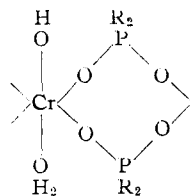


in benzene. The resulting solution is then separated from the small quantity of benzene insolubles (less than 0.3 g.) by filtration and evaporated at room temperature in a stream of nitrogen to yield II. Final drying is at 120°. *Anal.* Calcd. for $C_{12}H_{13}CrO_6P_2$: C, 55.25; H, 4.43; Cr, 10.0; P, 11.88. Found: C, 56.39; H, 4.36; Cr, 9.7; P, 11.93. Yields vary from 70 to 95%. The intrinsic viscosity of II prepared in this manner is 0.6 to 0.7 in chloroform. Less rigorously controlled conditions lead to polymers with intrinsic viscosities from 0.1 to 0.5. Even unfractionated samples with viscosities in the range 0.12 to 0.20 have number average molecular weights greater than 10,000 as determined by ebulliometry and vapor pressure osmometry in chloroform. Consequently, the higher-viscosity samples certainly have molecular weights of at least several tens of thousands.

Although any of the groups present in II could serve as bridging groups, the most probable structure contains a double-bridged backbone similar to that suggested for $Cr(AcCHAc)(OP(C_6H_5)_2O)_2^1$ except that a *cis* configuration is not required. The infrared spectrum of II contains absorption peaks characteristic of PO_2 stretching with virtually the same frequency and absorption profile as found for polymeric $Cr(AcCHAc)(OP(C_6H_5)_2O)_2$.¹ This is strong evidence that the diphenylphosphinate anion is functioning in the same way in both polymers. Furthermore, the hydroxyl group and the water O-H stretching vibrations can be identified separately at frequencies which suggest they are normally coordinated groups. Thus infrared indicates that the hydroxyl groups are not bridging groups. The solubility of II in benzene or chloroform accompanied by marked swelling and the high intrinsic viscosity values are good evidence for the presence of linear chains as the predominating species with cross-linking only of minor importance. The indications are, then, that the repeat unit is



Thermogravimetric analysis of II shows initial weight loss at 375° with a step in the 410–430° region which corresponds to a 3–10% weight loss. No polymer melt temperature has been observed up to or well beyond the decomposition point. Surprisingly the polymer shows remarkable resistance to hydrolysis and other chemical degradation. For example, no change in intrinsic viscosity is observed upon refluxing a suspension of the polymer in water for several hours. A cast film of high-viscosity II plasticized with 30% Aroclor 1254 has a tensile strength of over 1900 p.s.i.

In addition to the diphenyl species described here we have also been able to prepare the analogs with phenylmethylphosphinate, dimethylphosphinate and cacodylate bridging groups. The mechanism by which this kind of polymer forms is not clear. It would appear that the intermediate I could be a polymer somewhat analogous to the phosphinate polymers involving zinc, beryllium and cobalt.² The oxidation step then may serve to increase the oxidation state of the chromium and introduce the additional ligands. Alternatively polymerization may be involved in the oxidation step.

Acknowledgment.—This investigation was supported in part by the Office of Naval Research. We are in-

debted to several of our colleagues for assistance with various experiments. Analytical data were supplied by our Analytical Department.

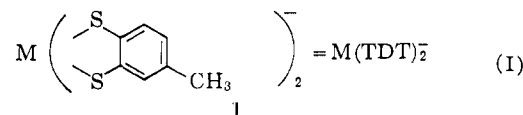
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RECEIVED APRIL 25, 1963

The Electronic Structures of Square-Planar Metal Complexes. III. High-Spin Planar Cobalt(I) and Iron(I)^{1,2}

Sir:

The reaction between toluene 3,4-dithiol and a number of divalent transition metal ions gives complexes which have the general formula



Formula I is established from analytical and conductance data in Table I. Magnetic susceptibility data in Table I indicate that the copper complex has $S = 0$, the nickel complex has $S = 1/2$, the cobalt complex has $S = 1$ and the iron complex has $S = 3/2$. The e.s.r. spectrum of an acetone solution of $Ni(\text{TDT})_2^-$ gives $\langle g \rangle = 2.08$; the $[(n-C_4H_9)_4N][Ni(\text{TDT})_2]$ powder gives $g_{\perp} = 2.045$ and $g_{\parallel} = 2.193$.³ The g -values show that the unpaired electron is mainly localized on the nickel. Further, the anisotropy in the g tensor is consistent with a d^9 planar situation. For comparison, planar $Cu(acac)_2$ has $g_{\perp} = 2.075$ and $g_{\parallel} = 2.254$.⁴

TABLE I
PROPERTIES $M(\text{TDT})_2^-$ COMPLEXES

Complexes	Analytical	Calcd.	Found	μ_{eff} (B.M.)	Λ°
$[(C_6H_5)_3As(CH_3)][Cu(\text{TDT})_2]$	C	57.17	56.79		
	H	4.36	4.97	Diamagnetic	85
$[(C_6H_5)_3As(CH_3)][Ni(\text{TDT})_2]$	C	57.57	57.49		
	H	4.39	4.37	1.89	91
$[(C_6H_5)_3As(CH_2)][Co(\text{TDT})_2]$	C	57.55	57.00		
	H	4.39	4.58	3.27	96
$[(C_6H_5)_3As(CH_3)][Fe(\text{TDT})_2]$	C	57.62	57.18		
	H	4.41	4.46	4.39	94

^a For 0.0001 M solutions in nitromethane at 25°; expressed in $\text{cm}^2 \text{mole}^{-1} \text{ohm}^{-1}$.

The electronic spectra of the $M(\text{TDT})_2^-$ complexes in acetonitrile show the following weak bands, which may be assigned to d-d transitions: $M = Ni$, 7300 cm^{-1} (ϵ 190); $M = Co$, 9300 cm^{-1} (ϵ 58), and a shoulder, indicative of a maximum at 11,300 cm^{-1} ($\epsilon \sim 100$); $M = Fe$, 7100 cm^{-1} (ϵ 45), 7900 cm^{-1} (ϵ 55), 9200 cm^{-1} (ϵ 65) and 10,300 cm^{-1} (ϵ 95). The X-ray powder patterns show that the $[(C_6H_5)_3As(Me)][M(\text{TDT})_2]$ complexes are isomorphous.

We conclude from the above evidence that the complexes are planar and are composed of M^+ and two dithiolate radical anion moieties. The unpaired electron which each radical anion would possess must be paired

(1) Paper II: E. Billig, R. Williams, I. Bernal and H. B. Gray, *Inorg. Chem.*, in press.

(2) The support of the National Science Foundation is gratefully acknowledged.

(3) Details of these experiments and e.s.r. experiments on similar Cu^{2+} complexes will be published by H. B. Gray, E. Billig and I. Bernal.

(4) B. R. McGarvey, *J. Phys. Chem.*, **60**, 71 (1956). Also, planar $Cu(\text{sali-cylaldimine})_2$ gives $g_x = 2.04$, $g_y = 2.05$ and $g_z = 2.20$: A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 35 (1958).

with its partner in the planar complex in one of the π -molecular orbitals of the complex.⁵

The $\text{Co}(\text{TDT})_2^-$ anion is the first example of a high-spin, planar d^8 metal complex. The exceptionally weak field of the TDT ligand is indicated from the position of the first band in $\text{Ni}(\text{TDT})_2^-$, which is tentatively assigned to the $d_{xy} \rightarrow d_{x^2-y^2}$ transition. For a Δ_1 ($xy \rightarrow x^2 - y^2$) in the neighborhood of 7000 cm.^{-1} , the planar Co^+ complex is predicted to be high-spin, even in the absence of axial interactions.⁶ Since the electronic spectrum of $[(\text{C}_6\text{H}_5)_3\text{As}(\text{CH}_3)][\text{Co}(\text{TDT})_2]$ is the same in acetone, acetonitrile and pyridine, axial effects probably are of no importance in this case.

The $\text{M}(\text{MNT})_2^{2-}$ complexes, which we reported earlier,⁷ on oxidation give $\text{M}(\text{MNT})_2^-$ complexes,⁸ which apparently are composed of M^+ and MNT radical anion moieties.⁹ Of interest is the reaction of Fe^{2+} and MNT, which gives $\text{Fe}(\text{MNT})_2^-$ directly. The $\text{Fe}(\text{MNT})_2^-$ complex has $S = 3/2$, with d-d electronic bands at practically the same energies as planar, high-spin $\text{Co}(\text{MNT})_2^{2-}$. Thus $\text{Fe}(\text{MNT})_2^-$ and $\text{Fe}(\text{TDT})_2^-$ are probably the first examples of high-spin Fe^+ in a planar situation. It is important to note that the ligand field strength of MNT is the same as a dianion with $d^7 \text{ Co}^{2+}$ and as a radical anion with $d^7 \text{ Fe}^+$.

(5) Evidence has been presented that the $\text{Ni} \left(\begin{array}{c} \text{S} \quad \text{C} \quad \text{Ph} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{S} \quad \text{C} \quad \text{Ph} \end{array} \right)_2$ complex

is planar and contains Ni^{2+} and two radical anions. The two odd electrons are supposedly paired in the π -molecular system of the complex; see G. N. Schrauzer and V. Mayweg, *J. Am. Chem. Soc.*, **84**, 3221 (1962). The

$\text{Ni} \left(\begin{array}{c} \text{S} \quad \text{C} \quad \text{Ph} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{S} \quad \text{C} \quad \text{Ph} \end{array} \right)_2$ complex can be reduced to $\text{Ni} \left(\begin{array}{c} \text{S} \quad \text{C} \quad \text{Ph} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{S} \quad \text{C} \quad \text{Ph} \end{array} \right)_2^-$, which

has $S = 1/2$ and shows a highly anisotropic e.s.r. spectrum; see ref. 8. The reduced complex may be electronically similar to $\text{Ni}(\text{TDT})_2^-$.

(6) C. J. Ballhausen and A. D. Liehr, *ibid.*, **81**, 538 (1959), suggested that high-spin, rigorously planar $d^8 \text{ Ni}^{2+}$ is possible for a Δ_1 less than $10,000 \text{ cm.}^{-1}$.

(7) The $\text{M}(\text{MNT})_2^{2-}$ complexes have been shown to consist of M^{2+} and two MNT $\left(\begin{array}{c} \text{S}^- \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{S}^- \\ \text{CN} \quad \text{CN} \end{array} \right)$ dianions. See ref. 1 and also H. B. Gray,

R. Williams, I. Bernal and E. Billig, *ibid.*, **84**, 3596 (1962).

(8) For $\text{M} = \text{Ni}$, Pd and Pt , see A. Davison, N. Edelstein, R. H. Holm and A. H. Maki, *ibid.*, **85**, 2029 (1963). We thank Dr. R. H. Holm for allowing us to see a preprint of these results prior to publication.

(9) Thus for the coplanar ring system, a stable electronic situation exists for either ten or twelve electrons in the π -molecular orbitals composed of the nine p (π) valence orbitals. We are now carrying out a complete molecular orbital analysis of these systems.

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RECEIVED APRIL 23, 1963

An Unusual Boron Exchange Reaction¹

Sir:

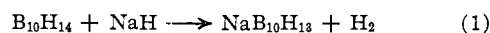
We wish to report an unprecedented type of exchange reaction involving complete isotopic substitution in a B_{10} framework. Previous studies of exchange and interconversion processes in boron hydrides and boron hydride ions containing ten or more boron atoms have concentrated almost exclusively² on exchange and tracer experiments using deuterium. Deuterated decaboranes have been prepared specifically labeled in a variety of positions by exchange of

(1) Interconversion of Boranes. VII. For paper VI of this series see D. F. Gaines, R. Schaeffer and F. Tebbe, *Inorg. Chem.*, **2**, 526 (1963).

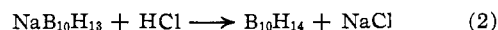
(2) Absence of boron exchange between ^{10}B labeled diborane, $^{10}\text{B}_2\text{H}_6$, and normal decaborane, $\text{B}_{10}\text{H}_{14}$, has been demonstrated: I. Shapiro and R. E. Williams, *J. Am. Chem. Soc.*, **81**, 4787 (1959).

decaborane with diborane- d_6 ,³ deuterium oxide,^{4,5} or deuterium chloride,⁶ and by reaction of the monosodium salt of decaborane, $\text{NaB}_{10}\text{H}_{13}$, with deuterium chloride.⁴ Although within the limits of these experiments decaborane and the closely related salt $\text{NaB}_{10}\text{H}_{13}$ have appeared immune to framework disruptions, the initial results in the present study of skeletal rearrangements in the higher boron hydrides indicate that diborane undergoes complete boron interchange with $\text{NaB}_{10}\text{H}_{13}$ in ethereal solution.

A sample of $\text{NaB}_{10}\text{H}_{13}$ was prepared^{4,7} by reaction of decaborane (0.778 mmole) of normal (20% ^{10}B) isotopic content with sodium hydride in diethyl ether solution. Hydrogen evolution according to the equation



was complete (97.3% of calculated) within 25 min. at room temperature. The solution was filtered under vacuum to give a pale yellow filtrate. Diborane, 96.4% ^{10}B (4.58 mmoles), was condensed into the flask and the contents were warmed to 0° and shaken for 1 hr., during which time no hydrogen formed. By mass spectrometric analysis the ^{10}B content of the recovered diborane was shown to have decreased to 62.7%, in close agreement with the value calculated (61.9% ^{10}B , taking into account the incomplete hydrogen evolution for (1)) for diborane exchange with all ten borons of the $\text{NaB}_{10}\text{H}_{13}$. Boron-10 enriched decaborane was recovered by treatment of the solution with hydrogen chloride^{4,7} according to the equation



With suitable recorder amplitude variation, the ^{11}B n.m.r. spectrum of the ^{10}B enriched decaborane was nearly coincident with an isotopically normal decaborane spectrum, in agreement with the mass spectral determination of participation of all boron positions.

Although the $\text{NaB}_{10}\text{H}_{13}$ structure has not been determined, it is probable, from the n.m.r. spectrum⁸ and the ready interconversion of decaborane and the salt by (1) and (2) (presumably involving primary removal and replacement of a bridge proton⁴), that the boron skeleton is similar to that of decaborane. With the implication that, in the absence of diborane, the boron framework of $\text{NaB}_{10}\text{H}_{13}$ undergoes neither dissociative nor internal rearrangement,⁴ it therefore seems more probable that in ^{10}B exchange the borane- ^{10}B ($^{10}\text{BH}_3$) adds to the normal $\text{B}_{10}\text{H}_{13}^-$, forming an exchange intermediate of over-all composition $\text{B}_{11}\text{H}_{16}^-$, capable of losing an isotopically normal borane to regenerate $\text{B}_{10}\text{H}_{13}^-$ containing the labeled boron in a position different from that originally occupied by the leaving boron. Considering only the boron framework, a model meeting these requirements can be formed by adding a boron to a decaborane-like cage between the 5 and 10 positions⁹ to produce an icosahedral fragment with 11 of the 12 positions occupied, similar to the boron structure proposed¹⁰ for the known¹¹ $\text{B}_{11}\text{H}_{14}^-$ ion. If the labeled boron is capable of losing its identity among the five top borons, perhaps by tautomerism of the ten

(3) J. J. Kaufman and W. S. Koski, *ibid.*, **78**, 5774 (1956).

(4) J. J. Miller and M. F. Hawthorne, *ibid.*, **81**, 4501 (1959).

(5) I. Shapiro, M. Lustig and R. E. Williams, *ibid.*, **81**, 838 (1959).

(6) (a) M. F. Hawthorne and J. J. Miller, *ibid.*, **80**, 754 (1958); (b) J. A. Dupont and M. F. Hawthorne, *ibid.*, **84**, 1804 (1962).

(7) W. V. Hough and L. J. Edwards, Abstracts of Papers, 133rd National Meeting of the American Chemical Society, San Francisco, Calif., 1958, p. 28-L.

(8) N. J. Blay, R. J. Pace and R. L. Williams, *J. Chem. Soc.*, 3416 (1962).

(9) The numbering system used is reproduced in ref. 5.

(10) E. B. Moore, L. L. Lohr and W. N. Lipscomb, *J. Chem. Phys.*, **35**, 1329 (1961).

(11) V. D. Aftandilian, H. C. Miller, G. W. Parshall and E. L. Muetterties, *Inorg. Chem.*, **1**, 734 (1962).