

of chloride ion as the reaction proceeded, four chlorides being released per palladous ion reaction. Two runs were made in the presence of finely divided palladium metal. The rate was unaffected.

The following form was assumed in calculating the equilibrium constant K

$$K = \frac{[(\text{PdCl}_3\text{C}_2\text{H}_4)^-][\text{Cl}^-]}{[\text{PdCl}_4^{2-}][\text{C}_2\text{H}_4]}$$

The net ethylene uptake was converted to moles of complex and this subtracted from the total palladous ion concentration to give $[\text{PdCl}_4^{2-}]$. The value of $[\text{Cl}^-]$ was then equal to total chloride $- 3[(\text{PdCl}_3\text{C}_2\text{H}_4)^-] - 4[\text{PdCl}_4^{2-}]$.

Constant Volume Reactor.—The constant volume reactor was essentially a 250-ml. Florence flask connected to a mercury capillary manometer. The flask was creased to increase the stirring efficiency of the magnetic stirring bar. An outlet equipped with stopcock was used to transfer gas into the apparatus or to pull a vacuum. The volume of the reactor was found to be 253.8 ml. by measuring the pressure before and after the injection of a weighed amount of mercury.

The reactions were run at an ethylene pressure of about 70 mm. Since at this pressure the concentration of complex is small, eq. 2 can be written

$$d[\text{C}_2\text{H}_4]/dt = k_2[\text{Pd}^{+2}][\text{C}_2\text{H}_4]$$

where

$$[\text{Pd}^{+2}] = [\text{I}] + [\text{PdCl}_4^{2-}] \text{ and } k_2 = \frac{k'K}{[\text{Cl}^-]^2[\text{H}^+]}$$

The solution of this equation for a constant volume reactor is

$$\frac{(\alpha + \beta)2.3}{\alpha(\beta P_0 - [\text{Pd}^{+2}]_0)} \times \log \frac{(\alpha + \beta)P[\text{Pd}^{+2}]}{\beta P_0([\text{Pd}^{+2}]_0 - \beta P_0) + (\alpha + \beta)P} = k_2 t$$

where α is the Henry's law constant, $[\text{Pd}^{+2}]_0$ is the initial palladous ion concentration, and β is an instrument constant³⁹ whose value is 8.5×10^{-6} for this reactor when 100 ml. of solution is used. The plots of the log term vs. t for all runs were linear, indicating the reaction is first order in palladous ion and first order in ethylene.

Acknowledgment.—The author gratefully acknowledges helpful discussions with Dr. H. G. Tennent and Professors M. Kilpatrick, S. Winstein, and H. Taube. The author also acknowledges the assistance of Mr. John Jackson with experimental work.

(39) P. Brandt and O. Plum, *Acta Chem. Scand.*, **7**, 97 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA, IOWA CITY, IOWA]

Crystal Structure of Diammonium Croconate and Molecular Orbital Calculations on the Croconate Ion

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The crystal structure of $(\text{NH}_4)_2\text{C}_5\text{O}_5$ was determined, and the molecular geometry of the croconate ion is reported. Molecular orbital calculations were carried out to check the effect of the parameters h and k on the calculated bond orders, electron densities, and delocalization energies. Values of the parameters which give the best agreement with the experimental bond orders and prescribed electron densities are reported.

Recent interest in a series of aromatic ions of general formula $\text{C}_n\text{O}_n^{2-}$ has sparked renewed interest in the structure of the croconate ion.^{1,2} A normal coordinate analysis of the infrared and Raman spectral data of the croconate ion indicates an anion of D_{5h} symmetry.³ The structure of $(\text{NH}_4)_2\text{C}_5\text{O}_5$ was undertaken to determine the molecular geometry (bond distances, bond angles) of the croconate ion. A preliminary account of the structure was reported.⁴

Bond orders, electron densities, and delocalization energies (obtained from Hückel molecular orbital (HMO) calculations) have been reported for a whole series of oxygenated anions. The parameters used in these calculations were $h = 1.0$ and $k = 0.8$.⁵

The molecular orbital calculations reported in this paper were carried out to test the dependence of the calculated bond orders, bond lengths, and delocalization energies on the parameters h and k . It was hoped that a set of h and k could be found that would give the observed bond orders, reasonable electron densities,⁶ and a maximum delocalization energy. The

effect of including the overlap parameters in the calculation was also investigated.

Experimental

The Crystal Structure of Ammonium Croconate.— $(\text{NH}_4)_2\text{C}_5\text{O}_5$ crystallizes from aqueous solution as monoclinic needles or laths with unit cell dimensions $a = 7.444 \pm 0.003 \text{ \AA}$, $b = 13.345 \pm 0.002 \text{ \AA}$, $c = 3.582 \pm 0.001 \text{ \AA}$, $\beta = 99.4 \pm 0.3^\circ$, $D_{\text{meas}} = 1.66 \text{ g./cm.}^3$ (pycnometrically), $Z = 2$, $D_x = 1.60 \text{ g./cm.}^3$. The cell constants were determined by a least-squares fitting of the $(h0l)$, $(hk0)$, and $(0kl)$ Weissenberg back-reflection data with extrapolation to $\theta = 90^\circ$. The systematic absences, (hkl) when $h + k = 2n + 1$, indicate space groups $C2/m$, $C2$, or Cm . Space group $C2/m$, which requires the croconate ion to have a symmetry center, seemed unlikely from previous information.

The intensity data were taken using crystals (approximate cylinders) maintained at 80°K . by use of a gas-flow dewar designed in our laboratory.⁷ The data were taken using the equi-inclination Weissenberg camera, multiple film technique, and Cu $K\alpha$ radiation ($\lambda 1.5418 \text{ \AA}$). Some diffraction spots at high angles were split into two spots due to thermal shock damage to the crystal. The amount of splitting varied from crystal to crystal, but the crystals used to take the intensity data showed little effect of the splitting. The splitting was observed only when the crystal was aligned along the needle (c) axis.

(1) R. West, H. Y. Niu, D. L. Powell, and M. D. Evans, *J. Am. Chem. Soc.*, **82**, 6204 (1960).

(2) R. West and H. Y. Niu, *ibid.*, **84**, 1324 (1962).

(3) M. Ito and R. West, *ibid.*, **85**, 2580 (1963).

(4) N. C. Baenziger, J. J. Hegenbarth, and D. G. Williams, *ibid.*, **85**, 1539 (1963).

(5) R. West and D. L. Powell, *ibid.*, **85**, 2577 (1963).

(6) Reasonable electron densities were determined by using the equations: $q_c = 5E_c^p/12(E_o^p + E_c^p)$; $q_o = 5E_o^p/12(E_o^p + E_c^p)$; E_c^p and E_o^p are Pauling's electronegativity numbers for carbon and oxygen. With the use of the above equations, q_c is calculated to be 1.0, q_o to be 1.4.

(7) G. F. Richards Thesis, Feb., 1964.

TABLE I

FINAL PARAMETERS AND STANDARD DEVIATIONS

| | x | y | z | b ₁₁ | b ₂₂ | b ₃₃ | b ₁₂ b ₁₃ b ₂₃ | | |
|---------------------|--------|--------|--------|-----------------|-----------------|-----------------|---|------|-----|
| | | | | | | | (× 10 ⁴) | | |
| C ₁ | 0.4457 | 0.5891 | 0.0003 | 54 | 21 | 80 | -25 | -13 | -7 |
| e.s.d. ^a | .0012 | .0006 | .0025 | 15 | 4 | 62 | 43 | 59 | 25 |
| (in Å.) | .009 | .008 | .009 | | | | | | |
| C ₂ | .1208 | .0545 | .9142 | 56 | 35 | -22 | 19 | 130 | 3 |
| | .0011 | .0007 | .0022 | 16 | 5 | 59 | 16 | 54 | 27 |
| | .008 | .009 | .008 | | | | | | |
| C ₃ | .3429 | .5000 | .0639 | 18 | 22 | 16 | .. | 161 | .. |
| | .0012 | .. | .0024 | 17 | 7 | 102 | .. | 77 | .. |
| | .009 | .. | .009 | | | | | | |
| O ₁ | .3939 | 0.6770 | .0210 | 83 | 11 | 396 | -7 | -129 | 4 |
| | .0011 | .0005 | .0018 | 12 | 3 | 66 | 34 | 53 | 21 |
| | .008 | .007 | .006 | | | | | | |
| O ₂ | .2478 | .1117 | .8465 | 53 | 39 | 216 | -46 | 57 | -20 |
| | .0009 | .0005 | .0022 | 11 | 4 | 58 | 14 | 38 | 27 |
| | .007 | .007 | .008 | | | | | | |
| O ₃ | .1815 | .5000 | .1507 | 22 | 12 | 369 | .. | 191 | .. |
| | .0011 | .. | .0022 | 14 | 4 | 89 | .. | 60 | .. |
| | .008 | .. | .008 | | | | | | |
| N | .0498 | 0.3324 | .5044 | 43 | 33 | 72 | 20 | 190 | -76 |
| | .0011 | .0006 | .0022 | 10 | 5 | 53 | 14 | 43 | 26 |
| | .008 | .008 | .008 | | | | | | |

^a e.s.d. = estimated standard deviations in parameters from error matrix. Thermal parameters are from $f = f^{\circ} \times e^{-(h^2b_{11} + k^2b_{22} + l^2b_{33} + hb_{12} + kb_{13} + lb_{23})}$.

A total of 338 out of a possible 370 reflections were observed. The intensities were obtained by visual comparison with a calibrated set of exposures of one reflection and were corrected for Lorentz and polarization effects but not for absorption. The absorption correction for cylinders with $\mu R = 0.24$ and 0.21 is insignificant.

Trial structures were calculated for space groups C2 and Cm assuming a planar ion of D_{3h} symmetry and reasonable C-C and C-O distances. In order for two molecules to be in the unit cell, it is necessary for the molecule to lie on the 2-fold axis of C2 or the mirror plane of Cm. The nitrogen atoms were placed in positions that allowed reasonable N-O distances and packing. Structure factor calculations, with block-diagonal least-squares refinement (BDLS), were carried out using the space groups C2 and Cm and the (hk0) data. Individual isotropic thermal parameters were included for all the atoms. The atomic scattering factors were calculated using the equation and constants of Forsyth and Wells.⁸ The trial structure in C2 did not refine below $R = 0.40$ ($R = \sum w |F_{obsd}| - |F_{calcd}| / \sum w F_{obsd}$). The trial structure in Cm refined to an R value of 0.116 for the (hk0) data.

The z parameters of the atoms in the croconate ion were given initial values of 0.0, and the nitrogen was placed at $z = 0.5$. The R value for all the three-dimensional data decreased to 0.128 after six cycles of BDLS. All present reflections were given unit weight.

At this point the results of an independent estimation of the intensity data were averaged with the original intensity estimates. Sufficient estimates of the same reflections were available that statistical weights of $1/\sigma^2(F)$ could be assigned to each reflection. Equivalent F^2 values obtained from different settings of the crystal were averaged and these reflections given appropriate weights.

The two-dimensional (projection on (001)) and three-dimensional electron density maps were calculated in an attempt to locate the hydrogen atoms. Approximate hydrogen atom positions were obtained from the rather poor electron density detail which appeared around the nitrogen atom on these plots and from the assumption of normal N-H distances. The hydrogen atoms were given isotropic thermal parameters of 3.5 \AA^2 and were included in the calculation but not refined. Five BDLS cycles reduced the discrepancy factor R to 0.098.

The final three-dimensional refinement was carried out by full-matrix least-squares methods. (The earlier BDLS refinement was carried out with a least-squares program written for the LGP-30 by R. Medrud. The full matrix program was written for the IBM-7070. The program permits intermixing of either anisotropic or isotropic temperature factors for any atom. Atom scattering factors are found by interpolation from the values

TABLE II

INTERATOMIC DISTANCES AND ANGLES

| | Dist. | S.d. | Angle | S.d. | |
|---|-------|-------|--|--------|-------|
| | | | | | In Å. |
| C ₁ -C ₂ ^a | 1.463 | 0.013 | C ₂ -C ₁ -C ₃ | 106.6° | 0.5° |
| C ₁ -C ₃ | 1.452 | .010 | C ₁ -C ₃ -C ₁ ' | 110.0 | .7 |
| C ₂ -C ₂ ' | 1.455 | .018 | C ₁ -C ₂ -C ₂ ' | 108.4 | .6 |
| C ₁ -O ₁ | 1.241 | .011 | C ₂ '-C ₂ -O ₂ | 127.0 | .8 |
| C ₂ -O ₂ | 1.269 | .011 | C ₁ -C ₂ -O ₂ | 124.6 | .7 |
| C ₃ -C ₃ | 1.289 | .013 | C ₂ -C ₁ -O ₁ | 127.4 | .8 |
| | | | C ₃ -C ₁ -O ₁ | 126.1 | .6 |
| N-O ₁ | 2.827 | .010 | C ₁ -C ₃ -O ₃ | 125.0 | .7 |
| N-O ₃ | 2.825 | .011 | | | |
| N-O ₂ | 2.831 | .011 | O ₁ -N-O ₂ | 100.6 | |
| N-O ₁ ' | 2.906 | .011 | O ₁ -N-O ₃ | 116.4 | |
| | | | O ₁ -N-O ₁ ' | 126.1 | |
| N-O ₂ ' | 3.070 | .011 | O ₂ -N-O ₃ | 110.1 | |
| N-O ₁ | 3.127 | .010 | O ₂ -N-O ₁ ' | 114.6 | |
| N-O ₃ | 3.253 | .011 | O ₃ -N-O ₁ ' | 89.2 | |
| N-O ₁ ' | 3.321 | .011 | | | |
| O ₁ -O ₂ | 2.938 | .011 | | | |
| O ₂ -O ₂ | 2.982 | .012 | | | |
| O ₁ -O ₃ | 2.922 | .007 | | | |

^a For comparison, in the earlier publication⁴ at the end of the BDLS refinement the distances in order were: 1.449, 1.442, 1.466; 1.258, 1.253, 1.249 Å. The final distances reported above are not significantly different.

listed in the "International Tables for X-Ray Crystallography," Vol. 3.) In space group Cm the x and z coordinates of one atom must be arbitrarily fixed; carbon atom C₁ was chosen for this purpose. After three cycles of refinement with individual isotropic temperature factors, the calculated parameter shifts were less than 0.0002 parameter unit. The discrepancy factor was 0.094. Individual anisotropic temperature factors were then refined, reducing R to 0.069. The final parameters are shown in Table I. The calculated and observed structure factors are given in Table III.

The calculation of errors is complicated by the dependence of the x and z coordinates and their covariances on the choice of origin, and the fact that no errors are calculated for the fixed parameters of atom C₁. The interatomic vectors and their errors should be independent of the choice of origin.⁹ As a result, the diagonal elements in the error matrix for the x and z coordinates of the remaining atoms must be correspondingly larger, and the correlation coefficients between the x coordinates of different atoms (and also between the z coordinates) should approximate 0.5. The variances (in Å.²) for x and z were found to be roughly twice as large as those for y , and the correlation coefficients calculated for the final refinement ranged from 0.5 to 0.7, though most were about 0.5. The estimated standard deviations in the bond distances were calculated using the full error matrix and are listed in Table II. For simplicity of presentation, however, standard deviations have been assigned to all atom parameters in Table I (including x and z of C₁) which yield almost identical standard deviations in bond distances. The estimated standard deviations obtained in this manner are essentially the same as those obtained from the BDLS refinement.

Discussion

A projection of the structure of diammonium croconate on the a, b plane is shown in Fig. 1. The structure consists of a pseudo-hexagonal array of NH₄⁺ ions at $z \sim 0.5$, surrounding the planar croconate ring. The NH₄⁺ ions are bonded to four oxygen atoms in a distorted tetrahedral configuration at distances of 2.825 to 2.906 Å. The O-N-O angles range from 89 to 126° with a mean value of 109.5° for the six tetrahedral angles. Two of the bonded oxygens are in the molecular plane below the N atom and two are in the

(8) J. B. Forsyth and M. Wells, *Acta Cryst.*, **12**, 412 (1959).(9) D. H. Templeton, *ibid.*, **12**, 771 (1959).

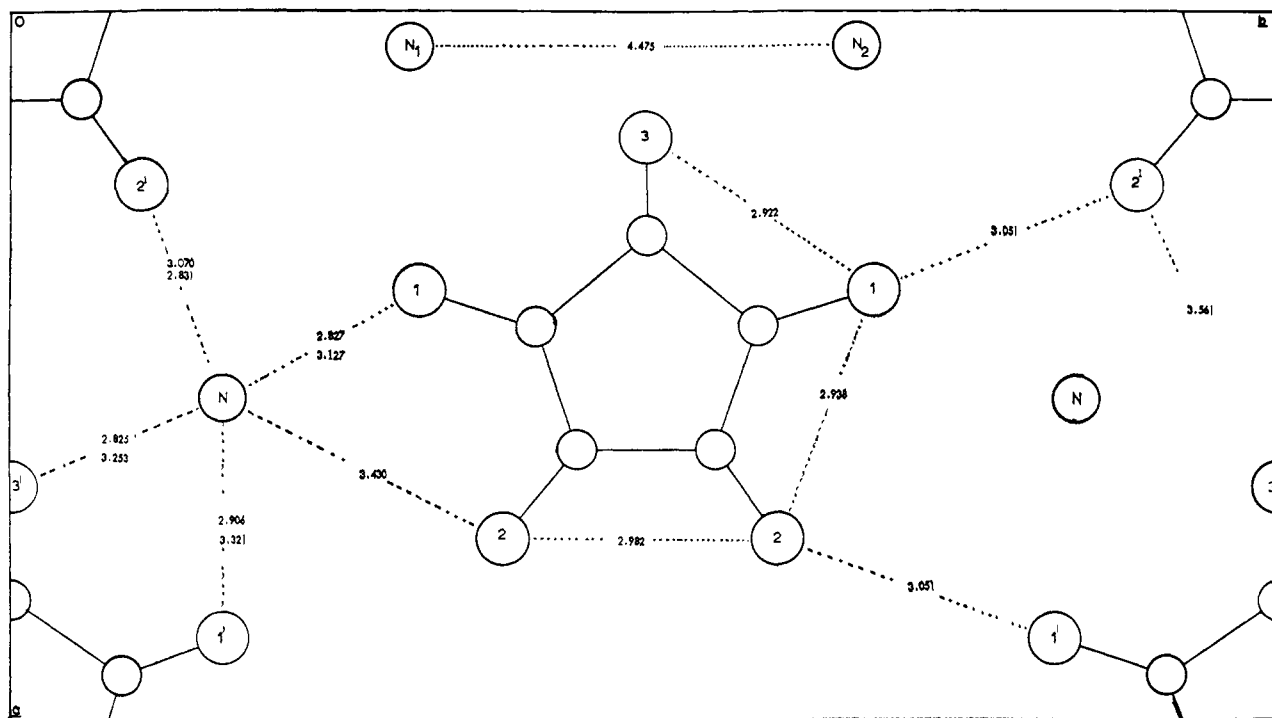


Fig. 1.—Projection onto (001) showing the intermolecular distances and packing of the ions.

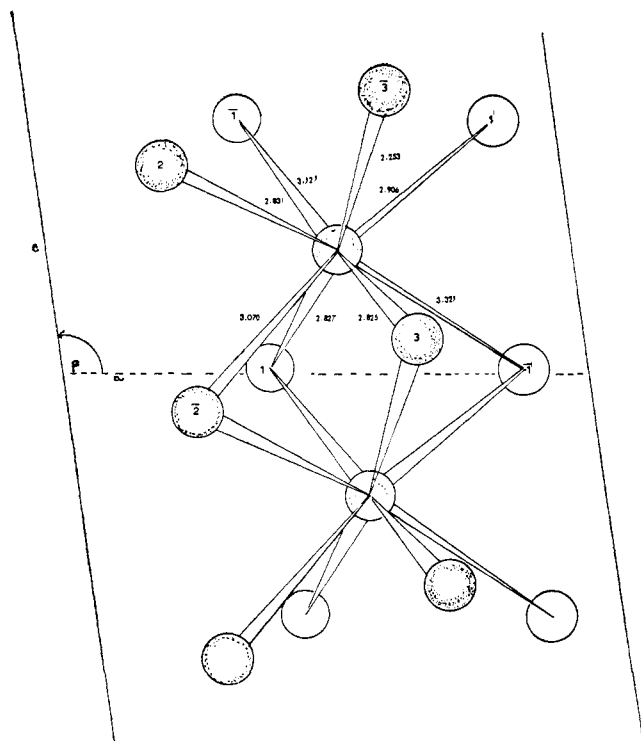


Fig. 2.—Coordination of the oxygen atoms around the nitrogen atom. The primed numbers denote crystallographic equivalent oxygen atoms which belong to different ions in the same molecular plane, while the numbers with "bars" denote oxygen atoms with the same x and y parameters as the numbers without bars, but belonging to the unit cell above or below.

and \bar{k} perpendicular to the ion.) The errors are quite large, so the results are not too significant. For example, T_{33} cannot really be negative and is probably close to zero. (The large errors may signify that the assumption that intramolecular motions are small

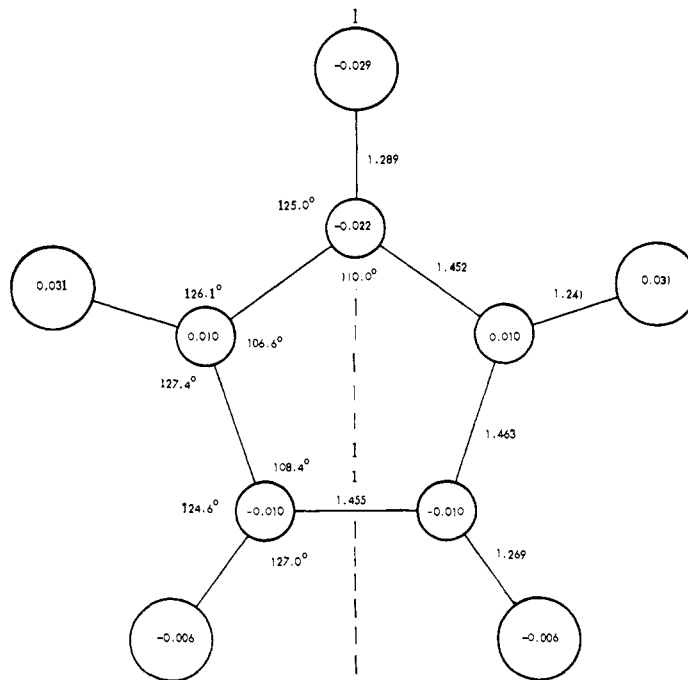


Fig. 3.—The bond lengths, angles, and deviations of the atoms from the least-squares plane of the croconate ion.

compared to the motion of whole ion is not valid.) The larger values of ω_{11} and ω_{22} indicate more motion perpendicular to the croconate ion plane than in the plane. Corrections in bond lengths based on this analysis amount to 0.003 Å. in the C-O bond distance and a negligible change in the C-C distances.

The spread of the C-C bond lengths, 1.442 to 1.466 Å., is less than two times the estimated standard deviation of a C-C bond and is not significant. The carbon-oxygen bond lengths deviate to a greater extent, but they are still within a little more than two standard

| $T \times 10^{-2}, \text{\AA}^2$ | | | $\sigma_T \times 10^{-2}, \text{\AA}^2$ | | |
|----------------------------------|------|-------|---|------|------|
| 1.08 | 0.0 | 0.25 | 0.32 | 0.27 | 0.33 |
| | 1.85 | 0.0 | | 0.32 | .33 |
| | | -0.34 | | | .52 |
| $\omega, \text{deg.}^2$ | | | $\sigma\omega, \text{deg.}^2$ | | |
| 13.4 | 0.0 | 3.9 | 4.7 | 2.7 | 3.5 |
| | 10.3 | 0.0 | | 4.7 | 3.4 |
| | | 6.0 | | | 2.8 |

deviations from the mean. The mean C-C distance is 1.457 Å.; the mean C-O distance is 1.262 Å., which with correction of bond lengths for thermal oscillation becomes 1.265 Å. The carbon-oxygen bonds are

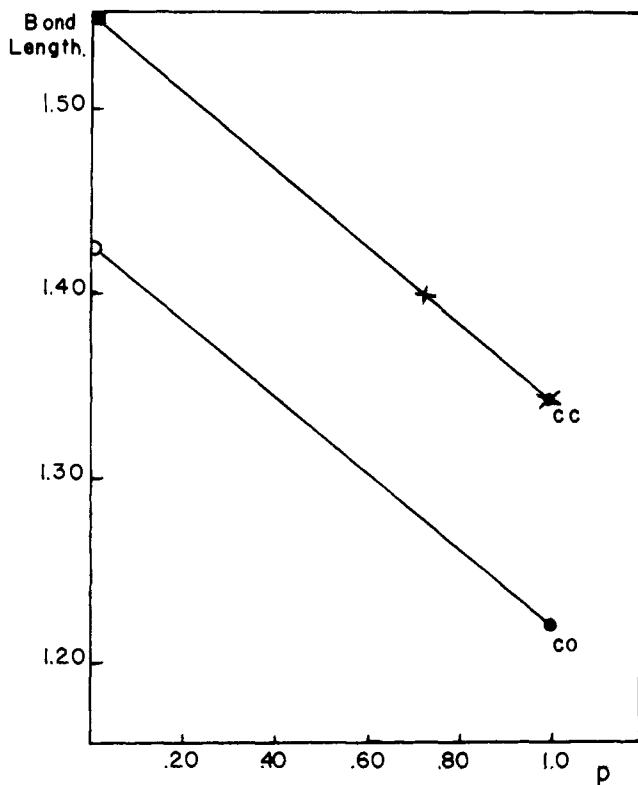


Fig. 4.— π -Bond order-bond length curves: ■, 1.543 Å. (ref. 12); ×, 1.397 Å. (ref. 13); ⊙, 1.335 Å. (ref. 14); ○, 1.427 Å. (ref. 15); ●, 1.222 Å. (ref. 16).

much shorter than the average hydroxyl C-O bond (1.43 Å.) and are close to the average carbonyl C-O distance of 1.23 Å. The C-O bonds are shorter than one may predict from the force constants of Ito and West.³ If the average C-C and C-O distances are used with the bond order-bond length curve of Fig. 4,¹²⁻¹⁶ the C-C bond order is 0.45 and the C-O bond order is 0.77. The range of C-C and C-O bond orders within the spread of observed bond lengths is 0.42 to 0.48 and 0.66 to 0.88.

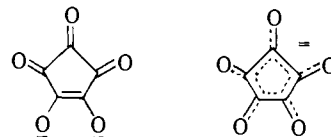
The bond angles in the carbon ring for an ion of D_{5h} symmetry are 108° , and the C-C-O angles are 126° . The observed angles have mean values of 108° and 126.1° . Deviations from the mean do not exceed three standard deviations of a single angle. Thus

the croconate ion has D_{5h} symmetry within the limits of error.

Molecular Orbital Calculations

Molecular orbital calculations were carried out on the croconate ion for values of the parameter, h , of 0.2 to 1.4 and for the parameter, k , from 0.4 to 1.6 at parameter intervals of 0.2.¹⁷ This range includes the values previously reported in the literature. Hückel molecular orbital calculations, HMO, and calculations including overlap were carried out. Overlap was included by using Löwdin's matrix, H' , instead of the usual "one-electron Hamiltonian" matrix H .¹⁸ The values of S_{CC} and S_{CO} used were 0.25 and 0.20. Calculations carried out in this manner will be denoted as orthogonal atomic orbital molecular orbital (OAOMO) calculations.

Bond orders, p , and electron densities, q , were calculated using the formulas of Coulson.¹⁹ The delocalization energy is defined as the difference in total π -electronic energy calculated assuming the two structures



The eigenvalues (energy levels) and eigenvectors (expansion coefficients of the atomic orbitals) of the tenth-order matrix were determined by Givens' method using an IBM-7070 computer.²⁰ The D_{5h} point group was used to check the results obtained and not to reduce the order of the matrix. The eigenvalues and eigenvectors for the results reported are completely consistent with D_{5h} point group symmetry.

The energy levels and delocalization energies from the HMO calculations are given in β_0 units, where $E_{\beta_0} = (\alpha_0 - E_{HMO})/\beta_0$. The energy levels and delocalization energies for the OAOMO calculations are given in β' units, where $E_{\beta'} = (\alpha_0 - E_{OAOMO})/\beta_0$. The energy, E_{HMO} , is given by $\alpha_0 + m_i\beta_0$, while the energy for calculations including overlap, E_{OAOMO} , is given by $\alpha_i + n_i\gamma_i$, where $\gamma_i = \beta_i - S_i\alpha_i$.²¹ When the calculations are carried out for hydrocarbons, α_0 and S_{CC} are known and the energy is easily converted to β_0 units. In the case of the croconate ion (or any molecule containing atoms other than carbon), there is no easy way of determining the contribution of β_0 , $k\beta_0$, α_0 , $(\alpha_0 + h\beta_0)$, S_{CC} , and S_{CO} to $E_{OAOMO}(\text{calcd.})$; therefore, there is no convenient way of putting the energy on the same scale as the HMO energy; $E_{OAOMO}(\text{calcd.})$ is dependent on h through $(\alpha_0 + h\beta_0)$ and on k through $k\beta_0$. The graphs of $DE(\beta')$ vs. h and k should not be expected to show the trends shown by the HMO delocalization energy.

The HMO and OAOMO energy levels are given in Fig. 5. The lower energy levels are compressed in the

(17) See A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 117, for a definition of the h and k parameters.

(18) P. Löwdin, *J. Chem. Phys.*, **13**, 365 (1950).

(19) C. A. Coulson, *Proc. Roy. Soc. (London)*, **A169**, 413 (1939).

(20) W. Givens, Oak Ridge National Laboratory Bulletin 1574, 1954.

(21) J. Ketelaar, "Chemical Constitution," Elsevier Publishing Co., New York, N. Y., 1958.

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(13) A. Langseth and B. P. Stoicheff, *Can. J. Phys.*, **34**, 350 (1956).

(14) L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, **31**, 400 (1959).

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(16) J. Trotter, *Acta Cryst.*, **13**, 86 (1960).

OAOMO calculation, and for calculations using some of the parameters, the energy difference became as small as the accuracy of the eigenvalues. This "computer degeneracy" is contrary to the D_{3h} point group symmetry, and, therefore, the symmetry in the bond orders and electron densities was destroyed. Multiplying the elements of H' by a constant (± 1.0) overcame this difficulty.

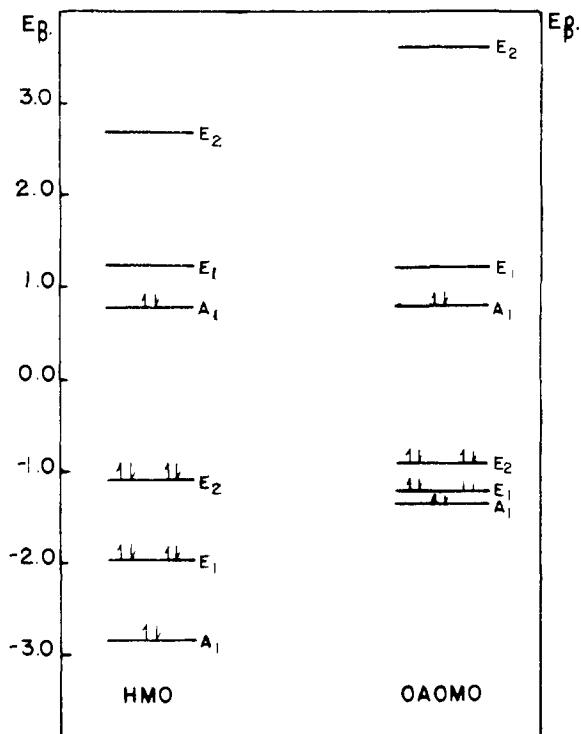


Fig. 5.—Energy level diagram of the croconate ion for HMO and OAOMO methods ($h = 0.2, k = 1.6$).

The results of the MO calculations are given in tabular and graphic form. The π -bond orders for C-C and C-O, the electron densities of carbon and oxygen, and the calculated delocalization energies are plotted independently against h at the various contours of k and independently against k at various contours of h . Graphs are given for both the HMO results and for the OAOMO methods. In all cases the broken lines identify carbon-carbon bond order or carbon electron densities, while the solid lines identify carbon-oxygen bond order or oxygen electron density. The various constant h or k contours are shown by the numbers on the edge of the graph. The graphs are given mainly to show the trends of the calculated quantities, and the table is given to show the absolute values of these quantities.

Table IV contains the numerical results of the HMO and OAOMO calculations. The table contains some entries for the OAOMO results where the delocalization energy is given but bond orders or densities are not. It was in these cases that the nondegenerate energy levels became so close that the energy difference was equal to the round-off errors in the computed values (see earlier discussion). Since these were not close to reasonable bond orders and electron densities, they were not recalculated. Figure 6 shows the graphs of the HMO π -bond orders, π -electron densities, and

delocalization energies vs. h and k . Figure 7 shows the graphs of the OAOMO bond orders and electron densities vs. h and k .

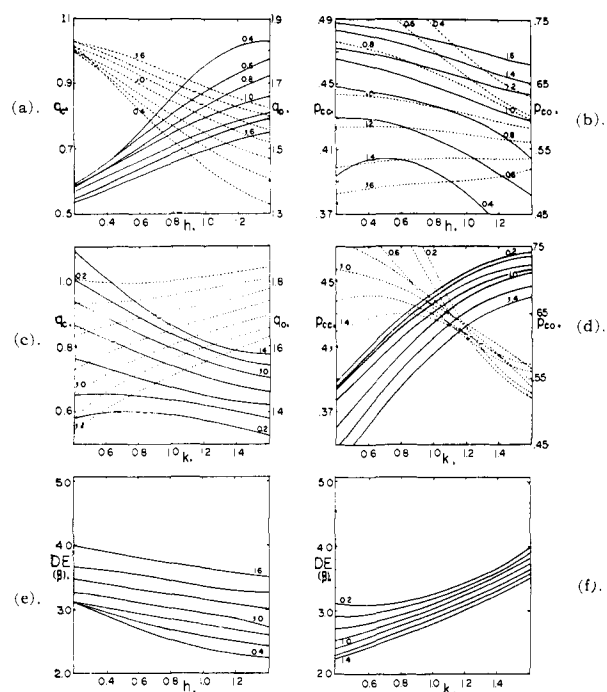


Fig. 6.—(a) HMO π -electron density vs. h at constant contours of k . (b) HMO π -bond order vs. h at constant contours of k . (c) HMO π -electron density vs. k at constant contours of h . (d) HMO π -bond order vs. k at constant contours of h . (e) HMO π -delocalization energy vs. h at constant contours of k . (f) HMO π -delocalization energy vs. k at constant contours of h .

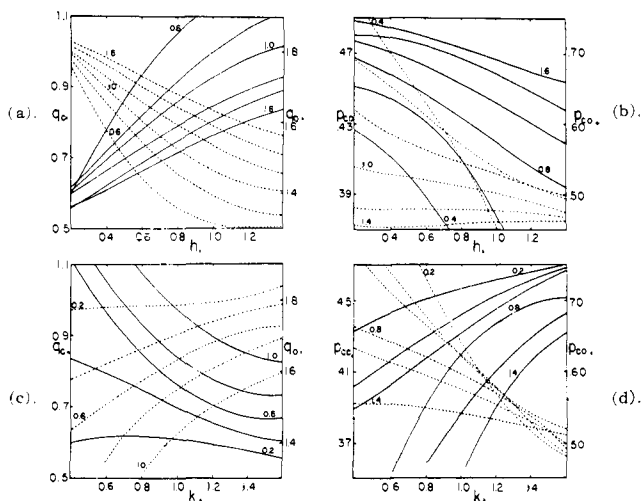


Fig. 7.—(a) OAOMO π -electron density vs. h at constant contours of k . (b) OAOMO π -bond order vs. h at constant contours of k . (c) OAOMO π -electron density vs. k at constant contours of h . (d) OAOMO π -bond order vs. k at constant contours of h .

It can be seen from the figures that the calculated quantities are dependent on the values of h and k used in the calculation. The calculated electron densities seem to be more dependent on h while the bond orders are more dependent on k . The delocalization energy increases with decreasing h . For higher values of k , the dependence of the delocalization energy on h

TABLE IV
RESULTS OF THE MOLECULAR ORBITAL CALCULATIONS

| h | HMO | | | | | OAOMO | | | | |
|-----------|----------|----------|-------|-------|-------------|----------|----------|-------|-------|-------------------|
| | p_{CC} | p_{CO} | q_C | q_O | $DE(\beta)$ | p_{CC} | p_{CO} | q_C | q_O | $DE(\beta')$ |
| $k = 0.4$ | | | | | | | | | | |
| 1.4 | 0.421 | 0.398 | 0.530 | 1.87 | 2.24 | | | | | |
| 1.2 | .439 | .432 | .580 | 1.81 | 2.31 | | | | | 0.54 |
| 1.0 | .456 | .479 | .646 | 1.76 | 2.41 | | | | | .53 |
| 0.8 | .479 | .515 | .730 | 1.66 | 2.54 | | | | | .52 |
| .6 | .507 | .534 | .832 | 1.55 | 2.72 | | | | | .51 |
| .4 | .536 | .522 | .934 | 1.42 | 2.92 | | | | | .56 |
| .2 | .558 | .506 | 1.02 | 1.38 | 3.11 | | | | | 1.00 |
| $k = 0.6$ | | | | | | | | | | |
| 1.4 | 0.433 | 0.483 | 0.610 | 1.79 | 2.43 | 0.393 | 0.219 | 0.430 | 1.96 | 0.41 |
| 1.2 | .444 | .516 | .657 | 1.74 | 2.50 | ... | ... | ... | .. | .41 |
| 1.0 | .456 | .546 | .715 | 1.68 | 2.59 | ... | ... | ... | .. | .42 |
| 0.8 | .469 | .570 | .783 | 1.62 | 2.70 | 0.409 | 0.424 | 0.536 | 1.88 | .45 |
| .6 | .487 | .585 | .853 | 1.53 | 2.81 | ... | ... | ... | .. | .51 |
| .4 | .502 | .592 | .911 | 1.49 | 2.96 | 0.460 | 0.588 | 0.814 | 1.56 | .63 |
| .2 | .510 | .600 | 1.00 | 1.40 | 3.38 | 0.511 | 0.592 | 0.976 | 1.43 | .79 |
| $k = 0.8$ | | | | | | | | | | |
| 1.4 | 0.432 | 0.546 | 0.671 | 1.72 | 2.61 | | | | | 0.36 |
| 1.2 | .438 | .573 | .715 | 1.69 | 2.69 | | | | | .39 |
| 1.0 | .447 | .596 | .765 | 1.63 | 2.77 | 0.417 | 0.553 | 0.662 | 1.73 | .43 ^a |
| 0.8 | .456 | .618 | .821 | 1.58 | 2.85 | .418 | .557 | .663 | 1.73 | .47 |
| .6 | .465 | .634 | .880 | 1.52 | 2.94 | .432 | .609 | .758 | 1.63 | .54 |
| .4 | .471 | .644 | .940 | 1.46 | 3.03 | ... | ... | ... | .. | .63 |
| .2 | .475 | .649 | 1.00 | 1.40 | 3.11 | 0.465 | 0.656 | 0.968 | 1.43 | .72 |
| $k = 1.0$ | | | | | | | | | | |
| 1.4 | 0.423 | 0.595 | 0.722 | 1.67 | 2.73 | | | | | 0.38 |
| 1.2 | .430 | .615 | .762 | 1.64 | 2.88 | 0.395 | 0.535 | 0.623 | 1.77 | .42 |
| 1.0 | .435 | .635 | .808 | 1.59 | 2.95 | ... | ... | ... | .. | .47 |
| 0.8 | .440 | .654 | .856 | 1.54 | 3.03 | 0.409 | 0.624 | 0.747 | 1.65 | .53 |
| .6 | .451 | .670 | .921 | 1.51 | ... | ... | ... | ... | .. | ... |
| .4 | .445 | .679 | .959 | 1.44 | 3.20 | 0.428 | 0.681 | 0.904 | 1.48 | 0.67 |
| .2 | .444 | .685 | 1.01 | 1.39 | 3.26 | 0.430 | 0.697 | 0.984 | 1.42 | 0.75 |
| $k = 1.2$ | | | | | | | | | | |
| 1.4 | 0.417 | 0.622 | 0.761 | 1.62 | 3.03 | | | | | 0.43 |
| 1.2 | .416 | .650 | .801 | 1.60 | 3.09 | 0.390 | 0.600 | 0.693 | 1.70 | .49 |
| 1.0 | .419 | .663 | .841 | 1.55 | 3.16 | ... | ... | ... | .. | .55 |
| 0.8 | .420 | .681 | .900 | 1.50 | 3.26 | 0.396 | 0.664 | 0.806 | 1.59 | .62 |
| .6 | .421 | .693 | .931 | 1.46 | 3.32 | .402 | .684 | .871 | 1.51 | .69 |
| .4 | .426 | .700 | .973 | 1.43 | 3.39 | .401 | .706 | .936 | 1.46 | .78 |
| .2 | .418 | .713 | 1.02 | 1.38 | 3.47 | .406 | .720 | 1.00 | 1.40 | .86 |
| $k = 1.4$ | | | | | | | | | | |
| 1.4 | 0.404 | 0.656 | 0.798 | 1.59 | 3.26 | 0.380 | 0.617 | 0.707 | 1.69 | 0.53 |
| 1.2 | .405 | .672 | .834 | 1.56 | 3.29 | 0.378 | 0.650 | 0.753 | 1.65 | .60 |
| 1.0 | .404 | .689 | .873 | 1.53 | 3.27 | ... | ... | ... | .. | .68 |
| 0.8 | .403 | .701 | .912 | 1.49 | 3.47 | 0.380 | 0.696 | 0.853 | 1.55 | .76 |
| .6 | .402 | .713 | .954 | 1.44 | 3.55 | .380 | .714 | .909 | 1.49 | .84 |
| .4 | .399 | .722 | .996 | 1.40 | 3.64 | .382 | .724 | .964 | 1.43 | ... |
| .2 | .394 | .732 | 1.01 | 1.38 | 3.56 | .378 | .746 | .996 | 1.40 | 1.10 ^a |
| $k = 1.6$ | | | | | | | | | | |
| 1.4 | 0.393 | 0.679 | 0.830 | 1.57 | 3.51 | 0.370 | 0.654 | 0.757 | 1.64 | 0.68 |
| 1.2 | .390 | .688 | .863 | 1.52 | 3.58 | .367 | .681 | .800 | 1.61 | 0.75 |
| 1.0 | .390 | .706 | .899 | 1.50 | 3.65 | .368 | .698 | .844 | 1.55 | .83 |
| 0.8 | .388 | .718 | .936 | 1.46 | 3.73 | ... | ... | ... | .. | .92 |
| .6 | .385 | .727 | .974 | 1.42 | 3.82 | 0.367 | 0.731 | 0.939 | 1.46 | 1.02 ^a |
| .4 | .382 | .734 | 1.01 | 1.39 | 3.90 | .366 | .742 | 0.988 | 1.41 | 1.12 ^a |
| .2 | .378 | .738 | 1.05 | 1.34 | 3.99 | .364 | .750 | 1.03 | 1.37 | 1.22 ^a |

^a "Computer degeneracy" removed by multiplying H' matrix by 4.0.

is not as great. It should be noted that the delocalization energy is 30% greater for $h = 0.2$ to 0.4 and $k = 1.6$ than for the parameters used by West and Powell ($h = 1.0, k = 0.8$).⁵ The delocalization energy increases almost linearly with k . For smaller values of h , the slope decreases, indicating a decreased dependence on k .

The value of h that gives the prescribed electron densities (in the HMO and OAOMO calculations) is between 0.2 and 0.4 . The increased delocalization energy as h decreases also lends weight to the choice of this range for h . This range for h is close to the value 0.15 which was determined by Brown and Hefferman²² by reproducing with HMO calculations the electron densities predicted by "self-consistent electronegativity" MO calculations.

The value of k that gives the observed bond orders is between 1.4 and 1.6 ; these values can be used in either the HMO or OAOMO calculations. The choice of the value of k in this range is made more plausible by the increased delocalization energy calculated for the higher values of k . The range above includes the value (1.56) used by Vincow and Fraenkel to give

(22) R. D. Brown and M. L. Hefferman, *Trans. Faraday Soc.*, **54**, 757 (1958).

the spin density distribution observed in the e.s.r. spectra of semiquinone ions.²³

Table IV shows the difference between the calculated quantities using the HMO and OAOMO methods. In all cases the differences between the bond orders and electron densities are small. These differences are not large enough to make the extra calculations necessary in the OAOMO method worthwhile. Calculations using S_{CO} values of $0.1, 0.2, 0.3,$ and 0.4 resulted in little change for the bond orders and electron densities.

As a result, the most appropriate parameters for use in HMO and OAOMO calculations of the oxocarbons are $h = 0.2$ to 0.4 and $k = 1.4$ to 1.6 . The appropriateness of these parameters in the MO calculations of the squarate ($C_4O_4^{-2}$) and rhodizionate ($C_6O_6^{-2}$) ions will be known when the molecular geometry of these ions has been determined.

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Rates of Substitution Reactions of Square-Planar Platinum(II) Complexes. II.¹ Reactions of *trans*-Dichlorobis(piperidine)platinum(II)

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The rates of the reactions of *trans*-[Pt(C₅H₁₁N)₂Cl₂] with ³⁶Cl⁻, NO₂⁻, and N₃⁻ and of *trans*-[Pt(C₅H₁₁N)₂NO₂Cl] (C₅H₁₁N = piperidine) with NO₂⁻ are reported. These are compared with the rates obtained previously for similar reactions of *trans*-[Pt(PEt₃)₂Cl₂]. The relative increase in reactivity of NO₂⁻ in the reaction with [Pt(C₅H₁₁N)₂Cl₂] is discussed. It is observed that the ligands in the *cis* position influence the *trans* effect of the *trans* ligand.

The first paper of this series reports¹ the nucleophilic substitution reactions of ³⁶Cl⁻ and NO₂⁻ with *trans*-[Pt(PEt₃)₂Cl₂] in methanol. In this system nitrite ion is a poorer reagent than chloride ion. This is believed to result from the π -bonding of phosphine with platinum(II) which in turn makes less important the electrophilic contribution of the entering reagent, e.g., NO₂⁻.

This paper reports investigations of the reactions of *trans*-[Pt(C₅H₁₁N)₂NO₂Cl] with NO₂⁻ and of *trans*-[Pt(C₅H₁₁N)₂Cl₂] (C₅H₁₁N = piperidine) with ³⁶Cl⁻, NO₂⁻, and N₃⁻ in methanol. This complex was chosen because Stuart models show that the steric hindrance caused by piperidine is approximately the same as that of triethylphosphine in the previously studied *trans*-[Pt(PEt₃)₂Cl₂]. Moreover *cis*-*trans* isomerization is known not to occur² for the piperidine compound under the conditions of these experiments. Hence replacement of triethylphosphine with piperidine is expected to affect the kinetic process solely through changes of the electronic features caused by

the different bonding properties of the two ligands. In the course of this investigation it was also felt necessary to study the reaction of *trans*-[Pt(PEt₃)₂Cl₂] with N₃⁻.

Experimental

Preparation of Materials.—*trans*-[Pt(C₅H₁₁N)₂Cl₂] was prepared from [Pt(SMe₂)₂Cl₂] and piperidine in *n*-butyl ether.² The compound was recrystallized from ethanol, m.p. 252–253°. *Anal.* Calcd. for C₁₀H₂₂N₂Cl₂Pt: N, 6.4. Cl, 16.5. Found: N, 6.3; Cl, 16.7. The compound is a nonelectrolyte in methanol ($\Lambda_M < 1$ ohm⁻¹ cm.⁻² mole⁻¹). [Pt(SMe₂)₂Cl₂] was prepared by the reaction of K₂PtCl₄ with S(CH₃)₂ in water solution.³ The S(CH₃)₂ used was obtained from the reaction between CH₃I and Na₂S in a water-ethanol mixture.⁴

trans-[Pt(C₅H₁₁N)₂(NO₂)₂] was obtained by the reaction of *trans*-[Pt(C₅H₁₁N)₂Cl₂] (10⁻³ M) with NaNO₂ (10⁻¹ M) at 30° in methanol, containing 10⁻² M toluenesulfonic acid, for 4 days. The compound was recrystallized from methanol, m.p. 258–260°. *Anal.* Calcd. for C₁₅H₂₂N₄O₄Pt: N, 12.25. Found: N, 12.1.

trans-[Pt(C₅H₁₁N)₂(N₃)₂] was obtained by the reaction of *trans*-[Pt(C₅H₁₁N)₂Cl₂] (10⁻³ M) with NaN₃ (5 × 10⁻² M) in methanol at 30° for 4 days. The product was recrystallized from methanol, m.p. 172–173°. *Anal.* Calcd. for C₁₀H₂₂N₈Pt: N, 24.9. Found: N, 24.4.

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