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Molecular Orbital Theory for the Pentachlorocuprate(II) Ion

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The modified Wolfsberg–Helmholz method has been used to calculate the energy levels in the pentachlorocuprate(II) ion. The Coulomb energies of copper were estimated by an iteration process to be −110,000, −82,000, and −40,000 cm.$^{-1}$ for the 3d, 4s, and 4p orbitals, respectively. The hydride ion ionization potential method was used to estimate the Coulomb energies for chlorine. The values used in the calculation were −103,000, −114,600, and −184,600 cm.$^{-1}$ for the 3pπ, 3pσ, and 3s orbitals, respectively. The agreement between the observed spectrum and the calculated energies is satisfactory.

A number of applications[1-5] of the semi-empirical molecular orbital treatment of transition metal complexes devised by Wolfsberg and Helmholz[6] and modified by Ballhausen and Gray[7] have been made recently. The limitations of the modified Wolfsberg–Helmholz method have been discussed.[8] Here the results of the calculations of the energy levels of the pentachlorocuprate(II) ion are reported.

Molecular Orbital Calculation

Linear Combinations of Ligand Orbitals.—The coordinate system used is shown in Figure 1. Linear combinations of ligand orbitals transforming as irreducible representations of the point group D_{3h} were constructed by standard methods, and linear combinations of these corresponding to the metal orbitals are given in Table I.

TABLE I

ORBITAL TRANSFORMATION SCHEME

Irreducible representation	Metal orbitals	Linear combinations of ligand orbitals
a_1'	s	$1/\sqrt{5}(z_1 + z_2 + z_3 + z_4 + z_5)$
	d_{z^2}	$\sqrt{3/10}(z_4 + z_5) - \sqrt{2/15}(z_1 + z_2 + z_3)$
a_2''	p_z	$1/\sqrt{2}(z_4 - z_5)$
		$1/\sqrt{3}(x_1 + x_2 + x_3)$
a_2'	None	$1/\sqrt{3}(y_1 + y_2 + y_3)$
e'	p_x, p_y	$(p_x)\ 1/\sqrt{6}(2z_1 - z_2 - z_3)$
		$(p_y)\ 1/\sqrt{2}(z_2 - z_3)$
		$(p_x)\ 1/\sqrt{2}(y_2 - y_3)$
		$(p_y)\ 1/\sqrt{6}(2y_1 - y_2 - y_3)$
		$(p_x)\ 1/\sqrt{2}(x_5 - x_4)$
		$(p_y)\ 1/\sqrt{2}(x_4 - y_5)$
	d_{xy}, $d_{x^2-y^2}$	$(d_{x^2-y^2})\ 1/\sqrt{6}(2z_1 - z_2 - z_3)$
		$(d_{xy})\ 1/\sqrt{2}(z_2 - z_3)$
		$(d_{x^2-y^2})\ 1/\sqrt{2}(y_2 - y_3)$
		$(d_{xy})\ 1/\sqrt{6}(2y_1 - y_2 - y_3)$
e''	d_{xz}, d_{yz}	$(d_{xz})\ 1/\sqrt{6}(2x_1 - x_2 - x_3)$
		$(d_{yz})\ 1/\sqrt{2}(x_2 - x_3)$
		$(d_{xz})\ 1/\sqrt{2}(x_5 + y_4)$
		$(d_{yz})\ 1/\sqrt{2}(x_4 + y_5)$

Overlap Integrals.—Atomic overlaps were computed for us by the Molecular Structure Group at the University of Chicago using the SCF functions for Cu^+ reported by Richardson and his co-workers[9] and Slater functions for chlorine.[10] Interatomic distances for the $CuCl_5^{3-}$ ion in $[Cr(NH_3)_6][CuCl_5]$ have been reported by Mori.[11] The values of the atomic overlap integrals are given in Table II.

Group overlap integrals were computed. The expressions and corresponding numerical values are given in Table III.

Valence State Ionization Energies.—The energy levels were obtained from the secular equation

$$|H_{ij} - G_{ij}E| = E$$

The diagonal terms, H_{ii}, were estimated to be the VSIE for the Cu ion of appropriate charge which was determined by the previously described iteration process.[1] The ionization energies for various valence states of integral charge were obtained from Moore's[12] tables of atomic spectra. The Coulomb energies corresponding to the self-consistent electronic charge and configuration are given in Table IV.

The hydride ion ionization potential method[1-3] was used to estimate the H_{ii} for chlorine. The ionization energy of HCl has been determined by three methods[13] and the results are summarized below.

Method	Ionization potential, cm.$^{-1}$
Electron impact	101,818
Photon impact	102,786
Spectroscopic	104,077

The mean of the three values, ~ 103,000, was taken to be the ionization potential for the 3pπ level. From the spectroscopic data for chlorine[12] the 3s and 3pσ levels were placed at −184,600 and −114,600 cm.$^{-1}$, respectively.

The off-diagonal terms were approximated from

$$H_{ij} = -2G_{ij}\sqrt{H_{ii}H_{jj}}$$

Energy Level Diagram.—The secular equations

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(1) H. D. Bedon, S. M. Horner, and S. Y. Tyree, *Inorg. Chem.*, **3**, 647 (1964).

(2) R. F. Fenske and C. C. Sweeney, *ibid.*, **3**, 1105 (1964).

(3) A. Viste and H. B. Gray, *ibid.*, **3**, 1113 (1964).

(4) H. D. Bedon, W. E. Hatfield, S. M. Horner, and S. Y. Tyree, *ibid.*, **4**, 743 (1965).

(5) F. A. Cotton and T. E. Haas, *ibid.*, **3**, 1004 (1964).

(6) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

(7) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

(8) R. F. Fenske, *ibid.*, **4**, 33 (1965).

(9) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962); J. W. Richardson, R. R. Powell, and W. C. Nieuwpoort, *ibid.*, **38**, 796 (1963).

(10) L. L. Lohr and W. N. Lipscomb, *Inorg. Chem.*, **2**, 911 (1963).

(11) M. Mori, *Bull. Chem. Soc. Japan*, **34**, 295 (1961).

(12) C. E. Moore, "Atomic Energy Levels," U. S. National Bureau of Standards Circular 467, 1949 and 1952.

(13) J. E. Collins, *Can. J. Chem.*, **40**, 2172 (1962).

TABLE II

VALUES OF ATOMIC OVERLAP INTEGRALS

Interatomic distance, Å.	$S_{3d\sigma,3s\sigma}$	$S_{4s\sigma,3s\sigma}$	$S_{4p\sigma,3s\sigma}$	$S_{3d\sigma,3p\sigma}$	$S_{4s\sigma,3p\sigma}$	$S_{4p\sigma,3p\sigma}$	$S_{3d\pi,3p\pi}$	$S_{4p\pi,3p\pi}$
2.32[a]	0.05578	0.26504	0.43567	0.07712	0.22465	0.28613	0.03112	0.14962
2.35[b]	0.05311	0.25688	0.42600	0.07384	0.22048	0.28533	0.02904	0.14403

[a] Axial copper–chlorine interatomic distance. [b] Equatorial copper–chlorine distance.

TABLE III

GROUP OVERLAP INTEGRALS

Irreducible representation	Group overlap[a]
a_1'	$3/\sqrt{5}S_{4s\sigma,3s\sigma_e} + 2/\sqrt{5}S_{4s\sigma,3s\sigma_a} = 0.5827$
	$3/\sqrt{5}S_{4s\sigma,3p\sigma_e} + 2/\sqrt{5}S_{4s\sigma,3p\sigma_a} = 0.4968$
	$\sqrt{6/5}S_{3d\sigma,3s\sigma_e} + \sqrt{3/10}S_{3d\sigma,3s\sigma_a} = 0.0902$
	$\sqrt{6/5}S_{3d\sigma,3p\sigma_e} + \sqrt{3/10}S_{3d\sigma,3p\sigma_a} = 0.1239$
a_2''	$\sqrt{2}S_{4p\sigma,3s\sigma_e} = 0.6161$
	$\sqrt{2}S_{4p\sigma,3p\sigma_e} = 0.4045$
e'	$\sqrt{3/2}S_{4p\sigma,3s\sigma_e} = 0.5219$
	$\sqrt{3/2}S_{4p\sigma,3p\sigma_e} = 0.3495$
	$\sqrt{3/2}S_{4p\pi,3p\pi_e} = 0.1764$
	$\sqrt{2}S_{4p\pi,3p\pi_a} = 0.2116$
	$3/2\sqrt{2}S_{3d\sigma,3s\sigma_e} = 0.5635$
	$3/2\sqrt{2}S_{3d\sigma,3p\sigma_e} = 0.07834$
	$\sqrt{3/8}S_{3d\pi,3p\pi_e} = 0.01778$
e''	$\sqrt{3/8}S_{3d\pi,3p\pi_e} = 0.01778$
	$\sqrt{2}S_{3d\pi,3p\pi_a} = 0.04401$

[a] Subscripts of a and e denote axial and equatorial overlaps, respectively.

TABLE IV

COULOMB ENERGIES FOR COPPER ORBITALS

	Charge	Electronic configuration	Orbital	$-H_{ii}$, cm.$^{-1}$
Input	$Cu^{+0.22}$	$3d^{9.95}4s^{0.59}4p^{0.24}$	4s	82,000
Output	$Cu^{+0.23}$	$3d^{9.95}4s^{0.58}4p^{0.24}$	4p	40,000
			3d	110,000

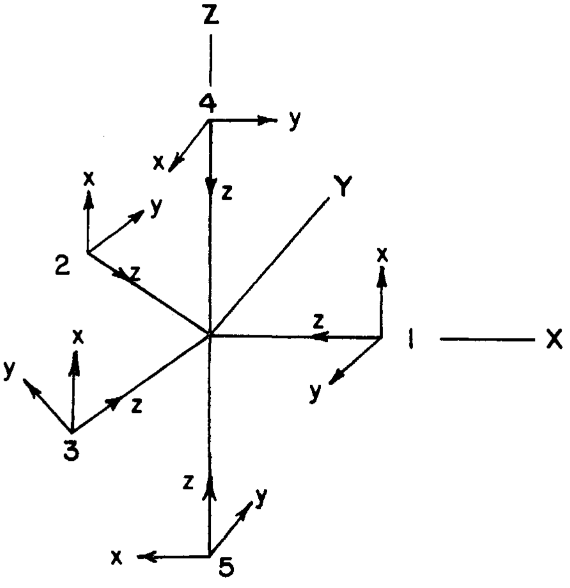

Figure 1.—The coordinate system that was used to construct the linear combinations of ligand orbitals. The metal coordinates are denoted by capital letters and the ligand coordinates by small letters.

were solved using a GAT program written for the UNIVAC 1105 computer. The energy level diagram is presented in Figure 2.

Discussion

The spectrum of the pentachlorocuprate(II) ion has been considered previously.[14–16] The selection rules for optical transitions for D_{3h} are: $a_1' \nleftrightarrow a_2'$; $a_1' \leftrightarrow a_2''$; $a_1' \leftrightarrow e'$; and $a_1' \nleftrightarrow e''$. In Figure 3 the energies of the allowed transitions predicted from the theoretical energy levels are compared to the observed spectrum. The spectrum corresponds closely to the predicted transitions. The assignments of the bands as indicated by the results of these calculations are given in Table V. Perhaps the transitions $5a_1' \leftarrow 4a_1$ and $5a_1' \leftarrow 3a_1'$ are not as energetic as predicted and are also included under the high energy band envelope. In order to measure this band the compound $[Rh(NH_3)_6][CuCl_5]$ was prepared,[14] since the bands of the $[Co(NH_3)_6]^{3+}$ ion occur in the same region.

TABLE V

CALCULATED AND OBSERVED TRANSITIONS IN $CuCl_5^{3-}$

Band maxima, cm.$^{-1}$	Assignment	Calculated energy, cm.$^{-1}$
8,200	$5a_1' \leftarrow 5e'$	7,700
10,400	$5a_1' \leftarrow 3a_2''$	9,400
	$5a_1' \leftarrow 4e'$	9,500
	$5a_1' \leftarrow 3e'$	10,200
24,000	$5a_1' \leftarrow 2a_2''$	21,300
~26,000	$5a_1' \leftarrow 2e'$	26,400

Day[15] reported only one band in the spectrum of a single crystal of $[Co(NH_3)_6][CuCl_5]$, apparently at room temperature. We have resolved this envelope into two bands[14] at liquid nitrogen temperature on samples of both $[Rh(NH_3)_6][CuCl_5]$ and $[Co(NH_3)_6][CuCl_5]$ mulled in hexachlorobutadiene. By diffuse reflection, we, too, observed only one band.

Day and Jørgensen[16] have used a one-parameter empirical molecular orbital method to describe the energy levels in $CuCl_5^{3-}$. Their treatment predicted bands at 3.8, 9.2, and 23.9 kK. which they assigned to the transitions $A_1' \rightarrow E'$, $A_1' \rightarrow E''$, and "charge transfer," respectively. Their charge of +0.19 on the copper ion agrees closely with our self-consistent value of +0.22. Our treatment places the highest e'' level (at −100.1 kK.) above an e' level at −101.7 kK. However, it is unlikely that any significance can be placed on such small energy differences.

In conclusion we wish to make some general comments on this semi-empirical molecular orbital treat-

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[14] W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, **3**, 841 (1964).
[15] P. Day, *Proc. Chem. Soc.*, 18 (1964).
[16] P. Day and C. K. Jørgensen, to be published.

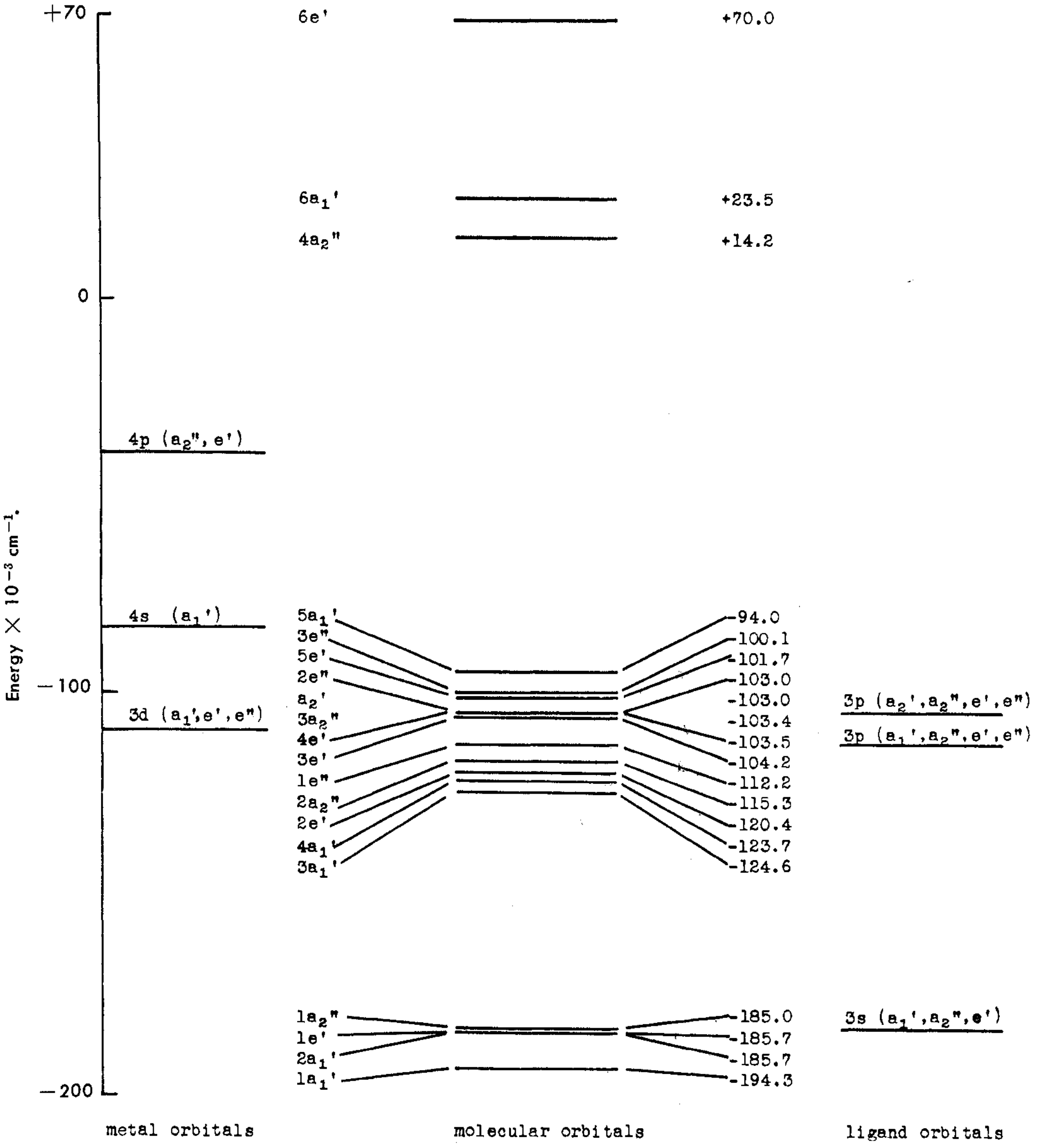

Figure 2.—Energy level diagram for $CuCl_5^{3-}$ (the usual connecting lines are not shown).

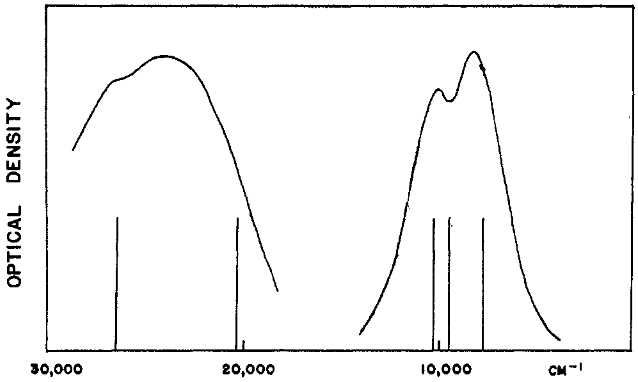

Figure 3.—The spectrum of the $CuCl_5^{3-}$ ion. The high energy band was obtained by the reflection method and the low energy band from a hexachlorobutadiene mull at 77°K., hence intensities cannot be compared. Predicted transitions are indicated by vertical lines.

ment of the electronic structure of inorganic complexes. In some instances[1,4,7] the method has predicted energy levels in good agreement with the observed spectra using hybridized ligand orbitals for σ-bonding. Hybridization of the oxygen atoms in permanganate by the criterion that $VSIE(\sigma)/S(\sigma)$ be a minimum did not prove to be successful for Fenske and Sweeney.[2] However, when both σ-bonding orbitals were included in the secular equation satisfactory agreement with the spectrum of MnO_4^- was obtained.[3] In this work, the ligand σ orbitals were not hybridized but both chlorine 3s and 3pσ orbitals were included in the secular equation. These arbitrary changes in the calculational procedures have been required because of the difficulty of estimating, among other things, the effect of the metal ion and other ligands on the Coulomb energies of the ligands. In an octahedral molecule the metal ion may alter these energies of the ligands to a different degree than the same metal ion would in a tetrahedral molecule. These difficulties are, of course, magnified in the estimation of the off-diagonal terms in the secular equation. After a complete series of compounds have been treated by a more rigorous theory it will be possible to make further modifications on this semi-empirical scheme.

For completeness we have calculated the energy level diagram using (1) hybridized ligand orbitals and (2) just chlorine p orbitals. The agreement between the predicted transitions and the observed spectrum was poor in both cases. However, we must point out that the apparent agreement between the predicted and observed transitions may only be an artifact of the calculational procedures. It would be desirable to have polarization data from spectral investigations of single crystals in order to confirm by selection rules the indicated assignments. We have been unable to find a suitable crystal for this experiment.

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Isotopic Fractionation in Electron-Transfer Reactions. The Role of Nonbridging Ligands

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The kinetic fractionation factors, d ln $[N^{14}]$/d ln $[N^{15}]$, for the nitrogen atoms in the ammine ligands of $Co(NH_3)_5OH_2^{3+}$, $Co(NH_3)_5Cl^{2+}$, $Co(en)_2NH_3Cl^{2+}$, and $Co(en)_2NH_3OH_2^{3+}$ during reactions with $Cr^{+2}(aq)$ have been measured. It is significant that they are very small (1.002 and 1.001) for the first two ions and that they are identical for NH_3 *cis* or *trans* to the bridging group. Thus, in these particular reactions, there seems to be little rearrangement in the Co–NH_3 residue attendant on electron transfer.

Some work has been done on oxidation–reduction reactions between metal ions in which a bridging ligand is involved.[2] In the reaction between $(H_3N)_5CoOH^{2+}$ and chromous ion,[3] the complexes containing O^{16} react faster than those made up of O^{18}, the fractionation factor[4] having the high value of 1.035. The observation indicates that in the transition state of the reaction, the Co–O distance is considerably greater than in the starting compound. As the formal charge on the cobalt atom falls from +3 to +2 during the reaction, part of this increase might be attributed to the concomitant expansion of the coordination shell as a whole.

We have investigated here the extent to which the stretching of bonds between the cobalt center and any nonbridging ligands occurs during oxidation–reduction processes, by studying the fractionation of N^{14} compared with N^{15} in the NH_3 groups of various cobaltic complexes.

A further point was also investigated. If one accepts Orgel's suggestion[5] that the electron entering the cobalt complex goes into the d_{z^2} orbital, which assumes that the tetragonal (C_{4v}) symmetry of the N_5CoX system is retained in the transition state (X being the bridging ligand and *z* the axis on which it lies), then the greatest fractionation should occur in the nitrogen atoms *trans* to the bridging group. By using bis-(ethylenediamine) complexes containing ammine and bridging ligands differently arranged, we have attempted to assess the amount of fractionation in the *trans* position and have compared it with that in the *cis*.

Experimental

The salt $[Co(NH_3)_5Cl](ClO_4)_2$ was obtained from its chloride, which was prepared following the procedure of Hynes, Yanowski, and Shiller.[6] $[Co(NH_3)_5OH]_2(ClO_4)_3$ was made by the action of perchloric acid on $[Co(NH_3)_5CO_3]NO_3$, generated by the method of Basolo and Murmann.[7] *trans*-$[Co(en)_2Cl_2]Cl$ was prepared by Bailar's[8] method and used to obtain *cis*- and *trans*-$[Co(en)_2NH_3Cl]Cl$ and crude *trans*-$[Co(en)_2NH_3H_2O]Br_3$ following the procedure of Werner.[9] The crude aquoammine complex was recrystallized from aqueous ethanol several times. We were unable, however, to obtain in sufficient quantity (2 g.) *trans* complex containing less than 10% of the *cis* isomer, our criterion of purity being the spectra of Nyholm and Tobe.[10] *cis*-$[Co(en)_2NH_3H_2O]Br_3$ was prepared utilizing Tobe's[11] observation that the *trans* isomer is converted entirely to *cis* at equilib-

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(1) Department of Chemistry, Stanford University, Stanford, Calif. 94305.

(2) For reviews, see H. Taube, *Can. J. Chem.*, **37**, 129 (1959); R. T. M. Fraser, *Rev. Pure Appl. Chem.*, **11**, 64 (1961).

(3) (a) R. K. Murmann, H. Taube, and F. A. Posey, *J. Am. Chem. Soc.*, **79**, 262 (1957); (b) H. R. Hunt and H. Taube, *J. Phys. Chem.*, **63**, 124 (1959).

(4) An isotopic fractionation factor, *f*, is defined as $X'\,dX/X\,dX'$ or d ln X/d ln X', where X and X' refer to the mole concentrations of two isotopes of a particular element. The fractionation factors used here are d ln $[O^{16}]$/d ln $[O^{18}]$ and d ln $[N^{14}]$/d ln $[N^{15}]$.

(5) L. E. Orgel, *Inst. Intern. Chim. Solvay, X^e Conseil Chim.*, 289 (1956).

(6) W. A. Hynes, L. K. Yanowski, and M. Shiller, *J. Am. Chem. Soc.*, **60**, 3053 (1938).

(7) F. Basolo and R. K. Murmann, *Inorg. Syn.*, **4**, 171 (1953).

(8) J. C. Bailar, *ibid.*, **2**, 222 (1946).

(9) A. Werner, *Ann.*, **386**, 1 (1912).

(10) R. S. Nyholm and M. L. Tobe, *J. Chem. Soc.*, 1707 (1956).

(11) M. L. Tobe, *ibid.*, 3776 (1959).