

directly within the microwave cavity by reduction of millimolar solutions of the neutral parent molecule using acetonitrile as solvent.¹ Detailed e.s.r. and polarographic data for compounds in the table as well as several related compounds currently being studied will be presented in detail elsewhere.

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BIRADICALS IN THE KETYL SERIES¹

Sir:

We have reported previously that the paramagnetic molecules formed on reduction of hexamethylacetone and pentamethylacetone by sodium or lithium are characterized by hyperfine splittings in which each unpaired electron spin is coupled to the nuclei in one ketone molecule and two equivalent alkali metal nuclei.² Dimeric molecules in which the two organic radicals are joined through two equivalent alkali metal ions could account for the observations. Such molecules are biradicals with each electron spin belonging predominantly to one-half of the dimer but sharing the two alkali metal nuclei with the other electron spin. The sharing refers to a time average and does not imply simultaneous presence of the electron spins at a particular site.

We have carried out new experiments with ketyls of the alkaline earths which suggest the formation of biradicals in which the two radicals are joined by a single divalent alkaline earth ion. Reduction of xanthone or benzophenone by magnesium, calcium, or barium in ethereal solvents leads in each case to a single paramagnetic species with hyperfine couplings to the protons in one molecule of the original ketone. The proton coupling constants are slightly dependent on the positive ion, varying monotonically with size of the positive ion. No trace of the dissociated ions is observed. The electron transfer reactions between the dimeric ketyls, both aliphatic and aromatic, and their parent ketones are too slow ($k < 10^5 M^{-1} \text{sec}^{-1}$) to be measured by e.s.r. spectroscopy, while the reaction of the monomeric aromatic ketyls of the alkali metals are very rapid ($k > 10^8 M^{-1} \text{sec}^{-1}$)³

Use of magnesium enriched to 93% of ²⁵Mg yields further evidence bearing on the constitution of the ketyls. In the case of benzophenone magnesium ketyl the expected splitting by one ²⁵Mg nucleus ($I = 5/2$) is observed. The interval between adjacent components is 0.3 gauss. The other ketyls with ²⁵Mg exhibit a broadening of all lines, but no well-resolved ²⁵Mg splitting.

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(2) N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **82**, 4424 (1960).

(3) F. Adam and S. Weissman, *ibid.*, **80**, 1518 (1958).

The lack of observable coupling between the electronic spin in the biradicals here reported as well as in others previously described is a matter of some theoretical interest.⁴ We are continuing experimental studies of radicals bound together by various metal ions, including tripositive ones, in order to gather further information concerning spin couplings in many electron systems.

(4) H. M. McConnell, *J. Chem. Phys.*, **33**, 115 (1960); *ibid.*, **33**, 1868 (1960).

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THE STEREOCHEMISTRY OF AN ETHYLENEDIAMINETETRAACETATO COMPLEX OF MANGANESE(II)¹

Sir:

In further elucidation of the frequently unorthodox stereochemistry^{2,3} of ethylenediaminetetraacetato (EDTA, Y⁻⁴) chelates, we have utilized spectrometrically measured X-ray diffraction data from the acid salt, Mn[Mn(OH₂)HY]₂·8H₂O, to give the remarkable structural features noted below. The monoclinic cell containing 2Mn[Mn(OH₂)HY]₂·8H₂O has $a = 9.21$, $b = 16.10$, $c = 11.88 \text{ \AA}$, $\beta = 90.60^\circ$; the space group is P2₁/n. Intensity counts were taken with MoK α radiation for all forms $\{hkl\}$ in the range, $0 < (\sin \theta)/\lambda < 0.96$. Results given herein are based upon the data for $(\sin \theta)/\lambda < 0.67$, comprising 4440 forms of which 90% are recordable above background. Objective analysis by Patterson and Fourier methods, with subsequent partial refinement by difference syntheses, yield structural configurations with rather accurate bond parameters. Thermal parameters range from 1.50 \AA^2 for manganese in the anion to above 3 \AA^2 for oxygen in some water molecules. The discrepancy index for all 4440 forms is 0.10.

Manganous ions in fourfold positions of P2₁/n are centered in sexadentate seven-coördinate aquo complexes, [Mn(OH₂)HY]⁻. The geometry of the inner coördination group is not that reported³ for [Fe(OH₂)Y]⁻, but is roughly that of the sterically superior NbF₇⁼ configuration^{2,4} (*cf.* ref. 4 for diagram). Bond lengths, to the nearest 0.005 \AA , are Mn-O, 2.210–2.260 \AA , average of five, 2.235 \AA ; Mn-N, 2.350, 2.395 \AA . Apart from those angles and bonds which involve the central atoms, the geometry of ring systems is very like that expected from earlier studies^{5,6} of CoY⁻ and Ni(OH₂)H₂Y. Manganous ions in twofold ($\bar{1}$) positions of P2₁/n display octahedral coördination; each such ion is bonded to four water molecules and two not otherwise complexed oxygen

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(2) *Cf.* J. I. Hoard, G. S. Smith and M. Lind in "Advances in the Chemistry of Coördination Compounds," C. Stanley Kirschner, The Macmillan Company, New York, N. Y., July, 1961.

(3) J. L. Hoard, M. Lind and J. V. Silverton, *J. Am. Chem. Soc.*, **83**, 2770 (1961).

(4) J. L. Hoard, *ibid.*, **61**, 1252 (1939).

(5) H. A. Weakliem and J. I. Hoard, *ibid.*, **81**, 549 (1959).

(6) Gordon S. Smith and J. L. Hoard, *ibid.*, **81**, 556 (1959).