DALTON
FULL PAPER

1,3-Bis(*N*,*N*,*N*′,*N*′-tetramethylguanidino)propane: synthesis, characterization and bonding properties of the first bidentate, peralkylated guanidine ligand †

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The first bidentate, peralkylated guanidine based ligand has been synthesized and its complexation chemistry examined by the preparation of three representative coordination compounds. The novel chelate ligand 1,3-bis(*N*,*N*,*N*′,*N*′-tetramethylguanidino)propane (btmgp, **1**) has been synthesized by the reaction of *N*,*N*,*N*′,*N*′-tetramethylguanidine (TMG) with 1,3-dibromopropane and subsequent deprotonation of the resulting guanidinium salt with sodium ethoxide. The bifunctional N-donor compound was treated with copper(I) iodide, copper(II) chloride and iron(II) iodide in a 1 : 1 molar ratio to yield the corresponding electroneutral complexes [CuI(btmgp)] **2**, [$CuCl_2$(btmgp)] **3** and [FeI_2(btmgp)] **4**. The structures of the dihydrochloride of **1** (**1b**) and of the complexes **2**–**4** have been determined by X-ray crystallography. A comparison of the molecular structures (**2**–**4**) shows that, in each case, btmgp acts as a bidentate ligand which is able to stabilize not only trigonal-planar (**2**), but also (distorted) square-planar (**3**) and tetrahedral coordination environments (**4**).

Introduction

In recent years, an increasing effort has been focused on the preparation of mono- or di-nuclear mixed ligand transition metal complexes containing neutral, chelating nitrogen ligands. Early and late transition metal complexes of this type have extensively been used as catalysts for a wide variety of reactions, including olefin polymerization[1] and oxygen activation.[2] In this context, diverse chelating Schiff-base type ligands, amines and pyridine derivatives[1–3] have successfully been applied in the preparation of these homogeneous catalysts. However, in processes where reactive species are involved such as the formation of coordinatively unsaturated cationic alkyl complexes $[L_nMR]^+$ in olefin polymerization, neutral chelating, sterically demanding ligands with an increased basicity are often desirable. Similar ligands are also required to stabilize neutral, mixed ligand metal complexes in different oxidation states.

Guanidine, the imide of urea, is one of the strongest organic bases,[4] since the resulting positive charge upon protonation can be delocalized throughout the molecule (Fig. 1). Although it has been shown that tetraalkylguanidines readily form transition metal complexes [*e.g.* with Cr^{II}, Co^{II}, Ni^{II}, Pd^{II}, Pt^{II} and Zn^{II}],[5,6] the literature on such complexes is very limited and their coordination chemistry poorly developed. To the best of our knowledge, only a few examples of structurally characterized complexes exist.[6–9] This is somewhat surprising since the high basicity, solubility and inherent steric strain of tetra- or penta-substituted guanidines can readily be modified by introducing various alkyl or aryl residues at the nitrogens of the guanidine core. This makes these substances an interesting and relatively unexplored class of N-donor ligands. In particular, peralkylated bis-guanidine ligands, wherein both guanidine subunits are connected by an alkyl chain *via* their imino nitrogen atoms, have not previously been reported.

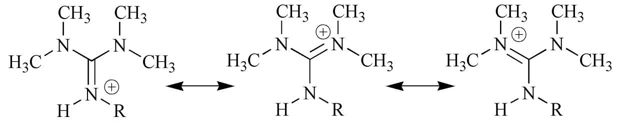

Fig. 1 Delocalization of the positive charge over all N atoms in the tetramethylguanidino unit upon protonation. R = $\{(CH_2)_3\text{-}NH{=}C[NMe_2]_2\}^+$.

As has been described elsewhere,[10] warming of alkyl halides with guanidine or its derivatives containing the free =NH group results in alkylation of nitrogen with the preferential formation of peralkylated guanidines. This fact prompted us to examine the reaction behavior of tetramethylguanidine (TMG) with alkyl dihalides. We were able to show that tetramethylguanidine readily reacts with 1,3-dibromopropane to yield the dihydrobromide of 1,3-bis(*N*,*N*,*N*′,*N*′-tetramethylguanidino)propane (btmgp), which, after deprotonation, gave the free bidentate ligand. The new compound shows a high solubility in a variety of aprotic solvents. This property, combined with the steric demands of the two tetramethylguanidine residues, the flexible trimethylene backbone, and the strong basicity, should make this ligand a versatile tool in metal complex chemistry. As a starting point we examined its coordination behavior towards various metal ions in different oxidation states. In this paper we report the syntheses of [CuI(btmgp)], [$CuCl_2$(btmgp)] and [FeI_2(btmgp)] (**2**–**4**, respectively) by the reaction of btmgp with the corresponding metal salts. The spectroscopic properties and

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† Electronic supplementary information (ESI) available: IR and Raman spectra of compound **1**, Raman data for **1**, **1b** and **2**. See http://www.rsc.org/suppdata/dt/b0/b002554m/

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the molecular structures of these new complexes have been determined and are discussed in detail.

Results and discussion

The compound btmgp **1** can readily be prepared by the reaction of an excess of tetramethylguanidine with 1,3-dibromopropane (Scheme 1). Initially, **1**·2HBr was obtained and converted into the free base on further treatment with sodium ethoxide in THF–ethanol (1 : 1) solvent. **1** was purified by distillation under reduced pressure whereby unchanged TMG was successfully recovered. Attempts to prepare derivatives of **1** by reaction of TMG with various alkyl dibromides (*e.g.* 1,4-dibromobutane, 1,5-dibromopentane, α,α′-dibromo-*o*-xylene) under similar reaction conditions to those described above led to complicated and intractable product mixtures. The ligand as such is highly moisture sensitive and found to be reactive towards chloroform. As expected, treatment of **1** with gaseous HCl in diethyl ether, or reaction of **1** with NH_4Cl, led to the formation of the more air stable **1**·2HCl **1b**. The formation of a dihydrochloride indicates that the ligand can easily be protonated at both nitrogen donor positions. As a result, the crystal structure of **1b** consists of discrete dicationic ions with an unfolded trimethylene bridge between the two guanidinium moieties (Fig. 2).

In order to evaluate the coordination behavior of compound **1** towards different metal ions, the bifunctional ligand was treated with various metal salts. We found that complexes **2**–**4** are readily prepared by dissolving or suspending the metal halides in aprotic solvents such as THF or acetonitrile, followed by the addition of btmgp (eqn. 1; M = Cu^I, Cu^{II} or Fe^{II}; X = Cl

$$MX_n + \text{btmgp} \longrightarrow [MX_n(\text{btmgp})] \qquad (1)$$

or I). The isolation of the complexes can either be achieved by vapor diffusion of ether into the reaction mixture (**2**) or by filtration of the precipitated complex (**3**,**4**). In all cases analytically pure materials were obtained in yields above 86%. All the complexes are highly air-sensitive but under an inert gas atmosphere are stable, even after several days in solution.

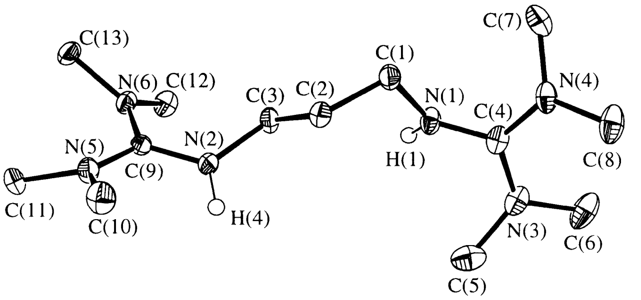


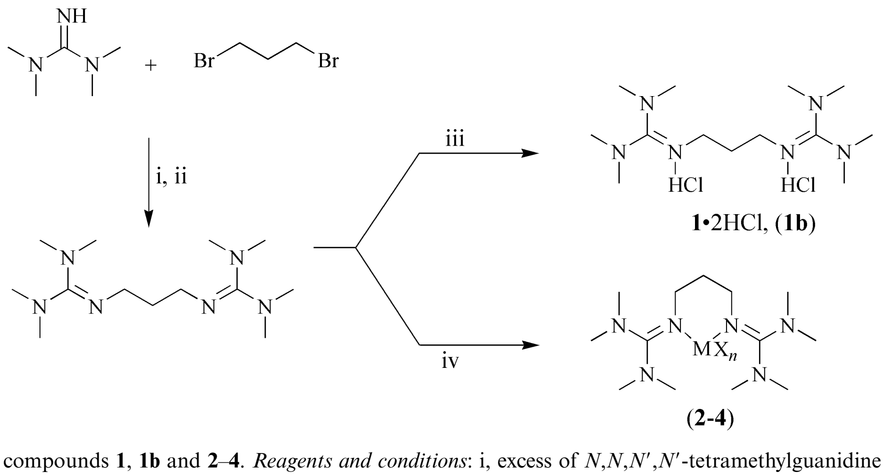
Fig. 2 An ORTEP[11] drawing (50% probability ellipsoids) of $[H_2btmgp]^{2+}$ **1b**.

Since attempts to crystallize the uncomplexed ligand have not yet been successful, no detailed structural data of **1** in the solid state are available. However comparison between the Raman and IR spectra of **1** shows the absence of a center of inversion, because most bands in the two spectra are coincident (ESI material).

The complexation of compound **1** is confirmed by a shift of the $\nu_{C=N}$ stretching frequency to lower wavenumbers accompanied by a splitting of the other modes into complicated patterns (Fig. 3). For the ligand **1**, the $\nu_{C=N}$ stretching frequency is observed at 1621 cm^{-1} (compared to 1608 cm^{-1} for TMG).[12] For complexes **2**, **3**, and **4**, these frequencies were found at 1565/1515, 1618/1579/1548, and 1615/1579/1537 cm^{-1}, respectively. The shift of the C=N band towards lower wavenumbers has previously been observed when tetramethylguanidine is complexed with transition metal ions.[5] This behavior clearly indicates that the imine nitrogens act as donor sites in these complexes. Unsurprisingly, a similar result is found for the protonated ligand, where a splitting into a doublet accompanied with a bathochromic shift (1618/1588 cm^{-1}) is observed.

The ^1H NMR spectra of compounds **1**, **1b** and of the diamagnetic complex **2** show the characteristic signals of two chemically different dimethylamino groups. With respect to the trimethylene substituent, one of the dimethylamino groups adopts the *cis* [H(**c**)], the other the *trans* [H(**d**)] position of the imine double bond (Fig. 4). The allocations are not quite clear because NOE difference spectroscopy shows no clear NOE effects. In the uncomplexed ligand, this differentiation causes a chemical shift difference of 0.09 ppm (δ 2.56, 2.65). As expected, this chemical shift difference slightly increases upon coordination [0.16 ppm, **2**] (see Fig. 4). Furthermore the observed signals of the terminal methyl groups shifted to lower fields (δ 2.74, 2.90), which is due to a decreased electron density of the imine donor function. The strong shift to lower fields in the case of **1b** (δ 2.94, 3.02), wherein both imine functions are protonated, gives clear evidence for this trend. This deshielding is in accordance with an effective electron donation of the sp^2 nitrogen donor to the metal center and has also been observed for the diprotonated ligand.

The crystal structures of the metal complexes **2**–**4** (Figs. 5–7, Table 1) show that the coordination geometry of the metal sites varies from trigonal planar in **2** [Cu^I] *via* distorted square planar [Cu^{II}] in **3** to tetrahedral [Fe^{II}] in **4**. A six-membered chelate ring is formed in all these cases by the coordination of the trimethylene-bridged N-donor functions. In complexes **2**



Scheme 1 Synthesis of compounds **1**, **1b** and **2**–**4**. *Reagents and conditions*: i, excess of *N*,*N*,*N*′,*N*′-tetramethylguanidine (TMG), 100 °C, 12 h; ii, NaOMe, distillation; iii, NH_4Cl, THF, reflux, 2 h; iv, anhydrous CuI (**2**), $CuCl_2$ (**3**) or FeI_2 (**4**), THF, reflux.

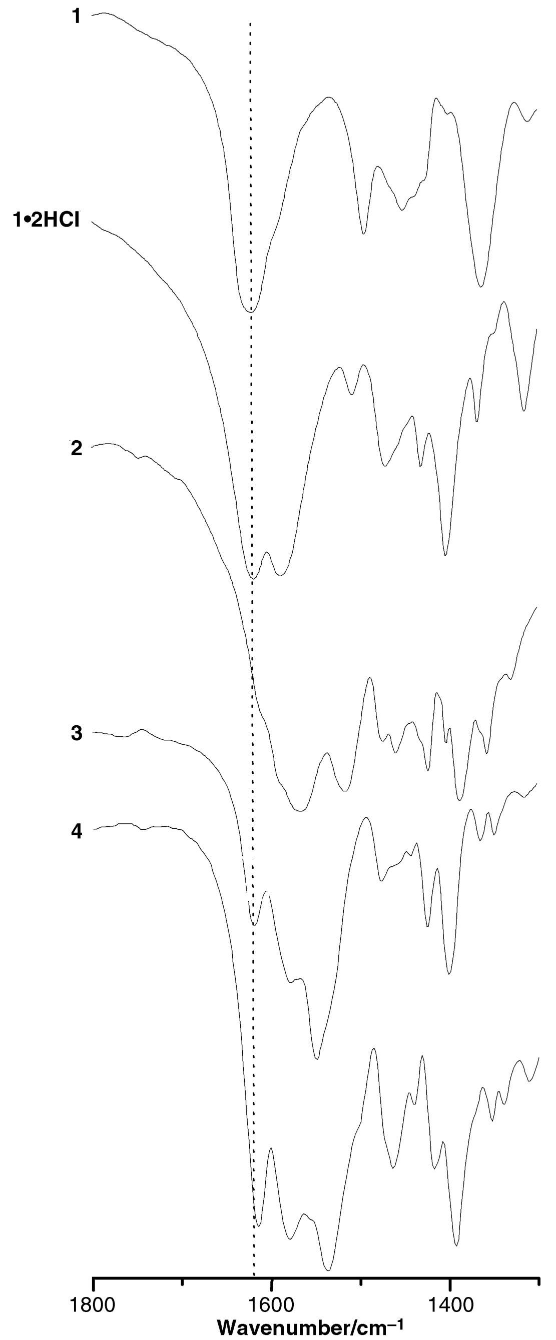


Fig. 3 Comparison of the infrared spectra of compounds **1**–**4** and **1b** in the region 1300–1800 cm^{-1}.

and **4** this chelate ring adopts the chair conformation. This conformation is required if the local symmetry of the metal coordination site is in accordance with a mirror plane that passes through the metal atom normal to the line connecting the nitrogen atoms. In principle, such a mirror plane is not only in agreement with trigonal-planar or tetrahedral ligand spheres as observed in **2** and **4** but could also be a component of square-planar coordination sites. In the case of **3**, however, the sterically demanding $(Me_2N)_2$–C groups, which are attached to the nitrogen donor functions, do not allow for an undistorted square-planar ligand arrangement. Consequently, the CuN_2 und $CuCl_2$ triangles of the idealized CuN_2Cl_2 square are twisted against each other. This notable deviation from square planar can be described by the Cu(1)N(1)N(2)/Cu(1)Cl(1)Cl(2) dihedral angle of 42.9°. As a result of the tetrahedral distortion, the local mirror plane of the idealized geometry is lost, and the six-membered chelate ring must adopt the observed twist conformation.

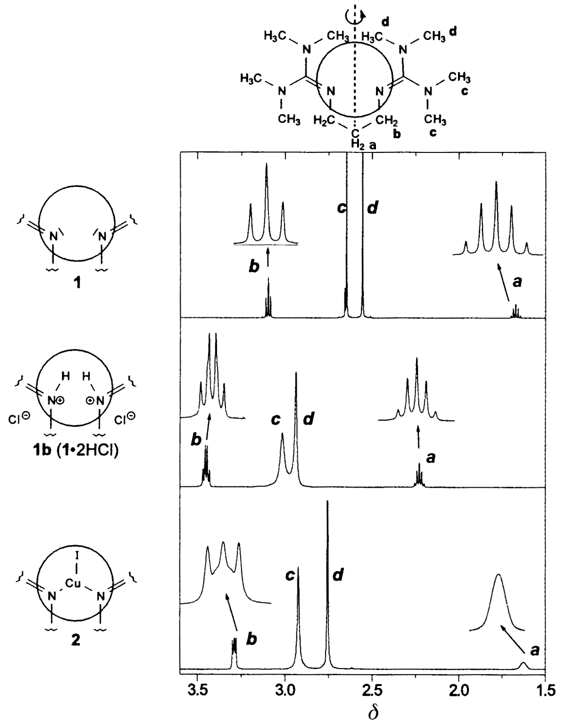


Fig. 4 ^{1}H NMR spectra of compounds **1**, **1b** and **2**.

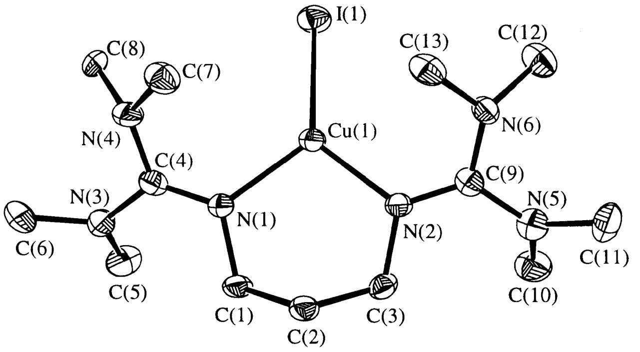


Fig. 5 Perspective drawing of [CuI(btmgp)] **2**, with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

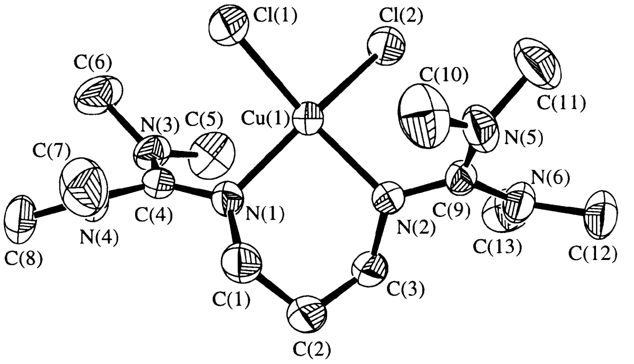


Fig. 6 Perspective drawing of $[CuCl_2(btmgp)]$ **3**. Details as in Fig. 5.

The unique plane of the six-membered chelate ring in its chair conformation in complexes **2** and **4** is defined by the atoms N(1), N(2), C(1) and C(3). The corresponding metal atom and C(2) are displaced in opposite directions from this plane by values of −0.46 and 0.76 Å (**2**) and −0.98 and 0.72 Å (**4**), respectively.

The geometry about the iron atom in complex **4** is best described as distorted tetrahedral with a bite angle of the ligand of 94.0(1)° and N–Fe–I angles ranging from 101.75(8) to 125.00(8)°. In comparison to the dihedral angles in regular

Table 1 Selected interatomaric distances (Å) and angles (°)

[H_2btmgp]Cl_2, **1b**					
N(1)–C(1)	1.468(2)	N(1)–C(4)	1.335(2)	N(2)–C(3)	1.467(2)
N(2)–C(9)	1.333(2)	N(3)–C(4)	1.338(3)	N(3)–C(5)	1.463(3)
N(3)–C(6)	1.460(3)	N(4)–C(4)	1.340(3)	N(4)–C(7)	1.456(3)
N(4)–C(8)	1.463(3)	N(5)–C(9)	1.341(2)	N(5)–C(10)	1.461(3)
N(5)–C(11)	1.462(2)	N(6)–C(9)	1.344(2)	N(6)–C(12)	1.463(2)
N(6)–C(13)	1.459(2)				
C(4)–N(1)–C(1)	124.9(2)	C(4)–N(3)–C(6)	122.1(2)	C(4)–N(3)–C(5)	122.1(2)
C(6)–N(3)–C(5)	115.5(2)	C(4)–N(4)–C(7)	122.3(2)	C(4)–N(4)–C(8)	122.9(2)
C(7)–N(4)–C(8)	114.7(2)	N(1)–C(4)–N(3)	118.6(2)	N(1)–C(4)–N(4)	121.4(2)
N(3)–C(4)–N(4)	120.0(2)				
[CuI(btmgp)], **2**					
Cu(1)–N(1)	2.010(5)	Cu(1)–N(2)	2.002(5)	Cu(1)–I(1)	2.491(1)
N(1)–C(1)	1.474(8)	N(2)–C(3)	1.461(8)	N(1)–C(4)	1.287(8)
N(4)–C(4)	1.363(8)	N(3)–C(4)	1.387(8)	N(3)–C(5)	1.448(9)
N(3)–C(6)	1.45(1)	N(4)–C(7)	1.454(9)	N(4)–C(8)	1.445(9)
N(2)–C(9)	1.302(8)	N(6)–C(9)	1.376(8)	N(5)–C(9)	1.371(8)
N(5)–C(10)	1.460(9)	N(5)–C(11)	1.442(9)	N(6)–C(12)	1.457(9)
N(6)–C(13)	1.450(9)				
N(2)–Cu(1)–N(1)	103.3(2)	N(2)–Cu(1)–I(1)	130.3(2)	N(1)–Cu(1)–I(1)	126.1(2)
N(1)–C(1)–C(2)	111.9(5)	C(1)–C(2)–C(3)	114.8(6)	N(2)–C(3)–C(2)	111.9(5)
N(1)–C(4)–N(4)	120.7(6)	N(1)–C(4)–N(3)	124.5(6)	N(4)–C(4)–N(3)	114.8(6)
N(2)–C(9)–N(6)	120.5(6)	N(2)–C(9)–N(5)	124.4(6)	N(6)–C(9)–N(5)	115.0(6)
C(4)–N(1)–C(1)	119.8(5)	C(4)–N(1)–Cu(1)	123.5(4)	C(1)–N(1)–Cu(1)	114.4(4)
C(9)–N(2)–C(3)	119.2(5)	C(9)–N(2)–Cu(1)	125.2(4)	C(3)–N(2)–Cu(1)	114.5(4)
C(4)–N(3)–C(5)	121.0(6)	C(4)–N(3)–C(6)	121.7(6)	C(4)–N(4)–C(7)	119.5(6)
C(4)–N(4)–C(8)	120.7(6)	C(9)–N(5)–C(10)	121.3(6)	C(9)–N(5)–C(11)	122.9(6)
C(9)–N(6)–C(13)	120.5(6)	C(9)–N(6)–C(12)	120.5(5)		
[$CuCl_2$(btmgp)], **3**[a]					
Cu(1)–N(1)	1.988(5)	Cu(1)–N(2)	1.992(4)	Cu(1)–Cl(1)	2.245(2)
Cu(1)–Cl(2)	2.247(2)	N(1)–C(4)	1.315(7)	N(1)–C(1)	1.474(7)
N(2)–C(9)	1.306(7)	N(2)–C(3)	1.465(7)	N(4)–C(4)	1.353(8)
N(3)–C(4)	1.354(8)	N(3)–C(5)	1.445(9)	N(3)–C(6	1.469(8)
N(4)–C(8)	1.459(9)	N(4)–C(7)	1.464(9)	N(5)–C(9)	1.351(8)
N(6)–C(9)	1.353(8)	N(5)–C(10)	1.446(9)	N(5)–C(11)	1.462(9)
N(6)–C(13)	1.461(9)	N(6)–C(12)	1.472(9)		
N(1)–Cu(1)–N(2)	89.7(2)	N(1)–Cu(1)–Cl(1)	94.5(1)	N(2)–Cu(1)–Cl(1)	148.1(2)
N(1)–Cu(1)–Cl(2)	149.2(2)	N(2)–Cu(1)–Cl(2)	93.7(1)	Cl(1)–Cu(1)–Cl(2)	98.55(7)
C(4)–N(1)–C(1)	120.9(5)	C(4)–N(1)–Cu(1)	120.6(4)	C(1)–N(1)–Cu(1)	112.7(4)
C(9)–N(2)–C(3)	120.7(5)	C(9)–N(2)–Cu(1)	120.2(4)	C(3)–N(2)–Cu(1)	113.1(3)
N(1)–C(1)–C(2)	110.1(5)	C(3)–C(2)–C(1)	113.8(5)	N(2)–C(3)–C(2)	110.6(5)
N(1)–C(4)–N(4)	123.6(6)	N(1)–C(4)–N(3)	119.0(5)	N(4)–C(4)–N(3)	117.4(5)
C(4)–N(3)–C(5)	120.1(5)	C(4)–N(3)–C(6)	121.1(6)	C(4)–N(4)–C(8)	124.3(6)
C(4)–N(4)–C(7)	120.9(6)	N(2)–C(9)–N(5)	118.6(5)	N(2)–C(9)–N(6)	124.0(6)
N(5)–C(9)–N(6)	117.4(5)	C(9)–N(5)–C(10)	120.2(5)	C(9)–N(5)–C(11)	120.7(6)
C(9)–N(6)–C(13)	121.7(5)	C(9)–N(6)–C(12)	123.6(7)		
[FeI_2(btmgp)], **4**					
I(1)–Fe(1)	2.6878(7)	I(2)–Fe(1)	2.6296(7)	Fe(1)–N(1)	2.038(3)
Fe(1)–N(2)	2.040(3)	N(1)–C(4)	1.317(4)	N(1)–C(1)	1.476(4)
N(2)–C(9)	1.320(4)	N(2)–C(3)	1.477(4)	N(3)–C(4)	1.361(4)
N(3)–C(6)	1.451(4)	N(3)–C(5)	1.456(5)	N(4)–C(4)	1.361(4)
N(4)–C(8)	1.447(5)	N(4)–C(7)	1.458(5)	N(5)–C(9)	1.357(4)
N(5)–C(10)	1.452(5)	N(5)–C(11)	1.463(5)	N(6)–C(9)	1.365(5)
N(6)–C(13)	1.450(5)	N(6)–C(12)	1.457(5)		
N(1)–Fe(1)–N(2)	94.0(1)	N(1)–Fe(1)–I(2)	125.00(8)	N(2)–Fe(1)–I(2)	120.49(8)
N(1)–Fe(1)–I(1)	101.75(8)	N(2)–Fe(1)–I(1)	106.04(9)	I(2)–Fe(1)–I(1)	106.99(2)
C(4)–N(1)–C(1)	118.9(3)	C(4)–N(1)–Fe(1)	123.0(2)	C(1)–N(1)–Fe(1)	112.7(2)
C(9)–N(2)–C(3)	118.9(3)	C(9)–N(2)–Fe(1)	124.7(2)	C(3)–N(2)–Fe(1)	111.8(2)
C(4)–N(3)–C(6)	123.1(3)	C(4)–N(3)–C(5)	121.1(3)	C(4)–N(4)–C(8)	121.4(3)
C(4)–N(4)–C(7)	122.0(3)	C(9)–N(5)–C(10)	123.5(3)	C(9)–N(5)–C(11)	120.9(3)
C(9)–N(6)–C(13)	121.2(3)	C(9)–N(6)–C(12)	122.7(3)	N(1)–C(1)–C(2)	111.2(3)
C(3)–C(2)–C(1)	115.5(3)	N(2)–C(3)–C(2)	110.7(3)	N(1)–C(4)–N(3)	124.0(3)
N(1)–C(4)–N(4)	119.6(3)	N(3)–C(4)–N(4)	116.4(3)	N(2)–C(9)–N(5)	123.5(3)
N(2)–C(9)–N(6)	119.7(3)	N(5)–C(9)–N(6)	116.8(3)		

[a] Data for one of the two symmetry independent molecules in the unit cell.

tetrahedral complexes (90°), the two planes defined by N(1), N(2), Fe(1) and I(1), I(2), Fe(1), respectively give rise to a slightly decreased dihedral angle (86.7°). It is interesting that the guanidine ligand in **2** and **4** adopts the same principal conformation. In this symmetric arrangement, the iodide ligand [I(2)] in the equatorial orientation of **4** is in close contact

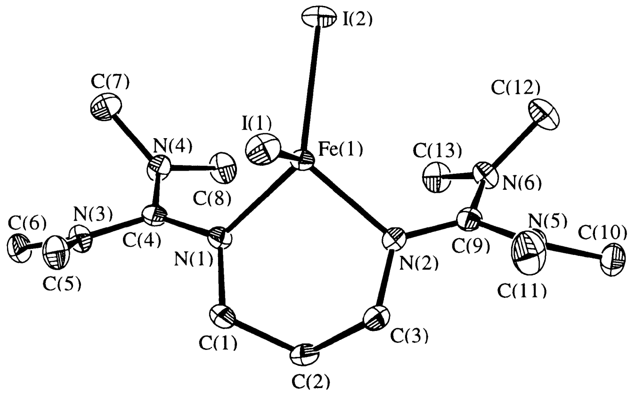


Fig. 7 Perspective drawing of [FeI$_2$(btmgp)] **4**. Details as in Fig. 5.

with the methyl groups of the bis(dimethylamino)methane residues which are arranged in the *trans* position of the imine double bond, with respect to the trimethylene chain. In the complex molecule **2** the iodide ligand occupies the same position. Obviously, this position corresponds with a pronounced energy minimum on the potential surface. The observed flattening of the six-membered C$_3$N$_2$M chair on going from **4** to **2** (and **3**) [metal to unique plane distances: −0.98 (**4**) and −0.46 Å (**3**)] must therefore be traced back to the driving force of the system to arrive at this minimum in energy.

Owing to steric repulsions introduced by the substituents bonded to the nitrogen atoms, the heavy atom frames of the guanidine subunits are not planar, but significantly twisted by rotation of the dimethylamino and the alkylimino groups around their C–N bonds. This twisting ranges from 34.7° (33.8–36.1°) in complex **4** to 39.6° (36.6–43.0°) in **2** for the planes containing the central guanidine core (N$_3$C) and the respective dimethylamino (NC$_2$) groups. As a consequence the σ- and π-bonding situation within the guanidine ligand of **2**, **3** and **4** is less influenced by the metal–nitrogen interaction as expected. Compared with the expected uncomplexed state, the coordination donor function remains an imino group in origin with C=N$_{\text{imin}}$ bonds ranging from (mean) 1.29(1) Å for the monovalent cation Cu$^{\text{I}}$ (**2**) to 1.31(1) and 1.319(6) Å for the divalent cations Cu$^{\text{II}}$ (**3**) and Fe$^{\text{II}}$ (**4**). The corresponding mean C–N$_{\text{amin}}$ bonds are 1.37(1) (**2**), 1.35(1) (**3**) and 1.361(6) (**4**) Å and thus significantly longer. From these values it can be concluded that the N$_{\text{imin}}$–M bond order is smallest for M = Cu$^{\text{I}}$ and increases for Fe$^{\text{II}}$ and Cu$^{\text{II}}$.

A slightly modified bonding situation is observed for the diprotonated guanidine dication (H$_2$btmgp)$^{2+}$. For this system, a resonance structure for the guanidinium moieties with two Me$_2$N–C bonds and one H(R)N–C bond of substantial π-bonding character is expected (Fig. 1), respectively.[13,14]

The decreased rotation with interplanar angles ranging from 26.4 to 32.6° for the dimethylamino groups and the guanidine backbone (N$_3$C) should result in a more efficient π interaction. As a result, the average H(R)N–C [1.334(3) Å] and Me$_2$N–C bonds [1.341(3) Å] show very similar values, which are comparable to the separations found in previous structural determinations of other substituted[15,16] and unsubstituted[14] guanidinium cations.

Conclusion

Examination of the literature reveals that the coordination chemistry of peralkylated guanidines is rather unexplored. The present investigation illustrates the formation of the first bidentate tetramethylguanidine based ligand, with an alkyl bridge linking the two guanidine units. As exemplified in our initial work, the novel ligand system offers a straightforward approach to the generation of neutral mixed ligand complexes with an N, X (X = Cl or I) environment around the metal atom. Extensive spectroscopic and structural examinations reveal coordination of the ligand *via* its diimine nitrogens. With regard to the high basicity and steric shielding of the diguanidine compound, the ligand offers the possibility to stabilize mixed ligand complexes with a wide range of oxidation states. Additionally, the synthesized complexes are potential precursors for the preparation of neutral, N/O-, N/S-mixed ligand complexes and clusters.

Experimental

General

All complexes were prepared under a nitrogen atmosphere using glovebox techniques. 1,3-Bis(*N*,*N*,*N*′,*N*′-tetramethylguanidino)propane **1** and its protonated form were prepared using Schlenk techniques. THF and ether were distilled from Na/K under a nitrogen atmosphere after being refluxed for 6 h. Commercial *N*,*N*,*N*′,*N*′-tetramethylguanidine was distilled under a nitrogen atmosphere prior to use.

Physical measurements

All measurements were performed under strictly anaerobic conditions. IR spectra were obtained using a Bruker IFS 66v spectrometer, Raman spectra on a Bruker RFS 100/S spectrometer [exitation source: Nd-YAG laser (1064 nm)], UV/Vis spectra on a Perkin-Elmer Lambda 900 spectrometer and ^{1}H and ^{13}C NMR spectra for **1** on a Bruker Avance DRX 500 and WM 300 spectrometer [solvent signals were used as an internal standard; calibrated on δ 7.240 (^{1}H)/77.00 (^{13}C)].

Crystal structure determinations

Molecular structures of compounds **1b**, **2** and **4**, were determined at 150 K, using a Siemens P4RA four-circle diffractometer fitted with graphite monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å), a rotating anode tube and a scintillation counter. An empirical absorption correction was applied in each case. Data for **3** were collected at room temperature on a Siemens-Stoe-AED-2 four-circle diffractometer using graphite monochromatized Mo-Kα ($\lambda = 0.71073$ Å) radiation. The structures were solved by direct methods (SHELXS 97)[17] and refined by full-matrix least-squares procedures based on F^2 (SHELXL 97).[17] The non-hydrogen atoms were refined anisotropically and hydrogen atoms were added in calculated positions; one scale factor and one isotropic extinction parameter were used. Crystal data are given in Table 2.

CCDC reference number 186/2131.

See http://www.rsc.org/suppdata/dt/b0/b002554m/ for crystallographic files in .cif format.

Syntheses

1,3-Bis(*N*,*N*,*N*′,*N*′-tetramethylguanidino)propane (btmgp) 1. 1,3-Dibromopropane (14 ml, 0.14 mol) was added to freshly distilled *N*,*N*,*N*′,*N*′-tetramethylguanidine (100 ml, 0.80 mol) and heated to 100 °C for 12 h. During this time the reaction mixture solidified. The excess of tetramethylguanidine was distilled off and a freshly prepared sodium ethoxide solution [6.5 g (0.28 mol) Na in 70 ml ethanol–70 ml tetrahydrofuran] was added to the pale brown residue. The mixture was stirred for 5 h. The resulting NaBr was filtered off and the solvents, together with any remaining tetramethylguanidine, were removed under reduced pressure at room temperature. The product was isolated by vacuum distillation (bp 110 °C/0.05 mbar). Yield: 15.2 g (41%). For elemental analytical data, the dihydrochloride **1b** of the highly air sensitive ligand was prepared. IR (silicon plates, cm^{-1}): 2994m, 2869s, 2798m, 1621vs, 1494s, 1451s, 1363vs, 1311m, 1234m, 1185m, 1135s, 1063m, 1011m, 984m, 913w, 811w, 643w, 577m, 492m and 427m. ^{1}H NMR (500 MHz, CDCl$_3$): δ 1.67 (q, 2 H, $J = 6.8$,

Table 2 Structure determination summary for compounds **1b** and **2**–**4**

	1b	**2**	**3**	**4**
Formula	$C_{13}H_{32}Cl_2N_6$	$C_{13}H_{30}CuIN_6$	$C_{13}H_{30}Cl_2CuN_6$	$C_{13}H_{30}FeI_2N_6$
M	343.35	460.87	404.87	580.08
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$C2/c$	$P2_1/n$	$Pbca$	$P\bar{1}$
a/Å	30.89(2)	7.839(2)	19.037(1)	9.466(2)
b/Å	7.897(4)	9.864(4)	13.646(1)	10.473(3)
c/Å	19.83(1)	25.026(8)	30.587(2)	12.860(3)
α/°				69.30(2)
β/°	128.53(3)	96.72(2)		87.65(2)
γ/°				63.96(2)
V/Å^3	3785(4)	1922.(1)	7945.9(9)	1061.6(5)
Z	8	4	16	2
D_{calc}/g cm^{-3}	1.205	1.593	1.354	1.815
μ/cm^{-1}	3.47	27.47	13.74	36.62
Reflections collected/observed	4644/3152	4479/3166	5911/4432	4844/4329
R,R_w	0.0409, 0.0846	0.0463, 0.1246	0.0601, 0.1338	0.0255 0.0681

$CH_2C\mathit{H}_2CH_2$), 2.56 (s, 12 H, NCH_3), 2.65 (s, 12 H, NCH_3) and 3.1 (t, 4 H, $J = 6.8$ Hz, $CH_2C\mathit{H}_2N$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 35.55 ($C\mathit{C}H_2C$), 38.76 (CH_3), 39.54 (CH_3), 47.54 ($N\mathit{C}H_2CH_2$) and 159.08 {$[(CH_3)_2N]_2\mathit{C}N$}.

btmgp·2HCl 1b. Compound **1** (541 mg, 2 mmol) was dissolved in THF (20 ml) and added to a suspension of ammonium chloride (214 mg, 4 mmol) in THF (10 ml). The reaction mixture was refluxed for 2 h and the solvent removed under reduced pressure. The colorless precipitate was resuspended in THF (20 ml) and the solvent removed again under reduced pressure with slight heating. The resulting precipitate was dissolved in acetonitrile (15 ml) and filtered. Ether was added to the pale yellow filtrate by vapor diffusion to form **1b** as small colorless needles. Yield: 500 mg (73%). Calc. for $C_{13}H_{32}Cl_2N_6$: C, 45.48; H, 9.39; N, 24.48%. Found: C, 45.31; H, 9.46; N, 24.32%. IR (KBr, cm^{-1}): 3472m, 3149m, 3053m, 2915s, 1618vs, 1588vs, 1508m, 1471s, 1430s, 1402vs, 1367m, 1314m, 1272m, 1240m, 1210m, 1170m, 1112m, 1069m, 1029m, 1007m, 947w, 931m, 896m, 884m, 801w, 760m, 736m, 708m, 550w and 517w. ^1H NMR (500 MHz, $CDCl_3$): δ 2.22 (q, 2 H, $J = 6.8$, $CH_2C\mathit{H}_2CH_2$), 2.94 (s, 12 H, NCH_3), 3.02 (s, 12 H, NCH_3), 3.45 (dt, 4 H $J_1 = 6.6$, $J_2 = 5.3$, CH_2CH_2NH) and 9.36 (t, 2 H, $J = 5.3$ Hz, NH=). ^{13}C NMR (125 MHz, $CDCl_3$): δ 29.65 (CH_2-$\mathit{C}H_2CH_2$), 40.13 (NCH_3), 40.48 (NCH_3), 42.92 ($N\mathit{C}H_2CH_2$) and 161.45 {$[(CH_3)_2N]_2\mathit{C}N$}.

[CuI(btmgp)], 2. btmgp (2300 mg, 8.5 mmol) was added dropwise to a suspension of CuI (1520 mg, 8.0 mmol) in 50 ml of THF. After 15 minutes a clear yellowish solution was obtained. The volume of the reaction mixture was reduced until the formation of a white precipitate occurred. After heating the mixture and redissolving the precipitate the solution was cooled to room temperature and crystallization initiated by diffusion of ether into the reaction mixture. Complex **2** was obtained as rectangular blocks, suitable for structure analysis. Yield 3300 mg (90% based on CuI). Calc. for $C_{13}H_{30}CuIN_6$: C, 33.88; H, 6.56; N, 18.24%. Found: C, 33.82; H, 6.55; N, 18.23%. IR (KBr, cm^{-1}): 2995m, 2920vs, 2901vs, 2874vs, 2838vs, 1565vs, 1515vs, 1459s, 1422s, 1402s, 1386vs, 1356s, 1235s, 1188m, 1157s, 1141s, 1111m, 1088m, 1063m, 1032s, 988m, 944s, 915m, 826w, 771m, 577w, 524vw and 492w. ^1H NMR (500 MHz, $CDCl_3$): δ 1.62 (‘q’, 2 H, $CH_2C\mathit{H}_2CH_2$), 2.74 (s, 12 H, NCH_3), 2.90 (s, 12 H, NCH_3) and 3.27 (t, 4 H, $J = 5.13$ Hz, $CH_2C\mathit{H}_2N$). ^{13}C NMR (75 MHz, CD_3CN): δ 37.18 ($CH_2\mathit{C}H_2CH_2$), 39.82 (NCH_3), 39.90 (NCH_3), 52.52 ($N\mathit{C}H_2CH_2$) and 165.57 {$[(CH_3)_2N]_2\mathit{C}N$}.

[CuCl$_2$(btmgp)], 3. Copper(II) chloride (269 mg, 2.0 mmol) was suspended in 20 ml of THF and btmgp (1082 mg, 4.0 mmol) was added dropwise. The resulting dark green mixture was heated for 2 h under reflux and then filtered. The filtrate was allowed to cool to room temperature and green crystals of complex **3**, suitable for X-ray studies, were obtained. Yield 721 mg (89%). Calc. for $C_{13}H_{30}Cl_2CuN_6$: C, 38.57; H, 7.47; N, 20.76%. Found: C, 39.02; H, 7.79; N, 20.36%. IR (KBr, cm^{-1}): 2995m, 2932vs, 2891vs, 1618m, 1579s, 1548vs, 1476m, 1423m, 1399s, 1363w, 1346w, 1314w, 1261m, 1237w, 1165m, 1147w, 1095m, 1069m, 1037m, 955w, 916w, 898w, 800w, 774w and 578w.

[FeI$_2$(btmgp)], 4. Iron (380 mg, 6.8 mmol) was added to a stirred solution of iodine (1160 mg, 4.6 mmol) in 100 ml THF. The reaction mixture was heated to reflux until the solution became gray-green (0.5–1 h). The excess of iron was removed with the magnetic stirring bar. To the stirred warm FeI_2 solution was added btmgp **1** (1240 mg, 4.6 mmol). Within 10 minutes a grayish white precipitate of [FeI$_2$(btmgp)] **4** formed. The suspension was stirred for 2 h and the product filtered off. It was washed with THF and dried *in vacuo*. Yield: 2300 mg (86%). Calc. for $C_{13}H_{30}FeI_2N_6$: C, 26.92; H, 5.21; N, 14.49%. Found: C, 26.78; H, 5.23; N, 14.36%. IR (KBr, cm^{-1}): 3219m, 2998m, 2923vs, 1615s, 1579vs, 1537vs, 1464s, 1417s, 1393vs, 1352m, 1339m, 1311m, 1234m, 1162m, 1064m, 1032m, 935m, 893m, 833w, 775m, 656m, 576m and 504w. Single crystals suitable for X-ray diffraction were obtained by recrystallization from hot acetonitrile.

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