aqueous NaOH. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$. The chloroform solution was dried over Na_2SO_4. Recrystallization from hexane gave 2.1 g (72.5%) (IVa), mp 68-69°C. Found: C 80.62; H 7.72; N 11.78%. Calculated for $C_{16}H_{18}N_2$: C 80.63; H 7.61; N 11.75%. PMR spectrum (δ, ppm): 0.96 t (CH_3-C), 1.43 sext (γ-CH_2), 1.80 q (β-CH_2), 2.95 t (α-CH_2), 3.79 (CH_3N), 7.11 (H^1), 7.3-7.5m (H^{5-7}), 8.10 d (H^8), 9.19 (H^4).

Analogous preparations were carried out for: (IVb), 62.8% yield, mp 114-115°C (from 1:2 benzene–hexane). Found: C 72.47; H 6.60; N 15.05%. Calculated for $C_{17}H_{19}N_3O$: C 72.57; H 6.81; N 14.93%. PMR spectrum (δ, ppm): 2.57 t (CH_2NCH_2), 3.76 t (CH_2OCH_2), 3.81 ($\rangle CH_2N$), 3.84 (CH_3N), 7.3-7.5 m ($H^{1,5-7}$), 8.12 d (H^8), 9.22 (H^4). (IVc), 62.1% yield, mp 106-107° (from hexane). Found: C 83.59; H 5.67; N 11.00%. Calculated for $C_{18}H_{14}N_2$: C 83.69; H 5.46; N 10.84%. PMR spectrum (δ, ppm): 3.85 (CH_3N), 7.3-8.1 m ($H^{1,5-7}$, Ph), 8.15 d (H^8), 9.34 (H^4).

CONCLUSIONS

3-Formyl-2-acetylenyl-1-methylindole oximes readily undergo intramolecular heterocyclization with closure of a pyridine ring and formation of substituted γ-carboline N-oxides.

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REACTIONS OF 15-CROWN-5 AND BIS-15-CROWN-5 ETHERS WITH METAL ACETYLACETONATE IONS IN THE GAS PHASE

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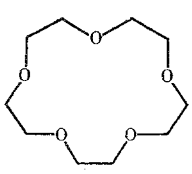
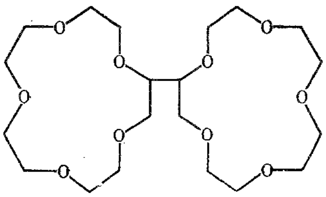
The composition and stability of complexes of crown ethers with metal ions in solution are determined to a significant extent by the nature of the solvent [1]. The reactivity of the macroring may be evaluated independently by carrying out the complexation in the gas phase in the absence of solvent by mass spectrometric methods. In our previous work [2, 3], we showed that 18-crown-6 and macrocyclic thiourea derivatives in the gas phase form 1:1 complexes with Group III elements. In the present work, we studied the gas-phase complexation reactions between 15-crown-5 (L^1) and bis-15-crown-5 (L^2) and cations containing transition metals, Group III metals, and rare-earth elements



L^1



L^2

Acetylacetonate complexes $(acac)_nM$, where M = Co (n = 3), Fe (n = 3), Cr (n = 3), Ni (n = 2), Mn (n = 2), Ga (n = 3), In (n = 3), Nd (n = 3) were used as the sources of metal-containing cations. The electron impact

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[*] Deceased.

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TABLE 1. Relative Yields of Secondary Ions* in the Mass Spectra Obtained by the Combined Ionization of $(acac)_nM$ and 15-Crown-5 ($L = L^1$) or Bis-15-crown-5 ($L = L^2$)

Ion	Cr ($n=3$)		Ni ($n=2$)		Mn ($n=2$)	Fe ($n=3$)	
	L^1	L^2	L^1	L^2	L^1	L^1	L^2
$(acac)_{n-1}ML^+$	0,77	0,87	0,77	0,80	1,0	–	–
$(acac)_{n-2}ML^+$	0,23	0,13	0,23	0,20	–	1,0	1,0
$(acac)_{n-2}M(L-H)^+$	–	–	–	–	–	–	–

Ion	Co ($n=3$)		Nd ($n=3$)		In ($n=3$)	Ga ($n=3$)
	L^1	L^2	L^1	L^2	L^1	L^1
$(acac)_{n-1}ML^+$	–	–	0,83	0,87	1,0	1,0
$(acac)_{n-2}ML^+$	1,0	1,0	–	–	–	–
$(acac)_{n-2}M(L-H)^+$	–	–	0,17	0,13	–	–

* The peak amplitudes are 0.01-0.1% of the amplitudes of the peaks for the $(acac)_{n-1}M^+$ ions.

mass spectra of these compounds at low ionizing potential (10 V) show peaks for the molecular ions $(acac)_nM^+$ and fragment ions $(acac)_{n-1}M^+$. The products of the ion–molecule reactions of the metal-containing ions with neutral macrocyclic polyether molecules ($L = L^1$ or L^2) are given in Table 1.

The combined ionization of vapors of metal acetylacetonates and these crown ethers give secondary ions $[(acac)_{n-1}ML]^+$, $[(acac)_{n-2}ML]^+$, and $[(acac)_{n-2}M(L-H)]^+$ (see Table 1). The products of the addition of a crown ether molecule to the molecular ion of the metal complex, $(acac)_nML^+$ were not observed in any case. The most likely pathway for the formation of $(acac)_{n-1}ML^+$ ions is reaction (1) involving the adition of $(acac)_{n-1}M^+$ ions to the macroring molecule and not the substitution of the acetylacetonate ligand in the molecular ion. This hypothesis is supported by the mass spectrum for In trisacetylacetonate, in which the intensity of the molecular ion peak is negligible. Nevertheless, $[(acac)_2InL]^+$ ions are formed in the combined ionization of this complex with the crown ether.

There were no $(acac)_{n-2}M^+$ ions in the low-potential spectra of the complexes studied. Thus, the appearance of $[(acac)_{n-2}ML]^+$ secondary ions also may be considered to result from the replacement of the acetyacetonate ligand in $(acac)_{n-1}M^+$ ions into the macroring molecule (reactions 2)). During this process, the metal ion is reduced to the nearest low oxidation state. Thus, we may assume that the ratio of the intensities of the $[(acac)_{n-1}ML]^+$ and $[(acac)_{n-2}ML]^+$ ions is a function of the ease of converting the metal ion to the lower oxidation state. This is supported by the data given in Table 1. For example, there are no $[(acac)_{n-2}ML]^+$ ions for complexes of Nd, Ga, and In which do not have stable +2 oxidation states. In the case of chromium, which has a small positive electrode potential (+0.407 V) for the reaction Cr(III) → Cr(II) [4], we find both these ions, while for cobalt and iron, which have negative potentials (−1.808 and −0.771 V, respectively), only $[(acac)ML]^+$ ions are formed. In this case the ratio of the rate constants for the formation of $[acacCoL]^+$ and $[acacFeL]^+$ ions* obtained experimentally in the combined ionization of $(acac)_3Co$, $(acac)_3Fe$ and bis-15-crown-5 is greater than unity, which is in accord with the greater ease of reducing Co(III) to Co(II).

In contrast to transition metals which display variable valence, only reactions (1) and (3) are found for Group III metal and rare-earth trisacetylacetonates

$$(acac)_{n-1}M^+ + L \rightarrow [(acac)_{n-1}ML]^+ \quad (1)$$

$$(acac)_{n-1}M^+ + L \rightarrow [(acac)_{n-2}ML]^+ + acac \quad (2)$$

$$(acac)_{n-1}M^+ + L \rightarrow [(acac)_{n-2}M(L-H)]^+ + Hacac \quad (3)$$

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* $K_{rel} = \frac{[acacCoL^+]}{[(acac)_2Co^+]\cdot[L^+]} : \frac{[acacFeL^+]}{[(acac)_2Fe^+]\cdot[L^+]} = 4.2$

The square brackets indicate the peak intensities of the corresponding ions; the intensity of the ions of ligand L^2 which characterizes the concentration of neutral molecules remained constant during the experiment.

In both cases, the metal ion is found in the stable +3 oxidation state in the secondary ions formed. We observed similar reactions in a study of the reaction of rare-earth acetylacetonates with macrocyclic thiourea derivatives [3]. The $[\mathrm{acacNd}(L-H)]^+/[(\mathrm{acac})_2\mathrm{NdL}]^+$ ion intensity ratio for the thiourea macrorings is significantly greater than the corresponding ratio for 15-crown-5 and its dimer which lack labile hydrogen atoms.

We especially note the formation of L^1 and L^2 complexes with nickel ions completely lacking a ligand environment (see Table 1). This finding indicates the possibility, in principle, of using 15-crown-5 and its analogs for fixing transition metals in unstable oxidation states.

Table 1 indicates that there are no qualitative differences in the reaction of $(\mathrm{acac})_{n-1}M^+$ ions with 15-crown-5 or with bis-15-crown-5, while the relative yields of the products of the ion–molecule reactions for L^1 and L^2 are similar. This indicates a similarity in the mechanisms of these reactions for 15-crown-5 and its dimer.

EXPERIMENTAL

The mass spectra were taken on an AEI MS-30 mass spectrometer by our previous method [3]. The error in the relative ion peak intensities given in Table 1 was not greater than ±10%. The crown ethers were prepared according to our previous procedure [5].

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CONCLUSIONS

1. A study was carried out on the ion–molecule reactions of ions arising in the dissociation of ferric, cobaltic, chromic, manganous, neodymium(II), gallium(III), and indium(III) acetylacetonates upon electron impact with 15-crown-5 and bis-15-crown-5.

2. The ratio of the yields of $(\mathrm{acac})_x M^+L$ and $(\mathrm{acac})_{x-1}M^+L$ ions (M is a metal, L is a macrocyclic ligand, and $x = 1$ or 2) is determined by the case of reduction of $M^{(x+1)+}$ to M^{x+} and for $(\mathrm{acac})_3M$ complexes, this ratio decreases in the series Nd, In, Ga > Cr > Fe, Co. The rate constant for the formation of $\mathrm{acacCoL}^+$ ions is greater than for $\mathrm{acacFeL}^+$ ions.

3. The possibility of fixing transition metals in unstable oxidation states by crown ethers was demonstrated in the case of nickel.

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