

Inorganica Chimica Acta 337 (2002) 163-172

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Copper complexes with non-innocent ligands: probing Cu^{II}/catecholato-Cu^I/o-semiquinonato redox isomer equilibria with EPR spectroscopy

Wolfgang Kaim^{a,*}, Matthias Wanner^a, Axel Knödler^a, Stanislav Záliš^b

^a Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70550 Stuttgart, Germany ^b J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-18223 Prague, Czech Republic

Received 1 March 2002; accepted 17 May 2002

Dedicated to Professor Karl Wieghardt

Abstract

The temperature-dependent intramolecular metal/ligand electron transfer equilibrium (L)Cu^{II}(Q²⁻) \rightleftharpoons (L)Cu^I(Q^{•-}) has been quantitatively analyzed by EPR as a function of the non-innocent *o*-quinonoid ligand Q and of the co-ligand L. Suitable co-ligands were 1-methyl-(2-methylthiomethyl)-1*H*-benzimidazole and 1-diphenylphosphino-2-dimethylaminoethane (dde) which can tolerate both copper oxidation states. EPR hyperfine data were extracted for a variety of alkyl- and methoxy-substituted *o*-semiquinones and their copper(I) complexes in solution. A close match of Q and Cu redox orbitals is essential for observing the redox isomer equilibrium which has been similarly reported for aminoxidase enzymes. Efforts to isolate the mixed-ligand compounds from solution failed due to coordination disproportionation. The new [Cu(dde)₂](ClO₄) was structurally characterized with comparable Cu–N and Cu–P distances of 2.24–2.27 Å and a P–Cu–P angle of 142.41(5)°, the '2+2' coordination pattern could be reproduced by DFT calculations.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Copper compounds; EPR spectroscopy; Quinone ligands; Redox isomerism; Structure

1. Introduction

Jørgensen's concept of non-innocent ligands [1] in coordination chemistry has been usually employed in a static sense, e.g. questioning whether e.g. 2,2'-bipyridine [2], a dithiolene [3] or an *o*-quinone ligand [4] coordinates as a neutral species (with the metal in a low oxidation state) or as a negatively charged species with high-valent metal. Recently, Wieghardt's group has extended this approach to imino- and thio-*o*-quinones [5]. However, there is also a dynamic aspect to 'noninnocence': Intramolecular metal-to-ligand electron transfer equilibria have been observed in complexes and were circumscribed as valence tautomerism or redox isomerism [6]. This unusual phenomenon has been observed mainly for low-spin $Co^{III}(Q^{2-})/high-spin$ $Co^{II}(Q^{\bullet-})$ systems [6,7] and for $Mn^{IV}(Q^{2-})/Mn^{III}(Q^{\bullet-})$ equilibria [8]; the temperature-dependence of Eq. (1) involving copper has been found in enzymes [9] (where it may contribute to the O₂ activation by amine oxidases [10]) and, more recently, in small systems by us [11] and others [12].

$$(\mathbf{Q}^{2-})\mathbf{C}\mathbf{u}^{II}\mathbf{L} \rightleftharpoons (\mathbf{Q}^{\bullet-})\mathbf{C}\mathbf{u}^{I}\mathbf{L}$$
(1)

A first recent report on the variation of Q [11b] has indicated the very narrow range where such an equilibrium can be observed (Scheme 1).

Herein we present detailed EPR studies on the redox isomer equilibrium (1) as a function of L and Q, analyzing the position of the equilibrium and the EPR characteristics, including the EPR hyperfine structure of the semiquinones and of their Cu^{I} complexes. In addition to a more detailed EPR analysis of the

0020-1693/02/\$ - see front matter \odot 2002 Elsevier Science B.V. All rights reserved. PII: S 0 0 2 0 - 1 6 9 3 (0 2) 0 1 0 8 1 - 2

^{*} Corresponding author. Tel.: +49-711-685 4170; fax: +49-711-685 4165

E-mail address: kaim@iac.uni-stuttgart.de (W. Kaim).





combination with L = mmb = 1-methyl-2-(methylthiomethyl)-1*H*-benzimidazole and $Q = Q^1 - Q^6$, we now studied a wider variety of components in order to probe the conditions for such redox isomer equilibria (Scheme 2).

In one approach, the *o*-quinone/catechol ligand system was replaced by the imino-*o*-quinone/*o*-aminophenol pair Q^A/H_2Q^A while keeping mmb as auxiliary, Cu^{I} - and Cu^{II} -tolerant [13] ligand. We also used an electron-poor biological *o*-quinone, pyrroloquinolinequinone (PQQ) [14] as the trimethyl ester PQQTME [15], in combination with copper and mmb. In yet another variation we combined the standard 3,5-di-*tert*butyl-*o*-quinone Q³ with 1-diphenylphosphino-2-dimethylaminoethane (dde) [16]. As in mmb [11], the mixed donor set of dde was introduced to stabilize both Cu^{II} (through N) and Cu^{I} (through P), thereby allowing us to detect both states of equilibrium (1) with their very different EPR signature [17].

In the course of attempts to isolate corresponding mixed-ligand compounds we also obtained a structure of $[Cu(dde)_2](ClO_4)$, which was reproduced by DFT calculations.

2. Results and discussion

2.1. Redox isomer equilibrium analysis

The equilibrium (1) can be produced by combining the components L, Q^{n-} and Cu^{n+} (n = 0, 1 or 2) [11]. A most convienient method, if the quinone state (n = 0) is available, is to use activated copper metal [11b]. The new systems with Q = PQQTME and L = mmb or Q = Q³ and L = dde have been produced accordingly in THF or toluene solution. As an alternative, a copper(II) salt may be used (n = 2) in combination with a dihydro form H₂Q in the presence of a base. *o*-Aminophenol H₂Q⁴, the related *o*-aminothiophenol H₂Q^B and *o*-phenylenediamine H₂Q^C have thus been reacted in dry THF with anhydrous CuCl₂, the H₂Q compounds serving simultaneously as deprotonating base. The following results were obtained.

2.1.1. Q = PQQTME, L = mmb

PQQTME, a rather electron-poor quinone [15b] (Table 1), yields only the copper(II)/catecholate form (mmb)Cu^{II}(PQQTME²⁻) according to EPR spectroscopy between 110 and 320 K in toluene or THF solution. The experiment in THF gave poorly resolved spectra due to a temperature-dependent equilibrium between two copper(II) species, which we tentatively attribute to coordination mode changes of the isoambialterdentate ligand PQQTME [14,15] in the presence of potentially coordinating THF. The EPR data are summarized in Table 2.

The comparatively less negative potential of PQQTME°/ \bullet^- at -0.80 V versus ferrocenium/ferrocene (Table 1) is responsible for this result, i.e. the absence of EPR-detectable redox isomerism.

2.1.2. $Q = Q^3$, L = dde

The standard *o*-quinone, 3,5-di-*tert*-butyl-*o*-quinone Q^3 , was reacted with copper and the mixed N–P donor bidentate ligand dde. Similarly as mmb [11], dde combines a Cu^{II}-preferring nitrogen donor atom (here trialkylamine N) and a Cu^I-preferring 'soft' donor center, here phosphane P instead of thioether S. As will be shown later through the structure of [Cu(dde)₂]⁺, dde can coordinate to Cu^I to form a five-membered chelate ring with relatively stronger Cu–P than Cu–N bonds.

The product of this reaction is a redox isomer equilibrium (1) as evident from temperature-dependent EPR spectroscopy (Fig. 1)

At the low- and high-temperature limits the EPR spectra could be analyzed, however, the g_{\perp} region of the Cu^{II} was poorly resolved. As previously noted for the amine oxidase enzyme [9] and for synthetic systems (1) with L = mmb [11b], the copper(II) form is the more stable, the low-temperature form; the semiquinone EPR spectrum of the high-temperature species (dde)Cu^I- [(Q³)[•]] is shown in Fig. 2.

The EPR data, g-factors and hyperfine information, are listed in Tables 2 and 3.

The equilibrium (1) has been quantitatively analyzed as described previously [11b]: the relative amounts I_k of the Cu^I/o-semiquinonato (I_I) and Cu^{II}/catecholato (I_{II}) forms were approximated at various temperatures through double integration of the EPR spectrum. Parameters A and B of the linear Eq. (2) are summarized in Table 1.

$$\ln(\mathbf{I}_{\mathrm{I}}/\mathbf{I}_{\mathrm{II}}) = A/T + B \tag{2}$$

For the $(dde)Cu(Q^3)$ system the parameters A and B are rather small, indicating a relatively low activation barrier (reorganization energy) for equilibrium (1) in



comparison to the sterically less encumbered systems with mmb.

2.1.3. $Q = Q^A - Q^C$, L = mmb

The reaction of *o*-aminophenol H_2Q^A with anhydrous CuCl₂ in dry THF in the presence of mmb also produced temperature-dependent EPR signals with the Cu^{II} form dominating at low temperature and a Cu^I/ imino-*o*-semiquinone species at high temperature. No extra supporting base was necessary, obviously, H_2Q^A can serve simultaneously as a ligand and as a deproto-

nating base. Tables 1 and 2 contain EPR and equilibrium parameters, the EPR spectrum of the semiquinone form of $(mmb)Cu(Q^A)$ could not be analyzed due to the low symmetry and coupling from several non-equivalent nuclei.

Reaction under identical conditions with *o*-aminothiophenol H_2Q^B did not produce paramagnetic species while *o*-phenylenediamine H_2Q^C gave poorly resolved EPR signals attributable to copper(II) species.

Table 1			
Redox isomer equilibri	um data for complexes	$(L)Cu^{n+}(Q^{n-})$ i	n THF solution ^a

Quinone	$E^{\rm b}$	L	A ^c	B ^c	R^2	Reference
PQQ	-0.80	mmb	only Cu ^{II} (Q ²⁻) forms observed	only Cu ^{II} (Q ²⁻) forms observed	only Cu ^{II} (Q ²⁻) forms observed	this work
Q^3	-1.09	dde	- 308	-0.99	0.990	this work
\mathbf{Q}^{A}	n.a.	mmb	-1107	+0.85	0.919	this work
Q^1	$-0.83^{\ d}$	mmb	-1120	+1.22	0.986	[11b]
Q^2	-1.01	mmb	-2639	+4.07	0.975	[11b]
Q^3	-1.09	mmb	-2903	+6.15	0.995	[11b]
Q^4	-1.11	mmb	only $Cu^{I} (Q^{\bullet})$ forms observed	only $Cu^{I} (Q^{\bullet})$ forms observed	only $Cu^{I} (Q^{\bullet})$ forms observed	[11b]
Q^5	-1.14	mmb	only $Cu^{I}(Q^{\bullet})$ forms observed	only Cu^{I} (Q [•] ⁻) forms observed	only Cu^{I} (Q [•] ⁻) forms observed	[11b]
Q^6	-1.21	mmb	only $Cu^{I} (Q^{\bullet}^{-})$ forms observed	only $Cu^{I} (Q^{\bullet}^{-})$ forms observed	only $Cu^{I} (Q^{\bullet}^{-})$ forms observed	[11b]

^a Parameters A and B from Eq (2).

^b Redox potential for the Q/Q^{• -} transition vs. ferrocenium/ferrocene.

^c $A \pm 5, B \pm 0.2.$

^d Irreversible; cathodic peak potential given at 100 mV s⁻¹ scan rate.

Table 2 EPR data of complexes (L)Cu(Q) in frozen solution at 110 K a

Q	L	$g_{ }$	G_{\perp}	$A_{ }$ (⁶³ Cu/ ⁶⁵ Cu)	A_{\perp} (Cu)	Medium	
PQQTME	mmb	2.250	2.057	20.0/18.6	2.1	toluene	
O^3	dde	2.26	с	17 ^ь	с	THF	
\tilde{Q}^A	mmb	2.253	2.058	16.5 ^b	с	THF	
\tilde{Q}^1	mmb	2.263	2.059	19.7/18.3	3.3	toluene	
\tilde{Q}^2	mmb	2.244	2.048	19.6/18.3	3.3	THF	
\hat{Q}^3	mmb	2.248	2.058	20.0/18.6	2.7	toluene	
\hat{Q}^5	mmb	2.035	2.0045	3.5 ^b	с	toluene	
Q ⁶	mmb	2.035	2.0048	3.5 ^b	с	toluene	

^a Coupling constants A in mT.

^b ⁶³Cu and ⁶⁵Cu hyperfine coupling not resolved.

^c g_{\perp} -region not sufficiently resolved.

2.1.4. $Q = Q^{1} - Q^{6}$, L = mmb

As previously described [11], the combination of copper, mmb and the six *o*-quinone ligands Q^1-Q^6 produces EPR-detectable redox isomer equilibria (1) for the first three members of the series whereas Q^4-Q^6 produce only copper(I)/*o*-semiquinone complexes (Table 1). However, temperature variation now showed the formation of at last two different such species in the latter case. We thus studied the EPR spectra, especially the hyperfine splitting of the copper(I)/*o*-semiquinonato complexes, in more detail.

2.2. EPR analysis

2.2.1. EPR spectra in frozen solution

The parameters of the low-temperature EPR spectra from frozen solution in Table 2 illustrate the stark difference between copper(II) and copper(II)/radical systems. The latter exhibit lower g anisotropy and much lower metal hyperfine coupling constants [17]. Within the series of Cu^{II}/catecholate species there is little spectral difference, confirming rather invariant structures [11b,18].

2.2.2. EPR spectra of o-semiquinones

In view of the fragmentary EPR information on the semiquinones of compounds Q^1-Q^6 [19–21], we studied all these radical anions under comparable conditions by



Fig. 1. Temperature dependent EPR spectra of the $(dde) \mbox{Cu}(\mbox{Q}^3)$ system in THF solution.



Fig. 2. EPR spectrum of (dde)Cu^I[(Q³) $^{\bullet}$] in THF at 315 K with computer simulation.



Fig. 3. EPR spectrum of $(Q^1)^{\bullet -}$ in THF at 250 K with computer simulation.

Table 3 EPR data of copper(I)/e-semiguinonato complexes (L)Cu^I(O^{•-}) ^a

Table 4					
EPR data	of o-semiquinones	Q• - in	n THF	solution ^a	

Q	g	$a(\mathrm{H}^4)$	<i>a</i> (CH ₃), <i>a</i> (OCH ₃)	a(¹³ C) ^b	T (K)
Q^1 Q^2	2.0049	0.087 0.316 °	0.580	n.o. 0 185	250 305
Q^3	2.0047	0.300	n.o.	n.o.	320
Q^{+} Q^{5}	2.0048 2.0047	0.368 0.355	0.089 0.031	n.o. n.o.	290 280
Q^6	2.0047		< 0.012	0.370	305

^a Coupling constants in mT.

^b From 4 equiv. C.

^c H^4 and H^5 .

EPR. A typical spectrum is shown in Fig. 3, the data are summarized in Table 4.

o-Benzosemiquinones typically have the a b_1 -orbital (Scheme 3) as singly occupied molecular orbital (SOMO) with little spin density in the 3,6-positions [4,17,20,21]. Accordingly, the substituents in those positions exhibit only small, frequently undetectable hyperfine coupling whereas the groups in positions 4 and 5 contribute largely to the observed EPR splitting patterns.

Whereas the high-symmetry species $(Q^2)^{\bullet}$ exhibits EPR-detectable ¹³C isotope coupling (Table 4) [20,22], the unsymmetrical $(Q^1)^{\bullet}$ shows larger coupling from the 5-methyl β -protons than from the α -proton in 4-position (Fig. 3). γ -Protons from *tert*-butyl or methoxy substituents have generally small coupling constants, the largest such value was determined for the 5-methoxy group in $(Q^4)^{\bullet}$ (Table 4).

2.2.3. EPR spectra of copper(I)/o-semiquinonato complexes

The isotropic g-values of the copper(I)/o-semiquinonato complexes described here (Table 3) do not differ much from the values around 2.0046 of the free radical

Er K data ör copper(1)/0-semiquinonato complexes (E)/cu (Q)								
L	medium (T (K))	$A(^{63}{\rm Cu}/^{65}{\rm Cu})$	$a(H_{\alpha})$	a(other)	g			
mmb	toluene (370)	0.51/0.54	0.34	0.06 (Me-H)	2.0048			
mmb	toluene (320)	0.53/0.56	0.33	n.o.	2.0055			
mmb	toluol (380)	0.51/0.54	0.30	n.o.	2.0052			
dde	THF (315)	0.56/0.60	0.35	n.o.	2.0039			
mmb	THF (340)	0.40/0.43	0.40	0.11 (OMe-H)	2.0046			
mmb	THF (240)	0.92/0.98	0.38	0.11 (OMe-H)	2.0044			
mmb	toluene (290)	0.40/0.43	0.40	n.o.	2.0050			
mmb	toluene (230)	0.92/0.98	0.37	0.10 (OMe-H)	2.0045			
mmb	THF (330)	0.46/0.50	0.36	n.o.	2.0053			
mmb	THF (210)	0.77/0.82	0.36	n.o.	2.0046			
mmb	toluene (330)	0.41/0.44	0.36	n.o.	2.0047			
mmb	THF (320)	0.44/0.47		n.o.	2.0048			
mmb	THF (190)	0.75/0.81		n.o.	2.0046			
mmb	toluene (310)	0.39/0.42		0.21 (2 × 13 C)	2.0047			
	L mmb mmb dde mmb mmb mmb mmb mmb mmb mmb mmb mmb	Lmedium (T (K))mmbtoluene (370)mmbtoluene (320)mmbtoluol (380)ddeTHF (315)mmbTHF (240)mmbtoluene (290)mmbtoluene (230)mmbTHF (330)mmbTHF (320)mmbTHF (320)mmbTHF (190)mmbtoluene (310)	Lmedium (T (K)) $A(^{63}Cu/^{65}Cu)$ mmbtoluene (370) $0.51/0.54$ mmbtoluene (320) $0.53/0.56$ mmbtoluol (380) $0.51/0.54$ ddeTHF (315) $0.56/0.60$ mmbTHF (240) $0.92/0.98$ mmbtoluene (230) $0.40/0.43$ mmbtoluene (230) $0.92/0.98$ mmbTHF (330) $0.46/0.50$ mmbTHF (210) $0.77/0.82$ mmbtoluene (330) $0.41/0.44$ mmbTHF (320) $0.75/0.81$ mmbtoluene (310) $0.39/0.42$	Lmedium (T (K)) $A(^{63}Cu/^{65}Cu)$ $a(H_{\alpha})$ mmbtoluene (370) $0.51/0.54$ 0.34 mmbtoluene (320) $0.53/0.56$ 0.33 mmbtoluol (380) $0.51/0.54$ 0.30 ddeTHF (315) $0.56/0.60$ 0.35 mmbTHF (240) $0.92/0.98$ 0.38 mmbtoluene (230) $0.40/0.43$ 0.40 mmbtoluene (230) $0.92/0.98$ 0.37 mmbTHF (330) $0.46/0.50$ 0.36 mmbTHF (210) $0.77/0.82$ 0.36 mmbtoluene (330) $0.41/0.44$ 0.36 mmbTHF (190) $0.75/0.81$ mmbmmbtoluene (310) $0.39/0.42$	Lmedium (T (K)) $A(^{63}Cu/^{65}Cu)$ $a(H_{\alpha})$ $a(other)$ mmbtoluene (370)0.51/0.540.340.06 (Me-H)mmbtoluene (320)0.53/0.560.33n.o.mmbtoluol (380)0.51/0.540.30n.o.ddeTHF (315)0.56/0.600.35n.o.mmbTHF (340)0.40/0.430.400.11 (OMe-H)mmbTHF (240)0.92/0.980.380.11 (OMe-H)mmbtoluene (290)0.40/0.430.40n.o.mmbtoluene (230)0.92/0.980.36n.o.mmbtoluene (230)0.92/0.980.36n.o.mmbtoluene (330)0.46/0.500.36n.o.mmbTHF (320)0.41/0.440.36n.o.mmbTHF (320)0.44/0.47n.o.mmbTHF (190)0.75/0.81n.o.mmbtoluene (310)0.39/0.420.21 ($2 \times ^{13}C$)			

^a Hyperfine coupling in mT.



Scheme 3.

ligands (Table 4). For the compounds (mmb)Cu^I(Q[•]⁻) they are marginally higher, the g_{iso} for (dde)Cu^I[(Q³)[•]⁻] is slightly lower than for (Q³)[•]⁻, in agreement with the presence of low-lying unoccupied orbitals on the phosphorus atom. This result stands in contrast to the copper(I)/*o*-semiquinonato complexes of chelating bisor tris(thioethers) which exhibit higher values between 2.0058 and 2.0093, in agreement with some Cu–S bond covalency [17].

Correspondingly, the semiquinone hyperfine parameters from the EPR spectra (Fig. 4) are little changed relative to the slightly smaller values of the free ligands, except for (mmb)Cu^I[(Q¹)•⁻] which exhibits a typical large 4-H and small 5-methyl coupling constant, in contrast to free (Q¹)•⁻ with its opposite splitting pattern (Table 4). Apparently, coordination of copper(I) to (Q¹)•⁻ reverses the unsymmetry of the b₁ SOMO, possibly through differences in the metal bonding to the semiquinone oxygen atoms.

Fig. 4 illustrates the asymmetric line broadening due to insufficiently averaged contributions from the A and g-tensors in the radical complexes.

The metal coupling constants from the 63 Cu (69.2% nat. abundance) and 65 Cu (30.8%) isotopes, both with



Fig. 4. EPR spectrum of (mmb)Cu^I[(Q^2)[•] ⁻] in THF at 320 K with computer simulation.

I = 3/2 but ⁶⁵Cu with 7% higher nuclear magnetic moment, lie between 0.5 and 0.6 mT for the mmb-Cu^I or dde-Cu^I complexes with the alkyl-substituted osemiquinones $(Q^1)^{\bullet} - (Q^3)^{\bullet}$. In contrast, complexes $(L_2)Cu^{I}[(Q^3)^{\bullet}]$ with $L = PR_3$ or SR_2 have distinctly higher coupling constants $a(^{63,65}Cu) > 1$ mT whereas those with L = carbon donors have copper splittings between 0.6 and 0.7 mT [17]. This comparison suggests that the coordination at the metal is unsymmetrical (non-tetrahedral), perhaps in the direction of a trigonal pyramid which would be typical for (3+1)-coordinated copper(I) [23]. We thus propose that the larger 3pelement (E = S or P) adopts a qualitatively different position from the nitrogen donor atom in complexes (L)Cu¹(Q[•]⁻), L = mmb or dde (Scheme 4). If only 3pdonor elements E are available, this differentiation is not possible.

Support for this model comes from the observation of temperature-dependent EPR spectra for the *o*-semiquinonato complexes (mmb)Cu^I(Q[•]⁻), $Q = Q^4 - Q^6$ (Fig. 5, Table 3).

Generally, the low-temperature forms have higher metal coupling constants (0.7–1.0 mT) and slightly higher g-factors than the high-temperature species (0.4–0.5 mT), in agreement with the observations stated above. Based on the conspicuous absence of EPR-detectable ³¹P hyperfine coupling for (dde)Cu^I[(Q³)•⁻] (Fig. 2) we tentatively associate the high-temperature form with the lower metal hyperfine value to a configuration with a largely coplanar semiquinone–Cu–E arrangement (Scheme 4: B). Small metal and donor atom coupling is expected when the Cu–E bond lies in the nodal plane of the spin-bearing π -system [24].

2.3. Crystal structure analysis of $[Cu(dde)_2](ClO_4)$

All attempts to isolate mixed-ligand complexes $(L)Cu^{n+}(Q^{n-})$ from EPR-active solutions for crystal structure analysis have failed so far. Slow evaporation typically produces the well-known homoleptic species $Cu^{II}(Q^{\bullet-})_2$ [25]. For the approach to use EXAFS in structure determination [26], we have set out to structurally characterize also the corresponding homoleptic compounds $[Cu(L)_2]^{n+}$, reports on the systems with L = nmb and n = 1 or 2 have appeared [13a], as has a structure analysis of $(Me_3TACN)Cu^{II}[(Q^3)^{2-}]$,



Scheme 4.



Fig. 5. Temperature dependent EPR spectra of (mmb)Cu^I[(Q^{5})•⁻] in THF solution.

Me₃TACN = 1,4,7-trimethyl-1,4,7-triazacyclononane [11b]. Herein we have used the dde ligand in connection with copper and have obtained a crystalline copper(I) complex [Cu(dde)₂](ClO₄) from the reaction of excess dde with Cu(ClO₄)₂·6H₂O in THF under argon. The function of triorganophosphanes as reductants towards copper(II) is not uncommon [27].

Fig. 6 shows the molecular cation of $[Cu(dde)_2](ClO_4)$ in the crystal, Tables 5 and 6 list the crystallographic and essential bond parameter information.

Table 6 also includes the results from a DFT calculation of the cation $[Cu(dde)_2]^+$ and bond parameters of comparable copper complexes with P–N donor ligands A–C [28–30] (Scheme 5).

The correspondence between DFT calculation results and experiment is very good except for the unusually extended Cu–N bonds which are calculated longer than they actually are. Apart from the not uncommon overestimation of Cu–N bonds [13a], we attribute this



Fig. 6. Molecular structure of the cation in the crystal of $[Cu-(dde)_2](CIO_4)$.

discrepancy to a shallow energy minimum for this 'secondary' bond. Both the similarity of Cu–P and Cu–N bond distances and the wide P–Cu–P angle of about 142° suggest a '2+2' coordination pattern with the P-atoms as primary donors and the trialkylamine nitrogen atoms as secondary donors. A related effect had been reported for [Cu(mmb)₂]⁺ where the imine Natoms occupy the primary sites ($d_{Cu-N} = 1.920$ Å) with a close to linear angle N–Cu–N of 169.8° whereas the thioether S-atoms are in a secondary position with long bonds of >2.6 Å to the metal [13a]. Obviously, copper(I) prefers imine–N over thioether–S but phosphane–P over amine–N.

The comparison with other copper complexes of N,Pdonor ligands A–C in Table 6 confirms the special configuration in $[Cu(dde)_2]^+$ with unusually long Cu–N bonds and rather large P–Cu–P and N–Cu–N angles, illustrating a typical 2+2 coordination pattern.

2.4. Summary

This study has confirmed that an *o*-quinone/copperbased redox isomer equilibrium (1) can be detected through EPR only in a rather narrow range of matching copper- d_{π} and quinone π^* -orbitals (Scheme 1). With the P–N mixed donor ligand dde there is a larger temperature range for the simultaneous observation of individual copper(I)/*o*-semiquinonato and copper(II)/ 170

Table 5

Crystal	data	and	structure	refinement	information	for	[Cu(dde) ₂]-
(ClO_4)							

Empirical formula Formula weight (g mol ^{-1})	C ₃₂ H ₄₀ ClCuN ₂ O ₄ P ₂ 677.59
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	hexagonal
Space group	P3121
Unit cell dimensions	
a (Å)	10.0961(14)
b (Å)	10.0961(14)
<i>c</i> (Å)	27.304(6)
α (°)	90
β (°)	90
γ (°)	120
V (Å ³)	2410.3(7)
Ζ	3
$D_{\text{calc}} (\text{mg m}^{-3})$	1.400
$\mu (\mathrm{mm}^{-1})$	0.901
F(000)	1062
Crystal size (mm)	0.6 imes 0.4 imes 0.2
θ Range (°)	2.24-29.04
Index ranges	$-3 \le h \le 13, -13 \le k \le 11,$
	$-36 \le l \le 37$
Number of reflections	13 480
Number of independent reflections	4294 ($R_{\rm int} = 0.0737$)
Data/restraints/parameters	4294/0/191
Goodness-of-fit in F^2	1.106
$R \ [I > 2\sigma(I)]$	$R_1 = 0.0487, wR_2 = 0.1060$
R (all data)	$R_1 = 0.0668, wR_2 = 0.1151$
Residual electron density (greatest	0.710 and -0.385
maximum and minimum) (e $Å^{-3}$)	

catecholate forms, however, all spectroscopic results indicate negligible covalency and metal-ligand orbital mixing.

There are thus two quite different manifestations of the 'non-innocence' of quinonoid ligands.

- Strongly interacting metal centers such as ruthenium(II) produce complexes with highly mixed states, where e.g. both $Ru^{II}(Q^{2-})$ and $Ru^{II}(Q^{\bullet-})$ or $Ru^{II}(\mu-Q^{\bullet-})Ru^{II}$ and $Ru^{II}(\mu-Q^{2-})Ru^{III}$ 'resonance' forms contribute to one delocalized state according to

Table 6 Selected bond distances (Å) and angles (°) in copper complexes with P–N ligands

EPR and other spectroscopic techniques [31,32]. Both the smaller conformational change and thus smaller reorganization energy of the d^6/d^5 transition as well as stronger π -interaction from the second row transition metal may be responsible for this result.

– On the other hand, the smaller π -interaction from copper complex fragments and the larger conformational change expected for the d¹⁰/d⁹ transition causes typically dichotomous states, either copper(II) species or copper(I) radical forms [17,33]. Only under special conditions are both forms detectable simultaneously, we shall, therefore, devote further experimental and computational efforts to investigate this remarkable dichotomy.

3. Experimental

3.1. Instrumentation

EPR spectra were recorded in the X-band on a Bruker System ESP 300 equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter. ¹H NMR spectra were taken on a Bruker AC 250 spectrometer. Cyclic voltammetry was carried out at 100 mV s^{-1} scan rate in THF/0.1 M Bu₄NPF₆ using a threeelectrode configuration (glassy carbon working electrode, Pt counter electrode, Ag/AgCl reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium couple served as internal reference.

3.2. Radical generation

o-Semiquinone radicals were prepared for EPR spectroscopy in sealed tubes using freshly distilled potassium as reductant in THF solution. The paramagnetic copper complexes (L)Cu(Q) were typically obtained in such sealed apparatuses by combining L, Q and activated Cu powder (the latter in excess) with the condensed solvent. As a variation, Q and Cu can be

Bond distances (Å) and bond angles (°)	[Cu(dde) ₂](ClO ₄)		$[Cu(A)_2](ClO_4) \cdot C_2H_5OH$	$[Cu(B)](BF_4)$	$[Cu(C)](ClO_4)_2 \cdot C_6H_6^{a}$			
	exp.	DFT	-					
Cu–N	2.250(3)	2.340	2.177(3)	2.169(8)	2.06(1)			
Cu–P	2.2630(8)	2.258	2.258(1)	2.197(2)	2.325(4)			
N-Cu-N(0A)	114.67(15)	113.1	111.7(2)	85.7(4)	86.3(4)			
N-Cu-P	86.78(8)	86.6	82.7(1)	87.0(2)	84.9(3) ^b			
P-Cu-P(0A)	142.40(5)	142.9	131.3(1)	132.8(1)	101.8(1)			
N-Cu-P(0A)	113.83(8)	114.3	129.7(2)	126.2(1)	166.3(2) ^b			
ref.	this work	this work	[28]	[29]	[30]			

^a Copper(II) complex.

^b Average value.



reacted to $Cu(Q)_2$ first and then combined with L in a controlled fashion. The reactions of H_2Q species were carried out with anhydrous $CuCl_2$ in THF.

3.3. Syntheses

3.3.1. Starting materials

The quinones were obtained commercially or were prepared as described before [11b]. The ligands dde [16] and PQQTME [15] were obtained according to the literature.

3.3.2. $[Cu(dde)_2](ClO_4)$

Addition of 57.7 mg (0.155 mmol) Cu(ClO₄)₂·6H₂O to a THF solution (5 ml) of 80.2 mg (0.311 mmol) dde resulted in a discoloring after 5 min of stirring. Reduction to about 1/3 of the volume and cooling to -17 °C produced 35 mg (30%) of a colorless material which contained a few single crystals suitable for X-ray diffraction. *Anal*. Found: C, 51.74; H, 6.00; N, 3.31. Calc. for C₃₂H₄₈ClCuN₂P₂O₈ (749.7): C, 51.27; H, 6.43; N, 3.72%. ¹H NMR (CD₂Cl₂): $\delta = 2.30$ (s, 12H, NMe₂), 2.42–2.53 (m, 4H, CH₂), 2.62–2.71 (m, 4H, CH₂), 7.32–7.57 (m, 20H, PPh₂).

3.4. Crystallography

Single crystals of $[Cu(dde)_2](ClO_4)$ were obtained from the raction solution. X-ray diffraction was carried out with a Siemens P4 instruement using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods using the SHELXTL program package [34]. All nonhydrogen atoms were refined anisotropically, and hydrogen atoms were introduced at calculated positions with coupled isotropic temperature factors. Further information is summarized in Table 5.

3.5. DFT calculation procedures

Ground state electronic structure calculations on $[Cu(dde)_2]^+$ have been done by the density functional theory (DFT) method using the ADF-2000.2 [35] program package.

Slater type orbital (STO) basis sets of double- ζ quality with polarization functions for H and C atoms within phenyl ligands and triple- ζ quality with polarization functions for the remaining atoms of the system were employed. Inner shells were represented by the frozen core approximation (1s for C, N; 1s-2p for P; 1s-3s for Cu). Within ADF the functional including Becke's gradient correction [36] to the local exchange expression in conjunction with Perdew's gradient correction [37] to the local density approximation (LDA) with VWN parametrization of electron gas data (ADF-BP) was used.

The geometry optimization was performed without symmetry constrains.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 179337. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

This work has been supported by the Deutsche Forschungsgemeinschaft (project KA 618/18) and by the Fonds der Chemischen Industrie. We thank Dr. W. Schwarz for the crystallographic data collection and Dr. K.-W. Klinkhammer for assistance in the space group identification.

References

- C.K. Jørgensen, Oxidation Numbers and Oxidation States, Springer, Berlin, 1969, p. 291.
- [2] W.R. McWhinnie, J.D. Miller, Adv. Inorg. Chem. Radiochem. 12 (1969) 135.
- [3] R.P. Burns, C.A. McAuliffe, Adv. Inorg. Chem. Radiochem. 22 (1979) 303.
- [4] C.G. Pierpont, C.W. Lange, Prog. Inorg. Chem. 41 (1994) 331.
- [5] D. Herebian, E. Bothe, E. Bill, T. Weyhermüller, K. Wieghardt, J. Am. Chem. Soc. 123 (2001) 10012.

- [6] C.G. Pierpont, Coord. Chem. Rev. 216-217 (2001) 99.
- [7] A. Caneschi, A. Dei, F. Fabrizi de Biani, P. Gütlich, V. Ksenofontov, G. Levchenko, A. Hoefer, F. Renz, Chem. Eur. J. 7 (2001) 3926.
- [8] M.W. Lynch, D.N. Hendrickson, B.J. Fitzgerald, C.G. Pierpont, J. Am. Chem. Soc. 106 (1984) 2041.
- [9] D.M. Dooley, M.A. McGuirl, D.E. Brown, P.N. Turowski, W.S. McIntire, P.F. Knowles, Nature (Lond.) 349 (1991) 262.
- [10] C.M. Wilmot, J. Hajdu, M.J. McPherson, P.F. Knowles, S.E.V. Phillips, Science 286 (1999) 1724.
- [11] (a) J. Rall, E. Waldhör, B. Schwederski, M. Schwach, S. Kohlmann, W. Kaim, in: A.X. Trautwein (Ed.), Bioinorganic Chemistry: Transition Metals in Biology and their Coordination Chemistry, VCH, Weinheim, 1997, p. 476;
 (b) J. Rall, M. Wanner, M. Albrecht, F.M. Hornung, W. Kaim, Chem. Eur. J. 5 (1999) 2802.
- [12] (a) G. Speier, Z. Tyeklár, P. Töth, E. Speier, S. Tisza, A. Rockenbauer, A.M. Whalen, N. Alkire, C.G. Pierpont, Inorg. Chem. 40 (2001) 5653;
 (b) See also G.A. Abakumov, V.A. Garnov, V.I. Nevodchikov,

V.K. Cherkasov, Dokl. Akad. Nauk SSSR 304 (1989) 109. [13] (a) M. Albrecht, K. Hübler, S. Zalis, W. Kaim, Inorg. Chem. 39

(2000) 4731; (2000) 4731;

(b) M. Albrecht, K. Hübler, T. Scheiring, W. Kaim, Inorg. Chim. Acta 287 (1999) 204.

- [14] (a) B. Schwederski, V. Kasack, W. Kaim, E. Roth, J. Jordanov, Angew. Chem. 102 (1990) 74;
 (b) B. Schwederski, V. Kasack, W. Kaim, E. Roth, J. Jordanov, Angew. Chem., Int. Ed. Engl. 29 (1990) 78.
- [15] (a) M. Wanner, T. Sixt, K.-W. Klinkhammer, W. Kaim, Inorg. Chem. 38 (1999) 2753;
 (b) S. Itoh, H. Kawakami, S. Fukuzumi, J. Am. Chem. Soc. 120 (1998) 7271 (and references therein);

(c) S. Itoh, H. Kawakami, S. Fukuzumi, J. Am. Chem. Soc. 119 (1997) 439.

- [16] R. Malet, M. Moreno-Manas, T. Parella, R. Pleixats, J. Org. Chem. 61 (1996) 758.
- [17] J. Rall, W. Kaim, J. Chem. Soc., Faraday Trans. 90 (1994) 2905 (and literature cited).
- [18] (a) B.A. Goodman, J.B. Raynor, Adv. Inorg. Chem. Radiochem. 13 (1970) 135;
 (b) F.F. Mabs. D. Collison. Electron Paramagnetic Resonance

(b) F.E. Mabbs, D. Collison, Electron Paramagnetic Resonance of d-Transition Metal Compounds, Elsevier, Amsterdam, 1992.

- [19] E. Müller, F. Günter, K. Scheffler, P. Ziemek, A. Rieker, Liebigs. Ann. Chem. 688 (1965) 134.
- [20] L.S. Lybchenko, S.G. Lakaev, Y.A. Lyulkin, A.I. Prokof'ev, Zh. Fiz. Khim. 55 (1981) 1216.
- [21] A. Vlcek, Jr., J. Organomet. Chem. 306 (1986) 63.

- [22] G. Vincow, G.F. Fraenkel, J. Chem. Phys. 34 (1961) 1333.
- [23] (a) C. Vogler, W. Kaim, H.-D. Hausen, Z. Naturforsch. 48b (1993) 1470;
 (b) A.F. Stange, T. Sixt, W. Kaim, J. Chem. Soc., Chem. Commun. (1998) 469.;
 (c) M. Schwach, H.-D. Hausen, W. Kaim, Inorg. Chem. 38 (1999) 2242.
- [24] (a) A. Alberti, C.M. Camaggi, J. Organomet. Chem. 181 (1979) 355;

(b) W. Kaim, Coord. Chem. Rev. 76 (1987) 187.

- [25] G.A. Abakumov, A.V. Lobanov, V.K. Cherkasov, G.A. Razuvaev, Inorg. Chim. Acta 49 (1981) 135.
- [26] M. Wanner, M. Seiler, W. Kaim, H. Bertagnolli, work in progress.
- [27] (a) N. Doslik, T. Sixt, W. Kaim, Angew. Chem. 110 (1998) 2521;
 (b) N. Doslik, T. Sixt, W. Kaim, Angew. Chem., Int. Ed. 37 (1998) 2403.
- [28] E.W. Ainscough, A.M. Brodie, S.L. Ingham, J.M. Waters, Inorg. Chim. Acta 217 (1994) 191.
- [29] F. Tisato, F. Refosco, G. Bandoli, G. Pilloni, B. Corain, J. Chem. Soc., Dalton Trans. (1994) 2471.
- [30] G. Pilloni, G. Bandoli, F. Tisato, B. Corain, Chem. Commun. (1996) 433.
- [31] (a) M. Haga, E.S. Dodsworth, A.B.P. Lever, Inorg. Chem. 25 (1986) 447;
 (b) A.B.P. Lever, P.R. Auburn, E.S. Dodsworth, M. Haga, W. Liu, M. Melnik, W.A. Nevin, J. Am. Chem. Soc. 110 (1988) 8076;
 (c) H. Masui, A.B.P. Lever, P.R. Auburn, Inorg. Chem. 30 (1991) 2402;

(d) A.B.P. Lever, H. Masui, R.A. Metcalfe, D.J. Stufkens, E.S. Dodsworth, P.R. Auburn, Coord. Chem. Rev. 125 (1993) 317.

- [32] (a) S. Ernst, P. Hänel, J. Jordanov, W. Kaim, V. Kasack, E. Roth, J. Am. Chem. Soc. 111 (1989) 1733;
 (b) V. Kasack, W. Kaim, H. Binder, J. Jordanov, E. Roth, Inorg. Chem. 34 (1995) 1924.
- [33] (a) W. Kaim, M. Moscherosch, J. Chem. Soc., Faraday Trans. 87 (1991) 3185;
 (b) M. Moscherosch, J.S. Field, W. Kaim, S. Kohlmann, M. Krejcik, J. Chem. Soc., Dalton Trans. (1993) 211.;
 (c) A.-L. Barra, L.-C. Brunel, F. Baumann, M. Schwach, M. Moscherosch, W. Kaim, J. Chem. Soc., Dalton Trans. (1999) 3855
- [34] G.M. Sheldrick, SHELXTL-PLUS, Relat. 5.03, Siemens Analytical X-ray Insturments Inc, Madison, WI, 1989.
- [35] C. Fonseca Guerra, J.G. Snijders, G. te Velde, E.J. Baerends, Theor. Chem. Acc. 99 (1998) 391.
- [36] A.D. Becke, Phys. Rev. A 38 (1988) 3098.
- [37] J.P. Perdew, Phys. Rev. A 33 (1986) 8822.