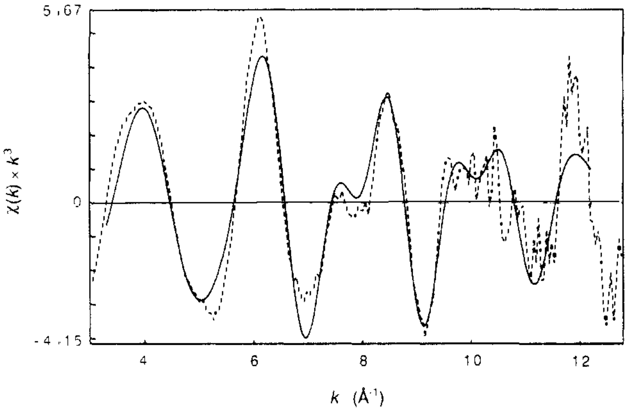

Figure 3. Comparison of the least-squares fit (dark line) to the EXAFS data of protein A of MMO (dashed line). Three waves (O, N, Fe) were used to fit data over a range of $k = 3.5 - 12.2$ Å^{-1}. The filter window for the back transform was $R = 0.52 - 3.33$ Å.

first coordination shell is thus composed of approximately six nearest N/O neighbors at an average distance of ~2.05 Å. A short Fe–O distance could not be fit to the data at any stage of the refinements and consistently gave negative coordination numbers. We have previously shown the high sensitivity of EXAFS to the presence or absence of a short μ-oxo bridge in binuclear iron centers.[10c]

The second-shell and two-shell curve-fittings showed a remarkable consistency in indicating the presence of a pair of iron atoms. Irrespective of the initial values of Fe–N, Fe–O, and Fe–Fe bond distances, the fits gave an Fe–Fe distance of 3.41 Å and a coordination number of 0.8. Carbon atoms are most probably present at distances around 3.0–3.3 Å from the iron atoms. In second-shell and two-shell fits which included an Fe–C wave, an insignificant improvement in F of 7% and 6%, respectively, occurred when adding an Fe–C wave (Table I). Replacing the Fe–Fe wave by only an Fe–C wave did, however, not give an acceptable fit. A comparison of the data and the best fit including O, N, and Fe backscattering waves is given in Figure 3 and a comparison of corresponding Fourier transforms in Figure 2.

Tests were further made to ensure that the Fe–Fe distance was not biased due to the fact that the backscattering parameters were extracted from the μ-hydroxo model. The μ-oxo model data were thus fitted by using these Fe–Fe backscattering parameters, and this fit gave the correct distance of 3.16 Å. Extracting Fe–Fe backscattering parameters from the μ-oxo model data and applying them in fits on the μ-hydroxo model data as well as the protein A data gave the expected long distance in the model compound and further confirmed the previously derived protein results.

We can therefore conclude that protein A of MMO in its semireduced form has a binuclear iron center with an Fe–Fe distance of 3.41 Å and no short μ-oxo bridge.[22]

Acknowledgment. This work was supported by grants from the National Science Foundation (CHE 85-12129 to K.O.H.), the Gas Research Institute (5086-260-1209 to H.D.), and the National Institute of General Medical Sciences (GM 32134 to S.J.L.). The EXAFS experiments were performed at Stanford Synchrotron Radiation Laboratory, which is supported by the Department of Energy, Office of Basic Energy Sciences, and the National Institutes of Health, Biotechnology Resource Program, Division of Research Resources. A.E. is a visiting graduate student supported in part by the Department of Inorganic Chemistry, Lund University, Sweden. J.G.B. acknowledges support under NCI Training Grant CA 09112 and as an American Cancer Society Postdoctoral Fellowship award recipient.

Registry No. 1, 90886-32-1; **2**, 86177-70-0; Fe, 7439-89-6; methane monooxygenase, 51961-97-8; [Fe(1,10-phenanthroline)$_3$](ClO$_4$)$_2$, 14586-54-0.

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[22] These results suggest a similarity with the binuclear iron center in semimethemerythrin azide, which has an Fe–Fe distance of 3.46 Å.[11a] The Fe–Fe distance is different from that of 3.05 Å being reported for oxidized protein A from *Methylobacterium* CRL-26 (Prince, R. C.; George, G. N.; Savas, J. C.; Cramer, S. P.; Patel, R. N. *Biochim. Biophys. Acta* **1988**, *952*, 220–229).

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Synthesis and Structure of [CpRu(PPh$_3$)$_2$(SC$_2$H$_4$)]OSO$_2$CF$_3$. A Transition-Metal Analogue of an Episulfonium Salt

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Recent studies in this laboratory and elsewhere have demonstrated the broad applicability of CpRu(PPh$_3$)$_n$ derivatives in probing metal–sulfur interactions.[1-6] The CpRu(PPh$_3$)$_2^+$ fragment is an unusually soft electrophile; as we indicated in a recent paper,[4] CpRu(PPh$_3$)$_2^+$ is a close relative to Ru(NH$_3$)$_5^{2+}$ which has so fruitfully been studied by Taube and co-workers.[7] This report describes an innovation in CpRu(PPh$_3$)$_2$X chemistry which appears to be generally useful and which we have employed in the synthesis of a stable metal complex of the simplest sulfur heterocycle, thiirane (ethylene sulfide).

Thiirane is often used in transition-metal chemistry as a source of sulfur atoms,[8] and we were interested in using it to generate [CpRu(PPh$_3$)$_2$S]$^+$.[4] In order to facilitate the expected sulfur atom transfer reaction we preactivated the ruthenium center by preparing CpRu(PPh$_3$)$_2$OTf (**1**, OTf is OSO$_2$CF$_3$).[9,10] Compound **1** was synthesized by the straightforward reaction of CpRu(PPh$_3$)$_2$Cl and AgOTf in dichloromethane solution. After removal of the AgCl, the pale yellow complex was precipitated with hexanes. Recrystallization from dichloromethane–hexane gave a 75% yield of **1**. Compound **1** is soluble in aromatic and chlorinated organic solvents and is stable toward traces of water. The triflate complex is a versatile reactant. For example, it forms well-behaved derivatives with a variety of Lewis bases, hydrogen, olefins, and all of the chalcogens.

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[9] CpRu(PPh$_3$)$_2$OTf: ^{1}H NMR (C$_6$D$_6$) δ 4.34 (5 H, s), 6.9–7.3 (30 H, m); ^{31}P{^{1}H} NMR (C$_6$D$_6$/toluene) 46.43 ppm. Anal. Calcd for C$_{42}$H$_{35}$F$_3$O$_3$P$_2$RuS: C, 60.07; H, 4.17. Found: C, 60.75; H, 4.54.

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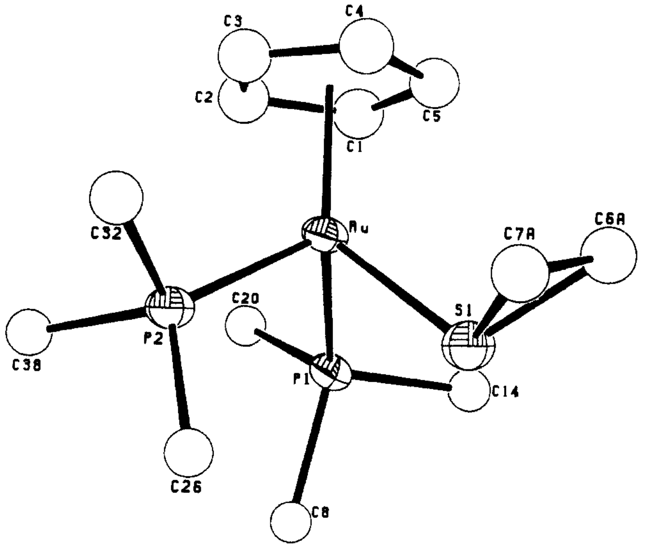


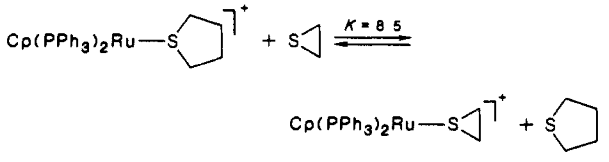
Figure 1. The molecular structure of the non-hydrogen atoms of $[CpRu(PPh_3)_2(SC_2H_4)]^+$; for clarity, only the ipso phenyl carbon atoms are shown. The thermal ellipsoids are drawn at the 35% probability level. Selected bond distances (Å) and angles (deg) are as follows: Ru–S_1 = 2.367 (3), Ru–P_1 = 2.362 (3), Ru–P_2 = 2.363 (3), Ru–C_5H_5 centroid = 1.860 (8), S_1–Ru–P_1 = 91.2 (1), S_1–Ru–P_2 = 88.2 (1), P_1–Ru–P_2 = 102.9 (1), S_1–Ru–Cp = 128.7 (2), C6A–S_1–C7A = 46 (1), S_1–C6A–C7A = 66 (2), S_1–C7A–C6A = 68 (2), Ru–S_1–[SC_2H_4plane] = 112 (1).

Thiirane does not serve as a sulfur donor in its reaction with **1**, instead we isolated $[CpRu(PPh_3)_2(SC_2H_4)]OTf$ (**2**).[11] The air stable yellow crystals of **2** were obtained in 80% yield by precipitation from dichloromethane–diethyl ether. The ^1H NMR spectrum of **2** in $CDCl_3$ indicates that it is stereochemically rigid with respect to inversion at sulfur since we observe distinct resonances for both the endo and exo protons. Further support for the stereochemical rigidity of the thiirane ligand was provided by simulation of the $SC_2\mathit{H}_4$ portion of the ^1H NMR spectrum which required two chemical shifts and four coupling constants.[11]

Because **2** is so unusual we characterized it further by single-crystal X-ray diffraction (Figure 1).[12] The $CpRu(PPh_3)_2$ portion of the cation is unexceptional. The structural parameters for the thiirane fragment closely resemble those for the free heterocycle;[13,14] for example, the C–S–C angles are 46° and 48° for **2** and the free ligand, respectively. The Ru–S bond length is 2.367 (3) Å which is within the range assigned Ru–S single bonds.[1] The sulfur is pyramidal; the angle defined by the Ru–S vector and the C_2S plane is 112 (1)°.

Compound **2** is an analogue of the extremely unstable episulfonium salts, i.e., $RSC_2H_4^+$. Such species have not been structurally characterized previously but have been the subject of lively discussion for many years.[15] In view of the elusiveness of episulfonium cations, the stability of **2** was examined under various conditions. Solid samples of **2** are stable for months if stored anaerobically. $CDCl_3$ solutions of **2** are unchanged after boiling for 5 min. However, in accord with the known properties of episulfonium salts,[14] **2** is very reactive toward weak nucleophiles. Addition of PPh_4Cl (1.1 equiv) to a CD_2Cl_2 solution of **2** at 0 °C followed by warming to room temperature resulted in complete disappearance of **2** and gave ca. 50% yield of $CpRu(PPh_3)_2Cl$ together with 1,4-dithiane (2.89 ppm, s) and a precipitate of $(C_2H_4S)_n$ (IR identification). Thiirane is not formed under these conditions even though solutions of thiirane are stable with respect to $CpRu(PPh_3)_2Cl$ as well as PPh_4Cl. Possibly relevant to our observations is the fact that cationic complexes of conventional thioethers are known to undergo nucleophilic attack at carbon in their reactions with soft nucleophiles like I^- and SCN^-.[16]

A series of ligand competition experiments were conducted in order to evaluate the stability of the Ru–SC_2H_4 interaction vis-a-vis more conventional thioethers. The addition of thiirane to a solution of $[CpRu(PPh_3)_2(tht)]^+$[17] gave a mixture of the thiirane and tetrahydrothiophene (tht) complexes where the equilibrium is in favor of the smaller ring. This equilibrium was achieved from both directions, and on the basis of ^1H NMR integrations the mean K_{eq} was calculated to be 8.5 (eq 1). In a more dramatic demonstration of this stability trend, solutions of the thiirane complex were found to be stable in the presence of elemental sulfur under conditions ($CDCl_3$ solution, 60 °C, 5 min, 1 equiv of S_8) where the tht complex was rapidly (seconds) converted to $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}$.[18] For comparison, the formation of this green μ-S_2 dication from the reaction of S_8 and **1** is complete in minutes at room temperature. The reaction of **1** and S_8 is slowed but is not redirected when conducted in the presence of ethylene; **2** is not formed under these conditions.



(1)

In summary, **2** is a stable analogue of the long sought episulfonium salts.[14,15,19] Our studies indicate that thiirane is a relatively basic ligand compared to more conventional thioethers. The rarity of thiirane complexes can be traced to the heightened reactivity which attends the coordination of thiirane ligands, and the successful isolation of **2** is attributed to the low nucleophilicity of the triflate anion.

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[11] $CpRu(PPh_3)_2(SC_2H_4)OTf\cdot 0.5CH_2Cl_2$: ^1H NMR ($CDCl_3$) δ 2.62 (m, 2 H), 2.93 (m, 2 H), 4.56 (5 H, s), 5.32 (1 H, s, CH_2Cl_2), 7.0–7.4 (30 H, m); $^{31}P\{^1H\}$ NMR ($CDCl_3$) 47.62 ppm. Anal. Calcd for $C_{44.5}H_{40}ClF_3O_3P_2RuS_2$: C, 56.72; H, 4.24; S, 6.79. Found: C, 56.50; H, 4.24; S, 6.73. A computer simulation of the $C_2\mathit{H}_4S$ proton resonances (ITRCAL from Nicolet) gave the following values: $|\delta_{H(1,3)} - \delta_{H(2,4)}| = 0.300$ ppm, $J(1,2) = J(3,4) = -3.38$ Hz, $J(1,4) = J(2,3) = 7.84$ Hz; $J(1,3) = 7.24$ Hz; $J(2,4) = 6.75$ Hz. The RMS value of the error between observed and calculated chemical shifts of the ten more intense transitions in a given envelope was 0.078. Each envelope of transitions contained two weak lines that were not used in the fit. The ^1H NMR spectrum of **2** is strongly solvent dependent, and only a singlet is observed for the $C_2\mathit{H}_4S$ for a CD_2Cl_2 solution of **2**.

[12] Crystal data for $C_{44}H_{39}ClF_3O_3P_2RuS_2$: transparent orange columnar crystal, 0.1 × 0.1 × 0.7 mm, monoclinic, space group $I2/a$. (This alternate space group setting was chosen to avoid the correlations between positional parameters anticipated for the conventional C-centered setting where β = 129.07°. The centric choice was suggested by the average values of the normalized structure factors, supported by an acentric refinement which converged slowly, did not resolve the disorder, and failed to significantly improve agreement, and confirmed by a successful centric refinement.) a = 22.935 (14) Å, b = 14.112 (2) Å, c = 24.787 (8) Å, β = 96.85 (3)°, V = 7965 (9) Å^3 and ρ_{calcd} = 1.501 g/cm^3 for $Z = 8$. Diffraction data: Enraf-Nonius CAD4 automated κ-axis diffractometer, Mo radiation ($\lambda(K\bar{\alpha}$ = 0.71073 Å), range $3.0 < 2\theta < 46.0°$ ($-h-k\pm l$ for $h+k+l = 2n$), 6320 reflections (5515 unique, $R_i = 0.022$, 2865 observed, $I > 2.58\sigma(I)$); corrected for anomalous dispersion, absorption (max and min numerical transmission factors, 0.940 and 0.658), Lorentz and polarization effects. Solution: Patterson methods (SHELXS-86), difference Fourier syntheses; atoms C6 and C7 were disordered in two positions, relative site occupancy 0.50 (3); extreme anisotropy of anion F and O atoms indicated some rotational disorder about the triflate S–C bond was likely. Refinement: H atoms included as fixed contributors in idealized positions, aromatic rings refined as rigid ideal groups and the remaining atoms were independently refined (SHELX). Final: difference Fourier map (range $-0.48 < e/Å^3 < 0.86$) located maximum residual electron density in vicinity of rigid phenyl rings; agreement factors, $R = 0.061$ and $R_w = 0.063$.

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[17] $CpRu(PPh_3)_2(SC_4H_8)BF_4$: ^1H NMR ($CDCl_3$) δ 2.04 (4 H, m), 2.76, (4 H, m), 4.72 (5 H, s), 6.9–7.4 (30 H, m); $^{31}P|H^1\}$ NMR ($CDCl_3$) 46.00 ppm. Anal. Calcd for $C_{45}H_{43}BF_4P_2RuS$: C, 62.43; H, 4.97. Found: C, 62.35; H, 5.19.

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[19] Lorenz, I.-P.; Kull, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 261. These workers have spectroscopically characterized a material assigned as $Pt(PPh_3)_2(SC_2H_4)$.

Acknowledgment. This research was supported by the National Science Foundation. During part of this research, J.A. was supported by a fellowship provided by University of Illinois.

Registry No. **1**, 113322-93-3; **2**, 113322-95-5; $CpRu(PPh_3)_2Cl$, 32993-05-8; PPh_4Cl, 2001-45-8.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond angles and distances (4 pages); tables of structure factors (12 pages). Ordering information is given on any current masthead page.

Mechanism of Formation of Coordination Polymers: A Structural Model for Polymer Chain Growth

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Although coordination polymers composed of metal ions linked by organic bridges have an extensive history, synthesis of well-defined materials is often problematical.[1] Knowledge of potential chain growth processes required in the synthesis of these materials should facilitate the rational design of metal-containing polymers with potentially useful properties.[2] We have recently demonstrated[3] that crystalline polymers derived from the ligands[4] **1** and silver ion can be prepared from soluble precursors (see Scheme I). We now report the isolation and crystallographic characterization of a dimeric silver complex which has structural parameters that suggest it is an intermediate in the chain growth process. This work provides the first evidence for a well-defined chain-growth step in the formation of coordination polymers.

Soluble complexes of the formula $[Ag(\mathbf{1})_2]OTf$[5] are readily isolated by cooling methanol solutions containing stoichiometric quantities of AgOTf and **1**.[6] The structure of $[Ag(\mathbf{1b})_2]OTf$ as a methanol solvate was determined by single-crystal X-ray diffraction[7] (Figure 1). Each ligand is coordinated to silver by two imine nitrogens to afford a four-coordinate complex with a distorted tetrahedral geometry. The average silver–nitrogen bond length of 2.33 (1) Å is long[8] and consistent with the lability of these complexes in solution.[9] In contrast the average silver–nitrogen distance in polymeric $[Ag(\mathbf{1a})]OTf$ is 2.15 (2) Å.[3]

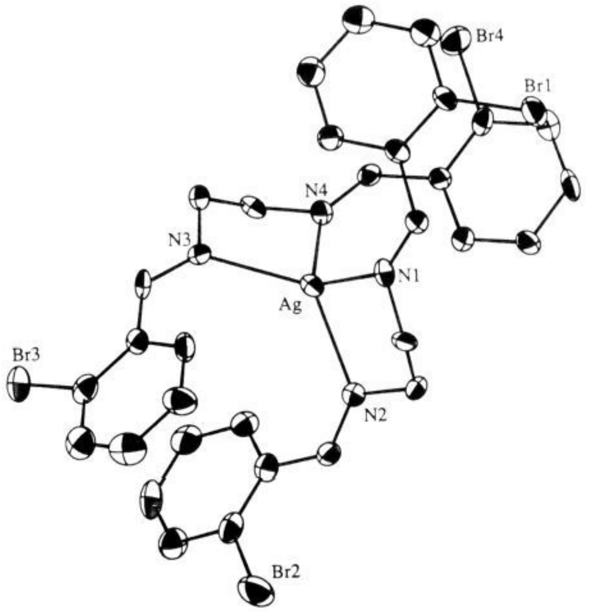
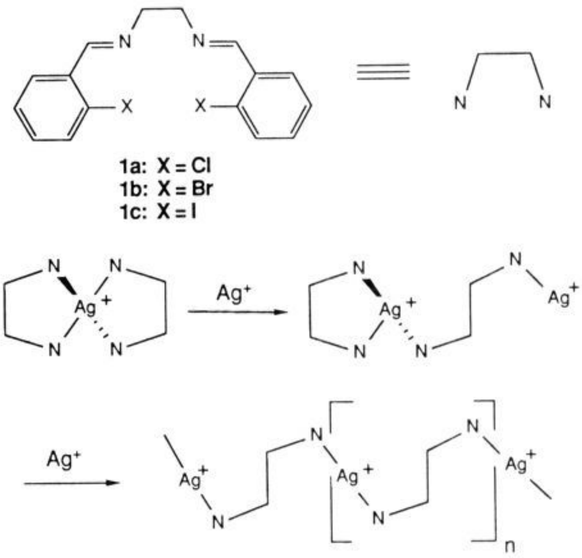


Figure 1. ORTEP representation of $[Ag(\mathbf{1b})_2]^+$. Selected bond distances (Å) are as follows: Ag–N1, 2.349 (9); Ag–N2, 2.327 (8); Ag–N3, 2.325 (8); Ag–N4, 2.330 (8). Selected bond angles (deg) are as follows: N1–Ag–N2, 76.1 (3); N3–Ag–N4, 76.6 (3); N1–Ag–N3, 133.8 (3); N1–Ag–N4, 120.4 (3); N2–Ag–N3, 127.0 (3), N2–Ag–N4, 131.6 (3).

Scheme I



Interaction of stoichiometric quantities of the ligand **1c** and AgOTf affords the dimeric complex $[Ag_2(\mathbf{1c})_3OTf][OTf]\cdot THF$ in 95% yield by crystallization from THF solution upon addition of Et_2O.[10] Crystallographic investigation reveals a novel dimeric structure in which the silver ions are linked by a bridging ligand and a bidentate trifluoromethanesulfonate counterion (Figure 2).[11]

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[5] Abbreviations: Et, ethyl; Me methyl; OTf, trifluoromethanesulfonate; THF, tetrahydrofuran.

[6] Analytical data: (a) $[Ag(\mathbf{1b})_2]OTf$. Anal. Calcd for $C_{33}H_{28}N_4AgBr_4F_3O_3S$: C, 37.92; H, 2.70; N, 5.36. Found: C, 37.74; H, 2.86; N, 5.09. (b) $[Ag(\mathbf{1c})_2]OTf$. Anal. Calcd for $C_{33}H_{28}N_4AgI_4F_3O_3S$: C, 32.14; H, 2.29; N, 4.54. Found: C, 32.24; H, 2.28; N. 4.40.

[7] Crystal data for $[Ag(\mathbf{1b})_2]OTf\cdot MeOH$: $AgBr_4SF_3O_4N_4C_{34}H_{18}$, colorless, monoclinic, $P2_1/c$, $a = 14.491$ (3) Å, $b = 21.005$ (7) Å, $c = 13.677$ (3) Å, $\beta = 108.75$ (2)°, $V = 3942.2$ Å^3, $Z = 4$, Mo Kα. Unique reflections (3095) were collected at ambient temperature (Nicolet R3m, $3.5° < 2\theta < 40°$) and used in the solution and refinement (SHELXTL program). Final refinement included phenyl rings as rigid regular hexagons, all other non-hydrogen atoms as anisotropic, and hydrogen atoms as idealized isotropic contributions. For 412 parameters, $R = 0.068$ and $R_w = 0.053$, GOF = 1.29.

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[9] For example, room temperature 300 MHz ^1H NMR data shows only averaged resonances for mixtures of $[Ag(\mathbf{1})_2]OTf$ and **1**.

[10] Analytical data for $[Ag_2(\mathbf{1c})_3OTf]OTf\cdot THF$. Anal. Calcd for $C_{54}H_{50}N_6Ag_2F_6I_6O_7S$: C, 31.63; H, 2.46; N, 4.10. Found: C, 31.56; H, 2.33; N, 3.86.

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