$$Ni^{2+} + 2HCQE + H_2NdpNH_2 + 2CH_3CN \rightarrow Ni(HCQEdpCQE)(CH_3CN)_2{}^+ + H^+ + 2H_2O \quad (3)$$

of elemental analytical results, octahedral structures such as those shown in Figures 5–7 may be suggested for the complex. The infrared spectrum of the complex shows absorptions at 2250, 2280, and 2310 $cm^{-1}$ in the region characteristic of coordinated $CH_3CN$ ligands.[20] The IR spectrum also shows bands at 1620 and 1650 $cm^{-1}$, which may be attributed to the $\nu$(C=N) modes of the oxime and imine groups, although a specific assignment is not possible. The magnetic moment (Table I) and electronic spectrum (Table III) are also consistent with octahedral coordination for the Ni(II).

Whether the complex has the structure shown in Figure 5, 6, or 7 cannot be established on the basis of the available data. However, it might be noted that the formation of six-membered chelate rings such as those shown in Figures 6 and 7 is not unreasonable in view of the known[1] structure of bis($\delta$-camphorquinone dioximato)nickel(II) in which the ligands form six-membered rings by coordinating via N and O atoms.

**$(HCQM)_2(H_2NdpNH_2)$.** When the procedure used by Uhlig[13] for the condensation of 1,3-diaminopropane with diacetyl monooxime to give *N,N′*-(1,3-propane)(diacetyl oxime imine) was followed, HCQM failed to react with $H_2NdpNH_2$ to give the desirable monooxime imine ligand. Instead, a product of the composition $(HCQM)_2(H_2NdpNH_2)$, in which HCQM and $H_2NdpNH_2$ cocrystallized, was obtained.

The IR spectrum of this pale yellow crystalline solid in $CHCl_3$ or in a KBr pellet shows both $\nu$(C=O) and $\nu$(C=N) absorptions at 1751 and 1653 $cm^{-1}$, respectively, which are identical with those of unreacted HCQM.[3] The $\nu$(N—H) absorptions of the $H_2NdpNH_2$ are found at 3280 and 3350 $cm^{-1}$. The $^1H$ NMR spectrum taken in $CDCl_3$ shows proton signals which are merely a combination of those of the reactants since no changes in chemical shifts from those of HCQM[3] and $H_2NdpNH_2$ are observed. It is uncertain what causes this unusual cocrystallization of the two organic compounds. However intermolecular H bonding between the amino groups of $H_2NdpNH_2$ and the carbonyl or the oxime group of HCQM probably plays a role.

**$[Ni_2(CQM)_2(OH)(H_2NdpNH_2)]B(C_6H_5)_4 \cdot MeOH \cdot H_2O$.** This green solid was obtained by adding $(HCQM)_2(H_2NdpNH_2)$ to a MeOH solution containing $NiCl_2 \cdot 6H_2O$ and $NaB(C_6H_5)_4$. Conductivity data (Table I) indicate that the compound is a 1:1 electrolyte, which suggests that the oxime ligands are deprotonated. The magnetic moment after correction for the diamagnetic contributions of the ligands is 2.28 $\mu_B$, smaller than the normal value (2.8–3.4 $\mu_B$[19]) for octahedral Ni(II) complexes.

Its IR spectrum taken on a KBr pellet is very similar to that of $[Ni(CQM)(py)_3(H_2O)]PF_6 \cdot H_2O$ with intense absorptions at 1540 and 1670 $cm^{-1}$. These may be assigned to the $\nu$(C=N) and $\nu$(C=O) modes, respectively, of the coordinated $CQM^-$ ligand. The $\nu$(N—H) absorptions are observed as medium-intensity bands at 3290 and 3350 $cm^{-1}$, as in the case of $Ni(CQdpNH_2)_2[B(C_6H_5)_4]_2$.

In an attempt to confirm the presence of the various ligands in this nickel complex, it was dissolved in $CHCl_3$-*d* containing a few drops of MeOH-$d_4$ and KCN. After the cyano nickel complex $(K_2Ni(CN)_4)$ which formed was filtered off, the $^1H$ NMR spectrum of the resulting solution indicated the presence of $CQM^-$ and $H_2NdpNH_2$ as well as $B(C_6H_5)_4^-$ and free MeOH. This spectrum suggested that both $CQM^-$ and $H_2NdpNH_2$ are present as ligands in the complex. The presence of $OH^-$ in the complex was deduced from the analytical results and the overall charge required by the conductivity data. A possible structure for the complex would be one in which the two Ni atoms are bridged by an $OH^-$ group and possibly by another ligand or donor group.

Although it was expected that HCQM might react with $H_2NdpNH_2$ to yield a Schiff-base complex of the type $[Ni(HCQEdpCQE)(CH_3CN)_2]^+$, formed in the analogous reaction with HCQE, Schiff-base condensation with HCQM does not occur. This is presumably prevented for steric reasons by the methyl group at the C(1) atom. This is probably the same reason why only the C(3) carbonyl group of CQ condensed with $H_2NdpNH_2$ to give $Ni(CQdpNH_2)_2{}^{2+}$ and $Zn(CQdpNH_2)_2{}^{2+}$ rather than forming the macrocyclic complex shown in Figure 3.

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**Registry No.** $[Ni(CQM)(py)_3(H_2O)]PF_6$, 72581-91-0; $[Ni(CQE)(py)_3(H_2O)]PF_6$, 72581-93-2; $Ni(CQdpNH_2)_2[B(C_6H_5)_4]_2$, 72581-95-4; $Zn(CQdpNH_2)_2[B(C_6H_5)_4]_2$, 72599-25-8; $[Ni(HCQEdpCQE)(CH_3CN)_2]B(C_6H_5)_4$, 72708-87-3; $[Ni_2(CQM)_2(OH)(H_2NdpNH_2)]B(C_6H_5)_4$, 72708-85-1; $(HCQM)_2(H_2NdpNH_2)$, 72581-88-5; CQ, 465-29-2; HCQE, 72581-89-6; HCQM, 663-17-2; 1,3-diaminopropane, 109-76-2.

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Contribution from the Department of Chemistry, Ithaca College, Ithaca, New York 14850, and the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

# Synthesis and Characterization of Copper(II) Squarate Complexes

JAMES T. REINPRECHT,[1] JAMES G. MILLER,[1] GLENN C. VOGEL,*[1] MUIN S. HADDAD,[2] and DAVID N. HENDRICKSON*[2]

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A number of new copper(II) complexes containing an oxocarbon dianion (squarate, croconate, or rhodizonate ion) and nitrogenous counterligands have been prepared. Both monomeric and dimeric mixed-ligand complexes were isolated when the oxocarbon dianion used was the squarate ion. In these dimeric complexes the squarate ion functions as a bis-monodentate bridging ligand when the counterligand is 2,2′-bipyridine or 1,10-phenanthroline and as a bis-bidentate bridging ligand when the counterligand is 1,1,7,7-tetraethyldiethylenetriamine. In addition to normal spectral characterization, a temperature-dependent study of the magnetic susceptibility of several of the squarate dimers, indicating weak antiferromagnetic exchange interaction, is reported.

Although the chemistry of cyclic oxocarbon systems has been studied for over 100 years,[3,4] it was not until the synthesis of 1,2-dihydroxycyclobutenedione,[5] $H_2C_4O_4$, commonly referred to as squaric acid, that the coordination chemistry of

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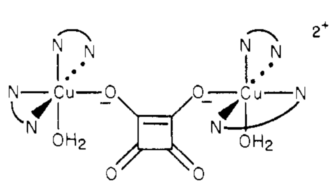
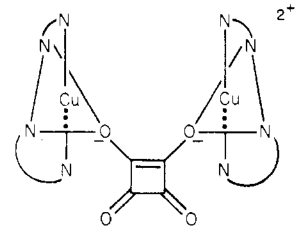
oxocarbon dianions had been studied in some detail. Several reports on the metal complexes formed by $C_4O_4^{2-}$, the squarate ion, have recently appeared.[6-13] In this paper we report the synthesis and characterization of a series of mixed-ligand copper(II) oxocarbon complexes. The specific complexes reported in this paper contain one of the oxocarbon dianions squarate ion (Sq), $C_4O_4^{2-}$, croconate ion (CR), $C_5O_5^{2-}$, and rhodizonate ion (RH), $C_6O_6^{2-}$, and one of the counterligands 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), and 1,1,7,7-tetraethyldiethylenetriamine ($Et_4$dien). Both monomeric and dimeric mixed-ligand complexes were isolated when the oxocarbon dianion employed was the squarate ion. In previously reported dimeric complexes, $[Cu_2(Et_5dien)_2Sq](BPh_4)_2$[12] and $[Ni_2(macro)_2Sq](ClO_4)_2$,[13] the squarate ion functions as a bis-bidentate bridging ligand. On the basis of the IR and EPR data reported in this paper, the squarate ion is bridging in a bis-monodentate fashion when the counterligand is bipyridine or phenanthroline. The structures proposed for these dimeric complexes can be schematically represented as I and II.



bpy-Sq
I



phen-Sq
II

## Experimental Section

**Materials.** Squaric acid was obtained from Columbia Chemicals and was recrystallized from water. 1,10-Phenanthroline monohydrate and 2,2′-bipyridine were obtained from Aldrich Chemical, and 1,1,7,7-tetraethyldiethylenetriamine was obtained from Fairfield Chemical Co. All were used without further purification.

**Compound Preparation. Cu(bpy)Sq·$H_2O$.** A solution containing 1.0 mmol of bipyridine (bpy) in 2 mL of methanol was added to 6 mL of an aqueous solution containing 1.0 mmol of sodium squarate. To this solution was added 1.0 mmol of $CuCl_2·2H_2O$ (or $Cu(ClO_4)_2·6H_2O$) in 2 mL of 75% aqueous methanol, and a green material precipitated. The solution was stirred and heated for 10 min. During this time the precipitate turned a darker green. The solution was filtered, and the precipitate was washed with $H_2O$ and methanol and dried in vacuo at 100 °C over $P_2O_5$. During drying the compound changed color to dark brown. The mass change in going from an air-dried sample to a vacuum-dried one showed that approximately four waters were lost in the transformation from the green to the brown compound.

**Cu(phen)Sq.** A solution containing 1.0 mmol of $Cu(NO_3)_2·3H_2O$ (or $Cu(ClO_4)_2·6H_2O$) and 1.0 mmol of phenanthroline (phen) was prepared in 10 mL of 75% aqueous ethanol. A hot 75% aqueous ethanol solution containing 1.0 mmol of sodium squarate was added, the solution turned brown, and a medium-brown precipitate formed, which was washed with ethanol and water and air-dried. This complex was analyzed as Cu(phen)Sq·$H_2O$. Upon drying at 100 °C, 3 mmHg over $P_2O_5$, the complex slowly lost its $H_2O$ to form an anhydrous complex. This $H_2O$ loss was accompanied by a color change from light brown to dark brown. Samples of **Cu(phen)(CR)·$H_2O$, Cu(bpy)(CR)·$H_2O$, Cu(phen)(RH)·$H_2O$,** and **Cu(bpy)(RH)·$H_2O$** were prepared in the same manner.

**Cu($Et_4$dien)Sq.** Cu(Sq)·$2H_2O$[11] (1.0 mmol) was suspended in 10 mL of warm methanol, and 1.3 mmol of 1,1,7,7-tetraethyldiethylenetriamine ($Et_4$dien) was added. The solution was stirred and moderately heated for 1 h while the solution volume was reduced to 2–3 mL. Upon cooling of the solution, a deep green complex precipitated and was filtered, washed with methanol, and air-dried. The green complex appeared to be the dihydrate as upon heating to 100 °C, 3 mmHg over $P_2O_5$, two waters of hydration were lost. The complex also changed from a green to a purple complex, which analyzed as Cu($Et_4$dien)Sq. The purple complex was obtained directly when the air-dried material was recrystallized from methanol.

**$[Cu_2(bpy)_4Sq](BF_4)_2·2H_2O$.** $Cu(BF_4)_2·xH_2O$ (~1.0 mmol) and bipyridine (2.0 mmol) were mixed together in a solution of warm 75% aqueous ethanol. A hot aqueous solution containing 1 mmol of sodium squarate was added, forming a deep green solution. Upon cooling of the solution to room temperature, large dark green needles formed. These crystals were filtered, washed with $H_2O$ and ethanol, air-dried, and recrystallized from hot $H_2O$. Upon drying at 100 °C, 3 mmHg over $P_2O_5$, the crystals changed to a very dark green. Weighing the compound before and after vacuum drying indicated that two water molecules were lost during the drying process. Elemental analysis of the vacuum-dried material showed that two waters still remained hydrated. Samples of **$[Cu_2(phen)_4Sq](ClO_4)_2·2H_2O$** and **$[Cu_2(phen)_4Sq](BF_4)_2·2H_2O$** were prepared in a similar manner.

**$[Cu_2(Et_4dien)_2Sq](PF_6)_2$.** This complex was prepared in the same manner as $[Cu_2(Et_5dien)_2Sq](BPh_4)_2$[12] by using $NaPF_6$, producing a deep brown complex.

**$[Cu_2(phen)_4Ox](BF_4)_2$.** A warm solution containing 1.0 mmol of $Cu(BF_4)_2·xH_2O$ and 2.0 mmol of phenanthroline was prepared in 15 mL of 75% aqueous ethanol, and a warm solution containing 0.5 mmol of sodium oxalate in 10 mL of $H_2O$ was added to the first solution. The resulting solution was brought to boiling, the volume was reduced to ~20 mL, and the dark blue precipitate that formed was filtered off. The resulting mother liquor was cooled to room temperature. A light blue precipitate was formed, washed with $H_2O$ and methanol, and dried at 100 °C, 1 mmHg over $P_2O_5$, for 24 h. The resulting compound was dark gray.

**Physical Measurements.** Elemental analyses were performed by the analytical laboratories at the University of Illinois and Galbraith Laboratories. Analytical data are given in the supplementary material. Molecular weights were determined by Galbraith.

Infrared spectra were recorded on Perkin-Elmer Model 237B and 337 infrared spectrophotometers as KBr pellets and Nujol mulls. UV–visible solution and reflectance spectra were run on a Cary 14 spectrophotometer. Conductance measurements were performed by using a Wayne-Kerr universal bridge 13221, employing a Sargent platinum electrode. Room-temperature magnetic moments were measured by the Gouy method.

Magnetic susceptibilities (4.2–224 K) were determined with a PAR Model 150A vibrating-sample magnetometer at a field setting of 13.5 kG. A sample of $CuSO_4·5H_2O$ was used as a standard, and all data were corrected for background, sample diamagnetism, and sample TIP (taken as $120 \times 10^{-6}$ cgsu/mol of copper dimer). The data were handled as previously reported.[12]

EPR spectra were recorded on Varian E-9 X-band and E-15 Q-band spectrometers. Low temperatures were obtained on the X-band unit with a liquid-nitrogen-cooled gas-flow system, and a similar system was used on the Q-band spectrometer.

## Results and Discussion

**Synthesis.** For the squarate complexes containing nitrogenous counterligands, elemental analyses, conductance measurements, and infrared data show that two types of complexes form, depending on the relative ratio of copper(II) ion to nitrogenous ligand in solution during complex preparation. The first type of complex, which was prepared with a copper(II) ion to nitrogenous ligand ratio of 1:1, contains no anion bands for $ClO_4^-$, $BF_4^-$, or $PF_6^-$ in the infrared

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**Table I.** Conductivity Data for Squarate Complexes in Various Solvents

| compd | solvent | measd conductance × $10^6$, $\Omega^{-1}$ | $\Lambda_M$,[a] $\Omega^{-1}$ $cm^2$ $mol^{-1}$ |
|---|---|---|---|
| $MeNO_2$ | $MeNO_2$ | 5.0 | |
| $[Cu_2(phen)_4Sq](ClO_4)_2 \cdot 2H_2O$ | $MeNO_2$ | 188 | 186 |
| $[Cu_2(phen)_4Sq](BF_4)_2 \cdot 2H_2O$ | $MeNO_2$ | 189 | 189 |
| MeOH | MeOH | 14.2 | |
| $Cu(bpy)Sq \cdot H_2O$ | MeOH | 16.6 | *b* |
| $Cu(Et_4dien)Sq$ | MeOH | 18.3 | *b* |
| $[Cu_2(bpy)_4Sq](BF_4)_2 \cdot 2H_2O$ | MeOH | 187 | 187 |
| $[Cu_2(bpy)_4Sq](BF_4)_2 \cdot 2H_2O$ | $H_2O$ | 334 | 335 |

[a] Normal range of 2:1 conductors: $MeNO_2$, 150–180; MeOH, 160–220; $H_2O$, 235–273 [Angelici, R. "Synthesis and Techniques in Inorganic Chemistry"; W. B. Saunders: Philadelphia, 1977]. [b] Nonconductor.

spectrum and is a nonconductor at ca. $10^{-3}$ M concentration (Table I). Elemental analyses indicate that these complexes have a 1:1:1 stoichiometry of Cu:Sq:(bpy, phen, *or* $Et_4dien$) and are subsequently referred to as 1:1 complexes. $Cu(Et_4dien)Sq$ and $Cu(bpy)Sq \cdot H_2O$ are soluble in polar organic solvents, the best solvent being methanol. These complexes are nonconductors and are clearly monomeric in methanol.[14] Cu(phen)Sq is only slightly soluble in the same solvents, suggesting stronger interactions between planar monomeric units.

The second type of complex, prepared with a ratio of copper(II) ion to bpy (*or* phen) of 1:2, has infrared spectral bands characteristic of tetrahedral $ClO_4^-$ or $BF_4^-$ ions. Elemental analyses for the complexes indicated a 1:$^1/_2$:2:1 stoichiometry of Cu:Sq:(bpy *or* phen):($ClO_4^-$ *or* $BF_4^-$). This type of complex is a 2:1 conductor in methanol and nitromethane (Table I) and is a dimer with the squarate ion functioning as the bridging ligand. When the tridentate nitrogenous ligand $Et_4dien$ was employed as the counterligand, the complex $[Cu_2(Et_4dien)_2Sq](PF_6)_2$ was isolated. Analogous complexes employing $Et_5dien$ in place of $Et_4dien$ are dimers with the squarate ion bridging in a bis-bidentate fashion.[12]

It is interesting to note that the copper(II) ion to squarate ion ratio was varied from 1:2 to 2:1 during the preparation of both types of complexes without any change in the stoichiometry of the complexes from what would be expected according to the ratio of copper(II) ion to nitrogenous ligand. Attempts to prepare analogous compounds with other oxocarbon dianions such as croconate, $C_5O_5^{2-}$, and rhodizonate, $C_6O_6^{2-}$, resulted in the preparation of only complexes of the 1:1 type: $Cu(phen)(CR)H_2O$, $Cu(phen)(RH)H_2O$, $Cu(bpy)(CR)H_2O$, and $Cu(bpy)(RH)H_2O$. Because of limited solubility, molecular weights of these complexes were not obtained.

**Infrared and Electronic Spectra.** Infrared spectra of squarate-containing complexes are quite characteristic of the mode of coordination. Complexes in which the squarate is coordinated through all four oxygen atoms exhibit a strong, broad-band center near 1500 $cm^{-1}$, which has been assigned to a mixture of C–C and C–O stretching vibrations.[11] Two additional bands have been observed above 1600 $cm^{-1}$ for complexes involving 1,2 bidentate coordination of the squarate ion.[7,9,10] The compound $(\eta^5\text{-}C_5H_5)_2Ti^{IV}(C_4O_4)$ was indicated to be either monomeric or polymeric, but in both cases the squarate ion is binding in a 1,2 fashion to either one or two titanium(IV) ions, respectively.[10] Medium-intensity IR bands at 1786 and 1691 $cm^{-1}$ were taken as evidence for the presence of localized C=O bonds. Similar evidence was used in postulating the structure of $V^{III}(OH)(C_4O_4)$ as a dihydroxo-bridged dimer with a squarate ion bonded to each metal ion in a 1,2 fashion.[9] Magnetism, Mössbauer, and IR data were used to deduce the structure of $Fe(C_4O_4)(OH)(H_2O)_3$ as a dihydroxo-bridged dimer with the squarate ion bonded in a 1,2 fashion.[6,7] Recently the X-ray structural determination of a nickel(II) complex was reported[8] in which the molecular structure contained chains of nickel(II) ions bridged by squarate ions bonding in a 1,3 fashion. In contrast to the infrared data for a squarate ion bonded in a 1,2 fashion, the highest energy IR band assigned to the squarate moiety occurred at 1480 $cm^{-1}$, and only the Raman spectrum contained a weak band at 1799 $cm^{-1}$.

**Table II.** Infrared Spectral Bands Attributable to the Squarate Moiety in the Region 1850–1500 $cm^{-1}$ [a]

| compd | $\nu(C{=}O)$ | $\nu(C{=}C)$ | $\nu(C{-}C)$ + $\nu(C{-}O)$ |
|---|---|---|---|
| $Cu(Et_4dien)Sq$ | 1775 w | 1620 m | 1500 s, br |
| $Cu(bpy)Sq \cdot H_2O$ | 1775 w | 1640 m | 1500 s, br |
| Cu(phen)Sq[b] | 1775 w | 1635 m | 1510 s, br |
| $Cu(phen)Sq \cdot H_2O$[c] | 1720 w | 1585 m | ~1500 s, br |
| $[Cu_2(phen)_4Sq](ClO_4)_2 \cdot 2H_2O$ | 1775 w | 1640 m | 1525 s, br |
| $[Cu_2(bpy)_4Sq](BF_4)_2 \cdot 2H_2O$ | 1775[d] | | 1545 s |
| $[Cu_2(Et_4dien)_2Sq](PF_6)_2$ | | | 1525, 1490 s, br |
| $[FeSq(OH)(H_2O)_2]_2 \cdot 2H_2O$[e] | 1815 m, sh | 1640 m, sh | 1500 s, br |
| $[VSq(OH)(H_2O)_2]_2 \cdot 2H_2O$[f] | 1801 w | 1615 w | 1515 vs, br |
| $(\pi\text{-}C_5H_5)_2TiSq$[g] | 1786 m | 1691 m | 1540 s |
| $[Ni_2(macro)_2Sq](ClO_4)_2$[h] | | | ~1520 vs |
| $[Cu_2(Et_5dien)_2Sq](BPh_4)_2$[i] | | | 1550 s |
| squaric acid[j] | 1822 w | 1643 m | 1513 s |

[a] Band assignment taken from ref 7. [b] Dried in vacuo at 100 °C over $P_2O_5$. [c] Air-dried. [d] This band is found only in $MeNO_2$ solutions of the complex. [e] Reference 7. [f] Reference 9. [g] Reference 10; 1691-$cm^{-1}$ band was assigned to CO stretch. [h] Reference 13. [i] Reference 12. [j] Reference 15; 1643-$cm^{-1}$ band was assigned to CO stretch.

The infrared bands attributable to the squarate moiety in the region 1500–1850 $cm^{-1}$ for the 1:1 copper complexes are listed in Table II. In addition to a strong, broad band at ca. 1500 $cm^{-1}$, two other bands are found at higher energy, ca. 1640 and ca. 1775 $cm^{-1}$. The position and intensities of the bands in this region are remarkably similar to those found in squaric acid[15] (Table II). This similarity and a comparison with infrared spectral data for complexes in which the squarate ion is bonding in a 1,2 fashion indicate that the squarate in these complexes is bonded in a 1,2 bidentate fashion with two uncoordinated oxygen atoms. For the 1:1 complexes the squarate ion is functioning as a chelating ligand. In the case of the Cu(phen)Sq complex, the positions of the two higher energy bands are very sensitive to the water of hydration or the drying procedure. For the air-dried complex these bands occur at 1720 and 1585 $cm^{-1}$, while for the complex dried in vacuo at 100 °C these bands become sharper and shift ca. 50 $cm^{-1}$ to 1775 and 1635 $cm^{-1}$, respectively. Only the position of bands assigned to the squarate ion is affected, suggesting that the water molecule is hydrogen bonding to the uncoordinated oxygen atoms.

The infrared bands of the dimers listed in Table II indicate that the squarate ion functions as a bridging ligand in two different fashions. For complexes with spectra containing only the strong band at ca. 1500 $cm^{-1}$, the squarate ion is functioning as a bis-bidentate ligand, while in complexes exhibiting spectra similar to those of the 1:1 type, the squarate ion is functioning as a bis-monodentate ligand. The infrared spec-

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(14) For $Cu(Et_4dien)Sq$ the experimental molecular weight in methanol was found to be 376 (theoretical 391) and for $Cu(bpy)Sq \cdot H_2O$ the experimental value obtained was 388 (theoretical 351). Because of limited solubility the molecular weight of Cu(phen)Sq could not be measured.

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**Table III.** Visible Spectral Bands of Complexes Containing Coordinated Squarate[a]

| $Cu(bpy)Sq{\cdot}H_2O$ | | $Cu(Et_4dien)Sq$ | | $Cu(phen)Sq$ | |
|---|---|---|---|---|---|
| reflectance | MeOH | reflectance | MeOH | reflectance | MeOH |
| ~740 | 665 (120) | ~740 | 690 (190) | 740 | 670 (87) |
| 490 | 420 (940) | 475 | 440 (770) | 490 | 428 (890) |
| $[Cu_2(bpy)_4Sq](BF_4)_2{\cdot}2H_2O$ | | $[Cu_2(Et_4dien)_2Sq](PF_6)_2$ | | $[Cu_2(phen)_4Sq](BF_4)_2{\cdot}2H_2O$ | |
| reflectance | MeOH | reflectance | MeOH | reflectance | MeOH |
| 710 | 690 (340) | 665 | 665 (540) | ~700 | 665 (310) |
| 465 | 453 (1100) | 400 | 415 (920) | 490 | 450 (1300) |

[a] $\lambda_{max}$ values are reported in nm; quantities in parentheses are molar extinction coefficients.

trum of $[Cu_2(phen)_4Sq](BF_4)_2{\cdot}2H_2O$ is very similar to those of the 1:1 complexes, indicating that the squarate ion is bridging in the latter fashion. In contrast, the infrared spectrum of $[Cu_2(Et_4dien)_2Sq](PF_6)_2$ contains only one band in the 1500–1800-cm$^{-1}$ region. $[Cu_2(Et_5dien)_2Sq](BF_4)_2$[12] and $[Ni_2(macro)_2Sq](ClO_4)_2$[13] are two previously reported complexes in which the squarate is bridging in a bis-bidentate fashion and their infrared spectra show one strong band in this region (Table II). The solid-state infrared spectrum of $[Cu_2(bpy)_4Sq](BF_4)_2{\cdot}2H_2O$ suggests that the squarate ion is coordinated through all four oxygen atoms. However, solution spectra of the complex show a band at 1775 cm$^{-1}$. The other bands in this region are obscured by the solvent. A possible explanation is that one mode of bonding is preferred in the solid while the other is more favorable in solution. EPR data (vide infra) indicate that the copper(II) ion coordination geometry in this complex is that of a distorted octahedron. If the squarate ion bonds in a bis-bidentate fashion in the solid, the copper(II) ion would have octahedral geometry. An alternative explanation is that the water molecules are coordinated to the copper with the squarate ion acting as a bis-monodentate ligand. In the solid, the coordinated water molecules undergo intramolecular hydrogen bonding with an uncoordinated CO group, resulting in higher site symmetry for the squarate ion and the loss of the 1775-cm$^{-1}$ band. In solution this hydrogen bonding is disrupted, and the 1775-cm$^{-1}$ band is present. In contrast to $[Cu_2(bpy)_4Sq](BF_4)_2{\cdot}2H_2O$, the solution infrared spectrum of $[Cu_2(Et_4dien)_2Sq](PF_6)_2$ does not contain a band near 1775 cm$^{-1}$.

Table III summarizes the electronic absorption spectra in the visible region for several squarate complexes. Both the reflectance and solution data are given. In general there is good agreement between the solid and solution spectra. The visible spectra of both the 1:1 and 1:2 type complexes are very similar, having two characteristic bands, one at ca. 450 nm and one at ca. 700 nm. The UV spectra of all the complexes contain a band at ca. 275 nm characteristic of the squarate ion.[3] The position of this band is insensitive to the mode of squarate coordination and to the nitrogenous counterligand.

**Magnetic Susceptibility and EPR.** The room-temperature magnetic moments for all squarate, croconate, and rhodizonate complexes lie in the range 1.85–1.90 $\mu_B$, indicating a normal d$^9$ configuration. However, temperature-dependence studies of the magnetic susceptibility of several of the dimers indicate weak antiferromagnetic exchange interaction.

Magnetic susceptibility data were collected between 224 and 4.2 K for $[Cu_2(bpy)_4Sq](BF_4)_2{\cdot}2H_2O$, $[Cu_2(phen)_4Sq](ClO_4)_2{\cdot}2H_2O$, and $[Cu_2(phen)_4Ox](BF_4)_2$. The data for these three compounds are given in Tables IV–VI[16] and are illustrated in Figures 1 and 2, respectively. There is no evidence of a magnetic exchange interaction down to 4.2 K for the oxalate-bridged complex, whereas the data for the two squarate-bridged complexes clearly indicate the presence of an antiferromagnetic exchange interaction for each complex. Susceptibility vs. temperature maxima occur at 6.2 and 17.2 K for the bpy–Sq and phen–Sq complexes, respectively. The susceptibility data for these latter two complexes were least-squares fit to the Bleaney–Bowers equation[17] for isotropic exchange interaction ($\hat{H} = -2J\hat{S}_1{\cdot}\hat{S}_2$) in a copper(II) dimer. The data for $[Cu_2(bpy)_4Sq](BF_4)_2{\cdot}2H_2O$ were fit to $J = -3.4$ cm$^{-1}$ and $g = 2.14$, while the data for $[Cu_2(phen)_4Sq](ClO_4)_2{\cdot}2H_2O$ were fit to $J = -10.1$ cm$^{-1}$ and $g = 2.17$. The solid lines in Figures 1 and 2 illustrate these two fits to the theoretical equation. It is clear that the phen–Sq exhibits the stronger antiferromagnetic exchange interaction of the two squarate-bridged complexes.

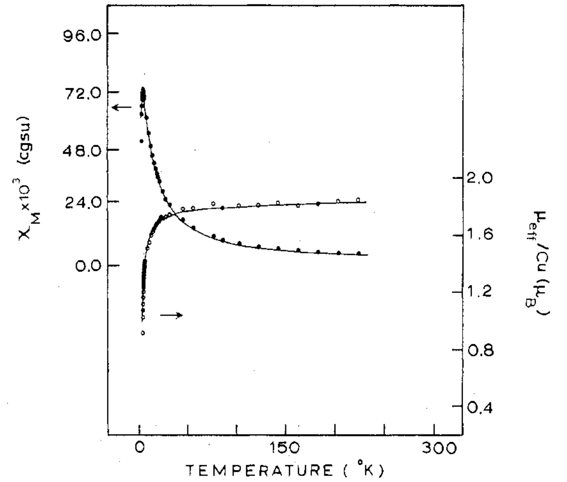

**Figure 1.** Experimental molar paramagnetic susceptibility (●) per mole of binuclear complex and effective magnetic moment (○) per Cu(II) ion vs. temperature for $[Cu_2(bpy)_4Sq](BF_4)_2{\cdot}3.5H_2O$. Solid lines represent the least-squares fit to the theoretical equation.

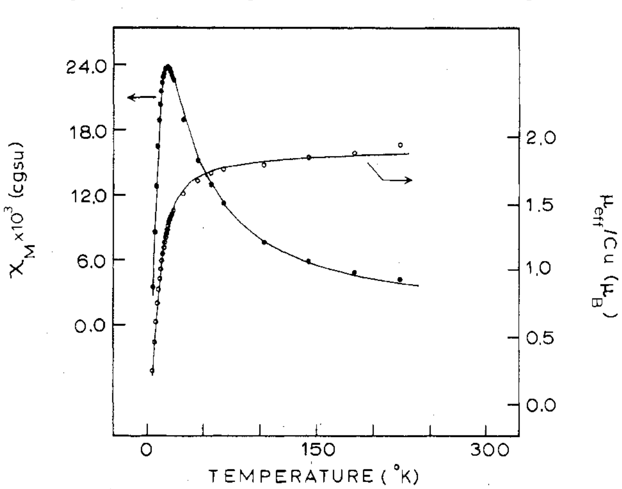

**Figure 2.** Experimental molar paramagnetic susceptibility (●) per mole of binuclear complex and effective magnetic moment (○) per Cu(II) ion vs. temperature for $[Cu_2(phen)_4Sq](ClO_4)_2{\cdot}2H_2O$. Solid lines represent the least-squares fit to the theoretical equation.

Q-Band EPR spectra were recorded at both room temperature and ca. 110 K for the three binuclear complexes. The ca. 110 K spectra are illustrated in Figure 3. The spectrum for the bpy–Sq complex does not change in the temperature range investigated, whereas the spectra for the other two bi-

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(16) Supplementary material.

(17) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451.

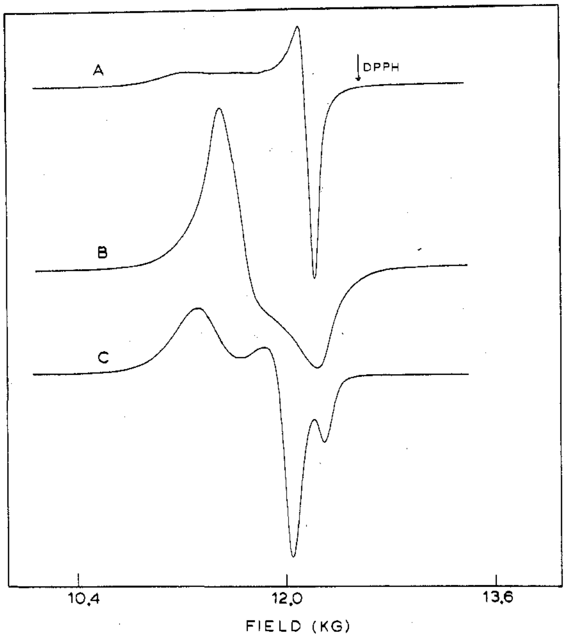


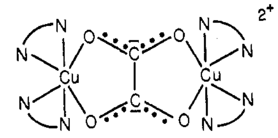
**Figure 3.** Liquid-nitrogen temperature Q-band EPR spectra: A, $[Cu_2(bpy)_4Sq](BF_4)_2{\cdot}3.5H_2O$; B, $[Cu_2(phen)_4Sq](ClO_4)_2{\cdot}2H_2O$; C, $[Cu_2(phen)_4Ox](BF_4)_2$.

nuclear complexes show greater resolution of signals at the lower temperature. The axial spectrum seen for $[Cu_2(bpy)_4Sq](BF_4)_2{\cdot}2H_2O$ has features at $g_{\parallel} = 2.237$ and $g_{\perp} = 2.065$, which clearly indicates that the copper(II) ion coordination geometry is that of a distorted octahedron. An octahedral coordination geometry is also indicated for $[Cu_2(phen)_4Ox](BF_4)_2$, because the "parallel" signal is seen at lower field, $g_{\parallel} = 2.225$, than the "perpendicular" signal at $g_{\perp} = 2.110$. The weak signal seen for this compound at even higher field in tracing C is due to an impurity as evidenced by the observation that the relative intensity of this signal changes from one sample to another.

An axial EPR spectrum is also seen for $[Cu_2(phen)_4Sq](ClO_4)_2{\cdot}2H_2O$; however, unlike the case for the other two binuclear complexes, the copper(II) ion coordination geometry in this complex is most likely trigonal bipyramidal. The $g_{\parallel}$ (2.048) signal occurs at higher field than the $g_{\perp}$ (2.152) signal.

As mentioned above (Table II), the IR spectra of the bpy–Sq and phen–Sq complexes show a band at ca. 1775 $cm^{-1}$, which is attributable to an uncoordinated C=O bond. The squarate dianion in these two complexes is, thus, not functioning as a bis-bidentate bridge but bridges as a bis-monodentate ligand. Taken together with the conclusions about coordination geometry from the EPR data, the structures of the binuclear cations in the two squarate complexes can be schematically represented by I (bpy–Sq) and II (phen–Sq). No X-ray structural reports have appeared yet to establish the possibility of 1,2 binding of the squarate ion.

In $[Cu_2(phen)_4Ox](BF_4)_2$, the copper(II) ions are octahedrally coordinated, which means that the oxalate dianion is bridging in a bis-bidentate manner. The IR data are in agreement with this. The binuclear cation has the structure



There is no evidence of a magnetic exchange interaction for this complex in the susceptibility data measured down to 4.2 K, which means that $|J| <$ ca. 0.5 $cm^{-1}$. The same observation has been made for $[Cu_2(tren)_2Ox](BPH_4)_2$, where tren is 2,2′,2″-triaminotriethylamine.[12,13] As advanced before, the explanation for the weak interaction lies in the fact that the unpaired electron for each copper(II) ion resides in a metal 3d orbital which is perpendicular to the plane of the oxalate bridge. The oxalate dianion propagates magnetic exchange interactions largely by $\sigma$-type orbitals.[12,13,18]

The exchange interaction is greater for $[Cu_2(phen)_4Sq](ClO_4)_2{\cdot}2H_2O$ than for the phen–Ox compound largely because the copper(II) ions in the former complex are trigonal bipyramidal. The $d_{z^2}$ ground state can interact effectively via a bridging ion bonded in an equatorial site. In $[Cu_2(phen)_4CN](PF_6)_3$, the cation $[Cu_2(phen)_4(CN)]^{3+}$ consists of two trigonal-bipyramidal copper(II) moieties bridged from one equatorial site to another by a cyanide ion in an end-to-end fashion. In this case, $J$ was found[19] to be $-29$ $cm^{-1}$. It is also important to note that the 1,2-bridging squarate ion has a nonaromatic character, which is most likely better situated to propagate an exchange interaction than the aromatic bis-bidentate squarate bridge. Aromaticity in the squarate ion indirectly stabilizes the $\sigma$ orbitals of the bridge, and this reduces the interaction between the squarate ion $\sigma$ orbitals and the metal unpaired-electron orbital.[12,13,18]

The presence of an exchange interaction in $[Cu_2(bpy)_4Sq](BF_4)_2{\cdot}2H_2O$ is probably due to an octahedral coordination geometry which is distorted to allow the same $\sigma$ interaction between the metal unpaired-electron orbital and the squarate orbitals. A crystal structure determination is needed to understand the origin of the interaction in this compound.

**Registry No.** $Cu(bpy)Sq{\cdot}H_2O$, 72541-48-1; Cu(phen)Sq, 72541-49-2; $Cu(bpy)(CR){\cdot}H_2O$, 72541-50-5; $Cu(phen)(RH){\cdot}H_2O$, 72541-51-6; $Cu(bpy)(RH){\cdot}H_2O$, 72541-52-7; $Cu(phen)(CR){\cdot}H_2O$, 72541-53-8; $Cu(Et_4dien)Sq$, 72541-54-9; $[Cu_2(bpy)_4Sq](BF_4)_2{\cdot}2H_2O$, 72541-56-1; $[Cu_2(phen)_4Sq](ClO_4)_2$, 72541-58-3; $[Cu_2(phen)_4Sq](BF_4)_2$, 72597-27-4; $[Cu_2(Et_4dien)_2Sq](PF_6)_2$, 72541-60-7; $[Cu_2(phen)_4Ox](BF_4)_2$, 72541-62-9.

**Supplementary Material Available:** Tables IV–VII giving magnetic susceptibility data and analytical data (5 pages). Ordering information is given on any current masthead page.

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(19) Bieksza, D. S.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 924.