Use of eq 1 and substitution of the relevant G matrix elements give

$$\lambda_{CO} = \mu_{CO}[F_{CO}(\Gamma) - 2xF_{MC,CO}(\Gamma) + x^2F_{MC}(\Gamma)]$$

where the $F(\Gamma)$ are the relevant combinations of force constants (f) leading to a symmetry force constant. This equation is identical with (3).

Registry No. $Cr(^{13}CO)_6$, 25941-09-7; $Cr(C^{18}O)_6$, 25875-16-5; $Cr(^{13}C^{18}O)_6$, 65392-05-4; $Mo(^{13}CO)_6$, 25941-10-0; $Mo(C^{18}O)_6$, 25875-17-6; $W(^{13}CO)_6$, 25941-11-1; $W(C^{18}O)_6$, 25941-12-2; $Ni(^{13}CO)_4$, 17594-06-8; $Ni(C^{18}O)_4$, 17099-52-4; $Fe(^{13}CO)_5$, 16997-09-4; $Fe(C^{18}O)_5$, 37766-06-6; $Co(^{13}CO)_3{}^{14}N^{16}O$, 17594-03-5; $Co(^{13}CO)_3{}^{15}N^{18}O$, 41582-03-0; $Co(C^{18}O)_3{}^{14}N^{16}O$, 41582-01-8; $Co(C^{18}O)_3{}^{15}N^{18}O$, 41582-02-9; $Cr(^{12}C^{16}O)_6$, 13007-92-6; $Cr(^{12}C^{16}O)_5(^{13}C^{16}O)$, 53109-01-6; $Cr(^{12}C^{16}O)_5(^{12}C^{18}O)$, 65392-04-3; $Cr(^{12}C^{16}O)_5(^{13}C^{18}O)$, 65392-03-2; *cis*-$Cr(^{12}C^{16}O)_4(^{13}C^{16}O)_2$, 53109-00-5; *cis*-$Cr(^{12}C^{16}O)_4(^{12}C^{18}O)_2$, 65437-10-7; *cis*-$Cr(^{12}C^{16}O)_4(^{13}C^{18}O)_2$, 65437-09-4; *trans*-$Cr(^{12}C^{16}O)_4(^{13}C^{16}O)_2$, 53108-99-9; *trans*-$Cr(^{12}C^{16}O)_4(^{12}C^{18}O)_2$, 65378-94-1; *trans*-$Cr(^{12}C^{16}O)_4(^{13}C^{18}O)_2$, 65378-93-0; *fac*-$Cr(^{12}C^{16}O)_3(^{13}C^{16}O)_3$, 53108-98-8; *fac*-$Cr(^{12}C^{16}O)_3(^{12}C^{18}O)_3$, 65391-67-5; *fac*-$Cr(^{12}C^{16}O)_3(^{13}C^{18}O)_3$, 65378-92-9; *mer*-$Cr(^{12}C^{16}O)_3(^{13}C^{16}O)_3$, 53109-02-7; *mer*-$Cr(^{12}C^{16}O)_3(^{12}C^{18}O)_3$, 65378-91-8; *mer*-$Cr(^{12}C^{16}O)_3(^{13}C^{18}O)_3$, 65378-90-7; *cis*-$Cr(^{12}C^{16}O)_2(^{13}C^{16}O)_4$, 53109-11-8; *cis*-$Cr(^{12}C^{16}O)_2(^{12}C^{18}O)_4$, 65437-66-3; *cis*-$Cr(^{12}C^{16}O)_2(^{13}C^{18}O)_4$, 65378-89-4; *trans*-$Cr(^{12}C^{16}O)_2(^{13}C^{16}O)_4$, 53042-53-8; *trans*-$Cr(^{12}C^{16}O)_2(^{12}C^{18}O)_4$, 65378-88-3; *trans*-$Cr(^{12}C^{16}O)_2(^{13}C^{18}O)_4$, 65391-68-6; $Cr(^{12}C^{16}O)(^{13}C^{16}O)_5$, 53109-12-9; $Cr(^{12}C^{16}O)(^{12}C^{18}O)_5$, 58167-58-1; $Cr(^{12}C^{16}O)(^{13}C^{18}O)_5$, 65378-99-6; $Co(^{13}CN)_6{}^{3-}$, 32648-15-0; $Co(C^{15}N)_6{}^{3-}$, 32648-16-1; $Ni(^{13}CN)_4{}^{2-}$, 52540-56-4; $Ni(C^{15}N)_4{}^{2-}$, 52540-55-3; $Pd(^{13}CN)_4{}^{2-}$, 52540-58-6; $Pd(C^{15}N)_4{}^{2-}$, 52540-57-5; $Pt(^{13}CN)_4{}^{2-}$, 52540-60-0; $Pt(C^{15}N)_4{}^{2-}$, 52540-59-7; $Au(^{13}CN)_2{}^{-}$, 65378-98-5; $Au(C^{15}N)_2{}^{-}$, 65378-97-4; $Fe(^{13}CN)_6{}^{3-}$, 65378-96-3; $Fe(C^{15}N)_6{}^{3-}$, 65378-95-2.

Supplementary Material Available: Table III, which lists experimental frequencies for $M(^xC^yO)_6$ (M = Cr, Mo, W; x, y = 13, 16; 12, 18; 13, 18), $Ni(^xC^yO)_4$ (x, y = 13, 16; 12, 18), $Fe(^xC^yO)_5$ (x, y = 13, 16; 12, 18), and $Co(^xC^yO)_3{}^zN^pO$ (x, y, z, p = 13, 16, 14, 16; 13, 16, 15, 18; 12, 18, 14, 16; 12, 18, 15, 18) and the calculated frequencies by the method of eq 9; Table IV, which gives experimental frequencies for $Cr(^{12}C^{16}O)_n(^xC^yO)_{6-n}$ (n = 0–6; x, y = 13, 16; 12, 18; 13, 18) and the calculated values using both fixed and floating R values and employing the energy factored force field; Table VI, which gives experimental frequencies for $^{13}C^{14}N$ and $^{12}C^{15}N$ complexes of Co, Ni, Pd, Pt, Au, and Fe and the calculated values by method of eq 9 (13 pages). Ordering information is given on any current masthead page.

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Thermodynamics of Chelation

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The enthalpy and entropy of solution of various species in chelation reactions, obtained from the literature or estimated by standard procedures, are compiled. These are used in Born–Haber-type cycles to calculate enthalpy and entropy of gas-phase reactions. A basic postulate is that the entropy change in the gas phase for $Cd(MeNH_2)_4{}^{2+} \rightarrow Cd(en)_2{}^{2+}$ (where en = 1,2-ethanediamine) is essentially the same as for $CEt_4 \rightarrow$ spiro[4.4]nonane. The analyses show that the enthalpy of solution of ligands generally is not ideal, and this affects the equilibrium as much as or more than the increase in the theoretical ideal translational entropy, 16 eu for two rings. The Cd–N bond strength is in general not the same in the monodentate and chelate structures; this holds especially for the ligands above. The entropies of solution of all species contribute to the $\Delta G°$ of reaction and are generally not ideal. In particular, the $\Delta S°$ of solution of the coordinated ionic species containing hydrocarbon groups (such as $Cd(MeNH_2)_4{}^{2+}$) are more negative, by as much as 34 eu, than $Cd(NH_3)_4{}^{2+}$. Some reactions have $\Delta H° \simeq 0$ and $\Delta S°$ near the calculated value. This is due to the confluence of several large and opposing enthalpy and entropy changes.

It is well known that many chemical processes differ considerably when carried out in the gas phase, as compared to aqueous solution. An example of this is the proton affinity of amines and ammonia.[1] So far the process of chelation has

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Table I. Factors[a] Influencing Solution Stabilities of Complexes

Enthalpy effects	Entropy effects
Variation of bond strength[d] with electronegativities of metal ions and ligand donor atom	Number of chelate rings[b] Size of chelate ring[b,d]
Ligand field effects	Changes of solvation on complex[b,c] formation
Steric and electrostatic[b] repulsion between ligand donor groups in the complex	Arrangement of chelate rings[b] Entropy variations in uncoordinated ligands[d]
Enthalpy effects related to the conformation of the uncoordinated ligand	Effects resulting from differences in configurational entropies of the ligand in complex compounds
Other coulombic forces involved in chelate ring formation	*Entropy of solution of ligands*[d]
Enthalpy of solution of ligands[d]	*Entropy of solution of coordinated metal ions*[d]
Change of bond strength when ligand is changed (same donor and acceptor atom)[d]	

[a] Taken from Martell,[2] plus the addition of the last items in each column. [b] Considered an important contribution by Martell. [c] Not applicable here, because no charged ligands are considered. [d] Considered an important contribution by this author.

been considered only in solution. This makes it difficult to sort out and consider the various solvation effects, and some have even been ignored. This paper computes thermodynamic data in the gas phase for some typical chelation reactions.

The chelate effect is usually described as due to the entropy increase resulting from the fact that more molecules of monodentate ligand are liberated, in solution, than molecules of chelating ligand are used in the reaction. The overall process is more complicated than this, as Martell[2] has pointed out.

This paper quantifies many of the variables which influence the process of chelation—factors which have heretofore been discussed only qualitatively—and in so doing reveals other decisive variables which have been overlooked, or not considered as being important. Martell's summary table is duplicated here, with these additional effects added in italics, as Table I. (The presence of charged ligands is not considered, because the present analysis involves only neutral ligands.)

The net increase in number of molecules in solution during chelation results in an increase in entropy, given by $\Delta S^\circ = XR \ln 55.5 = 8.0x$ eu, where x is the number of chelate rings. (When two chelate rings are formed then the entropy contribution to ΔG° will be −4.8 kcal.) The enthalpy change must also be known in order to compute the standard free energy change and therefore the equilibrium constant. More sophisticated analyses have been made, e.g., by Rasmussen,[3] summarized by Munro,[4] but the assumption is still that of ideal solutions. However, as pointed out previously,[5] solutions of many hydrogen-bonded substances in water are far from ideal.

Many authors assume that the metal–ligand bond strength remains nearly the same if other bonds of the ligated atom do not change. For example, it is assumed that the metal–nitrogen bond strength remains the same when 1,2-ethanediamine, en, is substituted for $MeNH_2$, but changes when it is substituted for NH_3. We will find that the assumption of zero ΔH is not justified, even for the substitution of en for $MeNH_2$.

By use of the Born–Haber-type calculation, and the experimentally determined ΔH for the reaction in solution, a fairly accurate figure can be calculated for the enthalpy change involved in formation of a chelate. Before we make these calculations it is necessary to collect a data base.

Table II. Standard Enthalpy of Solution of Gases

Substance	ΔH_s°, kcal/mol	Substance	ΔH_s°, kcal/mol
$H_2O(g)$	−10.519	$H_2N(CH_2)_3NH_2(g)$	−18.1[b]
$NH_3(g)$	−8.17	$CH_3OH(g)$	−10.82
$CH_3NH_2(g)$	−11.28	$HOCH_2CH_2OH(g)$	−17.3[a]
$H_2NCH_2CH_2NH_2(g)$	−18.5[a]		

[a] Estimated from data for dilute solutions, see text. [b] See Text.

The standard states are as follows: enthalpies of solution are for infinite dilution, entropies of solution are for 1 *m* ideal solutions, entropies of ideal gases are at 1 atm, all at 298 K.

Effects of Solution

The actual reactions occur in aqueous solution (pn = 1,3-propanediamine).

$$Cd(NH_3)_4{}^{2+}(aq) + 2en(aq) \rightarrow Cd(en)_2{}^{2+}(aq) + 4NH_3(aq) \tag{1}$$

$$Cd(MeNH_2)_4{}^{2+}(aq) + 2en(aq) \rightarrow Cd(en)_2{}^{2+}(aq) + 4MeNH_2(aq) \tag{2}$$

$$Cd(NH_3)_4{}^{2+}(aq) + 2pn(aq) \rightarrow Cd(pn)_2{}^{2+}(aq) + 4NH_3(aq) \tag{3}$$

$$Cd(MeNH_2)_4{}^{2+}(aq) + 2pn(aq) \rightarrow Cd(pn)_2{}^{2+}(aq) + 4MeNH_2(aq) \tag{4}$$

$$Cd(H_2O)_4{}^{2+}(aq) + 2eg(aq) \rightarrow Cd(eg)_2{}^{2+}(aq) + 4H_2O(l) \tag{5}$$

Consequently data for enthalpy and entropy of solution are needed, as well as the entropy of the chemical species themselves.

Enthalpy Factors

Enthalpy of Vaporization and Solution. Good and Moore[6] have determined the enthalpy of formation of en(g) to be −4.07 and the enthalpy of vaporization to be 10.99 kcal/mol. The enthalpy of solution of liquid en in 200 mol of water is −7.50 kcal/mol;[7] this should be virtually the same as the value under standard conditions. The standard enthalpy of solution of gaseous en is therefore −18.5 kcal/mol. Corkhill, Goodman, and Tate[8] found the integral heat of solution of the linear polymethylenediols to be almost constant up to about 6 carbons. The hydrogen-bonding diamines will behave similarly, so the enthalpy of solution of 1,3-propanediamine, pn, will be about the same as for en. From the known enthalpy of vaporization from Good and Moore,[6] we compute an enthalpy of solution of gaseous pn of −18.1 kcal/mol.

The trend of values for heat of solution of liquid 1,2-ethanediol (eg) shows that the most dilute solution, 1 mol in 15 mol of water, is approaching an asymptote. By analogy with the correction to standard conditions of CH_3OH, C_2H_5OH, and CH_3COOH, we will assume a standard enthalpy of formation of eg in aqueous solution to be −110.3 kcal/mol. This gives a standard enthalpy of solution of eg(g) of −17.3 kcal/mol. A summary is given in Table II for all ligands.

It is notable that the value for the enthalpy of solution of en and pn is not double that of the monodentate ligands NH_3 and $MeNH_2$. In the chelation reaction 2 mol of chelate ligand are taken out of solution and 4 mol of monodentate ligand go into solution. If the enthalpy change for the chelation reaction is to be zero, then the enthalpy of solution needs to be in the ratio 2:1. The same is true when one compares 1,2-ethanediol and methanol.

Enthalpy Analysis. The enthalpy data are reasonably accurate except perhaps for pn, to within ±0.5 kcal, and therefore the calculations below make possible valid and useful conclusions about enthalpy changes, for the reactions in the gas phase. Although never stated explicitly, it has been assumed heretofore that the enthalpy of solution is the same for large ions of the same charge and similar size. We will use this

Table III. Thermodynamic Data for Chelation Reactions[a]

Reaction	Positive ion	Chelating ligand	ΔH, kcal/mol (this paper)	ΔH_{exptl}, kcal/mol	ΔS_{exptl}, eu	ΔH_j,[b] kcal/mol
1	$Cd(NH_3)_4^{2+}$	en	$\Delta H_a^\circ + 4.3$	−0.6	+10.5	−4.9
2	$Cd(MeNH_2)_4^{2+}$	en	$\Delta H_b^\circ - 8.1$	+0.7	19	8.8
3	$Cd(NH_3)_4^{2+}$	pn	$\Delta H_c^\circ + 3.5$	+2.7	+7.5	−0.8
4	$Cd(MeNH_3)_4^{2+}$	pn	$\Delta H_d^\circ - 8.9$	+4	+16	12.9
5	$Cd(H_2O)_4^{2+}$	eg	$\Delta H_e^\circ - 7.5$			
6	$Cu(NH_3)_4^{2+}$	en	$\Delta H_f^\circ + 4.3$	−3.5	+24.2	−7.8
7	$Cu(MeNH_2)_4^{2+}$	en	$\Delta H_g^\circ - 8.1$			
8	$Cu(NH_3)_4^{2+}$	pn	$\Delta H_h^\circ + 3.5$	−0.4	+21	−3.9
9	$Cu(MeNH_2)_4^{2+}$	pn	$\Delta H_i^\circ - 8.9$			

[a] From ref 13. The experimental values are not at zero ionic strength and differ from the standard values by about 0.5 kcal or 1.0 eu. [b] In the first horizontal row ΔH_j is the value for ΔH_a°, and so on down the columns; probable error is about ±1 kcal.

Table IV. Calculated Entropy Data for Chelation Reactions

Reaction	Positive ion	Chelator	ΔS_r°	$\Delta S_{\text{ex}}^\circ$	$\Delta S_{\text{chel}}^\circ$	$\Delta S_{\text{lig}}^\circ$	$\Delta S_{\text{theo}}^\circ$
1	$Cd(NH_3)_4^{2+}$	en	+21.6	27.9	50	22	16
2	$Cd(MeNH_2)_4^{2+}$	en	−15.5	76.6	61	34	16
3	$Cd(NH_3)_4^{2+}$	pn	+23.2	3.9	27	10	16
4	$Cd(MeNH_2)_4^{2+}$	pn	−14.1	51.9	39	21	16
5	$Cu(H_2O)_4^{2+}$	eg	+21.6	25.7	47	−22	−16[a]

[a] The water is liberated at mole fraction 1, rather than 1 *m*.

assumption for the time being.

For reaction 1

$$\begin{tikzcd}
Cd(NH_3)_4^{2+}(g) + & 2en(g) \arrow[r, "\Delta H_a^\circ"] & Cd(en)_2^{2+}(g) \arrow[d, "-\Delta H_s^\circ"] + & 4\,NH_3(g) \arrow[d, "4(-8.17)"] \\
Cd(NH_3)_4^{2+}(aq) \arrow[u, "\Delta H_s^\circ"] + & 2en(aq) \arrow[u, "2(18.5)"'] \arrow[r, "\Delta H_1^\circ"] & Cd(en)_2^{2+}(aq) + & 4NH_3(aq)
\end{tikzcd}$$

$$\Delta H_1^\circ = \Delta H_s^\circ + 37.0 + \Delta H_a^\circ - \Delta H_s^\circ - 32.68 = \Delta H_a^\circ + 4.3 \text{ kcal}$$

The term ΔH_a° represents the difference in Cd–N bond strengths in $Cd(NH_3)_4^{2+}$ and $Cd(en)_2^{2+}$, four bonds total. A similar analysis for the other reactions yields the enthalpies of reaction in aqueous medium.

$$\Delta H_2^\circ = \Delta H_b^\circ - 8.1 \text{ kcal}$$

$$\Delta H_3^\circ = \Delta H_c^\circ + 3.5 \text{ kcal}$$

$$\Delta H_4^\circ = \Delta H_d^\circ - 8.9 \text{ kcal}$$

$$\Delta H_5^\circ = \Delta H_e^\circ - 7.5 \text{ kcal}$$

(For the corresponding Cu(II) coordination compounds the enthalpy changes will be the same, except that the Cu–N bond strengths will differ.)

These calculated enthalpies for the chelation reactions can now be compared with the experimental values, Table III. It can be seen that the reaction of $Cd(MeNH_2)_4^{2+}$ is actually endothermic by 0.7 kcal: $\Delta H_b^\circ - 8.1 = 0.7$. Each bond in $Cd(en)_2^{2+}$ is therefore *weaker* by about 2 kcal/mol, as compared with the $MeNH_2$ complex. Likewise, each Cd–N bond in $Cd(pn)_2^{2+}$ is weaker by about 3 kcal/mol than the corresponding $MeNH_2$ complex. In the Cu(II) complex, each bond is *stronger* by about 2 kcal/mol when en is substituted for NH_3. In any event, the enthalpy change due to change in ligands is usually as large as, or larger than, the "chelate effect" of 4.8 kcal. It follows also from Table III that there is no regularity, and it is impossible to predict the relative strength of metal–ligand bonds.

All these computations have assumed that the enthalpy of solution of the various ions is the same. If this assumption is false, then another variable is added to increase the complexity of the chelation process. When the entropy changes are considered later the suggestion will be that the enthalpies of solution of the various ions are probably not the same.

Table V. Standard Molar Entropy of Solution of Hydrogen-Bonding Gases in Water, 298 K, Unit Molality

NH_3	−19.4	H_2O	−20.4[a]
CH_3NH_2	−28.6	CH_3OH	−25.5
$C_2H_5NH_2$	−32[c]	C_2H_5OH	−32.0
		C_3H_7OH	−37.0[b]

[a] At hypothetical molality of 1. [b] From Lucas.[11] [c] Estimated from ref 11, using average temperature coefficients.

Entropy Factors

The Standard Entropy of Gaseous Diamines. The above evaluation showed the enthalpy data to be sufficiently available and accurate to permit reliable calculations. On the other hand deductions about entropy changes are virtually impossible because of the paucity[9] of experimental data. This difficulty is surmounted by the estimation procedures developed here, which permit valid qualitative comparisons between similar reactions.

The entropy of gaseous en has not been determined; however, it can be accurately estimated. Stull, Westrum, and Sinke[7] have pointed out that the rotational symmetry of the bent OH group and the pyramidal NH_2 group are the same, $\sigma_r = 1$. Therefore no rotational corrections for entropy need to be considered when one is substituted for the other.

Consider the following group substitutions, with the experimentally determined entropy changes noted (all substances gases). The entropy change for substitution of CH_3 by NH_2

$$CH_3\text{-}CH_2CH_2\text{-}CH_3 \xrightarrow{3.51} CH_3\text{-}CH_2CH_2\text{-}OH \xrightarrow{-0.30} HO\text{-}CH_2CH_2\text{-}OH$$

$$CH_3\text{-}CH_2CH_2\text{-}CH_3 \xrightarrow{3.36} CH_3\text{-}CH_2CH_2\text{-}NH_2 \xrightarrow{(\ )} H_2N\text{-}CH_2CH_2\text{-}NH_2$$

is inherently 0.15 eu less than the corresponding substitution by OH. The last process should therefore have ΔS° of 0.45 eu. The measured entropy of $PrNH_2$ is 77.48, so that S° of en(g) is 77.0.

Also consider the following parallel processes, again all gases and with the same symmetry changes. From the known entropy of $EtNH_2$, 68.08 eu, the S° of en(g) can be calculated.

$$CH_3CH_3 \xrightarrow{12.69} CH_3CH_2\text{-}OH \xrightarrow{9.79} HO\text{-}CH_2CH_2\text{-}OH$$

$$CH_3CH_3 \xrightarrow{13.23} CH_3CH_2\text{-}NH_2 \xrightarrow{(\ )} H_2N\text{-}CH_2CH_2\text{-}NH_2$$

$S_{en}{}^{\circ} = (13.23 - 12.69) + 9.79 + 68.08 = 78.4$ eu

We can consider other gas-phase processes with similar symmetries.

$CH_3CH_2\text{-}OH \xrightarrow{+0.54} CH_3CH_2\text{-}NH_2$
$CH_3(CH_2)_2\text{-}OH \xrightarrow{-0.15} CH_3(CH_2)_2\text{-}NH_2$
$CH_3(CH_2)_3\text{-}OH \xrightarrow{-0.04} CH_3(CH_2)_3\text{-}NH_2$

Substitution of NH_2 for OH results in virtually no entropy change, so the entropy of en will be the same as for eg, i.e., 77.3 eu.

Finally, consider the parallel processes

$2HO\text{-}CH_3 \xrightarrow{-37.25} HO\text{-}CH_2CH_2\text{-}OH$
$2H_2N\text{-}CH_3 \xrightarrow{(\,)} H_2N\text{-}CH_2CH_2\text{-}NH_2$

From the known entropy of $MeNH_2$, 57.98 eu, we compute the $S°$ of en to be $2(57.98) - 37.25 = 78.7$ eu. Averaging these four values gives 78.0 ± 0.5 as the entropy of gaseous en.

When estimating the entropy of even more flexible molecules such as 1,3-propanediamine, pn, the symmetry considerations become more complex and diffuse and therefore less determining. For example, consider the $\Delta S°$ for insertion of a CH_2 group into various fairly large compounds of differing symmetry.

$CH_3\text{-}CH_2CH_2\text{-}CH_3 \xrightarrow{9.28} CH_3\text{-}CH_2CH_2CH_2\text{-}CH_3$
$CH_3\text{-}CH_2CH_2\text{-}OH \xrightarrow{9.17} CH_3\text{-}CH_2CH_2CH_2\text{-}OH$
$CH_3\text{-}CH_2CH_2\text{-}Cl \xrightarrow{9.31} CH_3\text{-}CH_2CH_2CH_2\text{-}Cl$
$CH_3\text{-}CH_2CH_2\text{-}NH_2 \xrightarrow{9.28} CH_3\text{-}CH_2CH_2CH_2\text{-}NH_2$
$Cl\text{-}CH_2CH_2\text{-}Cl \xrightarrow{14.1} Cl\text{-}CH_2CH_2CH_2\text{-}Cl$
$H_2N\text{-}CH_2CH_2\text{-}NH_2 \xrightarrow{(\,)} H_2N\text{-}CH_2CH_2CH_2\text{-}NH_2$

Considering the somewhat similar symmetry changes in the last two reactions, and the average entropy changes in the first four, we conclude that $\Delta S°$ for the last process is slightly higher than 9.2, but not as high as 14.1. Let us use 11 for the last reaction. If the $S°$ of en is 78.0, then the S° for pn is about 89 eu. Consider also the following:

$CH_3CH_3 \xrightarrow{13.23} CH_3CH_2\text{-}NH_2$
$CH_3CH_2CH_3 \xrightarrow{12.97} CH_3CH_2CH_2\text{-}NH_2$
$CH_3(CH_2)_3CH_3 \xrightarrow{12.64} CH_3(CH_2)_3\text{-}NH_2$
$CH_3CH_2CH_2\text{-}NH_2 \xrightarrow{(\,)} H_2N\text{-}(CH_2)_3\text{-}NH_2$

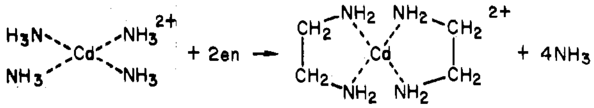
The last conversion should have a $\Delta S°$ of about 13 eu, which when added to 77.48, the $S°$ of *n*-$PrNH_2$, gives 90.5 eu as the entropy of pn.

Finally, the following can be used for calculation, in which an NH_2 substitutes for a CH_3 group.

$CH_3CH_2CH_3 \xrightarrow{3.57} CH_3CH_2\text{-}NH_2$
$CH_3(CH_2)_2CH_3 \xrightarrow{3.36} CH_3(CH_2)_2\text{-}NH_2$
$CH_3(CH_2)_3CH_3 \xrightarrow{3.36} CH_3(CH_2)_3\text{-}NH_2$
$CH_3(CH_2)_3\text{-}NH_2 \xrightarrow{(\,)} H_2N\text{-}(CH_2)_3\text{-}NH_2$

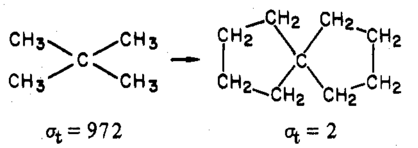
The last should have a $\Delta S°$ of 3.4 eu, which when added to the $S°$ of *n*-$BuNH_2$, 86.76 eu, gives 90.2 eu as the standard entropy of gaseous pn. The average of these three values gives 90 ± 1.5 as the $S°$ of pn. An error of this magnitude is of little significance (vide infra).

Entropy of Ring Formation. Formation of the chelate ring itself represents a change in entropy, and it is necessary to determine in some way the amount of the change. One way is to find data for structures which are as close as possible to those in chelate formation and to use these data as a good approximation. For example, consider reaction, a, which is the gas-phase equivalent of reaction 1,



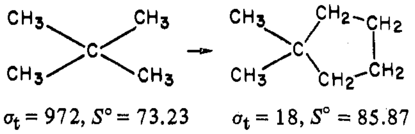
(a)

This will have the same configurational changes as the following, where σ_t is the total symmetry number.



(b)

The entropy of spiro[4.4]nonane has not been measured but can be accurately estimated by standard procedures.[7] Consider the partial process, following the method outlined in ref 7.



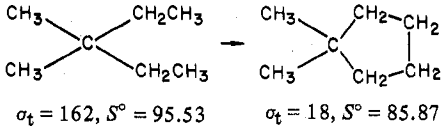
$\Delta S°$ for the formation of the cyclopentane ring from the two methyl groups is

$$\Delta S° = 85.87 + R \ln 18 - (73.23 + R \ln 972) = +4.71$$

Going back to process (b), the estimated $S°$ for spiro[4.4]nonane is then

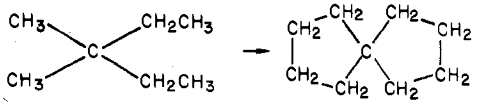
$$S° = 73.23 + R \ln 972 + 2(4.71) - R \ln 2 = 94.94 \text{ eu}$$

We can confirm this via another analogous process.



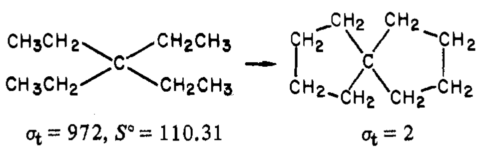
$$\Delta S° = 85.87 + R \ln 18 - (95.53 + R \ln 162) = -14.03$$

Using the following we can again compute the entropy of spiro[4.4]nonane.



$$S° = 95.53 + R \ln 162 + 4.71 - 14.03 - R \ln 2 = 94.94$$

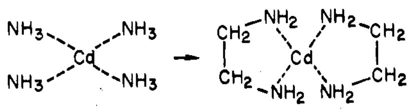
Finally we can use the following and obtain the entropy.



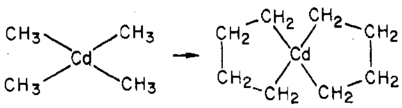
$$S° = 110.31 + R \ln 972 - 2(14.03) - R \ln 2 = 94.54$$

The average of these three gives 94.8 ± 0.2 as the standard entropy of spiro[4.4]nonane.

The process in reaction (b) is not quite the same as reaction (a), because NH_3 becomes NH_2 in the ring in (a) and CH_3 becomes CH_2 in the ring in (b). It is possible to show that this has virtually no effect on entropy changes. Geiseler[10] has proposed an accurate empirical equation for entropies of polyatomic molecules. If we use that equation to compare the *hypothetical* process

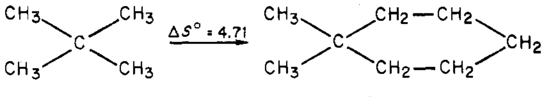


with the process



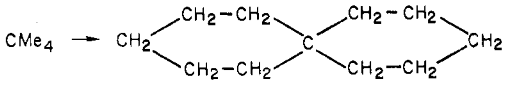
we find that the *change* in entropy in both reactions differs by only 0.3 eu. Therefore the change in entropy for reaction (a) will be the same as the change for (b), within 1 eu. The entropy change for the cyclization part of reaction (a) is therefore 94.8 − 73.23 = 21.6 eu.

1,3-Diaminopropane forms a six-membered ring, whose analogous structure is spiro[5.5]undecane. We therefore need the entropy of that compound. This can be obtained by a similar analysis



$\sigma_t = 972$, $S° = 73.23$ $\sigma_t = 9$, $S° = 87.24$

Therefore the following gives the entropy of the desired compound.



$$S°(\text{product}) = 73.23 + R \ln 972 + 2(4.71) - R \ln 1 = 96.32$$

Using similar processes with CMe_2Et_2 and CEt_4, we obtain 96.32 and 95.94 eu, giving an average of 96.2 ± 0.2 eu for the $S°$ of gaseous spiro[5.5]undecane.

The $\Delta S°$ for the cyclization part of reactions 1–4 is computed to be 21.6, −15.5, 23.2, and −13.9 eu, respectively, Table IV. Reaction 5 should be nearly the same as reaction 1, i.e., +22 eu.

Admittedly, the two situations are not precisely analogous. The central attachment is to Cd, not C, and the bond strengths are not the same. However, the actual configurational changes are external to this central structure, which remains unchanged. (The comparison will not apply as well to a planar Cu(II) chelate, models show slightly more strain in the ring than for the tetrahedral configuration. In any event, any errors in comparing the model to the original will be the same in reactions 1 and 3, and therefore the calculations will be quite valid for comparisons of these reactions.)

Entropy Change of Chelation. We are now in position to compute the overall entropy change upon chelation, when all substances are gases. Given the standard entropy of $NH_3(g)$ of 45.97 eu, we can compute $\Delta S°$ for reaction a.

$$\Delta S_a° = 4(45.97) - 2(78.0) + 21.6 = 50 \text{ eu}$$

By the same process, given the entropy of CH_3NH_2 of 58.15, we compute for reaction b

$$\Delta S_b° = 4(58.15) - 2(78.0) - 15.5 = 61 \text{ eu}$$

In other words, in the gas-phase reaction there is an entropy change due to ring formation, $\Delta S_r°$, and an entropy change due to the replacement of four molecules of monodentate ligand by two molecules of chelating ligand, $\Delta S_{cx}°$. The data of all five reactions are tabulated in Table IV. (As pointed out earlier, the differences in $\Delta S°$ for reactions of en and pn are so large that an error of 1 or 2 eu in the absolute entropy of pn is not important.)

Entropy of Vaporization and Solution. Lucas[11] has discovered that at 4 °C the entropy of solution of gases in water is almost entirely a function of molecular size. This still holds true at 25 °C but now each functional group substituted on carbon has its own curve. This suggests that entropy of solution for each homologous series should be a function of molecular weight. The data in Table V for solutes which are hydrogen bonding indicate that, for small molecules, each added CH_2 group decreases the entropy of solution in water by about 6 eu. Using the entropy of solution of H_2O_2 and N_2H_4, and decreasing the entropy of solution of each by 12, gives −33 and −36 eu for the entropy of solution of eg and en, respectively. (These *relative* values are probably quite good, because the amines have a slightly more negative entropy of solution than alcohols. Whether or not the entropy of solution of, say, en is exact has little consequence when one makes qualitative comparisons of chelation reactions which involve en replacing other ligands.) By the same logic the $\Delta S_s°$ of pn is −42 eu.

Powell and Latimer[12] have proposed an empirical equation for the partial molal entropy of ions whose mass is M.

$$\bar{S}° = {}^3/_2 R \ln M + 37 - 270Z/R_e{}^2$$

The first term is the same as that which appears in the statistical–mechanical equation for the entropy of gaseous ions.

$$\bar{S}° = {}^3/_2 R \ln M + {}^5/_2 R \ln T - R \ln p + R \ln \rho_0$$

(T is temperature, p is pressure, and ρ_0 the contribution of unpaired electrons.) When the ion dissolves in water the entropy change is a function of only charge and radius. Therefore the entropy of solution of the various coordinated ionic species will vary with the size, with the smaller being more negative. The effect of size will not be great for such very large ions. For example, for Rb^+ and Cs^+ the values are −9.6 and −8.8, respectively. In fact, as Lucas has shown, an increase in size of solute tends to give a more negative entropy of solution. It may very well be that the species $Cd(MeNH_2)_4{}^{2+}$ will have a more negative $\Delta S_s°$ than $Cd(NH_3)_4{}^{2+}$, just because of its larger size.

The nature of the coordinated group must also be considered. It appears that, as the hydrogen-bonding capability of the solute is decreased, its entropy of solution is more negative. This is illustrated by the following sequence of molecules of about the same size: HOOH, −21.2; CH_3OH, −25.5; C_2H_6, −26.55. The ion $Cd(MeNH_2)_4{}^{2+}$ and the chelated structures have hydrocarbon groupings around their periphery. In contrast, $Cd(NH_3)_4{}^{2+}$ has a hydrogen-bonding "exterior". We conclude that the $\Delta S_s°$ of $Cd(MeNH_2)_4{}^{2+}$ should be considerably more negative than $Cd(NH_3)_4{}^{2+}$.

Entropy Analysis. We can now combine all the contributions of entropy to the process of chelation in a Born–Haber type analysis. For reaction 1 the result is as follows

$$\begin{tikzcd}
\mathrm{Cd(NH_3)_4{}^{2+}(g)} + & \mathrm{2en(g)} \arrow[r, "27.9", "+21.6"'] & \mathrm{Cd(en)_2{}^{2+}(g)} + \arrow[d, "\Delta S_{en}°"] & \mathrm{4NH_3(g)} \arrow[d, "4(-19.4)"] \\
\mathrm{Cd(NH_3)_4{}^{2+}(aq)} + \arrow[u, "-\Delta S_{am}°"] & \mathrm{2en(aq)} \arrow[u, "2(36)"'] \arrow[r, "\Delta S_1°"] & \mathrm{Cd(en)_2{}^{2+}(aq)} + & \mathrm{4NH_3(aq)}
\end{tikzcd}$$

$$\Delta S_1° = -\Delta S_{am}° + 72 + 49.5 + \Delta S_{en}° - 77.6 = -\Delta S_{am}° + \Delta S_{en}° + 44 \text{ eu}$$

A similar analysis for the others yields the following.

$$\Delta S_2° = -\Delta S_{me}° + \Delta S_{en}° + 18.5 \text{ eu}$$

$$\Delta S_3° = -\Delta S_{am}° + \Delta S_{pn}° + 33 \text{ eu}$$

$$\Delta S_4° = -\Delta S_{me}° + \Delta S_{pn}° + 7 \text{ eu}$$

$$\Delta S_5° = -\Delta S_{aq}° + \Delta S_{eg}° + 0 \text{ eu}$$

The entropy analysis up to now did not evaluate the entropy of solution of the ions. This can be done—at least approximately—from the data in the literature[7,13] for various reactions, Table III. These values are not all at standard conditions, yet they are probably within ±2 eu, so can be used to obtain rather good results. In comparing reactions 1 and 2 we see that $-\Delta S_{am}° + \Delta S_{en}° + 44 = 10.5$ and $\Delta S_{me}° + \Delta S_{en}° + 18.5 = 19$. Combining these yields

$$\Delta S_{me}° - \Delta S_{am}° = -34$$

Similarly, combining reactions 3 and 4 yields

$$\Delta S_{me}° - \Delta S_{am}° = -34.5$$

Considering the accuracy of the experimental data and the various estimations, the close agreement is probably fortuitous. Yet it is abundantly clear that the larger ion, with the "hydrocarbon exterior" has a much more negative entropy of solution. This is expected, both from size considerations and from the effect of the hydrophobic groups.

The large difference in entropy of solution (up to 34 eu) is, at first, very surprising. The question soon arose whether other systems exist for which accurate data were available. Examples were easily found:

$$\begin{tikzcd}
Cd(H_2O)_4{}^{2+}(g) + & 4NH_3(g) \arrow[r, "\Delta S_{ex}°", "-3.46\ eu"'] & Cd(NH_3)_4{}^{2+}(g) + \arrow[d, "+\Delta S_{am}°"'] & 4H_2O(g) \arrow[d, "4(-28.39)"] \\
Cd(H_2O)_4{}^{2+}(aq) + \arrow[u, "-\Delta S_{aq}°"] & 4NH_3(aq) \arrow[u, "4(19.4)"'] \arrow[r, "\Delta S°", "-8.5\ eu"'] & Cd(NH_3)_4{}^{2+}(aq) + & 4H_2O(l)
\end{tikzcd}$$

$$-8.5 = -\Delta S_{aq}° + 77.6 + \Delta S_{ex}° - 3.46 + \Delta S_{am}° - 113.56$$

This yields

$$\Delta S_{aq}° - \Delta S_{am}° = -31 + \Delta S_{ex}°$$

$\Delta S_{ex}°$ is the entropy change for exchanging NH_3 for H_2O. Our knowledge of the similarity in the entropy of alcohols and amines indicates this will be quite low; the equation of Geiseler[10] proves it to be almost zero. Therefore the entropies of solution of $Cd(H_2O)_4{}^{2+}$ and $Cd(NH_3)_4{}^{2+}$ differ by approximately 31 eu. For the corresponding Zn^{2+} and Cu^{2+} compounds the differences are 32 and 22 eu.

The relative entropies of solution of other coordinated ions can be calculated. For example, using reactions 1 and 3, and 2 and 4, we find the following relations: $-\Delta S_{am}° + \Delta S_{en}° + 44 = 10.5$, $\Delta S_{me}° + \Delta S_{en}° + 18.5 = 19$, $-\Delta S_{am}° + \Delta S_{pn}° + 33 = 7.5$, and $\Delta S_{me}° + \Delta S_{pn}° + 7 = 16$. Combining these yields

$$\Delta S_{pn}° - \Delta S_{en}° = 8.0\ \text{eu}$$

$$\Delta S_{pn}° - \Delta S_{en}° = 8.5\ \text{eu}$$

Both of these species have hydrophobic exteriors and both have about the same geometry and size, so the entropy of solution should be fairly close, as calculated. Considering the high accuracy of the various entropy estimations, the differences, although small, are probably real.

A similar calculation shows that the entropy of solution of $Cd(MeNH_2)_4{}^{2+}$ is close to that of the chelates, as one would expect.

The effects can be sorted out in convenient form, Table IV, to make them more easily visualized. We have already designated as $\Delta S_r°$ the entropy change involved when $Ml_4{}^{2+}$ is changed into $ML_2{}^{2+}$, where l and L represent the monodentate and chelate ligands, respectively. Likewise $\Delta S_{lig}°$ will represent the overall change $2L(aq) \rightarrow 2L(g) \rightarrow 4l(g) \rightarrow 4l(aq)$, i.e., two chelate ligands are replaced in solution by four monodentate ligands. If the solutions are ideal, and the reactions satisfy the "chelate effect", then this latter will be +16 eu, designated as $\Delta S_{chel}°$. (In the case where the ligand is water, it is evolved at mole fraction one, rather than molality one. The value of 16 eu must be corrected by an amount $-4R \ln 55.5$, or −32 eu.) It can easily be seen that when the coordinating atom is nitrogen the $\Delta S_{lig}°$ can differ significantly from the ideal case. When four $MeNH_2$ are replaced by two en the entropy change is very much more positive. When the coordinating atom is oxygen, reaction 5, the actual $\Delta S_{lig}°$ is more negative than the ideal case.

Evidence from Other Reactions. We have become accustomed to thinking of chelated substances as being more stable (in solution) than the corresponding monodentate compound. Let us examine some additional evidence to test this assumption.

Ethylene glycol chelates of such ions as Cu^{2+}, Ni^{2+}, Co^{2+}, and Cd^{2+}, have been prepared. However, in order to prepare them the corresponding metal salt is dissolved warm in essentially pure glycol and then cooled. There is little tendency for chelation. This is verified by the fact that the reaction has a rather large positive $\Delta G°$.

$$Cu(H_2O)_4{}^{2+}(aq) + 2eg(aq) \rightarrow Cu(eg)_2{}^{2+}(aq) + 4H_2O(l)$$

The evidence for this is that when eg is added to a saturated aqueous solution of $Cu(IO_3)_2$ it does not become deeper in color. (The spectrum of the chelated Cu(II) is virtually identical with the aqueous solution, and the molar absorptivity is higher,[14] so any increased Cu(II) in solution will be readily apparent.) The same negative result is obtained when ethylene glycol is added to a saturated aqueous solution of $ZnCrO_4$; there is no deepening of the yellow color, indicating no special stability of the eg chelate of Zn^{2+}. The reason for this lack of reaction is probably in part related to the fact that H_2O is liberated at mole fraction 1 and therefore has more negative entropy.

If the reaction were carried out in nonaqueous solution this unfavorable entropy change would be removed, and a more normal "chelate effect" should cause a reaction. However, addition of eg to saturated solutions of $Cu(IO_3)_2$ in DMF, CH_3OH, or Me_2CO (containing a small amount of water) does not result in a deeper color. Shu[15] studied Ni^{2+} solutions in $MeOH-H_2O$ mixtures. The "visible spectral data...indicate that the solvated species $Ni(H_2O)_6{}^{2+}$, $Ni(H_2O)_5(MeOH)^{2+}$, and $Ni(H_2O)_4(MeOH)_2{}^{2+}$ are the predominant species in the solvent region 0–98% methanol...". Therefore in a 90% MeOH solution the major part of the Ni(II) will be coordinated with at least four water molecules, and the "chelate effect" should operate for replacement of the H_2O molecules. Presumably the same should hold true for Cu(II). As noted above, addition of ethylene glycol to the Cu(II) and Zn(II) solutions did not result in the formation of a chelate, even when the entropy change is favorable in the nonaqueous solutions. In these reactions the enthalpy change is apparently very unfavorable and cancels out the expected "chelate effect".

Summary

It can be seen from the forgoing analysis that there are many contributions to the chelate effect. These push the reaction in different directions and are of such different magnitudes that it is probably a coincidence if the standard enthalpy change for a chelation reaction turns out to be near zero and the entropy change is positive and near the theoretical value of +16 eu (for two rings). This is especially emphasized when one considers the resistance which ethylene glycol shows to formation of chelate complexes with metal ions.

Undoubtedly there is an increase in translational entropy when molecules are released in solution in the chelation process ($T\Delta S = -4.8$ kcal). But the evidence presented here shows that the solutions are far from ideal, and therefore the actual entropy of solution of all species is needed in order to discuss the direction of the reaction. Most especially, the entropy of solution of the monodentate and chelated cations can differ by as much as 34 eu. It is largely coincidental if the entropy change for a chelation reaction is close to the ideal value. The same is true for the enthalpies of solution of the ligands. These can easily deviate from ideal by more than 4.8 kcal. (The enthalpies of solution of the coordinated cations probably differ also, but we are not in a position to estimate the amount.)

Registry No. $Cd(NH_3)_4^{2+}$, 18373-05-2; $Cd(MeNH_2)_4^{2+}$, 65516-97-4; $Cd(H_2O)_4^{2+}$, 15906-02-2; $Cu(NH_3)_4^{2+}$, 16828-95-8; $Cu(MeNH_2)_4^{2+}$, 30809-52-0; en, 107-15-3; pn, 78-90-0; eg, 107-21-1.

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(9) The scarcity of data is indeed unfortunate and is a real handicap to our understanding of this as well as other processes. For example, 1,2-ethanediamine, which may be considered one of the most important compounds in inorganic chemistry, has not had its entropy measured nor has the standard enthalpy and entropy of solution been measured. A concerted effort needs to be made to acquire basic thermodynamic data for common substances.

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Ionic Conductivity in $Na_5YSi_4O_{12}$-Type Silicates

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A new series of Na ion conductors of the type $Na_5MSi_4O_{12}$, where M = Fe, In, Sc, Y, and the rare earths Lu–Sm, has been prepared by hydrothermal and solid-state reactions. Na ion conductivities, measured with Na electrodes at $\sim 10^3$ Hz, are proportional to the size of M^{3+} and range from 2×10^{-3} $(\Omega\ cm)^{-1}$ for $Na_5ScSi_4O_{12}$ to 3×10^{-1} $(\Omega\ cm)^{-1}$ at 300 °C for $Na_5SmSi_4O_{12}$. This behavior is consistent with a structure consisting of $Si_{12}O_{36}$ rings stacked to form columns held apart by MO_6 octahedra. Immobile Na atoms are situated within the rings and mobile Na atoms between the columns. The size of the channels is dictated by the size of the MO_6 octahedra. $Na_5GdSi_4O_{12}$ and $Na_{5-x}Gd_{1-x}Zr_xSi_4O_{12}$, which can be sintered to 95% theoretical density and appear to be resistant to attack by Na, are probably the most practical materials for use as a solid electrolyte.

Introduction

The discovery of ionic conductivity in Na-β-Al_2O_3 has led to an intensive search for other conductive compositions.[1-7] The only oxide to show comparable Na ion conductivity has been $Na_3Zr_2PSi_2O_{12}$[8] (for $Na_3Zr_2PSi_2O_{12}$ $\sigma(300\ °C) \simeq 2 \times 10^{-1}$ $(\Omega\ cm)^{-1}$ and $E_a = 6.7$ kcal/mol[8] whereas for β-Al_2O_3 $\sigma(300\ °C) \simeq 2 \times 10^{-1}$ $(\Omega\ cm)^{-1}$ and $E_a = 3.8$ kcal/mol[9]).

$Na_5FeSi_4O_{12}$ was first discovered by Bowen, Schairer, and Willems[10] in their investigation of the Na_2O–Fe_2O_3–SiO_2 system. They prepared birefringent, hexagonal-prismatic crystals, but no x-ray data were reported. Hydrothermal synthesis of isotypic $Na_5YSi_4O_{12}$, $Na_5ScSi_4O_{12}$, and $Na_5ErSi_4O_{12}$ and the crystal structure of $Na_5YSi_4O_{12}$ was reported by Maksimov et al.[11-13] Because they could locate only 48/90 of the Na atoms in $Na_5YSi_4O_{12}$, we suspected that the remaining Na atoms might be mobile, making this compound a good Na ion conductor. Subsequent conductivity measurements showed $\sigma(200\ °C) = 4 \times 10^{-2}$ $(\Omega\ cm)^{-1}$ and $E_a = 7.1$ kcal/mol for $Na_5YSi_4O_{12}$. Further investigation showed that the Na rare earth silicates prepared by Maksimov hydrothermally could be made by solid-state reaction and that compounds with rare earth ions having even larger ionic radii than that of Y could be prepared.

In this paper we report ionic conductivities comparable to that of β-Al_2O_3 and $Na_3Zr_2PSi_2O_{12}$ in a series of compositions $Na_5MSi_4O_{12}$ where M = Fe, In, Sc, Y, and the rare earths Lu → Sm.

Experimental Section

Starting materials were reagent grade Na_2CO_3, $NaHCO_3$, SiO_2, GeO_2, ZrO_2, HfO_2, and rare earth oxides. In a typical preparation stoichiometric compositions were intimately mixed in an agate ball mill, heated in air to ~900–1050 °C in Pt crucibles for 16 h, quenched, ball milled again, reheated, and quenched.

Crystals of $Na_5YSi_4O_{12}$ were grown hydrothermally. A $^3/_8$ in. diameter gold tube, 6 in. long and sealed at one end, was charged with 4.26 g of $Na_2SiO_3{\cdot}9H_2O$, 1.20 g of NaOH pellets, and 0.11 g of Y_2O_3. After sealing, the tube was heated to 900 °C under 3000 atm of external hydrostatic pressure, cooled over 90 h to 400 °C, and then quenched. Removal of the flux with hot water left a residue of 0.36 g of 3–4 mm euhedral crystals of $Na_5YSi_4O_{12}$. Only a small range of Na/Si ratios is possible—if this ratio is too small, $Na_3YSi_3O_9$ is stable; if too large, $Na_3YSi_2O_7$ and $NaYSiO_4$ form.

X-ray patterns were obtained on a Hägg–Guinier camera using Cu Kα_1 radiation and a KCl internal standard (a = 6.2931 Å). Table I gives powder diffraction data for $Na_5FeSi_4O_{12}$ and $Na_5YSi_4O_{12}$; Table II gives cell dimensions of some of the silicates and germanates prepared in this study. A low-temperature x-ray diffractometer pattern of $Na_5YSi_4O_{12}$ (NYS) was taken at 9 K; no superstructure lines were observed.

DTA scans were made with a du Pont thermal analyzer. High-temperature x-ray patterns were obtained with a Nonius Guinier camera. The results of the DTA investigations are summarized in Table III. The Fe, Sc, In, Lu, and Er compositions show small unexplained exothermic peaks at about 500–600 °C. Most compositions show small unexplained endotherms at ~800 °C. $Na_5FeSi_4O_{12}$ melts at 815 °C, whereas most of the other compositions melt between 1100 and 1250 °C, probably incongruently. Quenching experiments on $Na_5YSi_4O_{12}$ (NYS) showed NYS at 1150 °C, NYS + $Na_3YSi_2O_7$ at 1200 °C, and $Na_3YSi_2O_7$ at 1250 °C. Similar experiments on $Na_5GdSi_4O_{12}$ (NGS) showed NGS at 1060 °C and NGS + a $Ca_3Al_2O_6$-like phase at 1080 °C.

High-temperature Guinier photographs were obtained to explain some of the DTA thermal events. The high-temperature run for $Na_5ScSi_4O_{12}$ was carried out under vacuum. At 500 °C, lines appeared from a phase similar to $Ca_3Al_2O_6$ (C$_3$A). Formation of this phase may be responsible for the 600 °C exotherm. From 500 to 815 °C, $Na_5ScSi_4O_{12}$ and the C$_3$A phase coexist. At 850 °C, both these phases disappear and a new unidentified phase with strong lines at 4.45, 4.15,

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