$r_{i,j}$ = radius of ion i or j, m
R = gas constant, Nm K^{-1} mol^{-1}
ΔS_m = entropy of fusion, Nm K^{-1} mol^{-1}
T_m = melting point in absolute temperature scale, K
u_o = pair potential at equilibrium distance r_o, Nm mol^{-1} N_A^{-1}
u_s = energy of sublimation per atom or molecule at 0K, Nm mol^{-1} N_A^{-1}
V_o = volume per mole or kg-atom at 0K, m^3 mol^{-1}
Z = number of charges per ion active in electrostatic interaction between adjacent ions, –

Greek Letters

α_s = cubic thermal expansion coefficient, K^{-1}
ρ^* = packing density, –
θ_D = Debye temperature = $\omega_D h/k$, K
ω_D = Debye frequency, s^{-1}

Basic Units

N = Newton
m = meter
K = Kelvin
kg = kilogram
mol = kg mole or atom
s = second

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Thermochemistry of *N,N*-Dimethyl-*p*-nitrosoaniline Complexes

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Enthalpies of formation of crystalline, oxygen-bonded $MnLCl_2$, CoL_2Cl_2, and $NiLCl_2$ (L = *N,N*-dimethyl-*p*-nitrosoaniline) from crystalline anhydrous metal chlorides and ligand have been obtained by reaction calorimetry. The values found at 25° ± 0.001°C are, respectively, −8.85 ± 0.15; −10.12 ± 0.24; −11.71 ± 0.16 kcal/mol. The enthalpies of formation of gaseous complexes cannot be measured, since these decompose without any phase transition when heated, as indicated by thermal analysis.

N,N-dimethyl-*p*-nitrosoaniline complexes with some transition metals were previously investigated; the ligand behaves as a monodentate and coordinates through the nitroso oxygen (*2*). Successively Popp and Ragsdale (*5*) came to the same conclusion; Batten and Johnson do not preclude that, in the Pd-*N,N*-dialkyl-*p*-nitrosoaniline complexes, the ligands coordinate through the nitroso oxygen. Other papers (*1, 2, 5*) deal with the use of *N,N*-dialkyl-*p*-nitrosoanilines as reagents in the spectrophotometric determination of Pt group metals and in the preparation of several complexes having fungicidal properties.

Continuing our studies on nitroso derivative ligands we report now the calorimetric determination of the enthalpies of formation of crystalline complexes $MnLCl_2$, CoL_2Cl_2, and $NiLCl_2$ (L = *N,N*-dimethyl-*p*-nitrosoaniline) from crystalline anhydrous metal chlorides and crystalline ligands.

Experimental

Materials. $MnCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, and *N,N*-dimethyl-*p*-nitrosoaniline (C. Erba RP) were employed. $Mn(C_8H_{10}N_2O)Cl_2$, $Co(C_8H_{10}N_2O)_2Cl_2$, and $Ni(C_8H_{10}N_2O)Cl_2$ were prepared as previously described (*2*). All salts and complexes are completely soluble in 1.00*M* aqueous HCl.

Calorimetric measurements. A calorimetric equipment LKB Model 8700-1 was employed. The measurements were performed at 25° ± 0.001°C.

The calorimetric cell was charged with 100 ml of aqueous 1.00*M* HCl. After equilibration the reaction was started by breaking a thin-walled glass ampul containing 2–3 mmoles of solid reactant; the reaction periods for all experiments were short and the rates of heat evolution were exponential with time.

The expression $(R_i - R_f)/(R_i + R_f)$ was considered proportional to the temperature change.

The mean temperature of the reaction period was calculated to the time for 0.632 of total heat evolution (*6*).

In each experiment two electrical calibrations of the system were performed before and after reaction. Since the heat evolution is linear with time, the mean temperature corresponds to the time for half the temperature rise (*6*). The reproducibility of the electrical equivalent was usually better than ±0.2%. The enthalpies of reaction were calculated by using a Hewlett-Packard 9100 B calculator and an appropriate program.

Thermal analysis. Simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) were performed using a Mettler thermoanalyzer, at different heating rates, in vacuum and dynamic nitrogen atmosphere.

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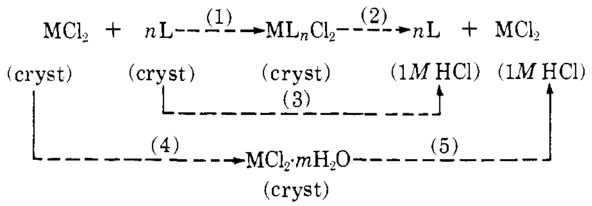
Results

The enthalpies of formation of crystalline complexes from crystalline anhydrous metal chlorides and crystalline ligand have been determined by considering the following cycle:



The enthalpy values are reported in Table I and are expressed in terms of thermochemical kcal/mol; the uncertainty intervals are twice the standard deviation of the mean of five determinations (*3*).

The enthalpy of solution of *N,N*-dimethyl-*p*-nitrosoaniline in an excess of 1.00*M* aqueous HCl does not change if, in this media, twice the stoichiometric amount of metal chloride is dissolved (Table I, Reaction 3), indicating that the ligand does not coordinate. Hence, since the final solutions produced by Reactions 2 and 3 are the same, Reaction 2 may be considered complete. The composition of the final solution is not required for the thermochemistry of the considered complexes. The enthalpy values of Reaction 4 were taken from ref. *4*. No detectable heat change was produced by diluting 100 ml of 1.00*M* aqueous HCl with ten- to fifteenfold the quantity of the hydration water contained in metal salts employed in Reaction 5. The enthalpies of formation of crystalline complexes result from the sum of enthalpies of Reactions 3-5 minus the enthalpy of Reaction 2.

The gas-phase enthalpies of formation of complexes from gaseous ligand and gaseous metal chlorides may give information about metal-oxygen bond strength. For the calculation of these enthalpies it is necessary to know the enthalpies of sublimation of all species involved in the reaction. The enthalpies of sublimation of complexes and ligand are not determinable because, when heated, the complexes decompose without any phase transition and the ligand decomposes after melting, as showed by simultaneous thermogravimetric and differential thermal analysis carried in dynamic N_2 atmosphere or in vacuum. The first step of thermal decomposition is a loss of the nitroso group as was observed in static air atmosphere (*2*).

Table I. Enthalpies of Reaction, Kcal/Mol at 25°C

Compound	Reaction	ΔH
$Mn(C_8H_{10}N_2O)Cl_2$	(1)	−8.85 ± 0.15
$Co(C_8H_{10}N_2O)_2Cl_2$	(1)	−10.12 ± 0.24
$Ni(C_8H_{10}N_2O)Cl_2$	(1)	−11.71 ± 0.16
$Mn(C_8H_{10}N_2O)Cl_2$	(2)	−8.519 ± 0.066
$Co(C_8H_{10}N_2O)_2Cl_2$	(2)	−10.595 ± 0.02
$Ni(C_8H_{10}N_2O)Cl_2$	(2)	−8.102 ± 0.124
$C_8H_{10}N_2O$	(3)	−1.686 ± 0.095[a]
$MnCl_2 \cdot 4H_2O$	(4)	−15.0 ± 0.1[b]
$CoCl_2 \cdot 6H_2O$	(4)	−21.0 ± 0.2[b]
$NiCl_2 \cdot 6H_2O$	(4)	−19.80 ± 0.01[b]
$MnCl_2 \cdot 4H_2O$	(5)	−0.688 ± 0.020
$CoCl_2 \cdot 6H_2O$	(5)	+3.655 ± 0.022
$NiCl_2 \cdot 6H_2O$	(5)	+1.672 ± 0.032

[a] Mean of values obtained dissolving the ligand in 1.00*M* aqueous HCl and in 1.00*M* aqueous HCl containing every time each kind of metal chloride. [b] From ref. *4*.

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