

# 'Inverse Cryptate' Structure of an Exceptionally Stable Dicopper(I) Semiquinonoid Intermediate†

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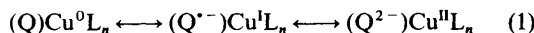
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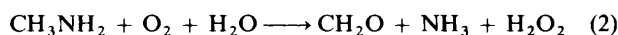
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Dinuclear diphosphinecopper(I) complexes of the bis(chelating) 'S-frame' ligand di-*tert*-butyl azodiformate exhibit a remarkable kinetic and thermodynamic stability of the deep blue *o*-semiquinonoid intermediate as evident from its facile formation, stability towards air and protic media, and from the electrochemical potential range. The comproportionation constant of  $[\text{Cu}^{\text{I}}_2\{\mu\text{-N}_2[\text{CO}(\text{OBu}^t)]_2\}\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2\}_2]^+$  was established at  $10^{19.7}$ . The crystal structure of the tetraphenylborate salt has been determined. It shows an 'inverse cryptate' structure; two bridging diphosphine ligands span the two bridgehead copper(I) centres which are fixed at 4.82 Å apart by the bis(chelating) azodicarboxylate anion radical. In contrast to the neutral (reduced) form of the complex, the dicationic oxidised state could only be studied spectroelectrochemically.

*o*-Semiquinone ( $\text{Q}^{\cdot-}$ ) complexes of copper(I) can be related *via* intramolecular electron-transfer equilibria to the copper(0)-*o*-quinone<sup>1</sup> and copper(II)-catecholate forms [equation (1)].<sup>2</sup> A

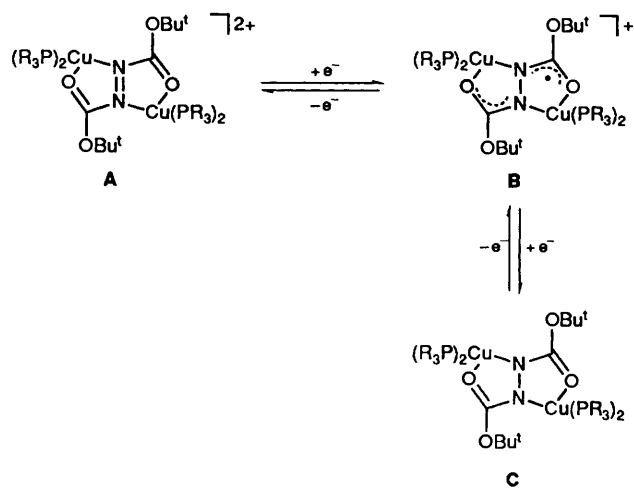


reversible equilibrium between the copper(I)-semiquinone and copper(II)-catecholate states has recently been invoked in the functioning of certain amine oxidases.<sup>3,4</sup> It was suggested that methylamine oxidase of *arthrobacter* P1 contains an *o,p*-quinonoid cofactor, identified as 6-hydroxydopa<sup>5</sup> [(3,4,6-trihydroxyphenyl)alanine] which interacts with a copper centre in order to bring about the two-electron reduction of methylamine to formaldehyde by dioxygen [equation (2)].<sup>3,4</sup> Although



no evidence for direct coordination of the copper centre with the cofactor could be provided, specific copper-cofactor interactions were deduced from absorption, resonance-Raman and reactivity studies of copper-containing and -depleted enzymes.<sup>4</sup>

In this report we demonstrate that radical-ion intermediates **B** in Scheme 1 of the semiquinone type can be stabilized to an exceptional extent through chelate co-ordination of two copper(I) species  $\text{Cu}(\text{PR}_3)_2^+$ .<sup>6,7</sup> The stabilization of compound **B** in Scheme 1 is both kinetic, facilitating isolation, and thermodynamic, as evidenced by an increase in the electrochemical potential range for the paramagnetic intermediates. As the bis(chelating) ligand we employed the di-*tert*-butyl ester of azodiformic acid (azodicarboxylic acid).<sup>8</sup> This 'S-frame'<sup>8,9</sup> ligand (see Scheme 2) contains two electronically coupled redox-active 1,4-dihetero-1,3-diene functions  $\text{O}=\text{C}=\text{N}=\text{N}$  which can co-ordinate to two metal centres forming edge-shared five-membered chelate rings. Since the co-ordinatively bifunctional azo group  $\text{N}=\text{N}$  has virtually the same electron affinity as that



Scheme 1

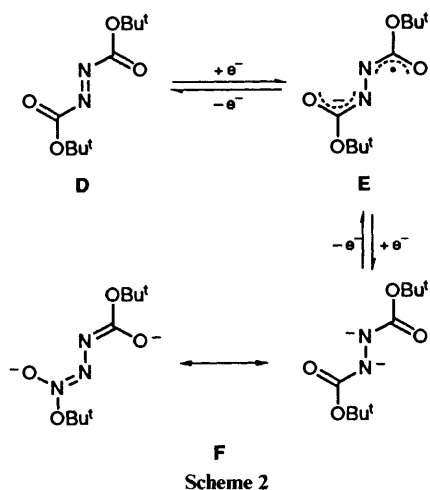
of a carbonyl group  $\text{C}=\text{O}$ ,<sup>10</sup> the azodicarbonyl ligands behave like a small, conjugated bis(*o*-quinonoid) two-step redox system (Scheme 2).<sup>8</sup> As in proper quinone redox systems, the doubly reduced form **F** is electronically stabilized, here by a carbonyl-amide-type resonance.

Arylphosphine complexes of  $\text{Cu}^{\text{I}}$  have attracted much attention recently because of their potential antitumour activities.<sup>11,12</sup> Another possible application is the use of such stable complexes with  $^{62}\text{Cu}$  ( $t_{1/2} = 9.7$  min) in positron emission tomography (PET).<sup>12</sup>

## Results and Discussion

**Synthesis and Electrochemistry.**—Tetraphenylborate salts of the dinuclear radical complexes  $[\text{Cu}^{\text{I}}_2\{\mu\text{-N}_2[\text{CO}(\text{OBu}^t)]_2\}\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}_2]^+$  ( $n = 6$   $1^+$  or  $5$   $2^+$ ) were obtained as stable deep blue compounds *via* the slow, stepwise reduction of di-*tert*-butyl azodiformate (dbadf) with elemental copper in the presence of phosphine, air and wet methanol [equation (3)].<sup>13a</sup> The necessity for  $\text{O}_2$  (activated by  $\text{Cu}^{\text{I}}$ )<sup>13b</sup> and water

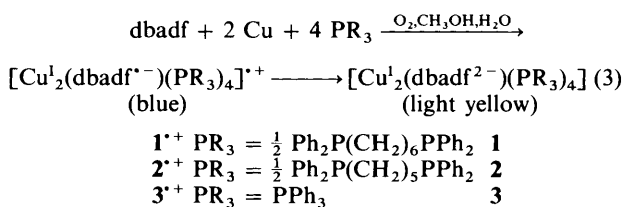
† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



**Table 1** Redox potentials of di-*tert*-butyl azodiformate and of its dicopper(I) complexes<sup>a</sup>

Compound (radical form)	$E_1$	$E_2$	$\Delta E_{pp}$ <sup>b</sup> $K_c$ <sup>c</sup>
$[\text{N}_2\{\text{CO}(\text{OBu}^t)\}_2]^{1-}$	-1.13	-1.84 (pc)	0.67 (10 <sup>11</sup> )
$1^{*+}$	+0.29 <sup>d</sup>	-0.87	1.16 (10 <sup>19.7</sup> )
$2^{*+}$	> +0.5 (pa) <sup>e</sup>	-0.85	> 1.3 (10 <sup>22</sup> )
$3^{*+}$	+0.25 (qr) <sup>f</sup>	-0.74 (pc) <sup>g</sup>	0.94 (10 <sup>16</sup> )

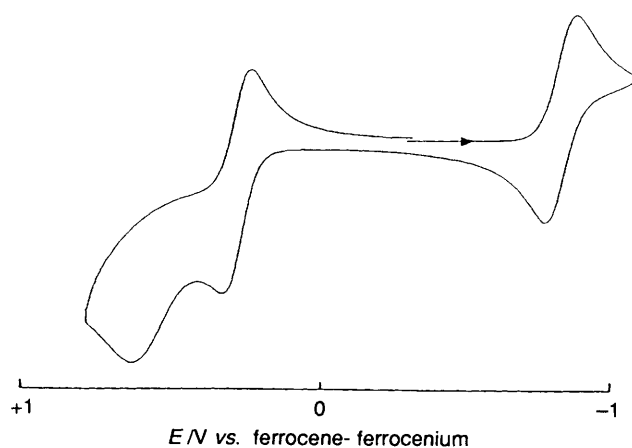
<sup>a</sup> Measurements in dichloromethane-0.1 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub>. Potentials in V vs. ferrocene-ferrocenium couple. Cathodic (pc) and anodic (pa) peak potentials from cyclic voltammetry at 100 mV s<sup>-1</sup> are listed for irreversible processes. <sup>b</sup> Differences between corresponding peak potentials for oxidation and reduction of intermediate. <sup>c</sup> Approximate values (upper limit) in parentheses for redox systems involving irreversible processes. <sup>d</sup> Followed by irreversible wave with anodic peak potential at +0.62 V. <sup>e</sup> Overlapping with irreversible oxidation wave at an anodic peak potential of +0.53 V. <sup>f</sup> Quasi-reversible wave with peak-potential difference of 100 mV, followed by irreversible oxidation wave at +0.7 V anodic peak potential. <sup>g</sup> Distorted wave with strongly shifted reverse peak potential at -0.42 V.



(stabilization of Cu<sup>II</sup>) suggests an electron-transfer mechanism involving the O<sub>2</sub>-O<sub>2</sub><sup>•-</sup>, Cu-Cu<sup>+</sup>-Cu<sup>2+</sup> and dbadf<sup>0/+/-2-</sup> couples.<sup>13a</sup> Coloured intermediates in the stepwise reactions of azodiformic acid esters with metal species have been reported.<sup>13c</sup>

Electron paramagnetic resonance data<sup>13a</sup> indicate unambiguously the anion radical complex character of the paramagnetic salts; small *g* anisotropies ( $\Delta g < 0.01$ ) as well as small <sup>63</sup>Cu, <sup>65</sup>Cu and <sup>31</sup>P coupling constants of less than 2 mT rule out a copper(II) formulation. The radical complexes thus bear some resemblance to the triple ions of reduced di-*tert*-butyl azodiformate with organometallic or alkali-metal cations.<sup>14</sup>

The anodic potential shifts corresponding to the reduction (Table 1) of the unsaturated  $\pi$  system in Scheme 2 upon metal complexation are typical;<sup>15</sup> this effect contributes to the decreased sensitivity of anion radical complexes towards electrophiles such as O<sub>2</sub> or H<sup>+</sup> and thus facilitates their



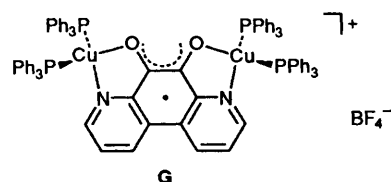
**Fig. 1** Cyclic voltammogram of  $1^{*+} \text{BPh}_4^-$  in CH<sub>2</sub>Cl<sub>2</sub>-0.1 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub> at 100 mV s<sup>-1</sup> scan rate

isolation. Most unexpected, however, is the vastly increased stability of the radical intermediates  $1^{*+}$ ,  $2^{*+}$ , or  $[\text{Cu}_2\{\mu\text{-N}_2[\text{CO}(\text{OBu}^t)]_2\}(\text{PPh}_3)_4]^{*+}$   $3^{*+}$  with respect to redox disproportionation [Scheme 1, equation (4)]. Whereas the semi-

$$K_c = \frac{[\text{semiquinone}]^2}{[\text{azo form}][\text{hydrazido form}]} = 10^{\Delta E/59 \text{ mV}} \quad (4)$$

quinonoid intermediate form of the free ligand (Scheme 2) and of its previously characterized dinuclear complex<sup>8</sup> with  $[\text{Ru}(\text{bipy})_2]^{2+}$  (bipy = 2,2'-bipyridine) show similar<sup>15</sup> stability ranges of about 0.6–0.7 V between oxidation to the azo and reduction to the hydrazido(2-) form, the copper complexes  $1^{*+}$  and  $2^{*+}$  display an increase of this stability range by more than eight orders of magnitude (Table 1).

The dicopper radical cation  $1^{*+}$  shows reversible waves (Fig. 1) for reduction and oxidation at potentials which yield the extremely large comproportionation constant of  $K_c = 10^{19.7}$  for the paramagnetic 'intermediate'. Beyond the reversible oxidation of the semiquinone ligand, there are irreversible oxidation processes, involving either the copper(I) centres or the phosphine ligands at higher potentials (Fig. 1). Dinuclear copper(I)-azodiformate radical complexes with other phosphine ligands<sup>13a</sup> such as  $2^{*+}$  or  $3^{*+}$  are not oxidized reversibly or display distorted reduction waves (Table 1). A previously characterized dinuclear copper(I) *o*-semiquinone complex **G** showed both irreversible (dissociative) oxidation and irreversible reduction.



**Molecular Structure.**—The enormous increase in electrochemical stability of the azodicarbonyl radical intermediates after co-ordination by copper(I) fragments may be caused by electronic or steric effects. It is well established that copper(I) is highly flexible in adopting unusual co-ordination arrangements,<sup>16</sup> thereby allowing unusual structures with the copper atom(s) in an environment of the 'supramolecular' type.

The radical salt  $[\text{Cu}_2\{\mu\text{-N}_2[\text{CO}(\text{OBu}^t)]_2\}(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2)_2] \text{BPh}_4$  crystallized from tetrahydrofuran (thf)-Et<sub>2</sub>O as a labile solvate which could be studied crystallographically despite some loss of solvent during the investigation. The unit cell contains discrete dicopper cations and tetraphenylborate anions separated by normal van der Waals contact distances. A

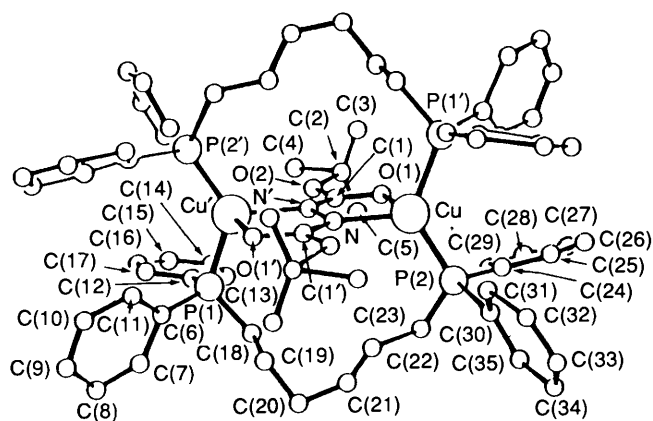


Fig. 2 Structure of the dicopper radical cation in the crystal of  $[\text{Cu}_2\{\text{N}_2[\text{CO}(\text{OBu}')]\}_2]\{\text{Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2\}_2\text{BPh}_4$ , showing the atom labelling scheme (side-view on the Cu–Cu axis). There are two crystallographically independent cations in the unit cell each at a centre of inversion; only one is shown since the other is geometrically equivalent

Table 2 Selected interatomic distances (Å) and angles (°) for  $[\text{Cu}_2\{\mu\text{-N}_2[\text{CO}(\text{OBu}')]\}_2]\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2\}_2\text{BPh}_4$

Cu(A)···Cu(A')	4.828(3)	Cu(B')···Cu(B')	4.819(3)
Cu(A)–P(1A')	2.249(4)	Cu(B)–P(1B')	2.244(4)
Cu(A)–P(2A)	2.247(4)	Cu(B)–P(2B)	2.242(5)
Cu(A)–O(1A)	2.324(17)	Cu(B)–O(1B)	2.316(14)
Cu(A)–N(A)	2.050(15)	Cu(B)–N(B)	2.007(13)
O(1A)–C(1A)	1.243(19)	O(1B)–C(1B)	1.236(19)
O(2A)–C(1A)	1.265(23)	O(2B)–C(1B)	1.235(21)
C(1A)–N(A')	1.369(20)	C(1B)–N(B')	1.369(22)
N(A)–N(A')	1.246(31)	N(B)–N(B')	1.308(26)
P(1A')–Cu(A)–P(2A)	122.9(2)	P(1B')–Cu(B)–P(2B)	122.9(2)
P(1A')–Cu(A)–O(1A)	105.6(3)	P(1B')–Cu(B)–O(1B)	99.1(3)
P(1A')–Cu(A)–N(A)	115.9(4)	P(1B')–Cu(B)–N(B)	115.5(4)
P(2A)–Cu(A)–O(1A)	102.1(4)	P(2B)–Cu(B)–O(1B)	107.4(3)
P(2A)–Cu(A)–N(A)	119.5(4)	P(2B)–Cu(B)–N(B)	120.4(4)
O(1A)–Cu(A)–N(A)	73.9(6)	O(1B)–Cu(B)–N(B)	73.0(5)

side-view of the structure of the paramagnetic cation is shown in Fig. 2. Table 2 lists selected interatomic distances and angles in the cation and Table 3 the fractional atomic coordinates.

In complex cation  $1^{+}$  the two approximately tetrahedrally co-ordinated copper centres are bridged by a virtually planar six-centre  $\pi$  system of the azodicarbonyl anion radical ligand. In contrast to what might have been expected,<sup>7,13a</sup> however, the rather long chain diphosphine ligands do not chelate at a single metal centre to give conformationally unfavourable nine-membered rings; instead, the rather small distance of 4.82 Å imposed<sup>8,9</sup> by the geometry of the edge-shared five-membered chelate rings of the S-frame bridging ligand (see Schemes 1 and 2) allows additional intramolecular bridging of the two copper(I) centres. The metals are thus bridged on the outside by two diphosphines and from within by the bis(chelating) radical ligand (Fig. 2). The eight phenyl rings and two Bu' groups are positioned so as effectively to protect the metal–radical–metal core from attack (Figs. 2 and 3).

By analogy with normal cryptates containing a labile metal cation fixed by bridgehead nitrogen atoms and protected from the outside by hydrophobic shielding groups,<sup>17</sup> the complex  $1^{+}$  may be viewed as an 'inverse cryptate' in which a central radical ion is stabilized through co-ordination by two copper(I) centres and protected from the environment *via* two bridging diphosphines.

Despite the relatively large standard deviations in the bonding parameters, certain bond lengths of the radical

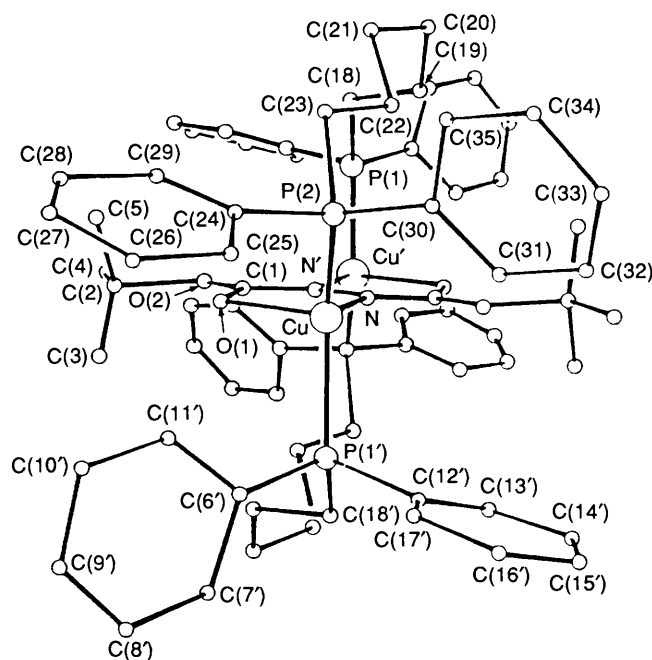
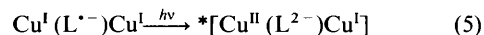


Fig. 3 Structure of the dicopper radical cation viewed along the Cu–Cu axis

complex (Table 2) allow an assessment of the contributions from resonance structures such as F in Scheme 2. The short Cu–N ( $\approx 2.02$  Å) but long Cu–O bonds ( $\approx 2.32$  Å) suggest that co-ordination of the soft copper(I) centres favours the hydrazido(2–) formulation which is also the result of a  $2e/2H$  reduction. The Cu–P bond lengths and P–Cu–P angles are normal,<sup>18</sup> there being no detectable tendency towards a  $3 + 1$  co-ordination which may occur with  $\text{Cu}^{\text{I}}$ .<sup>16</sup> The distances within the radical  $\pi$  system can only give a rough indication of how the bond orders change on co-ordination; the N=N and C=O bond distances are still in the region typical of double bonds<sup>9b</sup> whereas the N–C distance corresponds to a bond order of about 1.3.<sup>19</sup>

**Spectroelectrochemistry.**—While the yellow reduced forms  $1^{-}$ – $3^{-}$  are readily obtained as diamagnetic stable species by allowing reaction (3) to proceed to completion, the dicationic oxidized species of these two-step redox systems could not be isolated because of their high irreversible steps (Fig. 1). Nevertheless, careful application of spectroelectrochemical techniques using a specially designed cell<sup>20</sup> permitted the observation of the absorption spectrum of the species  $1^{2+}$  (Fig. 4).

Whereas the neutral complex **1** between electron-rich  $\text{Cu}^{\text{I}}$  and the reduced azodiformate ligand displays no low-energy absorption bands, the monocationic radical complexes such as  $1^{+}$  are distinguished by a single intense metal-to-ligand charge transfer (m.l.c.t.) band ( $d_{xz} \rightarrow \pi_1^*$ )<sup>16c</sup> in the visible region at about 700 nm (Fig. 4). Equation (5) involves a photoinduced intramolecular electron transfer formulation [*cf.* equation (1)].



In agreement<sup>8a</sup> with this assignment, the dication  $1^{2+}$  shows an m.l.c.t. transition at even lower energy, *i.e.* in the near-infrared region at about 1100 nm (Fig. 4); the filled metal d levels are strongly stabilized upon formation of the basic anion radical so that the energy of the m.l.c.t. transition to the ligand  $\pi_1^*$  level is larger for the singly reduced, *i.e.* the radical form, than for the non-reduced state.<sup>8a</sup> Eventual full occupation of  $\pi_1^*$  on double reduction leaves no possibility for low-lying

**Table 3** Fractional atomic coordinates ( $\times 10^4$ ) for  $[\text{Cu}_2\{\mu\text{-N}_2[\text{CO}(\text{O}i\text{Bu})]_2\}_2\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2\}_2]\text{BPh}_4$ 

Atom	x	y	z	Atom	x	y	z
Cu(A)	827(1)	788(1)	4 091(1)	Cu(B)	-4 045(1)	4 087(1)	9 310(1)
P(1A)	-430(3)	-2 174(2)	6 043(2)	P(1B)	-7 338(2)	6 446(2)	10 261(2)
P(2A)	1 938(2)	148(2)	3 440(2)	P(2B)	-4 511(2)	3 829(2)	8 286(2)
O(1A)	-349(10)	541(8)	3 632(7)	O(1B)	-4 149(7)	5 500(8)	8 964(7)
O(2A)	-1 380(9)	-6(9)	4 225(10)	O(2B)	-4 846(9)	6 577(8)	9 401(9)
N(A)	340(8)	83(8)	5 039(10)	N(B)	-4 900(8)	4 599(7)	10 031(8)
C(1A)	-672(9)	164(9)	4 220(8)	C(1B)	-4 651(9)	5 831(9)	9 414(8)
C(2A)	-1 847(13)	322(14)	3 365(12)	C(2B)	-4 481(13)	7 180(11)	8 720(14)
C(3A)	-2 177(17)	1 227(14)	3 165(16)	C(3B)	-5 009(27)	7 361(21)	8 046(17)
C(4A)	-2 695(16)	-47(22)	3 601(20)	C(4B)	-3 568(18)	6 988(15)	8 762(20)
C(5A)	-1 372(17)	-172(15)	2 917(11)	C(5B)	-4 930(32)	7 959(20)	8 846(27)
C(6A)	-116(7)	-2 849(5)	6 993(5)	C(6B)	-8 035(6)	5 987(6)	10 995(5)
C(7A)	220(7)	-3 717(5)	7 131(5)	C(7B)	-8 076(6)	5 187(6)	11 041(5)
C(8A)	478(7)	-4 224(5)	7 882(5)	C(8B)	-8 495(6)	4 771(6)	11 663(5)
C(9A)	400(7)	-3 865(5)	8 495(5)	C(9B)	-8 873(6)	5 156(6)	12 239(5)
C(10A)	64(7)	-2 998(5)	8 357(5)	C(10B)	-8 832(6)	5 956(6)	12 193(5)
C(11A)	-194(7)	-2 490(5)	7 606(5)	C(11B)	-8 413(6)	6 372(6)	11 571(5)
C(12A)	-1 291(7)	-2 493(7)	5 780(5)	C(12B)	-7 838(6)	7 556(8)	10 031(8)
C(13A)	-1 468(7)	-2 382(7)	5 001(5)	C(13B)	-8 737(6)	7 919(8)	9 983(8)
C(14A)	-2 178(7)	-2 584(7)	4 801(5)	C(14B)	-9 088(6)	8 789(8)	9 797(8)
C(15A)	-2 711(7)	-2 897(7)	5 381(5)	C(15B)	-8 540(6)	9 296(8)	9 661(8)
C(16A)	-2 534(7)	-3 007(1)	6 161(5)	C(16B)	-7 641(6)	8 933(8)	9 709(8)
C(17A)	-1 824(7)	-2 806(7)	6 360(5)	C(17B)	-7 290(6)	8 063(8)	9 894(8)
C(18A)	429(11)	-2 537(10)	5 429(9)	C(18B)	-7 562(11)	6 197(9)	9 378(8)
C(19A)	1 327(11)	-2 546(12)	5 700(11)	C(19B)	-7 142(10)	6 630(10)	8 682(10)
C(20A)	2 118(12)	-2 893(12)	5 273(12)	C(20B)	-7 322(10)	6 443(10)	7 932(9)
C(21A)	2 053(15)	-2 375(10)	4 412(13)	C(21B)	-6 989(10)	5 519(10)	7 943(10)
C(22A)	2 089(15)	-1 454(11)	4 392(12)	C(22B)	-6 024(9)	5 142(10)	8 039(10)
C(23A)	1 973(13)	-931(10)	3 524(9)	C(23B)	-5 685(8)	4 206(9)	8 133(9)
C(24A)	1 813(8)	591(8)	2 373(7)	C(24B)	-4 074(8)	4 268(8)	7 344(6)
C(25A)	2 188(8)	1 220(8)	1 991(7)	C(25B)	-3 453(8)	4 680(8)	7 326(6)
C(26A)	2 058(8)	1 589(8)	1 192(7)	C(26B)	-3 048(8)	4 956(8)	6 629(6)
C(27A)	1 553(8)	1 329(8)	774(7)	C(27B)	-3 264(8)	4 819(8)	5 949(6)
C(28A)	1 178(8)	700(8)	1 155(7)	C(28B)	-3 886(8)	4 406(8)	5 967(6)
C(29A)	1 308(8)	332(8)	1 954(7)	C(29B)	-4 291(8)	4 131(8)	6 664(6)
C(30A)	3 026(8)	159(9)	3 632(8)	C(30B)	-4 208(7)	2 731(7)	8 329(8)
C(31A)	3 124(8)	605(9)	4 135(8)	C(31B)	-4 801(7)	2 269(7)	8 458(8)
C(32A)	3 947(8)	639(9)	4 278(8)	C(32B)	-4 510(7)	1 410(7)	8 534(8)
C(33A)	4 672(8)	227(9)	3 919(8)	C(33B)	-3 625(7)	1 012(7)	8 482(8)
C(34A)	4 573(8)	-219(9)	3 416(8)	C(34B)	-3 033(7)	1 474(7)	8 353(8)
C(35A)	3 750(8)	-254(9)	3 273(8)	C(35B)	-3 324(7)	2 333(7)	8 276(8)
B	2 008(12)	2 510(12)	8 078(10)	C(48)	2 731(7)	1 571(7)	8 484(6)
C(36)	1 668(5)	3 054(6)	8 732(5)	C(49)	3 010(7)	986(7)	8 057(6)
C(37)	823(5)	3 218(6)	9 014(5)	C(50)	3 633(7)	221(7)	8 374(6)
C(38)	577(5)	3 688(6)	9 549(5)	C(51)	3 976(7)	40(7)	9 117(6)
C(39)	1 176(5)	3 994(6)	9 801(5)	C(52)	3 696(7)	625(7)	9 544(6)
C(40)	2 021(5)	3 830(6)	9 519(5)	C(53)	3 074(7)	1 390(7)	9 227(6)
C(41)	2 267(5)	3 360(6)	8 985(5)	C(54)	2 464(8)	3 078(7)	7 367(7)
C(42)	1 143(7)	2 292(6)	7 764(5)	C(55)	2 007(8)	3 917(7)	7 037(7)
C(43)	777(7)	1 739(6)	8 307(5)	C(56)	2 392(8)	4 430(7)	6 468(7)
C(44)	52(7)	1 566(6)	8 102(5)	C(57)	3 234(8)	4 103(7)	6 228(7)
C(45)	-308(7)	1 944(6)	7 354(5)	C(58)	3 692(8)	3 264(7)	6 557(7)
C(46)	58(7)	2 497(6)	6 811(5)	C(59)	3 307(8)	2 751(7)	7 127(7)
C(47)	784(7)	2 671(6)	7 016(5)				

m.l.c.t. transitions because there is a large energetic gap to the next unoccupied  $\pi_2^*$  molecular orbital.<sup>21</sup>

### Conclusion

While the interaction between copper, oxygen and quinonoid species is of some importance in the areas of bioinorganic chemistry [cf. equation (2)]<sup>22</sup> and catalysis,<sup>23</sup> it should be noted here that the combination of triarylphosphine, azodiformic acid diester and alcohol used in the syntheses of **1-3** is also essential for the Mitsunobu dehydration reaction which has found wide application in organic synthesis.<sup>24</sup> We therefore plan to study the influence of copper on this transformation.

Paramagnetic complex **1**<sup>+</sup>, although exceptionally stable, is not the first persistent dicopper(I) radical species; cation **G** could only be obtained as a radical<sup>6</sup> but cation **H** was suf-

ficiently stable for crystallographic studies.<sup>7</sup> The reasons for the remarkable stabilization of anion radical ligands by coordination of d<sup>10</sup> metal centres<sup>25</sup> are under further investigation.

### Experimental

Materials were used as commercially available. The complexes were prepared under air. Microanalyses were performed by Labor Paschen (Remagen, Germany).

*Instrumentation.*—The UV/VIS/NIR spectra were taken with a spectroelectrochemistry cell<sup>20</sup> on a Bruins Instruments Omega 10 spectrometer. The electrochemical equipment consisted of a PAR model 363/175 potentiostat and ramp generator. A three-electrode cell was used with a glassy carbon working electrode, a platinum counter electrode and Ag-AgCl

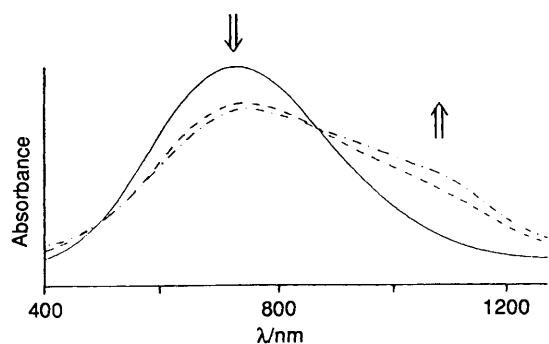
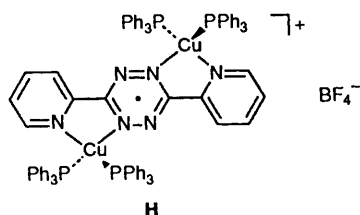


Fig. 4 Spectroelectrochemical (VIS/NIR) oxidation (—, ---, - · - · -) of  $[\text{Cu}_2\{\text{N}_2[\text{CO}(\text{O}i\text{Bu})]_2\}\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2\}_2]\text{BPh}_4$  in dichloromethane-0.1 mol  $\text{dm}^{-3}$   $\text{NBu}_4\text{ClO}_4$ . The arrows indicate the spectral changes caused by the conversion of the radical cation ( $\lambda_{\text{max}}$  725 nm,  $\epsilon_{\text{max}}$  4400  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) into the dication



as reference. The ferrocene-ferrocenium couple served as pilot system in dried and redistilled halogenocarbon solvents (0.1 mol  $\text{dm}^{-3}$   $\text{NBu}_4\text{ClO}_4$ ).

**Preparations.**— $[\text{Cu}_2\{\mu\text{-N}_2[\text{CO}(\text{O}i\text{Bu})]_2\}\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2\}_2]\text{BPh}_4$   $1^+ \text{BPh}_4^-$ . Di-*tert*-butyl azodiformate (115 mg, 0.5 mmol) and 1,6-bis(diphenylphosphino)hexane (454 mg, 1.0 mmol) were dissolved in methanol (2% water) (50  $\text{cm}^3$ ) and treated with copper powder (63 mg, 1 mmol). The mixture was heated briefly to reflux (10 min) and then vigorously stirred under air at room temperature. After 54 h a deep blue colour had developed. The product was precipitated by adding sodium tetraphenylborate (513 mg) in methanol (10  $\text{cm}^3$ ), was washed with methanol (50  $\text{cm}^3$ ) and diethyl ether (20  $\text{cm}^3$ ), dissolved in dichloromethane (25  $\text{cm}^3$ ) and filtered. Removal of the solvent and drying *in vacuo* yielded 407 mg (0.26 mmol, 51%) of the product (Found: C, 70.95; H, 6.55; B, 0.75; Cu, 6.8; N, 1.55; P, 7.65.  $\text{C}_{94}\text{H}_{102}\text{BCu}_2\text{N}_2\text{O}_4\text{P}_4$  requires C, 71.20; H, 6.50; B, 0.70; Cu, 8.00; N, 1.75; P, 7.80%). IR ( $\text{CH}_2\text{Cl}_2$ ): 1608  $\text{cm}^{-1}$ . UV/VIS (MeOH): 13 790  $\text{cm}^{-1}$ . EPR (MeOH, 300 K)  $g$  2.0104;  $a(^{63}\text{Cu})$  1.652,  $a(^{65}\text{Cu})$  1.769,  $a(^{31}\text{P})$  1.856,  $a(^{14}\text{N})$  0.640 mT; (frozen  $\text{CH}_2\text{Cl}_2$  solution) single line, peak-to-peak linewidth 5 mT.<sup>13a</sup>

$[\text{Cu}_2\{\mu\text{-N}_2[\text{CO}(\text{O}i\text{Bu})]_2\}\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_5\text{PPh}_2\}]\text{BPh}_4$   $2^+ \text{BPh}_4^-$ . This complex was obtained as a more sensitive, EPR-active species<sup>13a</sup> in an analogous fashion, using 1,5-bis(diphenylphosphino)pentane. Recrystallization from  $\text{thf-Et}_2\text{O}$  (5:1) and drying *in vacuo* yielded 21% of the product (Found: C, 70.60; H, 6.40; N, 1.70.  $\text{C}_{92}\text{H}_{98}\text{BCu}_2\text{N}_2\text{O}_4\text{P}_4$  requires C, 70.95; H, 6.30; N, 1.80%). UV/VIS (MeOH): 13 890  $\text{cm}^{-1}$ . EPR (MeOH, 300 K):  $g$  2.0098;  $a(^{63}\text{Cu})$  1.570,  $a(^{65}\text{Cu})$  1.681,  $a(^{31}\text{P})$  1.856,  $a(^{14}\text{N})$  0.634 mT.<sup>13a</sup>

$[\text{Cu}_2\{\text{N}_2[\text{CO}(\text{O}i\text{Bu})]_2\}(\text{PPh}_3)_4]$  **3**. Di-*tert*-butyl azodiformate (115 mg, 0.5 mmol) and triphenylphosphine (553 mg, 2.0 mmol) were dissolved in methanol (2% water) (50  $\text{cm}^3$ ) and treated with copper powder (63 mg, 1 mmol). The mixture was heated to reflux for 10 min and then vigorously stirred under air at room temperature. After 20 h the intermediate blue colour of the radical cation had disappeared and the compound was collected as a yellow precipitate together with some copper powder. Removal of remaining  $\text{PPh}_3$  by washing with diethyl ether, dissolution in acetone, filtration from Cu and removal of the solvent under vacuum yielded 525 mg (0.37 mmol, 75%) of

the product (Found: C, 69.25; H, 5.60; N, 2.15.  $\text{C}_{82}\text{H}_{78}\text{BCu}_2\text{N}_2\text{O}_4\text{P}_4$  requires C, 70.00; H, 5.60; N, 2.00%). UV/VIS ( $\text{CH}_2\text{Cl}_2$ ): 38 320  $\text{cm}^{-1}$ . EPR of the one-electron-oxidized form (in MeOH, 300 K):  $g$  2.0102;  $a(^{63}\text{Cu})$  1.607,  $a(^{65}\text{Cu})$  1.721,  $a(^{31}\text{P})$  1.872,  $a(^{14}\text{N})$  0.640 mT.<sup>13a</sup>

**X-Ray Crystallography.**—Deep blue crystals of  $1^+ \text{BPh}_4^-$  were grown by diffusion of  $\text{Et}_2\text{O}$  into a saturated  $\text{thf}$  solution. A crystal of approximate dimensions 0.57 × 0.15 × 0.19 mm was mounted in a thin-walled capillary. Preliminary Weissenberg photographs showed the reflections to be rather diffuse and generally fairly weak but it was not possible to locate another crystal which gave a better defined diffraction pattern. Lack of facilities precluded data collection at a low temperature.

**Crystal data.**  $\text{C}_{94}\text{H}_{102}\text{BCu}_2\text{N}_2\text{O}_4\text{P}_4$ ,  $M = 1585.7$ , triclinic, space group  $P\bar{1}$ ,  $a = 16.156(3)$ ,  $b = 17.430(2)$ ,  $c = 17.940(2)$  Å,  $\alpha = 73.25(1)$ ,  $\beta = 85.71(1)$ ,  $\gamma = 72.30(1)^\circ$ ,  $U = 4608(1)$  Å<sup>3</sup> (obtained from a least-squares refinement using the setting angles of 25 carefully centred reflections with  $\theta > 12^\circ$ ),  $Z = 2$ ,  $D_c = 1.147$  g  $\text{cm}^{-3}$ ,  $\lambda = 0.71069$  Å for Mo-K $\alpha$  radiation,  $F(000) = 1670$ ,  $\mu = 6.01$   $\text{cm}^{-1}$ .

**Data collection and reduction.** Data were collected at  $22 \pm 1$  °C on a Nonius CAD4 diffractometer using graphite-monochromated Mo-K $\alpha$  radiation. The  $\omega$ - $2\theta$  scan method was employed in the range  $2 \leq 2\theta \leq 46^\circ$ , with background counts made for half the total scan time on each side of the peak. An  $\omega$  scan angle of  $0.96 + 0.35 \tan \theta$  was used, except for certain intense and very diffuse reflections which showed very unequal background counts; these were remeasured individually using a larger  $\omega$  scan angle. Three standard reflections, measured every hour, showed a small decrease of 5% in intensity during the data collection for which a linear decay correction was applied. The data were also corrected for absorption on the basis of azimuthal scan profiles.<sup>26</sup> Of a total of 10 303 unique reflections measured 7062 had  $I > 2\sigma(I)$  and these were used in the solution and refinement of the structure.

**Structure solution and refinement.** Normal heavy-atom and Fourier methods were used to locate the Cu and other non-H atoms. Each of the cations in the unit cell is situated on a centre of symmetry midway between the two Cu atoms, while the tetraphenylborate anion is located on a general equivalent position. For the purposes of the final full-matrix least-squares refinement anisotropic thermal parameters were assigned to the non-H atoms and a single overall isotropic thermal parameter to the hydrogen atoms. The phenyl rings and methyl groups were refined as rigid groups of idealized geometry, all the H atoms being placed in calculated positions; because of the high thermal motion it was not possible to locate them all directly. Using the weighting scheme  $1/[\sigma^2(F) + gF^2]$  where  $g = 0.036$  the refinement of 839 parameters converged at  $R = 0.119$  and  $R' = 0.132$ . The final Fourier difference map was featureless except for a small amount of poorly defined electron density (height ca. 1.5 e Å<sup>-3</sup>) in a region of the crystal probably originally occupied by solvent molecules ( $\text{Et}_2\text{O}$  or  $\text{thf}$ , see text); indeed the volume occupied per non-H atom of 21.5 Å<sup>3</sup> is unusually large. Neutral atomic scattering factors corrected for anomalous dispersion were taken from ref. 27. All calculations were performed using the programs SHELX 86<sup>28</sup> and SHELX 76.<sup>28</sup>

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

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