Inorg. Chem. **1987**, *26*, 671–675 671

Contribution from the Dipartimento di Chimica Generale and Dipartimento di Genetica
e Microbiologia, Sezione di Cristallografia, dell'Università di Pavia, 27100 Pavia, Italy

Studies on Copper(II) Complexes of *o*-Quinone Monooximes. 3.[1] Reactivity of Bis(4-chloro-1-benzoquinone 2-oximato)copper(II) with Halides. Crystal Structure of Potassium Bis(μ-iodo)tris[bis(4-chloro-1-benzoquinone 2-oximato)cuprate(II)][2]

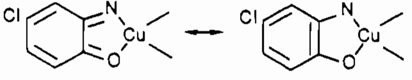
Carla Bisi Castellani,*[3a] Oliviero Carugo,[3a] and Alessandro Coda[3b]

Received July 30, 1986

The reactivity of bis(4-chloro-1-benzoquinone 2-oximato)copper(II), $[Cu(qo)_2]$, toward halides as Lewis bases was studied. While with chlorides and bromides the 1:1 adducts were formed, with iodides two different types of adducts were isolated, i.e. $Cu(qo)_2 \cdot 2Bu_4NI$ and $3Cu(qo)_2 \cdot 2KI$. X-ray crystal structure determination showed that $3Cu(qo)_2 \cdot 2KI$ is the potassium salt of a trinuclear anionic species, $[Cu(qo)_2–I–Cu(qo)_2–I–Cu(qo)_2]^{2-}$, in which copper(II) centers are linked by iodide bridges. The central Cu atom, which lies on an inversion center, reaches hexacoordination through tetragonally distorted octahedral geometry. The coordination of qo ligands around it is disordered. The outer Cu atoms have distorted square-pyramidal coordination. The compound, $C_{36}H_{18}Cl_6Cu_3K_2I_2N_6O_{12}$, crystallizes in the monoclinic space group $P2_1/c$ with cell parameters $a = 11.956$ (8) Å, $b = 15.506$ (7) Å, $c = 13.910$ (9) Å, $\beta = 110.97$ (7)°, $V = 2408$ (6) Å^3, $Z = 2$, and d(calcd) = 2.02 g·cm^{-3}. The structure converged to an unweighted R factor of 5.4% for 1843 observations and 275 parameters.

Introduction

Copper(II) bis-chelated derivatives of *o*-quinone monooximes are presently the focus of attention of many researchers because of their peculiar reactivity.[4] In fact, they react easily with many potentially basic compounds (i.e. dimethyl acetylenedicarboxylate, amines, triphenylphosphine, benzaldehyde, methanol) to give a wide variety of organic products. The mechanism of the reported reactions has been explained by assuming, as a preliminary step, the formation of adducts between the basic reagent and the copper ion; on this basis a systematic research on Lewis acidity of bis(4-chloro-1-benzoquinone 2-oximato)copper(II) [**1a** ↔ **1b**, referred to as $Cu(qo)_2$], taken as a typical example of Cu^{II} *o*-quinone monooximates, was undertaken in our laboratories. In a preceding paper, a series of $Cu(qo)_2$ adducts with etherocyclic N bases was described.[1a] In the present work we studied the reactivity of $Cu(qo)_2$ toward halides as Lewis bases. With chlorides and bromides the 1:1 adducts are formed, as in the case of the other described adducts with monodentate ligands. Instead, with iodides, two different types of adducts were obtained, i.e. $Cu(qo)_2 \cdot 2Bu_4NI$ and $3Cu(qo)_2 \cdot 2KI$. While for $Cu(qo)_2 \cdot 2Bu_4NI$ the octahedral coordination can be intuitively predicted, the stoichiometry of $3Cu(qo)_2 \cdot 2KI$ indicates a more interesting molecular structure. Therefore, X-ray determination of the structure of this compound was carried out; it was found to be the potassium salt of a quite unusual trinuclear anionic species in which copper(II) centers are linked by single iodide bridges. Cu^{II}–I linkages are seldom enountered,[5–7] since Cu^{II} is normally reduced by I^-. No other cases of iodine atoms bridging Cu^{II} centers have been reported, and thus the described structure appears to be of some interest.



1a **1b**

Experimental Section

Thermogravimetric measurements were carried out by means of the Du Pont 1090 System under a dry N_2 flow of 3 L/min. Magnetic susceptibility measurements were carried out by the Faraday method. Diamagnetic corrections were introduced.[8] Solution spectra were recorded with a Cary 2300 spectrophotometer. IR spectra were obtained with a 1330 Perkin-Elmer spectrophotometer.

Reaction with Halides. The reaction was carried out with halides whose cations are of different size and charge; the reaction medium was chosen on the basis of the solubility of the reagents. A suspension of $Cu(qo)_2$, prepared as described in the literature[9] (1 mmol in 30 cm^3 of the solvent), was refluxed for about 1 h with a large excess of the halide (10 mmol). The resulting solution was filtered and slowly evaporated at room temperature. The crystalline products, collected and washed with the reaction solvent, were dried in vacuo at room temperature.

(a) KI in Methanol. Product: dark red needles of potassium bis(μ-iodo)tris[bis(4-chloro-1-benzoquinone 2-oximato)cuprate(II)], $3Cu(qo)_2 \cdot 2KI$. Dec pt: 236 °C (weight loss 57%). Anal. Calcd for $C_{36}H_{18}Cl_6Cu_3K_2I_2N_6O_{12}$: C, 29.58; H, 1.24; Cu, 13.04; K, 5.35; N, 5.75. Found: C, 29.04; H, 1.21; Cu, 12.52; K, 5.56; N, 5.61. Cu was determined by potentiometric titration with EDTA;[10] K, by atomic absorption flame spectroscopy. As a useful alternative to the general procedure, $Cu(qo)_2$ can be Soxhlet-extracted into an excess of methanolic solution of KI.

(b) NH_4I in Ethanol. Product: dark red needles of $3Cu(qo)_2 \cdot 2NH_4I \cdot C_2H_5OH$. Anal. Calcd for $C_{38}H_{32}Cl_6Cu_3I_2N_8O_{13}$: C, 31.14; H, 2.20; N, 7.64. Found: C, 30.81; H, 2.16; N, 7.46.

The composition was confirmed by TGA. A first decomposition step was observed between 30 and 65 °C (weight loss 5.25%; calcd for 1 C_2H_5OH and 2 NH_3 5.40%). A second well-defined decomposition step occurred between 100 and 200 °C (weight loss 30.28%; calcd for 1 I and 2 qoH 30.15%; weight of the final total residue 64.38%; calcd for 1 CuI and 2 $Cu(qo)_2$ 64.38%).

Thus, it is presumable that the decomposition follows the scheme

$$3Cu(qo)_2 \cdot 2NH_4I \cdot C_2H_5OH \rightarrow C_2H_5OH + 2NH_3 + 2qoH + CuI + 2Cu(qo)_2$$

(c) NH_4I in Methanol. Product: dark red needles of bis(4-chloro-1-benzoquinone 2-oximato)(methanol)copper(II), $Cu(qo)_2 \cdot MeOH$. Dec pt: 105–110 °C. Anal. Calcd for $C_{13}H_{10}Cl_2CuN_2O_5$: C, 38.21; H, 2.47; N, 6.85. Found: C, 38.17; H, 2.32; N, 6.94. IR (Nujol): ν(methanol OH stretch) 3350–3450 cm^{-1}; ν(methanol C–O stretch) 1008 cm^{-1}. The composition was confirmed by crystal structure analysis.[11] Crystal data: space group $P\bar{1}$, with cell parameters $a = 12.389$ (9) Å, $b = 11.730$ (9) Å, $c = 5.462$ (3) Å, $\alpha = 87.21$, $\beta = 78.48$ (4)°, $\gamma = 74.84$ (5)°, $Z = 2$.

(d) Bu_4NI in Methanol. Products: after removal of a first precipitate consisting of the above described methanol adduct, dark red needles of tetrabutylammonium bis(4-chloro-1-benzoquinone 2-oximato)diiodocuprate(II), $Cu(qo)_2 \cdot 2Bu_4NI$ were obtained. Mp: 160–160.5 °C. Anal. Calcd for $C_{44}H_{78}Cl_2N_4O_4CuI_2$: C, 47.38; H, 7.05; N, 5.02. Found: C, 46.71; H, 7.09; N, 4.82.

(e) Bu_4NCl in 2-Propanol. Product: dark red needles of tetrabutylammonium chlorobis(4-chloro-1-benzoquinone 2-oximato)cuprate(II), $Cu(qo)_2 \cdot Bu_4NCl$. Mp: 148–149.5 °C. Anal. Calcd for $C_{28}H_{42}Cl_3CuN_3O_4$: C, 51.35; H, 6.47; N, 6.42. Found: C, 51.35; H, 6.42; N, 6.54.

---

(1) Parts 1 and 2 of this series: (a) Bisi Castellani, C.; Gatti, G.; Millini, R. *Inorg. Chem.* **1984**, *23*, 4004. (b) Bisi Castellani, C.; Millini, R. *J. Chem. Soc., Dalton Trans.* **1984**, 1461.

(2) Presented at IXth European Meeting of Crystallography, Torino, Italy, Sept 2–6, 1985.

(3) (a) Dipartimento di Chimica Generale. (b) Dipartimento di Genetica e Microbiologia, Sezione di Cristallografia.

(4) See references cited in ref 1.

(5) Barclay, G. A.; Hoskins, B. F.; Kennard, C. H. L. *J. Chem. Soc.* **1963**, 5691.

(6) Akhtar, F.; Goodgame, D. M. L.; Goodgame, M.; Rayner-Canham, G. W.; Skapski, A. C. *Chem. Commun.* **1968**, 1389.

(7) Rao, C. D.; Mohapatra, B. K. *J. Indian Chem. Soc.* **1977**, *54*, 432.

(8) O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 208.

(9) Charalambous, J.; Frazer, M. J.; Taylor, F. B. *J. Chem. Soc. A* **1969**, 2787.

(10) Stella, R.; Ganzerli Valentini, M. T.; Borroni, P. A. *Anal. Lett.* **1984**, *17*, 443.

(11) Bisi Castellani, C., submitted for publication in *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*

0020-1669/87/1326-0671$01.50/0

Table I. Information about Data Collection and Structure Refinement

space group	$P2_1/c$
a	11.956 (8) Å
b	15.506 (7) Å
c	13.910 (9) Å
β	110.97 (7)°
V	2408 Å^3
mol formula	$C_{36}H_{18}Cl_6Cu_3K_2I_2N_6O_{12}$
mol wt	1461.94
color	dark violet
Z	2
d(calcd)	2.02 g·cm^{-3}
radiation used for data colled	Mo Kα (λ = 0.7107 Å)
μ_{Mo}	32.2 cm^{-1}
specimen size	0.04 × 0.16 × 0.34 mm
scanning range for 2θ	$4 \leq 2\theta \leq 44°$
std for intens control	3
scan mode	$\omega/2\theta$
scan speed	4.5° min^{-1}
scan width	1.5° (in ω)
temp	293.0 (3) K
no. of unique reflcns used in last cycle of least squares ($I \geq 2\sigma(I)$)	1843 out of 2973
final R for 1843 reflcns (unit weight)	0.054
final R for the whole unique reflcns (2973)	0.089
scattering factors	from ref 13

Table II. Fractional Atomic Coordinates with Estimated Standard Deviations in Parentheses

atom	x/a	y/b	z/c
I	0.4190 (1)	0.1585 (1)	1.1075 (1)
Cu(1)	0.3543 (1)	0.3020 (1)	0.9882 (1)
Cu(2)	0.5000 (0)	0	1
K	0.3787 (2)	0.3414 (2)	0.2551 (2)
O(1)	0.2545 (7)	0.2552 (5)	0.8500 (5)
O(2)	0.1715 (6)	0.3527 (6)	1.0712 (6)
N(1)	0.1942 (7)	0.3206 (6)	0.9974 (7)
Cl(1)	−0.2526 (3)	0.2982 (4)	0.7695 (3)
C(1)	0.1444 (10)	0.2608 (8)	0.8335 (8)
C(2)	0.1034 (9)	0.2993 (8)	0.9090 (8)
C(3)	−0.0200 (11)	0.3106 (9)	0.8903 (9)
C(4)	−0.1014 (10)	0.2820 (9)	0.801 (1)
C(5)	−0.0623 (12)	0.241 (1)	0.726 (1)
C(6)	0.0563 (11)	0.2294 (9)	0.7419 (9)
O(3)	0.4326 (7)	0.3946 (5)	1.0893 (5)
O(4)	0.5302 (7)	0.2731 (6)	0.8916 (6)
N(2)	0.5030 (8)	0.3141 (6)	0.9554 (7)
Cl(2)	0.9051 (3)	0.4721 (3)	1.0786 (3)
C(7)	0.5338 (11)	0.4150 (7)	1.0874 (8)
C(8)	0.5804 (9)	0.3724 (7)	1.0174 (8)
C(9)	0.6948 (9)	0.3916 (8)	1.0135 (9)
C(10)	0.7622 (11)	0.4485 (9)	1.0781 (10)
C(11)	0.7207 (10)	0.4958 (8)	1.1488 (9)
C(12)	0.6127 (10)	0.4763 (8)	1.1536 (9)
O(5)	0.565 (2)	0.071 (2)	0.909 (2)
O(6)	0.717 (2)	−0.031 (2)	1.180 (2)
N(3)	0.666 (2)	0.001 (2)	1.098 (2)
Cl(3)	1.084 (1)	0.102 (1)	1.097 (1)
C(13)	0.676 (3)	0.084 (2)	0.955 (2)
C(14)	0.737 (3)	0.054 (3)	1.052 (2)
C(15)	0.866 (3)	0.055 (2)	1.104 (2)
C(16)	0.928 (3)	0.091 (2)	1.047 (2)
C(17)	0.870 (3)	0.128 (2)	0.949 (3)
C(18)	0.752 (3)	0.122 (2)	0.903 (2)
O(5′)	0.641 (2)	−0.020 (2)	1.129 (2)
O(6′)	0.592 (2)	0.096 (1)	0.869 (1)
N(3′)	0.610 (2)	0.063 (2)	0.949 (2)
Cl(3′)	1.066 (1)	0.117 (1)	1.058 (1)
C(13′)	0.735 (2)	0.011 (2)	1.107 (2)
C(14′)	0.734 (3)	0.050 (2)	1.023 (2)
C(15′)	0.831 (2)	0.090 (2)	1.006 (2)
C(16′)	0.937 (3)	0.070 (2)	1.085 (2)
C(17′)	0.947 (3)	0.032 (2)	1.170 (2)
C(18′)	0.852 (2)	−0.001 (2)	1.189 (2)

(f) Bu_4NBr in 2-Propanol. Product: dark red needles of tetrabutylammonium bromobis(4-chloro-1-benzoquinone 2-oximato)cuprate(II), $Cu(qo)_2 \cdot Bu_4NBr$. Mp: 121–122 °C. Anal. Calcd for $C_{28}H_{42}BrCl_2N_3O_4$: C, 51.35; H, 6.24; N, 6.00. Found: C, 48.19; H, 6.24; N, 6.00.

With Bu_4NCl or Bu_4NBr in MeOH, mixtures of the methanol and the halides adducts were obtained.

The reaction carried out with chlorides or bromides of cations other than Bu_4N^+ (NH_4^+, Na^+, K^+, Ca^{2+}, La^{3+}) invariably gave the methanol adduct. For the sake of comparison, the reaction was also carried out with ammonium, lithium, magnesium, and lanthanum perchlorates. While with lanthanum perchlorate the methanol adduct was obtained, with all the other perchlorates no reaction occurred and the unaltered $Cu(qo)_2$ was recovered.

Reaction with Potassium Cyanide. A suspension of $Cu(qo)_2$ in methanol was refluxed for about 1 h with an excess of KCN ($Cu(qo)_2$:KCN in the range 1:2 to 1:10). The solution filtered and added with benzene gave, on standing, brown needles of potassium 4-chloro-1-benzoquinone 2-oximate hemihydrate, $K(qo) \cdot {}^1/_2H_2O$. Crystal data: space group $C2/c$, with cell parameters a = 31.098 (9) Å, b = 3.897 (1) Å, c = 12.995 (3) Å, β = 102.29°, Z = 8. Dec pt: 110 °C. Anal. Calcd for $C_{12}H_8Cl_2K_2N_2O_5$: C, 35.21; H, 1.97; N, 6.87. Found: C, 34.74; H, 1.67; N, 6.80.

The composition was confirmed by crystal structure analysis.[11]

Crystallographic Study of $C_{36}H_{18}Cl_6Cu_3K_2I_2N_6O_{12}$. The data were collected on a Philips PW 1100 four-circle diffractometer using graphite-monochromatized radiation. Pertinent details are given in Table I. The only suitable sample was very thin, fractured, and irregular in shape. A total of 5928 reflections, $\pm h,\pm k,+l$ set, were measured; no intensity deterioration of standard reflections was detected. Lp correction and analytical absorption correction, for the sphere of the same volume as the crystal, plus North, Phillips, and Mathews'[12] empirical correction by azimuthal scan of six reflections ($\chi \simeq 90°$) were applied. The range of the absorption correction factor was 1.00–2.18; the averaging of reflections equivalent in pairs yielded the unique data set, with merging factors for the intensities R_I = 0.13 for the whole observed set and R_I = 0.11 for the observations with $I \geqslant 2\sigma(I)$. These rather high values reflect the poor quality of the sample. The structure was solved via Patterson synthesis and refined by unweighted least-squares full-matrix treatment, applied to anisotropic K, Cu(1), Cu(2), I, and Cu(1) coordinating qo and to isotropic Cu(2) coordinating qo, indicated in the following as qo′ (Table II). The hydrogen calculated coordinates were incorporated but not refined. The function minimized was $\sum_H ||F_o| - K|F_c||$ with unit weights. Anomalous dispersion corrections were applied.[13] An extinction correction according to Zachariasen[14] was also applied; it was small, but not negligible: $g = 5 \times 10^{-6}$ (2). A locally modified version of the Busing, Martin, and Levy ORFLS program was used.[15]

Cu(2)-coordinated qo′ appears as two "half-weigh" images, related by a local, noncrystallographic, mirror plane. The two images lie strictly on the same plane, and their chlorines and other atoms are partially superimposed, so that the settling of their coordinates was awkward; it was based on the superimposition of a transparent qo model on the F_o Fourier map, calculated on the molecular plane with a specifically written program. The anisotropic refinement of the atoms of the two half-weight qo's, partially superimposed, in the presence of heavy I, K, and two Cu's, was considered meaningless from the physical point of view. Thus, isotropic refinement was carried out for them only. Any sophisticated weight scheme in the refinement resulted in an unacceptable wandering of the coordinates of these atoms. The best behavior was obtained by using unit weights and omitting the weakest reflections from the refinement. It is well-known that a poor weighting scheme affects first the standard deviations (this was taken into account) and second the anisotropic thermal parameters of the lighter atoms (in our case isotropic refinement was carried out for them). The bond distances and angles for the Cu(2)-coordinated statistical qo's are of lower quality with respect to those of the Cu(1)-coordinated qo (Tables III and IV).

The strictly analogous complex $3Cu(qo)_2 \cdot 2NH_4I \cdot C_2H_5OH$ was only obtained in the form of extremely tiny crystals, not suitable for X-ray collection. However, there is no reason to believe that the anionic species has a different molecular structure.

---

(12) North, A. C. T.; Phillips, O. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

(13) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 99–101, 149–150.

(14) Zachariasen, W. H. *Acta Crystallogr.* **1963**, *16*, 1139.

(15) Busing, W. R.; Martin, K. O.; Levy, H. A. "ORFLS"; Report ORNL-TM-305; Oak Ridge National Laboratory: Oak Ridge, TN, 1962.

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

i	$x, y, z - 1$		
ii	$x, {}^1/_2 - y, z - {}^1/_2$		
iii	$1 - x, 1 - y, 1 - z$		
	Copper Bonds		
Cu(1)–I	2.717 (2)	Cu(2)–I	3.202 (2)
Cu(1)–O(1)	2.00 (1)	Cu(2)–O(5)	2.03 (2)
Cu(1)–N(1)	1.98 (1)	Cu(2)–N(3)	1.96 (3)
Cu(1)–O(3)	1.99 (1)	Cu(2)–O(5′)	2.00 (2)
Cu(1)–N(2)	2.00 (1)	Cu(2)–N(3′)	1.96 (2)
	qo Bonds		
N(1)–O(2)	1.26 (1)	N(3)–O(6)	1.20 (3)
N(1)–C(2)	1.36 (1)	N(3)–C(14)	1.47 (4)
O(1)–C(1)	1.26 (1)	O(5)–C(13)	1.27 (3)
C(1)–C(2)	1.44 (2)	C(13)–C(14)	1.37 (4)
C(2)–C(3)	1.42 (2)	C(14)–C(15)	1.46 (4)
C(3)–C(4)	1.35 (2)	C(15)–C(16)	1.38 (4)
C(4)–C(5)	1.43 (2)	C(16)–C(17)	1.42 (4)
C(5)–C(6)	1.37 (2)	C(17)–C(18)	1.33 (4)
C(4)–Cl(1)	1.72 (1)	C(16)–Cl(3)	1.74 (3)
N(2)–O(4)	1.23 (1)	N(3′)–O(6′)	1.18 (3)
N(2)–C(8)	1.36 (1)	N(3′)–C(14′)	1.49 (4)
O(3)–C(7)	1.26 (1)	O(5′)–C(13′)	1.34 (3)
C(7)–C(8)	1.44 (2)	C(13′)–C(14′)	1.32 (4)
C(8)–C(9)	1.42 (2)	C(14′)–C(15′)	1.40 (4)
C(9)–C(10)	1.31 (2)	C(15′)–C(16′)	1.39 (4)
C(10)–C(11)	1.45 (2)	C(16′)–C(17′)	1.30 (4)
C(11)–C(12)	1.35 (2)	C(17′)–C(18′)	1.35 (4)
C(10)–Cl(2)	1.75 (1)	C(16′)–Cl(3′)	1.85 (4)
	K Bonds[a]		
K–I	3.632 (3)	K–O(5)^{ii}	2.82 (2)
K–O(1)^{ii}	2.76 (1)	K–O(6)^{iii}	2.60 (2)
K–O(2)^{i}	2.86 (1)	K–O(5′)^{ii}	2.75 (2)
K–O(3)^{i}	2.73 (1)	K–O(6′)^{iii}	2.66 (2)
K–O(4)^{ii}	2.75 (1)		

[a] O(5′) and O(6′) are alternative to O(5) and O(6) because of the disorder of qo's around Cu(2).

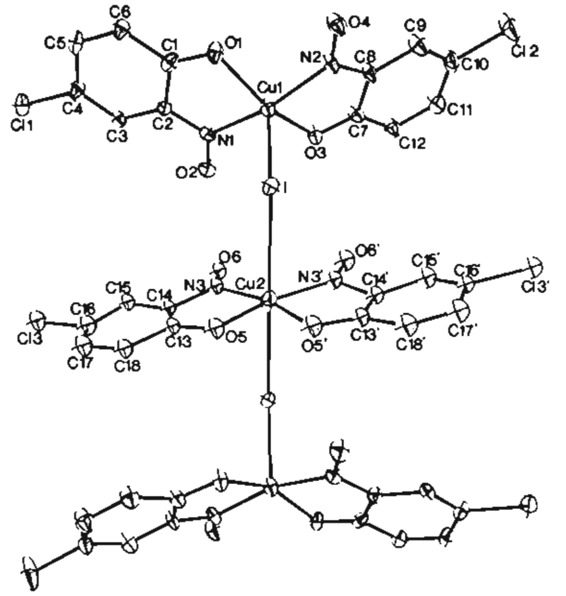


Figure 1. ORTEP view of the trinuclear anion. The coordination of qo ligands around Cu(2) is disordered and consists of the two half-occupancy qo ligands shown and the two half-occupancy qo ligands (not shown) related to the first two qo ligands by the inversion center located at the Cu(2) position.

Results and Discussion

Iodide Adducts. Crystal Structure of $3Cu(qo)_2\cdot 2KI$. The more interesting feature of the described structure is the presence of two different stereochemistries for the copper centers (Figure 1).

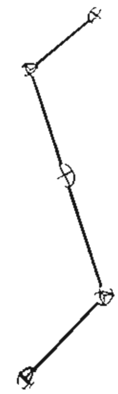


Figure 2. Perspective view of the Cu(1)–I–Cu(2)–I–Cu(1) chain that shows the angle of 114.3° about I.

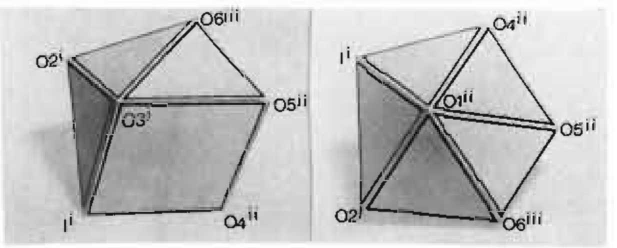


Figure 3. Two opposite views of K$^+$ coordination polyhedron, with the pentagonal basis in evidence. The superscripts bring to view the three different trinuclear anions that are involved.

The central Cu atom, which lies on a symmetry center, has tetragonally elongated octahedral coordination, with the two qo bidentate ligands occupying the equatorial positions. The outer Cu atoms have distorted square-pyramidal coordination, with the two qo ligands situated on the vertices of the square. Bridging I atoms occupy the shared axial positions of coordination polyhedra. The anion can thus be described as a chain of three Cu atoms with two μ-iodo bridges (Figure 2). Bond distances and angles of qo molecules bonded to the terminal Cu are in good agreement with values reported for other *o*-quinone monooxime complexes[1a,4] and with values recently found for $Kqo\cdot{}^1/_2H_2O$.[11] The Cu(1)–I bond length, 2.717 (2) Å, which compares well with the Cu–I distance found in the iodobis(2,2′-bipyridyl)copper(II) ion (2.70 Å),[5] is consistent with the sum of the covalent radii for copper(II) and iodine atoms (1.33 and 1.36 Å, respectively) and suggests a normal covalent copper–iodine bond. Cu(2)–I distance, 3.202 (2) Å, is long and suggests that the Cu(2)-I interaction is weak. A similar trinuclear structure, with asymmetric single halide bridges, was found for the $Cu_3Cl_{14}^{8-}$ anion.[16]

K coordinates as a distorted pentagonal bipyramid, with six oxygens and one iodine occupying the vertices (Figure 3). Three different trinuclear anions are bound to K$^+$, indicated in Table III, each with its appropriate superscript. The apical vertices are O(1)^{ii} and O(3)^{i}. The bipyramid is peculiar in that two triangular faces, i.e. I^{i}–O(3)^{i}–O(4)^{ii} and O(3)^{i}–O(4)^{ii}–O(5)^{ii}, are coplanar and fuse into a single quadrangular one.

The bridge angle Cu(1)–I–Cu(2) = 114.3 (2)°, close to the regular tetrahedral angle, allows one to conclude that the iodide ion utilizes two of its electron pairs to form metal–halogen bonds without any appreciable involvement of its two unshared electron pairs in delocalized bonding with the $Cu(qo)_2$ moieties. The magnetic behavior of the compound is consistent with this structure: in fact, the room-temperature magnetic moment is $\mu_{eff} = 3.3\ \mu_B$; this value does not point to any significant interaction between Cu^{II} ions via iodine bridges.

In the complex $(Bu_4N)_2[Cu(qo)_2I_2]$, the octahedral coordination around copper can easily be assumed, by analogy with the central unit of the trinuclear species described above.

---

(16) Antolini, L.; Marcotrigiano, G.; Menabue, L.; Pellacani, G. E. *J. Am. Chem. Soc.* **1980**, *102*, 5506.

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

iv	$1 - x, -y, 2 - z$		
	Angles around Cu(1)		
O(1)–Cu(1)–N(1)	81.8 (4)	N(1)–Cu(1)–N(2)	163.6 (4)
O(1)–Cu(1)–O(3)	155.1 (3)	N(1)–Cu(1)–I	98.6 (3)
O(1)–Cu(1)–N(2)	95.1 (4)	O(3)–Cu(1)–N(2)	82.1 (4)
O(1)–Cu(1)–I	103.4 (3)	O(3)–Cu(1)–I	101.5 (2)
N(1)–Cu(1)–O(3)	94.0 (4)	N(2)–Cu(1)–I	97.7 (3)
	Angles around Cu(2)		
O(5)–Cu(2)–N(3)	84.9 (4)	O(5′)–Cu(2)–N(3′)	86.6 (4)
O(5)–Cu(2)–I	97.0 (2)	O(5′)–Cu(2)–I	90.0 (2)
O(5)–Cu(2)–O(5)$^{\text{iv}}$	180	O(5′)–Cu(2)–O(5′)$^{\text{iv}}$	180
O(5)–Cu(2)–N(3)$^{\text{iv}}$	95.1 (4)	O(5′)–Cu(2)–N(3′)$^{\text{iv}}$	93.4 (4)
O(5)–Cu(2)–I$^{\text{iv}}$	83.0 (2)	O(5′)–Cu(2)–I$^{\text{iv}}$	90.0 (2)
N(3)–Cu(2)–I	93.9 (2)	N(3′)–Cu(2)–I	98.1 (2)
N(3)–Cu(2)–N(3′)$^{\text{iv}}$	180	N(3′)–Cu(2)–N(3′)$^{\text{iv}}$	180
N(3)–Cu(2)–I$^{\text{iv}}$	86.1 (2)	N(3′)–Cu(2)–I$^{\text{iv}}$	81.9 (2)
I–Cu(2)–I$^{\text{iv}}$	180		
	Iodine Angle		
Cu(1)–I–Cu(2)	114.3 (2)		
	qo Angles (Chelated Rings)		
O(1)–Cu(1)–N(1)	81.8 (4)	O(3)–Cu(1)–N(2)	82.1 (4)
Cu(1)–N(1)–C(2)	112.6 (8)	Cu(1)–N(2)–C(8)	112.2 (8)
Cu(1)–N(1)–O(2)	127.3 (8)	Cu(1)–N(2)–O(4)	127.3 (8)
C(1)–C(2)–N(1)	113.0 (10)	C(7)–C(8)–N(2)	113.2 (11)
O(1)–C(1)–C(2)	120.3 (11)	O(3)–C(7)–C(8)	120.3 (11)
C(1)–O(1)–Cu(1)	112.1 (7)	C(7)–O(3)–Cu(1)	112.2 (7)
O(2)–N(1)–C(2)	120.0 (10)	O(4)–N(2)–C(8)	120.5 (10)
O(5)–Cu(2)–N(3)	84.9 (4)	O(5′)–Cu(2)–N(3′)	86.6 (4)
Cu(2)–N(3)–C(14)	107.5 (5)	Cu(2)–N(3′)–C(14′)	108.8 (5)
Cu(2)–N(3)–O(6)	134.6 (5)	Cu(2)–N(3′)–O(6′)	129.9 (5)
C(13)–C(14)–N(3)	115 (3)	C(13′)–C(14′)–N(3′)	110 (3)
O(5)–C(13)–C(14)	122 (3)	O(5′)–C(13′)–C(14′)	129 (3)
C(13)–O(5)–Cu(2)	109.5 (5)	C(13′)–O(5′)–Cu(2)	104.1 (5)
O(6)–N(3)–C(14)	118 (3)	O(6′)–N(3′)–C(14′)	120 (3)
	Other qo Angles		
O(1)–C(1)–C(6)	122 (2)	O(3)–C(7)–C(12)	125 (2)
N(1)–C(2)–C(3)	125 (1)	N(2)–C(8)–C(9)	124 (1)
C(1)–C(2)–C(3)	121 (1)	C(7)–C(8)–C(9)	123 (1)
C(2)–C(3)–C(4)	119 (2)	C(8)–C(9)–C(10)	118 (2)
C(3)–C(4)–C(5)	120 (2)	C(9)–C(10)–C(11)	122 (2)
C(3)–C(4)–Cl(1)	122 (1)	C(9)–C(10)–Cl(2)	120 (2)
Cl(1)–C(4)–C(5)	118 (1)	Cl(2)–C(10)–C(11)	117 (1)
C(4)–C(5)–C(6)	122 (1)	C(10)–C(11)–C(12)	119 (2)
C(1)–C(6)–C(5)	120 (2)	C(7)–C(12)–C(11)	123 (2)
C(2)–C(1)–C(6)	117 (2)	C(8)–C(7)–C(12)	114 (2)
O(5)–C(13)–C(18)	122 (3)	O(5′)–C(13′)–C(18′)	115 (3)
N(3)–C(14)–C(15)	118 (3)	N(3′)–C(14′)–C(15′)	120 (2)
C(13)–C(14)–C(15)	125 (3)	C(13′)–C(14′)–C(15′)	128 (3)
C(14)–C(15)–C(16)	114 (3)	C(14′)–C(15′)–C(16′)	110 (3)
C(15)–C(16)–C(17)	123 (3)	C(15′)–C(16′)–C(17′)	127 (4)
C(15)–C(16)–Cl(3)	121 (3)	C(15′)–C(16′)–Cl(3′)	110 (3)
Cl(3)–C(16)–C(17)	116 (3)	Cl(3′)–C(16′)–C(17′)	123 (3)
C(16)–C(17)–C(18)	121 (3)	C(16′)–C(17′)–C(18′)	122 (3)
C(13)–C(18)–C(17)	121 (3)	C(13′)–C(18′)–C(17′)	117 (3)
C(14)–C(13)–C(18)	115 (3)	C(14′)–C(13′)–C(18′)	116 (3)

The formation of the described iodo complexes is surprising; in fact, copper(II) is normally reduced by iodide ions, and one could reasonably expect the formation of a complex of Cu$^{\text{I}}$ as happens in the case of the reaction of Cu(qo)$_2$ with triphenylphosphine.[17] As a matter of fact, the Cu$^{\text{II}}$–I system is stabilized by formation of the complex with *o*-quinone monooximate, as it has been only reported in the case of a few other ligands.[5–7] This might be related to the notable electron-withdrawing power of the qo ligand, already demonstrated in a preceding work.[1a] Moreover, we have recently found that by chemical or electrochemical reduction of Cu(qo)$_2$, the Cu(qo)$_2^-$ species is obtained, where the electron is mainly localized on the ligands, while the copper center remains in the Cu$^{\text{II}}$ form.[18]

Reactivity with Cyanide, Chlorides, and Bromides. In order to verify whether qo is also able to stabilize Cu$^{\text{II}}$ against reduction by cyanide (a potentially bridging ligand), the reaction between Cu(qo)$_2$ and KCN was carried out, but only copper(I) cyanide and the potassium salt of qo were obtained.

The ability of Cu(qo)$_2$ to form bridges with other halides was also investigated, but no polynuclear complexes were formed; in fact, with chlorides and bromides only the 1:1 adducts were obtained. These have been isolated as crystalline tetrabutylammonium salts, by operating in 2-propanol. In order to isolate the halide adducts, the choice of the cation and of the reaction medium is critical. For cations other than tetrabutylammonium (Na^+, K^+, Ca^{2+}, La^{3+}), the corresponding adducts could not be isolated, although an indication of their formation in concentrated solutions might be inferred from the increased solubility of Cu(qo)$_2$ and its color change (from violet to red-brown).

With methanol as a reaction medium, the 1:1 methanol adduct is generally obtained as the main product; however, it does not form in the absence of halides, and no significant interaction between Cu(qo)$_2$ and methanol can be demonstrated spectrophotometrically. This behavior may be explained as follows. Cu(qo)$_2$ is present in solution as a dimeric species,[9] and methanol is such a weak ligand that it is not able to break the intermolecular bonds between the copper center of one unit and the oxygen of the next. The bridging bonds are, however, broken when Cu(qo)$_2$ is refluxed with a large excess of halides, which behave as stronger Lewis bases toward Cu$^{\text{II}}$, and thus the monomer adducts can form. This view is supported by the fact that no reaction occurs in the presence of poorly coordinating perchlorates of ammonium, lithium, and magnesium, and the unaltered Cu(qo)$_2$ is recovered from the methanolic solution. In the presence of halides, several simultaneous equilibria are formed in the solution:

$$[\mathrm{Cu(qo)_2}]_2 + 2\mathrm{X}^- \rightleftarrows 2[\mathrm{Cu(qo)_2X}]^-$$

$$[\mathrm{Cu(qo)_2X}]^- + \mathrm{X}^- \rightleftarrows [\mathrm{Cu(qo)_2X_2}]^{2-}$$

$$[\mathrm{Cu(qo)_2X}]^- + \mathrm{MeOH} \rightleftarrows [\mathrm{Cu(qo)_2MeOH}] + \mathrm{X}^-$$

The crystallization of the methanol, rather than the halide, adduct depends on their relative solubilities and is therefore related to the nature of the counterion. For instance, with NH_4I the methanol adduct is formed, with KI the title compound is obtained, and with Bu_4NI first the methanol adduct crystallizes and then, separately, the adduct Cu(qo)$_2$·2Bu$_4$NI. With tetrabutylammonium chloride and bromide, both methanol and halide adducts crystallize from the solution as mixtures.

The reaction with lanthanum chloride and perchlorate requires some additional comment. Both these salts immediately react with Cu(qo)$_2$ in methanol at room temperature, and the usual adduct Cu(qo)$_2$·MeOH is obtained. This indicates that when La^{3+} is used as a cation, the reaction is not dependent on the coordinating power of the anion. We believe that, in this case, the Cu–O intermolecular bridges are disrupted by La^{3+}, which acts as a very hard Lewis acid toward the oxygen atoms. In fact, polynuclear species in which a d-metal complex (e.g. Cu$^{\text{II}}$ or Ni$^{\text{II}}$ Schiff base complexes) behaves as ligand toward lanthanoids are well-known,[19] although it has not been possible to demonstrate their formation in the present case.

In order to obtain more information about these equilibria, a spectrophotometric study of the Cu(qo)$_2$–halide systems in methanol was undertaken, but unfortunately in the range of concentrations suitable for the measurements (about 10^{-4} M) all the above described adducts were found to be completely dissociated.

Acknowledgment. We are grateful to Dr. D. Ajò, Istituto di Chimica e Tecnologia dei Radioelementi del CNR, Padova, Italy,

---

(17) Buckley, R. G.; Charalambous, J.; Kensett, M. J.; McPartlin, M.; Mukerjee, D.; Brain, E. G.; Jenkins, J. M. *J. Chem. Soc., Perkin Trans. 1* **1983**, 693.

(18) Bisi Castellani, C.; Buttafava, A.; Carugo, O.; Poggi, A., presented at the XIX National Congress of Inorganic Chemistry, Santa Margherita di Pula, Cagliari, Italy, Oct 6–10, 1986; paper A26.

(19) Harrison, D. W.; Bünzli, J. C. G. *Inorg. Chim. Acta* **1985**, *109*, 185.

for magnetic susceptibility measurements, to Dr. V. Berbenni, Dipartimento di Chimica Fisica, Università di Pavia, for thermogravimetric measurements, and to Professor L. Fabbrizzi for helpful discussions.

Registry No. $Cu(qo)_2$, 61721-88-8; $3Cu(qo)_2{\cdot}2KI$, 106400-05-9; $3Cu(qo)_2{\cdot}2NH_4I{\cdot}C_2H_5OH$, 106297-49-8; $Cu(qo)_2{\cdot}MeOH$, 106297-47-6; $Cu(qo)_2{\cdot}2Bu_4NI$, 106297-51-2; $Cu(qo)_2{\cdot}Bu_4NCl$, 106297-53-4; $Cu(qo)_2{\cdot}Bu_4NBr$, 106297-55-6; $K(qo){\cdot}{}^1/_2H_2O$, 106319-53-3.

Supplementary Material Available: Tables of calculated atomic coordinates for hydrogen atoms, torsion angles, and anisotropic thermal parameters (3 pages); a listing of observed and calculated moduli of structure factors (20 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Houston, Houston, Texas 77004

Polyaza Cavity Shaped Molecules. 11. Ruthenium Complexes of Annelated 2,2′-Biquinoline and 2,2′-Bi-1,8-naphthyridine

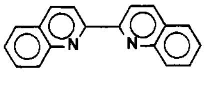
Randolph P. Thummel* and Francois Lefoulon

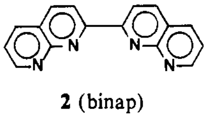
Received July 22, 1986

Ruthenium(II) complexes of the type $RuL_3(PF_6)_2$ and $Ru(bpy)_2L(PF_6)_2$ have been prepared, where bpy = 2,2′-bipyridine and L is a 3,3′-polymethylene-bridged derivative of 2,2′-biquinoline or 2,2′-bi-1,8-naphthyridine. Effects associated with steric crowding and nonplanarity of the bridged ligands are reflected in the coordination geometry of the RuL_3^{2+} complexes. These effects can be partially evaluated by consideration of NMR shielding effects and interpretation of ^1H spin–spin couplings along the polymethylene bridge. The energies of the long-wavelength MLCT absorption are sensitive to the delocalizing ability of the ligand as well as the effectiveness of coordination as dictated by steric effects. Varying the dihedral angle of the 1,4-bidentate chelating moiety affects the intensity more than the energy of charge transfer to the ligands. The oxidation potentials for the tris(biquinoline) complexes are more positive than for $Ru(bpy)_3^{2+}$ while those of the tris(binaphthyridine) complexes are more negative.

Introduction

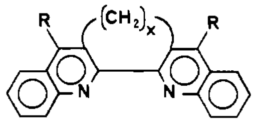
Ruthenium complexes of 2,2′-bipyridine (bpy) and related compounds have recently been the subject of intensive investigation.[1] Interest in these systems stems partly from their potential photocatalytic activity in the solar conversion of water into its elements.[2] Although the properties of the parent system, $Ru(bpy)_3^{2+}$, have been extensively studied, there have been relatively few attempts to vary the nature of the bipyridyl ligands in a regular fashion to evaluate the impact of steric and electronic factors on the complex.[3] We have undertaken such a study and herein report our initial results involving ruthenium complexes of annelated derivatives of 2,2′-biquinoline (**1**, biq) and 2,2′-bi-1,8-naphthyridine (**2**, binap).


1 (biq)


2 (binap)

We have chosen to prepare and study complexes of azabiaryl systems in which three variables are altered in a regular fashion so as to allow an evaluation of their relative importance in determining the properties of the system. The coordinating azaaryl nucleus has been varied from pyridine to quinoline to 1,8-naphthyridine. The two polynuclear biaryl systems are expected to differ from bipyridine with respect to steric bulk as well as electron delocalization and electronegativity. Second, we have varied the conformation of the biaryl system by connecting the 3- and 3′-positions with a polymethylene bridge. Third, we have examined complexes of the type RuL_3^{2+}, where three identical ligands are coordinated to the metal, and mixed-ligand complexes of the type $Ru(bpy)_2L^{2+}$, where one biq- or binap-type ligand is coordinated along with two bipyridines. In this report we will carefully examine the effect of ligand conformation on complexation as well as the complementary effect of coordination on ligand conformation.

In 1976, Klassen first reported preparation of the $Ru(biq)_3^{2+}$ complex and noted a significant red shift in the energy of its lowest lying triplet state.[4] Belser and von Zelewsky have prepared ruthenium complexes of a series of 4,4′-disubstituted 3,3′-annelated biquinolines (**3**) where the annelating bridge contained one to three methylene units and R was methyl or phenyl.[3c] In a subsequent study, they elucidated the photophysical and electron-transfer properties of $Ru(bpy)_{3-n}(DMCH)_{n+2}$, where n = 0–3 and DMCH was **3** (x = 2, R = CH_3).[5] Their results indicated that this complex where n = 1 is expected to be a more efficient mediator than $Ru(bpy)_3^{2+}$ in the water-splitting reaction. Uhlemann and co-workers have studied the spectroscopic properties and stability of copper(I) complexes of ligands of the type **3**.[6] Thomas and Rehorek have extended this work to include copper(II).[7]



3 (x = 1–3, R = CH_3, C_6H_5)

Although ruthenium complexes of 1,8-naphthyridine and substituted derivatives are known, no complexes have been reported for 2,2′-bi-1,8-naphthyridine (**2**).[8] Kaska and co-workers, however, have prepared a tris complex of the 3,3′-dimethylene-bridged derivative **5a**, for which they observe spectral and photophysical

---

(1) See for example: (a) Angel, S. M.; DeArmond, M. K.; Donohoe, R. J.; Hanck, K. W.; Wertz, D. W. *J. Am. Chem. Soc.* **1984**, *106*, 3688. (b) Barton, J. K.; Danishefsky, A. T.; Goldberg, J. M. *Ibid.* **1984**, *106*, 2172. (c) Durham, B.; Caspar, J. V.; Nagle, J. K.; Meyer, T. J. *Ibid.* **1982**, *104*, 4803. (d) Creutz, C.; Keller, A. D.; Sutin, N.; Zipp, A. P. *Ibid.* **1982**, *104*, 3618 and references cited therein.

(2) See for example: (a) Abruna, H. D.; Teng, A. Y.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 6745. (b) Lehn, J.-M.; Sauvage, J.-P.; Ziessel, R. *Nouv. J. Chim.* **1979**, *3*, 423. (c) Juris, A.; Barigelletti, F.; Balzani, V.; Belser, P.; von Zelewsky, A. *Isr. J. Chem.* **1982**, *22*, 87. (d) Connolly, J. S. *Photochemical Conversion and Storage of Solar Energy*; Academic: New York, 1981; Chapters 4 and 6 and references therein.

(3) (a) Allen, G. H.; White, R. P.; Rillema, D. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2613. (b) Lin, C.-T.; Bottcher, W.; Chou, M.; Creutz, C.; Sutin, N. *Ibid.* **1976**, *98*, 6536. (c) Belser, P.; von Zelewsky, A. *Helv. Chim. Acta* **1980**, *63*, 1675.

(4) Klassen, D. M. *Inorg. Chem.* **1976**, *15*, 3166.

(5) Juris, A.; Balzani, V.; Belser, P.; von Zelewsky, A. *Helv. Chim. Acta* **1981**, *64*, 2175.

(6) (a) Uhlemann, V. E.; Kurze, P. *J. Prakt. Chem.* **1970**, *312*, 1105. (b) Uhlemann, V. E.; Thomas, P.; Kempter, G. *Ibid.* **1965**, *30*, 273. (c) Uhlemann, V. E.; Thomas, P.; Kempter, G. *Z. Anorg. Allg. Chem.* **1965**, *341*, 11. (d) Uhlemann, V. E.; Thomas, P. *Ibid.* **1965**, *341*, 17.

(7) Rehorek, D.; Thomas, P. *Acta Chim. Acad. Sci. Hung.* **1977**, *93*, 149.

(8) Staniewicz, R. J.; Hendricker, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 6581.

0020-1669/87/1326-0675$01.50/0