

THERMOGRAVIMETRIC STUDY OF SOME DIVALENT TRANSITION METAL CHELATES OF SEVERAL AMINO ACIDS*

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Thermogravimetric studies of divalent metal chelates of eight common amino acids have revealed that no relationship exists between thermal stability orders of the chelates and hydrolytic stability orders, infrared band shifts or force constants. An attempt is made to relate thermal stability order to relative heats of formation and stereochemistry.

Amino acid chelates have been studied extensively during the last two decades. A variety of instrumental techniques have been used. Their thermal stabilities, however, have not been studied in any detail.

Most thermal stability work has been directed at the amino acids themselves, determining decomposition temperatures [1—3] and products of decomposition [4, 5]. Differential thermal analysis curves for copper glycinate mono- and dihydrate [6], cadmium glycinate monohydrate [7] and copper alaninate monohydrate [8] have been published, along with thermogravimetric curves for copper complexes of glycine and α -alanine [9] and cobalt(III) complexes of glycine, α -alanine and leucine [10]. It has been noted [2] that aliphatic amino acids are more stable when they have short, linear alkyl side chains rather than long branched chains. Other than this, however, no attempt has been made to correlate thermal stabilities with other structural or chemical properties.

Since a number of amino acid chelates were still easily available to us, it was decided to study the thermal properties of the compounds. Accordingly, thermogravimetric data for divalent transition metal chelates of glycine, DL- α -alanine, DL- β -alanine, DL-serine, DL- α -amino-*n*-butyric acid, DL- α -aminoisobutyric acid, DL-norvaline and DL-leucine were obtained. The resulting thermal data might then be compared with other available information such as infrared data and hydrolytic stability constants of amino acid chelates and thermal stabilities of other complexes of these transition metals.

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Experimental

Samples were obtained from either Fr. J. L. Walter, C.S.C., University of Notre Dame, or Sr. Mary Marina Kennelly, Mundelein College. Each sample was dried at 110°, for one-half hour before analyzing on the thermobalance. However, in some cases where an initial TG curve indicated an appreciable amount of absorbed water, the material was vacuum dried for one hour at 100° for the second determination. Syntheses of these compounds have been reported elsewhere [11—16].

The construction and method of operation of the manually-operated thermobalance used in this investigation have been previously described [17]. All TG curves were taken in an atmosphere of dry nitrogen obtained by passing nitrogen through the furnace before each run for one hour. A simple gas flow gauge was used to maintain a constant slow flow of nitrogen through the thermobalance during each run. The overall heating rate was nearly linear, approximately 4—5° per minute. The instrument was checked using calcium oxalate monohydrate.

Because of variations in the amounts of samples available, sample sizes varied from 8.3 to 52.9 mg. A 1-ml platinum crucible supported by a loop of nichrome wire was used as the sample container. After each run the platinum crucible was cleaned by removing the metal oxide powder, briefly boiling concentrated nitric-sulfuric acid cleaning solution in the crucible, rinsing, heating the crucible to red heat in a bunsen burner flame for a few seconds, then allowing to cool in a desiccator. This procedure effected the best reproducibility of the calibration curve for the empty crucible. For TG curves of the cadmium-amino acid complexes, the platinum crucible was lined with copper (by electroplating) to protect it from attack by CdO.

Results and discussion

Thermogravimetric curves for metal chelates of glycine, α -alanine, β -alanine, α -amino-*n*-butyric acid, α -amino-isobutyric acid, serine, norvaline, and leucine are presented in Figures 1—8, respectively. The decomposition temperatures, observed weight losses and theoretical weight losses, assuming the chelates decompose to metal oxides, are listed in Table 1. The observed weight loss was obtained by reweighing the crucible plus contents after each run and obtaining the difference between this value and the weight of crucible plus contents before the run. In several cases the amino acid chelates were hydrated, sometimes with stoichiometric quantities of water, e.g. $\text{Ni}(\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{COOH})_2 \cdot 2 \text{H}_2\text{O}$. The decomposition temperatures in Table 1 are of the anhydrous amino acid chelates. Dehydration ranges, the temperature ranges over which water is lost from the chelates, are listed as footnotes.

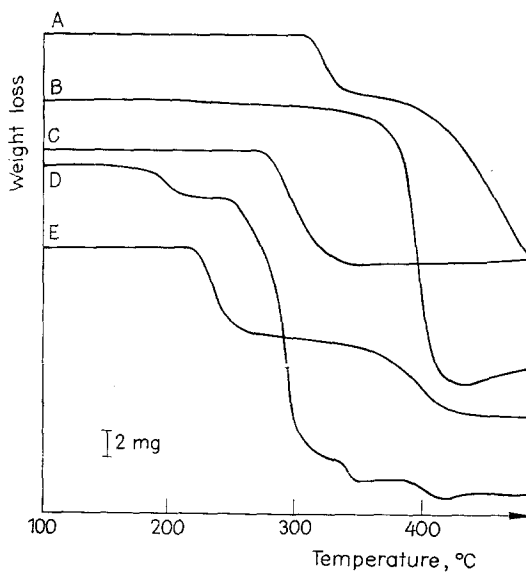


Fig. 1. TG curves of bis-(glycino)-metal chelates. A. Zinc dihydrate, B. Nickel, C. Platinum, D. Copper monohydrate, E. Palladium

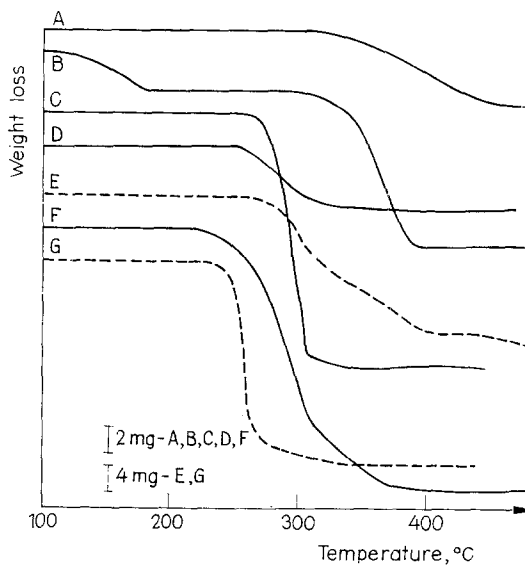


Fig. 2. TG curves of bis(DL- α -alanino)-metal chelates. A. Zinc, B. Nickel hydrate, C. Copper, D. Platinum, E. Cadmium, F. Cobalt, G. Palladium

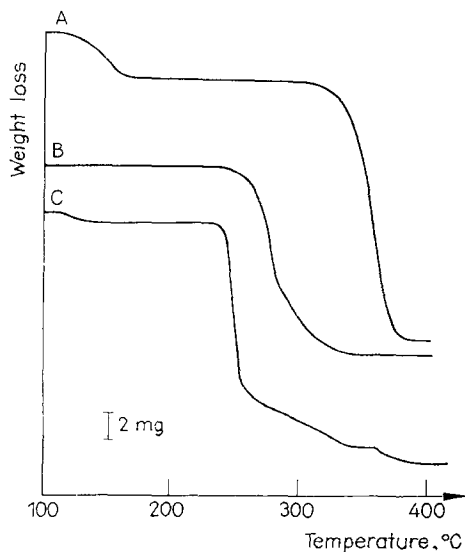


Fig. 3. TG curves of bis-(β -alanino)-metal chelates. A. Nickel dihydrate, B. Platinum, C. Copper

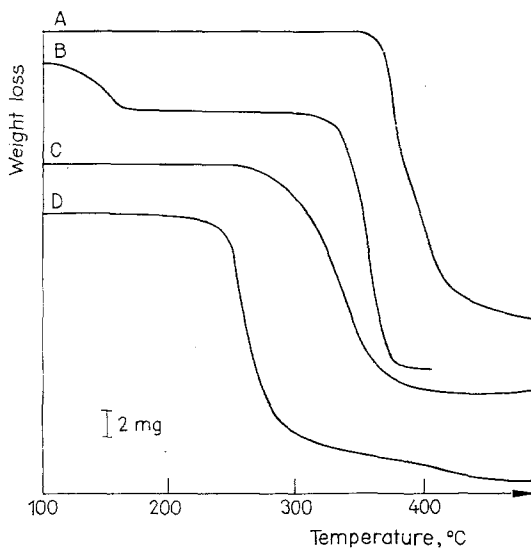


Fig. 4. TG curves of bis-(α -amino-*n*-butyro)-metal chelates. A. Zinc, B. Nickel dihydrate, C. Platinum, D. Copper

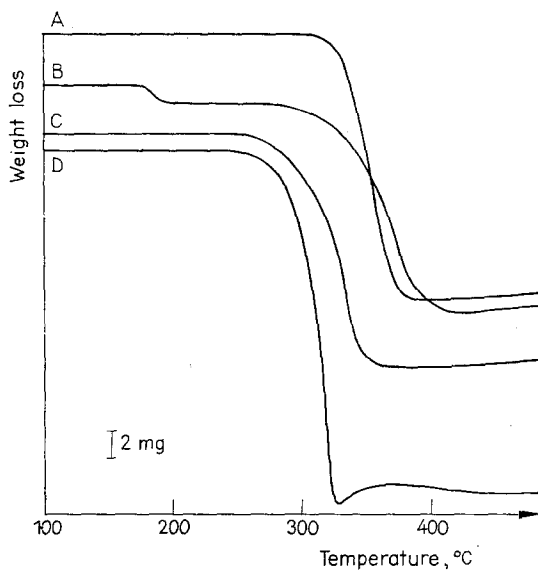


Fig. 5. TG curves of bis-(α -amino-isobutyro)-metal chelates. A. Nickel, B. Platinum monohydrate, C. Palladium, D. Copper

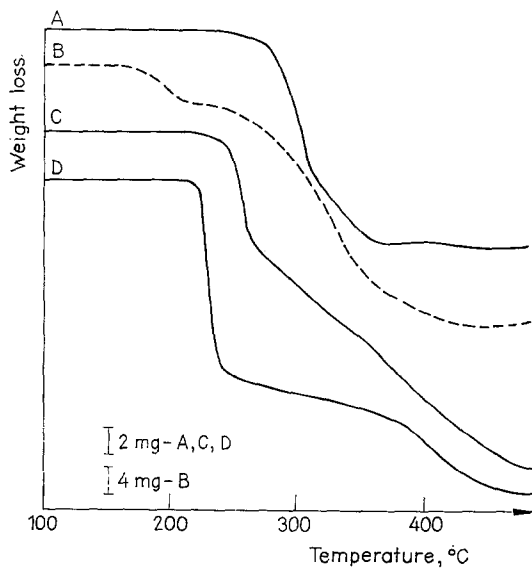


Fig. 6. TG curves of bis-(serino)-metal chelates. A. Platinum, B. Nickel dihydrate, C. Zinc, D. Copper

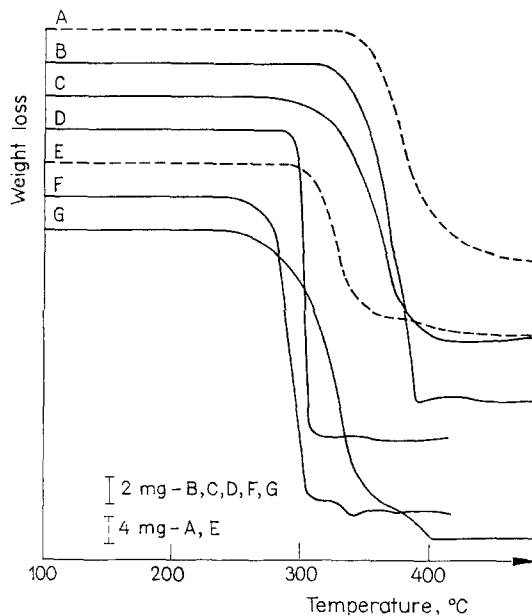


Fig. 7. TG curves of bis-(DL-norvalino)-metal chelates. A. Zinc, B. Nickel, C. Platinum, D. Palladium, E. Cadmium, F. Copper, G. Cobalt

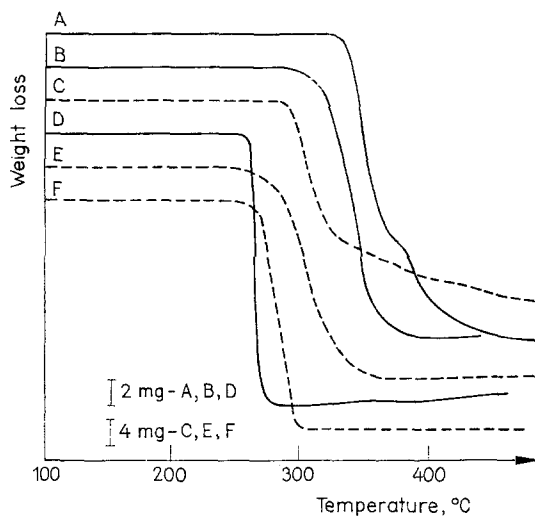


Fig. 8. TG curves of bis-(DL-leucino)-metal chelates. A. Zinc, B. Nickel, C. Cadmium, D. Palladium, E. Cobalt, F. Copper

Table 1
Decomposition temperatures and weight losses of metal chelates

Ligand	Metal	Sample wt., mg	Decomp. temp., °C	Observed wt. loss, mg	Theoretical wt. loss ^a , mg
Glycine	Ni	31.5	332	20.4	20.1
	Cu ^b	39.8	247	25.8	26.0
	Zn ^c	34.1	382	22.4	23.0
	Pd	23.6	218	13.3	12.3
	Pt	21.8	269	9.7	8.4
α -Alanine	Co	30.4	228	19.9	20.0
	Ni ^d	21.2	279	15.4	15.6
	Cu	29.5	262	19.5	19.7
	Zn	8.3	~300	5.2	5.5
	Cd	52.0	~250	26.9	28.8
	Pd	51.0	228	29.9	29.0
	Pt	10.7	255	4.4	4.6
β -Alanine	Ni ^e	31.7	298	22.9	23.0
	Cu	35.1	234	23.6	23.6
	Pt	36.3	242	14.8	15.7
α -Amino- <i>n</i> -butyric acid	Ni ^f	31.7	302	23.2	23.8
	Cu	32.3	218	21.3	22.7
	Zn	32.6	355	22.5	22.8
	Pt	32.8	247	17.4	16.4
α -Amino-isobutyric acid	Ni	28.9	310	20.6	20.7
	Cu	37.6	254	25.8	26.4
	Pt ^g	32.5	278	17.3	16.1
	Pd	27.9	265	18.0	16.9
Serine	Ni ^h	52.1	232	39.3	39.2
	Cu	33.2	220	23.4	23.5
	Zn	36.3	221	25.5	25.5
	Pt	31.0	240	16.3	14.8
Norvaline	Co	34.6	247	24.5	25.1
	Ni	37.2	319	26.7	27.6
	Cu	34.6	253	25.1	25.3
	Zn	52.9	331	37.2	38.4
	Cd	45.1	258	26.0	28.3
	Pd	37.0	278	23.7	23.6
	Pt	35.7	282	19.1	18.1
Leucine	Co	44.4	243	32.8	33.3
	Ni	30.2	292	21.7	23.1
	Cu	47.6	238	35.7	35.9
	Zn	33.4	329	23.8	25.0
	Cd	50.2	280	32.0	32.9
	Pd	31.4	258	20.8	20.9

a) For conversion of chelate to metal oxide; b) Dehydration range 160°–220°; c) Dehydration range 280°–360°; d) Dehydration range 80°–160°; e) Dehydration range 160°–215°; f) Dehydration range 115°–180°; g) Dehydration range 175°–205°; h) Dehydration range 140°–215°

The decomposition temperatures of copper chelates of glycine and α -alanine in nitrogen are higher (247 vs. 228 and 262 vs. > 200) than those run in air by Tomita [6] and Martin and Paris [9]. This is probably due to the oxygen of the air initiating degradation of the organic ligands at temperatures below their true thermal stabilities.

Several observations can be drawn from the data in Table 1. Glycine and α -amino-isobutyric acid form two of the most thermally stable chelate systems. Chelates of α -alanine are more thermally stable than those of β -alanine. Serine forms the least stable chelate system studied in this work. The presence of a hydroxy group on the pendant chain results in hydrolytic destabilization of chelates of this amino acid relative to chelates of α -alanine [18], and this is also observed in the thermal stability of the metal chelates.

Norvaline chelates are more stable than leucine chelates, in line with the previously observed [2] greater stability of straight chain pendant groups over branched chain groups. Table 2 gives thermal stability orders for each chelate system. The thermal stability order Ni > Cu > Zn is maintained for each amino acid chelate system observed in this work. For the systems in which cobalt has been studied, it always appears among the least thermally stable chelates.

Table 2

Thermal stability orders for each chelate system

Glycine	Zn > Ni > Pt > Cu > Pd
α -Alanine	Zn > Ni > Cu > Pt > Cd > Co ~ Pd
β -Alanine	Ni > Pt > Cu
α -NH ₂ - <i>n</i> -butyric acid	Zn > Ni > Pt > Cu
α -NH ₂ - <i>n</i> -isobutyric acid	Ni > Pt > Pd > Cu
Serine	Pt > Ni > Zn > Cu
Norvaline	Zn > Ni > Pt > Pd > Cd > Cu > Co
Leucine	Zn > Ni > Cd > Pd > Co > Cu

Comparison of the observed thermal stability orders with reported stability orders based on other phenomena shows little similarity. The Irving-Williams hydrolytic stability order, with copper forming the most stable chelate, is in part exactly opposed to the thermal stability order, where copper forms the least stable chelate in the given metal chelate series of Ni, Cu and Zn. That cobalt forms rather unstable chelates is true in both series. Comparison of hydrolytic and thermal stability orders of complexes of various ligands with a given metal also shows that there is no correlation between the two stability orders.

Contrasting the order of decreasing metal-nitrogen bond strengths, obtained from infrared analysis [12-15], with thermal stability orders reveals a similar situation. Comparing data in Tables 2 and 3, the order Pt > Pd is consistent in both series, but in the infrared series the platinum-nitrogen bond strength is greater than all others measured, with palladium the second in the series. In the

thermal stability orders these metals usually fall toward the middle of any given series, with palladium chelates much less stable than platinum chelates. The metal-nitrogen bond strengths of the rest of the metals roughly follow the Irving-Williams hydrolytic stability order, previously discussed.

Table 3

Relative order of metal-nitrogen bond stretching force constants for several amino acid-divalent transition metal chelates

Ligand	Decreasing order of force constants
Glycine [12]	Pt > Pd > Cu > Ni
α -Alanine [13]	Pt > Pd > Cu > Zn > Cd > Ni \approx Co
Leucine [14]	Pt > Pd > Cu > Zn > Cd > Ni \approx Co
Norvaline [15]	Pt > Pd > Cu > Zn > Cd > Ni \approx Co

Similar observations can be drawn from the orders of the carboxylate antisymmetric and symmetric stretching frequencies for metal complexes of the amino acid chelates of glycine [12], α -alanine [13], leucine [14] and norvaline [15]. The COO⁻ antisymmetric stretching frequencies decrease, and the COO⁻ symmetric stretching frequencies increase in the order Pt, Pd, Cu, Zn, Ni, Co and Cd. Again, this order bears little relationship to the thermal stability order for norvaline and leucine chelates of these metals.

It is evident that the mechanism of thermal degradation of these amino acid chelates differs from that of hydrolytic instability, and that the metal-nitrogen and metal-carboxylate bond strengths have no obvious influence on the thermal stabilities of these amino acid chelates. Prime causes for the observed stability orders must be sought elsewhere.

It has been shown by Drinkard et al. [19] that increasing the number of methylene groups in the coordination polymer backbone decreased the thermal stability of the compounds. This argument does not seem to hold in the case of monomeric amino acid chelates since norvaline chelates are more stable than α -alanine chelates and in some cases even more stable than glycinate.

One source of thermal instability is the availability of other valence states to which the central metal ion may possibly be oxidized and by so doing catalyze the decomposition of the chelate. Copper, palladium and cobalt may behave in this manner. On the other hand, zinc has no other oxidation state than Zn(II), and Ni(III) is unlikely to arise under conditions present in thermobalance. Hence, chelates of these metals evidence greater thermal stability than chelates of copper or palladium.

In Table 4 the thermal stabilities of the amino acid chelates are empirically arranged in two groups: complexes of zinc, nickel, cadmium and cobalt in Group 1 and complexes of platinum, palladium and copper in Group 2. The ligands have

been arranged to give the best fit for decreasing thermal stability, both horizontally and vertically in each group. Thermal stabilities generally decrease going down the table and also decrease in the order Zn > Ni > Cd > Co and Pt > Pd > Cu with surprisingly few exceptions.

Table 4
Decomposition temperatures of amino acid chelates, °C

Group 1					Group 2			
Ligand	Zn	Ni	Cd	Co	Ligand	Pt	Pd	Cu
Gly.	382	332	—	—	Norv.	282	278	253
Norv.	331	319	258	247	Isobut.	278	265	254
Isobut.	—	310	—	—	Gly.	269	218	247
<i>n</i> -But.	355	302	—	—	Leu.	—	258	238
Leu.	329	292	280	243	α -Ala.	255	228	262
α -Ala.	300	279	250	228	<i>n</i> -But.	247	—	218
β -Ala.	—	298	—	—	β -Ala.	242	—	234
Ser.	221	232	—	—	Ser.	240	—	220

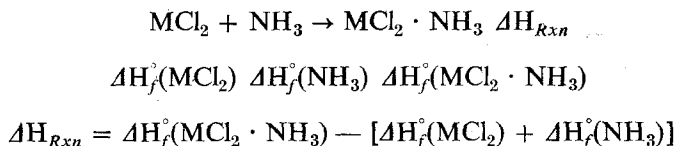
It is interesting to note that the metals in Group 2 generally occur in a square planar configuration, forming only weak bonds in the axial directions of an octahedron. Group 1 metals, on the other hand, usually prefer octahedral or tetrahedral environments. It should also be observed that, while the data is equally distributed between Groups 1 and 2, only one Group 2 complex (platinum norvalinate) decomposes above 280°, while twelve complexes in Group 1 decompose at/or above 300°. On the other hand, ten of the Group 2 complexes decompose below 250°, while only five of the Group 1 complexes decompose below 250°. Clearly complexes containing metals which prefer a square planar environment are less thermally stable, on the whole, than complexes containing metals which prefer octahedral or tetrahedral coordination.

One reason for the greater thermal stability of Group 1 metals over those in Group 2 may be the principle of polybonding, that is, linking each atom by as many bonds as possible. Metals in an octahedral or tetrahedral environment are fully coordinated, while the weak axial bonds of the Group 2 square planar metals are sites which may offer favorable routes to decomposition.

Another argument demonstrating a difference in thermal stability between the amino acid complexes of Group 1 and Group 2 metals can be obtained from thermochemical heats of reaction in the following manner. The ligand environment around each metal in the amino acid complexes is M(O,N). If the standard heat of formation of a given metal-oxygen species could be obtained for each metal and added to the standard heat of formation of the metal-nitrogen coordination bond for each metal (keeping conditions the same for all the metals), a qualitative estimate of the relative heat of formation of the amino acid chelate environment

for each metal could be obtained. While this would not be an accurate measure of the heat of formation of an individual amino acid chelate, a relative ordering of the metals in their affinity for the amino acid environment might be possible.

Heats of formation for the metal-ammine coordination complexes were derived from the following equations:



For copper, palladium and platinum, only data on the diammine complexes was available so the heat of reaction was halved to obtain a number average value for coordination of one ammine group to the metal dichloride.

Table 5 lists the relative heats of formation of the M(O,N) environment, using standard heats of formation of both the oxides and the hydroxides of the metals [20].

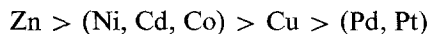
Table 5
Relative heats of formation of the metal-amino acid chelate environments

$\Delta H_f^\circ[\text{MO}] + \Delta H_{Rxn}[\text{MCl}_2 \cdot \text{NH}_3]$		$\Delta H_f^\circ[\text{M}(\text{OH})_2] + \Delta H_{Rxn}[\text{MCl}_2 \cdot \text{NH}_3]$	
Zn	-108.23 kcal	Zn	-178.56 kcal/mole
Ni	-80.26	Co	-152.66
Cd	-79.32	Cd	-151.76
Co	-78.66	Ni	-150.46
Cu	-58.4	Cu	-128.61
Pd	-40.1	Pt	-118.56
Pt	-	Pd	-111.86

The relative heat of formation of Pt(O,N) calculated from platinum oxide cannot be calculated since thermochemical data on platinum oxide have not been published.

In both the oxide and hydroxide tabulations in Table 5, the data are arranged in three groupings. In both cases the zinc complex has the highest heat of formation, exceeding the next closest value by approximately 27 kcal. This is followed by the grouping of nickel, cadmium and cobalt complexes, each having heats of formation within two kcal of each other. A relative order of stability within this grouping is not possible because the uncertainties in the respective values are greater than their differences. The third grouping consists of copper, palladium and platinum. In this grouping the maximum difference in relative heat of formation is 18 kcal, which is appreciable. The relative heat of formation data for this third group indicates that copper should form the more stable complex.

Thus, the relative heats of formation of the M(O,N) environment would indicate a stability order of:



Two results are evident from this calculated thermodynamic stability order: first, Group 1 metals (Zn, Ni, Cd and Co) should be more thermally stable in an amino acid chelating environment than Group 2 metals (Cu, Pd and Pt); second, zinc forms the thermally most stable chelate of the metals considered.

For the most part these theoretical results are confirmed in the thermal stability orders observed. The complicated kinetics and mechanics of interaction (e.g. valence state change in the metal) when a solid is heated to its decomposition temperature probably account for variations from the calculated stability order. Other differences may also arise from the fact that the calculated relative heats of formation are for crystalline materials at standard temperature and pressure, a condition not met in the thermobalance.

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RÉSUMÉ — L'étude thermogravimétriques des chélates de huit acides aminé communs avec des métaux divalents a montré qu'il n'existait pas de relation entre l'ordre de stabilité thermique et l'ordre de la stabilité hydrolytique, ni avec le déplacement des bandes infrarouges ou constantes de stabilité. On a essayé de constater une corrélation entre l'ordre de la stabilité thermique et la chaleur de formation et structure stéréochimique.

ZUSAMMENFASSUNG — Die thermogravimetrische Untersuchung der Chelatkomplexe von acht gewöhnlichen Aminosäuren mit zweiwertigen Metallen zeigte, daß keine Beziehung zwischen der Reihenfolge der Thermostabilität und der hydrolytischen Stabilität, der Verschiebung der infraroten Bänder oder den Stabilitätskonstanten besteht. Es wurde versucht, die thermische Stabilität mit den relativen Bildungswärmen und mit stereochemischen Deutungen in Beziehung zu bringen.

Резюме — Термогравиметрическое исследование хелатов восьми обычных аминокислот двухвалентного металла показало, что нет никаких соотношений между порядком термостабильности хелатов и порядком гидролитической стабильности, сдвигом инфракрасных полос или силовой постоянной связи. Проводился опыт для установления отношения порядка термостабильности к теплоте образования и структурного превращения.