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Synthesis and CharacterIsatIon of 4,4'-Di(AryItriazenIdo)DiphenyImetbane as New Bis-Triazenido Proligands. Copper(II) Complexes

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SYNTHESIS AND CHARACTERISATION OF 4,4'-DI(ARYLTRIAZENIDO)DIPHENYLMETHANES AS NEW BIS-TRIAZENIDO PROLIGANDS. COPPER(II) COMPLEXES

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ABSTRACT

The diazotation of p,p'-diaminodiphenylmethane and the coupling of the diazonium salt with substituted anilines yield p,p'-di(aryltriazenido)diphenylmethane proligands, H₂L=CH₂(C₆H₄NNHNR)₂, R = X-C₆H₄, X = p-Me (1), p-MeO (2), o-MeO (3) and p-F (4). Two copper(II) bis-triazenido complexes, [CuL]₂, X = p-Me- (5), and p-MeO- (6), were prepared as noncrystalline solids. The FT-IR, mass spectra and ¹H NMR characterisation support the bis-triazenido structure of all new proligands (1)-(4). The IR and ESR studies on the complexes (5) and (6) reveal N¹N³-η², N⁴N⁶-η² tetraconnective chelating coordination of bistriazenido anions and square-planar symmetry with MN₄ chromophores.

INTRODUCTION

Neutral triazenide (RNNHNR, R = aryl) acts as a monodentate ligand¹ (I), but deprotonation is facile and the triazenido anion (RNNNR⁻) is much more

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Fig. 1. The Coordination Behaviour of Neutral (I) and Anionic (II -V) Triazenido Ligands.¹⁻⁵

versatile as a ligand. It is able to coordinate as a monodentate (II), chelating (III), biconnective bridge²⁻⁴ (IV), or triconnective bridge⁵ (V) (Fig. 1).

The synthesis and structural characterisation of *ortho-* and *meta-*di(phenyltriazenido)benzenes and their use as ligands in Ag(I), Cu(I), Ni(II) and Tl(III) complexes has recently been reported.⁶⁻⁹ The bis-triazenido compounds reported so far have extended the possibilities of coordination and contact between metal atoms. The neutral ligand may act as a chelating (VI) and the mono- and dianions as chelating and/or bridging (VII), (VIII) (Fig. 2).

The synthesis of p,p'-di(phenyltriazenido)diphenylmethane and the X-ray structure of its thallium(III) complex have recently been described.¹⁰ No spectral studies on the neutral proligand or its thallium complexe were published so far.

Here we report the synthesis and spectral characterisation of new bistriazenido proligands with two 1-aryl-3-*para*-phenylenetriazenyl units connected by a methylene bridge, with the purpose of increasing the flexibility of the ligand. Preliminary investigations on their coordination properties produced dinuclear copper(II) complexes.

RESULTS AND DISCUSSION

The diazotation of $p_{,p}$ '-diamino-diphenylmethane, $(p,p'-H_2N-C_6H_4)_2CH_2$ [eq. (1)] and the coupling of the diazonium salt with substituted aniline



(VIII)

Fig. 2. The Coordination Behaviour of Neutral (VI) and Anionic (VII-VIII) Bis-triazenido Ligands.⁶⁻⁹

hydrochlorides [eq. (2)] yield p,p '-di(aryltriazenido)-diphenylmethane derivatives, CH₂(C₆H₄NNHNR)₂, R = X-C₆H₄, X = p-Me (1), p-MeO (2), o-MeO (3) and p-F (4) as yellow solids.

 $CH_{2}(C_{6}H_{4}-NH_{2})_{2} + 2 \operatorname{NaNO}_{2} + 4 \operatorname{HCl} \rightarrow CH_{2}(C_{6}H_{4}-N_{2}Cl)_{2} + 2 \operatorname{NaCl} + 4 \operatorname{H}_{2}O \quad (1)$ $CH_{2}(C_{6}H_{4}-N_{2}Cl)_{2} + 2 \operatorname{R-NH}_{3}Cl + 4 \operatorname{NaOAc} \rightarrow$ $\rightarrow CH_{2}(C_{6}H_{4}\operatorname{NNHNR})_{2} + 4 \operatorname{NaCl} + 4 \operatorname{HOAc} \quad (2)$

where: $\mathbf{R} = \mathbf{X} \cdot \mathbf{C}_6 \mathbf{H}_4$, $\mathbf{X} = p$ -Me, *p*-MeO, *o*-MeO and *p*-F.

The reaction of Cu(OAc)₂.H₂O with (1) and (2) in methanol/acetone [eq. (3)] yields dinuclear bis-triazenido Cu(II) complexes, [CuL]₂, $L = CH_2(C_6H_4NNNR)_2$, $R = X-C_6H_4$, X = p-Me (5) and p-MeO (6) as green non-crystalline solids.

$$2Cu(OAc)_2 H_2O + 2 H_2L \rightarrow [CuL]_2 + 4 HOAc + 2 H_2O$$
 (3)

All the new proligands (1)-(4) are relatively air- and light-stable and can be stored for a long period at low temperature. They are soluble in C_6H_6 , CH_2Cl_2 , $CHCl_3$, THF and slightly soluble in methanol. Alternatively, the bis-triazenido copper(II) complexes (5) and (6) are air- and light-stable. The lack of solubility prevents

Comp	X	Formula	Colour	Yield	M.p.	Ar	alysis ^a (%)
		Mol. Wt.		(%)	(°C)	С	Н	N
(1)	p-Me	$C_{27}H_{26}N_6$	brownish-	91	107-9	74.8	4.1	19.1
		434.55	-yellow			(74.6)	(3.7)	(19.3)
(2)	p-MeO	$C_{27}H_{26}N_6O_2$	yellow	92	83-6	69.9	5.9	18.0
		466.55				(69.5)	(5.6)	(18.0)
(3)	o-MeO	$C_{27}H_{26}N_6O_2$	orange-	86	74-6	69.5	5.8	17.9
		466.55	-yellow			(69.5)	(5.6)	(18.0)
(4)	<i>p-</i> F	$C_{25}H_{20}N_6F_2$	yellow	89	122-3	68.3	4.7	18.9
		442.47				(67.9)	(4.6)	(19.0)
(5)	p-Me	$C_{54}H_{48}N_{12}Cu_2$	green	50	143-5d	65.8	5.1	17.1
		992.15				(65.4)	(4.9)	(16.9)
(6)	p-MeO	$C_{54}H_{48}N_{12}O_4Cu_2$	green	62	185-6d	61.9	4.9	16.2
		1056.15				(61.4)	(4.6)	(15.9)

Table I. Analytical Data for H₂L (1)-(4) and [CuL]₂ (5), (6); L = CH₂(C₆H₄NNNR)₂, R = X-C₆H₄.

^a Calculated values are given in parantheses.

recrystallisation. The new compounds were characterised by elemental analyses and melting points. (Table I).

Structure characterisation was obtained by FT-IR, mass spectra (EI and FAB), ESR and ¹H NMR spectroscopy.

Infrared Spectra

Spectra were recorded in the range 4000-400 cm⁻¹. Bands characteristic of *ortho-* and *para*-phenylene and substituent (Me- and MeO-) groups were observed in the expected spectral regions for the title compounds.¹¹ According to the structure of the triazenido group (N:NN) in the proligands, the most important regions are 1405-1397 and 1214-1193 cm⁻¹ where the N=N and N-N stretchings are located. Also the bending vibration can be assigned^{11,12} between 657-647 cm⁻¹. There are other regions where the v(N-H) (3200-3167 cm⁻¹) and δ (N-H) (1525-1509 cm⁻¹) vibrations can be found. The assignement of the IR spectra of the bistriazenido proligands (1)-(4) is supported by comparison with the spectra of the

	(1)-(4) and then	r i riazem	uo nomon	gues Kin	innik (r.)-	$-(4), K = A - C_6 H_4.$
Comp.	. X	ν(N-H)	δ(N-H)	ν(N=N)	v(N-N)	δ(N:NN)	Other assignments
(1)	p-Me	3195m	1522vs	1399s	1193s	657m	
(1')	<i>p</i> -Me	3200m	1525vs	1397s	1193s	655m	
(2)	p-MeO	3186m	1517vs	1401s	1194s	653m	1241vs v(C-O-C)
(2')	p-MeO	3167m	1509vs	1401s	1206vs	653m	1245vs v(C-O-C)
(3) ^a	o-MeO	3190m	1517vs	1405s	1214s	647m	
(4)	<i>p</i> -F	3180m	1519vs	1401s	1197vs	651m	1226vs v(C-F)
(4')	<i>p</i> -F	3182m	1519vs	1398vs	1196vs	652s	1225vs v(C-F)

Table II. FT-IR Data (cm⁻¹) for the Bis-triazenido Compounds $CH_2(C_6H_4NNHNR)_2$, (1)-(4) and their Triazenido Homologues RNNHNR (1')-(4'), $R = X-C_6H_4$.

^a The compound *o*-MeOC₆H₄NNHNC₆H₄OMe-*o* could not be prepared.

Table III. FT-IR Data for Bis-triazenido Cu(II) Complexes, $[CuL]_2$, L = CH₂(C₆H₄NNNR)₂.

Comp.	Х	v _{as} (NNN)	v _s (NNN)	δ (NNN)
(5)	<i>p</i> -Me	1365vs	1220m	680w
(6)	p-MeO	1374vs	1225m	687w

corresponding mono-triazenido derivatives, RNNHNR, $R = X-C_6H_4$, X = p-Me (1'), *p*-MeO- (2') and *p*-F- (4') (Table II).

The IR data of bis-triazenido copper(II) complexes agree with the C_{2V} group symmetry of the triazenido units in the coordinated ligands^{12,13} (Table III).

Mass Spectra

For the bis-triazenido derivatives (1)-(4) EI and FAB mass spectra were recorded. The m/z values and the relative intensities of the main fragments are given in Table IV. It must be mentioned that only the FAB mass spectra reveal the molecular ion peak $CH_2(C_6H_4NNHNR)_2^+$, as (M+1) and (M-1) values.

The EI and FAB fragmentations are similar for all new compounds. The electron impact fragmentation (Fig. 3) of the parent ion can follow two alternative routes: the major one involves loss of two N₂ groups leading to the $CH_2(C_6H_4NHR)_2^+$ ion, which displays the highest m/z value in each spectrum and

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Fragment	X = I	9-Me (1)	M-d	leO (2)	M-0	leO (3)	-d	-F (4)	
	EI	FAB	EI	FAB	EI	FAB	EI	FAB	
$CH_2(C_6H_4N:NHNR)_2^+$ (M+1)		435(67)		467(65)		467(67)		443(21)	
(M-1)		433(6)		465(7)		465(7)		441(6)	
CH ₂ (C ₆ H ₄ NHR) ₂ ⁺	378(100)		410(100)		410(100)		386(2)		
CH ₂ (C ₆ H ₄ NR) ₂ ⁺	376(2)		408(3)		408(2)				
RNNHNC ₆ H ₄ CH ₂ C ₆ H ₄ N ₃ H ⁺		343(4)		359(3)	4	359(5)		347(3)	
RNNHNC ₆ H ₄ CH ₂ C ₆ H ₄ N ₂ H ⁺		329(93)			· .		-	333(28)	
RNNHNC ₆ H ₄ CH ₂ C ₆ H ₄ N ₂ ⁺				344(81)	· .	344(93)		- 16	
RNNHNC ₆ H ₄ CH ₂ C ₆ H ₄ N ⁺		314(8)	330(1)	330(5)	330(12)	330(13)		318(6)	
RNNNC ₆ H ₄ CH ₂ C ₆ H ₄ N ⁺		313(6)		329(52)		329(42)		317(4)	
RNNHNC ₆ H ₄ CH ₂ C ₆ H ₄ ⁺		300(28)	316(2)	316(69)		316(88)	-	304(29)	
RNC ₆ H ₄ CH ₂ C ₆ H ₄ ⁺		271(17)	287(23)	287(71)	287(25)	-287(63)	275(23)	275(10)	
$CH_2(C_6H_4NH)_2^+$	196(66)		196(14)		196(46)		196(7)	•	-
$\operatorname{CH}_2(\operatorname{C}_6\operatorname{H}_4)_2^+$	166(14)		166(34)		166(35)		166(23)		
RN_{2}^{+}	119(3)		135(71)		135(6)		123(34)		
RNH ⁺	106(34)		122(20)		122(83)		110(100)		
RN^{+}	105(2)		121(3)		121(12)				
RH ⁺	92(2)		108(90)		108(42)		96(50)		
R ⁺	91(15)		107(87)		107(81)		95(32)		
$C_6H_4NH^+$	91(15)		91(20)		91(18)		61(19)		_
$C_6H_5^+$	77(7)		77(42)		77(26)		77(10)		

Table IV. Mass Spectral Data for Bis-triazenido Derivatives, $CH_2(C_6H_4NNHNR)_2$, $R = X-C_6H_4$.

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Fig. 3. Electron Impact Fragmentation of $CH_2(C_6H_4N:NHNC_6H_4X)_2$, X = p-Me (1), p-MeO (2), o-MeO (3) and p-F (4).

produces the base peak of (1)-(3). Further fragmentation of this ion, by succesive loss of R groups, N and H, leads to the $CH_2(C_6H_4)_2^+$ fragment. Alternatively, the $CH_2(C_6H_4)_2$ radical can be lost at the beginning to form the RNH⁺ fragment which produces the base peak of (4). The loss of N and H leads to small aryl fragments (RH⁺, R⁺ and C₆H₅⁺).

The alternative route involves loss of two H radicals, leading to the $CH_2(C_6H_4NNNR)_2^+$ fragment, which was not observed. Further fragmentation of this ion, by losing two N₂ or one $CH_2(C_6H_4N)_2$ group, produces the fragments of the main route of the scheme.

Fragment	Chemical Shift (δ , ppm) and Coupling Constant (J, Hz)								
	1	1'							
-CH ₃	2.36 (6H, s)	2.36 (6H, s)							
-CH ₂	3.90 (2H, s)								
$-C_6H_4$ (<i>p</i> -tolyl)	7.18 (4H, d; J 7.8)	7.18 (4H, d, J 8.0)							
$-C_6H_4$ (<i>p</i> -tolyl)	7.31 (4H, d; J 7.7)	7.32 (4H, d, J 8.3)							
$-C_6H_4$ (diphenylmethane)	7.20 (4H, d; J 6.8)								
-C ₆ H ₄ (diphenylmethane)	7.34 (4H, d; J 6.7)								

Table V.	Ή	NMR	Data	for	the	Bis-f	riaze	nido	Proligand
	CH ₂	(C ₆ H ₄ NN	HNC ₆ H₄($CH_3-p)_2$	(1)	and	its	Mono	-triazenido
	Hon	ologue p-	Н₃СС₅Н	₄N:NHN	C ₆ H ₄	CH ₃ -p	(1') (CDCl ₃ S	Solvent).

The FAB fragmentation of the parent ion, which is less representative for triazenido derivatives, also presents successive loss of N, H and aryl radicals.

¹H NMR Spectra

A proton resonance spectrum was recorded for the proligand $CH_2(C_6H_4N:NHNC_6H_4CH_3-p)_2$ (1). The compounds (2)-(4) being less stable in solution could not be investigated. The assignment of the ¹H NMR spectrum of the bis-triazenido proligand (1) was made by comparison with the spectrum of the corresponding mono-triazenido derivative $p-H_3CC_6H_4N:NHNC_6H_4CH_3-p$ (1') (Table V) and confirms the equivalence of terminal Me-, C_6H_4 - and bridged C_6H_4 -groups, respectively; the resonance signal for N-H proton could not be observed. The spectrum shows no unusual features.

The microanalytical and spectral data confirm the presence of two triazenido units (N:NN) and the expected aryl and alkyl groups in the synthesised proligands (1)-(4) (Fig. 4).

Following the reactions of eqs. (1) and (2) the acid hydrogens should be bonded to the N(1) and N(6) atoms. Considering the behaviour of mono-triazenides, which show two equivalent aryl groups in the NMR spectra, we can suggest the



Fig. 4. The Proposed Molecular Structure of the Bis-triazenido Proligands $CH_2(C_6H_4N:NHNR)_2$, $R = X-C_6H_4$, X = p-Me- (1), p-MeO (2), o-MeO (3) and p-F (4).



Fig. 5. The Proposed Molecular Structure of the Bis-triazenido Copper(II) Complexes, [CuL]₂, L = CH₂(C₆H₄NNNR)₂, R = X-C₆H₄-, X = *p*-Me (5) and *p*-MeO (6).

tautomery¹⁴ of H between N(1) ... N(3) and N(4) ... N(6), respectively. Complete deprotonation of the bis-triazenides (1)-(4) leads to bis-triazenido anions, $L = CH_2(C_6H_4NNNR)_2$ which can act as chelating ligands^{10,13} in the synthesised complexes, [CuL]₂ (5) and (6) (Fig. 5).

The coordination geometry of copper(II) in (5) and (6) is supported by ESR spectra. Thus, the ESR X-band powder spectra of the [CuL]₂ complexes (5) and (6) show $g_{||}= 2.237$ and $g_{\perp}= 2.055$, the metal hyperfine splitting being resolved in the parallel band (A_{||} = 180G). These data are typical for square-planar local symmetry with a MN₄ chromophore.¹⁵

Further studies on the structure and coordination behaviour of new bistriazenido ligands are in progress and preliminary data confirm these possibilities.

EXPERIMENTAL

The preparation and purification of the compounds were carried out in air. All starting materials and solvents were purchased from the Aldrich Chemical Co., Inc.

FT-IR spectra were recorded using the KBr pellet technique, on a Perkin-Elmer FT-IR Spektrum 1000 spectrometer with calibration against the absorption band of polystyrene at 1601 cm⁻¹. Mass spectra (EI and FAB) were recorded on an A. E. I. MS 902 - 70 eV spectrometer. ¹H NMR spectra were recorded on a Varian-Gemini 300 instrument. The ESR measurements were performed using standard JEOL JES-3B equipment. Microanalysis were carried out by the Microanalytical Service of the School of Chemistry, University of Bristol, United Kingdom.

Synthesis of Proligands

p,p'-Di(p-tolyltriazenido)diphenylmethane, CH₂(C₆H₄NNHNC₆H₄CH₃-p)₂ (1).

In a stirred mixture of 60 mL of distilled water and 36% HCl solution (5.20 mL, 60.0 mmol) was dissolved $CH_2(C_6H_4NH_2-p)_2$ (3.00 g, 15.0 mmol). After cooling to 0-3°C with 25 g of crushed ice, NaNO₂ (2.10 g, 30.0 mmol) dissolved in 5 mL distilled water was added over a period of five minutes. To the cold, dark yellow solution was added first *p*-toluidine (3.20 g, 30.0 mmol) dissolved in a mixture of 60 mL distilled water and 36% HCl solution (2.60 mL, 30.0 mmol), over a period of five minutes. The coupling reaction was started by adding very fast to the mother liquid a solution of NaOAc.3H₂O (6.00 g, 73.2 mmol) dissolved in 15 mL distilled water. A yellow precipitate started to form at once. After stirring for 1.5 hours and keeping the temperature below 10°C the product was filtered on a Büchner funnel, washed with cold water and ethanol and dried at room temperature. Yield 5.98 g.

The following were prepared similarly:

p,p'-Di(p-methoxyphenyltriazenido)-diphenylmethane, CH₂(C₆H₄NNHNC₆H₄OCH₃-p)₂ (**2**);

p,p'-Di(o-methoxyphenyltriazenido)-diphenylmethane, $CH_2(C_6H_4NNHNC_6H_4OCH_3-o)_2$ (**3**); p,p'-Di(p-fluorophenyltriazenido)-diphenylmethane, $CH_2(C_6H_4NNHNC_6H_4F-p)_2$ (**4**).

Synthesis of Complexes

Bis[p,p'-di(p-tolyltriazenido)-diphenylmethane-copper(II)],

$[CuCH_2(C_6H_4NNNC_6H_4CH_3-p)_2]_2 (5).$

To Cu(OAc)₂.H₂O (0.20 g, 1.00 mmol) in boiling methanol (40 mL) was added a warm solution of CH₂(C₆H₄NNHNC₆H₄CH₃-p)₂ (0.43 g, 1.00 mmol) in acetone (40 mL). After stirring and refluxing for 1 hour the green precipitate was filtered on a Hirsch funnel, washed with warm methanol and acetone and dried at room temperature. Yield 0.25 g.

The following was prepared similarly:

Bis[p,p'-di(p-methoxytriazenido)-diphenylmethane-copper(II)][Cu CH₂(C₆H₄NNNC₆H₄OCH₃-p)₂]₂ (**6**) (yield 62%)

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REFERENCES

1. N. G. Connelly and Z. Demidowicz, J. Chem. Soc. Dalton Trans., 50 (1978).

2. J. T. Leman, H. A. Roman and A. R. Barron, J. Chem. Soc. Dalton Trans., 2183 (1992).

- 3. E. Hartmann and J. Strähle, Z. Naturforsch., 43b, 818 (1988).
- 4. E. Hartmann and J. Strähle, Z. Anorg. Allg. Chem., <u>583</u>, 31 (1990).
- N. G. Connelly, P. M. Hopkins, A. G. Orpen, G. M. Rosair and F. Viguri, J. Chem. Soc. Dalton Trans., 2907 (1992).
- M. Hörner, A. G. Pedroso, C. R. de Menezes Peixoto and J. Beck, Z. Naturforsch., <u>45b</u>, 689 (1990).
- 7. M. Hörner, H. Fenner, W. Hiller and J. Beck, Acta Cryst., C45, 204 (1989).
- 8. M. Hörner, H. Fenner, W. Hiller and J. Beck, Z. Naturforsch., <u>43b</u>, 1174 (1988).
- M. Hörner, H. Fenner, J. Beck and W. Hiller, Z. Anorg. Allg. Chem., <u>571</u>, 69 (1989).
- 10. M. Hörner, A. B. Oliveira and J. Beck, Z. Anorg. Allg. Chem., <u>623</u>, 65 (1997).
- N. B. Colthup, L. H. Daly and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy", Academic Press, New York, pp. 362-413 (1964).
- J. Beck, "Dissertation", Fakultät für Chemie und Pharmazie, Eberhard-Karls-Universität zu Tübingen, pp. 268-271 (1986).
- M. Venter, I. Haiduc, L. David and O. Cozar, J. Mol. Struct., <u>408-409</u>, 483 (1997).
- 14. L. Lunazzi, and M. Guerra, J. Chem. Soc. Perkin Trans., 2, 52 (1980).
- 15. R. K. Ray and G. B. Kauffman, Inorg. Chim. Acta, <u>173</u>, 207 (1990).

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