quartet peak was split into a doublet ($|J| = 2$ cps), caused by long-range coupling of the proton at C_1 through the exocyclic double bond. Assignment of the other resonances obtained for phycocyanobilin followed directly from those of mesobiliverdin.

Mass spectral analyses[5] showed both phycocyanobilin and mesobiliverdin dimethyl ester had a strong molecular ion which required the empirical formula $C_{35}H_{42}N_4O_6$ as its base peak at *m/e* 614. The stabilities of the fully conjugated pigment systems were analogous to that of alkylated dipyrrylmethenes[6] in which fragmentation occurred primarily at the side-chain positions rather than at the methine bridge. In the case of the tetrapyrrole pigments most of the peaks with a high *m/e* ratio could be accounted for by the successive fragmentation of the propionic ester side chains. They did, however, show appreciable cleavage at the central methine bridge. Phycocyanobilin differed from mesobiliverdin in that it had an intense peak (97% of base) at *m/e* 599, which would be consistent with cleavage of the methyl group at the saturated carbon atom C_1. The results presented above are in agreement with the structure[7] proposed for phycocyanobilin (Figure 1, top), or with the β substituents of rings A and D interchanged. A tetrapyrrolic structure with the same ring A substituents has recently been proposed for aplysioviolin.[8] The structure for phycocyanobilin is further validated by its simple isomerization, when boiled under reflux with 1 *N* potassium hydroxide in methanol for 15 min, to a product identical, chromatographically, and in melting point, ultraviolet–visible, infrared, and nmr spectra, with mesobiliverdin.

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(5) Determined with an AEI MS-9 mass spectrometer by W. Milne, National Institutes of Health, Bethesda, Md.

(6) A. H. Jackson, G. W. Kenner, H. Budzikiewicz, C. Djerassi, and J. M. Wilson, *Tetrahedron*, **23**, 3642 (1967).

(7) This structure is similar to but not identical with that proposed by H. L. Crespi, L. J. Boucher, G. Norman, J. J. Katz, and R. C. Dougherty, *J. Am. Chem. Soc.*, **89**, 3642 (1967).

(8) W. Rüdiger, *Z. Physiol. Chem.*, 348, 129 (1967).

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Tri(cyclopentadienylmanganese)tetranitrosyl. A Metal Cluster Compound with Doubly and Triply Bridging Nitrosyl Groups

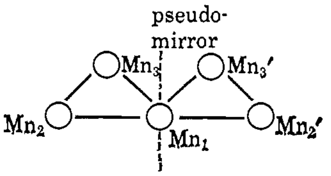
Sir:

King and Bisnette[1] have reported a compound which they formulated as $(\pi\text{-}C_5H_5)_6Mn_6(NO)_8$, and for which they proposed a cyclohexane-like ring of Mn atoms with six doubly bridging and two triply bridging NO groups (symmetry D_{3d}; should have two NO bands in the infrared). Other hexanuclear structures have also been proposed;[2] none of the structures fits the observed infrared spectrum if the three NO stretching bands (1520, 1475, 1313 cm^{-1} for the solid) are correctly assigned.

Because of the uncertainties regarding the structure of this unusual substance, further investigations were undertaken. A preliminary report is presented here.[3]

Single crystal X-ray diffraction studies have shown that this substance is, in fact, a trinuclear compound, $(\pi\text{-}C_5H_5)_3Mn_3(NO)_4$, containing a triangular array of manganese atoms in which the occurrence of bridging nitrosyl groups, of both the double and triple types, is substantiated for the first time by X-ray methods. Black, seemingly crystalline material, kindly supplied by Dr. R. B. King, was in the shape of hexagonal tablets, but examination with the precession camera showed it to be a microcrystalline mass. Recrystallization of this material yielded a small number of crystals which were twinned. A new batch of the compound was then prepared and recrystallized from a chloroform–pentane mixture. Most of these crystals were also twinned but three single crystals were obtained. The cell constants determined for the twinned crystals of King and the single crystals we prepared are the same, thus confirming the identity of our compound with that of the compound prepared by King. They are $a = 13.34 \pm 0.01$, $b = 7.95 \pm 0.03$, $c = 16.82 \pm 0.01$ A; $\beta = 107.8 \pm 0.1°$. The space group, determined uniquely from the systematic absences, is $P2_1/c$. From the density (1.88 ± 0.05 g cm^{-3}) the unit cell must contain 12 manganese atoms or one-half of the proposed hexanuclear molecule as the asymmetric unit.

Attempts to solve the structure by Patterson techniques showed a pseudo-centering translation in Patterson space and did not yield a useful model of the structure. Attempts to resolve the structure using superposition functions were equally fruitless. The heavy atom structure was finally determined by MAGIC,[4] a digital computer program using the Hauptman–Karle methods to determine the signs of reflections in centric structures. The structure is disordered by the presence of a pseudo-mirror plane perpendicular to the a axis at $x = {}^1/_4$. One of the manganese atoms lies approximately in this plane and is reflected into itself appearing at full weight in the Fourier synthesis. The remaining two metal atoms are reflected through this plane to form a second triangle, thus



The last four manganese atoms all appear at about one-half the height of the first one. This solution of a disordered structure seems indicative of the wide usefulness of such methods.

Successive Fourier syntheses computed with signs fixed by the model allowed the resolution of all nonhydrogen atoms except two of the carbon atoms, which, from the ring geometry, can be presumed to superpose on Mn_2 and Mn_2' due to the disorder. Least-squares refinement of positional and temperature parameters

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(1) R. B. King and M. B. Bisnette, *Inorg. Chem.*, 3, 791 (1964).

(2) *Cf.* B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, 7, 346 (1966). These include a more compact D_{3d} (not S_6) structure and a cubic structure (proposed independently by F. A. Cotton and E. L. Muetterties, assuming a hexanuclear molecule; the cubic structure should have but one NO stretch in the infrared).

(3) Further refinement of the crystal structure is being carried out by R. C. Elder at the University of Chicago and will be reported later.

(4) E. B. Fleischer, A. L. Stone, and R. B. K. Dewar, "MAGIC—Multiphase Automatic Generation from Intensities in Centric Crystals," program for IBM 7094 computer, University of Chicago, March 1966.

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 postulated[1] for the hexamer. The Mn–Mn distances, the only ones known with some accuracy at present, lie in the range 2.47–2.57 A (mean, 2.50 A).

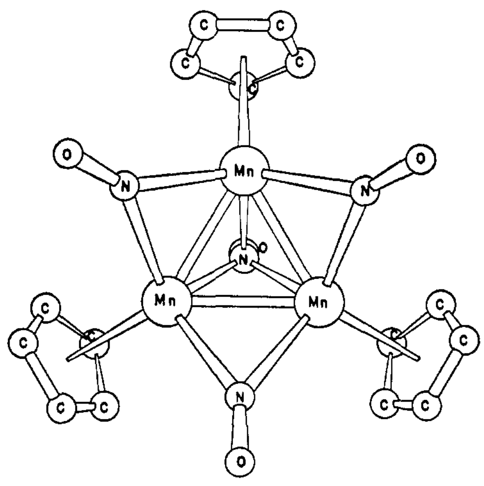

Figure 1. The idealized structure of $(\pi\text{-}C_5H_5)_3Mn_3(NO)_4$ showing C_{3v} symmetry.

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 ~1320 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 pressure osmometry yields a molecular weight of 500 ± 20 (calculated for trinuclear molecule, 480).[5]

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Optical Rotatory Dispersion Spectra of Bis- and Mono(α-substituted glycinato)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 strength[3] 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 mμ. The mixed complexes underwent a blue shift (*ca.* 25 mμ) and a red shift (*ca.* 25 mμ), respectively, for the diamino and oxalato mixing ligands. Small,

(1) (a) F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *J. Am. Chem. Soc.*, 85, 661 (1963); F. P. Dwyer, F. L. Garvan, and A. Shulman, *ibid.*, 81, 290 (1959); (b) A. J. McCaffery, S. F. Mason, and B. J. Norman, *Chem. Commun.*, 49 (1965).

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