The structure determination[9,11] (Figures 2 and 3) revealed that protonation had resulted in the placement of a proton between the carbon–molybdenum σ bond of **2** (Scheme II) with the principal changes in geometry occurring in the region of C(8) and Mo(2) (Figure 2, Table I), the Mo(2)–C(8) distance increasing from 2.096 (2) Å in **2** to 2.196 (5) Å in **3**. Such a shift is similar to, although slightly smaller than, those observed in M–H–M systems relative to their unprotonated analogoues,[12–14] since in these systems the bent C–H–Mo interaction, which is also reflected in the high-field ^{1}H shift of the hydrogen, is best described as three center two electron, with the (X-ray distorted) bond lengths and angles reflecting considerable Mo(2)–C(8) interaction. The effect of protonation on the remainder of the C_8 chain is slight, leaving the connectivity unchanged with only very minor modification of bond lengths and angles, reflecting the stability of this mode of coordination; bonds to Mo(2) are slightly lengthened (by ca. 0.02 Å), and the Mo–Mo bond is still within the range appropriate for a double bond at 2.614 (1) Å.

The anion was found to consist of two trifluoroacetate groups linked by a short, strong, nearly symmetrical hydrogen bond [O···O, 2.429 (5) Å] and the hydrogen located and refined without constraints [O(311)–H(34) = 1.34 (7), O(411)–H(34) = 1.10 (7) Å; O(311)–H(34)–O(411) = 175 (7)°].

In contrast with the C—H··M interactions previously observed,[15,16] the bent CHMo system present in the cation **3** closely resembles the kind of interaction which it has been postulated[17,18] leads to an α-hydrogen abstraction reaction. As is shown in Scheme II if protonation occurs at a carbon α to the molybdenum, then the cationic electron-deficient molybdenum center which is generated is ideally placed to participate in such a three-center interaction, thus providing strong support for Schrock's suggestion. Suitable neutron diffraction studies are planned to define the precise location of the bridging hydrogen.

Acknowledgment. We thank the S.R.C. for support and Dr. N. J. Connelly for help with the electrochemical observations.

Supplementary Material Available: Atomic positional and thermal parameters and bond lengths for complexes **2** and **3** (18 pages). Ordering information is given on any current masthead page.

(11) The bridging hydrogen atom was located as the highest difference electron density peak associated with the cation **3**, bridging the C(8)–Mo(2) vector at 1.10 Å from C(8) and 1.85 Å from Mo(2); unconstrained isotropic refinement of this hydrogen gave the bond lengths and angles given in Table I.

(12) Petersen, J. L; Stewart, Jr., R. P. *Inorg. Chem.* **1980**, *19*, 186–191.
(13) Petersen, J. L; Dahl, L. F; Williams, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 6610–6620.
(14) Petersen, J. L; Williams, J. M. *Inorg. Chem.* **1978**, *17*, 1308–1312.
(15) Cotton, F. A; La Cour, J; Stanislowski, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 754–760.
(16) Williams, J. M; Brown, R. K; Schultz, A. J; Stucky, G. D; Ittel, S. D. *J. Am. Chem. Soc.* **1978**, *100*, 7401–7409. Ittel, S. D; Van-Catledge, F. A; Hesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 6905–6911.
(17) Wood, C. D; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210–3222.
(18) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104.
(19) Sheldrick, G. M. SHELXTL structure analysis system, Göttingen, Federal Republic of Germany, 1980.

A New and Efficient Total Synthesis of Streptonigrin

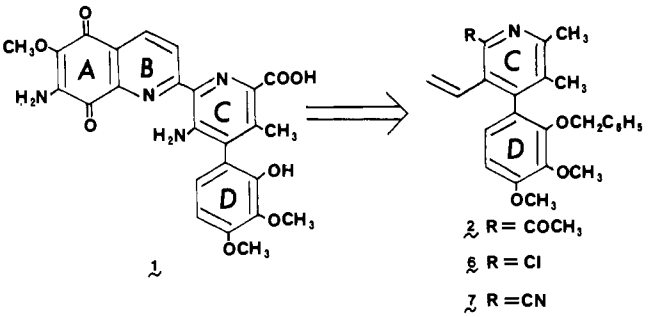
Andrew S. Kende,* Dennis P. Lorah, and Rodney J. Boatman

Department of Chemistry, University of Rochester Rochester, New York 14627

Received September 15, 1980

The antitumor antibiotic streptonigrin was shown in 1963 by Rao, Biemann, and Woodward to have the tetracyclic aminoquinone structure **1**.[1] Since that time a stream of publications have reported approaches to the synthesis of this polyfunctional molecule.[2–4] The first synthesis of its carbon framework was achieved in these laboratories in 1978,[3a] and an imaginative total synthesis of streptonigrin in 0.013% yield in over 30 steps from 2-benzyloxy-3,4-dimethoxybenzaldehyde was recently reported by Weinreb and co-workers.[5] We now describe concurrent studies in this area which have led to a short and efficient total synthesis of this intricate molecule by utilizing a more direct C-ring construction than the sequence employed by the Weinreb group.

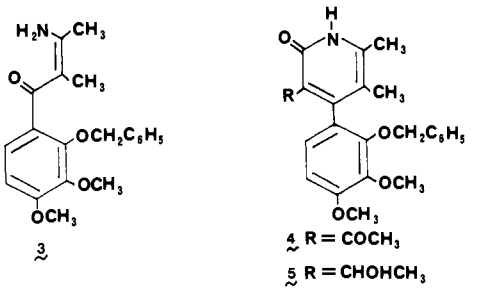
It is clear from our preliminary communication[3a] that synthesis of **1** requires early construction of the C–D arylpyridine rings containing substituents appropriate for facile conversion to those in the target antibiotic. In the Weinreb synthesis this was achieved by a nonregiospecific imino Diels–Alder reaction, aromatization, and a subsequent Sommelet–Hauser rearrangement sequence to introduce functionality at the vacant 3-position of the pyridine intermediate. Our strategy involves a regiospecific 3-acyl-2-pyridone construction, leading to the key C–D vinylpyridine **2**,



1 **2** **6** **7**

since Friedländer condensation should lead to attachment of rings A and B, while the stable vinyl group should serve as convenient precursor to the C-ring amino group.

Thus, condensation of the readily available β-keto enamine **3**[6]



3 **4** **5**

with methyl acetoacetate (xylenes, reflux, $-H_2O$, 14 h) led with unusual regiospecificity[7] to the acylpyridone **4** in 97% yield:[8] mp 216–217 °C;[9a] NMR[9b] δ 1.68 (3 H, s), 2.32 (3 H, s), 2.44 (3 H,

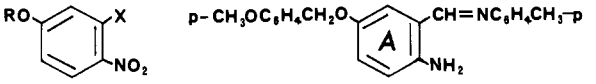
(1) Rao, K. V.; Biemann, K.; Woodward, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 2532.
(2) For a review, see: Hibino, S. *Heterocycles* **1977**, *6*, 1485.
(3) (a) Kende, A. S.; Naegely, P. C. *Tetrahedron Lett.* **1978**, 4775. (b) Kim, D.; Weinreb, S. M. *J. Org. Chem.* **1978**, *43*, 121. (c) *Ibid.* **1978**, *43*, 125. (d) Wittek, P. J.; Liao, T. K.; Cheng, C. C. *Ibid.* **1979**, *44*, 870. (e) Rao, K. V.; Kuo, H.-S. *J. Heterocycl. Chem.* **1979**, *16*, 1241.
(4) For fascinating recent studies on the biosynthesis of streptonigrin, see: Gould, S. J.; Darling, D. S. *Tetrahedron Lett.* **1978**, 3207. Gould, S. J.; Chang, C. C. *J. Am. Chem. Soc.* **1977**, *99*, 5496; **1978**, *100*, 1624; **1980**, *102*, 1702. Gould, S. J. Chang, C. C.; Darling, D. S.; Roberts, J. D.; Squillacote, M. *Ibid.*, **1980**, *102*, 1707.
(5) Basha, F. Z.; Hibino, S.; Kim, D.; Pye, W. E.; Wu, T.-T.; Weinreb, S. M. *J. Am. Chem. Soc.* **1980**, *102*, 3962.
(6) Liao, T. K.; Wittek, P. J.; Cheng, C. C. J. *Heterocycl. Chem.* **1976**, *13*, 1283.
(7) Breitmaier, E.; Gassenman, S.; Bayer, E. *Tetrahedron* **1970**, *26*, 5907. This reference describes the inverse regiochemistry from what we find in our system.
(8) The analogous condensation with ethyl nitroacetate failed under a variety of conditions.
(9) (a) All compounds for which a melting point is reported gave satisfactory combustion analyses. (b) All NMR spectra were recorded at 100 MHz in $CDCl_3$ unless otherwise noted.

0002-7863/81/1503-1271$01.25/0

s), 3.90 (3 H, s), 3.92 (3 H, s), 5.04 (2 H, s), 6.72 (2 H, s), 7.24 (5 H, m), 13.70 (1 H, br s). Reduction of ketone **4** ($NaBH_4$, 3:1 THF/*i*-PrOH, room temperature, 16 h) gave alcohol **5** in quantitative yield.

Treatment of alcohol **5** with $PhPOCl_2$ (170 °C, 3 h) gave a 67% yield of chloropyridine **6** (mp 88–89 °C), which on reflux in DMF with CuCN for 14 h gave nitrile **7** (mp 103–105 °C, 85% yield). Reaction of this nitrile with MeMgBr (C_6H_6, room temperature, 1.5 h, acid hydrolysis) produced the key vinylpyridine **2** in 83% yield: mp 105–106.5 °C; NMR δ 1.90 (3 H, s), 2.50 (3 H, s), 2.63 (3 H, s), 3.87 (3 H, s), 3.91 (3 H, s), 4.74–5.14 (2 H, AB of ABX), 6.44–7.20 (8 H, m).

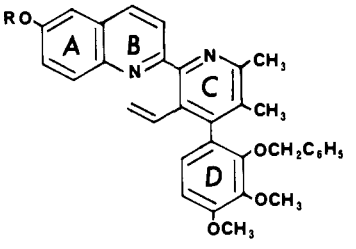
Despite moderate success in the use of the Friedländer quinoline synthesis in some streptonigrin model studies,[3a,10] that reaction could not be directly employed in the Weinreb synthesis and was, at first, consistently refractory for the conversion of our vinylpyridine **2** to a substituted quinoline derivative. After innumerable forays, a novel variant of the Borsche modification proved uniquely successful.[11] To this end, the A-ring precursor **11** was prepared in three steps (60% yield) from the known aldehyde **8**.[12] O-benzylation of **8** with *p*-methoxybenzyl bromide (K_2CO_3, KI, DMF, room temperature, 14 h) gave ether **9** (mp 89–90 °C), which with *p*-toluidine (C_6H_6, reflux, $-H_2O$, 14 h) gave the nitroimine **10** (mp 99–101 °C). This was reduced with Na_2S (CH_3OH, reflux, 2 h) to the amino imine **11** used in the Borsche condensation. Reaction of **11** (1.45 equiv) with vinylpyridine



8 R = H; X = CHO

9 R = p-$CH_3OC_6H_4CH_2$; X = CHO

10 R = p-$CH_3OC_6H_4CH_2$; X = CH$NC_6H_4CH_3$-p



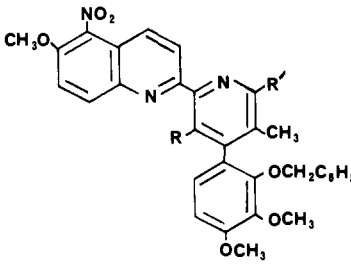
12 R = p-$CH_3OC_6H_4CH_2$

13 R = H

2 by using freshly prepared *t*-BuOK under strictly defined conditions (8.66 equiv of *t*-BuOK, 3.3:1 toluene/*t*-BuOH, N_2, reflux, 10 h)[13] led reproducibly to the desired tetracyclic olefin **12** in 90–96% yield after silica gel chromatography ($CHCl_3$): mp 151–152 °C (dec); NMR δ 2.00 (3 H, s), 2.62 (3 H, s), 3.74 (3 H, s), 3.86 (3 H, s), 3.91 (3 H, s), 4.56–4.92 (2 H, AB of ABX), 4.92 (2 H, s), 5.04 (2 H, s), 6.39–7.82 (15 H, m), 8.02 (1 H, d, *J* = 9 Hz), 8.10 (1 H, d, *J* = 9 Hz).

Selective debenzylation of **12** (TFA, 0 °C, 1 h) produced an 85% yield of phenol **13**: mp 158–160 °C (dec); NMR δ 1.96 (3 H, s), 2.63 (3 H, s), 3.88 (3 H, s), 3.92 (3H, s), 4.50–4.94 (2 H, AB of ABX), 4.88 (2 H, s), 6.18–6.48 (1 H, X of ABX), 6.65 (2 H, AB quartet, *J* = 9 Hz), 6.90–7.75 (10 H, m). A-ring nitration of phenol **13** (HNO_3, CH_3NO_2, 5–20 °C, 25 min) followed by direct O-methylation (Me_2SO_4, K_2CO_3, Me_2CO, reflux, 5 h) gave a 55% yield of nitroquinoline **14** after silica gel chromatography ($CHCl_3$/EtOAc, gradient elution): NMR δ 2.00 (3 H, s), 2.61 (3 H, s), 3.92 (6 H, s), 4.04 (3 H, s), 4.52–4.98 (2 H, AB of ABX), 4.92 (2 H, s), 6.38–6.68 (1 H, X of ABX), 6.76 (2 H, s), 6.94–7.28 (5 H, m), 7.54 (1 H, d, *J* = 9 Hz), 7.73 (1 H, d, *J* = 9 Hz), 8.06 (1 H, d, *J* = 9 Hz), 8.32 (1 H, d, *J* = 9 Hz).

The olefinic bond of **14** was cleaved to carboxylic acid **15** (75%)



14 R = CH=CH_2; R′ = CH_3

15 R = COOH; R′ = CH_3

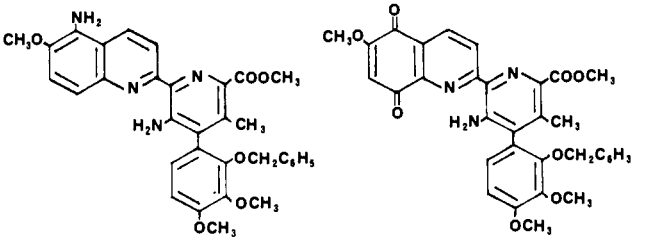
16 R = COOH; R′ = CHO

17 R = R′ = COOH

18 R = COOH; R′ = $COOCH_3$

19 R = NH_2; R′ = $COOCH_3$

by successive treatment with catalytic OsO_4 (*N*-methylmorpholine *N*-oxide, Me_2CO, H_2O, *t*-BuOH, room temperature, 20 h)[14] followed by glycol cleavage (9 equiv of $NaIO_4$ in 2.8:1 dioxane/H_2O, 80 °C, 18 h). Selenium dioxide oxidation[3d] (HOAc, reflux, 18 h) of this acid produced the aldehyde acid **16** (74%) which on sodium chlorite oxidation[15] (H_2NSO_3H, NaOAc, 2:1 dioxane/H_2O, room temperature, 1.5 h) gave diacid **17** in 92% yield. Selective esterification of the unhindered carboxyl of **17** (MeOH, AcCl, room temperature, 14 h) led to the acid ester **18** (95%). Application of the Yamada modification of the Curtius rearrangement[16] [$(PhO)_2PON_3$, Et_3N, C_6H_6, reflux 50 min, then H_2O, reflux 30 min] to **18** produced amino ester **19** in 43% yield: mp 162.5–163 °C; NMR δ 2.25 (3 H, s), 3.97 (6 H, s), 4.00 (3 H, s), 4.04 (3 H, s), 4.92 (2 H, s), 6.81 (2 H, s), 6.80–7.10 (5 H, m), 7.42 (1 H, d, *J* = 9 Hz), 7.97 (1 H, d, *J* = 9 Hz), 8.07 (1 H, d, *J* = 9 Hz), 8.92 (1H, d, *J* = 9 Hz). Dithionite reduction ($Na_2S_2O_4$, THF, aqueous MeOH, reflux, 3 h) of **19** gave diamine **20**, mp 148–150 °C, in 80% yield. Selective oxidation of the A



20 **21**

ring of **20** with Fremy's salt[3a,5] (Na_2HPO_4, aqueous Me_2CO, room temperature, 12 h) led to quinone **21** in 92% yield after preparative silica gel TLC (9:1 $CHCl_3$/EtOAc): mp 242–243 °C; NMR (400 MHz) δ 2.24 (3 H, s), 3.94 (3 H, s), 3.95 (3 H, s), 3.96 (3 H, s), 3.99 (3 H, s), 4.92 (2 H, AB quartet, *J* = 11.2 Hz), 6.29 (1 H, s), 6.85 (2 H, AB quartet, *J* = 8.3 Hz), 7.00–7.11 (5 H, m); 8.50 (1 H, d, *J* = 8.6 Hz), 9.04 (1 H, d, *J* = 8.6 Hz); UV (MeOH) λ_{max} 208 (ε 50 000), 254 (37 600), 281 sh (19 400), 368 (11 500), 449 nm (4300).

The TLC behavior and all spectroscopic properties of our quinone **21** were identical with those of a comparison sample kindly supplied by Professor Weinreb. Since introduction of the A-ring amino function by using our selective IN_3 procedure[3b] has been employed to convert quinone **21** in four steps (10% yield) to streptonigrin (**1**),[5] the above chemistry comprises a new total syntheis of this antitumor agent. Our synthesis leads from 2-benzyloxy-3,4-dimethoxypropiophenone to quinone **21** in 19 steps with an overall yield of ca. 1.3%, an order of magnitude higher than previously reported.

(10) Hibino, S.; Weinreb, S. M. *J. Org. Chem.* **1977**, *42*, 232.
(11) (a) Cheng, C. C.; Yan, S. J. *Org. React.* **1981**, *27*, in press. (b) Borsche, W.; Barthenheier, J. *Ann. Chem.* **1941**, *548*, 50.
(12) Horning, L. S. *J. Am. Chem. Soc.* **1952**, *74*, 4570.
(13) Dry, degassed solvent and potassium metal purified by the procedure of Pearson were employed, cf.: Pearson, D. E.; Keaton, O. D. *J. Org. Chem.* **1963**, *28*, 1557.
(14) VanRheenen, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.* **1976**, 1973.
(15) Lindgren, B. O.; Nilsson, T. *Acta Chem. Scand.* **1973**, *27*, 888.
(16) Shiori, T.; Ninomiya, K.; Yamada, S. *J. Am. Chem. Soc.* **1972**, *94*, 6203.

Acknowledgment. We thank the National Cancer Institute (USPHS) for Grant CA-18846 in partial support of this work. We are grateful to David Becker and Neil Feldstein for preparing large quantities of intermediates and Dr. Paul C. Naegely for valuable discussions and model studies.

Binuclear Copper Complexes: An Open and Shut Case. A Strong Antiferromagnetically Coupled μ-Monohydroxo Bridged Complex

Patrick L. Burk, John A. Osborn,* and Marie-Thérèse Youinou

Laboratoire de Chimie Inorganique Moléculaire et de Catalyse (ERA 721) Institut Le Bel, Université Louis Pasteur 67070 Strasbourg Cedex, France

Yvette Agnus, Rémy Louis, and Raymond Weiss*

Laboratoire de Christallochimie et de Chimie Structurale (ERA 008) Institut Le Bel, Université Louis Pasteur 67070 Strasbourg Cedex, France

Received October 22, 1980

Binuclear copper systems are implicated in a wide variety of biochemical processes, especially in transport and multielectron redox reactions of molecular oxygen. Recent interest has focused on the oxygen carrier, hemocyanin[1] and the oxidase enzymes, tyrosinase,[2] laccase,[3] and ceruloplasmin.[4] Particularly intriguing are the changes in spectroscopic, magnetic, and electron resonance data with reactions at the binuclear site.[5] For example, oxy- and methemocyanin,[6] although both formally $Cu(II)_2$ species, are ESR silent, and magnetic susceptibility studies place a lower limit of -550 cm^{-1} for the antiferromagnetic exchange interaction in the oxy form.[7] Chemical, spectroscopic, and EXAFS[8] studies suggest that the two coppers are held by an unknown[9] endogenous ligand at a distance of 3.4–3.7 Å. However, reaction of hemocyanin with NO or $NaNO_2$ (pH ~6)[10] causes conversion to a dimer form which, despite the similarity of its optical properties to the met form, is EPR active, and the Cu–Cu distance is estimated as ~6 Å. In this communication, we present studies on and X-ray structures of a binuclear copper system which demonstrates like properties.

We have previously described the ligand L (or $\langle\cdots\rangle$)[11] and the binuclear copper(I) complex **1**, $[\langle Cu(I)\cdots Cu(I)\rangle](BF_4)_2$, which in propylene carbonate (PC) solution absorbs CO (reversibly) and O_2 (partly reversibly).[12] Treatment of **1**, (in nitromethane) with NO yields a dark-green solution from which, on addition of THF, **2** crystallizes as the dark-green BF_4^- salt. The X-ray structure of **2** consists of discrete binuclear cations $[\langle Cu(II)NO_2\cdots Cu(II)NO_2\rangle]^{2+}$ (Figure 1) and BF_4^- anions.[13] Each Cu(II) has a distorted octahedral environment consisting of the ONS_2 donor set of the ligand and, surprisingly, a chelating NO_2^- group.[14] The approximate symmetry of the cation is C_{2v} with the crystallographic plane of symmetry containing the following atoms: 2 Cu, 2 NO_2, O(7), O(27), N(1), N(21), C(13), C(14), C(17), and C(20). Elongation along one axis produces asymmetrically coordinated NO_2^- groups, as reflected by the longer Cu–O distances 2.38 (3) and 2.50 (3) Å compared to the shorter ones 1.91 (3) and 1.95 (3) Å. The Cu(II)···Cu(II) intramolecular distance is 11.264 (6) Å since L is in an open configuration.

$[\langle Cu(II)(H_2O)_3\cdots Cu(II)(H_2O)_3\rangle](BF_4)_4$ (**3**) was prepared by addition of $Cu(BF_4)_2\cdot 6H_2O$ (2 mol) to L (1 mol) in PC. The resultant green crystals dissolved in PC show absorptions at 670 (ϵ_{Cu} ~500), 390 (ϵ_{Cu} ~4300), 315 (ϵ_{Cu} ~2000 cm^{-1} mol^{-1} L) and 275 nm (sh). The magnetic moment at 20 °C is 1.85 μ_B/Cu, and the solid-state ESR spectrum at 20 °C shows a resonance at g_{av} = 2.099 with no detectable $\Delta m = 2$ transition. Hence a normal

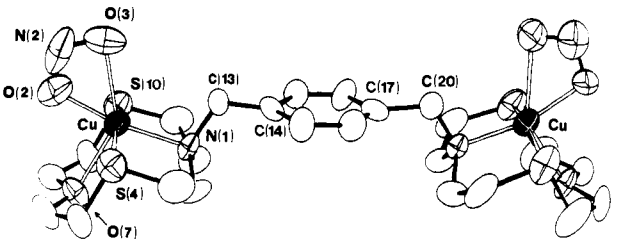


Figure 1. Structure of the $[\langle Cu(II)(NO_2)\cdots Cu(II)(NO_2)\rangle]^{4+}$ cation. The Cu···Cu interatomic distance is 11.264 (6) Å. Selected bond distances (in Å) (the second value corresponds to the related distances or angles for the unlabeled half of the molecule): Cu–O(2), 1.91 (3), 1.95 (3); Cu–O(3), 2.38 (3), 2.50 (3); Cu–N(1), 2.06 (3), 2.02 (3); Cu–S(4), 2.342 (6), 2.377 (6); Cu–O(7), 2.34 (2), 2.22 (2). Selected bond angles (in deg): N(1)–Cu–O(2), 169.6 (2), 163.8 (1); N(1)–Cu–S(4), 88.7 (5), 88.4 (5); N(1)–Cu–O(7), 100.8 (7), 103.6 (8); S(4)–Cu–O(2), 92.6 (6), 93.7(6); S(4)–Cu–O(7), 82.6 (5), 82.6 (4); O(7)–Cu–O(2), 89.6 (8), 92.6 (8).

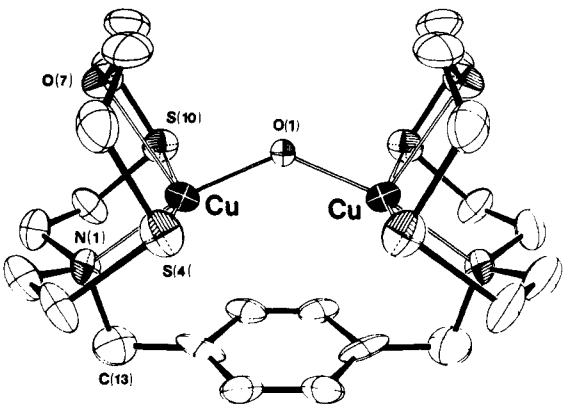


Figure 2. Structure of the $[\langle Cu(II)\cdots(OH)\cdots Cu(II)\rangle]^{3+}$ cation. The Cu···Cu interatomic distance is 3.384 (9) Å and the bond angle Cu–O(I)–Cu is 132.2 (4)°. Selected bond distances (in Å): Cu–O(1), 1.85 (2); Cu–N(1), 2.06 (5); Cu–S(4), 2.35 (2); Cu–O(7), 2.37 (4); Cu–S(10), 2.39 (2). Selected bond angles (in deg): O(1)–Cu–N(1), 167.2 (9); O(1)–Cu–S(4), 95.5 (8); O(1)–Cu–O(7), 98.1 (9); O(1)–Cu–S(10), 95.4 (8); N(1)–Cu–O(7), 94.8 (9); S(4)–Cu–S(10), 159.5 (7).

(1) (a) Himmelwright, R. S.; Eickman, N. C.; Solomon, E. I. *J. Am. Chem. Soc.* **1979**, *101*, 1576. (b) Himmelwright, R. S.; Eickman, N. C.; Lubien, C. D.; Solomon, E. I. *Ibid.* **1980**, *102*, 5378 and references therein.

(2) Eickman, N. C.; Solomon, E. I.; Larragee, J. A.; Spiro, T. G.; Lerch, K. *J. Am. Chem. Soc.* **1978**, *100*, 6529.

(3) (a) Farver, O.; Goldberg, M.; Wherland, S.; Pecht, J. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 5245. (b) Farver, O.; Goldberg, M.; Pecht, J. *FEBS Lett.* **1978**, *94*, 383.

(4) Dawson, J. H.; Dooley, D. M.; Gray, H. B. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 4078.

(5) Fee, J. A. *Struct. Bonding (Berlin)* **1975**, *23*, 1.

(6) It has recently been suggested[1b] that the "dimer" and "met" nomenclature used here be replaced by "EPR-detectable met" and "EPR-nondetectable met".

(7) Dooley, D. M.; Scott, R. A.; Ellinghaus, J.; Solomon, E. I. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 3019.

(8) Brown, J. M.; Powers, L.; Kincaid, B.; Larrpbee, J. P.; Spiro, T. G. *J. Am. Chem. Soc.* **1980**, *102*, 4210.

(9) In the oxy protein, the coordination around the Cu^{2+} ions is, as yet, unknown; however, recent EXAFS (cf. ref 8) and other studies suggest the presence of three imidazole groups, O_2, and a further bridging ligand.

(10) (a) Schoot Uiterkamp, A. J.; *FEBS Lett.* **1972**, *20*, 93. (b) Schoot Uiterkamp, A. J.; van der Deen, H.; Berendsen, H. C.; Boas, J. F. *Biochim. Biophys. Acta* **1974**, *372*, 407.

(11) L is 1,4-bis[(1-oxa-4,10-dithia-7-azacyclododecan-7-yl)methyl]-benzene which can bind two metal ions in an ear-muff configuration clearly demonstrated in Figure 2.

(12) Bulkowski, J. E.; Burk, P. L.; Ludmann, M. F., Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1977**, 498.

(13) **2** crystallizes in the monoclinic space group $P2_1/m$ with a = 14.471 (4), b = 17.201 (5), c = 8.835 (3) Å; β = 106.19(2)°; M_r = 909.56, ρ_{calcd} = 1.430 g cm^{-3} with Z = 2 formula units per cell. A total of 1910 independent nonzero reflections were measured on a Picker FACS 3 diffractometer, and 1220 reflections with $I > 3\,\sigma(I)$ were used in subsequent structure solution and least-squares refinement. R_f = 0.09 and R_{wf} = 0.10.

(14) The origin of the additional oxygen atom is unclear but may come from adventitious traces of oxygen or by disproportionation of NO on the complex.

0002-7863/81/1503-1273$01.25/0