4004 *Inorg. Chem.* **1984**, *23*, 4004–4008

exchange couplings. Owing to the chosen box-type distribution, it is clear that the results can only be qualitative. Notice that more sophisticated distributions, such as $P(J) = \lambda^{\alpha-1}|J|^{-\alpha}$ with $0 < |J| < \lambda$, provide the same divergence, $\chi = AT^{-\alpha}$, as $T \rightarrow 0$ K.[19] Further investigations, such as low-temperature specific heat studies, are now required for a better understanding of the critical parameter α.

Finally, whatever the kind of distribution, the $\lambda/|J|$ ratio must play a special role when the "degrees of disorder" in the EDTA amorphous complex series are compared. On account of their very close local structure[8] such a comparison should lead to a better knowledge of the correlations structure–exchange mechanisms in the amorphous state. Our groups are working in this way.

Acknowledgment. We thank Dr. C. Schwab and B. Meyer from the Laboratoire de Spectroscopie et d'Optique du Corps Solide (Strasbourg) for their assistance with EPR measurements.

Registry No. $Co_2(EDTA)\cdot 6H_2O$, 84222-22-0.

Contribution from the Dipartimento di Chimica Generale and Istituto di Cristallografia,
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Studies on Copper(II) Complexes of *o*-Quinone Monooximes. Adducts of Bis(4-chloro-1-benzoquinone 2-oximato)copper(II) with Some Heterocyclic Bases. Structure of the 2,2′-Bipyridine Adduct[1]

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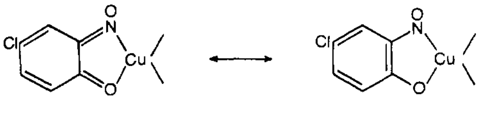
Stable 1:1 adducts of bis(4-chloro-1-benzoquinone 2-oximato)copper(II), $Cu(qo)_2$, with 2,2′-bipyridine, 1,10-phenanthroline, imidazole, and pyrazole, have been isolated. The crystal structure of bis(4-chloro-1-benzoquinone 2-oximato)(2,2′-bipyridine)copper(II), $C_{22}H_{14}Cl_2CuN_4O_4$, has been determined. The compound crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 15.499$ (14) Å, $b = 14.260$ (13) Å, $c = 11.097$ (15) Å, $\alpha = 71.26$ (8)°, $\beta = 75.25$ (4)°, $\gamma = 81.07$ (5)°, $V = 2238.8$ (4) Å^3, $Z = 4$, and d(calcd) = 1.581 g cm^{-3}. The structure converged to a weighted R factor of 3.37% for 6228 observations and 596 parameters. The copper ion attains coordinative saturation through cis,cis-octahedral geometry tetragonally distorted. The formation constants for $Cu(qo)_2(bpy)$ and $Cu(qo)_2(phen)$ are reported. A corresponding series of adducts containing benzene in the crystal lattice has been isolated.

Introduction

It is well-known that bis-chelated complexes of copper(II) behave as Lewis acids and react with donor ligands, thus increasing their coordination number.[3] The more usual product of the reaction with bases is the square-pyramidal 1:1 type of adduct; six-coordination is attained only when the electron-withdrawing nature of the chelating ligands increases the residual positive charge on the metal ion; for instance, this is the case for bis(hexafluoroacetylacetonato)copper(II), which forms octahedral isolable adducts with pyridine and bipyridine, whereas bis(acetylacetonato)copper(II) forms only an unstable 1:1 pyridine adduct, which loses the base on exposure to air.[4] Extensive research on this subject has been carried out on Cu(II) complexes derived from β-diketones and from salicylaldimine type ligands,[5] but very little information is reported about the Lewis acidity of Cu(II) bis-chelated derivatives of *o*-quinone monooximes. Moreover these compounds are presently the focus of attention of many researchers because of their peculiar reactivity. In fact, they react easily with many potentially basic compounds (i.e., dimethyl acetylenedicarboxylate,[6] amines,[7] triphenylphosphine,[8] benzaldehyde,[9] methanol[10]) to give a wide variety of organic products. The mechanism of these reactions (which do not occur if the *o*-quinone monooximes are not complexed with the metal) has been explained by assuming, as a preliminary step, the formation of adducts between the basic reagent and the copper ion;[6,7] therefore, in order to understand the reactivity of copper(II) complexes derived from *o*-quinone monooximes, it is advisable to know more about their Lewis acid behavior and the molecular structure of their adducts.

The number of adducts that have been isolated so far is very meager; as regards Cu(II) complexes of *o*-benzoquinone monooximes, only the 1:1 square-pyramidal adduct with pyridine has been characterized;[11] it is reported that other strong donors such as triethylamine, dimethyl sulfoxide, and acetonitrile fail to react,[12] and the existence of a water adduct is very doubtful.[10] Only if the chelated ligand is a naphthoquinone monooximate can a square-pyramidal monohydrate be obtained[13a] and a weak octahedral acetone adduct can be isolated.[13b]

In order to obtain more information on this subject, we investigated the reaction of bis(4-chloro-1-benzoquinone 2-oximato)copper(II) [**1a** ↔ **1b**, referred to as $Cu(qo)_2$] with



1a 1b

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[2] (a) Dipartimento di Chimica Generale. (b) Istituto di Cristallografia.

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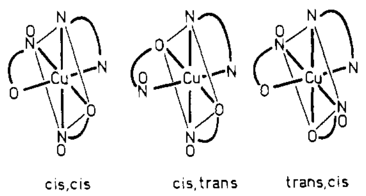

Figure 1. Possible diastereomeric forms of octahedral $Cu(qo)_2(bpy)$.

the heterocyclic bases 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), pyrazole (pz), and imidazole (im), and found that, in each case, only the 1:1 adduct is obtained. While for the 1:1 pyrazole and imidazole adducts the square-pyramidal coordination can be intuitively predicted by analogy to the pyridine complex, the 1:1 adducts with bpy and phen do not necessarily imply the hexacoordination around copper, despite the presence of three bidentate and potentially chelating ligands; for instance, it has been recently found that in Cu(acac)(hfac)(phen) (acac = acetylacetonato; hfac = hexafluoroacetylacetonate) copper is five-coordinate, hfac acting as monoligating anion.[14] Furthermore, if the octahedral coordination were proved, the arrangement of the donor atoms around copper should be settled. In fact, for octahedral $Cu(qo)_2(bpy)$ three diastereomeric forms are possible (cis,cis; cis,trans; trans,cis), where the first prefix refers to NO groups and the second to CO groups (Figure 1).

As ligand complexity prevents unambiguous conclusions to be drawn from infrared or electronic spectral data,[15,16] or similar physicochemical measurements, the X-ray determination of the crystal structure of $Cu(qo)_2(bpy)$ was carried out and the copper was found to be coordinatively saturated through cis,cis octahedral geometry tetragonally distorted.

Experimental Section

Solution spectra were recorded with a Carlo Erba Spectracomb 601 spectrophotometer; IR spectra were obtained with a 1330 Perkin-Elmer spectrophotometer; mass spectra were obtained with a Du Pont 21492B mass spectrometer.

Preparation of Adducts. Bis(4-chloro-1-benzoquinone 2-oximato)copper(II) (1 mmol), prepared according to ref 12, was suspended in acetonitrile (50 cm^3), treated with a slight excess of the appropriate base (1.1 mmol), and stirred for 1 h. The obtained solution was filtered, and on slow evaporation of the solvent, deep red crystals of the adduct precipitated. The crystals were washed with acetonitrile and Et_2O and dried at room temperature under vacuum for 3 h.

Bis(4-chloro-1-benzoquinone 2-oximato)(2,2′-bipyridine)copper(II). Mp 147–149 °C. Anal. Calcd for $C_{22}H_{14}Cl_2CuN_4O_4$: C, 49.62; H, 2.65; N, 10.52. Found: C, 48.89; H, 2.68; N, 10.50. Absorption spectrum: λ_{max} (MeCN) 430 sh, 500 nm (ϵ 7915 dm^3 mol^{-1} cm^{-1}).

Bis(4-chloro-1-benzoquinone 2-oximato)(1,10-phenanthroline)copper(II). Mp 208–209 °C. Anal. Calcd for $C_{24}H_{14}Cl_2CuN_4O_4$: C, 51.80; H, 2.54; N, 10.08. Found: C, 51.93; H, 2.49; N, 10.14. Absorption spectrum: λ_{max} (MeCN) 430 sh, 500 nm (ϵ 7220 dm^3 mol^{-1} cm^{-1}).

Bis(4-chloro-1-benzoquinone 2-oximato)(imidazole)copper(II). Mp 179–180 °C. Anal. Calcd for $C_{15}H_{10}Cl_2CuN_4O_4$: C, 40.51; H, 2.27; N, 12.6. Found: C, 41.00; H, 2.35; N, 12.92.

Bis(4-chloro-1-benzoquinone 2-oximato)(pyrazole)copper(II). Mp 170–171 °C. Anal. Calcd for $C_{15}H_{10}Cl_2CuN_4O_4$: C, 40.51; H, 2.27; N, 12.60. Found: C, 40.66; H, 2.22; N, 12.60.

Adducts Containing Benzene. These were prepared as outlined above with benzene as solvent instead of acetonitrile. The crystallization was obtained by adding *n*-hexane.

$Cu(qo)_2(bpy)\cdot{}^1/_2C_6H_6$. Dec pt 70–150 °C (weight loss: for $^1/_2C_6H_6$: calcd, 6.82%; found, 6%). Anal. Calcd for $C_{25}H_{17}Cl_2CuN_4O_4$: C, 52.50; H, 3.00; N, 9.80. Found: C, 51.39; H, 3.23; N, 9.66. IR (KBr): ν [out-of-plane C–H bending of benzene (A_{2u})] 685 cm^{-1}.

Table I. Information about Data Collection and Structure Refinement

space group	$P\bar{1}$
a	15.499 (14) Å
b	14.260 (13) Å
c	11.097 (15) Å
α	71.26 (8)°
β	75.25 (4)°
γ	81.07 (5)°
V	2238.8 (4) $Å^3$
mol formula	$C_{22}H_{14}Cl_2CuN_4O_4$
mol wt	532.6
color	dark red
Z	4
d(calcd)	1.581 g cm^{-3}
radiation used for data collcd	Mo Kα (λ = 0.7107 Å)
μ(Mo)	10.53 cm^{-1}
specimen size	0.08 × 0.04 × 0.025 cm
scanning range for 2θ	$4° \leqslant 2\theta \leqslant 46°$
std for intens control	3
scan mode	$\omega/2\theta$
scan speed	0.10°/min
scan width	1.5° (in ω)
no. of unique reflcns used in the last cycle of least squares	3860 out of 6228 ($I \geqslant 2\sigma(I)$)
final $R_w(F)$ ($w = 1/\sigma(F)^2$	0.034

$Cu(qo)_2(phen)\cdot{}^1/_2C_6H_6$. Dec pt 170 °C. Anal. Calcd for $C_{27}H_{17}Cl_2CuN_4O_4$: C, 54.42; H, 2.88; N, 9.40. Found: C, 54.20; H, 2.89; N, 9.41. IR (KBr): ν [out-of-plane C–H bending of benzene (A_{2u})] 685 cm^{-1}.

Mass spectra (EI 75 eV; 50 μA; source temperature 230 °C) were run at probe temperatures from 40 to 360 °C and acquired by a data system; computer-reconstructed ion current helped to localize benzene and phenanthroline.

$Cu(qo)_2(phen)\cdot{}^1/_2C_6D_6$ was prepared by the same outlined method, using hexadeuteriobenzene as reaction medium. IR (KBr): ν (out-of-plane bending of C–D) 500 cm^{-1}.

$Cu(qo)_2(im)\cdot C_6H_6$. Dec pt 150–195 °C. Anal. Calcd for $C_{21}H_{16}Cl_2CuN_4O_4$: C, 48.25; H, 3.08; N, 10.72. Found: C, 48.43; H, 3.29; N, 10.51. IR (KBr): ν [out-of-plane C–H bending of benzene (A_{2u})] 692 cm^{-1}.

$Cu(qo)_2(pz)\cdot{}^1/_2C_6H_6$. Dec pt 70–120 °C. Anal. Calcd for $C_{18}H_{13}Cl_2CuN_4O_4$: C, 44.68; H, 2.71; N, 11.58. Found: C, 44.18; H, 2.59; N, 11.21. IR (KBr): ν [out-of-plane C–H bending of benzene (A_{2u})] 692 cm^{-1}.

Crystallographic Study of $C_{22}H_{14}Cl_2CuN_4O_4$. The data were collected on a Philips PW1100 four-circle diffractometer using monochromatized radiation. Pertinent details are given in Table I.

An empirical absorption correction was applied,[17] by ψ scanning two axial reflections.

The structure was solved by Patterson method and anisotropically refined by block-diagonal least squares. Secondary extinction effects were found to be absent. The occupancies of both copper sites (Cu^{2+} against Cu^0) were refined, finding values around 1+ for each copper. Form factors with anomalous dispersion components were used.[18] All the 28 hydrogens were detected in the final ΔF Fourier map; however, the coordinates used in the final structure factor calculation were adjusted to theoretical bonds and angles. The final coordinates of the refined atoms appear in Table II; the calculated coordinates for H atoms and thermal parameters appear as supplementary material.

Results and Discussion

$Cu(qo)_2(bpy)$ Crystal and Molecular Structure. The asymmetric unit includes two molecules of complex. The geometry of both crystallographically nonequivalent molecules is quite similar (Figure 2).[19] All three ligands are chelated, giving

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Table II. Fractional Atomic Coordinates with Estimated Standard Deviations in Parentheses[a,b]

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
			Molecule A				
Cu	0.30891 (5)	0.45481 (6)	0.82866 (8)	C(8′)	0.2128 (4)	0.1946 (5)	1.1429 (7)
Cl(12′)	−0.0457 (2)	0.2353 (2)	1.3026 (2)	C(9′)	0.1305 (5)	0.1812 (5)	1.2219 (6)
Cl(12″)	0.3921 (2)	0.2107 (2)	0.3704 (3)	C(10′)	0.0591 (4)	0.2556 (5)	1.2011 (6)
N(1″)	0.2725 (4)	0.4118 (4)	0.6954 (5)	C(11′)	0.0740 (4)	0.3419 (5)	1.1060 (6)
N(3)	0.3530 (4)	0.4989 (4)	0.9601 (5)	C(6′)	0.1589 (4)	0.3575 (5)	1.0270 (6)
N(1′)	0.1820 (4)	0.4451 (4)	0.9354 (5)	O(5′)	0.1219 (3)	0.5141 (3)	0.9161 (4)
O(2″)	0.4312 (3)	0.4219 (3)	0.7241 (4)	C(13)	0.3801 (5)	0.4335 (5)	1.0639 (7)
O(2′)	0.3075 (3)	0.2921 (3)	0.9629 (4)	C(14)	0.4075 (5)	0.4624 (6)	1.1541 (7)
N(4)	0.3013 (4)	0.6164 (4)	0.7523 (5)	C(15)	0.4048 (5)	0.5615 (6)	1.1368 (7)
C(7″)	0.4243 (5)	0.3768 (5)	0.6482 (7)	C(16)	0.3758 (5)	0.6312 (5)	1.0327 (8)
C(8″)	0.4988 (5)	0.3321 (6)	0.5725 (7)	C(17)	0.3508 (4)	0.5957 (5)	0.9450 (6)
C(9″)	0.4890 (6)	0.2829 (6)	0.4914 (7)	C(18)	0.3225 (4)	0.6637 (5)	0.8289 (6)
C(10″)	0.4032 (6)	0.2769 (5)	0.4734 (7)	C(19)	0.3194 (5)	0.7637 (5)	0.7974 (7)
C(11″)	0.3292 (5)	0.3196 (5)	0.5352 (7)	C(20)	0.2951 (5)	0.8204 (5)	0.6858 (8)
C(6″)	0.3394 (5)	0.3700 (5)	0.6219 (6)	C(21)	0.2699 (5)	0.7759 (5)	0.6074 (6)
O(5″)	0.1929 (3)	0.4140 (4)	0.6827 (5)	C(22)	0.2749 (5)	0.6736 (5)	0.6451 (7)
C(7′)	0.2335 (4)	0.2827 (5)	1.0388 (6)				
			Molecule B				
Cu	0.80160 (5)	0.13651 (6)	0.84579 (8)	C(8′)	0.5132 (5)	0.1421 (5)	0.9195 (6)
Cl(12′)	0.4332 (2)	0.0249 (2)	0.6857 (2)	C(9′)	0.4623 (4)	0.1123 (5)	0.8560 (7)
Cl(12″)	0.9179 (2)	0.6095 (2)	0.5635 (3)	C(10′)	0.5024 (5)	0.0625 (5)	0.7604 (6)
N(3)	0.8345 (4)	0.0053 (4)	0.9692 (5)	C(11′)	0.5924 (4)	0.0455 (5)	0.7236 (6)
N(1″)	0.7850 (4)	0.2717 (4)	0.7242 (5)	C(6′)	0.6462 (4)	0.0794 (4)	0.7864 (6)
O(2″)	0.8531 (3)	0.2207 (3)	0.9325 (4)	O(5′)	0.7763 (3)	0.0372 (3)	0.6562 (4)
N(1′)	0.7373 (4)	0.0730 (4)	0.7477 (5)	C(13)	0.7779 (4)	−0.0385 (5)	1.0758 (6)
N(4)	0.9386 (4)	0.1001 (4)	0.7451 (5)	C(14)	0.7956 (5)	−0.1292 (5)	1.1584 (6)
O(2′)	0.6572 (3)	0.1449 (3)	0.9547 (4)	C(15)	0.8814 (5)	−0.1758 (5)	1.1293 (7)
C(6″)	0.8307 (4)	0.3419 (5)	0.7377 (6)	C(16)	0.9424 (5)	−0.1298 (5)	1.0197 (7)
C(11″)	0.8431 (5)	0.4359 (5)	0.6515 (7)	C(17)	0.9179 (5)	−0.0381 (5)	0.9373 (6)
C(10″)	0.8954 (5)	0.4934 (5)	0.6707 (7)	C(18)	0.9753 (5)	0.0143 (5)	0.8145 (6)
C(9″)	0.9363 (5)	0.4587 (6)	0.7769 (8)	C(19)	1.0625 (5)	−0.0202 (5)	0.7698 (7)
C(8″)	0.9209 (5)	0.3705 (5)	0.8674 (7)	C(20)	1.1095 (5)	0.0342 (6)	0.6522 (8)
C(7″)	0.8679 (4)	0.3050 (5)	0.8516 (6)	C(21)	1.0714 (5)	0.1201 (6)	0.5817 (7)
O(5″)	0.7441 (4)	0.2961 (3)	0.6345 (5)	C(22)	0.9859 (5)	0.1494 (5)	0.6358 (7)
C(7′)	0.6097 (5)	0.1229 (4)	0.8934 (6)				

[a] The following conventions are adopted in this and following tables: A and B denote two crystallographically nonequivalent molecules. Within each molecule the primes are used for the two nonequivalent *qo* ligands, i.e. prime for that with one short and one long coordinating bond double prime for the equatorially chelated one with two short bonds. [b] Esd's refers to the last digit printed.

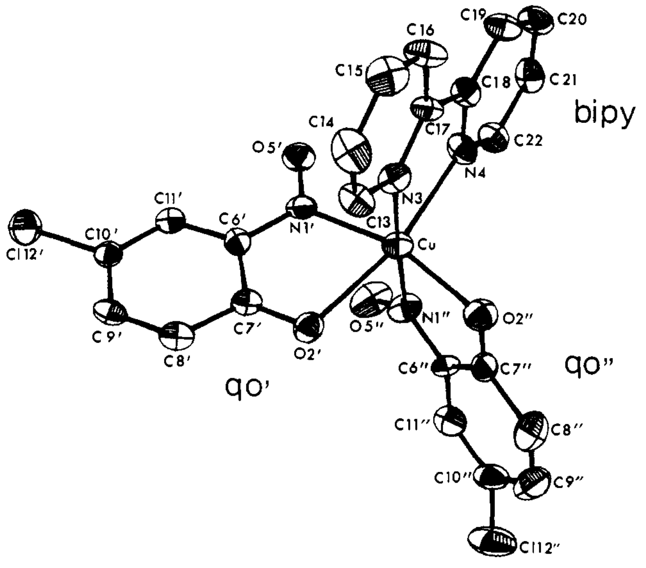

Figure 2. ORTEP view of Cu(qo)$_2$(bpy), molecule A, showing the anisotropic thermal ellipsoids with 20% probability. The octahedron is oriented as in Figures 1 and 4.

Table III. Selected Intramolecular Bond Distances (Å) for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses[a]

	A′	A″	B′	B″
		Copper Bonds		
Cu-N(1) (qo)	2.021 (5)	1.999 (6)	2.113 (7)	1.988 (5)
Cu-O(2) (qo)	2.320 (4)	2.028 (4)	2.262 (4)	2.106 (5)
Cu-N(3) (bpy)	2.055 (6)		2.012 (5)	
Cu-N(4) (bpy)	2.181 (5)		2.203 (5)	
		qo Bonds		
N(1)-O(5)	1.251 (6)	1.271 (8)	1.258 (7)	1.243 (7)
N(1)-C(6)	1.364 (7)	1.336 (8)	1.365 (8)	1.378 (9)
O(2)-C(7)	1.235 (6)	1.244 (9)	1.252 (9)	1.262 (6)
C(6)-C(7)	1.447 (8)	1.442 (10)	1.462 (10)	1.435 (10)
C(7)-C(8)	1.422 (8)	1.438 (9)	1.448 (9)	1.412 (11)
C(8)-C(9)	1.352 (8)	1.355 (13)	1.371 (11)	1.344 (9)
C(9)-C(10)	1.419 (8)	1.413 (13)	1.424 (10)	1.395 (12)
C(10)-C(11)	1.345 (7)	1.345 (10)	1.356 (8)	1.335 (11)
C(11)-C(6)	1.389 (8)	1.423 (11)	1.432 (10)	1.382 (8)
C(10)-Cl(12)	1.731 (6)	1.752 (9)	1.744 (8)	1.726 (6)

[a] A complete list of bond distances of bpy is available as supplementary material.

an octahedral polyhedron, tetragonally elongated, around copper.

Two equatorial positions are occupied by one qo-chelated ligand (indicated in Figure 2 as qo″); the other two are taken by the nitrogen donor atom of the other qo (indicated in Figure 2 as qo′) and a nitrogen atom of bpy (N(3)). The N(4) nitrogen atom of bpy and the carbonyl oxygen of qo′ occupy the axial positions. In Table III the interatomic distances are reported.

The symmetrical bpy ligand undergoes distortion, Cu–N(3) and Cu–N(4) bond lengths being respectively 2.055 (6) and 2.181 (5) Å. The features of the Cu–qo″-chelated ring sited in the equatorial plane do not differ essentially from those found in the four other Cu(II) complexes of *o*-quinone mo-

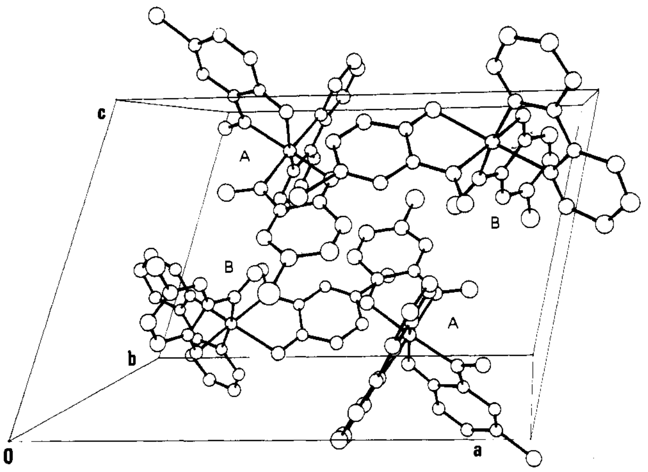

Figure 3. Perspective ORTEP view of a unit cell. The thermal spheres are drawn with 17% probability.

nooximes studied earlier.[13a] The only difference occurs in the Cu–O bond, which is lengthened to some extent; i.e., the value 2.028 (4) Å of the Cu–O(2″) bond in $Cu(qo)_2(bpy)$ compares with mean values 1.97 Å in bis(4-methyl-1-quinone 2-oximato)(pyridine)copper(II) and in aquo-bis(1,2-naphthoquinone 2-oximato)copper(II) and with 1.95 Å in diacetonebis(1,2-naphthoquinone 2-oximato)copper(II) and in diaquo(4-sulfonato-1,2-naphthoquinone 2-oximato)copper(II) trihydrate.

Correspondingly, the C(7″)–O(2″) distance, 1.244 (9) Å, is shorter than, or at least in the lower limit of, the values found in the other mentioned complexes, ranging between 1.26 and 1.30 Å. These features appear more marked in the qo′ ligand, the Cu–O(2′) bond being quite long (2.320 (4) Å), and the C(7′)–O(2′) bond (1.235 (6) Å) being the shortest found in this class of complexes; these values approach very closely those reported for metal complexes of quinone ligands[20] and indicate that in the present complex the *o*-quinone monooxime structure **1a** is predominating, and this occurs at a larger extent than in the other mentioned complexes.

A perspective projection of the structure of the complex is illustrated in Figure 3. The shortest intermolecular distances concern the two independent molecules, A and B: O(5″)–H(22) = 2.418 (6) Å and O(5′)–H(21) = 2.518 (5) Å. O(5′) and O(5″) are NO oxygens of qo′ and qo″, respectively; H(21) and H(22) pertain to the same bpy ligand.

These distances are not short enough to be considered true weak hydrogen-bond interactions.

The remaining structural features of the compound appear to be normal. Bond angles are given in Table IV.

With reference to the planarity of the chelated rings, the maximum distances (in Å) from the least-squares planes concern the two qo ligands, for which the following values have been obtained: molecule A C(7′) −0.062 (8), C(7″) −0.085 (8); molecule B C(7′) −0.084 (7), C(7″) −0.115 (8). The situation is inverted for bpy where the maximum distance for N(3) is 0.032 (7) (molecule A); bpy of molecule B appears to be nearly planar within the standard deviations.

The atoms of bpy are nearly coplanar. The individual rings are twisted 2.4 (2)° in molecule A and 4.0 (2)° in molecule B with respect to each other about the 2,2′ carbon bond.

The compound is in the cis,cis diastereomeric form, and during the preparation we found no evidence of formation of any other species; this is noteworthy since in the above-mentioned adducts with pyridine, water, and acetone the chelated ligands are in trans positions. This suggests that in the solution of $Cu(qo)_2$ cis–trans equilibrium might be present. Alternatively, if the trans structure is assumed as most likely for $Cu(qo)_2$, it follows that a rearrangement of the ligands occurs at an intermediate stage of $Cu(qo)_2(bpy)$ formation. Several pathways for such a rearrangement are possible; a likely hypothesis is preliminary formation of a square-pyramidal intermediate with bpy as an axial dangling ligand (analogous to the $Cu(qo)_2(py)$ adduct). A polytopal rearrangement of the ligands at this stage could easily occur, owing to the high plasticity of the five-coordinate copper atom.[21]

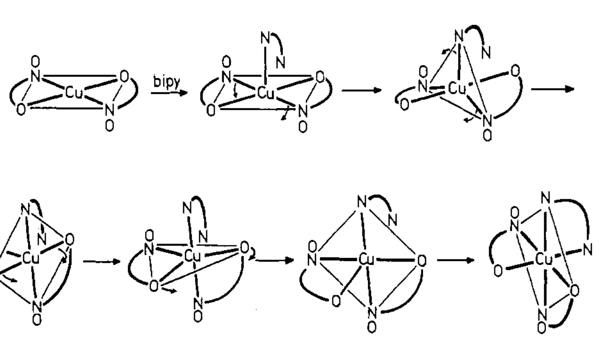

Figure 4. Possible pathway for the formation of *cis,cis*-$Cu(qo)_2(bpy)$.

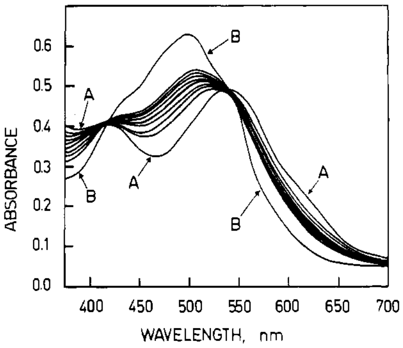

Figure 5. Absorption spectra of the system $Cu(qo)_2(bpy)$ in MeCN: A, 7.96×10^{-5} M $Cu(qo)_2$; B, molar ratio bpy:$Cu(qo)_2$ = 50; intermediate spectra, molar ratios bpy:$Cu(qo)_2$ = 0.2, 0.6, 0.8, 1, 1.4, 1.6, 2.

A hypothetical self-explanatory pathway is shown in Figure 4.

It is worthwhile to point out that the tetragonality parameter[22] is 0.899; this value significantly greater than 0.85 is consistent with a possible fluxional behavior of the CuL_6 chromophore.[21]

The cis-octahedral structure was also found for the anion in ferroverdin[23] and for tris(4-chloro-1-benzoquinone 2-oximato)nickelate(II) anion.[24]

In order to see whether the general features of the bipyridine adduct structure in solution are the same as in the crystalline state, the continuous-variation method and the molar ratio method[25] were applied to the $Cu(qo)_2$–bpy system in acetonitrile solution. The results confirmed the 1:1 adduct. Addition of successive amounts of bipyridine to $Cu(qo)_2$ in acetonitrile gives a series of absorption spectra passing through a well-defined isosbestic point (Figure 5), from which the

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Table IV. Selected Bond Angles (deg) for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses[a]

Angles around Cu

	A	B		A	B
N(1′)-Cu-N(1″)	89.3 (3)	92.0 (3)	N(1″)-Cu-O(2′)	89.5 (3)	91.4 (3)
N(1′)-Cu-N(3)	93.6 (3)	94.3 (3)	N(1″)-Cu-O(2″)	80.1 (3)	79.8 (3)
N(1′)-Cu-N(4)	96.4 (3)	95.5 (3)	N(3)-Cu-O(2′)	91.0 (2)	94.4 (3)
N(1″)-Cu-N(3)	177.0 (3)	172.2 (4)	N(3)-Cu-O(2″)	97.0 (3)	94.1 (3)
N(1″)-Cu-N(4)	103.9 (3)	96.6 (3)	N(4)-Cu-O(2′)	164.6 (2)	169.6 (3)
N(3)-Cu-N(4)	76.0 (3)	78.2 (3)	N(4)-Cu-O(2″)	99.6 (3)	89.6 (3)
N(1′)-Cu-O(2′)	76.0 (3)	77.6 (3)	O(2′)-Cu-O(2″)	90.0 (3)	98.2 (2)
N(1′)-Cu-O(2″)	162.5 (3)	170.9 (3)			

	A′	A″	B′	B″
	qo Angles (Chelated Rings)			
N(1)-Cu-O(2)	76.0 (3)	80.1 (3)	77.6 (3)	79.8 (3)
Cu-O(2)-C(7)	107.7 (5)	110.6 (6)	108.4 (5)	108.8 (5)
Cu-N(1)-C(6)	118.9 (5)	114.5 (6)	113.9 (5)	114.2 (5)
N(1)-C(6)-C(7)	113.0 (6)	110.9 (6)	115.3 (7)	111.8 (6)
O(2)-C(7)-C(6)	123.7 (6)	122.3 (7)	123.5 (7)	122.1 (7)
O(5)-N(1)-Cu	122.9 (5)	126.1 (5)	125.0 (6)	127.1 (5)
O(5)-N(1)-C(6)	118.1 (6)	119.1 (6)	121.0 (7)	118.5 (6)
	Other qo Angles			
C(6)-C(7)-C(8)	113.7 (6)	113.3 (6)	114.0 (7)	115.2 (6)
C(7)-C(8)-C(9)	123.1 (7)	122.9 (8)	121.3 (8)	120.3 (7)
C(8)-C(9)-C(10)	120.3 (6)	120.5 (8)	121.2 (7)	122.4 (8)
C(9)-C(10)-C(11)	120.0 (7)	121.5 (8)	122.3 (7)	120.0 (8)
C(10)-C(11)-C(6)	120.0 (7)	118.0 (8)	116.8 (6)	119.1 (7)
C(11)-C(6)-C(7)	122.8 (6)	123.7 (7)	123.9 (7)	122.7 (7)
C(11)-C(6)-N(1)	124.1 (7)	125.3 (8)	120.8 (6)	125.4 (7)
C(8)-C(7)-O(2)	122.5 (7)	124.4 (8)	122.5 (6)	122.7 (7)
Cl(12)-C(10)-C(9)	119.1 (5)	119.6 (6)	118.6 (6)	118.2 (6)
Cl(12)-C(10)-C(11)	120.8 (6)	118.9 (7)	119.1 (6)	121.8 (6)

[a] A list of bpy angles is available as supplementary material.

formation constant for the equilibrium $Cu(qo)_2 + bpy \rightleftarrows Cu(qo)_2(bpy)$ was obtained ($\log K_f = 4.3 \pm 0.1$). This value is consistent with the chelating behavior of bipyridine in copper complexes,[26] and therefore it seems correct to assume that the adduct in solution has the same molecular structure as in the solid state.

Adducts with Other Heterocyclic Bases. The spectra of the $Cu(qo)_2$–phen system, for molar ratios L:Cu ≥ 1 are quite similar to those reported above for $Cu(qo)_2(bpy)$. Thus, we assume that the 1:1 phenanthroline adduct has the same kind of cis,cis-octahedral structure as $Cu(qo)_2(bpy)$. The value obtained for the formation constant ($\log K_f = 3.7 \pm 0.1$) indicates a somewhat lower stability of the phenanthroline adduct. In the range of molar ratios phen:Cu ≤ 0.5 the spectra indicate the presence of a second equilibrium; the higher rigidity of the phenanthroline molecule, compared to bipyridine, might account for these results.

The spectra of pyrazole, imidazole, and pyridine adducts reveal that these compounds are largely dissociated in acetonitrile solution. At high values of L:Cu molar ratio (50:1), the absorption spectra of the system $Cu(qo)_2$–unidentate base indicate the formation of 1:2 adducts in solution. Investigation on these equilibria is in progress. The possibility of reaching hexacoordination and the remarkable stability of tris-chelated complexes indicate that the electron-withdrawing power of *o*-benzoquinone monooximate ligands is noticeable.

Adducts Containing Benzene in the Lattice. From benzene, the adducts with bpy, phen, pz, and im crystallize with solvent molecules, giving the series $Cu(qo)_2L \cdot nC_6H_6$ ($n = {}^1/_2$ for L = bpy, phen, pz; $n = 1$ for L = im). The same procedure repeatedly applied to the pyridine adduct did not result in an analogous compound. The presence of benzene, revealed by elemental analysis, was confirmed by mass spectrometry and IR spectra. Mass spectra, carried out on $Cu(qo)_2(phen) \cdot {}^1/_2C_6H_6$, chosen as a typical example of the series, showed at low probe temperature, an ion *m*/*z* 78 that is not observed in the fragmentation pattern obtained from pure phenanthroline under the same conditions.

IR spectra of pairs of compounds $Cu(qo)_2L$ and $Cu(qo)_2L \cdot nC_6H_6$ are similar, except that the last ones contain a band at 682–693 cm^{-1}. This band, assigned to the out-of-plane C–H bending of benzene (A_{2u}) and present in benzene clathrates,[27] is shifted to 500 cm^{-1} in the spectrum of $Cu(qo)_2(phen) \cdot {}^1/_2C_6D_6$, which was prepared for the sake of comparison.

Absorption spectra of these complexes, in benzene and in chloroform solutions, do not differ significantly, indicating that benzene is presumably trapped in the crystal lattice; their thermal stability depends on the ligands in the order phen > im > bpy > pz.

Further structural studies on this class of compounds are planned.

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Registry No. $Cu(qo)_2$, 61721-88-8; $Cu(qo)_2(bpy)$, 88383-79-3; $Cu(qo)_2(phen)$, 88383-75-9; $Cu(qo)_2(im)$, 88383-77-1; $Cu(qo)_2(pz)$, 88383-76-0.

Supplementary Material Available: Listings of torsion angles for chelated rings, bpy bond lengths and bond angles, least-squares planes with atomic deviations and angles, calculated positions for hydrogen atoms, anisotropic thermal parameters, and observed and calculated structure factors (71 pages). Ordering information is given on any current masthead page.

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