

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 analogues,¹²⁻¹⁴ since in these systems the bent C-H-Mo interaction, which is also reflected in the high-field ¹H 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 C₈ 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.

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A New and Efficient Total Synthesis of Streptonigrin

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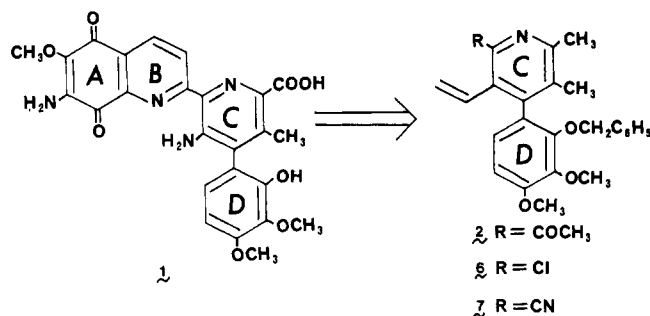
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The antitumor antibiotic streptonigrin was shown in 1963 by Rao, Biemann, and Woodward to have the tetracyclic aminoquinone structure **1**.¹ Since that time a stream of publications

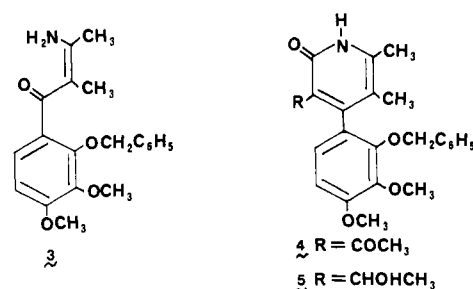
have reported approaches to the synthesis of this polyfunctional molecule.²⁻⁴ The first synthesis of its carbon framework was achieved in these laboratories in 1978,^{3a} and an imaginative total synthesis of streptonigrin in 0.013% yield in over 30 steps from 2-benzoyloxy-3,4-dimethoxybenzaldehyde was 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**,



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



with methyl acetoacetate (xylenes, reflux, -H₂O, 14 h) led with unusual regiospecificity⁷ 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,

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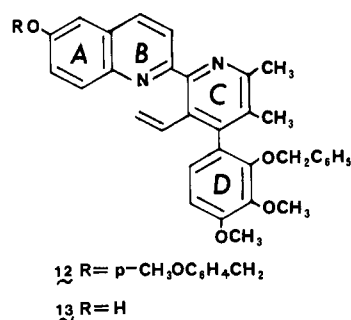
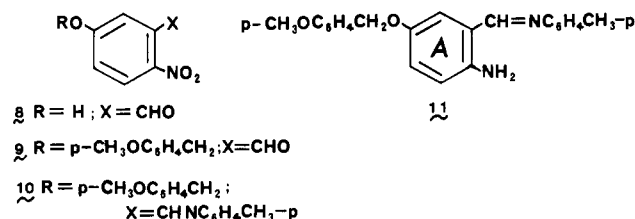
(8) The analogous condensation with ethyl nitroacetate failed under a variety of conditions.

(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 CDCl₃ unless otherwise noted.

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** (NaBH₄, 3:1 THF/*i*-PrOH, room temperature, 16 h) gave alcohol **5** in quantitative yield.

Treatment of alcohol **5** with PhPOCl₂ (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 (C₆H₆, 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-benzoylation of **8** with *p*-methoxybenzyl bromide (K₂CO₃, KI, DMF, room temperature, 14 h) gave ether **9** (mp 89–90 °C), which with *p*-toluidine (C₆H₆, reflux, –H₂O, 14 h) gave the nitroimine **10** (mp 99–101 °C). This was reduced with Na₂S (CH₃OH, reflux, 2 h) to the amino imine **11** used in the Borsche condensation. Reaction of **11** (1.45 equiv) with vinylpyridine

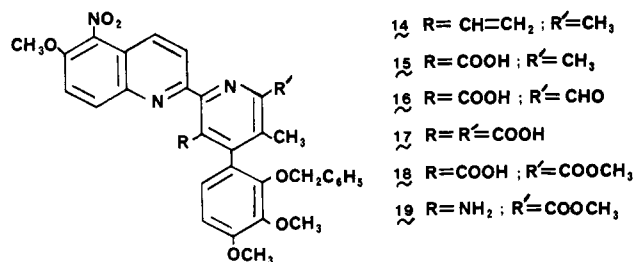


2 by using freshly prepared *t*-BuOK under strictly defined conditions (8.66 equiv of *t*-BuOK, 3.3:1 toluene/*t*-BuOH, N₂, reflux, 10 h)¹³ led reproducibly to the desired tetracyclic olefin **12** in 90–96% yield after silica gel chromatography (CHCl₃): mp 151–152 °C (dec); NMR δ 2.00 (3 H, s), 2.62 (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).

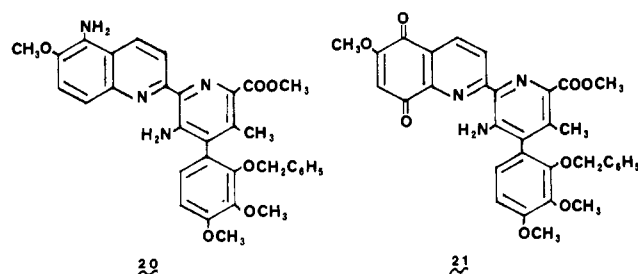
Selective debenzoylation of **12** (TFA, 0 °C, 1 h) produced an 85% yield of phenol **13**: mp 158–160 °C (dec); NMR δ 1.96 (3 H, s), 2.63 (3 H, s), 3.88 (3 H, s), 3.92 (3 H, s), 4.50–4.94 (2 H, AB of ABX), 4.88 (2 H, s), 6.18–6.48 (1 H, X of ABX), 6.65 (2 H, AB quartet, *J* = 9 Hz), 6.90–7.75 (10 H, m). A-ring nitration of phenol **13** (HNO₃, CH₃NO₂, 5–20 °C, 25 min) followed by direct O-methylation (Me₂SO₄, K₂CO₃, Me₂CO, reflux, 5 h) gave a 55% yield of nitroquinoline **14** after silica gel chromatography (CHCl₃/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%)



by successive treatment with catalytic OsO₄ (*N*-methylmorpholine *N*-oxide, Me₂CO, H₂O, *t*-BuOH, room temperature, 20 h)¹⁴ followed by glycol cleavage (9 equiv of NaIO₄ in 2.8:1 dioxane/H₂O, 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 oxidation¹⁵ (H₂NSO₃H, NaOAc, 2:1 dioxane/H₂O, 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 rearrangement¹⁶ [(PhO)₂PON₃, Et₃N, C₆H₆, reflux 50 min, then H₂O, 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 (1 H, d, *J* = 9 Hz). Dithionite reduction (Na₂S₂O₄, THF, aqueous MeOH, reflux, 3 h) of **19** gave diamine **20**, mp 148–150 °C, in 80% yield. Selective oxidation of the A



ring of **20** with Fremy's salt^{3a,5} (Na₂HPO₄, aqueous Me₂CO, room temperature, 12 h) led to quinone **21** in 92% yield after preparative silica gel TLC (9:1 CHCl₃/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 IN₃ 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 synthesis of this antitumor agent. Our synthesis leads from 2-benzyloxy-3,4-dimethoxypropionophenone to quinone **21** in 19 steps with an overall yield of ca. 1.3%, an order of magnitude higher than previously reported.

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

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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, hemocyanin¹ 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 $\sim 550 \text{ cm}^{-1}$ for the antiferromagnetic exchange interaction in the oxy form.⁷ Chemical, spectroscopic, and EXAFS⁸ studies suggest that the two coppers are held by an unknown⁹ 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, $[\langle \text{Cu(I)} \cdots \text{Cu(I)} \rangle](\text{BF}_4)_2$, which in propylene carbonate (PC) solution absorbs CO (reversibly) and O_2 (partly reversibly).¹² Treatment of 1, (in nitro-

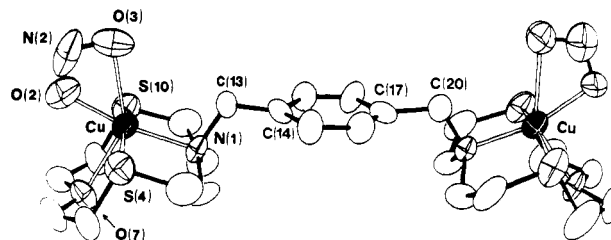


Figure 1. Structure of the $[\langle \text{Cu(II)(NO}_2 \rangle \cdots \text{Cu(II)(NO}_2 \rangle)]^{2+}$ cation. The Cu \cdots Cu interatomic distance is 11.264 (6) Å. Selected bond distances (in Å) (the second value corresponds to the related distances or angles for the unlabeled half of the molecule): 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).

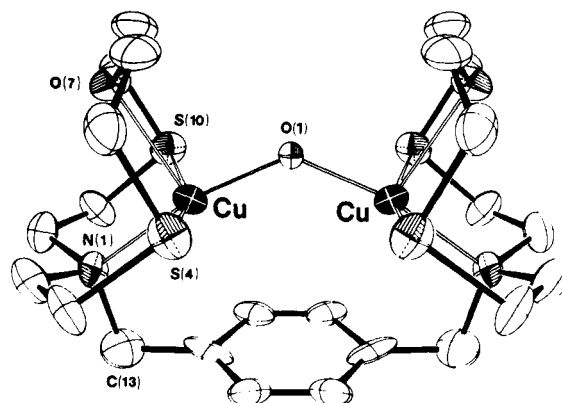


Figure 2. Structure of the $[\langle \text{Cu(II)} \cdots (\text{OH}) \cdots \text{Cu(II)} \rangle]^{3+}$ cation. The Cu \cdots Cu interatomic distance is 3.384 (9) Å and the bond angle Cu–O(1)–Cu is 132.2 (4)°. Selected bond distances (in Å): Cu–O(1), 1.85 (2); Cu–N(1), 2.06 (5); Cu–S(4), 2.35 (2); 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).

methane) 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 $[\langle \text{Cu(II)(NO}_2 \rangle \cdots \text{Cu(II)(NO}_2 \rangle)]^{2+}$ (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) \cdots Cu(II) intramolecular distance is 11.264 (6) Å since L is in an open configuration.

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

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(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.

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(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.

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(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; $\beta = 106.19(2)^\circ$; $M_r = 909.56$, $\rho_{\text{calcd}} = 1.430 \text{ g cm}^{-3}$ 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 $R_{w_f} = 0.10$.

(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.