

A proton induced conformational change in metal complexes with potential hydrogen bonding triplet motifs

Ian M. Atkinson,^a Michael M. Bishop,^{bc} Leonard F. Lindoy,^{*c} Srihari Mahadev^b and Peter Turner^c

^a James Cook University, Townsville, Australia. E-mail: ian.atkinson@jcu.edu.au; Fax: +61 7 4781 5230; Tel: +61 7 4781 4551

^b Sydney Grammar School, College Street, Sydney 2010, Australia. E-mail: mmb@sydgram.nsw.edu.au; Fax: +61 2 9331 5164; Tel: +61 2 9332 5820

^c The Centre for Heavy Metal Research, School of Chemistry, University of Sydney, Sydney 2006, Australia. E-mail: Lindoy@chem.usyd.edu.au; Fax: +61 2 9351 3329; Tel: +61 2 9351 4400

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Biguanide-like bidentate ligands in a variety of transition metal complexes of different geometries exhibit conformational changes upon protonation/deprotonation that alter their capacity to recognise complementary hydrogen bonding motifs.

Complementary hydrogen bonding motifs in organic molecules, inorganic complexes or combinations of the two have been used in the design of supramolecular structures.¹

Complexes of N-substituted or N,N'-disubstituted biguanide, dialkyl imidodicarbonimidoate esters and related molecules can be used in this way and, in these ligands, the N atom in the 4-position of the metallaring may be protonated (the neutral ligand) or lack a proton (anionic ligand). The alkyl substituents on the ligands may adopt conformations in which they are *syn* or *anti* with respect to the NH or O to which they are bonded. Only in the *syn-syn* conformation is there a potential triplet hydrogen bonding motif exposed and the energy barrier to changing another conformation to this may be too great to be overcome by the formation of a hydrogen bonded complex.

A search of the Cambridge Structural Database,² the results of which are summarised in Table 1, showed that only the *syn-syn* and *anti-anti* conformers were observed in such disubstituted ligands (Scheme 1). In all cases the neutral ligands were *syn-syn* and the anionic *anti-anti*; the X and R groups also lay in the plane of the ligand.

Only in one case (KAHQEQ, SEZJUC) were structures available for both the neutral and anionic forms of the same

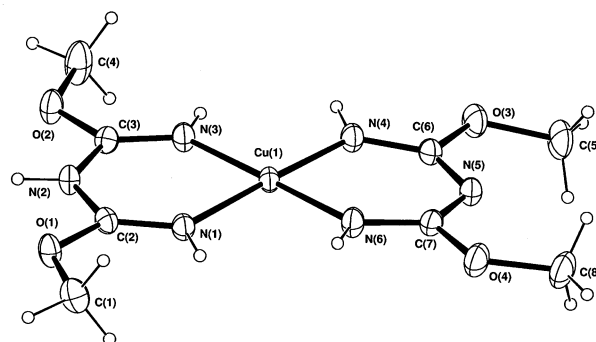


Fig. 1 ORTEP¹¹ depiction of complex cation **1** with 20% ellipsoids.

ligand. (There was a second instance, CMTCUB, VIYHOA/VIYHUG, but atomic coordinates were not available for one of the structures. However, so far as can be seen from the published structure the same applies for this ligand.)

To examine this phenomenon further, a third complex, [(dimethyl imidodicarbonimidoate)(dimethyl imidodicarbonimidoato)copper(II)]⁺, **1**, in the KHAREQ, SEZJUC family, but with one neutral and one anionic ligand in the same complex, was prepared in the present study. The synthesis involved the preparation of [bis(dimethyl imidodicarbonimidoato)zinc(II)] from sodium dicyanamide, zinc chloride and methanol^{4a} followed by the replacement of the zinc by copper(II).^{4b} The monocationic complex **1** was obtained as its hexafluorophosphate salt by heating the neutral complex with a two-fold excess of ammonium hexafluorophosphate in a mixture of methanol and acetonitrile. The crystals, † which formed on slow evaporation of the solvent, contain one molecule of acetonitrile, hydrogen bonded to N(2), per complex cation. The highly disordered PF₆⁻ ions lie in pockets formed by two pairs of complexes and so are surrounded by eight imino NH groups.

As can be seen in Fig. 1, the *syn-syn* and *anti-anti* conformations are as expected from the CSD survey. It is also clear from the figure that only in the case of the neutral ligand is a potential triplet motif observed.

The present report presents a further and unusual example of the induction of a major conformational change in a coordinated ligand involving protonation/deprotonation – a process documented in the solid state by an X-ray structure. Apart from its considerable intrinsic interest, the investigation points the way to the manner by which acid–base control might find application for inducing mechanical change in future molecular devices.

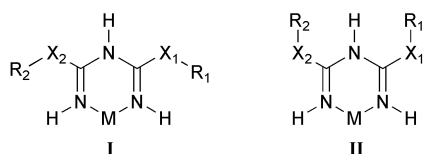
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Notes and references

† Data were collected on a Bruker SMART 1000 CCD diffractometer employing graphite monochromated MoK α radiation generated from a

Table 1 A summary of structures from the CSD

CODE	Form	M	X ₁	R ₁	X ₂	R ₂
KAHQEQ ^{3a}	I	Cu(II)	O	Me	O	Me
SEZJUC ^{3b}	II	Cu(II)	O	Me	O	Me
ZAQFUS ^{3c}	II	Co(III)	O	Me	O	Me
POWHAK ^{3d}	II	Pt(II)	NH	H	O	Me
TUPLAR ^{3e}	I	Cu(II) ⁺	NH	H	O	Me
YAXBAA ^{3f}	I	Cu(II) ⁺	NH	H	O	Me
TUJQOE ^{3g}	I	Zn(II)	NH	H	O	Et
DOPNIF ^{3h}	I	Cu(II)	NH	H	O	Et
DOPNOL ^{3h}	I	Cu(II)	NH	H	O	Et
JOFTUT ³ⁱ	I	Cu(II)	NH	H	O	Et
CMTCUB ^{3j}	I	Cu(II)	NH	Me	O	Me
VIYHOA ^{3k}	II	Cu(II)	NH	Me	O	Me
VIYHUG ^{3k}	II	Cu(II)	NH	Me	O	Me
WOJKUB ^{3l}	I	Cu(II)	NH	Me	O	Me



Scheme 1 The two observed conformations: **I**, *syn-syn*; **II** *anti-anti*.

sealed tube. A Gaussian absorption correction was applied to the data,^{5,6} as was a subsequent empirical correction determined with SADABS.⁷

The structure was solved by direct methods with SIR97,⁸ and extended and refined with SHELXL-97,⁹ using TEXSAN.¹⁰ The asymmetric unit contains a complex molecule, an acetonitrile solvate molecule and a highly disordered hexafluorophosphate counterion. In general the non-hydrogen atoms in the asymmetric unit of the model were modelled with anisotropic displacement parameters and a riding atoms model was used for the hydrogen atoms. A total of 18 partially occupied fluorine sites were used to model the disordered counterion, and isotropic temperature factors were used for these sites.

Formula $C_{10}H_{20}CuF_6N_7O_4P$, M 510.84, triclinic, space group $P\bar{1}(\#2)$, a 12.334(2), b 12.456(2), c 6.8257(13) Å, α 95.855(3), β 104.966(3), γ 90.591(3)°, V 1007.1(3) Å³, D_c 1.685 g cm⁻³, Z 2, crystal size 0.564 by 0.118 by 0.090 mm, colour red, habit columnar, $\lambda(\text{MoK}\alpha)$ 0.71073 Å, $\mu(\text{MoK}\alpha)$ 1.250 mm⁻¹, $T(\text{Gaussian})_{\text{min,max}}$ 0.645, 0.895, $2\theta_{\text{max}}$ 56.74, hkl range -16 16 , -16 16 , -9 8 , N 10273, N_{ind} 4577 (R_{merge} 0.0220), N_{obs} 3869 ($I > 2\sigma(I)$), N_{var} 285, residuals $R1(F)$ 0.0590, $wR2(F^2)$ 0.1893, $\text{GoF}(\text{all})$ 1.067, $\Delta\rho_{\text{min,max}}$ -0.702 , 0.768 e⁻ Å⁻³. $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\sum w(F_o^2 - F_c^2)^2 / \sum (wF_c^2)^2)^{1/2}$ all reflections; $w = 1/[\sigma^2(F_o^2) + (0.1271P)^2 + 0.667P]$ where $P = (F_o^2 + 2F_c^2)/3$. CCDC 190047. See <http://www.rsc.org/suppdata/cc/b2/b206898b/> for crystallographic data in CIF or other electronic format.

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