

would be similar to the drawing shown for $[\text{Co}(\text{CyDTA})]^-$, but where C_4 and C_8 are hydrogens.

By analogy to $[\text{Co}(\text{EDTA})]^-$, the interaction of H_1 and H_8 in $[\text{Co}(\text{PDTA})]^-$ is felt to be small. However, as the methyl group so strongly prefers the equatorial conformation that only two complexes of *dl*-PDTA are formed,³⁵⁻³⁷ it is felt that there exists a significant steric interaction of H_8 with the equatorial methyl protons. This steric interaction contributes to ν_{AB} of AB-one and to the observed difference in the isotopic exchange rate of H_8 and H_1 in a manner as previously pointed out in the case of $[\text{Co}(\text{CyDTA})]^-$. Moreover, it has been pointed out (Results) that H_8 was interchanged with H_1 in the liberation of the 3D-PDPA ligand and re-formation of the cobalt complex. Thus, H_8 is assigned to the lower-field members of AB-one of the $[\text{Co}(\text{PDTA})]^-$ nmr spectra. As the equatorial methyl is relatively removed from H_8' and H_1' and no steric interaction can be anticipated, no attempt is made to assign H_8' and H_1' to the respective nmr resonances.

Previous workers²⁵ in determining the protonation scheme of free PDPA⁴⁻ hypothesized that the chemical-shift difference between the protons nearest to the asymmetric atom which causes the difference is likely

to persist over the greater pH range. Although using a different basis in the present work to interpret the same protonation scheme, a concurring conclusion was reached.

The method of obtaining selectively deuterated chelates in fairly high yields reported here could be useful to obtain isotopically-labeled chelons to study various intermolecular rates of exchange, racemization rates, and electron-transfer processes. Furthermore, the postulate set forth here which relates isotopic reactivity and nmr spectra can be extended to elucidate other analogous chelate hyperfine splitting patterns. Mixed Co(III) chelates of racemic amino acids and selected asymmetric ligands are being evaluated as possible routes for obtaining optically pure amino acids.

Thus, it is anticipated that the chelate models chosen to study the scope of the acid-catalyzed isotopic exchange in heavy water will provide additional insight into the nature of the metal-Co(III) carboxylate bonding.

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Metal Complexes of the Amino Acid DL-Methionine

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The donor properties of the amino acid methionine, $\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$ (HMT), were investigated for a number of transition and nontransition metal ions, Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Al(III), Ag(I), Cd(II), Hg(II), Pb(II), Bi(III), Rh(III). Methionine behaves as an anionic ligand (Mt) and generally forms neutral complexes, $\text{M}^{\text{II}}\text{Mt}_2$ and $\text{M}^{\text{III}}\text{Mt}_3$, in which the metal attains its usual higher coordination number by linking with the N atom of the $-\text{NH}_2$ group and with one or both of the O atoms of the $-\text{COO}^-$ group. In these complexes the S atom of the $-\text{SCH}_3$ group is still available for coordination, as shown by the formation of mixed-metal complexes with Ag(I), for example, $\{\text{Cr}_2\text{Ag}_3\text{Mt}_6\}(\text{ClO}_4)_3$. Conversely, methionine forms with Ag(I) an anionic complex, $[\text{AgMt}_2]^-$, in which only the S atom coordinates, and mixed-metal complexes may then be formed by subsequent coordination of the $-\text{NH}_2$ and $-\text{COO}^-$ groups to metal ions such as Ni(II) and Cu(II). To help in the structural study of methionine complexes, a number of the corresponding complexes of the amino acid norleucine, $\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{NH}_2)\text{COOH}$, were prepared and investigated.

Introduction

It is well known¹⁻⁷ that aminocarboxylic acids act as negatively charged chelating ligands toward metal ions, coordinating both through the $-\text{NH}_2$ and the

$-\text{COO}^-$ groups. In contrast only sparse information is available on the donor ability of sulfur-containing amino acids, in which the sulfur atom is also a possible ligating site. For the anion of cysteine, $-\text{SCH}_2\text{CH}(\text{NH}_2)\text{COO}^-$, both sulfur-to-metal and oxygen-to-metal bonds have been shown⁸ to exist in solid complexes of Zn(II), Cd(II), and Hg(II), whereas sulfur and nitrogen appear to be the ligating atoms toward Ni(II) in aqueous solution.⁹ With methionine, $\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$ (HMT), formation constants

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in aqueous solution indicated that coordination occurs *via* the $-\text{NH}_2$ and $-\text{COO}^-$ groups for a number of transition and post-transition metal ions¹⁰⁻¹² and *via* the S atom for Ag(I).^{12,13} None of these methionine complexes, however, was isolated in the solid state, and no direct investigation of their structures was reported. Some complexes of methionine with Pt(II), obtained as solids,¹⁴ were assigned structures involving coordination of the S and N atoms on the basis of chemical behavior. The data available in the literature showed therefore that methionine is capable of coordination through the $-\text{SCH}_3$ as well as through the $-\text{NH}_2$ and $-\text{COO}^-$ groups and is potentially a tridentate chelating ligand. On the other hand, since the S atom of a thioether group (class b base¹⁵) differs markedly in its donor properties from the N atom of an amino group and the O atom of a carboxylate group (both class a bases), methionine may not tend to coordinate with a given metal ion as a tridentate chelating ligand (S, N, and O donor atoms). More likely, methionine could be expected to act as a bidentate chelating ligand and use different pairs of donor atoms (O and N, S and N) when coordinating to different metal ions. The third, and free, donor atom could then be the site of subsequent coordination to a different acceptor. Thus, a systematic study of the ligating ability of methionine promised to be chemically significant, and the biological importance¹⁶ of this amino acid added interest to the investigation.

In the present work, methionine complexes of some fifteen transition and nontransition metals have been prepared and their structures investigated, with particular regard to the coordination sites and the character of the coordinate bonds. The metals were chosen to include both class a and class b acceptors, as well as some of intermediate character. During the course of the research it became apparent that the properties of the metal-methionine complexes could be best interpreted if compared with those of the analogous complexes of an amino acid not containing sulfur. Therefore, a number of metal complexes of norleucine, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$ (HNorl), which differs from methionine only by having a $-\text{CH}_2-$ group in place of the $-\text{S}-$ atom, were also prepared and investigated.

Results and Discussion

Methionine and its alkali metal salts reacted with metal ions to form complexes containing the negative ligand, $\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COO}^-$ (Mt). Neutral complexes, $\text{M}^{\text{II}}\text{Mt}_2$ or $\text{M}^{\text{III}}\text{Mt}_3$, were generally obtained regardless of the experimental conditions

(metal/ligand ratio, order of addition of reagents, solvent); however, with Ni(II) and Cu(II) different preparative methods yielded cationic, neutral, or anionic complexes. The metal-methionine complexes (Table I) are crystalline, have rather high decomposition temperatures, are stable to air, and, with a few exceptions, are fairly stable to moisture. Most of these complexes, once isolated as solids, are insoluble in all solvents and consequently their structural study had to be limited to the solid state. For this reason, and because of the complexity of their infrared spectra, the geometric (*cis-trans*) form of the complexes was not investigated.

Complexes with Two Ligands, ML_2 (L = Mt and Norl; M = Mn(II), Co(II), Ni(II), and Cu(II)).—The magnetic moments (Table I) and visible spectra of the Mn(II), Co(II), Ni(II), and Cu(II) methionine complexes, MMt_2 , indicate that the central metal ion is six-coordinated with a high-spin, essentially octahedral, configuration. Therefore in these complexes each methionine anion ligates through three sites, and the two most likely possibilities are (a) coordination *via* the N and S atoms and one O atom of the $-\text{COO}^-$ group; (b) coordination *via* the N atom and both O atoms of the $-\text{COO}^-$ group. A comparison with the analogous complexes of norleucine, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$, helps to distinguish between these two possibilities. The significant regions of the infrared spectra of the methionine and norleucine complexes (Table II) are very similar and the following observations are of interest.

(1) The antisymmetric and symmetric carboxylate stretching vibrations, $\nu(\text{COO}^-)$, of the methionine and norleucine complexes have frequencies which agree within $\pm 6 \text{ cm}^{-1}$ and also have similar band contours, indicating that the carboxylate group has the same role in both series of complexes. The difference between the antisymmetric and symmetric $-\text{COO}^-$ stretching frequencies, $\Delta\nu(\text{COO}^-)$, which is reported⁶ to increase with the strength of the M-O coordinate bond, is greater for the methionine and norleucine complexes than for the NaMt and LiNorl salts and varies in the order Mn(II) < Co(II) < Ni(II) < Cu(II) > Zn(II), following the Irving-William series.

(2) The sodium salts of methionine and norleucine have three medium, well-resolved absorption bands between 3410 and 3270 cm^{-1} , all of which shift upon deuteration of the $-\text{NH}_2$ group. For this reason a well-defined trend in the $\nu(\text{NH}_2)$ frequencies is not observable for the MMt_2 and MNorl_2 complexes, although there is a general lowering of the absorption range. The range of the $\nu(\text{NH}_2)$ absorptions for the Cu(II) complex (3290–3136 cm^{-1}) is about 100 cm^{-1} lower than for the other complexes (3370–3270 cm^{-1}), suggesting that the M-N bond is—as expected—strongest for Cu(II).

(3) Should the S atom of the $-\text{SCH}_3$ group coordinate to the metal in the complexes of methionine, a regular shift of the CS stretching frequency would be expected. Unfortunately the CS stretching mode, which in aliphatic sulfides appears as a weak band in

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TABLE I
 FORMULAS, ANALYTICAL DATA, AND SOME PROPERTIES OF THE METAL COMPLEXES OF METHIONINE AND NORLEUCINE

Compound	Color	Mp or dec temp, °C	μ_{eff} B.M.	Prep method	Metal, %		Nitrogen, %		Solubility ^a
					Calcd	Found	Calcd	Found	
DL-Methionine									
[MnMt ₂] _n ^b	Light tan	300	5.84	II	15.56	15.50	7.98	7.80	<i>c</i>
[CoMt ₂] _n ^d	Pink	285	4.91	VI	16.51	16.22	7.88	7.77	<i>c</i>
[NiMt]ClO ₄	Blue-green	>300	3.18	II	19.17	19.19	4.57	4.70	<i>e, f</i>
[NiMt ₂] _n ^g	Light blue	>300	3.25	I	16.55	16.78	7.89	7.77	<i>c</i>
Li[NiMt ₃]	Light blue	220	3.06	III	11.50	11.31	8.24	8.43	<i>e</i>
[CuMt]ClO ₄	Blue-green	180	1.89	II	20.43	20.30	4.50	4.38	<i>c</i>
[CuMt ₂] _n ^h	Deep blue	270	2.05	IV	17.67	17.40	7.79	7.69	<i>c</i>
[ZnMt ₂] _n	White	280		V	18.00	18.08	7.75	7.43	<i>c</i>
[CdMt ₂] _n	White	214		II	27.45	26.99	6.86	6.52	<i>c</i>
[HgMt ₂] _n	Yellow	120		II	40.30	40.98	5.63	5.37	<i>c</i>
[PbMt ₂] _n	White	214		II	41.18	41.12	5.57	5.23	<i>c</i>
[AlMt ₃]	White	260		II	5.73	5.03	8.92	8.62	<i>c</i>
[CrMt ₃]	Red-purple	>300	3.73	II	10.48	10.40	8.47	8.39	Sol in all
[FeMt ₃]	Red-brown	203	5.63	II	15.90	16.11	8.41	8.40	Sol in all
[RhMt ₃]	Yellow-gray	205		VII	18.82	18.90	7.68	7.85	<i>e</i>
[BiMt ₃]	White	205		VII	31.85	32.63	6.43	6.33	<i>c</i>
Li[AgMt ₂]	White	107		II	26.64	26.90	6.87	6.59	<i>e</i>
DL-Norleucine									
[MnNorl ₂] _n	Light tan	220	5.78	II	17.14	17.21	8.88	8.83	<i>c</i>
[CoNorl ₂] _n	Pink	200	4.90	VI	18.40	18.28	8.77	8.76	<i>c</i>
[NiNorl ₂] _n	Light blue	210	3.21	I	18.40	18.27	8.77	8.76	<i>c</i>
[CuNorl ₂] _n	Blue-gray	>300	1.98	IV	19.49	19.38	8.59	8.62	<i>c</i>
[ZnNorl ₂] _n	White	>300		V	19.97	20.06	8.55	8.51	<i>c</i>
Li[AgNorl ₂]	White	155		II	28.76	29.03	7.46	7.48	<i>c</i>
[CdNorl ₂] _n	White	209		II	30.15	30.80	7.51	7.87	<i>c</i>
[HgNorl ₂] _n	Gray	118		II	43.51	42.92	6.07	6.24	<i>c</i>
[PbNorl ₂] _n	White	225		II	44.31	43.72	5.99	6.26	<i>c</i>

^a Solvents used: water, ethanol, methanol, diethyl ether, carbon tetrachloride, carbon disulfide, dichloromethane, acetonitrile. ^b Calcd: C, 34.18; H, 5.75. Found: C, 34.07; H, 6.28. ^c Insoluble in all solvents. ^d Calcd: C, 33.80; H, 5.68. Found: C, 33.96; H, 5.69. ^e Soluble in water. ^f Soluble in acetonitrile. ^g Calcd: C, 33.82; H, 5.69. Found: C, 33.76; H, 5.87. ^h Calcd: C, 33.63; H, 5.61. Found: C, 33.30; H, 5.98.

the 600–700 cm⁻¹ region,¹⁷ could not be identified with certainty in the spectra of methionine and its metal complexes, because several other modes absorb in the same region. However, indirect evidence that the S atom of methionine is not involved in coordination is the fact that the deformation vibrations of the –CH₃ group do not differ appreciably from those of the norleucine complexes.

The ML₂ metal complexes of methionine and norleucine have almost identical magnetic moments and visible absorption spectra, which indicate that methionine and norleucine produce the same average ligand field; these two series of complexes also have the same general properties in regard to solubility, thermal stability, and sensitivity to moisture. It may be concluded that in the methionine complexes the S atom is not involved in coordination and that both the methioninato and the norleucinato ligands are tridentate, coordinating through the N atom of the –NH₂ group and through both O atoms of the –COO⁻ group. Two different formulations are then possible for these six-coordinate complexes: if the bidentate –COO⁻ group functions as a chelate, a monomeric complex [ML₂] will result, whereas if it acts as an asymmetrically bridging ligand, the complex will be a polymer, [ML₂]_n. X-Ray analysis has shown

that the former type of coordination occurs in Zn(CH₃COO)₂·2H₂O¹⁸ and Na[UO₂(CH₃COO)₃]₁,¹⁹ and the latter type in the glycine complexes, Zn(gly)₂·H₂O and Cd(gly)₂·H₂O.²

Complexes with Three Ligands, MMT₃ (M = Al(III), Cr(III), Bi(III), Fe(III), and Rh(III)).—These complexes may be considered to have an octahedral stereochemistry, and the Fe(III) and Rh(III) complexes have high- and low-spin configurations, respectively. Since these trivalent metals are class a acceptors, the methioninato ligand may be expected to coordinate through the N and O atoms, and, again, the –COO⁻ and –NH₂ infrared absorptions (Table II) may be expected to show definite changes. In fact the values of Δν(COO⁻) show that the –COO⁻ group is coordinated and indicate that in general the M–O bond is, as expected, stronger for trivalent than for divalent transition metals. Because the antisymmetric ν(COO⁻) appears as a split band in the Fe(III) and Bi(III) complexes, a reliable order of the M–O bond strength for the trivalent complexes was not obtained; however, it is evident that the M–O bond is strongest for Cr(III). The –NH₂ stretching region shows the very broad, poorly resolved absorptions typical of strongly hydrogen-bonded –NH₂ groups, and an assignment of the

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TABLE II
SOME INFRARED ABSORPTION FREQUENCIES (CM⁻¹)^a OF DL-METHIONINE,
DL-NORLEUCINE, THEIR ALKALI METAL SALTS, AND THEIR METAL COMPLEXES

Compound	$\nu(\text{NH}_2)$ or $\nu(\text{NH}_2)$	$\delta(\text{NH}_2)$ or $\delta(\text{NH}_2)$	$\nu(\text{COO}^-)$ antisym	$\nu(\text{COO}^-)$ ^d sym	$\Delta\nu$ ^e (COO^-)
MtH ^{b,c}	2720 s, 2614 s, 2510 s, 2100 w	1660 s, 1580 s, 1515 w	1625 s, 1620 s	1412 s	210
NorIH ^{b,c}	2755 s, 2665 s, 2590 s, 2480 s, 2315 s, 2100 w	1660 s, 1585 s, 1520 w	1625 s, 1620 s	1430 s	192
NaMt ^b	3410 m, 3353 m, 3270 m	1550 sh	1584 s	1422 m	162
LiNorI	3356 sh, 3350 m, 3267 m	1613 s	1590 sh, 1582 sh, 1577 s	1446 s	131
MnMt ₂ ^b	3340 s, 3270 s	1567 s	1582 s	1409 m	173
MnNorI ₂ ^b	3342 s, 3271 s	1569 s	1580 s	1403 m	177
CoMt ₂ ^b	3360 sh, 3342 s, 3272 s	1565 sh	1585 s	1410 m	175
CoNorI ₂ ^b	3368 m, 3275 s	1566 sh	1582 s	1418 s, 1403 s	172
NiMt ₂ ^b	3338 m, 3276 m	1587 s	1617 s	1399 m	188
NiNorI ₂ ^b	3370 m, 3268 m	1580 s	1587 s	1408 s, 1402 s	182
CuMt ₂ ^b	3280 s, 3236 s, 3136 w	1574 s	1621 s	1400 s, 1392 s	225
CuNorI ₂ ^b	3290 s, 3240 s, 3137 m	1587 m	1625 sh, 1617 s	1397 m	224
AlMt ₃ ^b	3308 s, 3260 s, / 3140 s /	1584 m	1668 s	1418 m	250
CrMt ₃	3225 s, / 3118 s /	1580 sh	1648 s	1373 m	275
FeMt ₃	g	1585 m	1625 s, 1615 s	1415	205
RhMt ₃	g	1585 m	1630 s	1410 m	220
BiMt ₃	g	1585 m	1625 s, 1615 sh	1415 m	210
ZnMt ₂ ^b	3314 s, 3292 s, 3250 s, 3154 m	1572 m	1610 s	1390 m	220
ZnNorI ₂ ^b	3315 m, 3250 m, 3160 w, 3110 w	1570 m	1604 s	1394 m	210
CdMt ₂ ^b	3330 m, 3247 m, 3200 sh	1570 m	1590 s	1410 m	180
CdNorI ₂ ^b	3340 m, 3250 m	1581 m	1598 s	1410 m	178
HgMt ₂ ^b	3157 m, 3090 m	1573 s	1597 s	1400 s	197
HgNorI ₂	3425 w, br, 3225 m, 3080 sh	1584 s	1601 s	1411 m	190
PbMt ₂	3296 s, 3250 s, 3160 w	1553 s	1629 s	1400 s	229
PbNorI ₂	3315 s, 3250 s, 3160 w	1550 s	1629 s	1400 s	229
NiMtClO ₄	3600-3400 m, br, 3330 m, 3280 m	1610 sh	1630 s	1410	220
Li[NiMt ₃]	3500-3400 m, br, 3330 m, 3275 m	1585 sh	1595 s	1420	175
CuMtClO ₄	3600-3400 m, br, 3285 sh, 3240 m	1580 sh	1623 s	1394	229
Li[AgMt ₂]	3327 m, 3270 m	1592	1592	1422	170
Li[AgNorI ₂]	3250 m, 3160 m	1585	1585	1419	176

^a s, strong; m, medium; w, weak; sh, shoulder. ^b Assignments were confirmed by comparison with the spectra of the deuterated compounds. ^c The infrared spectra indicate that methionine and norleucine exist in the solid state as the zwitterions. ^d In some complexes, two absorptions of comparable intensity appeared in the region of the symmetric $\nu(\text{COO}^-)$, and both were assigned to this mode. ^e When the $\nu(\text{COO}^-)$ modes appeared as split bands, the average frequency value was used in estimating $\Delta\nu(\text{COO}^-)$. / Peaks superposed on a very broad, strong absorption (due to H bonding). ^g Very broad, strong absorption in the region 3400-3000 cm⁻¹.

$\nu(\text{NH}_2)$ frequencies was possible only for the Cr(III) and Al(III) complexes. These values indicate that the $-\text{NH}_2$ group is coordinated and also that the M-N bond is stronger in the Cr(III) than in the Al(III) complex.

Unlike the MMT₂ complexes, some of the MMT₃ compounds dissolve in a number of solvents (Table I); in water and alcohol, however, extensive solvolysis occurs.

The Li[AgMt₂] Complex.—The dissociation constants

of the [AgMt₂]⁻ ion indicate^{12,13} that in aqueous solution the methioninato ligand coordinates to Ag(I) through the S atom only. To decide whether the same coordination is present in the solid complex, Li[AgMt₂], a comparison was made with the analogous norleucine complex, Li[AgNorI₂]. The $-\text{COO}^-$ stretching frequencies of solid Li[AgMt₂] and Li[AgNorI₂] are very close to those of the uncoordinated ligands and suggest that the $-\text{COO}^-$ group is not involved in coordination. The $-\text{NH}_2$ stretching frequencies

are lower in solid $\text{Li}[\text{AgMt}_2]$ than in NaMt , but are still considerably higher (by about 100 cm^{-1}) than in solid $\text{Li}[\text{AgNorl}_2]$. Thus the infrared spectra suggest the presence of Ag-N bonds in the solid $\text{Li}[\text{AgMt}_2]$, although much weaker than in the analogous norleucine complex.

It is significant that the $\text{Li}[\text{AgMt}_2]$ and the $\text{Li}[\text{AgNorl}_2]$ complexes differ appreciably in some of their properties; for example, the methionine complex is very light sensitive, whereas the norleucine complex is fairly stable to light. If one keeps in mind that Ag(I) complexes containing Ag-N bonds are in general less light-sensitive than those with Ag-S bonds, this difference may be considered an additional indication that in $\text{Li}[\text{AgNorl}_2]$ the bonding occurs through the N atom whereas in $\text{Li}[\text{AgMt}_2]$ it occurs through the S atom, with possible weak coordination of the $-\text{NH}_2$ group.

Zinc(II), Cadmium(II), Mercury(II), and Lead(II) Complexes.—These post-transition metal ions form, with both methionine and norleucine, complexes of the type ML_2 , insoluble in all solvents. The infrared spectra of the complexes show that both the $-\text{NH}_2$ and $-\text{COO}^-$ groups are coordinated; the range of absorption of the $\nu(\text{NH}_2)$ modes indicates that Hg(II) forms the strongest M-N bonds, while the values of $\Delta\nu(\text{COO}^-)$ indicate that the strength of the M-O bond decreases in the order $\text{Pb} > \text{Zn} > \text{Hg} > \text{Cd}$. The similarity between the methionine and norleucine complexes is very marked and indicates that the sulfur atom of methionine is not involved in coordination even for these heavy post-transition metals, which may be expected to have an affinity for the $-\text{SCH}_3$ group. These complexes may then be considered to be structurally similar to the ML_2 complexes of the first-row transition metals.

Ni(II) and Cu(II) Complexes with One and Three Ligands.—By varying the metal/ligand ratio and the experimental conditions of the preparation, Ni(II) complexes with one and three methioninato ligands, NiMtClO_4 and $\text{Li}[\text{NiMt}_3]$, were prepared. Copper(II) gave a similar complex with one ligand, CuMtClO_4 , but a complex with three ligands was not obtained. For the other metals investigated, variation in the preparative method failed to yield pure compounds of different stoichiometries.

The compound $\text{Li}[\text{NiMt}_3]$ is soluble in water without appreciable solvolysis and the solution has a conductivity typical of a 1:1 electrolyte; the magnetic moment and electronic spectrum (solid and aqueous solution) indicate a high-spin octahedral configuration for Ni(II), similar to that of the glycinate complex, $\text{Na}[\text{Ni}(\text{gly})_3]$.

It is difficult to propose a structural formula for NiMtClO_4 . The magnetic moment and electronic spectrum of the solid indicate an octahedral environment for Ni(II); however, the ClO_4 group is not coordinated since the infrared spectrum shows the single absorption at 1100 cm^{-1} characteristic of the ClO_4^- ion. The presence of coordinated water was

considered but discounted because even one H_2O molecule would give a percentage composition markedly different from that observed. Therefore, it seems likely that in NiMtClO_4 the one methionine ligand generates an octahedral field around Ni(II) by coordinating through all its four donor atoms (N, S, and two O) and in addition by sharing two as bridging groups. The suggestion that the S atom of methionine is involved in coordination in $[\text{NiMt}]\text{ClO}_4$ may explain the failure to obtain an analogous complex with norleucine. It is significant that the $[\text{NiMt}]\text{ClO}_4$ compound is soluble in acetonitrile and the solution has a conductivity typical of a 1:1 electrolyte. However, the complex species in solution very likely contain coordinated acetonitrile, because the electronic spectrum of the solution differs somewhat from that of the solid, the value of the crystal field splitting being intermediate between that of the solid complex and that of $[\text{Ni}(\text{CH}_3\text{CN})_6]^{2+}$.

Some significant information can be obtained from the infrared spectra of the Ni(II)-methionine complexes. The $\nu(\text{COO}^-)$ frequencies show that in $[\text{NiMt}]\text{ClO}_4$ and $\text{Li}[\text{NiMt}_3]$ the $-\text{COO}^-$ group is coordinated. Moreover, the $\Delta\nu(\text{COO}^-)$ values for the series $[\text{NiMt}]^+$, NiMt_2 , and $[\text{NiMt}_3]^-$, 200, 188, and 175 cm^{-1} , respectively, indicate that the strength of the Ni-O bond decreases as the number of coordinated anions increases. In the $-\text{NH}_2$ stretching region, $\text{Li}[\text{NiMt}_3]$ has a broad intense absorption between 3600 and 3000 cm^{-1} (Figure 1(a)), similar to that of the $\text{M}^{\text{III}}\text{Mt}_3$ complexes, thus indicating that the $-\text{NH}_2$ group is strongly hydrogen bonded. A similar broad, unresolved absorption also appears at about 3500 – 3000 cm^{-1} in the spectrum of the $[\text{NiMt}]\text{ClO}_4$ compound. The fact that hydrogen bonding is present in both the $[\text{NiMt}_3]^-$ and $[\text{NiMt}]^+$, but not in the NiMt_2 complex, is not surprising. In the $[\text{NiMt}_3]^-$ ion, the three Mt ligands are bidentate (one N and one O donor atom) and each $-\text{COO}^-$ group still has one uncoordinated O atom available for hydrogen bonding with the neighboring $-\text{NH}_2$ groups. In the NiMt_2 complexes, as discussed previously, each Mt ligand is tridentate (one N and two O donor atoms), so that no O atom of the $-\text{COO}^-$ group is available for hydrogen bonding. In $[\text{NiMt}]^+$, although all donor atoms of methionine are involved in coordination, the presence of the ClO_4^- anion again makes possible the hydrogen bonding of the $-\text{NH}_2$ groups.

Mixed-Metal Polynuclear Complexes of Methionine.—In the MMT_2 and MMT_3 complexes the $-\text{SCH}_3$ group is not coordinated and therefore should be available for bonding with a good class b acceptor, for example Ag(I). In fact, the addition of Ag(I) to solutions of FeMt_3 , RhMt_3 , and $\text{Li}[\text{NiMt}_3]$ yields mixed-metal complexes of the formulas $[\text{Ag}_3\text{Fe}_2\text{Mt}_6](\text{NO}_3)_3$, $[\text{Ag}_3\text{Rh}_2\text{Mt}_6](\text{NO}_3)_3$, and $[\text{Ag}_3\text{Ni}_2\text{Mt}_6]\text{X}$ ($\text{X} = \text{ClO}_4, \text{NO}_3$), containing a Ag:S ratio of 1:2. In these mixed-metal complexes the $-\text{NH}_2$ and $-\text{COO}^-$ stretching vibrations (Table III) are very close to those of the parent complexes, showing that their bonding is not

TABLE III
 MIXED-METAL COMPLEXES OF METHIONINE

Compound	Color	Ag, %		Metal, %		N, %		Infrared absorption frequencies, cm ⁻¹			
		Calcd	Found	Calcd	Found	Calcd	Found	$\nu(\text{NH}_2)$	$\delta(\text{COO})$ antisymp	$\delta(\text{COO})$ sym	Anion
[Ag ₃ Fe ₂ Mt ₆](NO ₃) ₃ ^a	Red-brown	21.53	21.91			8.38	8.09	3400- 3100 br	1615 s	1382 s	1330 m
[Ag ₃ Rh ₂ Mt ₆](NO ₃) ₃ ^a	Yellow-white	20.26	19.80			7.86	8.10	3430- 3350 br	1628 s	1411 s	1385 m
[Ag ₂ Ni ₂ Mt ₆](NO ₃) ₂ ^a	Light blue	23.37	23.80	8.47	8.57	7.08	7.37	3320 s 3287 s 3168 m	1585 s	1393 s	1350 m
[Ag ₃ Ni ₂ Mt ₆](ClO ₄) ₃ ^a	Light blue	22.65	22.41	8.21	8.23	5.88	5.93	3353 s 3270 s	1580 s	1400 s	1085 s
[Ag ₃ Cr ₂ Mt ₆](ClO ₄) ₃ ^b	Dark red	20.12	20.48			5.22	4.97	3281 m 3250 m 3150 m	1638 s	1380 s	1090 s
[Ag ₃ Fe ₂ Mt ₆](ClO ₄) ₃ ^b	Gray-brown	19.95	19.86			5.17	5.28	3485 w, br 3335 m 3265 m	1625 s	1425 m	1088 s
[Ag ₃ Co ₂ Mt ₆](ClO ₄) ₃ ^b	Brown	22.74	23.12	8.28	8.31	5.90	5.74	3340 m 3284 m	1580 s	1395 s	1090 s
[Ag ₃ Ni ₂ Mt ₆](ClO ₄) ₃ ^b	Light blue	22.65	23.33	8.21	8.14	5.88	5.77	3430 m 3335 m 3265 m	1615 s	1390 s	1100 s
[AgCuMt ₂](ClO ₄) ₃ ^b	Blue	16.19	16.23	9.54	9.70	4.20	4.08	3165 m 3430 m 3312 m 3245 m 3150 m	1615 s	1387 s	1100 s

^a Prepared by addition of AgNO₃ to the metal-methionine complex. ^b Prepared by addition of the metal salt (perchlorate or nitrate) to the [Ag(Mt)₂]⁻ complex.

altered appreciably by coordination to Ag(I). Also, the electronic spectrum of [Ag₃Ni₂Mt₆]⁺, which is nearly identical with that of the parent [NiMt₃]⁻, indicates that in the mixed-metal complex Ni(II) is still octahedrally surrounded by three N and three O donor atoms.

On the other hand, in the [AgMt₂]⁻ ion in aqueous solution only the S atom is coordinated, so that both the -NH₂ and -COO⁻ groups should remain available for bonding with class a metal ions. And, in fact, the addition of the perchlorates of Cr(III), Fe(III), Co(II), Ni(II), and Cu(II) to Li[AgMt₂] yields the mixed-metal complexes [Ag₃Cr₂Mt₆](ClO₄)₃, [Ag₃Fe₂Mt₆](ClO₄)₃, [Ag₃Co₂Mt₆](ClO₄)₃, [Ag₃Ni₂Mt₆](ClO₄)₃, and [AgCuMt₂](ClO₄)₃. The -NH₂ and -COO⁻ stretching frequencies of these mixed-metal complexes are close to those of the MMT₃ complexes for Cr(III) and Fe(III), and to those of the MMT₂ complexes for Co(II) and Cu(II); for the latter two complexes, however, the -NH₂ absorptions show the presence of hydrogen bonding (very likely to the NO₃⁻ or ClO₄⁻ anions). Both the visible and the infrared spectra of the [Ag₃Ni₂Mt₆](ClO₄)₃ complex of this series differ somewhat from those of [NiMt₃]⁻ and also from those of the similar complex prepared from [NiMt₃]⁻ and AgClO₄, but still indicate that both the -NH₂ and -COO⁻ groups are coordinated octahedrally to Ni(II).

The mixed-metal complexes of methionine may be assigned polymeric structures, consistent with their insolubility. The different properties of complexes having the same empirical formula but prepared by different methods may result from different degrees of polymerization and/or different tridimensional arrangements.

Conclusions

A comparison between the properties of the M^{II}Mt₂ and M^{III}Mt₃ complexes is helpful in the assignment of their structural formulas. The MMT₂ complexes are insoluble in all solvents and their infrared spectra have sharp, well-resolved -NH₂ stretching absorptions. On the other hand, the MMT₃ complexes have very broad, unresolved absorption in the -NH₂ stretching region (Figure 1 (b)), indicating strong hydrogen bonding of the -NH₂ groups; also, some complexes have a moderate solubility. These differences, taken in conjunction with other properties of the two series of complexes and in particular their visible spectra, lead to the conclusion that the MMT₂ complexes are polymerized through asymmetric -COO⁻ bridges (for example as in Figure 2), whereas the MMT₃ complexes are essentially monomeric, although intermolecular association by hydrogen bonding occurs in the solid state. A similar structure involving asymmetric carboxylato bridges is assigned to the MNOr₁₂ complexes. Thus, in the [MMT₂]_n complexes the Mt ligand is both chelating and bridging, for it coordinates to one metal ion *via* its N atom and one O atom of the -COO⁻ group, and to a neighboring metal ion *via* the other O atom of the -COO⁻ group. On the other hand, in the [MMT₃] complexes the methioninato acts simply as a bidentate chelating ligand (N and O donor atoms). These conclusions are consistent with the few available X-ray studies of metal-amino acid complexes, which show that the amino acid anions can act as "simple" chelating ligands (monodentate -COO⁻) in some complexes, for example Ni(gly)₂·2H₂O,¹ and as bridging-chelating ligands (asymmetric bidentate -COO⁻) in others, for example Zn(gly)₂·H₂O and Cd(gly)₂·H₂O.² The X-ray data

TABLE IV
ELECTRONIC ABSORPTION FREQUENCIES OF SOLID
Ni(II) COMPLEXES OF METHIONINE AND RELATED COMPLEXES

Compound	Ligating atoms	Absorption maxima (cm ⁻¹ × 10 ⁻³) ^a				Ref
		9.3 (1.28)	12.2 sh	15.8 (0.96)	25.6 (1.00)	
[NiMt]ClO ₄		9.7 (0.38)		16.0 (0.37)	26.3 (1.00)	This work
[Ni(Mt) ₂] _n	2 N, 4 O (bridg)	9.1 (0.76)	11.2 (0.97)	15.4 (1.26)	25.6 (1.00)	This work
[Ni(Norl) ₂] _n	2 N, 4 O (bridg)	9.1 (0.67)	11.3 (0.72)	15.5 (1.00)	27.0 (1.00)	This work
Li[Ni(Mt) ₃]	3 N, 3 O	9.8 (0.93)	13.1 sh	16.7 (0.95)	27.8 (1.00)	This work
		10.2 (0.14)		16.7 (0.31)	27.8 (1.00)	This work
[Ag ₃ Ni ₂ Mt ₆]ClO ₄ ^d	3 N, 3 O	9.5 (1.58)	11.7 sh	15.9 (1.17)	26.3 (1.00)	This work
[Ag ₃ Ni ₂ Mt ₆]NO ₃ ^e	3 N, 3 O	10.1 (1.14)	13.0 (0.36)	16.8 (0.86)	27.8 (1.00)	This work
[Ag ₃ Ni ₂ Mt ₆]ClO ₄ ^e	3 N, 3 O	10.0 (0.75)	13.2 sh	16.7 (0.68)	27.4 (1.00)	This work
[Ni(H ₂ O) ₆] ²⁺	6 O	8.5	13.5	15.4	25.3	21
[Ni(gly) ₂ (H ₂ O) ₂]	2 N, 4 O	10.0	13.3	16.1	27.0	21
[Ni(gly) ₃] ⁻	3 N, 3 O	10.1	13.1	16.6	27.6	21
[Ni(gly) ₂ en]	4 N, 2 O	10.5	13.0	17.3	28.1	21
[Ni(en) ₃] ²⁺	6 N	11.2	12.4	18.35	29.0	21

^a Numbers in parentheses are relative absorbancies. ^b In acetonitrile solution. ^c In water solution. ^d Prepared from Li[Ag(Mt)₂] and [Ni(H₂O)₆](ClO₄)₂. ^e Prepared from Li[Ni(Mt)₃] and AgNO₃ or AgClO₄.

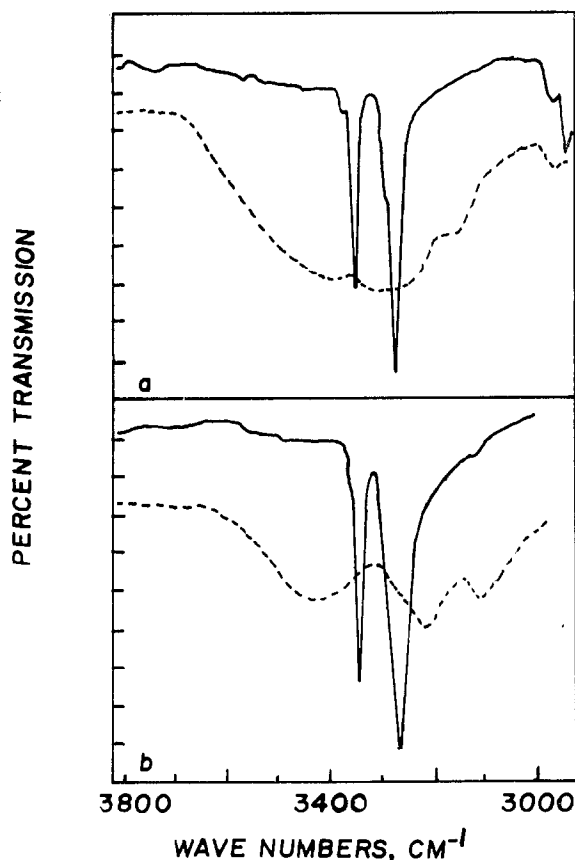


Figure 1.—Infrared spectra (—NH₂ stretching region) of: (a) ----, Li[NiMt₃]; —, [NiMt₂]_n; (b) ----, [CrMt₃]; —, [CoMt₂]_n.

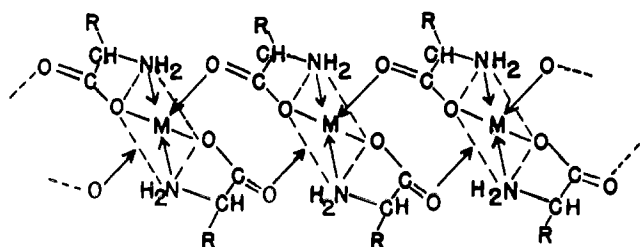


Figure 2.—Proposed structure of the [MMt₂]_n complexes.

for these glycine complexes also show that hydrogen bonding between the —NH₂ and —COO⁻ groups of neighboring entities occurs when the —COO⁻ group is monodentate, but not when it is bidentate (bridging). It may be observed that the polymeric formula of [NiMt₂]_n offers a satisfactory explanation for the difference between the visible spectrum (Table IV) of this complex and that of Li[NiMt₃]. The spectrum of [NiMt₃]⁻ is identical with that²⁰ of [Ni(gly)₃]⁻ (three N, three “negative” O), whereas for [NiMt₂]_n the average ligand field is close to that of [Ni(gly)₂(H₂O)₂] (two N, two “negative” O, two “neutral” O), as might be expected since the two O atoms of a bidentate —COO⁻ group correspond in field strength to one “negative” and one “neutral” O atom.

On the basis of these results, it is interesting to reconsider the structure of the numerous anhydrous complexes of the type ML₂ (L = amino acid anion) which have been extensively investigated by infrared spectroscopy (see, for example, ref 5, 6, and 21), assuming the central metal to be four-coordinate. By analogy with [MMt₂]_n and [M(Norl)₂]_n, any amino acid complex of the type ML₂—in which M is a (divalent) first-row transition metal ion—may be expected to be six-coordinate and have a polymeric, carboxylato-bridged structure. Since only sparse data were available in the literature in regard to the stereochemistry and solubility of such complexes, we investigated the Co(II), Ni(II), and Cu(II) complexes of a series of amino acids with C₃ to C₁₀ aliphatic chains.²² As expected, we found that the solid ML₂ complexes are six-coordinate and octahedral; also their solubility in both polar and nonpolar solvents is very low and does not follow a regular trend and may therefore be related to the polymeric structure of the complexes rather than to the size of the ligands.

(20) C. K. Jørgensen, “Absorption Spectra and Chemical Bonding in Complexes,” Pergamon Press, London, 1962, Table 31, p. 296.

(21) I. Nakagawa, R. J. Hooper, J. L. Walter, and T. J. Lane, *Spectrochim. Acta*, **21**, 1 (1965).

(22) C. A. McAuliffe, M.S. Thesis, Florida State University, April 1965.

Experimental Section

Starting Materials.—DL-Methionine, DL-norleucine (Nutritional Biochemicals Corp.), and analytical grade metal salts were used without further purification.

Preparation and Characterization of the Complexes. Preparation I.—The amino acid (1.3 g) and Na_2CO_3 (0.5 g) were dissolved in 70 ml of water at 80° and the metal nitrate (hexahydrate) was added with stirring (metal:amino acid mole ratio 1:2.3). The resulting solution was concentrated under reduced pressure on a steam bath and then cooled in a refrigerator. After several hours the crystals which formed were filtered off, washed with water and ethanol, and dried *in vacuo* over P_4O_{10} .

Preparation II.—The amino acid was added to a suspension of $\text{LiOH}\cdot\text{H}_2\text{O}$ (slight excess over 1:1 mole ratio) in ethanol and stirred at 60° for 20 min. After filtration of the unreacted $\text{LiOH}\cdot\text{H}_2\text{O}$, a solution of the metal perchlorate (hexahydrate) in ethanol was added slowly. (The metal:amino acid mole ratio was 1:2 for the $\text{M}^{\text{II}}\text{L}_2$ complexes and 1:3 for the $\text{M}^{\text{III}}\text{L}_3$ and $\text{M}^{\text{II}}\text{LCIO}_4$ complexes.) The precipitate which formed immediately was filtered, washed with ethanol, and dried *in vacuo* over P_4O_{10} . For the compounds $[\text{NiMt}]\text{ClO}_4$, $[\text{CuMt}]\text{ClO}_4$, $[\text{CoNorl}_2]_n$, $[\text{NiNorl}_2]_n$, and $[\text{CuNorl}_2]_n$, precipitation occurred after the reaction mixture was cooled in a refrigerator for several hours. For the compounds $[\text{CrMt}_3]$ and $[\text{FeMt}_3]$, the reaction mixture was heated on a steam bath for 30 min, until crystallization began.

Preparation III was carried out similarly to preparation II, except that the lithium methioninato solution was added to the metal perchlorate solution (metal:methionine mole ratio 1:3).

Preparation IV was carried out according to the general method of Abderhalden and Schnitzler.²³ Freshly prepared $\text{Cu}(\text{OH})_2$, suspended in a small volume of water, was added to a 10% aqueous solution of methionine (Cu:methionine mole ratio 1:2.2). The reaction mixture was stirred at 60° for 30 min; the deep blue crystals which formed were filtered off, washed with warm water and ethanol, and dried *in vacuo* over P_4O_{10} .

Preparation V.—A solution of sodium ethoxide in ethanol (0.12 g of sodium in 60 ml) was treated with 1.50 g of methionine and then with hydrated zinc(II) perchlorate (1.33 g) dissolved in a minimum volume of ethanol. The white precipitate which formed immediately was filtered, washed with ethanol, and dried *in vacuo* over P_4O_{10} .

(23) E. Abderhalden and E. Schnitzler, *Z. Physik. Chem.*, **163**, 96 (1927).

Preparation VI.—Methionine (1.3 g) was dissolved in 60 ml of water, treated with $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$ (0.6 g), and heated at 80° for 20 min. Hydrated cobalt(II) perchlorate (1.1 g in 20 ml of water) was then added to the warm sodium methioninato solution, and the pale pink precipitate which formed slowly was filtered off, washed with water and ethanol, and dried *in vacuo* over P_4O_{10} .

Preparation VII.—An ethanol solution of the anhydrous metal chloride was added to a hot ethanol solution of lithium methioninato, and the mixture was refluxed for 3 hr. The resulting solution was filtered hot and on cooling gave a precipitate which was filtered, washed with ethanol, and dried *in vacuo* over P_4O_{10} .

Preparation VIII.—An aqueous solution of the metal perchlorate hexahydrate (1.0 g in 20 ml) was added with stirring to an aqueous solution of the $\text{Li}[\text{AgMt}_2]$ complex (1.0 g in 30 ml). The precipitate which formed immediately was filtered, washed with water and ethanol, and dried in air.

Preparation IX.—The $[\text{M}^{\text{III}}\text{Mt}_3]$ and $\text{Li}[\text{NiMt}_3]$ complexes were dissolved in ethanol and treated with an ethanol solution of silver nitrate or perchlorate. The precipitate which formed immediately was filtered off, washed with ethanol, and dried in air.

Deuterated Compounds.—The details of the preparations, analytical data, and properties of the deuterated compounds are available elsewhere.²²

Measurements.—Analyses, magnetic susceptibility determinations, and infrared and electronic spectra and conductivity measurements were made as previously described.²⁴ The diffuse reflectance absorption maxima ($\text{cm}^{-1} \times 10^{-3}$) (a), and the molar conductivity values, Δ_M ($\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$) (b), of some complexes follow: (a) $[\text{CoMt}_2]_n$, 20.2, v br; 17.2 sh; $[\text{CoNorl}_2]_n$, 18.5; $[\text{CuMt}_2]_n$, 16.5; $[\text{CuNorl}_2]_n$, 16.5. (b) $[\text{FeMt}_3]$, $1.840 \times 10^{-3} M$ in water, $\Delta_M = 223.9$; $1.690 \times 10^{-3} M$ in methanol, $\Delta_M = 74.8$; $[\text{RhMt}_3]$, $1.675 \times 10^{-3} M$ in water, $\Delta_M = 55.6$; $2.100 \times 10^{-3} M$ in methanol, $\Delta_M = 5.9$; $\text{Li}[\text{NiMt}_3]$, $1.190 \times 10^{-3} M$ in water, $\Delta_M = 115.0$; $[\text{NiMt}]\text{ClO}_4$, $1.590 \times 10^{-3} M$ in acetonitrile, $\Delta_M = 58.4$.

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The Chloramination of Some Substituted Arsines

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The reactions of triphenylarsine and diphenylchloroarsine with chloramine and with mixtures of chloramine and ammonia have been carried out and a variety of aminoarsonium chlorides and cyclic arsenonitriles prepared. Similar compounds have been derived by the ammonolysis of di- and trichlorophenylarsanes. It has been shown that chloramination, like chlorination, of phenylarsines results, under some conditions, in the fission of some of the arsenic-phenyl bonds and the elimination of chlorobenzene.

H. H. S. has previously reported that chloramine reacts with triphenylarsine to yield impure samples of triphenylaminoarsonium chloride,¹ but the pure compound was not isolated and characterized. We have

now accomplished this objective and also have studied the chloraminations of diphenylchloroarsine and tri-

(1) H. H. Sisler, XVIIth International Union of Pure and Applied Chemistry, Munich, Sept 1959.