

# High-frequency (245 GHz) and X-band EPR study of stable dicopper radical complexes

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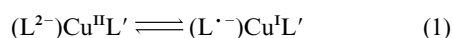
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Stable, readily accessible and in part even structurally established paramagnetic complex cations  $[\text{Cu}_2(\mu\text{-}\eta^4\text{-BL})\text{L}_2]^{++}$ , BL = bridging ligand, L =  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  or  $2 \text{PPh}_3$ , were studied by high-frequency (245 GHz) and X-band EPR spectroscopy. The dicopper(II)/anion radical ligand formulation as opposed to a mixed-valent dimetal description is supported by the high-frequency EPR results which show *g* components between 2.0220 and 1.9968. The largest (rhombic) *g* anisotropy  $\Delta g$  was found for the system with BL = azodi-*tert*-butyl formate and L =  $\text{Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2$ , and the smallest (axial)  $\Delta g$  splittings for 1,2,4,5-tetrazine-bridged species. There is a clear relation between  $\Delta g$  as obtained from the high-field measurements and the  $^{63,65}\text{Cu}$  hyperfine coupling as measured from solution spectra in the X band.

Paramagnetic co-ordination compounds of the copper(II) ion with its  $3d^9$  configuration have been extensively researched by EPR<sup>1</sup> due to their accessibility and relevance for biochemistry and catalysis.<sup>2</sup> Di- and oligo-nuclear systems have attracted special attention because of the magnetic and EPR spectroscopic consequences of exchange interaction.<sup>1c</sup> Copper(I), on the other hand, has a  $3d^{10}$  ground state configuration, and corresponding complexes are diamagnetic and EPR inactive unless a paramagnetic entity, ligand radical or other metal provides the spins necessary for detection.<sup>3-6</sup>

In EPR studies<sup>4-6</sup> which have eventually proven biochemically relevant<sup>7</sup> it was shown that copper(II) complexes  $\text{LCuL}'$  with a non-innocent (here: oxidizable) ligand  $\text{L}^{2-}$  may adopt a valence tautomeric copper(I)/radical form and even exhibit corresponding EPR-detectable equilibria (1).<sup>8</sup> Suitable



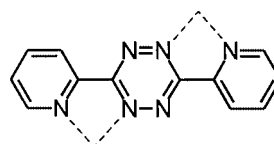
ligands L for the valence tautomer alternative (1) are *o*-quinones<sup>4-6,8</sup> and quinone-like  $\pi$  acceptor molecules which can form metal-co-ordinating radical anions.<sup>5</sup>

During the development of dinucleating redox-active ligands we have discovered<sup>9-14</sup> that azo-containing bis-chelate systems can react with copper and copper compounds to yield deeply coloured and surprisingly stable paramagnetic dicopper complexes, some of which could even be structurally characterized.<sup>11-14</sup> Structural and spectroscopic data, including high-resolution EPR in the X-band,<sup>9,10</sup> suggested predominantly ligand-based spin, however, the absolute values of the isotropic metal hyperfine coupling constants  $a(^{63,65}\text{Cu})$  for two metal centres<sup>10</sup> were quite large in comparison with those of typical copper(I) anion radical complexes,<sup>15</sup> amounting to about 25% of the average  $a(^{63,65}\text{Cu}) \approx 7 \text{ mT}$  in delocalized mixed-valent  $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$  systems.<sup>16</sup>

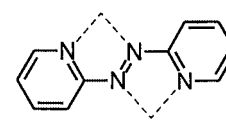
The often extensive hyperfine splitting from  $^{63,65}\text{Cu}$ ,  $^{31}\text{P}$ ,  $^{14}\text{N}$  and  $^1\text{H}$  nuclei<sup>9,10</sup> precluded meaningful studies of solids or glassy frozen solutions in the X-band; only broad, unstructured signals were observed. We have thus studied the following five paramagnetic dicopper complexes 1-5 by high-frequency EPR at 245 GHz to establish the *g* anisotropy in comparison with

genuine copper(II) compounds and to correlate these data with hyperfine information from high-resolution X-band studies.

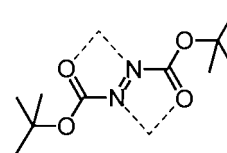
	BL	L
1	bptz	2 PPh <sub>3</sub>
2	bptz	Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>6</sub> PPh <sub>2</sub>
3	bptz	Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>8</sub> PPh <sub>2</sub>
4	abpy	Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>6</sub> PPh <sub>2</sub>
5	adcO <sup>t</sup> Bu	Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>6</sub> PPh <sub>2</sub>



bptz



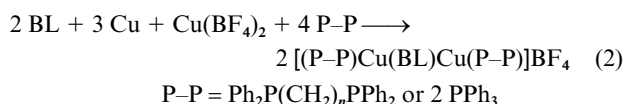
abpy



adcO<sup>t</sup>Bu

## Results and discussion

Compounds 1 and 5 have been previously reported and structurally characterized.<sup>9-11,14</sup> The radical complexes 2-4 were obtained as paramagnetic cation salts in analogy to 1 via self-assembly comproportionation reactions (2).<sup>14,17</sup>

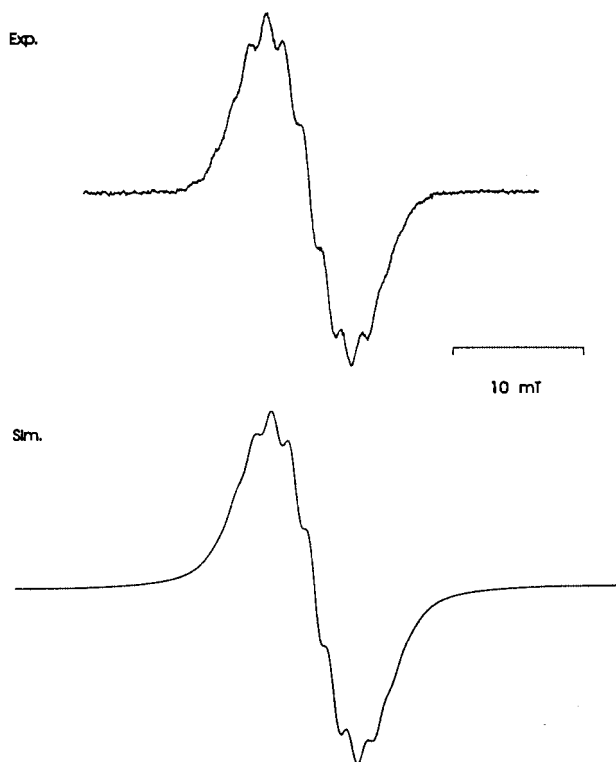


Partially resolved EPR spectra in solution at ambient temperature were obtained in the X-band for 1,<sup>9</sup> 5<sup>10</sup> and radical

**Table 1** X-Band EPR data<sup>a</sup> for the paramagnetic dicopper complexes

Complex	$g_{\text{iso}}$	$a(^{63/65}\text{Cu})$	$a(^{31}\text{P})$	$a(^{14}\text{N})$	Solvent
1	2.0055	0.758 <sup>b,c</sup>	0.910	0.605/0.463	CH <sub>2</sub> Cl <sub>2</sub>
2	2.0054	0.760/0.813 <sup>c</sup>	0.923	0.613/0.463	CH <sub>2</sub> Cl <sub>2</sub>
3	2.0054	0.785/0.840 <sup>c</sup>	0.944	0.628/0.468	CH <sub>2</sub> Cl <sub>2</sub>
4	2.0051	1.300/1.393 <sup>c</sup>	1.480 <sup>d</sup>		CH <sub>2</sub> Cl <sub>2</sub>
5	2.0104	1.652/1.769	1.856	0.640	CH <sub>3</sub> OH/ 2% water

<sup>a</sup> Coupling constants in mT, from computer-simulated spectra. <sup>b</sup> From ref. 9. <sup>c</sup> Isotope coupling not separated. <sup>d</sup> Not resolved.

**Fig. 1** X-Band EPR spectrum of radical 4 in CH<sub>2</sub>Cl<sub>2</sub> with computer simulation (hyperfine values from Table 1).

complexes 2–4 (Fig. 1). The corresponding data are listed in Table 1. As expected,<sup>9,10,15</sup> the <sup>63,65</sup>Cu ( $I = 3/2$ ) and <sup>31</sup>P ( $I = 1/2$ ) hyperfine splitting dominates the spectra. The presence of two equivalent copper centres with nuclei in natural abundance (<sup>63</sup>Cu, 69.2%; <sup>65</sup>Cu, 30.8%; gyromagnetic ratio <sup>63</sup>Cu/<sup>65</sup>Cu, 0.9345) gives rise to three sub-spectra for the <sup>63</sup>Cu–<sup>63</sup>Cu, <sup>63</sup>Cu–<sup>65</sup>Cu and <sup>65</sup>Cu–<sup>65</sup>Cu combinations which can be observed under favourable conditions.<sup>10,15b</sup> Hyperfine coupling from the tetrazine and azo <sup>14</sup>N nuclei<sup>18</sup> is also observed,<sup>9,10</sup> except for complexation 4 with its rather poorly resolved EPR spectrum (Fig. 1); radical anions of azo compounds usually suffer from strong anisotropic line broadening.<sup>13,19</sup> Attempts at ENDOR spectroscopy in fluid solution<sup>18a</sup> failed because of an inability to saturate the EPR transitions in the complexes.

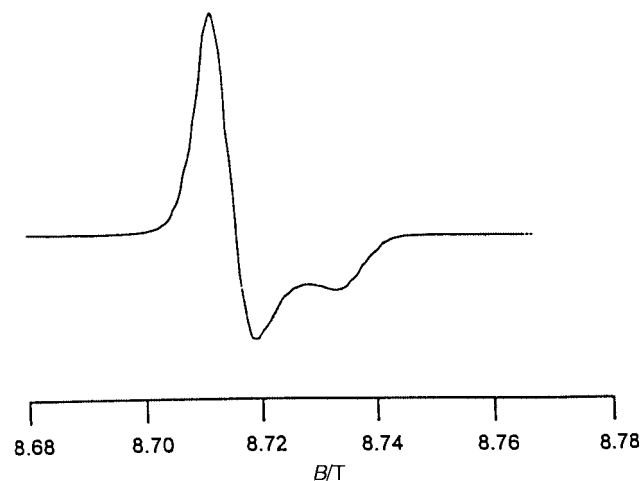
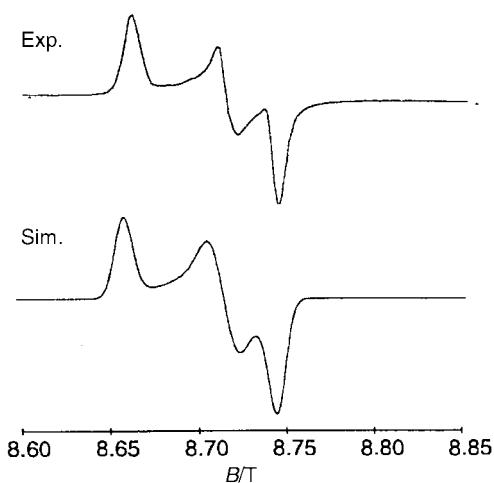
To establish the  $g$  anisotropy and thus gain more information on the electronic structure in comparison to copper(II) and mixed-valent dicopper species the stable paramagnetic species 1–5 were subjected to high-frequency (245 GHz) EPR measurements using far infrared laser techniques.<sup>20,21</sup> The spectra of two species are shown in Figs. 2 and 3, and the  $g$  components obtained are summarized in Table 2.

All five paramagnetic dicopper compounds showed splitting of  $g$  components under the high-field EPR conditions. With linewidths >6 mT the hyperfine information could not be observed. A first interesting observation is the rhombic  $g$  component pattern for the azo radical complexes 4 and 5 and the

**Table 2** High-field EPR data for the paramagnetic dicopper complexes<sup>a</sup>

Complex	$g_1$	$g_2$	$g_3$	$\Delta g^b$	$\langle g \rangle^c$	$a(^{63/65}\text{Cu})^d$
1	2.0067	2.0067	2.0026	0.0041	2.0053	0.758 <sup>e</sup>
2	2.0070	2.0070	2.0024	0.0046	2.0055	0.760/0.813
3	2.0070	2.0070	2.0022	0.0048	2.0054	0.785/0.840
4	2.0134	2.0047	1.9968	0.0166	2.0050	1.300/1.393
5	2.0220	2.0090	2.0020	0.0200	2.0110	1.652/1.769

<sup>a</sup>  $g$  Components from 245 GHz measurements of frozen acetone–ethanol (5:1) solutions at 4 K. <sup>b</sup>  $g_1 - g_3 = \Delta g$ . <sup>c</sup> Calculated. <sup>d</sup> From X-band measurements in CH<sub>2</sub>Cl<sub>2</sub> at 300 K, coupling constants in mT. <sup>e</sup> From ref. 9, isotope coupling not separated.

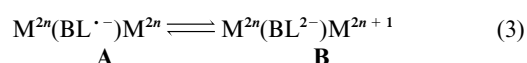
**Fig. 2** 245 GHz EPR spectrum of radical 1 in frozen acetone–ethanol (5:1) solution at 4 K.**Fig. 3** 245 GHz EPR spectrum of radical 5 in frozen acetone–ethanol (5:1) solution at 4 K with computer simulation ( $g$  components from Table 2).

axial pattern with overall smaller  $g$  anisotropy for the tetrazine radical species 1–3. The different magnitude of the  $g$  splitting confirms<sup>18</sup> that the azo group interacts more strongly with the metal than the tetrazine function, simply because of the smaller  $\pi$  system of the former. This argument also explains the difference between 4 and 5, where the latter with the smaller conjugated system (6 vs. 14  $\pi$  centres) exhibits the most pronounced effects. The extent of  $g$  anisotropy is significantly determined by the participation of the heavier elements Cu and P with their large spin–orbit coupling constants at the singly occupied molecular orbital (SOMO).<sup>22</sup> Accordingly, there is an approximate (non-linear) correlation between the  $g$  anisotropy and the metal hyperfine coupling as a more direct measure of the metal

contribution: the orange-red tetrazine radicals exhibit small  $\Delta g$  and  $a(^{63,65}\text{Cu})$  values, whereas the azo-containing species **4** (purple) and in particular **5** (blue) are distinguished by large  $\Delta g$  and  $a(^{63,65}\text{Cu})$  parameters.

The symmetry of the  $g$  component splitting reflects the symmetry of the spin-bearing azo or tetrazine functions in the radical ligands: whereas the less symmetrical azo compounds in *trans* configuration exhibit rhombic behaviour, the more symmetrical cyclic  $\pi$  radical system of the 1,2,4,5-tetrazine species is related to the axial splitting ( $\pi$  axis/ $\pi$  plane) typical for aromatic radical ions.<sup>23</sup>

The overall  $g$  component splitting  $\Delta g$  is distinctly larger in the complexes than for typical metal free  $\pi$  radical ions.<sup>23</sup> Nevertheless, this increase up to  $\Delta g = 0.02$  for **5** is still far from what would be expected for copper(II) ( $\Delta g \approx 0.2$ )<sup>1</sup> or mixed-valent dicopper(II,I) species ( $\Delta g > 0.13$ ).<sup>16</sup> Both the  $g$  anisotropy data from high-field EPR and the metal hyperfine results from X band studies [ $a(^{63,65}\text{Cu}) \approx 7.5$  mT for copper(II) species]<sup>1</sup> thus suggest only about 10–25% metal participation in the SOMO of the radical complexes presented here. This contribution is larger than typical for metal complexes of radical ligands,<sup>22</sup> however, the alternative **A** in eqn. (3) is still predominant for the dicopper



systems, in contrast to complexes of ruthenium(III,II) where relaxation and  $g$  anisotropy clearly point to comparable contributions from both resonance structures **A** and **B**.<sup>23</sup>

## Experimental

Compounds **1**(BF<sub>4</sub>)–**4**(BF<sub>4</sub>) were obtained by treating one equivalent of copper(II) bis(tetrafluoroborate), two equivalents of the bridging ligand, slightly more than three equivalents of HCl-activated copper powder and eight equivalents of triorganophosphine (four equivalents for diphosphines) in dichloromethane.<sup>14,17</sup> For the bptz derivatives, the 1,4-dihydro-3,6-di(2-pyridyl)-1,2,4,5-tetrazine side product formed from the water traces introduced with Cu(BF<sub>4</sub>)<sub>2</sub> was separated out.<sup>14</sup> Complex **5**(BF<sub>4</sub>)<sup>10,11</sup> was prepared as described previously.

X-Band EPR spectra were recorded on a Bruker System ESP 300 equipped with an ENI A500 RF amplifier, a Bruker ER033 field frequency lock, a Bruker ER035M gaussmeter and a HP 5350B microwave counter. High field EPR spectroscopy at 245 GHz was performed using a multifrequency spectrometer,<sup>20,21</sup> measuring the transmission of the exciting radiation through the sample (infrared laser as frequency source). An InSb bolometer (QMC Instruments) was used for detection. The main magnetic field was provided by a superconducting magnet (Cryogenics Consultant) which generates fields up to 12 T. Owing to different field sweep conditions the absolute values of the  $g$  components were obtained by calibrating the precisely measured  $g$  anisotropy data with the isotropic  $g$  value from X-band measurements. While this procedure does not account for the temperature dependence of  $g$ , the values extracted are identical with those obtained using an added standard.

## Acknowledgements

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