state expected for the mer isomer. The band at 27,200 cm^{-1} is assigned to the unsplit $^1A_{1g} \rightarrow {}^1T_{2g}$ transition of O_h symmetry. The visible spectrum includes intense ligand and charge-transfer absorption "tails" in the near-ultraviolet–visible region of the spectrum which raises the value of the apparent molar absorptivities above values expected for d–d transitions. The energy difference between the two components of the $^1T_{1g}$ state is quite large ($\sim$6200 cm^{-1}) but is comparable to the analogous splitting found for *trans*-$Co(en)_2Cl_2^+$ ($\sim$6400 cm^{-1}).[6] The assignment of the 27,200-cm^{-1} band is supported by the spectra of other complexes containing oxygen and nitrogen donors in which ligand transitions do not interfere with the crystal field transitions. For example, the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition is seen at 27,600 cm^{-1} in *trans*-(*O*),*cis*(*N*)-$[Co(gly)_2(l\text{-pn})]Cl \cdot 6H_2O$[10] and *trans*-$Co(en)_2F_2^+$[6] and at 27,000 cm^{-1} in *mer*-$Co(\beta\text{-ala})_3$.[9]

The ^1H and ^{19}F nuclear magnetic resonance spectra of $Co(TFAP)_3$ in acetone-d_6 and benzene, respectively, provide support for the contention that the synthesis provides the mer isomer in vast predominance. The proton resonance spectrum shows a complex pattern typical of 2-substituted pyridines centered at −7.5 ppm from TMS. There are three peaks of equal intensity at −5.89, −6.07, and −6.26 ppm from TMS which are assigned to the –CH=C< protons in the three unique environments of the mer isomeric structure of the six-coordinate complex. The ^{19}F spectrum confirms this assignment showing three peaks of equal intensity at 72.50, 72.55, and 72.66 ppm upfield from $CFCl_3$. Also, in support of these assignments, the ^1H spectrum of the zinc(II) complex, assumed to have pseudotetrahedral coordination, affirms the simple spectrum expected for the ligand when all ligands are geometrically equivalent. In acetone-d_6 there is a multiplet at about −7.7 ppm of intensity 4 times that of a singlet at −5.85 ppm from TMS.

There is some evidence that the stereospecificity of the reaction is not complete. Thin layer chromatograms of the product on silica gel H show two components, one present in very small quantity relative to the other. Toluene elutes only the major product whereas absolute ethanol moves both products at slightly different rates. Also, the ^1H spectra of some batches of $Co(TFAP)_3$ show absorption above noise level at −6.13 ppm downfield from TMS. These observations suggest that small amounts of the fac isomer are produced.

Although initial studies using high-speed liquid chromatography with uv detection produced only one major elution peak for $Co(TFAP)_3$ and $Fe(TFAP)_3$ using Carbowax-400–Porasil-C as the column packing and 2,2,4-trimethylpentane as the mobile phase; it is planned to examine the liquid chromatographic behavior of these compounds on other column materials in order to facilitate the quantitative measurement of isomer distribution.

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Circular Dichroism of Copper(II) and Palladium(II) Complexes of *N*-Methyl-L-amino Acids and Dipeptides[1]

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Four spin-allowed ligand field bands are identified in the solution circular dichroism of the 2:1 *N*-methyl-L-alanine complexes of Cu(II) and Pd(II). For the Cu(II) complex the CD extrema appear at 510, 560, 656, and 784 nm. Two spin-forbidden transitions are also observed in the Pd(II) complex. A persistent net negative sign is noted for the magnetic dipole allowed transitions of several transition metal ion complexes of L-amino acids and (*S*)-1,2-diaminopropane. A possible role is suggested for π-electron interactions in transmitting asymmetry in amino acid or peptide ligands so that optical activity appears in the ligand field bands of transition metal ion complexes. Both vicinal effects of substituents and chelate ring conformation contribute to the optical activity in the ligand field bands of complexes of *N*-methylamino acids.

From extensive investigations of the optical activity generated in the ligand field bands of tetragonal Ni (II),[2] Pd(II),[3] and Cu(II)[4] complexes by amino acid and small peptide ligands, a hexadecant rule appears to provide the simplest general description of the results. Octant or quadrant rules are unsatisfactory for these complexes. The single main feature leading to the hexadecant sector rule is the consistent negative sign and additivity of CD magnitudes observed for complexes of di- and tripeptides composed of L-amino acid residues.[2-5] Hexadecants may be constructed by dividing the coordination plane including the transition metal ion perpendicularly into eight wedge-shaped sectors with nodal planes along the metal ion–ligand bonds

(1) This research was supported by a grant from the National Science Foundation.

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and at 45° to these bonds. The coordination plane also defines a nodal surface, and alternate signs are assigned to each of the 16 sectors. In a tetragonal complex of a tripeptide composed of L-amino acid residues, all side chains appear in sectors of the same sign, assigned as negative to correspond to the net CD sign observed in the magnetic dipole allowed d–d transitions.[2-5] It is the net CD sign over all magnetic dipole allowed d–d transitions that is of significance in sector rules.[6] Signs of individual transitions provide a more difficult problem.

Compared to the puckering of the ethylenediamine (en) type of chelate rings, amino acids and peptides yield nearly planar rings with the side chains in relatively fixed positions in the case of the peptides.[7] For Co(III) complexes of approximate D_{4h} symmetry an octant rule has been proposed involving puckering of en type chelate rings.[8] A resolution of the conformational and vicinal contributions to the optical activity of d–d bands in Co(III) complexes of en type ligands led to the conclusions that vicinal effects are slight for C-substituted diamines and that both vicinal and conformational effects are important and oppose each other for N-substituted diamines.[9] The first conclusion is based on the observation of similar d–d CD magnitudes in bis-diamine complexes of Co(III) with one or two asymmetric centers in the ligands. This observation does not appear to hold for similar bis-diamine complexes of Pd(II), Pt(II), or Au(III).[10] The hexadecant rule suggested as applicable to the nearly planar peptide complexes is based empirically on the location of substituents which promote optical activity primarily through vicinal effects.[2-5] In this paper we report the results of the effect of N-methylation on the d–d CD of Cu(II) and Pd(II) complexes where according to the second conclusion above we might expect opposing vicinal and conformational contributions. Included are CD results for N-methylated amino acids and dipeptides (sarcosyl dipeptides).

Experimental Section

All chemicals were high-grade commercial products. They were routinely checked for purity by titration with standard base on a Radiometer TTT1a titrator–SBR2b titragraph combination. The sarcosyl-L-leucine from Cyclo Chemical gave only 88% of the correct equivalent weight but the remainder of the material appears to be inert. $CuCl_2$ was employed and Pd(II) was added as Na_2PdCl_4 obtained from Alfa Inorganics, Inc.[3] Absorption and CD spectra were taken on solutions containing ligands and metal ion in the appropriate molar ratios that had been titrated with standard base until the end point was reached as determined on the recording titragraph. An integral number of equivalents of base was always added assuring virtually complete formation of the indicated complexes. All measurements were performed at ambient temperatures, about 25°. Absorption spectra were recorded on a Cary 14R recording spectrophotometer. All molar absorptivities, ϵ, and differential molar absorptivities, $\Delta\epsilon$, between left and right circularly polarized light refer to 1 mol of transition metal ion. Circular dichroism spectra were recorded on a JASCO J-10B instrument. Intensities were standardized with a 1 mg/ml aqueous solution of camphorsulfonic-*10-d* acid in a 1-cm cell set at 236 mdeg at the CD maximum near 292 nm. For wavelengths longer than 700 nm an interfaced Spex 1400-II double monochromator was also employed. In this mode the Pockel's cell quarter-wave modulation voltage was set for 740 nm so that intensities reported at longer wavelengths are apt to be low.

Results

The CD and absorption spectra of Cu(II) complexes of α-*N*-methyl-L-amino acids are presented in Table I,

TABLE I
CIRCULAR DICHROISM AND ABSORPTION OF 2:1 COMPLEXES OF L-AMINO ACIDS AND Cu(II) AND MIXED COMPLEXES WITH GLYCINE

N-CH_3				*N*-H, 2:1	
2:1		1:1:1			
$\Delta\epsilon$ (ϵ)	λ, nm	$\Delta\epsilon$ (ϵ)	λ, nm	$\Delta\epsilon$ (ϵ)	λ, nm
		Alanine			
+0.003	784			+0.02	730
−0.080	656	−0.05	660	−0.09	625
+0.018	560	+0.02	557		
+0.015	510	+0.01	510		
(80)	612	(62)	620	(57)	620
		Lysine			
−0.24	634	−0.15	636	−0.16	600
−0.97	235	−0.32	235	−1.3	253
(85)	610	(49)	615	(57)	622
(4700)	243	(3460)	237	(6700)	235
		Glutamate			
+0.13	733			+0.04	765
−0.16	550	−0.08	549	−0.16	620
−0.85	247	−0.22	250	−1.2	255
+1.9	215	+0.9	207	+0.9	210
(100)	605	(57)	615	(58)	611
(3860)	245	(2920)	240	(6700)	235
		Valine			
+0.06	807			+0.05	765
−0.81	615	−0.44	620	−0.32	590
+1.7	276	+0.86	273	−1.3	250
−1.3	226	−0.63	223	+2.4	205
(96)	606	(56)	613	(58)	615
(4200)	242	(3570)	238	(6700)	235
		Leucine			
+0.01	843				
−0.47	630	−0.23	636	−0.15	620
+1.0	276	+0.27	270	−1.5	258
−0.7	228	−0.15	228		
(96)	618	(54)	618	(50)	625
(4970)	243	(2770)	236	(6250)	235
		Phenylalanine			
+0.12	790				
−0.87	600	−0.47	607	−0.44	592
				−0.45	278
+2.7	250	+1.4	255	+1.6	240
−3.8	219	−1.7	215	−4.8	218
(76)	584	(44)	618	(50)	620
(4970)	246	(3360)	240	(4350)	242
		Proline			
				+0.30	665
−0.25	622	−0.11	625	−0.07	525
+0.4	280	+0.4	286	−0.5	275
				+2.8	230
(140)	620	(80)	622	(72)	612
(3100)	283 s				
(4300)	248	(4800)	238	(5800)	242

and the CD spectra of Pd(II) complexes are in Table II. For both tables the first column of numbers lists the differential molar absorptivity at an extremum, the wavelength of which is listed in the second column, for 2:1 complexes of *N*-methyl-L-amino acids and the divalent transition metal ion. The third and fourth columns in both tables contain the same information for solutions containing equal numbers of moles of the *N*-methyl-L-amino acid, glycine, and metal ion. The

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TABLE II
CIRCULAR DICHROISM OF 2:1 COMPLEXES OF L-AMINO ACIDS AND Pd(II) AND MIXED COMPLEXES WITH GLYCINE

N-CH3				N-H, 2:1	
2:1		1:1:1			
Δε	λ, nm	Δε	λ, nm	Δε	λ, nm
		Alanine			
−0.012	450				
+0.018	413				
−0.10	374	−0.06	375		
+0.18	344	+0.08	344	+0.26	348
−0.22	313	−0.08	313	−0.68	307
+0.03	275	+0.02	280		
		Glutamate			
−0.22	364	−0.24	350	+0.25	355
−0.73	330	−0.30	323	−1.3	310
−0.08	275				
		Valine			
−1.09	350			+0.06	372
−1.21	330	−0.59	332	−1.8	313
+0.14	280	+0.07	280		

fifth and sixth columns show for comparison the results for 2:1 complexes of the nonmethylated ordinary L-amino acids of Cu(II) in Table I and Pd(II) in Table II. In addition Table I lists in parentheses the molar absorptivities at an absorption maximum for the Cu(II) complexes, the wavelengths of which are tabulated in the adjacent column.

For the Pd(II) complexes of Table II, the 2:1 complexes of *N*-methyl-L-amino acids exhibit an absorption maximum at 314 nm with ε 380. These values occur at 5 nm to shorter wavelength and with about a 25% increase in molar absorptivity compared to the values for the 2:1 complexes of L-amino acids.[3] Solutions containing the 1:1:1 mixtures of *N*-methyl-L-amino acid, glycine, and Pd(II) display only a shoulder in their absorption spectra at about 315 nm with an apparent ε greater than either of the above cases. Because ε <1300 even at 270 nm, all the bands reported in Table II evidently refer to predominantly d–d transitions.

The absorption maxima are consistent with two nitrogen and two oxygen donor atoms for both the tetragonal copper(II)– and palladium(II)–amino acid complexes. The pH of the nearly neutral solutions was adjusted so that ignoring the side chain all complexes in Tables I and II possess a net zero charge. Because of the positively and negatively charged side chains the lysine and glutamate complexes bear 2+ and 2− charges in the 2:1 complexes and 1+ and 1− charges, respectively, in the 1:1:1 complexes. The last complexes refer to solutions containing equal amounts of *N*-methyl-L-amino acid, glycine, and metal ion. Statistically the 1:1:1 complex should correspond to 50% of metal ion present but probably exceeds this amount as disproportionation to pure 2:1 complexes is not expected to be favored.

In the amino acid complexes of Cu(II), the charge-transfer band near 250 nm is shifted to longer wavelengths upon N-methylation. The mixed 1:1:1 Cu(II) complexes with glycine possess the lowest ε values near 240 nm. Occasionally the absorption bands reported in Table I are not symmetrical but are skewed to longer wavelengths with incipient shoulders. Charge transfer in this spectral region is due to transitions involving both amino and carboxylate groups and Cu(II).[11] All the ultraviolet CD results reported in Table I represent a single extremum or oppositely signed extrema from under the charge-transfer absorption band. The oppositely signed CD results reported at 220 and 255 nm for several other 2:1 complexes of amino acids and Cu(II)[12] should also be viewed as a splitting out from under the charge-transfer absorption band.

Considering together all the uv CD magnitudes for any one complex in Table I, the results for the 1:1:1 complexes are usually about half those of the 2:1 N-methylated complexes. The difference in the charge-transfer region between the CD magnitudes of the 2:1 N-methylated and their corresponding nonmethylated Cu(II) complexes is uniformly positive.

Except for proline, which undergoes a red shift, the visible absorption maximum of the 2:1 Cu(II) complexes in Table I exhibits a blue shift with an increase in intensity upon N-methylation. In contrast, N-methylation produces a red shift (where the same number of extrema appear) in the visible CD of the 2:1 complexes. Though N-methylation usually produces a 2:1 complex with a more negative visible CD, this generalization is not true for L-glutamate nor the L-alanine complexes. Except for a small blue shift a solution containing a 1:1:1 mixture of Cu(II), *N*-methyl-L-alanine, and sarcosine gives visible CD and absorption results similar to that of the solution where glycine replaces sarcosine in Table I. The visible CD magnitudes for the 1:1:1 complexes with glycine are usually half those of the 2:1 N-methylated complexes. This statement is more strictly true for ordinary amino acids, where a solution containing nonaromatic amino acid, glycine, and Cu(II) in equimolar amounts exhibits half the visible CD of a solution containing a 2:1 complex of the L-amino acid.

The magnitude of the visible CD extremum from 600 to 625 nm for 2:1 Cu(II) complexes of aromatic amino acids is more than double the value obtained for solutions containing the corresponding 1:1:1 mixture with glycine. The smallest augmentation occurs in the 1:1:1 complex of *N*-methyl-L-phenylalanine, glycine, and Cu(II) where Table I shows that the Δε value is only 8% more than Δε/[optically active ligand] in the 2:1 complex. The 2:1 complexes of Cu(II) with phenylalanine and tyrosine with either an un-ionized or ionized phenolic group on the side chain all yield for the 2:1 complex Δε = −0.44 to −0.46. The corresponding 1:1:1 solutions with glycine give Δε = −0.29, −0.30, and −0.41, respectively, equivalent to augmentations of about 31% for the first two cases and 80% for tyrosine with an ionized phenolic group.

The CD and absorption of equimolar dipeptide complexes of Cu(II) and Pd(II) with and without an *N*-methyl group at the amino terminus are reported in Table III. Both Cu(II) and Pd(II) promote ionization of amide nitrogens so that dipeptide complexes of these metal ions at neutral pH are tridentate with amino nitrogen, ionized amide nitrogen, and carboxylate oxygen donor atoms (CuL^0). In basic solutions the water in the fourth coordination position about the Cu(II) complex undergoes ionization with $pK_9 \simeq 9.5$ to give $CuLOH^-$. The donor atom in the fourth

(11) E. W. Wilson, Jr., M. H. Kasperian, and R. B. Martin, *J. Amer. Chem. Soc.*, **92**, 5365 (1970).
(12) J. M. Tsangaris, J. W. Chang, and R. B. Martin, *ibid.*, **91**, 726 (1969).

position of the neutral Pd(II) complexes is an equilibrium mixture of H_2O and Cl^-.[13]

Substitution of hydroxide ion for water in the Cu(II) complexes of glycine-L-alanine and glycyl-L-leucine results in separation of a broad negative CD into two peaks with little increase in total area.[4] CD curves for the glycyl-L-alanine case appear in the literature.[14] As Table III shows, the negative peaks are already

TABLE III
CD AND ABSORPTION OF DIPEPTIDE COMPLEXES OF Cu(II) AND Pd(II)

	CuL^0		$CuLOH^-$		PdL^0	
Ligand, H_2L^0	$\Delta\epsilon$ (ϵ)	λ, nm	$\Delta\epsilon$ (ϵ)	λ, nm	$\Delta\epsilon$ (ϵ)	λ, nm
Sarcosyl-L-alanine	−0.28	705	−0.26	710	−0.60	380
	−0.05	550	+0.07	582	+0.36	315
			−0.13	504	−0.38	256
	(100)	640	(88)	638	(815)	332
Glycyl-L-alanine	−0.35	650	−0.32	680	−0.80	378
	+0.23	310	−0.15	510	+0.25	324
	(90)	635	(80)	636	(652)	333
Sarcosyl-L-leucine	−0.58	660	−0.53	670	−0.28	420
			+0.06	568	+0.07	365
			−0.13	500		
	+0.15	320	+0.16	315		
	−2.2	270	−2.3	260		
	(112)	638	(93)	634	(920)	339
	(3900)	242	(5000)	240		
Glycyl-L-leucine	−0.62	654	−0.61	662	−0.96	376
	+0.33	317	−0.17	500	+0.07	316
	−1.5	270				
	(86)	632	(78)	633	(700)	332

separated in neutral solutions of the Cu(II) complex of sarcosyl-L-alanine and addition of base produces a new positive CD peak at intermediate wavelengths. Upon increasing the pH an isosbestic point occurs at 550 nm and again there is little change in net area or the sums given in Table III. No CD or absorption peaks other than those listed in Table III appear below 900 nm in the sarcosyl-L-alanine complex. The $CuLOH^-$ complex of sarcosyl-L-leucine also exhibits a small positive CD peak.

Discussion

Four CD bands are apparent in the visible region for the 2:1 complex of *N*-methyl-L-alanine and Cu(II) as shown in Table I. Apparently this is the first instance in which all four d–d transitions have been located approximately for a two nitrogen and two oxygen donor system of Cu(II).[15] All the bands appear at wavelengths longer than 500 nm and only one band occurs at a wavelength longer than 700 nm. This result contrasts with a claim of two CD bands between 700 and 900 nm in some 2:1 amino acid complexes of Cu(II).[16] We have conducted a careful search of the same and additional complexes in the CD to 900 nm for evidence of two bands at wavelengths longer than 700 nm. We find only one maximum beyond 700 nm and a smooth reduction in intensity as 900 nm is approached. We suggest that the irregularities previously reported[16] may be due to xenon arc lines. Some results from our long-wavelength studies are recorded in Table I. Assignments for the four transitions have been suggested.[4]

Six CD bands assigned to d–d transitions are tabulated for the 2:1 complex of *N*-methyl-L-alanine and Pd(II) in Table II. The four bands at wavelengths shorter than 400 nm are due to singlet–singlet transitions. Compared to the 2:1 L-alanine complex, an additional negative extremum appears at 374 nm. Evidently, only in the *N*-methyl complexes is this negative band sufficiently distinct from the shorter wavelength positive CD of greater intensity so that it appears as a separate entity. Applying the symbols of the D_{4h} parent group to the 2:1 *N*-methyl-L-alanine complex we suggest the following singlet assignments:[3] 374 nm to $A_{1g} \rightarrow A_{2g}$, oppositely signed CD at 344 and 313 nm to $A_{1g} \rightarrow E_g$, and 275 nm to $A_{1g} \rightarrow B_{1g}$. The last transition is magnetic dipole forbidden in the D_{4h} parent group and exhibits the lowest intensity. The two very weak CD bands observed at wavelengths longer than 400 nm are attributed to singlet–triplet transitions of the same designations as the nearest singlet–singlet transition with identical CD signs.

The relatively constant value $\Delta\epsilon = -0.44$ to -0.46 for the 2:1 Cu(II) complexes of L-amino acids with aromatic side chains suggests that they adopt a quasi-equatorial conformation so that they are directed toward the solvent in trans complexes. Side chains of L-amino acids appear on opposite sides of the chelate plane in cis complexes, but there seems to be little or no evidence for their being favored in aqueous solution.[17] In trans complexes side chains of L-amino acids may be able to interact with each other. However, the similar value $\Delta\epsilon = -0.45$ for the 2:1 L-tyrosine complex with negatively charged ionized phenolic groups suggests that the two side chains in one complex are directed away from each other. The augmentation of the visible CD magnitude in the 1:1:1 complexes of the aromatic amino acids with glycine above 50% of the 2:1 complexes suggests some restriction of motion perhaps by interaction of the aromatic ring with Cu(II) in the 1:1:1 complexes.[18]

A more dramatic change has been reported for the visible CD of 2:1 complexes of L-histidinol and Cu(II) and mixed 1:1:1 complexes with an optically inactive second ligand. The 2:1 complex exhibits a positive CD, 1:1:1 complexes of ligands with nitrogen donors exhibit less than half the magnitude of the 2:1 complex, and 1:1:1 complexes with glycine and oxalate exhibit a

(13) T. P. Pitner, E. W. Wilson, Jr., and R. B. Martin, unpublished experiments.

(14) R. S. Treptow, *J. Inorg. Nucl. Chem.*, **31**, 2983 (1969). In contrast to the negligible or small red shift due to the replacement of water by hydroxide ion observed upon adding base to the neutral copper(II)–dipeptide complexes, the neutral copper(II)–dipeptide–amide complexes exhibit a blue shift of about 35 nm. This blue shift coupled with the lack of an inflection point in the titration curve of only the dipeptide–amide complexes indicate that solutions containing copper(II)–dipeptide–amide complexes with average net zero charge are composed of mixtures of at least two complexes, CuL^0 and $CuHLOH^0$.

(15) S. W. Tang, J. E. Coleman, and Y. P. Myer, *J. Biol. Chem.*, **243**, 4286 (1968), have resolved the CD of the Cu(II) complex of glycylvaline at pH 10.4 into five bands by a Gaussian analysis. Since ionization of coordinated water occurs at about pH 9.5, the pH employed is low for exclusive occurrence of the $CuLOH^-$ complex. Nevertheless we feel that the resolution into one more band than the maximum permitted by theory is probably not due to the presence of more than one complex species but primarily to the failure of the CD envelope to be amenable to strict Gaussian analysis. This conclusion seems to be supported by the narrow bandwidths of the resolved bands. In other applications of Gaussian analysis these authors have assumed identity of frequency and bandwidths for transitions in absorption and CD spectra. These identities are not expected theoretically and to the extent that they are not borne out in practice additional resolved bands will be needed to fit observed spectra. In general the resolutions made by these authors appear to be over-Gaussed.

(16) T. Yasui, *Bull. Chem. Soc. Jap.*, **38**, 1746 (1965); T. Yasui, J. Hidaka, and Y. Shimura, *J. Amer. Chem. Soc.*, **87**, 2762 (1965).

(17) R. D. Gillard and S. H. Laurie, *J. Chem. Soc. A*, 59 (1970).

(18) D. van der Helm and W. A. Franks, *J. Amer. Chem. Soc.*, **90**, 5627 (1968); C. E. Tatsch and D. van der Helm, *Acta Crystallogr., Sect. A*, **25**, S192 (1969).

net negative CD with the latter magnitude about twice as negative as that for glycine.[19] The authors ascribed these differences to greater steric effects between bound nitrogen atoms than between nitrogen and carboxylate oxygen donors. However such pronounced differences due to steric effects are difficult to justify on the basis of space-filling molecular models, and we suggest that π bonding be considered as a source of the sign inversions observed. In support of this view we note that a 1:1:1 mixture of Cu(II), L-histidinol, and ethanolamine exhibits a positive CD peak with $\Delta\epsilon = +0.06$ at 560 nm. Furthermore, though the visible CD is negative for 2:1 L-alanine and 1:1:1 L-alanine complexes of Cu(II) with either glycine or 1,2-diaminoethane,[11] the 1:1:1 mixed complex of Cu(II) with L-alanine and histamine gives a small net positive CD with $\Delta\epsilon = +0.02$ and -0.01 at 550 and 638 nm, respectively. It does not seem to us possible to account convincingly for these results in terms of steric effects. We suggest instead that π bonding be considered as a mechanism for transmission of asymmetry in the ligand to the transition metal ion. In support of this view we note that the sign inversions occur in transitions involving the e_g orbitals of Cu(II) which are involved in out-of-chelate-plane π bonding. It is possible that some of the differences reported for CD of peptide complexes when the side chains are in the amino terminal rather than in the second or third residues and ascribed to steric effects of bulky side chains[4] are due in part to differences between the tetrahedral amino nitrogen and ionized amide nitrogens that are capable of π bonding.

It is striking that a net negative CD sign obtains for magnetic dipole allowed d–d transitions in transition metal ion complexes of typical L-amino acids such as L-alanine and their derivatives and of (+)-1,2-diaminopropane, which is related configurationally to L-amino acids (both ligands belong to the *S* configuration). From a perusal of the literature the list includes the tetragonal complexes of Ni(II),[2] Cu(II),[4,16] Pd(II),[3,10] Pt(II),[10] and Au(III)[10] and, where the arrangement of chelate rings about the metal ion is not a factor, the octahedral complexes of Cr(III),[20] Co(II)[21,22] (high- and low-spin components), Co(III),[23] Ni(II),[22] and Rh(III).[24] As we have pointed out previously for tetragonal Cu(II),[4] Ni(II),[2] and Pd(II)[3] complexes the CD magnitudes of alaninamide and 1,2-diaminopropane complexes are similar despite nearly planar and extensively puckered chelate rings in the two cases. Either the main contributor to the optical activity is vicinal effects of substituents in both kinds of complexes or, if conformational effects are dominant in the substituted diaminoethane type complexes, some other factor such as π-electron interactions must be important in generating optical activity of similar magnitude in the d–d bands of the more nearly planar amino acid complexes.

In the amino acid complexes the *N*-methyl group should appear on the opposite side of the chelate ring from the acid side chain for steric reasons. Assuming an approximate tetrahedral amino nitrogen, the methyl group appears in a hexadecant below the chelate plane of the same sign as that containing the amino acid side chain. The net CD magnitudes of the N-methylated amino acids should then be more negative than those of their nonmethylated counterparts. Since the magnitudes for the 2:1 complexes of nonaromatic amino acids are double those of the 1:1:1 complexes, the first and last columns of $\Delta\epsilon$ values in Tables I and II may be compared directly. Greater net negative visible CD magnitudes are observed for *N*-methyl-L-amino acids compared to L-amino acids with large side chains, in agreement with the prediction of the hexadecant rule. Quantitatively the net differences in visible and ultraviolet CD magnitudes of 2:1 Cu(II) complexes of N-methylated and ordinary amino acids fall into two groups. For the first three amino acids of Table I the difference in the visible CD is 0.0 ± 0.1 while for the last four amino acids the difference is -0.4 ± 0.1. The net differences for the Pd(II) complexes of Table II are +0.3, 0.0, and −0.4, respectively. Therefore the magnitude and even the sign of the difference in CD between N-methylated and ordinary amino acids appear to depend upon the size of the amino acid side chain. Similar uncertainties appear in comparing CD of stereospecific Co(III) complexes of *N*-methyl-L-alanine and *N*-methyl-L-leucine with the corresponding nonmethylated amino acid complexes.[25] Evidently both vicinal effects of substituents and conformational effects contribute to the CD of N-methylated amino acid complexes.

The consequences of a change in solvation of coordinated amino groups on CD have not been considered directly in this discussion. Rather than merely replacing a hydrogen atom with a methyl group, N-methylation might better be viewed as substitution of a methyl group for hydrogen with a hydrogen-bonded water molecule. The multiple effects expected might be unraveled by investigations of solvent variation and of N-alkylation with other groups.

An attempted application[26] of the hexadecant rule to Co(III) complexes of substituted ethanediamines with D_{4h} microsymmetry seems incomplete. Since it is the net CD sign over all magnetic dipole allowed d–d transitions that is significant, the CD spectra shown are not enantiomorphous as claimed and it is questionable whether sector rules may be applied to individual transitions.[6] In addition a separation of the CD into vicinal and conformational contributions was not attempted. Perusal of results[8] for Co(III) complexes of D_{4h} microsymmetry reveals that the CD magnitude of complexes composed of two optically active substituted diaminoethane ligands is not double that of a corresponding complex with one optically active center. This situation complicates interpretation of the CD of such complexes though synthesis and study of some interesting ligands[27] should aid in any attempt.

Though most of the changes are small, N-methylation of the dipeptide complexes of Cu(II) and Pd(II) shown in Table III tends to reduce the net negative CD for the d–d transitions. Examination of space-filling molecular

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models reveals no interaction between the *N*-methyl and *C*-methyl groups in sarcosyl-L-alanine. Therefore the distribution of *N*-methyl groups might be equal above and below the chelate plane, effecting a cancellation of any contribution to the optical activity from this source provided the contributions of *N*- and *C*-methyl groups are additive. The results for the first two compounds of Table III indicate that the situation is somewhat more complicated than the simple suggestion. Complexes of Cu(II) with but two nitrogen and two oxygen donors appear to require at least a fifth ligand in an apical position.[7] A water molecule in the fifth position might favor the situation where both methyl groups of sarcosyl-L-alanine lie on the same side of the Cu(II) chelate plane opposite that of the water molecule. Any effects ascribable to a fifth ligand in a Cu(II) complex should be diminished or absent in the corresponding more strongly tetragonal Pd(II) complex.

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Copper(III) and Nickel(III) Complexes of Biuret and Oxamide

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Bis-biuretato complexes of Cu(II) and Ni(II) $K_2M(Rbi)_2$ (where M is Cu or Ni, and Rbi is the dianion HNCONRCONH formed by deprotonation of the corresponding biuret, R = H or alkyl) can be oxidized to $KM(Rbi)_2$ in which the metal has the oxidation number III. Nmr, ir, and magnetic susceptibility studies of these compounds revealed that these ligands are bonded *via* their N atoms, most probably in a planar coordination around the metal. The oxidation occurs in aqueous solutions at a potential of 0.50–0.65 V (relative to a saturated calomel electrode); in DMSO the reaction is a reversible one-electron transfer at $E_{1/2} = -0.35$ V as was shown by polarographic measurements. Two H_2O or $RbiH_2$ molecules can be bonded to the coordinated biuretate groups, most probably *via* H bridges. A bis-oxamidato complex $KCu(HNCOCONH)_2$ could be prepared with analogous properties. The stabilizing influence of these ligands on the high oxidation states of the metals is thought to be due to the very strong electron-donating capacity of the deprotonated amine groups.

Introduction

In a previous short communication[1] we have reported the preparation and the properties of bis-biuretato complexes of Cu(III) and Ni(III) with compositions of $KCu(bi)_2$ and $KNi(bi)_2$, respectively, wherein bi is the dinegative ion HNCONHCONH formed by deprotonation of biuret ($H_2NCONHCONH_2$ = biH_2). The further study of these compounds was seriously hampered by their extremely low solubility. We now succeeded in preparing analogous complexes derived from the alkyl-substituted biuretate ions (of the type HNCONRCONH) which are soluble in acetone, alcohol, and DMSO, allowing a more detailed study. With respect to the oxidation to a Cu(III) complex the dianionic form of oxamide (HNCOCONH = oxam) behaves in the same way as the biuretate ion. We shall report here about the preparation and the properties of these compounds in which Cu and Ni have the uncommon oxidation state III. The specific influence of the ligands leading to a stabilization of these high oxidation states will be discussed.

Experimental Part

$K_2Cu(bi)_2$, $K_2Ni(bi)_2$, and $K_2Cu(oxam)_2$ were prepared according to known methods.[2,3]

Preparation of $KCu(bi)_2$.—(a) A solution of $K_2Cu(bi)_2$ was prepared by dissolving 2.2 g of biuret, 2.5 g of $CuSO_4 \cdot 5H_2O$, and 3 g of KOH in 25 ml of water. When an excess of $K_2S_2O_8$ was added to this solution, the compound $KCu(bi)_2$ precipitated immediately. The compound was filtered off, washed with hot water (70°), and dried in a vacuum desiccator.

(b) When the above-mentioned $K_2Cu(bi)_2$ solution was electrolyzed between Pt electrodes, $KCu(bi)_2$ was precipitated on the anode. The anode potential, measured with an auxiliary saturated calomel electrode, was 0.50 V. The compound was collected, washed with water, and dried.

(c) $KCu(bi)_2$ was formed when air with some hydrogen chloride was bubbled through a suspension of $K_2Cu(bi)_2$ in benzene. On further study, uv irradiation, formerly reported to be necessary,[1] appeared to be redundant.

Anal. Calcd for $KCu(bi)_2$: Cu, 20.85; K, 12.84; C, 15.76; H, 1.97; N, 27.58. Found: Cu, 20.95; K, 12.72; C, 15.61; H, 2.02; N, 27.25 (for a sample prepared according to method a, the other methods give analogous results).

Preparation of $KNi(bi)_2$.—The procedures a and b, as described for $KCu(bi)_2$, but now starting with $NiSO_4$, were possible. Method b gave a very poor yield. The electrode potential, measured relative to saturated calomel electrode was 0.50 V. Preparation according to procedure c was impossible. *Anal.* Calcd for$KNi(bi)_2$: Ni, 19.57; K, 13.04; C, 16.02; H, 2.02; N, 28.01. Found: Ni, 19.60; K, 13.10; C, 16.22; H, 2.13; N, 27.25.

Preparation of $KCu(Rbi)_2 \cdot 2H_2O$.—The preparation of pure 3-alkylbiuret appeared to be very difficult. The recipe of Weith[4] for the preparation of 3-phenylbiuret, modified to produce 3-alkylbiuret, yielded a mixture of products, among which were 3- and 1-alkylbiuret. The separation of 3-alkylbiuret was very difficult and will be published elsewhere. In the next sections we give methods to prepare $KCu(3\text{-}Rbi)_2 \cdot 2H_2O$, R = propyl, starting with pure 3-propylbiuret and with the just mentioned reaction mixture.

(a) When 1 g of KOH was added to a solution of 0.5 g of $CuSO_4 \cdot 5H_2O$ and 1 g of 3-propylbiuret in 10 ml of water, Cu-

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