concentration, and the concentration of small organic molecules. Further work is in progress. It seems clear, however, that nuclear relaxation studies of appropriately constituted enzymes may offer a powerful probe into the dynamics of the interactions between protein active sites and substrate-like molecules.

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[19] NDEA Fellow, 1966–1969.

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A New Type of Fluxional Molecule. Bis-μ-dimethylgermyl-dicobalt Hexacarbonyl

Sir:

We report here the observation of a type of intramolecular rearrangement which is rapid and interconverts equivalent nuclear configurations (*i.e.*, the molecule exhibiting it is fluxional) and which appears likely to have some scope and generality.

The molecule we have studied is $[(CH_3)_2Ge]_2Co_2(CO)_6$, **1**, which is one of several products isolated from reaction[1] of $(CH_3)_2GeH_2$ with $Co_2(CO)_8$ in toluene at $-78°$. The substance is characterized by satisfactory analyses for Co, C, and H, by its mass spectrum (*m/e* 491 (parent ion) and peaks corresponding to ions formed by loss of from one to six CO groups), ir spectrum (in CS_2 C–H stretches at 2960 (m) and 2900 (w) cm^{-1} and CO stretches at 2063 (s), 2028 (vs), 2002 (vs), 1990 (vs), 1960 (m, sh), and 1940 (w, sh, ^{13}C) cm^{-1}), as well as by its pmr spectrum described below.

Figure 1 shows the 100-MHz pmr spectrum of **1** at several temperatures. All methyl protons give a single sharp line at room temperature, but this line broadens, collapses, and is eventually replaced by two peaks of equal intensity which are sharp at $-89°$. Rates estimated from line widths follow the Arrhenius equation with $\Delta E = 15 \pm 1$ kcal/mol.

We propose that the molecule has structure I, which is analogous to that[3] of $Co_2(CO)_8$. The methyl groups on a given germanium atom lie in different environments, as emphasized by diagram II, which is similar to a Newman projection of an ethane-like structure. The low-temperature spectra are consistent with this structure and collapse of the two methyl peaks to a single one on raising the temperature shows that syn and anti methyl groups interchange rapidly at room temperature.

In a nonmechanistic sense the minimal required rearrangement steps can be described as II $\rightleftarrows$ III $\rightleftarrows$ IV, etc. From a more explicit or realistic point of view we consider traversal of the configuration V to be the most plausible of the various alternatives we have considered.[4,5] In each of its stable configurations,

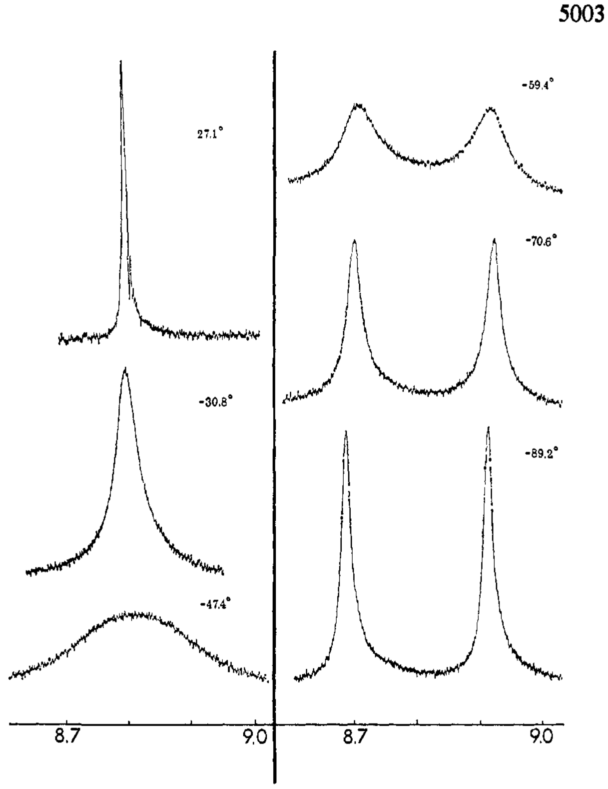
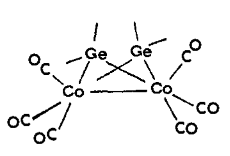
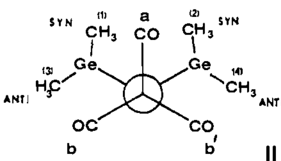


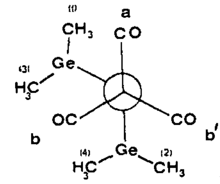
Figure 1. The pmr spectrum of $[(CH_3)_2Ge]_2Co_2(CO)_6$, **1**, at several temperatures. Recorded at 100 MHz in 2/1, v/v, CF_2Cl_2–CH_2Cl_2 solvent.



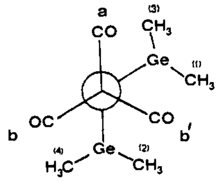
I



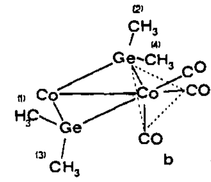
II



III



IV



V

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[1] Reaction[2] of $(C_6H_5)_2GeH_2$ with $Co_2(CO)_8$ apparently gave no digermyl product, but only $(C_6H_5)_2GeCo_2(CO)_7$.

[2] S. A. Fieldhouse, B. H. Freeland, and R. J. O'Brien, *Chem. Commun.*, 1297 (1969).

[3] G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Crystallogr.*, 17, 732 (1964).

[4] Simple inversion of the four-membered Co–Ge–Co–Ge ring is inadmissible; it cannot lead to an equivalent configuration unless accompanied by some rearrangement of the $Co(CO)_3$ groups tantamount to a rotation about the local approximate threefold axis.

[5] A transition state or intermediate having nonbridging $(CH_3)_2Ge$ groups behaving as carbene analogs, in which rotation about an unbridged Co–Co bond might lead to the observed methyl group interchange, is considered unlikely, though it is not actually ruled out by present evidence. Rapid bridged–nonbridged–bridged interconversion

the molecule has approximately square-pyramidal coordination about each cobalt atom; in II CO_a occupies the unique or axial position of the pyramid. In V the coordination about each cobalt atom is more nearly trigonal bipyramidal with $(CH_3{}^{(1)})(CH_3{}^{(3)})Ge–Co^{(1)}–CO_{b'}$, for example, constituting a pseudothreefold axis. A trigonal-bipyramidal configuration is simultaneously assumed at the other cobalt atom, but for clarity this is not explicitly shown in the sketch.

The proposed rearrangement pathway is interesting in that it is the converse of the now widely accepted Berry mechanism[9] for site exchange in trigonal-bipyramidal molecules by way of a square-pyramidal intermediate or transition state. We are not aware that there has been any previous proposal of the converse rearrangement, but, given the premise of a preferred square-pyramidal configuration, it is, *mutatis mutandis*, as natural and appealing as the Berry mechanism.

There are several aspects of the type of phenomenon reported here still to be explored, *e.g.*, the influence of the M–M bond on access to the postulated transition state, whether simultaneous site exchange of CO groups occurs in a manner consistent with the postulated mechanism, etc., and these are under study.[10]

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is believed to occur quite commonly where bridging CO groups are concerned,[6,7] but carbene-like, *i.e.*, terminal CO groups are decidedly stable, whereas stable carbene-like R_2Ge groups have not been observed.[8]

(6) E. A. C. Lucken, K. Noack and D. F. Williams, *J. Chem. Soc. A*, 148 (1967).

(7) J. G. Bullitt, F. A. Cotton, and T. J. Marks, *J. Amer. Chem. Soc.*, **92**, 2155 (1970).

(8) The transient existence of H_2Ge in the gas phase has been postulated by P. Estacio, M. D. Sefcik, E. K. Chan, and M. A. Ring, *Inorg. Chem.*, **9**, 1068 (1970).

(9) (a) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960); (b) G. M. Whitesides and H. L. Mitchell, *J. Amer. Chem. Soc.*, **91**, 5384 (1969); (c) K. E. DeBruin, K. Naumann, G. Zon, and K. Mislow, *ibid.*, **91**, 7031 (1969).

(10) This work was supported in part by the National Science Foundation under Grant No. GP-7034X. We thank Mr. C. M. Lukehart for generous assistance in recording spectra and Mr. T. J. Marks for useful discussions.

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Chemistry of the Iron–Dithiooxalate Complexes

Sir:

Our studies of the metal–dithiooxalato complexes[1] have revealed two unique characteristics of the coordinated dithiooxalate ligand: (a) the ability of the carbonyl groups to function as donors for Lewis acids,[1] and (b) a conjugated system different from that of the formally analogous 1,2-dithiolate ligands.[2]

The former of these characteristics makes it possible to alter the donor properties of the coordinated sulfur atoms by withdrawing electron density at the oxygen sites, while the latter accounts for the absence of redox properties due to thiol–thione interconversions. A study of the chemistry of the tris(dithiooxalato)iron(III) complex has produced two results which are attributed to the unique properties of the dithiooxalate ligand: (a) isolation of both the high-spin ($^6A_1$ ground state) and low-spin ($^2T_2$ ground state) forms of an iron–sulfur complex by altering the charge distribution within the sulfur ligand, and (b) reversible oxidation which gives rise to a chemically reactive oxidation product. These results, which are summarized in Table I and Figure 1, have not been previously encountered in the thoroughly studied[2,3] iron–sulfur coordination chemistry.

The tetraphenylarsonium, Ph_4As, salt of the tris(dithiooxalato)iron(III) trianion, $Fe(Dto)_3{}^{3-}$,[4] was prepared by extracting an aqueous solution of $K_3Fe(Dto)_3$ with a dichloromethane solution of Ph_4AsCl. The crude product isolated from the dichloromethane solution was recrystallized from cold nitromethane, whereby crystals of I were obtained. The magnetic moment of I (2.30 BM at 300°K)[6] and the abnormally large Curie–Weiss constant[7] of −42°K are values similar to those obtained for the ferric thioxanthate complexes,[9] in which both the $^6A_1$ and $^2T_2$ states are populated at room temperature.[10] We were unable to observe the existence of a $^2T_2$–$^6A_1$ equilibrium for the $Fe(Dto)_3{}^{3-}$ complex by epr spectroscopy, since spectra could not be obtained at either 300 or 78°K. At 1°K a strong absorption was observed which is attributed to the $^2T_2$ ground state.

In the $Fe(Dto)_3{}^{3-}$, the proximity of the ligand field to the $^2T_2$–$^6A_1$ cross-over point is suggested by the fact that perturbations reducing the ligand-field strength cause an unpairing of spins and result in a $^6A_1$ ground state.

Specifically, the $Fe(Dto)_3{}^{3-}$ complex was used as a ligand for the $(Ph_3P)_2Cu^+$ and $(Ph_3P)_2Ag^+$ cations, and by an extraction procedure identical with the one described for I, the crystalline, *high-spin*, X-ray-isomorphous $[(Ph_3P)_2Cu]_3Fe(Dto)_3$ (II) and $[(Ph_3P)_2Ag]_3$-$Fe(Dto)_3$ (III) complexes (Table I) were isolated. The carbonyl stretching frequencies at 1380 cm^{-1} and strong bands at 310 cm^{-1}, which we tentatively assign to the Fe–S stretching vibration, suggest a structure similar to that shown in Figure 1 for these complexes.[11] The epr powder spectrum of III is characteristic of a $S = {}^5/_2$ system with $g = 2.000 \pm 0.002$ and an estimated value for a of 0.5 Gc.[12a]

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(1) D. Coucouvanis, *J. Amer. Chem. Soc.*, **92**, 707 (1970).

(2) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

(3) (a) D. Coucouvanis, *ibid.*, **11**, 233 (1970); (b) D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *J. Amer. Chem. Soc.*, **90**, 3281 (1968), and references therein; (c) L. H. Pignolet and R. H. Holm, *ibid.*, **92**, 1791 (1970); (d) A. L. Balch, *ibid.*, **91**, 6962 (1969).

(4) The anilinium salt of this anion was first reported in ref 5, but was incorrectly formulated as the ferrous complex $(C_6H_5NH_3)_2Fe(Dto)_2$.

(5) C. S. Robinson and H. O. Jones, *J. Chem. Soc.*, 62 (1912).

(6) The moments of $KBaFe(Dto)_3 \cdot 6H_2O$[7] and $KBaFe(Dto)_3 \cdot 4H_2O$[8] have also been reported as 2.28 and 2.95 BM, respectively.

(7) R. L. Carlin and F. Canziani, *J. Chem. Phys.*, **40**, 371 (1964).

(8) F. A. Dwyer and A. M. Sargeson, *J. Amer. Chem. Soc.*, **81**, 2335 (1959).

(9) The tris(ethyl thioxanthate)iron(III) complex has been reported to have a magnetic moment of 2.57 BM at 300°K and a "pseudo" Curie–Weiss constant of −85°K.[10]

(10) A. H. Ewald and E. Sinn, *Aust. J. Chem.*, **21**, 927 (1968).

(11) Stannic chloride interacts in a similar fashion with the $Fe(Dto)_3{}^{3-}$ complex anion, and the anion $[Fe(Dto)_3(SnCl_4)_2]^{3-}$ was isolated as the crystalline Ph_4As^+ salt. The C–O absorptions were also observed at 1380 cm^{-1} in this complex.

(12) (a) The spectrum was tentatively analyzed with the spin Hamiltonian[12b]

$$H = g\beta\vec{H}\vec{S} + (a/6)[Sx^4 + Sy^4 + Sz^4 - {}^1/_5S(S + 1)(3S^2 + 3S - 1)]$$

A crystal structure determination of III is currently in progress. (b) B. Bleaney and K. W. H. Stevens, *Rep. Progr. Phys.*, **16**, 108 (1953).