Our results demonstrate the formation of superoxide in the oxidation of CuL_2^+ by molecular oxygen in aqueous solution. Superoxide potentiates the cleavage reaction because it increases the concentration of CuL_2^+ by reduction of CuL_2^{2+}, which subsequently reacts with hydrogen peroxide to yield the hydroxyl radicals. Our results seem to contradict this hypothesis. For example, the cuprous complex of 2,2'-bipyridyl, which does not cleave DNA, produces diffusible superoxide at rates comparable to those of 1,10-phenanthroline, while the cuprous complex of 5-nitro-1,10-phenantrholien, which damages DNA more effectively than 1,10-phenanthroline, produces the diffusible superoxide at a rate that is 100-fold lower than that of 1,10-phenanthroline. These results are in agreement with those observed earlier by Sigman.[2]

One might also assume that the difference in the DNA cleavage reaction is due to the different rates at which O_2^- reduces the Cu(II) complexes. Our results show that k_7 and k_{cat} have almost the same values for the various Cu(II) complexes. Moreover, according to our results, no correlation exists between the rate at which CuL_2^+ reacts with hydrogen peroxide to form OH· and its ability to damage the DNA.

Therefore, it seems that the main source of damage to DNA in these systems does not originate from OH· radicals being formed in the bulk of the solution.

We believe that the breakdown of the DNA depends on the binding or intercalating of the coordination complex to the DNA during the course of the reaction. One possibility is that the rate constants of the relevant reactions of free and bound CuL_2^+ may be different. Those cuprous complexes that cleave DNA may have higher rate constants when they are bound or intercalated to the DNA than those that do not cleave the DNA.

Another very probable possibility is that the cuprous complexes that cause the damage intercalate into the DNA in a unique orientation. This is in accord with the observation of Pope and Sigman[29] on the difference in the damage of cuprous 1,10-phenanthroline on the A, B, and Z forms of DNA. This seems to be a probable explanation for the inability of cuprous 2,2'-bipyridyl to cleave DNA even though its coordination chemistry is similar to that of 1,10-phenanthroline and the fact that complexes of 2,2'-bipyridyl may bind to DNA.[30]

We expect that a site-specific mechanism may operate in this system and therefore a different orientation in the intercalation of CuL_2^+ into the DNA will yield the hydroxyl radical, according to reaction 18, at different sites and thus will cause the difference in the ability to cleave the DNA for the various cuprous complexes.

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Registry No. $Cu(5\text{-Me-op})_2^+$, 17702-23-7; $Cu(5\text{-Cl-op})_2^+$, 52152-05-3; $Cu(5\text{-NO}_2\text{-op})_2^+$, 59751-73-4; $Cu(neocup)_2^+$, 21710-12-3; $Cu(2,2'\text{-bpy})_2^+$, 36450-97-2; O_2, 7782-44-7; H_2O_2, 7722-84-1.

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Preparation, Crystal Structure, and Spectroscopic Characterization of the Tetranuclear Copper–Thiolate Cluster $[Cu_4(o\text{-}(SCH_2)_2C_6H_4)_3]^{2-}$ as Its $[PPh_4]^+$ Salt

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$[Cu_4(o\text{-}(SCH_2)_2C_6H_4)_3]^{2-}$ has been prepared by reacting $K_2[o\text{-}(SCH_2)_2C_6H_4]$ with $[Cu(N\text{-methylimidazole})_4][BF_4]$ (1.1:1) in dried acetonitrile and by reacting $Cu(NO_3)_2\cdot 6H_2O$, NEt_3, and $o\text{-}(HSCH_2)_2C_6H_4$ (1:10:5) in ethanol. $[PPh_4]_2[Cu_4(o\text{-}(SCH_2)_2C_6H_4)_3]\cdot MeCN$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.900$ (2) Å, $b = 14.000$ (2) Å, $c = 21.550$ (3) Å, $\alpha = 82.09$ (2)°, $\beta = 81.06$ (2)°, $\gamma = 73.21$ (2)°, $V = 3379.1$ Å^3, and $Z = 2$. The structure was solved by direct methods, followed by least-squares refinement using 5374 reflections to a final R value of 0.072 ($R_w = 0.098$). The anion consists of a tetrahedron of copper atoms (Cu- - -Cu = 2.726 (16) Å), each edge of which is spanned by a μ-thiolato group, and each copper is coordinated by a trigonal-planar array of sulfur atoms (Cu–S = 2.272 (20) Å). The arrangement of the three chelate rings produces an overall symmetry for the anion that is approximately C_3. ^1H and ^{13}C NMR data are consistent with the maintenance of this structure in solution.

Copper–thiolate chemistry is of much current interest, as part of the sustained interest in the thiolate chemistry of the later 3d transition metals,[2–24] together with the cysteinyl ligation of this metal that has been established for plastocyanin[25] and other "blue" copper[26] and metallothionein[27] proteins. The latter are capable

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of binding several copper(I) atoms,[28] the maximum copper to cysteinyl ratio so far reported being ca. 1:1 in the low molecular weight metallothionein from *Neurospora crassa*.[29] In general, these proteins are considered to form oligomeric assemblies of the metal atoms via μ-thiolate groups, cf. the $Cd_4(Scys)_{11}$ and $Cd_3(Scys)_9$ groupings proposed on the basis of ^{113}Cd NMR data.[30] There is good chemical precedence for oligomeric copper(I)-thiolate species, with anions such as $[Cu_4(SR)_6]^{2-}$ (R = Ph[16,17] Me[17]), $[Cu_5(S\text{-}t\text{-}Bu)_6]^-$,[18] $[Cu_5(SPh)_7]^{2-}$,[19] and $[Cu^I{}_8Cu^{II}{}_6(SCMe_2CH(NH_2)CO_2)_{12}Cl]^{5-}$[20] having been structurally characterized.

In seeking further developments of copper-thiolate chemistry, we have examined reactions of Cu^I and Cu^{II} compounds with *o*-xylene-α,α'-dithiol ($(HS)_2$-*o*-xyl). This was considered of interest since the ligand has proven to be a versatile chelate,[5,8,9,14,15] since its initial employment[31] in the synthesis of $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{2-}$. Herein, we report two preparations and the structural characterization of $[PPh_4]_2[Cu_4(S_2\text{-}o\text{-}xyl)_3]$, the first structurally characterized copper-*o*-xylenedithiolate complex that, presently, represents the largest metal aggregate supported by this chelating 1,4-dithiolate.

Experimental Section

Preparation of $[PPh_4]_2[Cu_4(S_2\text{-}o\text{-}xyl)_3]$. All manipulations were performed in standard Schlenk-type apparatus under an atmosphere of purified dinitrogen. *o*-Xylene-α,α'-dithiol was prepared as described previously.[31] Two synthetic routes to the title complex were developed:

Method A. $K_2(S_2\text{-}o\text{-}xyl)$ was prepared by dissolving *o*-xylene-α,α'-dithiol (2.4 g, 14.1 mmol) in freshly distilled, degassed THF (ca. 100 mL) and stirring with potassium metal (1.1 g, 28.1 mmol) for ca. 2 days at room temperature (i.e., until all of the metal had reacted). The white precipitate of $K_2(S_2\text{-}o\text{-}xyl)$ was separated by filtration, washed with fresh THF, and dried in vacuo prior to use. $[Cu(N\text{-methylimidazole})_4][BF_4]$[32] (1.6 g, 3.3 mmol) was dissolved in dried (over CaH_2), freshly distilled, MeCN (ca. 20 mL) and the solution degassed prior to the addition of $K_2(S_2\text{-}o\text{-}xyl)$ (0.9 g, 3.7 mmol) that, initially, produced a mustard-colored solution and a white precipitate. After ca. 5 min, the solution became red-brown in color; $[PPh_4]Cl$ (2.5 g, 6.7 mmol) was added, and the solution gradually attained a yellow coloration. The reaction was considered to be complete after ca 2 h when essentially all of the $K_2(S_2\text{-}o\text{-}xyl)$ had reacted. The solution was filtered to remove a fine, off-white, precipitate, and the filtrate was concentrated by evaporation at room temperature in vacuo and allowed to stand at ca. −20 °C. The bright yellow microcrystalline precipitate that formed was separated by filtration and washed with several small (ca. 5 mL) portions of cyclohexane and then diethyl ether, prior to dissolution in the minimum volume of MeCN at ca. 40 °C. This solution was allowed to cool slowly to room temperature, when bright orange-red, trapezoidal crystals were obtained, which proved suitable for X-ray diffraction studies. Further concentration and cooling of the filtrate yielded more of the title compound, the overall yield being 2.9 g (60%). [*Note*: If, after it was washed, the crude material was redissolved in MeCN at room temperature and then stored at −20 °C, yellow needle-shaped crystals were formed. This product lost its crystallinity in vacuo, and the powder obtained was analytically and spectroscopically identical with the bright orange-red crystalline product].

Method B. $Cu(NO_3)_2\cdot 6H_2O$ (0.6 g, 2.0 mmol) and NEt_3 (2.0 g, 19.8 mmol) were dissolved in ethanol (60 mL), and the solution was degassed prior to the addition of *o*-xylene-α,α'-dithiol (1.7 g, 10.0 mmol). $[PPh_4]Br$ (2.6 g, 6.2 mmol), dissolved in ethanol (10 mL) was added to the resultant pale yellow solution, and after the solution was allowed to stand at room temperature for several hours, its color darkened and small orange crystals were formed. The yield at this stage was 2.1 g (70%) and could be improved by the addition of more $[PPh_4]Br$. The precipitate was collected by filtration, washed with small portions (ca. 1 mL) of ethanol and diethyl ether, and dried in vacuo.

Table I. Crystallographic Data for $[PPh_4]_2[Cu_4(S_2\text{-}o\text{-}xyl)_3]\cdot MeCN$[a]

chem formula	$C_{74}H_{67}Cu_4NP_2S_6$
form wt	1478.8
cryst color	orange-red
cryst size	0.3 × 0.4 × 0.55 mm
temp	291 K
diffractometer	Stoe-Siemens AED
radiation	Mo Kα, graphite monochromator
λ	0.710 69 Å
cryst syst	triclinic
space gp	$P\bar{1}$
a	11.900 (2) Å
b	14.000 (2) Å
c	21.550 (3) Å
α	82.09 (2)°
β	81.06 (2)°
γ	73.21 (2)°
V	3379.1 Å^3
Z	2
d_{calcd}	1.453 g cm^{-3}
μ	1.51 mm^{-1}
$F(000)$	1520
scan type	θ/ω, profile fitting[33]
2θ range	7–45°
index ranges: h	0 to 12
k	−15 to +15
l	−23 to +23
no. of reflcns measd	8799
no. of reflcns with $F > 6\sigma(F)$	5374
transmissn factors	0.48–0.67
R	0.072
wtd R	0.077
weighting	$w^{-1} = \sigma^2(F) + 0.003F^2$
shift/esd: max	0.020
mean	0.006
slope of normal prob plot	1.22
max peak in final diff map	+1.30 e Å^{-3}
max hole in final diff map	−1.07 e Å^{-3}

[a] The standard deviation of the least significant figure is given in parentheses in this and subsequent tables.

Anal. Calcd for $C_{72}H_{64}Cu_4P_2S_6$: C, 60.1; H, 4.5; Cu, 17.7; P, 4.3; S, 13.4. Found: C, 60.0; H, 4.8; Cu, 16.9; P, 4.0; S, 13.3.

Crystal Structure Determination. Crystal data and data collection parameters are given in Table I. Unit cell parameters were obtained by least-squares refinement from 2θ values of 30 reflections centered at $\pm\omega$ ($20 < 2\theta < 25°$).[33] Data were collected by an on-line profile-fitting method.[34] Problems with the X-ray generator caused slow variations of up to 15% in the intensities of three standard reflections: corresponding corrections were applied to the data. Semiempirical absorption corrections based on azimuthal scan measurements were also applied.[33]

The structure was solved by direct methods and refined on F by blocked-cascade least-squares methods, with anisotropic thermal parameters for all non-hydrogen atoms. Phenyl rings of the cations were constrained to ideal regular hexagons with C–C = 1.395 Å, and H atoms were included with constraints: C–H = 0.96 Å, H–C–H = 109.5° for CH_2, H on external bisectors of aromatic ring angles, $U(H) = 1.2U_{eq}(C)$. The acetonitrile solvent molecule was refined as a linear rigid group with C–C = 1.47 Å, C–N = 1.15 Å, and no H atoms. Complex scattering factors were taken from ref 35.

The relatively high R value is due to high thermal motion of the cations and solvent and probable disorder in the latter.

Final refined atomic coordinates are given in Table II, and a selection of interatomic distances is presented in Table III. Calculated atomic coordinates, anisotropic thermal parameters, isotropic thermal parameters

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Table II. Refined Atomic Coordinates ($\times10^4$) for $[PPh_4]_2[Cu_4(S_2\text{-}o\text{-}xyl)_3]\cdot MeCN$

atom	*x*	*y*	*z*
Cu(1)	555 (1)	963 (1)	6973 (1)
Cu(2)	229 (1)	2789 (1)	7382 (1)
Cu(3)	2304 (1)	1921 (1)	6678 (1)
Cu(4)	1826 (1)	1165 (1)	7879 (1)
S(11)	1855 (2)	886 (2)	6094 (1)
S(12)	1124 (2)	−169 (2)	7822 (1)
C(11)	3015 (9)	−311 (7)	6192 (6)
C(12)	2488 (9)	−1176 (7)	6358 (5)
C(13)	2253 (9)	−1644 (8)	5880 (6)
C(14)	1854 (9)	−2482 (9)	5970 (6)
C(15)	1640 (10)	−2890 (9)	6601 (6)
C(16)	1840 (9)	−2435 (9)	7090 (6)
C(17)	2248 (9)	−1580 (7)	6977 (5)
C(18)	2439 (10)	−1145 (9)	7535 (5)
S(21)	−1184 (2)	2142 (2)	7179 (1)
S(22)	700 (2)	2505 (2)	8399 (1)
C(21)	−1840 (10)	1703 (9)	7962 (5)
C(22)	−2315 (8)	2481 (8)	8424 (5)
C(23)	−3482 (10)	3076 (9)	8411 (5)
C(24)	−4014 (11)	3733 (9)	8854 (6)
C(25)	−3382 (13)	3878 (9)	9305 (6)
C(26)	−2222 (13)	3322 (9)	9321 (5)
C(27)	−1665 (9)	2607 (8)	8872 (5)
C(28)	−409 (10)	2013 (9)	8927 (5)
S(31)	1427 (2)	3566 (2)	6713 (1)
S(32)	3656 (2)	1131 (2)	7365 (1)
C(31)	2259 (9)	3989 (9)	7230 (6)
C(32)	3544 (9)	3772 (9)	6983 (6)
C(33)	3932 (10)	4454 (9)	6536 (6)
C(34)	5108 (11)	4309 (10)	6275 (6)
C(35)	5898 (10)	3410 (9)	6458 (6)
C(36)	5550 (9)	2729 (9)	6895 (5)
C(37)	4385 (9)	2881 (9)	7185 (5)
C(38)	4095 (11)	2106 (9)	7683 (5)
P(1)	1830 (2)	2741 (2)	4066 (1)
C(112)	209 (5)	2785 (4)	5132 (3)
C(122)	1939 (6)	4343 (5)	3166 (3)
C(132)	3150 (5)	747 (5)	4147 (4)
C(142)	4074 (6)	3005 (6)	3944 (3)
P(2)	4423 (2)	2142 (2)	954 (1)
C(212)	6178 (7)	358 (6)	922 (3)
C(222)	2416 (6)	1561 (5)	1410 (3)
C(232)	4469 (5)	3287 (6)	1912 (3)
C(242)	3306 (7)	2500 (5)	−125 (4)
N	9661 (13)	2843 (13)	819 (7)

Table III. Selected Interatomic Distances (Å) in $[Cu_4(S_2\text{-}o\text{-}xyl)_3]^{2-}$

Cu(1)-Cu(2)	2.722 (2)	Cu(1)-Cu(3)	2.739 (2)
Cu(1)-Cu(4)	2.738 (2)	Cu(2)-Cu(3)	2.737 (2)
Cu(2)-Cu(4)	2.720 (2)	Cu(3)-Cu(4)	2.699 (2)
Cu(1)-S(11)	2.245 (3)	Cu(1)-S(12)	2.298 (3)
Cu(1)-S(21)	2.269 (3)	Cu(2)-S(21)	2.248 (3)
Cu(2)-S(22)	2.300 (3)	Cu(2)-S(31)	2.262 (3)
Cu(3)-S(11)	2.264 (4)	Cu(3)-S(31)	2.244 (3)
Cu(3)-S(32)	2.294 (3)	Cu(4)-S(12)	2.280 (4)
Cu(4)-S(22)	2.286 (3)	Cu(4)-S(32)	2.276 (3)

for hydrogen atoms, remaining bond lengths and bond angles, and a list of $|F_o|$ and $|F_c|$ are available as supplementary material.

Spectroscopic Studies. NMR spectra were recorded for $(CD_3)_2SO$ solutions of the title compound at ambient temperature. ^1H (300-MHz) and ^{13}C (75 MHz) NMR spectra were obtained on a Varian XL-300 spectrometer by the pulse Fourier transform technique using Me_4Si as an internal reference. ^{13}C NMR (20 MHz) data were also obtained on a Bruker WP80 instrument.

UV-visible spectra were recorded on Pye Unicam SP8-500 and Perkin-Elmer 402 spectrometers, and IR spectra were obtained for Nujol mulls of the title compound held between CsI plates, in the range 4000–200 cm^{-1} on a Perkin-Elmer 577 spectrometer.

Results and Discussion

Description of the Structure. The molecular structure of the anion of $[PPh_4]_2[Cu_4(S_2\text{-}o\text{-}xyl)_3]\cdot MeCN$ is presented in Figure 1; selected bond lengths and interbond angles are detailed in Tables III and IV, respectively. The overall symmetry approximates to C_3 and comprises an essentially tetrahedral arrangement of copper atoms, each edge of which is spanned by a μ-sulfur atom; one atom from each chelate bridges across an edge of the base of the tetrahedron (Cu(1), Cu(2), Cu(3)) and the other links between a basal atom and the apical copper (Cu(4)). The three chelates form a "propeller" about the Cu_4S_6 core. This is the first example of a structure in which each S_2-*o*-xyl ligand involves two bridging sulfur atoms; previously[5,8,9,14,15,31] this ligand has provided either one bridging and one terminal sulfur or two terminal sulfur atoms.

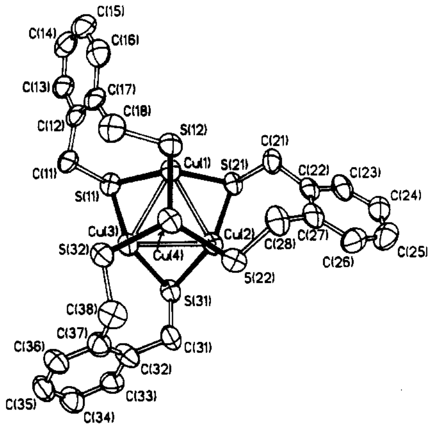

Figure 1. Structure of the $[Cu_4(S_2\text{-}o\text{-}xyl)_3]^{2-}$ anion, with thermal motion depicted as 50% probability ellipsoids.

Table IV. Selected Interbond Angles (deg) in $[Cu_4(S_2\text{-}o\text{-}xyl)_3]^{2-}$

S(12)-Cu(1)-S(21)	114.5 (1)	S(31)-Cu(3)-S(32)	118.7 (1)
S(11)-Cu(1)-S(21)	128.0 (1)	S(11)-Cu(3)-S(32)	114.6 (1)
S(11)-Cu(1)-S(12)	117.1 (1)	S(11)-Cu(3)-S(31)	126.3 (1)
S(22)-Cu(2)-S(31)	112.7 (1)	S(12)-Cu(4)-S(22)	121.1 (1)
S(21)-Cu(2)-S(31)	129.8 (1)	S(12)-Cu(4)-S(32)	117.1 (1)
S(21)-Cu(2)-S(22)	117.1 (1)	S(22)-Cu(4)-S(32)	121.7 (1)
Cu(2)-Cu(1)-Cu(3)	60.2 (1)	Cu(2)-Cu(1)-Cu(4)	59.8 (1)
Cu(3)-Cu(1)-Cu(4)	59.1 (1)	Cu(1)-Cu(2)-Cu(3)	60.2 (1)
Cu(1)-Cu(2)-Cu(4)	60.4 (1)	Cu(3)-Cu(2)-Cu(4)	59.3 (1)
Cu(1)-Cu(3)-Cu(2)	59.6 (1)	Cu(1)-Cu(3)-Cu(4)	60.5 (1)
Cu(2)-Cu(3)-Cu(4)	60.0 (1)	Cu(1)-Cu(4)-Cu(2)	59.8 (1)
Cu(1)-Cu(4)-Cu(3)	60.5 (1)	Cu(2)-Cu(4)-Cu(3)	60.7 (1)

Table V. Dimensions of the Cu_4S_6 Cores of Selected Copper(I)-Thiolate Clusters

	$[Cu_4(SPh)_6]^{2-}$ [a]	$[NMe_4]_2$-$[Cu_4(SMe)_6]$ [a]	$[PPh_4]_2[Cu_4$-$(S_2\text{-}o\text{-}xyl)_3]$ [b]
		Cu-S, Å	
range	2.247 (10)-2.349 (7)	2.247 (2)-2.315 (3)	2.244 (3)-2.300 (3)
mean	2.290 (29)	2.278 (20)	2.272 (20)
		Cu-Cu, Å	
range	2.640 (1)-2.846 (1)	2.673 (2)-2.791 (2)	2.699 (2)-2.739 (2)
mean	2.746 (65)	2.721 (41)	2.726 (16)
		S-Cu-S, deg	
range	104.9 (3)-143.7 (1)	111.1 (1)-128.2 (1)	112.7 (1)-129.8 (1)
mean	119.9 (10.5)	119.9 (5.8)	119.9 (5.6)

[a] Reference 17. [b] This work.

The type of Cu_4S_6 core observed for $[Cu_4(S_2\text{-}o\text{-}xyl)_3]^{2-}$ has been characterized previously for unidentate S-donor ligands, in $[Cu_4(SR)_6]^{2-}$ (R = Ph,[16,17] Me[17]) and $[Cu_4(SC(NH_2)_2)_6]^{4+}$,[36] and the dimensions of the $[Cu_4(S_2\text{-}o\text{-}xyl)_3]^{2-}$ and $[Cu_4(SR)_6]^{2-}$ anions are compared in Table V. The coordination about each copper of the $[Cu_4(S_2\text{-}o\text{-}xyl)_3]^{2-}$ anion is distorted trigonal planar, with

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[36] Griffith, E. H.; Hunt, G. W.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1976**, 432.

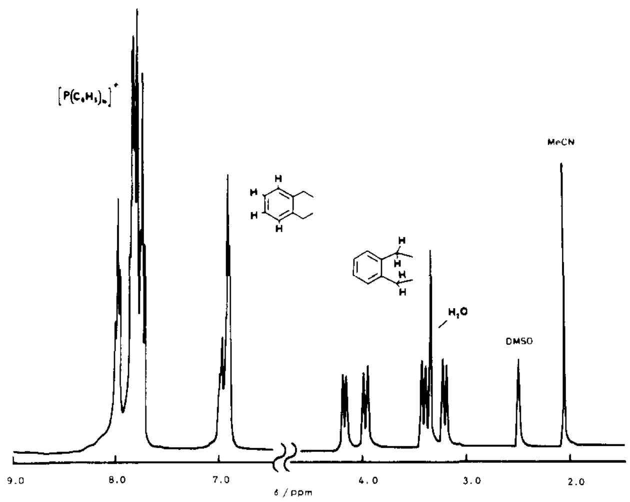

Figure 2. 300-MHz ^1H NMR spectrum of $[PPh_4]_2[Cu_4(S_2\text{-}o\text{-}xyl)_3]\cdot$MeCN in $(CD_3)_2SO$ at ambient temperature.

Cu–S bond lengths typical[16-19,37,38] of such coordination. The apical copper atom involves the least angular distortion from trigonal planar coordination (Table IV); for each of the other copper atoms, the Cu–S bonds spanning the basal edges involve an interbond angle at the copper of ca. 128° with one ∠S–Cu–S of ca. 118° and the other of ca. 114°. The Cu- - -Cu separations are consistent[39] with the presence of weak metal–metal bonding interactions. A detailed examination of the angular variations in the $[Cu_4(SR)_6]^{2-}$ (R = Me, Ph) cage structures by Dance et al.[17] has shown that intramolecular repulsions between the larger phenyl groups are responsible, at least in part, for the wider range of S–Cu–S interbond angles observed for R = Ph vs. R = Me but that these interactions have little effect on the Cu_4 framework. An extension of these ideas to $[Cu_4(S_2\text{-}o\text{-}xyl)_3]^{2-}$ indicates that the intramolecular repulsion of the ligands are small, as manifested in Figure 1. Thus, the presence of a Cu–S framework in $[Cu_4(S_2\text{-}o\text{-}xyl)_3]^{2-}$ with distortions from T_d symmetry of a magnitude similar to those found for $[Cu_4(SMe)_6]^{2-}$ is consistent with this view.

The dimensions of the ligands, the cations, and the MeCN molecule incorporated within the structure are unexceptional.

NMR Spectra. ^1H and ^{13}C NMR spectra of $[PPh_4]_2[Cu_4(S_2\text{-}o\text{-}xyl)_3]\cdot$MeCN, including off-resonance and broad-band-decoupled ^{13}C spectra, were recorded and assigned with the aid of a heteroscaler (^1H, ^{13}C) chemical shift correlation. The ^1H and the broad-band-decoupled ^{13}C NMR spectra are illustrated in Figures 2 and 3, respectively, and the resonances of the title compound are summarized in Table VI. The principal interest in the ^1H NMR spectrum concerns the appearance of the methylene proton resonances of the S_2-o-xyl ligands as four inequivalent, sharp, doublets. This profile is consistent with the molecular structure of the anion (Figure 1), since the nature of the chelation to the Cu_4 moiety results in the ligands being equivalent to each other while introducing an inequivalence of the corresponding atoms of each half of the ligand. The conformation of the seven-membered chelate ring renders the protons of each methylene group inequivalent. The ^1H NMR data are consistent with the structure depicted in Figure 1 being maintained in $(CD_3)_2SO$ solution at ambient temperature and with the absence of any rapid equilibration between different conformations of the chelate ring. These conclusions are supported by the ^{13}C NMR spectrum (Figure 3), which includes the resolution of the methylene carbon resonances.

Electronic and Vibrational Spectra. The UV–visible absorption spectrum of $[PPh_4]_2[Cu_4(S_2\text{-}o\text{-}xyl)_3]\cdot$MeCN dissolved in MeCN at ambient temperature consists of a structured maximum (λ_{max} = 270 nm, $\epsilon \sim 4 \times 10^4$ mol L^{-1} cm^{-1}), a prominent shoulder (λ_{max} = 290 nm, $\epsilon \sim 2.5 \times 10^4$ mol L^{-1} cm^{-1}), and a less well-defined shoulder at 320 nm ($\epsilon \sim 1.25 \times 10^4$ mol L^{-1} cm^{-1}). With reference to earlier comments,[38] these two bands to shorter wavelength are suggested to involve a considerable amount of cation and ligand aromatic $\pi \rightarrow \pi^*$ character.

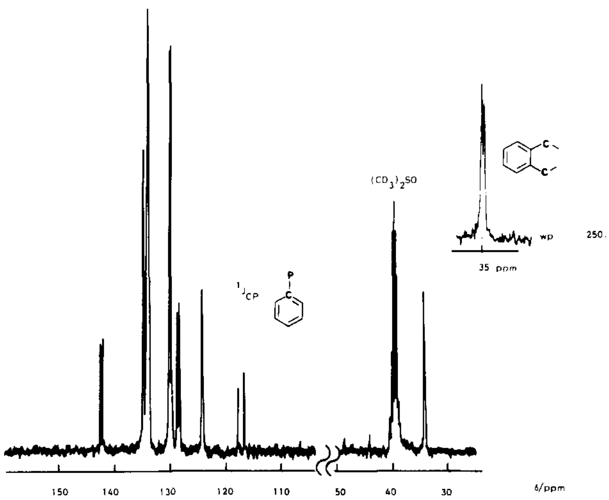

Figure 3. Broad-band-decoupled 75-MHz ^{13}C NMR spectrum of $[PPh_4]_2[Cu_4(S_2\text{-}o\text{-}xyl)_3]\cdot$MeCN, recorded in $(CD_3)_2SO$ at ambient temperature. The width of the plot was 15 000 Hz. Inset is the resolution achieved for the methylene resonances with a plot width of 250.7 Hz.

Table VI. ^1H and ^{13}C NMR Data Recorded[a] for $[PPh_4]_3[Cu_4(S_2\text{-}o\text{-}xyl)_3]\cdot$MeCN

chem shift, δ	rel intens	mult	J/Hz	assgnt
			^1H	
3.2	2.8	1:1 d	11.2	methylene
3.4	3.0	1:1 d	11.2	
3.9_5	3.0	1:1 d	11.2	
4.1_5	2.9	1:1 d	11.2	
6.9_5	12.3	m		aromatic protons of S_2-o-xyl
7.8	49.5	m		aromatic protons of $[PPh_4]^+$
			^{13}C	
34.2		s		methylene
34.3		s		
117.5		d	$^1J_{CP} = 88$	quaternary C of $[PPh_4]^+$
121.6		s		aromatic C(H) of S_2-o-xyl
124.5		s		
128.7		s		
129.1		s		
130.3		d	$^3J_{CP} = 14$	m-C of $[PPh_4]^+$
134.4		d	$^2J_{CP} = 11$	o-C of $[PPh_4]^+$
135.2		d[b]	$^4J_{CP} = 3$	p-C of $[PPh_4]^+$
142.4		s		aromatic C of S_2-o-xyl
142.8		s		

[a] Recorded in $(CD_3)_2SO$ at ambient temperature. [b] The resonance was not resolved into a doublet at the digital resolution employed at 75 MHz (i.e., 2.5 Hz); the coupling constant was obtained from a 20-MHz spectrum that employed a digital resolution of 1.4 Hz.

The IR spectrum of the title compound mulled in Nujol contains a relatively weak feature at ca. 322 cm^{-1}, which is considered to be one (or both) of the t_2 Cu–S stretching modes of the Cu_4S_6 (T_d) core. This value is similar to the features observed at ca. 342 cm^{-1} (Raman and IR) and at 314 cm^{-1} (Raman) attributed[38] to the ν(Cu–S) stretching modes of $[NEt_4]_2[Cu(SPh)_3]$.

Conclusions

The preparation of a new tetracopper(I)–thiolate cluster, $[Cu_4(S_2\text{-}o\text{-}xyl)_3]^{2-}$ is readily achieved, commencing from either copper(I) or copper(II). The structure of this anion involves the previously identified[16,17,36] Cu_4S_6 core; however, this is the first example involving chelating thiolate groups. This study has

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demonstrated that chelating thiolates can support an oligomeric array in which the metal atoms, although possessing essentially the same immediate coordination geometry, are rendered inequivalent by the chelate arrangement. This consideration should not be ignored in any interpretation of the spectroscopic inequivalence[30] of the metal centers of the metallothioneins and related proteins.

Acknowledgment. We thank S. Bristow for his considerable assistance and expertise in the recording and assignment of ^{13}C NMR spectra and the SERC for financial support (to J.R.N. and I.L.A.).

Registry No. $[PPh_4]_2[Cu_4(S_2\text{-}o\text{-}xyl)_3]$, 94957-36-5; $[Cu(N\text{-methylimidazole})_4][BF_4]$, 94957-37-6.

Supplementary Material Available: Listings of all the calculated atomic coordinates, anisotropic thermal parameters, isotropic thermal parameters for hydrogen atoms, remaining bond lengths and bond angles, and $|F_o|$ and $|F_c|$ values (40 pages). Ordering information is given on any current masthead page.

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Study of a Cyclometalated Complex of Ruthenium by 400-MHz Two-Dimensional Proton NMR

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Salts of the new cation $[Ru(bpy)_2(\mathbf{1})]^+$, where bpy = 2,2′-bipyridine and **1** = the cyclometalating ligand 2-(4-nitrophenyl)pyridine, have been prepared and characterized. A two-dimensional homonuclear decoupled autocorrelated Fourier transform ^1H NMR (HDCOSY) spectrum has allowed the assignment of all 23 of the distinguishable aromatic protons of the one benzene and five pyridine groups. This represents the first application of this new NMR technique to a metallic complex of this type.

Introduction

In recent years there has been an exponential increase in interest in the chemistry and physics of salts of tris(2,2′-bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$, and its substituted bipyridine and bipyridine-like derivatives.[1-3] Numerous complexes of the type $[Ru(bpy)_{3-x}L_x]^{n+}$, where x is 1 or 2 and L is some bidentate ligand that is not bipyridine-like, have also been prepared and studied spectroscopically,[1] but to our knowledge no such complexes have been prepared in which the ligand L is a cyclometalating species.

In the course of preparation of a series of new cyclometalated compounds of ruthenium, $[Ru(bpy)_{3-x}L_x]^{2-x}$ (bpy = 2,2′-bipyridine; L = 2-phenylpyridine; x = 1–3), which are being studied spectroscopically and electrochemically to evaluate their potential use as photocatalysts, it became apparent that the use of more sophisticated NMR techniques would be needed to properly interpret the spectra of these complexes. The first member of the new series to be prepared was $[Ru(bpy)_2(\mathbf{1})]PF_6$ (where **1** is 2-(4-nitrophenyl)pyridine). Its yield was low, but while alternative methods of preparation are being explored and other studies are in progress, we report here the use of two-dimensional Fourier transform ^1H NMR, which allows the ready interpretation of the three-dimensional structure of the complex and indeed the assignment of all 23 distinguishable aromatic protons! This represents, to our knowledge, the first application of such a technique to compounds of this type and complexity. We hope to be able to use this technique later in an NMR study of *photoexcited* molecules in this series.

Experimental Section

A. Compound Preparation. $[Ru(bpy)_2(\mathbf{1})]^+$ (bpy = 2,2′-bipyridine; **1** = 2-(4-nitrophenyl)pyridine) was prepared from the intermediate *cis*-$[Ru(bpy)_2(DME)]PF_6$ (DME = 1,2-dimethoxyethane), of which the preparation has already been described.[4] A freshly prepared solution of $[Ru(bpy)_2(DME)]PF_6$ in DME (10 mL, 5.0×10^{-2} M) was reacted with a DME solution of the ligand (40 mL, 200 mg, 100% excess) under argon. The solution was stirred and refluxed under argon for 30 min, and then an excess of triethylamine was added (to promote removal of the aromatic proton on the cyclometalating carbon). The mixture was refluxed for 24 h, the solvent distilled off, and the product chromatographed on an alumina column. The unreacted free ligand was eluted first with acetonitrile/toluene (1:1), and then the desired product came off. The dark red product was recrystallized from dichloromethane/ether, and the fine crystals were washed with ether and dried in vacuo. (Analytical analyses showed the compound to crystallize with 0.5 mol of water and 0.5 mol of methylene chloride, which is also the case for several other compounds in the series $[Ru(bpy)_2L]PF_6$, where L are other cyclometalating ligands such as azobenzene, substituted azobenzene, benzo[*h*]quinoline, and 2-phenylpyridine.)

B. NMR Experiments. The 2D COSY-45 and homodecoupled COSY (HDCOSY) spectra were acquired by using 2048 × 512 data matrices, resulting in 1024 × 1024 transforms after zero-filling in F1 and using the absolute value spectra. Both spectra were acquired with a 1024-Hz spectral window (SW).

The COSY-45 experiment uses a 45° mixing pulse to simplify the spectrum by limiting the cross peaks to directly connected transitions. The preparation and mixing pulses as well as the receiver reference phase were cycled for negative type peak selection. Matched Gaussian window functions were used in both domains.

The HDCOSY experiment[5] uses a 180° refocusing pulse between the preparation and mixing pulses to produce a spectrum in which the homonuclear coupling is collapsed in the F1 domain. There is a fixed delay between the preparation and mixing pulses set to half the normal acquisition time. The refocusing pulse follows an incremented delay. A 45° mixing pulse is necessary, and the 180° refocusing pulse must be carefully calibrated. All three pulses and the receiver reference phase are cycled so that only the coherence transfer echo is detected. A Gaussian window function was used in both domains.

All spectra were taken in $Me_2SO\text{-}d_6$ on a sample prepared by dissolving 20 mg of the compound in 0.5 mL of 100 atom % $Me_2SO\text{-}d_6$. Spectra were acquired at 400.133 MHz on a Bruker WH-400 spectrometer.

Results and Discussion

The low microsymmetry in the expected gross octahedral structure of $[Ru(bpy)_2(\mathbf{1})]^+$ (Figure 1) assures nonequivalence to all five pyridine groups. The molecule thus contains 23 nonequivalent aromatic protons, 20 on five monosubstituted pyridine rings and three on the trisubstituted benzene ring. Since the electronic environments of numerous pyridine hydrogen atoms would be very similar, their signals occur in a very narrow chemical shift range. Furthermore, their resonance patterns are made very

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