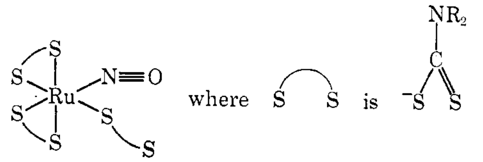
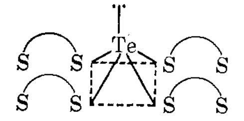
have observed CN and CS bands in the respective ranges of 1465–1490 and 960–985 cm^{-1} for sodium dialkyldithiocarbamates (*viz.*, dimethyl,[3,4] diethyl,[4] dipropyl,[4] and dibutyl[4]). Mann[5] observed a CN doublet at 1420 and 1482 cm^{-1} for sodium pentamethylenedithiocarbamate.

The CN vibration in tellurium tetrakis(tetramethylenedithiocarbamate) occurs as a strong band at 1440 cm^{-1} and as a broad band in the range 1452–1510 cm^{-1} with a peak at 1468 cm^{-1} followed by a succession of shoulders at 1475 and 1490 cm^{-1}. Moore and Rice[6] reported a very strong doublet at 1504 and 1515 cm^{-1} for dioxomolybdenum(VI) bis(tetramethylenedithiocarbamate).

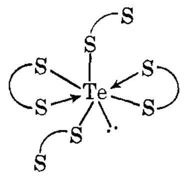
Domenicano, *et al.*,[7] observed for $Ru(NO)(S_2CNR_2)_3$, where R = CH_3 or C_2H_5, the CN vibration in the 1460–1470-cm^{-1} region, which is near the literature values for the sodium salts of dialkyldithiocarbamic acids (*vide supra*). However, the literature values[3–6] for the CN band for transition metal dialkyldithiocarbamates are in the 1490–1550-cm^{-1} region. They[7] concluded on the basis of the ir study and a priorly obtained X-ray result that one of the dialkyldithiocarbamates is unidentate and the other two are bidentate, *i.e.*



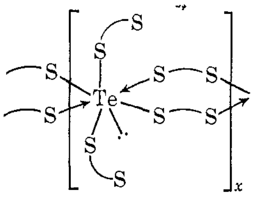
Our observation of relatively low-energy CN bands, *viz.*, 1468, 1475 (sh), and 1490 (sh) cm^{-1}, for tellurium tetrakis(tetramethylenedithiocarbamate) similarly suggests unidentate ligands. Plausible structures may be a square pyramid (A), a distorted octahedron (B), or a polymeric distorted octahedron (C). Molecular weight determinations would be helpful were it



A



B



C

not for the rather low solubility of the complex in the usual solvents. It is interesting that Chatt, *et al.*,[3] also observed low-energy CN vibrations for $((C_2H_5)_2NCS_2)_3M$ at 1490 (M = P), 1492 (M = As), and 1488 (M = Bi) cm^{-1}. These compounds were considered by them to possess possibly a distorted octahedral or a pyramidal stereochemistry. It is conceivable to us that such structures would contain a stereochemically active lone-electron pair on the phosphorus, arsenic, and bismuth atoms and unidentate ligands for the pyramidal stereochemistry and the appropriate combination of bridging and unidentate ligands for the distorted octahedral stereochemistry.

The CS vibration in tellurium tetrakis(tetramethylenedithiocarbamate) appears as a weak band at 1000 cm^{-1}. This is an increase of 8 and 20 cm^{-1} from the respective 992 and 980 cm^{-1} doublet which appears in the spectrum of APDC. Similar increases have been observed by Moore and Larson[4] for dialkyldithiocarbamates of Mo(VI), Mo(V), and Mo(II).

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(3) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Suomen Kemistilehti*, **B29**, 75 (1956).

(4) F. W. Moore and M. L. Larson, *Inorg. Chem.*, **6**, 998 (1967).

(5) J. Mann, *Trans. Inst. Rubber Ind.*, **27**, 232 (1951).

(6) F. W. Moore and R. E. Rice, *Inorg. Chem*, **7**, 2510 (1968).

(7) A. Domenicano, A. Vaciago, L. Zambonelli, P. L. Loader, and L. M. Venanzi, *Chem. Comm.*, 476 (1966).

Correspondence

The Linear Correlation of ΔH and ΔS of Complexation

Sir:

For a number of years there have been some very strong implications made[1,2] that a linear correlation of ΔH and ΔS for a series of analogous metal complexes is corroborative evidence for a common structure throughout the series. We wish to point out the incorrect reasoning of this interpretation, although the correct logic should have been obvious at a much earlier time, in order to prevent any later misguidance in the interpretation of these approximately linear relationships. It is not possible to interpret the free energy changes in metal complex equilibria as being diagnostic of the type of ion association without at the same time considering the accompanying enthalpy ΔH and entropy ΔS of complexation. In dismissing this idea we shall show that the linear correlation is no more informative than the free energy[3] in this regard.

From the Gibbs free energy (GFE) equation, a linear correlation of ΔH and ΔS for a series of n related reactions (for example the lanthanide ions with a common ligand) is an obvious result if the ΔG values for the reactions are zero or constant and the slope of the line is, by definition, $T\,^\circ\mathrm{K}/1000$, *i.e.*, $\Delta H_n = \Delta G_n + 0.298\Delta S_n$, for a temperature of 25°. In the real situation however there very often is variation in ΔG_n within the series. For the series of n related reactions, therefore,

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(1) J. F. Duncan and D. L. Kepert in "The Structure of Electrolytic Solutions," W. J. Hamer, Ed., John Wiley & Sons, Inc., New York, N. Y., 1959, pp 380–400.

(2) R. E. Mesmer and C. F. Baes, Jr., *J. Phys. Chem.*, **72**, 4721 (1968).

(3) G. H. Nancollas, "Interactions in Electrolyte Solutions," Elsevier Publishing Co., New York, N. Y., 1966, p 94 ff.

TABLE I

System of 1:1 complexes	Equation of line	Ionic strength, M	$\Delta(\Delta G)$, kcal/mol	$\Delta(\Delta H)$, kcal/mol	$\Delta(\Delta S)$, cal/mol deg	Max. abs dev in ΔH_{calcd}, kcal/mol	Av dev in ΔH_{calcd}, kcal/mol
Lanthanide fluoride[a]	$\Delta H_{\text{LS}} = -2.83 + 0.257\Delta S$	1.0	1.29	5.56	22.9	0.43	0.22
	$\Delta H_n = -4.50 + 0.298\Delta S_n$					0.87	0.36
	$\Delta H_{\text{MB}} = -2.38 + 0.246\Delta S$					0.50	0.19
Lanthanide EDTA[b]	$\Delta H_{\text{LS}} = -12.84 + 0.149\Delta S$	0.1	5.39	3.03	19.5	1.46	0.58
	$\Delta H_n = -23.47 + 0.298\Delta S_n$					2.75	1.45
Lanthanide diglycolate[b]	$\Delta H_{\text{LS}} = -7.18 + 0.292\Delta S$	0.1	0.98	2.78	8.7	0.60	0.18
	$\Delta H_n = -7.33 + 0.298\Delta S_n$					0.61	0.18
Lanthanide dipicolinate[b]	$\Delta H_{\text{LS}} = -11.42 + 0.286\Delta S$	0.5	1.46	2.84	8.4	0.91	0.24
	$\Delta H_n = -11.72 + 0.298\Delta S_n$					0.90	0.28
Alkaline earth formate[c]	$\Delta H_{\text{LS}} = -1.87 + 0.289\Delta S$	$\rightarrow 0$	0.07	2.87	10.3	0.07	0.06
	$\Delta H_n = -1.91 + 0.298\Delta S_n$					0.11	0.07
Alkaline earth acetate[c]	$\Delta H_{\text{LS}} = -1.63 + 0.296\Delta S$	$\rightarrow 0$	0.12	3.23	11.2	0.07	0.06
	$\Delta H_n = -1.63 + 0.298\Delta S_n$					0.07	0.06
Lanthanide sulfate[d]	$\Delta H_{\text{LS}} = -4.01 + 0.267\Delta S$	$\rightarrow 0$	0.26	1.19	4.4	0.11	0.03
	$\Delta H_n = -4.92 + 0.298\Delta S_n$					0.18	0.05
Lanthanide sulfate[e]	$\Delta H_{\text{LS}} = -4.41 + 0.438\Delta S$	2.0	0.39	0.69	2.0	0.25	0.10
	$\Delta H_n = -1.69 + 0.298\Delta S_n$					0.22	0.07
Lanthanide acetate[f]	$\Delta H_{\text{LS}} = -3.68 + 0.378\Delta S$	2.0	0.63	2.05	5.3	0.34	0.13
	$\Delta H_n = -2.38 + 0.298\Delta S_n$					0.40	0.17
Lanthanide propionate[f]	$\Delta H_{\text{LS}} = -3.45 + 0.360\Delta S$	2.0	0.66	2.42	6.2	0.41	0.10
	$\Delta H_n = -2.35 + 0.298\Delta S_n$					0.36	0.16
Sulfate[g] of Mg^{2+}, Ca^{2+}, Mn^{2+},	$\Delta H_{\text{LS}} = -2.88 + 0.280\Delta S$	$\rightarrow 0$	0.18	2.90	10.0	0.12	0.07
Co^{2+}, Ni^{2+}, or Zn^{2+}	$\Delta H_n = -3.18 + 0.298\Delta S_n$					0.18	0.06

[a] See ref 2. [b] See ref 3, p 191. [c] G. H. Nancollas, *J. Chem. Soc.*, 744 (1956). [d] D. P. Fay and N. Purdie, submitted for publication. [e] R. G. DeCarvalho and G. R. Choppin, *J. Inorg. Nucl. Chem.*, **29**, 737 (1967). [f] I. Grenthe, *Acta Chem. Scand.*, **18**, 283 (1964). [g] See ref 3, p 180.

in which this variation exists, one can construct, for each member, a line of slope T°K/1000 through the individual ΔH_n and ΔS_n values obtained by experiment and the corresponding intercept at $\Delta S_n = 0$ where $\Delta G_n = \Delta H_n$. When the ΔG_n values are zero or constant, the intercepts would be coincident and the various ΔH_n–ΔS_n values would fall on a single line.

This is precisely the situation observed by Mesmer and Baes[2] for the information of the LnF^{2+} complexes[4] in that the variation in ΔG_n for the series is small. The fact that there is a wide spread in the ΔH_n values across the series is of secondary importance. The equation for the line was calculated by Mesmer and Baes to be $\Delta H = -2.38 + 0.246\Delta S$, and the difference between the intercept ΔG at $\Delta S = 0$, obtained by a long extrapolation, as would be required in this case, and the average ΔG for the series, -4.50 ± 0.17 kcal/mol, readily compensates for the deviation from the slope of 0.298°K. From the remarks made above on the restrictions on ΔG, the linear correlation is not surprising.

In fact, from Table I, in which a comparison is made between the equations for the GFE or ΔH_n line and the least-squares ΔH_{LS} line, it is immediately apparent that the relationship is not limited to a few cases. The degree of agreement between the slope and intercept of each least-squares line and those of the ΔH_n lines is an indication of the relative variance in the individual ΔG_n values. For the lanthanide monofluoride complexes these lines give only a slightly worse fit than the Mesmer–Baes line, ΔH_{MB}.

In every system in Table I, with the exception of the lanthanide EDTA complexes, the average deviation in the calculated ΔH_n is probably still within the error limits on the experimentally determined heats and a good comparison is observed. For the EDTA complexes[5] $\Delta(\Delta G) = 5.4$ kcal/mol and the scatter in the ΔH–ΔS data is such that they cannot be fitted to a single straight line of any slope within the experimental error limits in ΔH for all members.

The alkaline earth acetates[6] and formates[6] are the two examples which best illustrate the validity of the added constraint of a virtually constant ΔG. In both systems $\Delta(\Delta G)$ is approximately 0.1 kcal/mol and *no* extrapolation to $\Delta S = 0$ is necessary, since values of ΔH are both positive and negative. The least-squares and ΔH_n lines give a nearly perfect fit to the experimental data and the intercepts are equal to the average ΔG values.

Since the linear correlation is contingent upon certain restrictions on ΔG and since ΔG tells us nothing about the structures of the complexes in solution, then conversely the linear dependence of ΔH–ΔS should be independent of the structural properties of the complexes. Therefore we see that inner-sphere complexes, *e.g.*, $LnSO_4^+$ and LnF^{2+}, as well as ion pairs,[1] comply with the relationship. Furthermore, the case of magnesium and calcium acetates is most striking in that although ΔG is constant, the signs of ΔH are opposite, a certain indication of dissimilar structures. The reason for the correlation is more fundamental than one of structure.

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(4) J. B. Walker and G. R. Choppin, Advances in Chemistry Series, No. 71, American Chemical Society, Washington, D. C., 1967, p 127.

(5) Reference 3, p 191.

(6) G. H. Nancollas, *J. Chem. Soc.*, 744 (1956).

(7) We wish to thank the National Aeronautics and Space Administration for a fellowship to D. P. F.