A question may arise as to the coordination geometry of the copper atom of higher homologues of $Cu(LB)_2$ complexes in the mesophase. On the basis of the following information, we think that destabilization of the mesophases of these complexes is not caused by tetrahedral distortion alone to a serious degree and their coordination geometries are planar, or nearly so, ensuring a lathlike molecular structure even at very large *m*. First of all, the mesomorphic behavior is completely lost in tetrahedral zinc(II) analogues of $Cu(LA)_2$ ($n = 10$ and 14); their isotropic melts can be supercooled down to about 20 °C below their melting points (153 and 148 °C, respectively) but yield no mesophase whatsoever. Besides, Marcos et al. mentioned on ESR (negative) evidence that the nickel(II) analogue of our $Cu(LB)_2$ ($m = 10$) is not paramagnetic,[5] supporting its square-planar configuration. Square planarity of related complexes in other phases has been established; bis[*N*-(*n*-alkyl)salicylaldiminato]copper(II) complexes containing up to six carbon alkyl chains also have a planar structure with minimal distortion in toluene,[9] and the $Cu(LA)_2$ ($n = 5$) containing propyl substituents is of planar configuration in the solid state, since the near-infrared band(s) is(are) absent from its reflectance spectrum.[10]

Experimental Section

Materials. Typical procedures for preparation of the compounds are outlined below.

Ligands (LA). 2,4-Dihydroxybenzaldehyde was subjected to DCC esterification[11] by an appropriate *p*-alkoxybenzoic acid[1] and purified by two or three recrystallizations from methanol (or ethanol for higher homologues). Yields: 40–60%. The product was then condensed with an equimolar amount of propylamine by refluxing in benzene with a Dean-Stark trap attached. After the solvent was removed by rotary evaporation, the desired Schiff base was isolated from the methanol-triturated residue by filtration and recrystallized twice from methanol. Yields: 70–80%, pale yellow microcrystals. ^1H NMR ($CDCl_3$) for L ($n = 9$): δ 14.08 (br s, 1 H, OH), 8.31 (s, 1 H, CH=N), 8.12 (d, $J = 8.8$ Hz, 2 H, benzoyl), 7.26 (d, $J = 8.2$ Hz, 1 H, salicylidene), 6.96 (d, 2 H, benzoyl), 6.79 (d, $J = 2.2$ Hz, 1 H, salicylidene), 6.72 (dd, 1 H, salicylidene), 4.04 (t, $J = 6.6$ Hz, 2 H, CH_2—O), 3.55 (t, $J = 6.6$ Hz, 2 H, CH_2—N), 1.82 (quintet, $J = 7$ Hz, 2 H, CH_2), 1.71 (hextet, $J = 7$ Hz, 2 H, CH_2), 1.47–1.29 (br m, 12 H, CH_2's), 0.98 (t, $J = 7$ Hz, 3 H, CH_3), 0.89 (t, $J = 7$ Hz, 3 H, CH_3). Anal. Found (calcd) for $C_{25}H_{33}NO_4$ ($n = 8$): C, 72.80 (72.96); H, 8.04 (8.09); N, 2.99 (3.40). Found (calcd) for $C_{26}H_{35}NO_4$ ($n = 9$): C, 73.36 (73.38); H, 8.45 (8.29); N, 3.49 (3.29).

Copper(II) Complexes ($Cu(LA)_2$). A 5-mmol sample of an LA homologue was dissolved in 30 mL of hot methanol, and to this was added a methanolic solution of 2.55 mmol of cupric acetate dihydrate. After refluxing for several hours, a greenish brown solid was collected by filtration, washed with methanol, and recrystallized from ethanol/chloroform mixtures until sharp and constant phase transitions were obtained. Yields: 50–70%, fibrous to platelike ($n \leq 12$) or powdery microcrystals ($n = 14$, 16, and 18). Anal. Found (calcd) for $C_{50}H_{64}N_2O_8Cu$ ($n = 8$): C, 67.73 (67.89); H, 7.30 (7.29); N, 3.13 (3.17). Found (calcd) for $C_{52}H_{68}N_2O_8Cu$ ($n = 9$): C, 68.34 (68.43); H, 7.58 (7.51); N, 3.00 (3.07).

$Cu(LB)_2$. Bis[4-((4-(hexyloxy)benzoyl)oxy)salicylaldehydato]copper(II) was prepared by using the aldehyde ligand, prepared above, in a manner similar to that for $Cu(LA)_2$. A 1-mmol quantity of this complex was allowed to react with 3 equiv of an alkylamine in 40 mL of boiling chloroform for several hours and then evaporated nearly to dryness. Crude solid was isolated and washed with methanol and purified as above. Yields: 30–60%, greenish brown fibrous to platelike crystals. Anal. Found (calcd) for $C_{58}H_{80}N_2O_8Cu$ ($m = 9$): C, 69.75 (69.89); H, 8.21 (8.09); N, 2.78 (2.81).

Physical Measurements. Calorimetric measurements were performed by using Rigaku Thermoflex, Rigaku TAS100, and Du Pont 9900 differential scanning calorimeters. The heating or cooling rate was 5 K min^{-1}.

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Nitronium (Trifluoroacetato)metalates. 1. Nitronium Hexakis(trifluoroacetato)stannate(IV)

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Received August 1, 1989

During an investigation by ^{14}NMR spectroscopy of the nature of the nitrogen species present in the solution of covalent tin(IV) nitrate in the reactive solvent $(CF_3CO)_2O$, it became apparent that solvolysis of the tin(IV) nitrate with the anhydride provides a synthetic method for the hitherto unknown nitronium salt of the hexakis(trifluoroacetato)stannate(IV) anion.

Addison has postulated a free radical mechanism[1,2] to account for the vigor of the bidentate nitrate reactions in nonaqueous media. Such a hypothesis would involve reduction of the metal ion, e.g.

$$Sn(NO_3)_4 \rightleftharpoons Sn(NO_3)_3 + NO_3^{\bullet}$$

The existence of the $NO_3^{\bullet}$ free radical is well established.[3–6]

However, the reactions of the bidentate tin(IV) nitrate described here can alternatively be regarded as reactions of coordinated nitrate ligands. The reactivity of the bidentate nitrate, due to perturbed electronic distribution, appears to be related to the oxidation state, electronic configuration, and the polarizing power of the metal, with small highly charged cations possessing a spherically symmetric electron distribution, such as d^{10} in $Sn(NO_3)_4$.

On the other hand the fluoroacetato compounds are well-known and established.[7–10]

Here, we report the synthesis, characterization, and spectroscopic properties of nitronium hexakis(trifluoroacetato)stannate(IV).

Experimental Section

Reagents. Tin(IV) nitrate was prepared as described in the literature.[1] Pure N_2O_5 was collected at −78 °C, and $SnCl_4$ was added in portions with continuous shaking. Excess of the reagents was removed by evacuating the flask, and the crude product was sublimed under vacuum at 50 °C.

Carbon tetrachloride, nitromethane, and acetonitrile were distilled twice from P_2O_5. Molecular sieves were used to dry other solvents.

Preparation of $(NO_2)_2[Sn(O_2C_2F_3)_6]$. The nitronium hexakis(trifluoroacetato)stannate(IV) is prepared by dissolving powdered $Sn(NO_3)_4$ (0.5 g) in pure and dry $(CF_3CO)_2O$ (ca. 5 mL). All manipulations were carried out in inert media. The mixture was allowed to stand overnight whereupon white needles and a clear supernatant liquid were obtained. The precipitate was filtered off under a nitrogen current, washed with dry CCl_4, and dried in vacuum at room temperature. Analysis was consistent with the formula $[SnO_{16}C_{12}N_2F_{18}]$. [Cald for $SnC_{12}F_{18}N_2O_{16}$: Sn, 13.35; C, 16.21; N, 3.15. Found: Sn, 13.55; C, 16.21, N, 3.15; H, 0.12.] The product is readily soluble and stable in acetonitrile and ethyl acetate, insoluble in CCl_4, CH_3Cl, and CH_2Cl_2, and reacts with effervescence with alcohol, acetone, and water.

Analysis. Nitrogen was determined by the refined Kjeldah method using stoppered breakable bulbs for the hydrolysis of the compound. Tin was determined as SnO_2.

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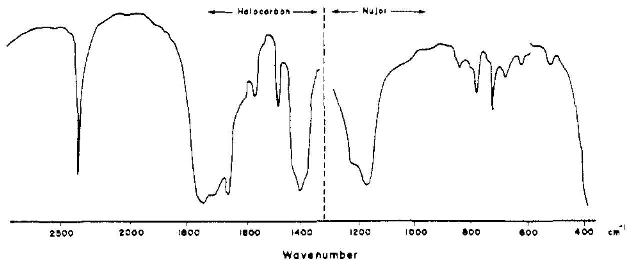

Figure 1. Infrared spectrum of $(NO_2^+)_2[Sn(OOCCF_3)_6]^{2-}$.

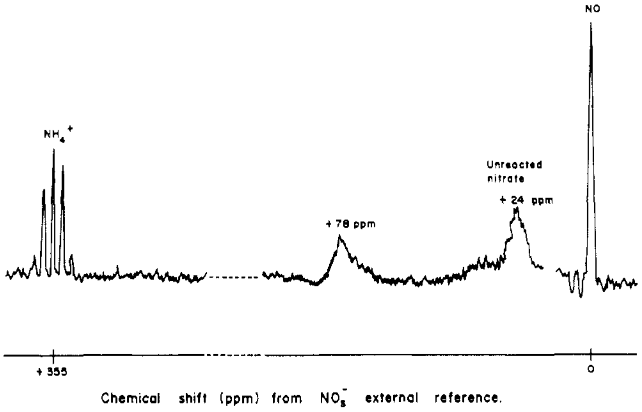

Figure 2. ^{14}N NMR spectrum of a solution of $Sn(NO_3)_4$ in excess $(CF_3CO)_2O$.

Table I. ^{14}N Chemical Shifts ($\delta(NO_3^-)$ in ppm) of Freshly Prepared Solutions (Excess Solvent)[a]

	MeCN	CF_3COOH	$(CF_3CO)_2O$	$MeNO_2$
100% HNO_3		41 (17)	62 (32)	
N_2O_5	58	59 (40)	62 (24)	
$Sn(NO_3)_4$	24 (55)	51 (55)	78 (41)[b] 24 (41)[c]	
product				120

[a] Half-height line width (Hz) in parentheses. [b] Resonance moves to high field with time. [c] Resonance decreases in intensity and disappears after about 35 min (assigned to unreacted nitrate).

Physical Measurements. Infrared spectra were obtained by using a Perkin-Elmer 457 spectrometer. Spectra of Nujol and halocarbon mulls are presented in Figure 1.

^{14}N NMR spectra were obtained with a Varian HA 100 spectrometer and saturated ammonium nitrate as an external reference standard. Results are presented in Table I and Figure 2.

^{119}Sn Mossbauer spectra were measured at −196 °C, with $BaSnO_3$ as the source. Results are presented in Figure 3.

Results and Discussion

The analytical data and infrared, ^{14}N NMR, and Mossbauer spectra are all consistent with the formulation of the product as

$$(NO_2^+)_2[Sn(OOCCF_3)_6]^{2-}$$

The infrared spectrum exhibits a strong and sharp band at 2393 cm⁻¹ (Figure 1), which was assigned to the antisymmetric stretching frequency of the nitronium ion, $\nu_{as}(NO_2^+)$. This band apeared only weakly in a Nujol mull, indicating reaction of NO_2^+ ion with the Nujol.

However, it was not possible to distinguish unequivocally between the different modes of coordination of trifluoroacetate groups on the basis of their IR frequencies.

The unidentate trifluoroacetate groups are identified by the absence of the frequency at ca. 1450 cm⁻¹ and the presence of a band assignable to C–O stretching motion at ca. 1200–1300 cm⁻¹. By comparison with the data in Table II it could be inferred that the compound might contain both bidentate and unidentate groups with 1740 cm⁻¹ being due to $\nu_{as}(COO)$ bidentate, 1483 cm⁻¹ being due to $\nu_s(COO)$ bidentate, and 1230 cm⁻¹ being due to $\nu_s(C-O)$ unidentate.

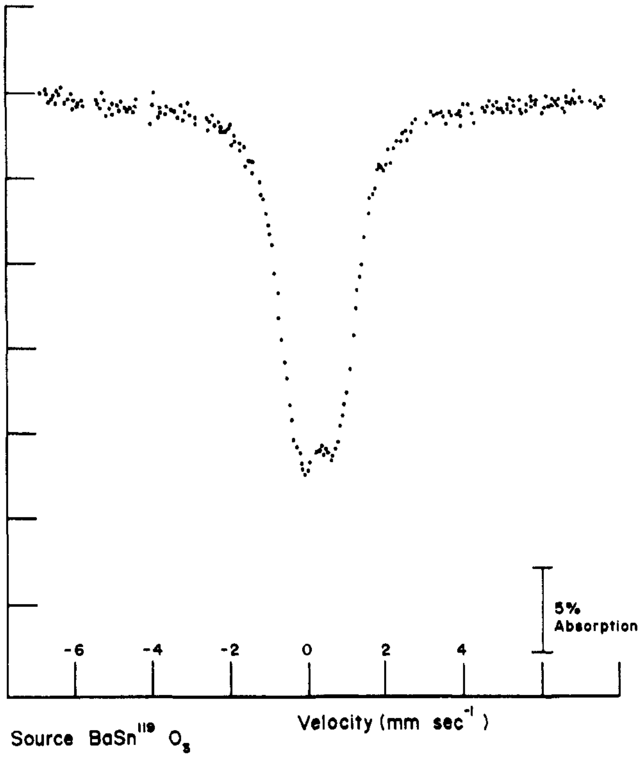

Figure 3. ^{119m}Sn Mossbauer spectrum of $(NO_2^+)_2[Sn(O_2C_2F_3)_6]$.

Table II. Symmetric and Asymmetric COO Stretching Frequencies (cm⁻¹) of Trifluoroacetate Compounds

compd	mode of bonding	$\nu_{as}(COO)$	$\nu_s(COO)$	Δ[a]	phase[b]	ref
$NH_4(O_2CCF_3)$	ionic	1731 1667	1465	202	s	7
$K(O_2CCF_3)$	ionic	1678	1437	241	s	8
$Th(O_2CCF_4)_4$	bidentate	1688	1481	207	soln	8
$Cr(O_2CCF_3)_3$	bidentate	1710	1490	220	soln	9
$Me_3Sn(O_2CCF_3)$	unidentate	1720	1290	430	soln	10
$Mn(CO)_5(O_2CCF_3)$	unidentate	1688	1205	483	soln	10
$(CF_3CO)_2O$	unidentate	1820 1885	1325	495	l	11

[a] $\Delta = (\nu_{as} - \nu_s)$ cm⁻¹. [b] s = solid ; soln = solution; l = liquid.

The presence of the nitronium ion is further confirmed by the ^{14}N NMR spectrum of a nitromethane solution of the product. The chemical shift observed at +120 ppm relative to NO_3^- is a value characteristic of NO_2+ but slightly lower than that obtained for NO_3^- (NO_3^-, +125 ppm);[12,13] see Table I.

The preservation of the +IV oxidation state of tin was indicated by the tin-119 Mossbauer spectrum, which exhibited resonances with isomer shifts identical with those of other tin(IV) compounds at ca. 0.29 mm s⁻¹. The spectrum consisted of a barely resolved doublet in the tin(IV) region (δ 0.29 mm/s; QS 0.96 mm/s; T_1 = 1.18 mm/s; T_2 = 1.25 mm/s); see Figure 3.

The preservation of the +IV oxidation state of tin indicates that the reaction between tin(IV) nitrate and $(CF_3CO_2)_2O$ appears to involve only substitution reactions of the nitrate ligands. Whether this is an S_N2 or S_N1 mechanism is arguable, but in view of the bulkiness of the approaching fluoroacetate ligand and the shield of the metal by the nitrate groups, it seems unlikely that the incoming ligand will coordinate to the metal ion to yield an acetate–nitrate intermediate that then yields the product.

The S_N1 mechanism is more attractive, which is envisaged to take place via an outer-sphere solvation of the metal nitrate

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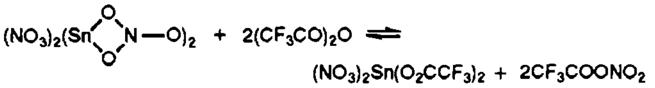
producing the trifluoroacetyl nitrate, i.e.



$$(NO_3)_2(Sn(O_2N{-}O)_2 + 2(CF_3CO)_2O \rightleftharpoons (NO_3)_2Sn(O_2CCF_3)_2 + 2CF_3COONO_2$$

The formation of NO_2^+ and CF_3COO^- ions will be favored by the electron-withdrawing character of the CF_3 group; i.e., the following equilibrium will be shifted to the right:

$$CF_3COONO_2 \rightleftharpoons NO_2^+ + CF_3COO^-$$

This shift is more enhanced by the removal of trifluoroacetate ions through coordination to the metal ion, giving the complex (trifluoroacetato)metalate anion.

This is evident from the upfield shift of the ^{14}N NMR resonance; see Table I and Figure 2.

Registry No. $(NO_2)_2[Sn(O_2C_2F_3)_6]$, 68462-15-7; $CF_3C(O)ONO_2$, 66693-89-8; $NO_2^+CF_3COO^-$, 129176-51-8; $Sn(O_2C_2F_3)_4$, 16424-89-8; $Sn(NO_3)_4$, 13826-70-5; $(CF_3CO)_2O$, 407-25-0.

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Synthesis and Characterization of Heptarhenium Carbido Clusters with (η^2-Olefin)iridium Capping Moieties

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Studies of transition-metal η^2-olefin compounds have played very important roles in understanding the metal–ligand bonding as well as mechanisms of catalytic processes involved in alkene transformations.[1] Mononuclear η^2-olefin compounds with six-electron polyene auxillary ligands, such as cyclopentadienyl (Cp$^-$), benzene, and their derivatives, have received increased attention in that several late-transition-metal compounds have been established as useful C–H bond activation reagents.[2] Compared with mononuclear species, fewer polynuclear η^2-olefin compounds have been reported.[3] When alkenes are allowed to react with cluster compounds, facile C–H and/or C–C bond cleavage or formation is frequently encountered, preventing the isolation and characterization of η^2-olefin adducts.[4]

In a series of recent reports from our group and others, mixed-metal carbido cluster anions with the general formula of $[Re_7C(CO)_{21}ML_n]^{2-}$ have been synthesized by redox-coupling[5] of $[Re_7C(CO)_{21}]^{3-}$ and various ML_n^+ (M = Rh, Ir, Pt, Pd, Cu, Ag, Au) moieties.[6,7] An isolobal analogy between the Cp$^-$ ligand and the anionic cluster compound $[Re_7C(CO)_{21}]^{3-}$ was proposed on the basis of the topological and expected frontier orbital similarities between them as well as the resemblance in the spectroscopic features of $[Re_7C(CO)_{21}ML_n]^{2-}$ and $CpML_n$.[6b] In terms of reactivity, metalloligand-supported metal centers also resemble their mononuclear analogues with respect to substitution reactions.[8] As part of our current attempt to extend the analogy between $[Re_7C(CO)_{21}]^{3-}$ and Cp$^-$, we report here the synthesis and characterization of the η^2-olefin-containing clusters $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ (C_8H_{14} = cyclooctene) and $[Re_7C(CO)_{21}Ir(C_2H_4)(CO)]^{2-}$.

Experimental Section

General Procedures. All reactions were carried out under a nitrogen atmosphere by using standard Schlenk techniques and were monitored by IR spectroscopy (carbonyl region). Solvents were distilled from appropriate drying agents and degassed immediately before use. Cyclooctene (Aldrich) was purified by passing it through an aluminum oxide column and tested for the absence of peroxide with $FeSO_4$ and KSCN immediately before use. CP grade ethylene (Matheson) and $AgBF_4$ (Ozark-Mahoning) were used as received. $[PPN]_3[Re_7C(CO)_{21}]$ or $[Et_4N]_3[Re_7C(CO)_{21}]$[9] and $[Ir(C_8H_{14})_2(CO)Cl]_2$[10] were prepared according to literature methods. ^{13}CO-enriched $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ was prepared from ca. 20% ^{13}CO-enriched $[PPN]_3[Re_7C(CO)_{21}]$.

IR spectra were recorded with a Perkin-Elmer 1750 FT-IR spectrometer. ^{1}H NMR spectra were obtained by using a GE GN-500 spectrometer at 500 MHz. The ^{13}C NMR spectrum was acquired on a GE QE-300 instrument at 75 MHz. Negative ion fast atom bombardment mass spectra (FAB-MS) and elemental analyses were obtained by the respective staffs of the Mass Spectrometry Center and the Microanalytical Laboratory of the School of Chemical Sciences.

$[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$. THF solutions of $AgBF_4$ (9.6 mg, 0.049 mmol) and $[Ir(C_8H_{14})_2(CO)Cl]_2$ (30.1 mg, 0.0316 mmol) were combined, and cyclooctene (2.0 mL, 15 mmol) was added immediately after mixing. The solution became turbid after stirring at ambient temperature for 2 h. After the precipitate was allowed to settle, the yellow solution was transferred via a filtering cannula and passed through a layer of Celite on a fritted filter. This solution was mixed with a dichloromethane solution of $[PPN]_3[Re_7C(CO)_{21}]$ (83.7 mg, 0.0238 mmol), resulting in an immediate color change to dark red. After 30 min of stirring at room temperature, the solvents were removed under vacuum. The residue was dissolved in a minimal amount of chloroform, and 2-propanol was carefully layered on top. Solvent diffusion at room temperature for 12 days gave a black solid (70.2 mg). A recrystallization using chloroform/2-propanol was carried out over 5 days, giving dark red crystals (35.1 mg, 45%). Anal. Calcd for $C_{104}H_{75}N_2Cl_3IrO_{22}P_4Re_7$ ($[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]\cdot CHCl_3$): C, 36.41; H, 2.20; N, 0.82; Cl, 3.10. Found: C, 36.48; H, 2.12; N, 0.84; Cl, 2.89.[11] IR (acetone): ν_{CO} 2048 (w), 1996 (vs), 1973 (w), 1940 (w), 1921 (w), 1888 (vw) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 7.80–7.40 (m, 60 H, C_6H_5 in PPN$^+$), 2.79 (m, 2 H, H_v), 2.16 (m, 2 H, $H_{\alpha 1}$), 1.72–1.50 (m, 10 H, $H_\beta + H_\gamma + H_{\alpha 2}$). ^{13}C NMR ($CDCl_3$, 20 °C): δ 204.7 (s, 3 C, Re(*CO*)$_3$ cap), 195.3 (s, 9 C), 191.2 (s, 9 C), 167.1 (s, 1 C, Ir–*CO*). FAB-MS (negative ion): *m/z* (^{187}Re, ^{193}Ir) 2778 (M – PPN), 2668 (M – PPN – C_8H_{14}), 2130 (M – 2PPN – C_8H_{14}).

$[PPN]_2[Re_7C(CO)_{21}Ir(C_2H_4)(CO)]$. $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ (21.4 mg, 0.006 46 mmol) was dissolved in acetone (ca. 40 mL) in a 250-mL heavy-walled glass pressure bottle. The bottle was pressurized with ethylene (15 psig), (15 psi), and the solution was stirred at room temperature for 13 h. After the removal of the solvent, the residue

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(11) An analytically pure sample without solvent molecules was obtained as the Et_4N^+ salt $[Et_4N]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$. Anal. Calcd for $C_{47}H_{54}N_2IrO_{22}Re_7$: C, 22.63; H, 2.18; N, 1.12. Found: C, 22.39; H, 2.17; N, 1.10.

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