like metal complexes are addressed and discussed, whenever possible.

Experimental

Materials.—All chemicals were used as purchased from Aldrich. Microanalyses were performed by the Analytische Laboratorien of Professor H. Malissa and G. Reuter Gmbh, Gummersbach, Germany and UV/VIS and ^1H NMR spectra were carried out using a 2300 Cary and a 300 MHz Bruker spectrometer respectively.

Synthesis of [Cu(tmtaa)].—The intermediate Li_2(tmtaa)[2e,5] was prepared as described in the literature and was characterized by UV/VIS and ^1H NMR spectroscopies. The complex [Cu(tmtaa)] was prepared as follows. To a solution of $Cu(O_2CMe)_2$ (1.8 g, 9.6 mmol) in ethanol (50 cm^3) was added a suspension of Li_2(tmtaa) (3.4 g, 9.5 mmol) in tetrahydrofuran (thf) (20 cm^3) under stirring, at −10 °C. After warming to ≈20 °C the volume of the solution was reduced to ≈10 cm^3 and the resulting dark green precipitate was collected by filtration and washed with ethanol. Recrystallization from CH_2Cl_2–pentane afforded 3.7 g of greenish brown pleocroic platelets of [Cu(tmtaa)] (>98%, based on Cu).

UV/VIS, CH_2Cl_2 [λ_{max}/nm (log ε)]: 248 (4.30), 292 (4.11), 320sh (3.96), 384 (4.37), 416sh (4.08), 624 (3.00), 644 (3.10) and 660 (3.00) (Found: C, 65.10; H, 5.65; N, 13.70. $C_{22}H_{22}CuN_4$ requires C, 65.10; H, 5.40; N, 13.80%).

Crystallography.—A crystal of dimensions 0.30 × 0.20 × 0.07 mm was mounted with epoxy resin on the tip of a glass fibre. The space group ($P2_1/c$) was determined using the Weissenberg photographic technique. Diffraction measurements were carried out on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu-Kα radiation. A summary of the data collection and refinement results are reported in Table 1. Cell parameters were obtained from 20 reflections with θ angles in the range 25.67–29.08°. An ω–2θ

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: eV ≈ 1.60 × 10^{-19} J.

Table 1 Data collection and structure refinement parameters for [Cu(tmtaa)]

Formula	$C_{22}H_{22}CuN_4$
M	405.98
Crystal system	Monoclinic
Space group	$P2_1/c$
λ(Cu-Kα)/Å	1.541 78
a/Å	14.332(1)
b/Å	16.443(2)
c/Å	16.313(1)
β/°	100.03(1)
U/Å^3	3785.5(5)
Z	8
D_c/g cm^{-3}	1.420
μ/cm^{-1}	16.8
T/K	296
F(000)	1688
h,k,l Range	−17 to 17, 0–20, 0–19
Unique reflections	7276
Observed reflections [$I > 3\sigma(I)$]	4986
Goodness of fit	1.86
No. of parameters	487
Maximum Δ/σ	0.02
Maximum, minimum Δρ/e Å^{-3}	0.45, −0.22
R^a	0.051
R'^b	0.063

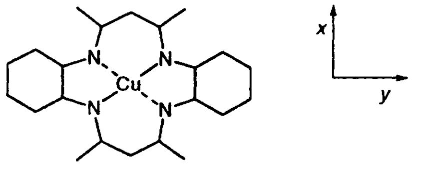
[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $R' = [\Sigma(w(||F_o| - |F_c||)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

scan mode and scan range were chosen from the examination of the reflection profiles. The intensities of two reflections were measured every 1 h during data collection. The crystal orientation was checked after every 200 intensity measurements using two control reflections. A total of 7276 unique reflections were collected in the θ range 1–70°. Data reduction included corrections for background, Lorentz and polarization effects. No absorption correction was applied. A total of 4986 reflections with $I > 3\sigma(I)$ were used in the refinement. The structure was solved by Patterson and Fourier methods and anisotropically refined by a full-matrix least-squares procedure. The function minimized was $\Sigma w = (|F_o| - |F_c|)^2$, with $w = 4F_c^2/[\sigma(F_o)^2 + (pF_c^2)]^2$ where p is an instability factor.[6] Hydrogen atoms, included in the structural model in stereochemically calculated positions, were not refined. Atomic scattering factors and anomalous dispersion corrections were taken from ref. 7. All the computations were performed by the MOLEN package[6] running on a DEC VAX 6510.

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

Photoelectron Spectroscopy.—The He I photoelectron spectrum was recorded on an ES 320 I spectrometer using a heated inlet probe system. The spectrum was measured at 320 °C and there was no evidence of thermal decomposition of the sample. The mean energy resolution was *ca.* 55 meV. The PE spectrum was calibrated with xenon. The measured ionization energies are accurate to ± 0.01 eV.

Computational and Methodological Details.—The calculations reported in this paper are based on the Amsterdam DF package[8,9] characterized by the use of a density fitting procedure to obtain accurate Coulomb and exchange potentials in each self-consistent field (SCF) cycle, by accurate and efficient numerical integration[9] of the effective one-electron Hamiltonian matrix elements, and by the possibility to freeze core orbitals.[8a] All calculations were spin unrestricted. Electron correlation was treated within the local density approximation (LDA) in the parametrization of Vosko *et al.*[10] The vertical ionization energies (i.e.s) have been computed using a ΔSCF procedure, in order to fully include electronic relaxation effects.



Scheme 1

The final energies of the ground and excited states included Becke's[11] non-local exchange correlation to the local expression of the exchange energy and Perdew's[12] non-local corrections to the local expression of correlation energy. Singlet–triplet splitting was computed according to the method of Ziegler *et al.*[13] The molecular orbitals were expanded in an uncontracted double-ζ Slater type orbital (STO) basis set for all atoms with the exception of the Cu 3d orbital for which we used a triple-ζ STO basis set. As polarization functions one 4p orbital was used for copper. The cores (Cu: 1s, 2p; C: 1s; N: 1s) have been kept frozen. Atomic coordinates were taken from the crystal structure. Atomic positions were averaged in accordance to the C_{2v} symmetry which is the closest one to that deduced for [Cu(tmtaa)] from the X-ray crystallographic analysis. We use a coordinate system where the z axis is perpendicular to the N_4 plane (Scheme 1) with Cu at $x = 0.0, y = 0.0, z = 0.07$ Å.

Results and Discussion

Synthesis.—It is known that [Cu(tmtaa)] can be prepared by template condensation,[3c] of *o*-phenylenediamine and pentane-2,4-dione in the presence of $Cu(O_2CMe)_2{\cdot}xH_2O$ or by direct reaction[3a] of this salt with H_2tmtaa. However these synthetic routes are characterized by a low yield and are rather time consuming. We have found that, according to equation (1), the

$$Li_2(\text{tmtaa}) + Cu(O_2CMe)_2 \xrightarrow[\text{thf-EtOH}]{-10\,^{\circ}\text{C}} [Cu(\text{tmtaa})] + 2Li(O_2CMe) \quad (1)$$

complex can be obtained in high yield (>98%) when a thf solution of Li_2(tmtaa) is mixed at a temperature of −10 °C with an equimolar amount of $Cu(O_2CMe)_2$ dissolved in ethanol.

The reaction is very fast and clean and is complete as soon as the dark green mixture is allowed to warm to room temperature; no detectable amounts of by-products are observed. Dark greenish brown platelet-like crystals of X-ray quality were grown within two weeks by slow evaporation of solutions of [Cu(tmtaa)] in CH_2Cl_2–pentane at room temperature. It should be noted however that any attempt to recrystallize the complex from mixtures of solvents containing aliphatic alcohols, led to the slow formation of a yellow-green flocculent precipitate, which was characterized by electronic spectroscopy as an oligomer.[3c] Repeating the above crystallization procedure under anaerobic conditions led to layered crystals which were amorphous to X-rays.

Crystal and Molecular Structure.—The crystal structure of [Cu(tmtaa)] reveals two independent molecules (denoted A and B) in the asymmetric unit. For sake of simplicity Fig. 1(*a*) shows only the ORTEP diagram of molecule A with the labelling scheme for the non-hydrogen atoms. Final fractional coordinates for molecules A and B, selected bond distances and bond angles are reported in Tables 2 and 3. In the two molecules all chemically equivalent bond parameters are essentially identical. Superimposition of the structures by least-squares minimization of the deviation of the distance between corresponding atoms, in the best relative orientation, gives a root mean square value of 0.092 Å. As shown in Fig. 1(*b*) where a side view of the molecule A is presented, the 14-membered tmtaa ring forms a saddle-like shape around the Cu atom with the benzene rings and the diiminato chelate rings tilted on opposite sides of the N_4 co-ordination plane. The interplanar angles of

Table 2 Final fractional coordinates for [Cu(tmtaa)] with estimated standard deviations (e.s.d.s) in parentheses

	Molecule A			Molecule B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Cu	0.181 78(4)	0.017 54(3)	0.091 84(4)	0.298 18(4)	0.000 18(3)	0.376 59(4)
N(1)	0.083 9(2)	0.024 7(2)	0.158 5(2)	0.368 4(2)	0.029 0(2)	0.290 4(2)
N(2)	0.143 1(2)	−0.086 7(2)	0.042 2(2)	0.224 6(2)	−0.084 3(2)	0.313 6(2)
N(3)	0.273 1(2)	0.015 7(2)	0.018 1(2)	0.232 1(3)	−0.033 2(2)	0.464 1(2)
N(4)	0.216 2(2)	0.125 4(2)	0.135 8(2)	0.381 0(2)	0.076 4(2)	0.443 3(2)
C(1)	0.001 6(3)	−0.014 1(3)	0.137 4(3)	0.381 6(3)	−0.023 1(3)	0.230 9(3)
C(2)	−0.010 4(3)	−0.077 9(3)	0.080 3(3)	0.328 9(3)	−0.094 5(3)	0.215 2(3)
C(3)	0.054 2(3)	−0.114 3(3)	0.036 6(3)	0.254 2(3)	−0.124 3(3)	0.252 5(3)
C(4)	0.214 4(3)	−0.120 5(3)	0.003 5(3)	0.143 8(3)	−0.102 7(2)	0.348 5(3)
C(5)	0.226 7(4)	−0.202 2(3)	−0.015 5(3)	0.059 8(3)	−0.136 0(3)	0.306 5(3)
C(6)	0.303 6(4)	−0.227 4(3)	−0.049 8(3)	0.019 2(4)	−0.141 2(3)	0.343 3(3)
C(7)	0.371 6(4)	−0.172 9(3)	−0.063 2(3)	0.016 1(3)	−0.111 9(3)	0.423 2(3)
C(8)	0.364 2(3)	−0.092 3(3)	−0.041 6(3)	0.066 4(4)	−0.078 3(3)	0.466 8(3)
C(9)	0.285 8(3)	−0.064 1(3)	−0.010 2(3)	0.147 6(3)	−0.073 7(2)	0.431 2(3)
C(10)	0.302 9(3)	0.083 3(3)	−0.013 9(3)	0.271 7(4)	−0.028 3(3)	0.544 8(3)
C(11)	0.294 6(3)	0.159 9(3)	0.022 7(3)	0.352 4(4)	0.018 9(3)	0.571 2(3)
C(12)	0.255 6(3)	0.180 8(2)	0.093 1(3)	0.402 9(3)	0.069 0(2)	0.526 1(3)
C(13)	0.177 1(3)	0.140 5(3)	0.207 9(3)	0.425 5(3)	0.128 0(2)	0.392 8(3)
C(14)	0.209 1(3)	0.197 2(3)	0.269 7(3)	0.466 8(3)	0.202 8(3)	0.415 8(3)
C(15)	0.167 6(4)	0.203 6(3)	0.339 5(3)	0.505 3(3)	0.250 0(3)	0.359 7(4)
C(16)	0.097 4(4)	0.149 2(4)	0.351 5(3)	0.496 3(4)	0.226 0(3)	0.278 0(3)
C(17)	0.066 9(4)	0.089 7(3)	0.293 2(3)	0.451 3(3)	0.153 2(3)	0.253 0(3)
C(18)	0.104 5(3)	0.085 3(3)	0.220 1(3)	0.418 2(3)	0.102 3(3)	0.309 0(3)
C(19)	−0.086 3(3)	0.010 9(3)	0.169 8(3)	0.460 3(4)	−0.012 7(3)	0.181 0(3)
C(20)	0.016 0(4)	−0.182 9(3)	−0.020 7(4)	0.216 0(4)	−0.206 6(3)	0.222 8(3)
C(21)	0.342 9(4)	0.084 0(3)	−0.093 2(4)	0.235 9(5)	−0.077 9(4)	0.610 3(3)
C(22)	0.255 5(3)	0.270 3(3)	0.110 6(4)	0.488 4(4)	0.110 9(3)	0.575 6(3)

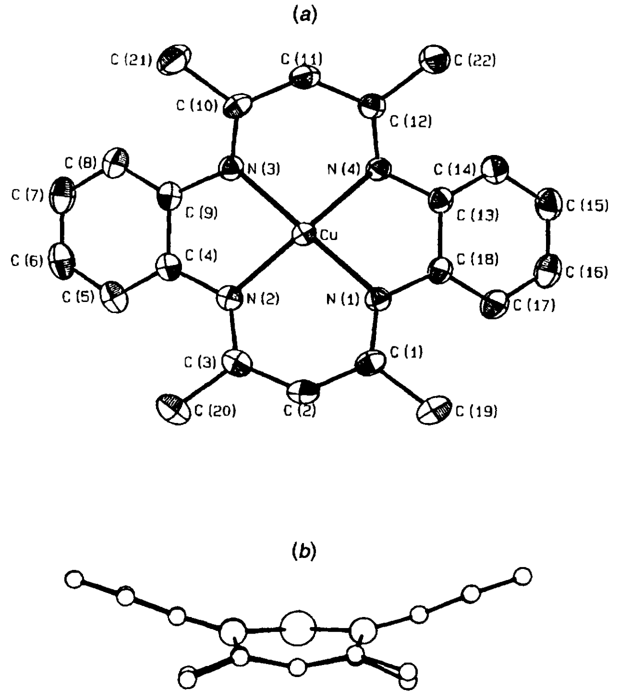


Fig. 1 (*a*) An ORTEP[14] diagram and labelling scheme for [Cu(tmtaa)] (molecule A). Thermal ellipsoids represent the 50% probability level; (*b*) side view (PLUTO[15] diagram) showing the saddle-shape conformation of [Cu(tmtaa)]

the benzodiimine/N_4 and pentane-2,4-diiminato/N_4 planes are 20.8 and 24.9° respectively in A and 23.0 and 24.8° in B. The tilting of the benzene and diiminato chelate rings is comparable to that found in the congeneric complexes with Ni^{II},[16] Fe^{II}[17] and Co^{III}.[18] The free ligand, H_2tmtaa,[16] shows larger tilting angles, 25 and 37° respectively. Our crystal structure contradicts the suggestion by Cotton and Czuchajowska[1] that [Cu(tmtaa)], considering the strong preference of copper(II) for square co-ordination, should have a stepped conform-

Table 3 Selected bond distances (Å) and angles (°) for [Cu(tmtaa)]

	Molecule	
	A	B
Cu–N(1)	1.922(4)	1.925(4)
Cu–N(2)	1.935(3)	1.929(3)
Cu–N(3)	1.925(4)	1.925(4)
Cu–N(4)	1.944(3)	1.927(3)
N(1)–C(1)	1.333(5)	1.333(6)
N(2)–C(3)	1.341(6)	1.324(6)
N(3)–C(10)	1.330(6)	1.342(5)
N(4)–C(12)	1.331(6)	1.339(5)
N(1)–C(18)	1.409(5)	1.405(5)
N(2)–C(4)	1.406(6)	1.408(6)
N(3)–C(9)	1.413(5)	1.405(5)
N(4)–C(13)	1.411(6)	1.410(6)
C(1)–C(2)	1.394(6)	1.395(6)
C(2)–C(3)	1.398(7)	1.408(7)
C(10)–C(11)	1.407(6)	1.398(7)
C(11)–C(12)	1.405(7)	1.389(7)
C(4)–C(9)	1.427(6)	1.422(6)
C(13)–C(18)	1.421(6)	1.417(6)
N(1)–Cu–N(2)	96.1(2)	95.5(1)
N(3)–Cu–N(4)	95.0(1)	95.8(1)
N(1)–Cu–N(4)	84.2(1)	84.4(1)
N(2)–Cu–N(3)	84.3(2)	84.0(1)
C(1)–C(2)–C(3)	130.3(4)	129.9(4)
C(10)–C(11)–C(12)	129.9(4)	130.2(4)
Cu–N(1)–C(1)	121.7(3)	122.1(3)
Cu–N(2)–C(3)	121.9(3)	122.8(3)
Cu–N(3)–C(10)	122.2(3)	122.1(3)
Cu–N(4)–C(12)	122.4(3)	121.6(3)
Cu–N(1)–C(18)	111.3(3)	111.3(3)
Cu–N(2)–C(4)	111.1(3)	110.5(3)
Cu–N(3)–C(9)	111.0(3)	110.7(3)
Cu–N(4)–C(13)	110.9(3)	111.0(3)

ation, as found for [Ru(tmtaa)($PPh_2Me)_2$]. Woodruff and coworkers[3a,b] however, previously assumed a saddle-shape conformation of the ligand in [Cu(tmtaa)] in order to interpret the non-structural, electronic effects of different metal ions upon the ligand vibrational frequencies in resonance Raman spectra of the [M(tmtaa)] (M = Fe, Co or Cu) series.

In the complex each copper atom is co-ordinated through the four nitrogens of the macrocyclic ligand with an average Cu–N bond distance of 1.932 Å for A and 1.927 Å for B. This bond length is comparable to that observed in copper phthalocyanine[19] (1.93 Å) but is significantly shorter than that observed in (5,10,15,20-tetraphenylporphyrinato)copper(II) (1.98 Å).[20] The displacement out of the N_4 plane of the copper centre is only 0.069 Å for A and 0.071 Å for B, in line with the general trend[1] that the extent of metal pyramidalization in tmtaa complexes decreases on going from early to late transition metals. As it is inferred from the bond lengths of Table 2, the delocalization is limited primarily to the pentane-2,4-diiminato ring (the average C–N and C–C bond lengths are 1.33 and 1.39 Å respectively) and to the benzenoid rings. It is broken by the C–N bonds of the *o*-phenylenediamine residues, which have predominantly single-bond character (the average C–N bond length is 1.41 Å). These patterns of delocalization of the macrocycle are virtually identical to those found in other tmtaa complexes[16–18] and in the congeneric unmethylated dibenzo[*b,i*][1,4,8,11]tetraaza[14]annulene (taa) complexes.[21]

Electronic Structure.—Table 4 lists the one-electron energies of the highest occupied and the lowest unoccupied molecular orbitals obtained by spin-unrestricted density functional calculations. According to the occupation of the one-electron levels the ground state of [Cu(tmtaa)] is $^2A_2$. The spin unrestricted orbital energies are representative of a general pattern in metal–organic compounds. The delocalized ligand orbitals show little exchange effect and the splitting between spin-up and spin-down levels is very small. By contrast, the molecular orbitals that are largely localized on the metal, such as the $22a_1$, $18b_1$, $16b_2$, $20a_1$, have sizable splitting. The orbital splitting is also accompanied by significant changes of the amount of metal character, indicating that the lower lying spin-up metal orbitals mix more favourably with tmtaa ligand orbitals. In agreement with ESR experiments[3c] the unpaired electron is found to reside in the $15a_2$ α orbital which is principally an antibonding Cu–N state composed of $3d_{xy}$ (33%) and nitrogen lone pairs. The bonding counterpart of the $15a_2$ (not reported in Table 4) is much lower in energy because of the strong Cu–N σ interaction. The $d_{x^2-y^2}$ orbital which is suitable for π in-plane interaction with the four nitrogens mixes very little with N in-plane p_π orbitals, due to small overlap and energy mismatch between these orbitals. It is found indeed almost purely in the $20a_1$ molecular orbital. The d_{z^2} orbital has pure metal character and occurs in the $22a_1$ and $21a_1$ molecular orbitals where it mixes with the 4s and $d_{x^2-y^2}$ orbitals respectively. The out-of-plane d_π (d_{xz}, d_{yz}) orbitals interact weakly with the p_z nitrogen orbitals, as indicated by the small spacing of the resulting π Cu–tmtaa bonding/antibonding pairs $16b_2/18b_2$ and $18b_1/19b_1$. These metal–ligand interaction features do not differ significantly from those found in other copper tetraazamacrocycles[22] including the unmethylated analogue [Cu(taa)].[22b] It is noteworthy that the relevant aspects of the electronic structure of [Cu(taa)] and [Cu(tmtaa)] are very similar, in spite of the quite different conformation of the two macrocyclic ligands. The reason resides in that deformation from planarity on going from taa to tmtaa has negligible electronic effects on the nature and energy of the macrocycle orbitals involved in the interactions with the metal.

When comparing the electronic structure of copper[22b] and nickel[22,23] tetraazamacrocycles the outstanding differences are: (*i*) a less effective mixing between metal and ligand orbitals in the copper compounds and, (*ii*) a downward energy shift of the metal states when going from nickel to copper.

Table 4 Eigenvalues and Cu percentage for the lowest unoccupied and the highest occupied molecular orbitals of [Cu(tmtaa)]

Orbital	Spin *	Energy/eV	Percentage Cu
Unoccupied orbitals			
$20b_1$	–	−2.58	1.9 (d_{xz})
$16a_2$	–	−2.59	11.8 (d_{xy})
$20b_1$	+	−2.63	1.7 (d_{xz})
$16a_2$	+	−2.75	5.9 (d_{xy})
$15a_2$	–	−3.97	32.5 (d_{xy})
Occupied orbitals			
$15a_2$	+	−4.47	32.6 (d_{xy})
$23a_1$	–	−5.00	3.0 ($d_{x^2-y^2}$), 2.7 ($4p_z$)
$23a_1$	+	−5.06	2.4 ($d_{x^2-y^2}$), 2.6 ($4p_z$)
$18b_2$	–	−5.49	8.9 (d_{yz})
$18b_2$	+	−5.57	6.6 (d_{yz})
$19b_1$	–	−5.96	4.3 (d_{xz}), 1.4 ($4p_x$)
$19b_1$	+	−6.05	3.0 (d_{xz}), 1.1 ($4p_x$)
$14a_2$	–	−6.70	1.9 (d_{xy})
$14a_2$	+	−6.75	1.8 (d_{xy})
$22a_1$	–	−6.76	70.0 (d_{z^2}), 9.6 (4s)
$22a_1$	+	−7.00	60.0 (d_{z^2}), 9.3 (4s)
$17b_2$	–	−7.02	1.9 (d_{yz}), 1.3 ($4p_y$)
$17b_2$	+	−7.10	1.1 ($4p_y$)
$18b_1$	–	−7.16	75.2 (d_{xz})
$16b_2$	–	−7.24	77.0 (d_{yz})
$18b_1$	+	−7.40	71.0 (d_{xz})
$16b_2$	+	−7.50	77.5 (d_{yz})
$21a_1$	–	−7.54	11.1 (d_{z^2}), 30.3 ($d_{x^2-y^2}$)
$21a_1$	+	−7.66	21.6 (d_{z^2}), 6.8 ($d_{x^2-y^2}$)
$20a_1$	–	−7.76	2.1 (d_{z^2}), 58.0 ($d_{x^2-y^2}$)
$20a_1$	+	−8.00	77.8 ($d_{x^2-y^2}$)

* +, α spin; –, β spin.

Photoelectron Spectra.—The relevant features of the electronic structure of [Cu(tmtaa)], outlined above, are reflected in the ultraviolet photoelectron spectrum displayed in Fig. 2. This spectrum, although showing strong analogies with that of the unmethylated congener [Ni(taa)],[23] is much better resolved. The spectrum can be divided into three regions: the 6–8 eV region contains three distinct bands; the region 8–9 eV appears to contain two bands one of which manifests itself as a shoulder at 8.32 eV while the third region (> 9 eV) contains many overlapping bands.

The ionization energies (i.e.s) appearing as separate spectral bands and the maxima of overlapping bands are listed in Table 5, together with the calculated values. According to our calculations, the first band at 6.35 eV can be assigned to the $^1A_1$ state due to $15a_2$ ionization and to $^{1,3}A_2$ states due to $(23a_1)^{-1}$. The $^{1,3}B_1$ states due to $18b_2$ ionization correspond to the second band. The $(19b_1)^{-1}$ leading to $^{1,3}B_2$ states is unequivocally responsible for the band centred at 7.54 eV. The band centred at 8.73 eV and its shoulder arise from three ionizations, $(14a_2)^{-1}$, $(17b_2)^{-1}$, $(22a_1)^{-1}$, as inferred from the energies of the corresponding singlet and triplet states. This assignment is in good agreement with the areas of these bands which are in the ratio 1.5 : 1.5 : 1 : 3. The [Cu(tmtaa)] ionizations that correspond to metallic states consist of $(22a_1)^{-1}$, $(18b_1)^{-1}$, $(16b_2)^{-1}$ and $(20a_1)^{-1}$. The first belongs to the band centred at 8.73 eV, while the last three, considering the two spin components, span the region 9.16–9.80 eV that correspond to the third region of the ultraviolet photoelectron spectrum. When comparing the energies of d-like states computed for [Cu(tmtaa)] and for [Ni(taa)],[23] the increase of the binding energy for 3d-like orbitals on going from nickel to copper is evident.

Conclusion

The copper(II) complex of 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine has been pre-

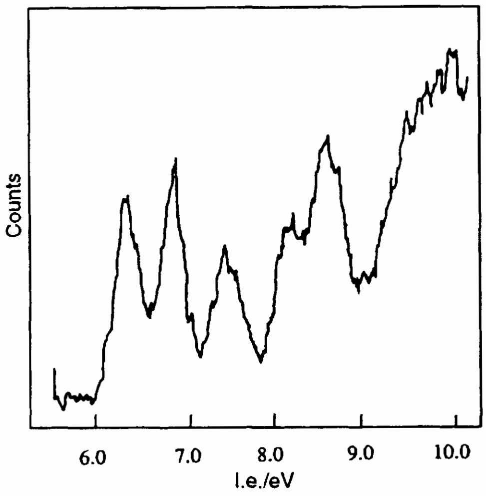


Fig. 2 The He I photoelectron spectrum of [Cu(tmtaa)]

Table 5 Experimental and calculated ionization energies (eV) for [Cu(tmtaa)]

MO	State	Calc.	Exptl.
$15a_2$	$^1A_1$	6.36	
			6.35
$23a_1$	$^1A_2$	6.59	
	$^3A_2$	6.48	
			6.91
$18b_2$	$^1B_1$	7.12	
	$^3B_1$	6.99	
			7.54
$19b_1$	$^1B_2$	7.59	
	$^3B_2$	7.43	
			8.32
$14a_2$	$^1A_1$	8.25	
	$^3A_1$	8.14	
$17b_2$	$^1B_1$	8.53	
	$^3B_1$	8.44	
			8.73
$22a_1$	$^1A_2$	8.80	
	$^3A_2$	8.64	
$18b_1$	$^1B_2$	9.38	
	$^3B_2$	9.16	
			9.66
$16b_2$	$^1B_1$	9.80	
	$^3B_1$	9.37	
$21a_1$	$^1A_2$	9.77	
	$^3A_2$	9.49	
$20a_1$	$^1A_2$	9.67	
	$^3A_2$	9.75	

pared by a new and efficient synthetic route and its molecular structure has been determined by single-crystal X-ray diffraction. It is found that the ligand co-ordinates to the metal through four nitrogen atoms and adopts the usual saddle-like conformation with the metal only slightly displaced out of the N_4 plane. A combined theoretical and UV photoelectron spectroscopic investigation of the electronic structure of this complex has been presented. Our results indicate that the relevant features of the metal–macrocycle interaction are typical of other copper–tetraazamacrocycle complexes. In particular, the electronic structure of [Cu(tmtaa)] strongly resembles that of the unmethylated congener [Cu(taa)], in spite of the quite different conformation of the two macrocyclic ligands. This has been explained in terms of negligible electronic effects of the deformation from planarity on going from taa to tmtaa on the nature and energy of the macrocycle orbitals involved in the interactions with the metal.

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