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Mass Spectrometric Observation of Gaseous EuCN and the Determination of its Atomization Energy

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Summary The gaseous molecule EuCN has been observed in a high-temperature mass spectrometer and its atomization energy, $\Delta H^\circ_{\mathrm{atm},298}$ has been determined as 283 ± 8 kcal mol^{-1}.

OBSERVATIONS of gaseous metal cyanides have been quite rare;[1-5] however, recently more attention has been given to such molecules owing to their interesting structural and bonding properties.[2a,5-7] Here, is reported the first observation of a gaseous transition-metal cyanide and in particular, the first gaseous lanthanide cyanide. In this connection, it is noteworthy that only recently have the first simple condensed lanthanide cyanides been prepared.[8]

The EuCN$^+$ ion was observed in the effusing vapour from a graphite-lined tantalum Knudsen cell initially containing an intimate powdered mixture of EuN, ZrN, Rh, and excess of graphite along with a piece of gold wire. The EuCN$^+$ ion was identified by its isotopic distribution and shown to be parent by its ionization efficiency curve. It was found to have an approximate appearance potential of 5·5 ± 1·5 eV.

The mass spectrometer used, experimental techniques, and standard third-law treatment of the ion intensity *vs.* temperature data have been described previously.[9] The pressure-dependent equilibrium reaction (1) was measured

$$2\mathrm{Eu(g)} + \mathrm{N_2(g)} + 2\mathrm{C(s)} = 2\mathrm{EuCN(g)} \qquad (1)$$

and its enthalpy obtained by the third-law method according to the relation $\Delta H_{298} = -RT\ln K_{\mathrm{p}} - T\Delta[(G^\circ_T - H^\circ_{298})/T]$. The data and results of the evaluation are given in the Table. Here, the ion intensities, I_{i}, were multiplied by experimentally determined calibration constants before they were used in the determination of the equilibrium constant, K_{p}. These calibration constants, k_{i}, were determined from measurements of the well known equilibrium $\mathrm{Au_2(g)} = 2\mathrm{Au(g)}$[10] as 0·156, 0·881, and 0·165 atm/A K for Eu, N_2, and EuCN, respectively. They include correction parameters for ionization cross sections, multiplier gains, maximum ionization efficiency, and isotopic abundances. Partial pressures are obtained from ion intensities, I_{i}, by the relation $P_{\mathrm{i}} = k_{\mathrm{i}} I_{\mathrm{i}} T$.

TABLE. *Third-law enthalpies for the reaction* $2\mathrm{Eu(g)} + \mathrm{N_2(g)} + 2\mathrm{C(s)} = 2\mathrm{EuCN(g)}$

	Ion intensities/A					
T/K	$I(^{153}\mathrm{Eu}^+)$	$I(^{28}\mathrm{N_2}^+)$	$I(^{179}\mathrm{EuCN}^+)$	$-\log K_{\mathrm{p}}$	$\Delta[(G^\circ_T - H^\circ_{298})/T]$/(cal K^{-1})	ΔH°_{298}/kcal
1735	$1{\cdot}39 \times 10^{-7}$	$1{\cdot}60 \times 10^{-7}$	$1{\cdot}69 \times 10^{-10}$	2·170	7·69	3·9
1707	$1{\cdot}24 \times 10^{-7}$	$7{\cdot}31 \times 10^{-8}$	$1{\cdot}26 \times 10^{-10}$	1·979	7·68	2·4
1652	$9{\cdot}21 \times 10^{-8}$	$8{\cdot}09 \times 10^{-8}$	$1{\cdot}00 \times 10^{-10}$	1·951	7·65	2·1
1742	$2{\cdot}80 \times 10^{-7}$	$7{\cdot}93 \times 10^{-8}$	$3{\cdot}51 \times 10^{-10}$	1·840	7·69	1·3
1794	$4{\cdot}16 \times 10^{-7}$	$1{\cdot}39 \times 10^{-7}$	$5{\cdot}90 \times 10^{-10}$	1·990	7·72	2·5

Average: 2·4 ±0·8

Free-energy functions, $-(G^\circ_T - H^\circ_{298})/T$, were taken from the literature for Eu(g),[11] N_2(g), and C(s).[12] For EuCN(g), the free-energy functions were calculated by statistical thermodynamic methods for an assumed linear structure and the estimated molecular parameters ($r_{\mathrm{Eu-C}} = 2{\cdot}10$ Å, $r_{\mathrm{C\equiv N}} = 1{\cdot}16$ Å; $\nu_1 = 938$, $\nu_2 = 384$, and $\nu_3 = 2150\ \mathrm{cm}^{-1}$) with an arbitrary 5 entropy unit electronic contribution as 76·21 and 77·49 cal $\mathrm{mol}^{-1}\ \mathrm{K}^{-1}$ for 1600 and 1800 K, respectively. Free-energy functions for the alternative structure EuNC are not expected to differ appreciably from those given above.

The enthalpy change ΔH°_{298}, for reaction (1) was determined as 2·4 ± 7·5 kcal where the error limits include all estimated uncertainties. This value in appropriate combination with the dissociation energy[12] $D^\circ_{298}(N_2) = 226 \pm 2$ kcal mol^{-1} and the heat of formation of C(g),[12] $\Delta H^\circ_{298} = 170{\cdot}9 \pm 0{\cdot}4$ kcal mol^{-1} yields a heat of atomization $\Delta H^\circ_{\mathrm{atm,298}}$ of EuCN(g) as 283 ± 8·0 kcal mol^{-1} or 1184·1 ± 33·5 kJ mol^{-1}. This value is comparable to, but somewhat smaller than, the atomization energies in kcal mol^{-1} determined for other metal or metalloid gaseous cyanides: BCN(301 ± 5),[3] AlCN(297 ± 5),[2] and SiCN[4] (298 ± 6).

Assuming the C–N bond energy is the same as in gaseous CN,[13] $D^\circ_{298}[\mathrm{CN(g)}] = 178$ kcal mol^{-1}; the bond energy D(Eu–CN) is derived as 105 kcal mol^{-1}. This quite high value suggests a sizeable ionic contribution to the bond energy.

In this work, EuCN(g) was assumed to have metal–carbon bonding. The alternative isocyanide structure with nitrogen metal bonding is also possible. The mass spectrometric data did not permit a decision as to which structure should be preferred, but it is interesting that both EuN^+ and EuC^+ fragments were observed with approximately 14 eV appearance potentials. The EuN^+ and EuC^+ ion intensities were observed in the ratio $\mathrm{EuN}^+/\mathrm{EuC}^+ = 0{\cdot}9$ and their ion intensities were *ca.* 0·1% of that of EuCN^+ with 15 eV electrons.

Determination of the true isomeric structure will have to come from optical spectroscopic studies and it may well be, that, as in the case of LiNC[5,6] and BNC,[7] the isocyanide structure is the more stable.

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