

of all of the nonhydrogen atoms yields a conventional reliability factor of 0.17. A difference Fourier computed with this model shows no peaks greater than 1.3 electrons. The carbon-carbon ring distances vary considerably, and this as well as the high-temperature factors of the carbon atoms may indicate that the rings are rotationally disordered, that they are undergoing large librations, or that some of the carbon atoms are still incorrectly positioned.

The idealized molecular structure, with virtual C_{3v} symmetry, is shown in Figure 1. The equilateral triangle of manganese atoms has directly below it one triply bridging nitrosyl and, along each side and bent up above the metal atom plane, a doubly bridging nitrosyl group. The cyclopentadienyl rings are placed off the points of the triangle and slightly bent down away from the doubly bridging nitrosyls. Interestingly, the local environment of the manganese atoms in this trimeric structure is identical with that first postulated¹ for the hexamer. The Mn-Mn distances, the only ones known with some accuracy at present, lie in the range 2.47–2.57 Å (mean, 2.50 Å).

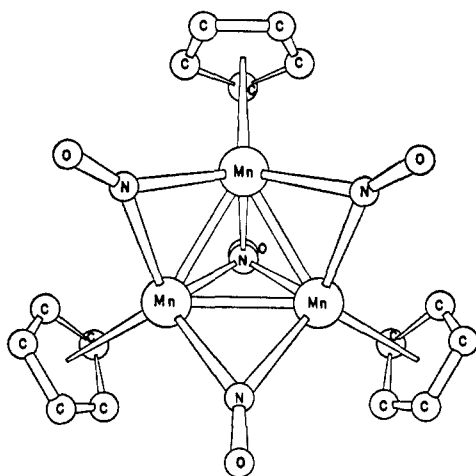


Figure 1. The idealized structure of $(\pi\text{-C}_5\text{H}_5)_3\text{Mn}_3(\text{NO})_4$ showing C_{3v} symmetry.

The infrared spectrum of a KBr pellet consists of three bands as reported earlier.¹ In CHCl_3 solution, strong bands appear at 1543, 1481, and 1328 cm^{-1} with a shoulder at 1348 cm^{-1} . The bands at ~ 1480 and 1530 cm^{-1} can presumably be assigned to the A_1 and E modes of the set of three doubly bridging NO groups, while the band at $\sim 1320\text{ cm}^{-1}$ is due to the triply bridging NO. Thus the trinuclear structure explains the spectrum. Only a single nmr peak (τ 4.94 in CHCl_3) is observed, and there is a very weak parent ion peak at 480 in the mass spectrum.

Finally, the only direct evidence originally given for the hexanuclear formula, molecular weight measurements (apparently by vapor pressure osmometry in benzene), has been reexamined. It appears that the solubility of the compound in benzene is too low to permit reliable molecular weight determinations. Moreover, the solutions are so intensely colored as to obscure the presence of undissolved solid. Thus spuriously high results could be obtained. However, measurement of CHCl_3 solutions at 37° by vapor pres-

sure osmometry yields a molecular weight of 500 ± 20 (calculated for trinuclear molecule, 480).⁶

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Optical Rotatory Dispersion Spectra of Bis- and Mono(α -substituted glycinate)copper(II) Complexes

Sir:

The steric interaction between chelate rings in octahedral cobalt(III) complexes with diamines is well established.^{1a} This interaction in cobalt(III) complexes is clearly reflected in their optical activity.^{1b} In the case of bis chelate complexes of copper(II) the situation is not clear. Recently Gillard and co-workers have interpreted spectroscopic and stability constant results to imply no stereoselectivity.² In any case, the consequence of electronic and/or steric effects of one chelate ring upon the optical rotatory dispersion (ORD) of the cross-plane chelate ring in these bis complexes is unanswered. It is to this question that this communication is directed.

In order to study these effects, it was desired to measure a mixed bis complex composed of optically active amino acid, optically inactive ligand, and cupric ion. ORD measurements of these labile complexes in solution were accomplished by taking advantage of the unique feature of ORD and circular dichroism (CD) for detecting only the optically active species in solution. Thus, mixing an excess of a bis copper(II) complex containing the desired mixing ligand with a bis-(amino acid)-copper(II) complex will yield a solution containing the mixed, optically active complex and excess inactive complex. Using this technique the ORD curves in the visible region were measured for a variety of 1:1:1 amino acid-mixing ligand-copper(II) complexes. The Cotton effect amplitudes, which are a measure of the rotational strength³ of the d-d metal band absorption, are shown in Table I; mixing ligands are glycine (Gly), α,α -dimethylglycine (DMG), DL-alanine (DL-Ala), ethylenediamine (en), DL-propylenediamine (DL-pn), and oxalic acid (ox). In general, the bis(amino acid) complexes have a Cotton effect centered near $615\text{ m}\mu$. The mixed complexes underwent a blue shift (*ca.* $25\text{ m}\mu$) and a red shift (*ca.* $25\text{ m}\mu$), respectively, for the diamino and oxalato mixing ligands. Small,

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(2) R. D. Gillard, H. M. Irving, R. M. Parkins, N. C. Payne, and L. D. Pettit, *J. Chem. Soc., Sect. A*, 1159 (1966).

(3) A. Moscovitz in "Optical Rotatory Dispersion: Applications to Organic Chemistry," C. Djerassi, Ed., McGraw-Hill Book Co., Inc. New York, N. Y., 1960, Chapter 12.

Table I. Molecular Amplitudes [ϕ] (in Degrees) of 2:1 and 1:1:1 Square-Planar Copper(II) Complexes^a (ca. 10^{-3} M, pH \sim 8)

Amino acid of parent 2:1 Cu(II) complex	Parent 2:1 complex	[ϕ] $\times 10^{-2}$					
		Mixing ligands ^b (%)					
		Gly	DL-Ala	DMG	en	DL-pn	Oxalate
L- α -Alanine	-3.40	-1.70 (50)	-1.80 (53)	-1.90 (56)	-1.43 (42)	-1.48 (43)	-1.90 (56)
L- α -Aminobutyric acid	-7.4	-3.60 (49)	-3.80 (52)	-4.20 (57)	-2.99 (41)	-3.10 (42)	-3.60 (49)
L-Norvaline	-7.8	-3.85 (49)	-4.10 (53)	-4.50 (58)	-3.43 (44)	-3.45 (44)	
L-Leucine	-6.3 ^c	-3.15 (50)		-3.15 (50)			
L-Valine	-13.1	-6.40 (49)	-6.65 (51)	-7.35 (57)	-5.52 (42)	-5.68 (43)	-6.20 (47)
L-Isoleucine	-15.0	-7.41 (49)	-7.60 (51)	-7.95 (53)	-6.90 (46)	-6.91 (46)	-7.90 (53)
L-Phenylglycine ^d	-25.0	-12.5 (50)	-13.0 (52)	-13.4 (54)	-11.8 (47)	-11.8 (47)	-11.7 (47)

^a A Cary Model 60 spectropolarimeter was used for all measurements. Reproducibility varied from ca. $\pm 3\%$ in the L- α -alanine series to $\pm 1\%$ in the L-phenylglycine series. Because the mixed diamine complexes were in a more accessible spectral region, the precision is better; the reverse is true for the mixed oxalate complexes. ^b Values in parentheses are [ϕ]_{1:1}/[ϕ]_{2:1} $\times 100$. ^c This value was estimated from the value for the 1:1:1 mixed glycine complex since the parent 2:1 complex was insoluble. ^d The material used was D-phenylglycine, which was generously furnished by Kay-Fries, Chemicals, Inc.

random shifts were observed when the mixing ligand was an amino acid. A fivefold excess of inactive mixing ligand as the bis complex gave essentially a completely mixed 1:1:1 complex since larger excesses gave identical results.

An interesting feature of the data in Table I is that, whereas there is a sevenfold variation in the amplitude of the metal band Cotton effects, the diminution in amplitude in the bis(amino acid) complexes *vs.* the 1:1:1 mixed complex is approximately 50% in all cases (see values in parentheses in Table I). This is particularly evident with the glycine mixing ligand whose 1:1:1 complexes exhibit precisely a 50% diminution within experimental error. The mixed complexes with DL-Ala show only a slightly higher amplitude (ca. 2%) than the glycine complexes even though the mixed DL-Ala complexes are most certainly a composite of diastereomers. The trend to higher amplitudes for the mixed complexes with α substitution in the mixing ligand is amplified with DMG, the increase over the glycine complexes being an average of ca. 5%. On the basis of these results, where the ligand field about the metal is changing negligibly, it can be concluded that changing steric requirements of the mixing ligand has a negligible or small effect on the Cotton effect amplitude of the d-d transition. The lack of a cross-plane steric effect as a factor in the magnitude of the metal band rotational strength is further evidenced by the Cotton effects of the mixed ethylenediamine and DL-propylenediamine complexes. Again, the mixed DL-propylenediamine-amino acid complexes are undoubtedly diastereomeric mixtures; nevertheless, the Cotton effects for the mixed en and DL-pn complexes are identical within experimental error.

On the other hand, changes in the ligand field strength as a result of changing from 2:1 amino acid complexes to 1:1:1 mixed complexes involving either a diamine or oxalate ligand also exert only a small effect upon the d-d Cotton effect. Thus, the ethylenediamine mixed complexes show a diminution to 41-47% of that for the parent 2:1 amino acid complex, whereas the mixed oxalate complexes give Cotton effect amplitudes on the order of 48-56% of the amplitudes of the 2:1 complexes.⁴

It is evident from these results that *cross-plane, steric, and electronic interactions between ligands and ligand*

(4) In the case of mixed oxalate complexes, preliminary CD data indicate the diminution is actually 43-49%.

field changes have small or negligible effects on the Cotton effect amplitudes of a d-d transition in an amino acid-copper(II) complex.

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Relationship of Ring Conformation to Rotational Strengths of d-d Transitions in Amino Acid-Copper(II) Complexes

Sir:

In the preceding communication¹ data are presented which demonstrate negligible vicinal interactions on the visible optical rotatory dispersion (ORD) curves of a variety of amino acid-copper(II) complexes. On the other hand, the rotational strengths, as measured by the Cotton effect amplitudes, were found to be very sensitive to the substituted glycine (RCHNH₂COOH). Thus, the d-d transition amplitudes for the 2:1 or 1:1:1 complexes show a sevenfold variation with the effect of the R group being in the order CH₃ < CH₂-CH₃ < CH₂CH₂CH₃ < CH(CH₃) < CH₂Ph \leq Ph.

In order to gain further insight into the nature of substituent effects on the ORD spectra of copper(II) chelate systems, we have measured the spectra of several amino acid-copper(II) complexes with special emphasis placed on those amino acids which could act as tridentates. The Cotton effect amplitudes for the d-d transition are given in Table I. The visible region ORD curves of several 1:1:1 amino acid-glycine-copper(II) complexes are presented in Figure 1 for comparison.

Recently, Mason and Norman have argued that the optical activity of trigonal complexes is due in a large measure to mixing of d-d with charge-transfer transitions involving both the chelate ligand and metal.² Hence, the optical activity can be expected to be sensi-

(1) K. M. Wellman, T. G. Mecca, W. Mungall, and C. R. Hare, *J. Am. Chem. Soc.*, **89**, 3646 (1967).
(2) S. F. Mason and B. J. Norman, *Chem. Commun.*, 48 (1965).