

- 248, 5211 (1973).
- (3) (a) H. Brunner and H. Sussner, *Biochim. Biophys. Acta*, **310**, 20 (1973);
(b) H. Brunner, A. Mayer, and H. Sussner, *J. Mol. Biol.*, **70**, 153 (1972).
 - (4) T. G. Spiro and T. C. Strekas, *J. Am. Chem. Soc.*, **96**, 338 (1974).
 - (5) J. J. Weiss, *Nature (London)*, **202**, 83 (1964).
 - (6) L. Pauling, *Nature (London)*, **203**, 182 (1964).
 - (7) L. Rimal, I. Salmeen, and D. H. Petering, *Biochemistry*, **14**, 378 (1975).
 - (8) L. Pauling and C. D. Coryell, *Proc. Natl. Acad. Sci. U.S.A.*, **22**, 210 (1936).
 - (9) T. Iizuka and M. Kotani, *Biochim. Biophys. Acta*, **181**, 275 (1969); **194**, 351 (1969).
 - (10) F. Conti and M. Paci, *FEBS Lett.*, **17**, 149 (1971).
 - (11) R. B. Moon and J. H. Richards, *J. Am. Chem. Soc.*, **94**, 5093 (1972).
 - (12) P. J. Vergamini, N. A. Matwiyoff, R. C. Wohl, and T. Bradley, *Biochem. Biophys. Res. Commun.*, **55**, 453 (1973).
 - (13) I. Morishima, T. Inubushi, T. Yonezawa, and T. Iizuka, to be submitted for publication.
 - (14) G. Lang and W. Marshall, *Proc. Phys. Soc., London*, **87**, 3 (1966).
 - (15) G. Lang, *J. Appl. Phys.*, **38**, 915 (1967).
 - (16) M. I. Saito, T. Kitagawa, T. Iizuka, and Y. Kyogoku, *FEBS Lett.*, **50**, 233 (1975).
 - (17) T. Kitagawa, Y. Kyogoku, T. Iizuka, M. I. Saito, and T. Yamanaka, *J. Biochem.*, **78**, 719 (1975).
 - (18) T. Kitagawa, H. Ogoshi, E. Watanabe, and Z. Yoshida, *Chem. Phys. Lett.*, **30**, 451 (1975).
 - (19) T. Kitagawa, H. Ogoshi, E. Watanabe, and Z. Yoshida, *J. Phys. Chem.*, **80**, 1181, (1976).
 - (20) T. Kitagawa, Y. Kyogoku, T. Iizuka, and M. I. Saito, *Chem. Lett.*, 849 (1975).
 - (21) J. C. Chien, *J. Chem. Phys.*, **51**, 4220 (1969).
 - (22) T. Yonetani, H. Yamamoto, J. E. Erman, J. S. Leigh, Jr., and G. H. Reed, *J. Biol. Chem.*, **247**, 2447 (1972).
 - (23) D. L. Drabkin, *J. Biol. Chem.*, **164**, 703 (1946).
 - (24) T. Omura and S. Takesue, *J. Biochem.*, **67**, 249 (1970).
 - (25) A. L. Verma and H. J. Bernstein, *J. Raman Spectrosc.*, **2**, 163 (1974).
 - (26) T. C. Strekas, A. J. Packer, and T. G. Spiro, *J. Raman Spectrosc.*, **1**, 197 (1973).
 - (27) F. S. Mathews, M. Levine, and P. Argos, *J. Mol. Biol.*, **64**, 449 (1972).
 - (28) T. C. Strekas and T. G. Spiro, *Biochim. Biophys. Acta*, **351**, 237 (1974).
 - (29) G. Rakshit and T. G. Spiro, *Biochemistry*, **13**, 5317 (1974).
 - (30) P. Stein, J. M. Burke, and T. G. Spiro, *J. Am. Chem. Soc.*, **97**, 2304 (1975).
 - (31) M. Abe, T. Kitagawa, and Y. Kyogoku, *Chem. Lett.*, 249 (1976).
 - (32) L. Stryer, J. C. Kendrew, and H. C. Watson, *J. Mol. Biol.*, **8**, 96 (1964).
 - (33) J. P. Collman, R. R. Gagne, C. A. Reed, T. R. Halbert, G. Lang, and W. T. Robinson, *J. Am. Chem. Soc.*, **97**, 1427 (1975).
 - (34) Y. Seno, J. Otsuka, O. Matsuoka, and N. Fuchikami, *J. Phys. Soc. Jpn.*, **33**, 1645 (1972).
 - (35) J. Otsuka, M. Matsuoka, N. Fuchikami, and Y. Seno, *J. Phys. Soc. Jpn.*, **35**, 854 (1973).
 - (36) M. Zerner, M. Gouterman, and H. Kobayashi, *Theor. Chim. Acta*, **6**, 363 (1966) (from Figure 2 case VII).
 - (37) C. H. Barlow, J. C. Maxwell, W. J. Wallace, and W. S. Caughey, *Biochem. Biophys. Res. Commun.*, **55**, 91 (1973).
 - (38) J. C. Maxwell, J. A. Volpe, C. H. Barlow, and W. S. Caughey, *Biochem. Biophys. Res. Commun.*, **58**, 166 (1974).
 - (39) G. Herzberg, "Spectra of Diatomic Molecules", Van Nostrand Princeton, N.J., 1965, p 62.
 - (40) H. Siebert, "Schwingungsspektroskopie in der Anorganischen Chemie", Springer Verlag, Berlin, 1966, pp 40, 51.
 - (41) See Figures 5 and 6 of ref 36.
 - (42) J. O. Alben and W. S. Caughey, *Biochemistry*, **7**, 175 (1968).
 - (43) T. Iizuka, H. Yamamoto, M. Kotani, and T. Yonetani, *Biochim. Biophys. Acta*, **263**, 830 (1972).

Tetrakis(methyl isocyanide)palladium(II) Tetrakis(7,7,8,8-tetracyano-*p*-quinodimethane), [Pd(CNMe)₄](TCNQ)₄·2MeCN: Synthesis, Structure, and Physical Properties

Stephen Z. Goldberg,^{1a} Richard Eisenberg,*^{1a} Joel S. Miller,*^{1b}
and Arthur J. Epstein^{1b}

*Contribution from the Department of Chemistry, University of Rochester, Rochester,
New York 14627, and Xerox Corporation, Webster Research Center, Webster,
New York 14580. Received July 28, 1975*

Abstract: The title compound has been synthesized from the reaction of [Pd(CNMe)₄](PF₆)₂, LiTCNQ, and TCNQ in acetonitrile. Its crystal and molecular structure have been determined from three-dimensional x-ray data obtained by counter techniques. The compound crystallizes in the triclinic space group *P* $\bar{1}$ with one formula unit/unit cell. Cell dimensions are: *a* = 7.730 (2), *b* = 14.978 (7), *c* = 14.389 (4) Å; α = 65.08 (2), β = 81.29 (2), γ = 73.46 (2)°. The conventional *R* factors (refinement on *F*) at convergence for 2266 reflections with $F^2 \geq 3\sigma(F^2)$ and $2\theta \leq 45^\circ$ are 0.0459 and 0.0472. The molecular parameters of the two crystallographically independent TCNQ moieties are equivalent. The crystal structure is such that the TCNQ's stack to give tetrameric groups with interplanar distances of 3.29 and 3.32 Å between molecules in the tetramer. At the junction between tetramers the two independent interplanar ring-ring distances are 3.15 and 3.69 Å. The [Pd(CNMe)₄]²⁺ ion has the expected square planar coordination sphere. There are no stacking interactions between the cation and the TCNQ system. Infrared and reflectance spectra are reported, as are magnetic measurements. Conductivity measurements have been made on both pressed pellet and single-crystal samples. The interpretation of the conductivity data is complicated by the triclinic nature of the crystal cell; however, the results are consistent with a quasi-two-dimensional semiconductor behavior.

An active area of recent research has been the synthesis and characterization of new materials which as solids exhibit anisotropic electrical and magnetic properties, and in particular unidirectional metallic behavior. Although limited in number, materials of this latter type, which are called one-dimensional (1-D) metals, span both organic and inorganic chemistry. To date, the most successful organic systems in this area have been based on the anion of 7,7,8,8-tetracyano-*p*-quinodimethane, TCNQ,²⁻⁵ while the best inorganic systems have been developed around the tetracyanoplatinate anion, Pt(CN)₄²⁻.^{2,3,6-8} It is now well established that partial oxidation of potassium

tetracyanoplatinate(II) with bromine or chlorine leads to the formation of a lustrous, homogeneous material of stoichiometry K₂Pt(CN)₄X_{0.3}(H₂O)₃ which has a partially filled electron energy band arising from the overlap of orbitals comprised mainly of platinum d_{z²} functions.^{2,3,6-8} Similarly, the reaction of tetrathiafulvalene, TTF, with TCNQ results in the formation of the charge transfer salt (TTF)(TCNQ) which possesses partially filled electron energy bands arising from the overlap of π molecular orbitals on the segregated stacks of donor and acceptor molecules.²⁻⁵ The structural arrangement in both of these systems which allows band formation involves the

stacking of planar anionic units. The existence of these *partially filled* electron energy bands manifests itself in shorter than van der Waal's spacings between adjacent molecules and in high conductivity along the stacking directions, as well as in a variety of other physical properties.²⁻⁸

A large number of TCNQ systems have been studied in which both organic and inorganic electron donors have been employed.^{4,9,10} Cations used include simple metal ions,^{9,10} metal complexes,^{9,10} clusters,¹¹ and open³⁻⁵ and closed⁹⁻¹⁰ shell organic cations. TCNQ systems have thus been obtained in which the formal charge per TCNQ molecule lies in the range between 0 and -1 .²⁻⁴ For one-dimensional systems having a fractional charge per TCNQ, both uniform delocalization of charge along a stack and localization of charge at specific sites have been observed.¹²⁻¹⁴ Several systems of the former type have been characterized as having a 1-D metallic state.²⁻⁵

Because of the importance of correlating physical properties with structure, single-crystal x-ray diffraction studies have been carried out on a number of TCNQ systems. These studies have been reviewed recently,^{12,13} and the TCNQ groupings have been classified by structural type,¹²⁻¹⁵ i.e., infinite chains, monomers, dimers, trimers, and tetramers, with a variety of overlap interactions between adjacent TCNQ molecules in the stacked units.

The possibility of forming systems in which square planar complexes would serve as counterions to negatively charged TCNQ moieties seemed to us attractive in light of the role of such complexes in the known inorganic 1-D metals. Of special interest would be the possible extent of interaction between the metal d_{z^2} orbital and the partially filled π^* function of the TCNQ anion. The cation chosen for this purpose was tetrakis(methylisocyanide)palladium(II). Herein we report the synthesis, structural characterization, and physical properties of $[\text{Pd}(\text{CNMe})_4](\text{TCNQ})_4 \cdot 2\text{MeCN}$.

Experimental Section

Preparation of Samples. A hot filtered acetonitrile solution of 129.6 mg of $\text{Pd}(\text{CNMe})_4(\text{PF}_6)_2$ ¹⁶ (0.231 mmol) was added to a hot filtered acetonitrile solution containing 99.6 mg of LiTCNQ ⁹ (0.481 mmol) and 99.9 mg of TCNQ (0.489 mmol). The solution was cooled to -8°C and after 12 h at this temperature dark purple homogeneous crystals separated and were collected (165.4 mg; 0.141 mmol; 61%). Large single crystals were grown by maintaining the filtrate at -8°C for extended periods of time. Crystals for magnetic susceptibility measurements were prepared from quartz ware. Commercially available TCNQ and LiTCNQ were crystallized from commercial acetonitrile of satisfactory quality.⁹ Anal. Calcd for $[\text{Pd}(\text{CNMe})_4](\text{TCNQ})_4 \cdot 2\text{MeCN}$: C, 61.62; N, 26.35; H, 2.93. Found: C, 61.61; N, 25.96; H, 2.83.

Instrumentation. The reflectivity spectra were obtained on a Cary 14 spectrophotometer equipped with a diffuse reflectance accessory. The sample was diluted with magnesium carbonate. The baseline was obtained from blocks of magnesium carbonate. Infrared spectra were obtained on a Beckman IR-12 spectrophotometer in KBr pellets. Polycrystalline conductivity measurements were made with a Triplet 801 VOM meter. Four probe conductivity measurements were made with a Keithly 225 current source, Model 180 nanovoltmeter, and 616 electrometer. Temperature control was provided by a Delta oven. The magnetic susceptibility apparatus used has been previously described.¹⁷

Collection and Reduction of the Single-Crystal X-Ray Data. Single crystals of $[\text{Pd}(\text{CNMe})_4](\text{TCNQ})_4 \cdot 2\text{MeCN}$ suitable for diffraction study were obtained as described above. The space group and preliminary lattice constants were determined from zero and upper level precession photographs. These photographs showed no systematic absences and only $\bar{1}$ symmetry, thus limiting the possible space groups to $P1$ and $P\bar{1}$.¹⁸ Precise cell constants at 22°C were determined from a least-squares refinement¹⁹ of the setting angles of 12 well-resolved reflections ($\sin \theta/\lambda > 0.35$) which were carefully centered (using $\text{Mo K}\alpha_1$ radiation, λ 0.709 261 Å) on a Picker FACS-I diffractometer equipped with a graphite monochromator. The lattice constants are $a = 7.730$ (2) Å, $b = 14.978$ (7) Å, $c = 14.389$ (4) Å, $\alpha = 65.08$ (2)°,

$\beta = 81.29$ (2)°, $\gamma = 73.46$ (2)°, and $V = 1447.3$ (9) Å³. A cell reduction²⁰ confirmed that the crystal had only triclinic symmetry, but revealed that the cell determined above was not the reduced cell. Transformation to the reduced cell is given by the following equation:

$$\begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix}_{\text{reduced}} = \begin{pmatrix} 0 & 0 & -1 \\ -1 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix}_{\text{experimental}}$$

and parameters for the reduced cell are $a = 14.389$ Å, $b = 14.771$ Å, $c = 7.730$ Å, $\alpha = 103.57^\circ$, $\beta = 98.71^\circ$, $\gamma = 110.37^\circ$, and $V = 1447.3$ Å³. Data were collected, and the structure was solved using the initially assigned cell. An experimental density of 1.37 (1) g/cm³ as determined by flotation in $\text{CHCl}_3\text{-CCl}_4$ was in disagreement with a density of 1.25 g/cm³ calculated for one formula unit of $[\text{Pd}(\text{CNMe})_4](\text{TCNQ})_4$ per unit cell. Subsequent solution of the structure, however, revealed the presence of two molecules of acetonitrile for each cation. The calculated density when the solvent is taken into account is 1.34 g/cm³, which is in good agreement with the experimental value. It should be noted that during the experimental determination of the density, the density of the crystal appeared to increase, possibly due to absorption of additional solvent. Thus, the above quoted experimental value of 1.37 (1) g/cm³ should be taken as an upper limit.

Intensity data were collected using the same crystal which was used for the determination of the space group and lattice constants. The crystal dimensions were approximately $0.34 \times 0.17 \times 0.09$ mm, and the crystal was mounted so that the a^* axis (the a axis corresponds to the long dimension and makes an angle of 16.66° with a^*) was nearly parallel to the ϕ axis of the diffractometer. Mosaic spread was checked by means of narrow source, open counter ω scans.²¹ Full widths at half maximum for some typical strong reflections were in the range 0.05–0.08°.

Intensities were measured by the θ - 2θ scan technique. The takeoff angle for the x-ray tube was set at 1.4° so that the intensities of typical strong reflections were roughly 80% of their maximum value as a function of takeoff angle. Data were collected at a scan rate of $1^\circ/\text{min}$ with scans being made from 0.7° below the $\text{K}\alpha_1$ peak to 0.7° above the $\text{K}\alpha_2$ peak. Background counts of 10 s were made at each end of the scan. Attenuator foils were automatically inserted when the intensity of the diffracted beam reached 10 000 counts/s. The pulse height analyzer was set for a 90% window centered on $\text{Mo K}\alpha$ radiation.

Data were collected for the hemisphere with $h \geq 0$ for $3 \leq 2\theta \leq 45^\circ$. Three standard reflections were monitored after every 80 observations. The standards showed a slow linear decay during data collection with the total decay being 7.2%. A total of 4156 reflections were observed, of which 343 with $h = 0$ were observed as Friedel pairs. The values of $\sigma^2(I)$ were estimated using the expression:

$$\sigma^2(I) = \left[q \left\{ 10\text{CT} + 12.75 + \left[\left(\frac{t_c}{2t_b} \right)^2 (10(\text{BL} + \text{BH}) + 25.5) \right] \right\} + (pI)^2 \right]$$

where q is the attenuator factor; t_c is the scan time; t_b is the time spent counting background at each end of the scan; CT, BL, and BH are the counts for the scan and the low and high backgrounds, respectively. The numerical factors arise from the fact that CT, BL, and BH are truncated values obtained from the Picker instrument rather than actual counts. The intensity, I , is given by:

$$I = q \left\{ 10\text{CT} + 4.5 - \left[\left(\frac{t}{2t_b} \right) (10(\text{BL} + \text{BH}) + 9) \right] \right\}$$

The term $(pI)^2$ is included in the expression for the variance to prevent the overweighting of strong reflections,²² and the value of p was chosen as 0.04. Values of I and $\sigma^2(I)$ were converted to F^2 and $\sigma^2(F^2)$ by application of Lorentz and polarization corrections.²⁰

The observed linear decrease in the intensities of the standards was used as the basis of a decay correction. The absorption coefficient for $\text{Mo K}\alpha$ radiation is 3.80 cm^{-1} and no correction for absorption was made. On the assumption that the correct space group was $P\bar{1}$, the Friedel pairs were averaged. The R factor for averaging was 2.3%. The final data set consisted of 3813 reflections of which the 2266 with $F_o^2 \geq 3\sigma(F_o^2)$ were used in the refinement.

Table I. Positional and Thermal Parameters for $[Pd(CNMe)_4](TCNQ)_4 \cdot 2MeCN$

Atom	x	y	z	B_{11}^a	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	0	0	0	153.5 (22) ^b	72.1 (7)	52.6 (6)	-36.4 (9)	-6.0 (8)	-27.0 (5)
C (1)	-0.2379 (10)	0.0695 (5)	-0.0628 (5)	174. (20)	82. (6)	64. (5)	-52. (10)	1. (8)	-39. (5)
C (2)	-0.0147 (9)	0.1200 (5)	0.0307 (5)	193. (17)	93. (7)	50. (5)	-40. (9)	-3. (7)	-33. (5)
C (3)	-0.5485 (10)	0.1622 (6)	-0.1411 (5)	183. (19)	113. (7)	102. (6)	-32. (10)	-42. (9)	-33. (6)
C (4)	-0.0355 (11)	0.2761 (5)	0.0661 (5)	168. (27)	77. (6)	74. (5)	-79. (10)	-17. (10)	-40. (5)
C (5)	0.1844 (10)	0.3728 (4)	0.3946 (5)	215. (19)	43. (5)	45. (5)	-22. (7)	-11. (8)	-13. (4)
C (6)	0.2620 (9)	0.3595 (4)	0.4856 (5)	185. (18)	49. (5)	55. (5)	-20. (7)	-10. (8)	-18. (4)
C (7)	0.1557 (9)	0.3613 (4)	0.5700 (5)	188. (18)	48. (5)	54. (5)	-15. (7)	-31. (8)	-18. (4)
C (8)	-0.0350 (9)	0.3789 (4)	0.5693 (5)	207. (18)	44. (5)	48. (5)	-12. (7)	-9. (8)	-20. (4)
C (9)	-0.1109 (9)	0.3932 (4)	0.4777 (5)	172. (19)	54. (5)	62. (5)	-8. (7)	-26. (8)	-26. (4)
C (10)	-0.0058 (10)	0.3898 (4)	0.3949 (5)	219. (19)	51. (5)	51. (5)	-18. (8)	-23. (8)	-23. (4)
C (11)	0.2949 (10)	0.3678 (5)	0.3108 (5)	230. (20)	45. (5)	55. (5)	-27. (8)	-14. (9)	-18. (4)
C (12)	-0.1430 (10)	0.3815 (4)	0.6551 (5)	221. (20)	48. (5)	60. (5)	-15. (8)	-9. (9)	-24. (4)
C (13)	0.4879 (13)	0.3485 (5)	0.3111 (5)	279. (24)	56. (6)	63. (5)	-44. (11)	9. (11)	-20. (4)
C (14)	0.2219 (10)	0.3828 (5)	0.2189 (6)	276. (21)	30. (6)	60. (6)	-48. (9)	23. (9)	-32. (5)
C (15)	-0.3352 (13)	0.3974 (5)	0.5591 (5)	274. (25)	40. (7)	66. (6)	-29. (12)	6. (11)	-33. (5)
C (16)	-0.0656 (10)	0.3684 (5)	0.7459 (5)	336. (23)	70. (6)	53. (6)	-46. (9)	-1. (9)	-26. (5)
C (17)	0.3683 (8)	0.1208 (4)	0.3604 (4)	156. (16)	44. (5)	44. (4)	-17. (7)	-8. (7)	-17. (4)
C (18)	0.4307 (8)	0.1212 (4)	0.4495 (4)	142. (16)	42. (5)	45. (4)	-13. (7)	-13. (7)	-18. (4)
C (19)	0.3164 (8)	0.1272 (4)	0.5265 (4)	142. (16)	34. (4)	52. (5)	-12. (7)	-20. (7)	-17. (4)
C (20)	0.1282 (8)	0.1343 (4)	0.5270 (4)	138. (15)	41. (5)	40. (4)	-15. (7)	-16. (7)	-13. (4)
C (21)	0.0651 (8)	0.1361 (4)	0.4374 (5)	120. (16)	70. (5)	54. (5)	-29. (7)	-7. (7)	-27. (4)
C (22)	0.1796 (9)	0.1293 (4)	0.3593 (4)	156. (17)	66. (5)	49. (5)	-21. (7)	-16. (7)	-29. (4)
C (23)	0.4841 (8)	0.1122 (4)	0.2797 (4)	151. (16)	57. (5)	50. (5)	-29. (7)	-13. (7)	-26. (4)
C (24)	0.0130 (9)	0.1373 (4)	0.6094 (4)	158. (17)	60. (5)	40. (4)	-27. (7)	-13. (7)	-18. (4)
C (25)	0.4290 (8)	0.1043 (5)	0.1947 (5)	133. (17)	96. (6)	71. (6)	-27. (8)	9. (8)	-43. (5)
C (26)	0.6717 (11)	0.1066 (5)	0.2782 (4)	209. (20)	58. (5)	40. (4)	-33. (9)	-5. (8)	-23. (4)
C (27)	0.0749 (8)	0.1270 (4)	0.7032 (5)	144. (16)	58. (5)	53. (5)	-30. (7)	10. (7)	-17. (4)
C (28)	-0.1758 (11)	0.1449 (5)	0.6117 (5)	181. (20)	103. (7)	58. (5)	-46. (10)	7. (9)	-44. (5)
N (1)	-0.3745 (8)	0.1112 (4)	-0.0974 (4)	157. (16)	39. (5)	73. (5)	-39. (8)	-16. (7)	-35. (4)
N (2)	-0.0253 (7)	0.1884 (5)	0.0469 (4)	234. (16)	80. (5)	60. (4)	-49. (8)	-5. (6)	-32. (4)
N (3)	0.6400 (10)	0.3336 (5)	0.3122 (5)	254. (19)	109. (6)	118. (6)	-59. (10)	19. (10)	-42. (5)
N (4)	0.1626 (10)	0.3352 (5)	0.1450 (5)	465. (23)	141. (7)	69. (5)	-84. (10)	4. (9)	-56. (5)
N (5)	-0.4873 (10)	0.4095 (6)	0.5600 (5)	259. (19)	142. (7)	108. (6)	-47. (11)	18. (10)	-55. (5)
N (6)	0.0005 (10)	0.3578 (5)	0.8163 (5)	509. (25)	123. (7)	60. (5)	-71. (10)	-14. (9)	-40. (5)
N (7)	0.3857 (8)	0.0966 (5)	0.1255 (5)	284. (18)	179. (8)	92. (5)	-74. (9)	-7. (8)	-84. (6)
N (8)	0.8205 (8)	0.1060 (4)	0.2757 (4)	198. (15)	94. (5)	76. (5)	-52. (8)	-1. (7)	-38. (4)
N (9)	0.1245 (8)	0.1190 (4)	0.7775 (4)	265. (16)	93. (5)	53. (4)	-72. (7)	-7. (7)	-23. (4)
N (10)	-0.3260 (9)	0.1511 (5)	0.6145 (5)	165. (16)	169. (7)	108. (6)	-61. (9)	12. (8)	-73. (5)
C (29)	0.2820 (15)	0.4608 (8)	-0.1059 (8)	11.4 (3) ^c					
C (30)	0.4394 (22)	0.3966 (11)	-0.0689 (11)	14.7 (4) ^c					
N (11)	0.5484 (20)	0.3239 (11)	-0.0240 (10)	19.7 (5) ^c					

^a The anisotropic thermal parameters have been multiplied by 10^4 . The form of the anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^b In this and subsequent tables the standard deviations of the least significant figures are given in parentheses. ^c Isotropic thermal parameter, B in \AA^2 , in the expression $\exp[-B(\sin \theta/\lambda)^2]$.

Solution and Refinement of the Structure. The structure was solved and refined using standard Patterson, Fourier, and least-squares methods.²⁰ In all least-squares refinements the quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where the weights, w , were taken as $(1/\sigma(F))^2 = 4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for neutral Pd, N, and C were taken from the tabulation of Cromer and Mann.²³ Corrections for anomalous dispersion of Pd were made using the $\Delta f'$ and $\Delta f''$ values of Cromer and Lieberman.²⁴ The scattering factor for hydrogen was that of Stewart et al.²⁵

The space group was assumed to be $P\bar{1}$. The absence of a single intense peak in the three-dimensional Patterson map, assignable as a Pd-Pd vector, confirmed the presence of only a single cation in the unit cell. The prominent features of the map could not be interpreted in terms of metal-carbon vectors but rather in terms of overlapping

carbon-carbon vectors (vide infra). A careful examination of some of the less intense peaks of the map clearly revealed the positions of the two crystallographically independent TCNQ molecules. Refinement of the trial model resulted in values of R_1 and R_2 of 0.23 and 0.28, respectively.²⁶ A difference Fourier revealed the positions of the carbon and nitrogen atoms of the isocyanide ligands. Isotropic refinement of the full structure yielded $R_1 = 0.12$, $R_2 = 0.17$. Anisotropic thermal parameters were introduced for all the nonhydrogen atoms in the structure and after two cycles of refinement the values of R_1 and R_2 dropped to 0.084 and 0.097.

A difference Fourier at this point revealed three peaks which could be interpreted as the atoms of a trapped molecule (either CH_3CN or CH_3NC). Since it seemed much more reasonable to assume a trapped solvent molecule than a dissociated but trapped ligand moiety, re-

Table II. Positional and Thermal Parameters for Hydrogen Atoms

Atom	x	y	z	B, Å ²
H(6) ^a	0.4074 ^b	0.3447	0.4886	5.5 (15)
H(7)	0.2167	0.3502	0.6381	5.3 (14)
H(9)	-0.2562	0.4073	0.4751	3.8 (13)
H(10)	-0.0684	0.3998	0.3280	5.7 (15)
H(18)	0.5726	0.1171	0.4512	4.7 (14)
H(19)	0.3693	0.1261	0.5945	4.0 (12)
H(21)	-0.0764	0.1441	0.4325	4.8 (14)
H(22)	0.1285	0.1280	0.2936	5.3 (14)
H(31) ^c	-0.5520	0.2398	-0.1969	6.0 ^d
H(32)	-0.5868	0.1225	-0.1802	6.0
H(33)	-0.6543	0.1677	-0.0820	6.0
H(41)	0.0995	0.2878	0.0651	6.0
H(42)	-0.1124	0.3461	0.0079	6.0
H(43)	-0.1001	0.2709	0.1407	6.0

^a TCNQ hydrogens are numbered according to the carbons to which they are bonded. ^b Positional parameters were not refined. ^c Methyl hydrogens are numbered such that the first digit indicates the carbon to which they are bonded. ^d Thermal parameters for methyl hydrogens were not refined.

finement was continued on this assumption. Two additional cycles of refinement reduced R_1 and R_2 to 0.0593 and 0.0547. A difference Fourier revealed the positions of all the hydrogen atoms of the TCNQ molecules at distances ranging from 1.07 to 1.15 Å from the carbon atoms to which they were bonded. The hydrogens were placed at idealized positions with a C-H distance of 1.08 Å. The isotropic thermal parameters were varied and a single cycle of refinement yielded $R_1 = 0.0484$ and $R_2 = 0.0514$. A difference Fourier map then showed the position of the methyl hydrogen atoms. Their inclusion in the final calculations at idealized positions (assuming C-H = 1.08 Å and H-C-H = 109°28', with fixed isotropic temperature factors of 6 Å²) led to convergence after two additional cycles with $R_1 = 0.0459$ and $R_2 = 0.0472$. On the final cycle no parameter shifted by more than half its estimated standard deviation and most of the shifts were less than 0.04σ. A final difference Fourier map showed no peaks larger than 0.5 e/Å³ or 10% of the height of a typical carbon atom in this structure. The largest peaks in the difference map were located near the solvent molecule. The value of the quantity $\sum w(|F_o| - |F_c|)^2$ showed no general trends as a function of either $|F_o|$ or $\sin \theta/\lambda$ although it was somewhat larger than average for the largest and smallest values of $|F_o|$ and at small values of $\sin \theta/\lambda$. The error in an observation of unit weight²⁶ was 1.34 e⁻ for 2266 reflections and 369 variables.

The success of the refinement confirms the choice of the centric space group $P\bar{1}$ (but see the comment regarding the *acentric* space group $P1$ below). The model for the molecule of crystallization is clearly unsatisfactory based on solvent bond distances and angles calculated from the final least-squares parameters. However, since even the complete removal of the solvent from the model led to virtually no change in the other structural parameters it was not considered worthwhile to attempt the development of alternative models.

The final positional and thermal parameters and their estimated errors, as obtained from the final cycle of least squares, are given in Tables I and II. A listing of the observed and calculated structure factors for the reflections used in refinement of the structure is available.²⁷

Results and Discussion

Description of the Structure. The crystal and molecular structure described by the unit cell parameters, the crystallographic symmetry, and the parameters of Table I consist of the packing of isolated square planar Pd(II) dications and tetrameric groupings of planar TCNQ species with delocalized negative charge in a general stacked arrangement which is discussed below. Tables III and IV present intramolecular distances and angles for the structure.

The [Pd(CNMe)₄]²⁺ Cation. The cation [Pd(CNMe)₄]²⁺ is the first simple tetrakis(isocyanide) complex to be structurally determined. Its structural parameters are in accord with those expected for a Pd(II) d⁸ square planar system. A drawing

Table III. Bond Distances of [Pd(CNMe)₄](TCNQ)₄·2 MeCN (in Å)

Atoms	Distance	Atoms	Distance
Pd-C(1)	1.975 (7)	C(5)-C(6)	1.431 (8)
Pd-C(2)	1.993 (7)	C(5)-C(10)	1.419 (8)
	Av ^a 1.984 (9)	C(7)-C(8)	1.422 (8)
		C(8)-C(9)	1.433 (8)
N(1)-C(3)	1.433 (8)	C(17)-C(18)	1.427 (7)
N(2)-C(4)	1.430 (8)	C(17)-C(22)	1.433 (8)
	Av 1.432 (1)	C(19)-C(20)	1.431 (7)
C(1)-N(1)	1.129 (7)	C(20)-C(21)	1.428 (7)
C(2)-N(2)	1.123 (7)		Av 1.428 (2)
	Av 1.126 (3)	C(5)-C(11)	1.385 (8)
C(13)-N(3)	1.134 (9)	C(8)-C(12)	1.401 (8)
C(14)-N(4)	1.145 (8)	C(17)-C(23)	1.383 (7)
C(15)-N(5)	1.137 (9)	C(20)-C(24)	1.384 (7)
C(16)-N(6)	1.135 (8)		Av 1.388 (4)
C(25)-N(7)	1.148 (7)	C(11)-C(13)	1.437 (10)
C(26)-N(8)	1.137 (7)	C(11)-C(14)	1.421 (9)
C(27)-N(9)	1.138 (7)	C(12)-C(15)	1.433 (10)
C(28)-N(10)	1.134 (8)	C(12)-C(16)	1.422 (9)
	Av 1.138 (2)	C(23)-C(25)	1.423 (8)
		C(23)-C(26)	1.433 (9)
C(6)-C(7)	1.368 (8)	C(24)-C(27)	1.427 (8)
C(9)-C(10)	1.347 (8)	C(24)-C(28)	1.428 (9)
C(18)-C(19)	1.359 (7)		Av 1.428 (2)
C(21)-C(22)	1.350 (7)		
	Av 1.356 (5)	C(29)-C(30)	1.336 (15)
		C(30)-N(11)	1.167 (17)

^a All average values and their errors are calculated from: $\bar{x} = \sum x_i/n$, $\sigma(\bar{x}) = [\sum (x_i - \bar{x})^2/n(n-1)]^{1/2}$ where n is the number of independent values obtained.

of the cation is presented in Figure 1. Because the Pd atom is located at a crystallographic inversion center, the inner coordination geometry is rigorously planar. The deviation from perfect tetragonal symmetry is only slight with a C-Pd-C bond angle of 88.4 (3)°. The average Pd-C bond length is 1.984 (9) Å. The methyl isocyanide C≡N triple bond distance averages 1.126 (3) Å, while the mean N-Me bond length is 1.432 (3) Å. The PdCNMe unit is essentially linear with average bond angles at the isocyanide carbon and nitrogen atoms of 178.4 (4) and 178.8 (4)°, respectively.

The Pd-C bond length of 1.984 (9) Å obtained in the present study may be compared with values of 2.03 (3), 2.04 (3), and 1.99 (3) Å reported²⁸ for the Pd-terminal isocyanide distances in the trinuclear cluster Pd₃(SO₂)₂(CN-*t*-Bu)₅, and with values of 2.049 (6) and 1.963 (5) Å found for the axial and equatorial bond lengths in the Pd(I) dimer [Pd₂(CNMe)₆]²⁺.²⁹ While no other Pd-C distances seem appropriate for comparison, there exists considerably more data in the literature on Pt(II)-isocyanide complexes. It is expected that the Pt-C and Pd-C distances in these systems should be of similar length. In *trans*-[Pt(CNMe)₂Cl(NHMe)(SEt)]₂²⁺ the metal-isocyanide carbon bond length is 1.968 (9) Å³⁰ and in [Pt(C₅H₁₁N₄)(CNMe)₂]⁺ the corresponding distance is 1.96 (2) Å.³¹ Other isocyanide complexes with shorter platinum-carbon distances have also been reported.³²

The TCNQ Species. Within the unit cell there are two crystallographically independent molecules of TCNQ which are designated A and B, and are illustrated in Figures 2 and 3, respectively. Both molecules have the same structural parameters to within experimental error (Table V) leading to the hypothesis that each TCNQ species carries the equivalent of one-half unit negative charge. Least-squares planes through the six-membered rings of the TCNQ species are given in Table VI, and in each case the dicyanomethylene groups exhibit slight but significant deviations from their respective planes.

Structural equivalence between crystallographically independent TCNQ molecules has been observed previously,^{12,13} although in certain cases it has been thought possible to dis-

Table IV. Bond Angles of $[Pd(CNMe)_4](TCNQ)_4 \cdot 2MeCN$ (in deg)

Atoms	Angle	Atoms	Angle
C(1)–Pd–C(2)	88.4 (3)	C(6)–C(5)–C(11)	120.0 (6)
Pd–C(1)–N(1)	178.0 (6)	C(10)–C(5)–C(11)	122.2 (6)
Pd–C(2)–N(2)	178.8 (6)	C(7)–C(8)–C(12)	120.5 (6)
	Av ^a 178.4 (4)	C(9)–C(8)–C(12)	121.8 (6)
C(1)–N(1)–C(3)	178.8 (7)	C(18)–C(17)–C(23)	121.9 (6)
C(2)–N(2)–C(4)	178.7 (7)	C(22)–C(17)–C(23)	120.9 (5)
	Av 178.77 (2)	C(19)–C(20)–C(24)	121.1 (5)
C(6)–C(5)–C(10)	117.9 (6)	C(21)–C(20)–C(24)	121.5 (5)
C(7)–C(8)–C(9)	117.7 (6)		Av 121.2 (3)
C(18)–C(19)–C(22)	117.1 (5)	C(5)–C(11)–C(13)	122.2 (6)
C(19)–C(20)–C(21)	117.5 (5)	C(5)–C(11)–C(14)	121.3 (7)
	Av 117.53 (17)	C(8)–C(12)–C(15)	122.3 (6)
C(5)–C(6)–C(7)	120.9 (6)	C(8)–C(12)–C(16)	121.0 (7)
C(6)–C(7)–C(8)	120.8 (5)	C(17)–C(23)–C(25)	123.4 (6)
C(8)–C(9)–C(10)	121.4 (6)	C(17)–C(23)–C(26)	121.4 (5)
C(5)–C(10)–C(9)	121.3 (6)	C(20)–C(24)–C(27)	122.7 (6)
C(17)–C(18)–C(19)	121.4 (5)	C(20)–C(24)–C(28)	123.1 (5)
C(18)–C(17)–C(20)	121.1 (5)		Av 122.2 (3)
C(20)–C(21)–C(22)	121.2 (5)	C(11)–C(13)–N(3)	179.3 (8)
C(17)–C(22)–C(21)	121.6 (5)	C(11)–C(14)–N(4)	179.7 (8)
	Av 121.23 (10)	C(12)–C(15)–N(5)	178.6 (8)
C(13)–C(11)–C(14)	116.4 (6)	C(12)–C(16)–N(6)	178.2 (8)
C(15)–C(12)–C(16)	116.7 (6)	C(23)–C(25)–N(7)	179.1 (8)
C(25)–C(23)–C(26)	115.2 (5)	C(23)–C(26)–N(8)	179.7 (7)
C(27)–C(24)–C(25)	114.1 (5)	C(24)–C(27)–N(9)	179.8 (6)
	Av 115.6 (6)	C(24)–C(28)–N(10)	179.0 (7)
			Av 179.2 (2)
		C(29)–C(30)–N(11)	162.6 (17)

^aSee note in Table III.

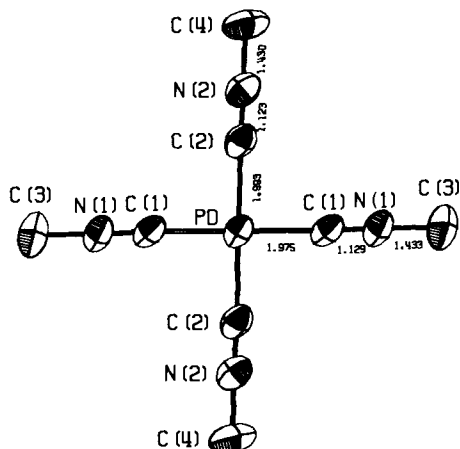


Figure 1. The tetrakis(methyl isocyanide)palladium(II) cation. Thermal ellipsoids enclose 50% of the electron distribution.

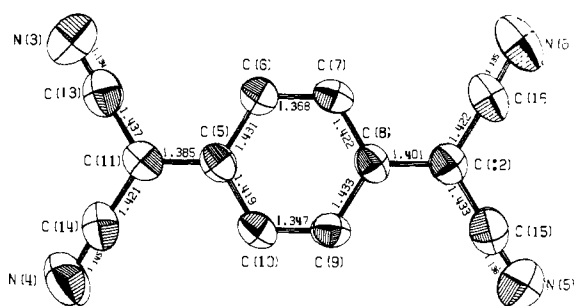


Figure 2. TCNQ (molecule A). The thermal ellipsoids enclose 50% of the electron distribution.

tinguish between $TCNQ^0$ and $TCNQ^-$ within a given structure.^{33,34} Since the space group is not uniquely determined in the present study, the possibility of a random disorder of $TCNQ^0$ and $TCNQ^-$ with the correct structure in space group

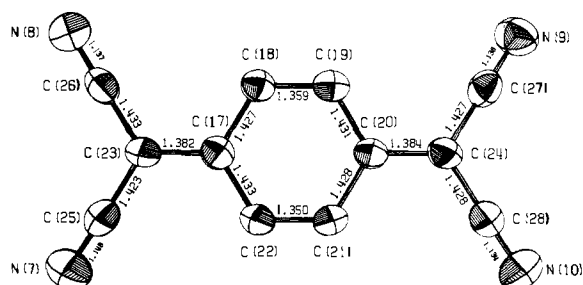
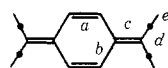


Figure 3. TCNQ (molecule B). The thermal ellipsoids enclose 50% of the electron distribution.

$P1$ must be considered. However, examination of the thermal ellipsoids (Table VII for root mean square amplitudes of vibration and Figures 2 and 3) reveals nothing unusual about them and it is therefore felt that $P1$ is indeed the correct space group with structurally equivalent TCNQ species.

The observed structural parameters strongly support the notion of one-half unit negative charge per TCNQ species. Previously, molecular orbital calculations^{35a} and empirical bond length–bond order relationships^{35b} have indicated that bond lengths for TCNQ should vary according to the net charge of the species.³⁶ The structure of TCNQ itself³⁷ may be taken as providing the molecular parameters for the neutral species, while that of $RbTCNQ^{38}$ provides the parameters for the radical anion. In Table V the structural parameters for these two TCNQ systems, as well as those for a number of others, are presented. The trends in the observed bond distances of the neutral and anionic species parallel the conclusions derived from the theoretical considerations.

While differences in the corresponding bond lengths in the TCNQ structures may not be highly significant in a statistical sense, the trends in bond length variation do offer considerable insight. In Cs_2TCNQ_3 ,³³ for example, two crystallographically independent TCNQ species are found with one at a crystallographic inversion center and the other located in general positions of the space group $P2_1/c$. It is thought that in this

Table V. Molecular Parameters^a for Selected TCNQ Systems

Compound	a	b	c	d	e	Charge	Ref	
TCNQ	1.346 (3)	1.448 (4)	1.374 (3)	1.441 (4)	1.140 (1)	0	37	
RbTCNQ	1.373 (1)	1.423 (3)	1.420 (1)	1.416 (8)	1.153 (7)	-1	38	
Cs ₂ TCNQ ₃	1.341 (5)	1.444 (4)	1.371 (5)	1.428 (4)	1.140 (4)	0	33	
(TEA)(TCNQ) ₂ ^b	1.355 (4)	1.427 (3)	1.410 (4)	1.419 (3)	1.152 (3)	-1		
(TMA) ₂ (TCNQ) ₃ ^c	1.345 (8)	1.444 (5)	1.389 (4)	1.422 (12)	1.153 (14)	0	34a	
	1.377 (2)	1.433 (17)	1.409 (4)	1.408 (9)	1.158 (11)	-1		
	1.340 (8)	1.447 (5)	1.368 (7)	1.433 (6)	1.138 (7)	0	34b	
	1.367 (6)	1.419 (4)	1.421 (6)	1.423 (5)	1.147 (7)	-1		
(TMPD)(TCNQ) ₂ ^d	1.354 (2)	1.434 (2)	1.395 (2)	1.427 (3)	1.17 (1)	-1/2	39	
(TPP)(TCNQ) ₂ ^e	1.354 (2)	1.434 (2)	1.396 (2)	1.428 (3)	1.17 (1)	-1/2	36	
(TTF)(TCNQ) ^f	1.356 (3)	1.433 (3)	1.402 (3)	1.423 (3)	1.151 (3)	g	40	
[Pd(CNCH ₃) ₄](TCNQ) ₄	1.356 (5)	1.428 (2)	1.388 (4)	1.428 (2)	1.138 (2)	-1/2	This study	
	1.358 (11)	1.426 (3)	1.393 (8)	1.428 (4)	1.138 (2)	-1/2		Molecule A
	1.355 (5)	1.430 (1)	1.384 (1)	1.428 (2)	1.139 (3)	-1/2		Molecule B
Theoretical	1.350	1.457	1.361	1.464	—	0	38 ^h	
Theoretical	1.365	1.433	1.395	1.448	—	-1		

^aIn those cases where librational corrections have been applied the tabulated distances are the corrected ones. Librational effects are small except for the lengthening on the CN bonds. ^bTEA = triethylammonium. ^cTMA = trimethylammonium. ^dTMPD = *N,N,N',N'*-tetramethyl-*p*-phenylenediamine. ^eTPP = tetraphenylphosphonium. ^fTTF = tetrathiafulvalene. ^gSee text and ref 41. ^hBased on bond order calculation in ref 35a.

Table VI. Weighted Least-Squares Planes^a of the Ring Systems of the Independent TCNQ Molecules

Atom	Deviation from plane, Å	Atom	Deviation from plane, Å
C(5)	-0.002 (6)	C(17)	0.004 (5)
C(6)	0.000 (6)	C(18)	-0.007 (5)
C(7)	0.002 (6)	C(19)	0.002 (5)
C(8)	0.000 (6)	C(20)	0.007 (5)
C(9)	-0.002 (6)	C(21)	-0.012 (6)
C(10)	0.003 (6)	C(22)	0.005 (6)
C(11)	0.022 ^b	C(23)	0.029
C(12)	0.004	C(24)	0.055
C(13)	0.045	C(25)	0.135
C(14)	0.006	C(26)	-0.023
C(15)	0.023	C(27)	0.189
C(16)	-0.010	C(28)	0.057
N(3)	0.059	N(7)	0.239
N(4)	-0.009	N(8)	-0.069
N(5)	0.047	N(9)	0.292
N(6)	-0.024	N(10)	0.056
Coefficients for Plane			
A	-1.272		-0.533
B	-13.97		-13.23
C	-1.108		0.324
D	-5.879		-1.682

^aPlane is referred to triclinic coordinates and has the form $Ax + By + Cz - D = 0$; see W. C. Hamilton, *Acta Crystallogr.*, 14, 185 (1961). ^bIn those cases where no estimate of the error in the deviation is given the atom was given zero weight in the calculation of the plane.

system negative charge is localized on the latter type of TCNQ species, and the observed structural parameters lend credence to this view. A second structure proposed to contain two different types of TCNQ species is the 1:2 triethylammonium salt, (Et₃NH)(TCNQ)₂.^{34a} Although the bond lengths in this structure have a relatively poor degree of precision, the averaged molecular parameters reveal the same differences as were seen for Cs₂(TCNQ)₃ indicating that one TCNQ may be considered as neutral and the other as the anion radical.

Structural equivalence among crystallographically independent TCNQ species is found in the 1:2 complex salts (PPh₄)(TCNQ)₂³⁶ and (*p*-(Me₂N)₂(C₆H₄))(TCNQ)₂³⁹ as well as in the present study. In these structures the averaged bond lengths are intermediate between those obtained for the

Table VII. Root Mean Square Amplitudes of Vibration (Å)

	Min	Intermed	Max
Pd	0.1899 (14)	0.2137 (12)	0.2525 (13)
C(1)	0.187 (13)	0.224 (10)	0.274 (11)
C(2)	0.190 (11)	0.228 (10)	0.270 (11)
C(3)	0.203 (13)	0.304 (10)	0.331 (10)
C(4)	0.200 (12)	0.266 (10)	0.362 (10)
C(5)	0.188 (11)	0.211 (10)	0.246 (11)
C(6)	0.206 (10)	0.222 (10)	0.230 (11)
C(7)	0.188 (11)	0.208 (10)	0.250 (10)
C(8)	0.193 (11)	0.202 (10)	0.247 (10)
C(9)	0.197 (11)	0.212 (10)	0.252 (10)
C(10)	0.192 (11)	0.211 (11)	0.256 (10)
C(11)	0.199 (11)	0.215 (10)	0.255 (11)
C(12)	0.200 (11)	0.226 (10)	0.255 (11)
C(13)	0.213 (11)	0.242 (10)	0.282 (12)
C(14)	0.212 (11)	0.259 (10)	0.289 (11)
C(15)	0.229 (11)	0.264 (11)	0.285 (12)
C(16)	0.209 (11)	0.244 (11)	0.306 (11)
C(17)	0.193 (10)	0.197 (10)	0.211 (10)
C(18)	0.185 (11)	0.191 (10)	0.211 (10)
C(19)	0.171 (11)	0.183 (11)	0.226 (10)
C(20)	0.171 (11)	0.194 (10)	0.208 (10)
C(21)	0.174 (12)	0.213 (10)	0.249 (10)
C(22)	0.174 (11)	0.216 (11)	0.244 (9)
C(23)	0.172 (11)	0.217 (11)	0.225 (10)
C(24)	0.176 (11)	0.212 (11)	0.234 (10)
C(25)	0.189 (12)	0.234 (11)	0.293 (10)
C(26)	0.175 (11)	0.221 (11)	0.242 (11)
C(27)	0.186 (11)	0.221 (11)	0.238 (10)
C(28)	0.199 (10)	0.218 (12)	0.301 (10)
N(1)	0.189 (11)	0.251 (8)	0.279 (9)
N(2)	0.212 (10)	0.243 (8)	0.273 (9)
N(3)	0.252 (10)	0.311 (9)	0.330 (8)
N(4)	0.217 (9)	0.335 (9)	0.368 (9)
N(5)	0.259 (10)	0.310 (9)	0.356 (9)
N(6)	0.214 (9)	0.327 (9)	0.376 (9)
N(7)	0.213 (9)	0.282 (9)	0.398 (9)
N(8)	0.219 (9)	0.250 (8)	0.289 (8)
N(9)	0.212 (8)	0.235 (8)	0.308 (8)
N(10)	0.205 (11)	0.280 (8)	0.386 (8)
C(29)	0.380 (5) ^a		
C(30)	0.432 (6)		
N(11)	0.449 (6)		

^aAcetonitrile atoms refined isotropically.

neutral and monoanionic forms. Thus there appears to exist only a single type of TCNQ species in these structures with

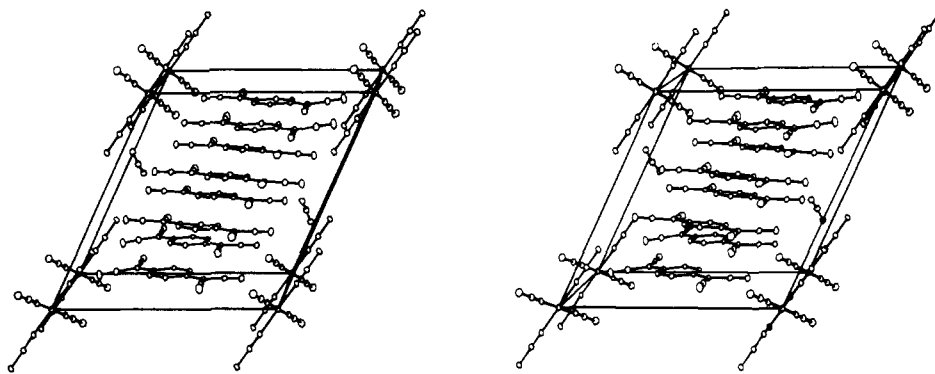


Figure 4. A stereoscopic packing diagram for $[\text{Pd}(\text{CNMe})_4](\text{TCNQ})_4 \cdot 2\text{MeCN}$. The c axis is horizontal and the b axis is mostly vertical. For clarity, the isotropic thermal parameters for MeCN have been set to 5 \AA^2 . Thermal ellipsoids enclose 10% of the electron distribution.

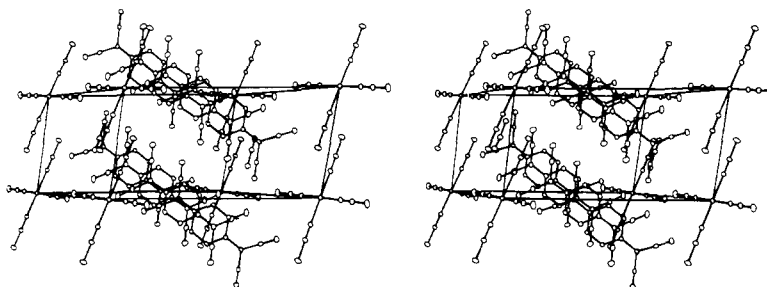


Figure 5. A stereoscopic packing diagram for $[\text{Pd}(\text{CNMe})_4](\text{TCNQ})_4 \cdot 2\text{MeCN}$. The c axis is horizontal and the a^* axis is vertical. For clarity, the isotropic thermal parameters for MeCN have been set to 5 \AA^2 . Thermal ellipsoids enclose 10% of the electron distribution.

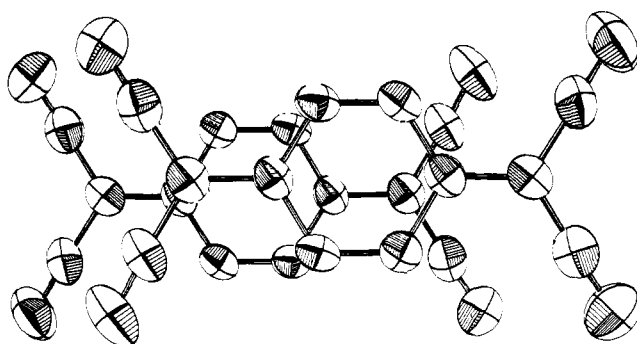


Figure 6. Interaction between TCNQ molecules A and A' where A' is related to A by the inversion center at $(0, 1/2, 1/2)$. The view is normal to the TCNQ plane. Thermal ellipsoids enclose 50% of the electron distribution.

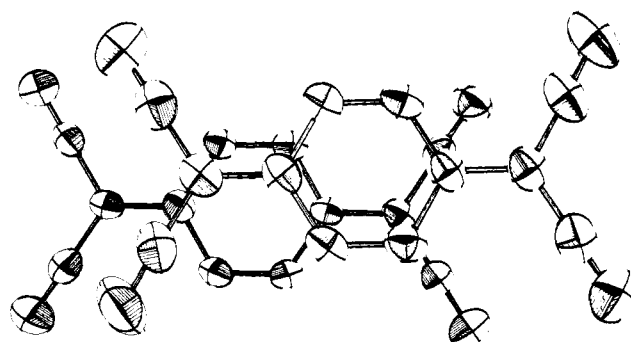


Figure 7. Interaction between TCNQ molecules A and B. The view is normal to the plane of molecule B. Thermal ellipsoids enclose 50% of the electron distribution.

charge uniformly delocalized. Each TCNQ species carries approximately one-half unit negative charge.

In the light of these results, the charge assignment in the case of the well-studied tetrathiafulvalenium system (TTF)-(TCNQ)⁴⁰ poses an interesting question. Based on the parameters presented in Table V, it would appear that only partial charge transfer occurs in (TTF)(TCNQ) since the bond lengths obtained for TCNQ in this system agree closely with those of TCNQ species bearing a fractional negative charge. However, Kistenmacher et al.⁴⁰ have suggested that the molecular parameters obtained by them in their study of (TTF)(TCNQ) imply that the TCNQ species bears approximately a 1⁻ charge. The matter is not completely resolvable via x-ray crystallography; however, recent x-ray diffuse scattering experiments⁴¹ have led to estimates of 0.55 excess electrons per TCNQ in (TTF)(TCNQ).

The TCNQ Stacking Arrangement. The TCNQ species pack together in the crystal as tetrameric units of the form BAA'B' where the primes denote molecules related to the unprimed species by a crystallographic inversion center. Views of the

tetrameric grouping are shown in Figures 4 and 5. The A and B molecules are not perfectly parallel, having an angle of 7.4° between the normals of the least-squares planes. The vector from the center of molecule A to the center of molecule B makes an angle of 177.2° with the vector from the center of A to the center of A'. The tetramer stacking direction is at an angle of approximately 32° to the normals of the molecular planes, and it forms angles of 88 , 20 , and 60° with the crystallographic axes a , b , and c , respectively.

There are three types of interactions between TCNQ species to be considered in the present structure, and they are illustrated in Figures 6–8. The A–A' and A–B interactions, which are within the tetrameric grouping, have the exo double bond of one TCNQ moiety located over the ring system of the neighboring molecule. The plane-to-plane distance between adjacent A molecules is 3.32 \AA while the mean interplanar separation between neighboring A and B moieties is 3.29 \AA .

The third type of interaction between TCNQ species occurs at the tetramer junctions between molecules of the B type. In Figure 8a the central molecule may be viewed as the bottom

Table VIII. Stacking Arrangements in Some Representative TCNQ Systems

Compound	Stack type	Interplanar distances, Å	Ref
TCNQ	Uniform	3.45	37
(TMPD)(TCNQ)	Uniform	3.24	39
(TTF)(TCNQ)	Uniform	3.17	40
(TMA) ₂ (TCNQ) ₃	Monomeric	—	34b
RbTCNQ	Dimeric	(3.26)	
(TPP)(TCNQ) ₂	Dimeric	(3.159), ^a 3.484	38
Cs ₂ (TCNQ) ₃	Trimeric	(3.22), 3.35	36
(TEA)(TCNQ) ₂	Trimeric	(3.22, 3.22), 3.26	33
(DBBP)(TCNQ) ₂	Tetrameric	(3.24, 3.32, 3.24), 3.30	34a
(DBBP)(TCNQ) ₄ ^b	Tetrameric	(3.16, 3.24, 3.16), 3.62	42
[Pd(CNCH ₃) ₄](TCNQ) ₄	Tetrameric	(3.29, 3.32, 3.29), 3.69, 3.15	This study

^aDistances between planes of the repeating unit are enclosed in parentheses. ^bDBBP = (*N,N'*-dibenzyl-4,4'-bipyridylum)²⁺.

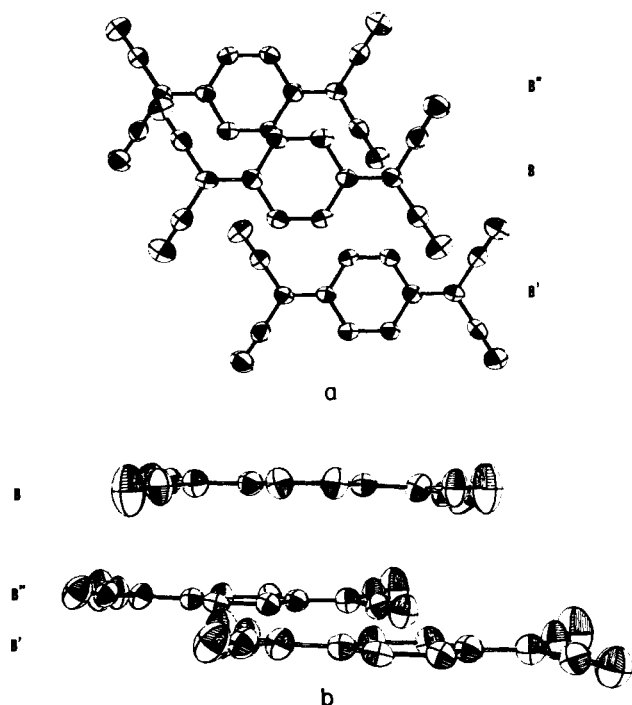


Figure 8. Two views of the interactions of B type rings at the tetrameric junction. Ring B is the bottom molecule of one tetramer while B' and B'' are the top molecules of two other tetramers. Rings B' and B'' are related to B by inversion through (0, 0, 1/2) and (1/2, 0, 1/2). Ring B'' is related to B' by translation along the *a* axis. The thermal ellipsoids enclose 50% of the electron distribution.

member of one tetrameric grouping with the other two TCNQ molecules as the top members of the nearest neighbor tetramers. The interplanar distances for the two types of B-B' interactions illustrated are 3.15 and 3.69 Å. There is a close C(18)-C(18') contact of 3.204 (11) Å which represents the shortest nonbonded interaction between atoms of adjacent TCNQ species. This particular intermolecular contact is such that even though it occurs between termini of the tetrameric groupings, some interaction between π systems of adjacent B type molecules seems probable.

Crystal structures of TCNQ systems reveal a large variation in the packing arrangements of the TCNQ molecules.^{12,13} In many cases TCNQ species have as their nearest neighbors other TCNQ molecules, and a stacked arrangement is observed. This arrangement may be uniform with equally spaced TCNQ species or nonuniform with dimeric, trimeric, or tetrameric groupings as the basic repeat unit. In other cases, the TCNQ molecules do not exhibit an extended stacking arrangement and instead occur as isolated monomers or dimers. Stacking arrangements for a number of representative TCNQ systems are given in Table VIII.

The present structural results show an extended, nonuniform stacking arrangement with tetrameric groupings. In the structures of TCNQ³⁷ and (TTF)(TCNQ),⁴⁰ uniform stacking arrangements are observed with interplanar spacings of 3.45 and 3.17 Å, respectively. The overlap between adjacent molecules in these systems is of the ring-exo double bond type similar to that shown in Figures 6 and 7. In nonuniform stacking arrangements, differences in nearest neighbor interactions arise because of differences in TCNQ overlap as well as because of differences in interplanar separations. The complex salt Cs₂(TCNQ)₃, for example, exhibits trimeric groupings delineated by the nature of nearest neighbor overlap interactions.³³ Within the trimeric units, the overlap is of the ring-exo double bond type, whereas at the junction of the trimeric groupings the overlap is of a ring-ring type.

In (DBBP)(TCNQ)₄ (DBBP = *N,N'*-dibenzyl-4,4'-bipyridylum),⁴² the TCNQ to cation ratio is the same as it is in the present case. While the general features of these two structures are similar, there exist major differences in the interactions at the tetramer junctions. In particular, the close contact between carbon atoms of the TCNQ rings reported here (see Figure 8) is not observed in the DBBP structure. The closeness of the C(18)-C(18') nonbonded contact is taken to mean that extended interactions between the TCNQ groupings occur.

Other Structural Features. The important interaction which we wished to investigate was that between the square planar cationic species and the planar TCNQ anions. As Figures 4 and 5 show, there is essentially no interaction of this type. The angles between the normals of the cation plane and the TCNQ species are 63.3 and 61.5° for A and B, respectively. Thus, despite the possibility for interaction between the planar cationic and anionic species, no such interaction is observed.

The acetonitrile of crystallization is poorly defined in our model. The C-C and C-N distances are 1.34 (2) and 1.17 (2) Å, respectively, while the C-C-N angle is 163 (2)°. The isotropic thermal parameters for the three atoms are in the range 11.4-19.7 Å². The molecule's closest nonbonded interactions are with the hydrogens of a methyl isocyanide ligand, N(11)-H(42) = 2.86 (1) Å, C(29)-H(41) = 3.23 (1) Å, and C(30)-H(41) = 3.40 (1) Å. Inclusion of the MeCN molecule in the model resulted in a significant improvement in the agreement factors and in a substantial reduction in the estimated standard deviations of the structural parameters; however, no significant changes in bond lengths or angles resulted from its inclusion.

Physical Properties

Conductivity. Four-probe single-crystal dc conductivities of [Pd(CNMe)₄](TCNQ)₄·2MeCN were measured. Conductivity as a function of reciprocal temperature is shown in Figure 9 for measurements taken along the crystal *a* axis. The results show a semiconducting behavior with a room temper-

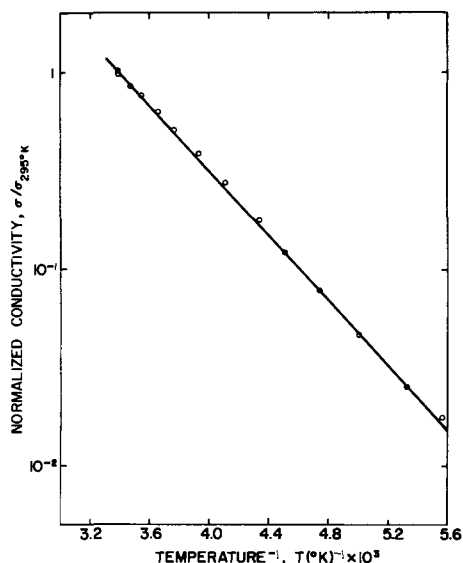


Figure 9. Temperature dependence of the conductivity along a for a single crystal of $[\text{Pd}(\text{CNMe})_4](\text{TCNQ})_4 \cdot 2\text{MeCN}$.

ature conductivity of $5.4 \times 10^{-3} (\Omega \text{ cm})^{-1}$. Using the expression

$$\sigma = \sigma_0 \exp(-E_g/kT)$$

an energy gap, E_g , of 0.16 eV (1300 cm^{-1}) is found together with $\sigma_0 = 3.5 (\Omega \text{ cm})^{-1}$.

Because of the triclinic habit of crystals of $[\text{Pd}(\text{CNMe})_4](\text{TCNQ})_4 \cdot 2\text{MeCN}$ and their relatively small dimensions in directions perpendicular to the a axis ($<1 \text{ mm}$), direct measurement of the other components of the conductivity tensor was not possible. An estimate of the conductivity along the b axis, which is presumed to be the highest conducting direction because of TCNQ stacking, was obtained by taking samples of rectangular parallelepiped geometry and making independent electrical contact to each of four corners of one face, extending the silver paint contact down each edge to the base of the sample. The ratio of the voltage between two adjacent electrodes to the current between the other two electrodes was obtained. A similar measurement was then performed with the sample rotated by 90° . From these measurements, assuming orthorhombic (not the observed triclinic) symmetry and utilizing an algorithm due to Montgomery,⁴³ estimates of the sample conductivity parallel to the chosen face were made. Typically, values of 0.02 – $0.04 (\Omega \text{ cm})^{-1}$ were obtained. Comparison of these results with compressed powder sample conductivities of $\sim 1.3 \times 10^{-2} (\Omega \text{ cm})^{-1}$ shows that the conductivity parallel to the b axis is higher than that along the a (needle) axis.

Magnetic Susceptibility. Attempts were made to measure the intrinsic magnetic susceptibility of $[\text{Pd}(\text{CNMe})_4](\text{TCNQ})_4 \cdot 2\text{MeCN}$ between 2 and 320 K. However, it was found to be masked by ferromagnetic and paramagnetic impurities (which saturated at magnetic fields greater than 8 kG) for $T > 280 \text{ K}$ and paramagnetic impurities with a Curie law dependence for $T < 280 \text{ K}$. An upper limit of $+7.5 \times 10^{-5} \text{ emu/mol}$ is therefore placed upon the total intrinsic susceptibility at room temperature after correction for the ferromagnetic and paramagnetic impurities. The core diamagnetic susceptibility is estimated as $-6.80 \times 10^{-4} \text{ emu/mol}$ using the measured room temperature susceptibilities of $\text{Pd}(\text{CNCH}_3)_4(\text{PF}_6)_2$ ($-2.70 \times 10^{-4} \text{ emu/mol}$, this study) TCNQ^0 ($-1.21 \times 10^{-4} \text{ emu/mol}$),⁴⁴ and acetonitrile ($-0.28 \times 10^{-4} \text{ emu/mol}$),⁴⁵ and Pascal's constants⁴⁶ for hexafluorophosphate ($-0.64 \times 10^{-4} \text{ emu/mol}$). Therefore the upper limit for the room temperature para-

magnetic contribution to the susceptibility of $[\text{Pd}(\text{CNMe})_4](\text{TCNQ})_4 \cdot 2\text{MeCN}$ is $+7.55 \times 10^{-4} \text{ emu/mol}$.

Optical Properties. The absorption spectrum of $[\text{Pd}(\text{CNMe})_4](\text{TCNQ})_4 \cdot 2\text{MeCN}$ was measured in a KBr pellet using the method of Iida.^{47a} The results are in qualitative agreement with those reported for other complex TCNQ salts.^{47,48} S and α bands^{47a} were observed at 11 500 and 16 400 cm^{-1} , whereas two absorptions at 23 000 and 30 800 cm^{-1} occurred in the region assignable to the β bands. The diffuse reflectance spectrum was also recorded for a finely ground sample of $[\text{Pd}(\text{CNMe})_4](\text{TCNQ})_4 \cdot 2\text{MeCN}$ mixed with magnesium carbonate as diluent. Absorptions were observed at 11 900, 12 300, 13 200, 13 500, 23 000, 24 000, 29 200, 44 600, and $\leq 50\,000 \text{ cm}^{-1}$. The high energy bands at 44 600 and $\leq 50\,000 \text{ cm}^{-1}$ are characteristic of $[\text{Pd}(\text{CNMe})_4]^{2+}$ ($\text{R} = \text{Me}$,⁴⁹ Et ,⁵⁰) while the low energy absorptions (12 300–11 900) are qualitatively similar to the S absorptions reported by Iida.^{47a} The observed differences between the absorption spectrum and the diffuse reflectance spectrum probably arise from sample preparation. Although KBr is frequently used as a medium for the measurement of the optical properties of TCNQ salts, the KBr pellet in the present study was green (transmitted light), whereas the mixture of $[\text{Pd}(\text{CNMe})_4](\text{TCNQ})_4 \cdot 2\text{MeCN}$ and MgCO_3 was purple (reflected light). These differences are being investigated further.

In the infrared region, $[\text{Pd}(\text{CNMe})_4](\text{TCNQ})_4 \cdot 2\text{MeCN}$ exhibits a variety of broad absorptions characteristic of TCNQ, cyano, and isocyano groups. The most prominent feature is a broad absorption at 2180 cm^{-1} assigned to the $\text{C}\equiv\text{N}$ stretches of $[\text{Pd}(\text{CNMe})_4]^{2+}$, MeCN , and of the tetracyanoquinodimethane moieties.

Summary

A novel TCNQ charge transfer salt has been synthesized utilizing a planar transition metal cation and the donor. The resultant compound shows no significant interaction between the π orbitals of the TCNQ and the d_{z^2} orbitals of the Pd atom. The TCNQ molecules form tetramer groups with two excess electrons per tetramer. The arrangement of these tetramer groups in two-dimensional arrays (bc plane) isolated by planes of the closed shell $\text{Pd}(\text{CNCH}_3)_4^{2+}$ cation suggest quasi-two-dimensional semiconducting behavior within the planes and lower conductivity in the out-of-plane (a) direction. These expectations are supported by the conductivity and magnetic measurements outlined above. The compound reported here appears to be part of a new class of compounds with a two-dimensional array of TCNQ molecules.

Acknowledgments. R.E. and S.Z.G. gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. A.J.E. gratefully acknowledges the cooperation of J. C. Scott, A. F. Garito, and A. J. Heeger in performing the magnetic susceptibility measurements.

Supplementary Material Available: A listing of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) (a) University of Rochester; (b) Xerox Corporation.
- (2) I. F. Shchegolev, *Phys. Status Solidi A*, **12**, 9 (1972).
- (3) H. R. Zeller, *Adv. Solid State Phys.*, **13**, 31 (1973).
- (4) A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, **7**, 232 (1974).
- (5) A. J. Heeger and A. F. Garito, *NATO Adv. Study Inst.*, **7**, 89 (1975).
- (6) J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, **20**, 1 (1976).
- (7) K. Krogmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 35 (1969).
- (8) T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev.*, **1**, 99 (1972).
- (9) L. R. Meiby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962).
- (10) D. S. Acker and D. C. Blomstrom, U.S. Patent 3 162 641.
- (11) S. Z. Goldberg, G. Stanley, B. Spivack, R. Eisenberg, D. M. Braitsch, and J. S. Miller, manuscript in preparation.

- (12) R. B. Shibaeva and L. O. Atovmyan, *J. Struct. Chem. (Engl. Transl.)*, **13**, 514 (1972).
- (13) F. H. Herbstein, *Perspect. Struct. Chem.*, **4**, 269 (1971).
- (14) Z. G. Soos, *Annu. Rev. Phys. Chem.*, **24**, 121 (1974).
- (15) D. J. Dahm, P. Horn, G. R. Johnson, M. G. Miles, and J. D. Wilson, *J. Cryst. Mol. Struct.*, **5**, 27 (1975).
- (16) J. S. Miller and A. L. Balch, *Inorg. Chem.*, **11**, 2069 (1972).
- (17) J. C. Scott, Ph.D. Thesis, University of Pennsylvania, 1975.
- (18) "International Tables for X-Ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1969.
- (19) The programs for refinement of lattice constants and automated operation of the diffractometer are those of Busing and Levy as modified by Picker Corporation.
- (20) All computations were carried out on an IBM 360/65 computer. Cell reduction was done using Lawton's TRACER II. Locally modified versions of the following programs were used: Raymond's URFACTS for data reduction; Ibers' NUCLS, a group least-squares version of the Busing-Levy ORFLS program; Zalkin's FORDAP Fourier program; ORFFE, a function and error program by Busing, Martin, and Levy; Johnson's ORTEP2 thermal ellipsoid plotting program. A number of local programs were also used.
- (21) T. C. Furnas, "Single Crystal Orienter Instruction Manual", General Electric Co., Milwaukee, Wis., 1957.
- (22) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).
- (23) D. T. Cromer and B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
- (24) D. T. Cromer and D. Lieberman, *J. Chem. Phys.*, **53**, 1891 (1970).
- (25) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
- (26) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. Estimated standard deviation of an observation of unit weight = $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$ where N_o and N_v are the number of observations and variables, respectively.
- (27) See paragraph at end of paper regarding supplementary material.
- (28) S. Otsuka, Y. Tatsuna, and M. Miki, *J. Chem. Soc. Chem. Commun.*, 445 (1973).
- (29) D. J. Doonan, A. L. Balch, S. Z. Goldberg, R. Eisenberg, and J. S. Miller, *J. Am. Chem. Soc.*, **97**, 1961 (1975); S. Z. Goldberg and R. Eisenberg, *Inorg. Chem.*, **15**, 535 (1976).
- (30) W. M. Butler and J. H. Enemark, *Inorg. Chem.*, **12**, 540 (1973).
- (31) W. M. Butler, J. H. Enemark, J. Parks, and A. L. Balch, *Inorg. Chem.*, **12**, 451 (1973).
- (32) (a) B. Jovanovic and Lj. Manojlovic-Muir, *J. Chem. Soc., Dalton Trans.*, 1176 (1972); (b) B. Jovanovic, Lj. Manojlovic-Muir, and K. W. Muir, *ibid.*, 1178 (1972).
- (33) C. J. Fritchie, Jr., and P. Arthur, Jr., *Acta Crystallogr.*, **21**, 139 (1966).
- (34) (a) H. Kobayashi, Y. Ohashi, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **26**, 459 (1970); (b) H. Kobayashi, T. Danno, and Y. Saito, *Acta Crystallogr., Sect. B*, **29**, 2693 (1973).
- (35) (a) H. T. Jonkman and J. Kommandeur, *Chem. Phys. Lett.*, **15**, 496 (1972); (b) J. L. de Boer and A. Vos, *Acta Crystallogr., Sect. B*, **28**, 835 (1972), and references therein.
- (36) P. Goldstein, K. Seff, and K. N. Trueblood, *Acta Crystallogr., Sect. B*, **24**, 778 (1968).
- (37) R. E. Long, R. A. Sparks, and K. N. Trueblood, *Acta Crystallogr.*, **18**, 932 (1965).
- (38) A. Hoekstra, T. Spoelder, and A. Vos, *Acta Crystallogr., Sect. B*, **28**, 14 (1972).
- (39) A. W. Hanson, *Acta Crystallogr., Sect. B*, **24**, 768 (1968).
- (40) T. J. Kistenmacher, T. E. Phillips, and D. O. Cowan, *Acta Crystallogr., Sect. B*, **30**, 763 (1974); T. E. Phillips, T. J. Kistenmacher, J. P. Ferraris, and D. O. Cowan, *J. Chem. Soc., Chem. Commun.*, 471 (1973).
- (41) F. Denoyer, R. Comes, A. F. Garito, and A. J. Heeger, *Phys. Rev. Lett.*, **35**, 445 (1975).
- (42) T. Sundaresan and S. C. Wallwork, *Acta Crystallogr., Sect. B*, **28**, 2474 (1972).
- (43) H. C. Montgomery, *J. Appl. Phys.*, **42**, 2971 (1971).
- (44) J. C. Scott, A. F. Garito, and A. J. Heeger, *Phys. Rev. B*, **10**, 3131 (1974).
- (45) R. C. Weast, Ed., "Handbook of Chemistry and Physics", 53rd ed, Chemical Rubber Co., Cleveland, Ohio, 1972, p E-114.
- (46) J. Lewis and R. G. Wilkins, Ed., "Modern Coordination Chemistry", Interscience, New York, N.Y., 1960, p 403. Values for P and F are -26.3 and -6.3×10^{-6} emu/(g atom), respectively.
- (47) (a) Y. Iida, *Bull. Jpn. Chem. Soc.*, **42**, 71, 367 (1969); (b) Y. Ohashi and T. Sakata, *ibid.*, **46**, 330 (1973).
- (48) J. B. Torrence, B. A. Scott, and F. B. Kaufman, *Solid State Commun.*, **17**, 1369 (1975).
- (49) J. S. Miller and D. G. Marsh, unpublished results.
- (50) H. Isci and W. R. Mason, *Inorg. Chem.*, **14**, 913 (1975).

Metal to Ligand Charge-Transfer Spectra in Tetra-*n*-butylammonium Dicyanoaurate(I)

W. Roy Mason

Contribution from Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115. Received December 22, 1975

Abstract: Electronic absorption spectra at 1.6 K are reported for thin polycrystalline films of $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Au}(\text{CN})_2]$ on quartz plates, together with some polarized spectra at 300 K for oriented single crystals grown on quartz or LiF plates. The 1.6 K spectra reveal considerable structure in the major band systems which are observed in the region 40–53 cm^{-1} . The spectra of the single crystals show strong polarization in the ultraviolet region 40–47 cm^{-1} and in the infrared cyanide stretching region (2150–2130 cm^{-1}). The structured bands in the 1.6 K spectra are assigned as allowed metal to ligand charge-transfer (MLCT) transitions ($\text{Au } 5d \rightarrow \pi^*\text{CN}^-$) accompanied by vibrational excitation. Several progressions in the totally symmetric ν_1 (CN stretch) and ν_2 (AuC stretch) modes are identified and electronic origins are tentatively located. The polarized spectra allow differentiation of transitions to allowed Σ_u^+ states (z -polarized) and Π_u states (xy -polarized) below 47 cm^{-1} . Electronic excited states for $\text{Au}(\text{CN})_2^-$ are interpreted by means of a model which includes spin-orbit coupling in MLCT excited configurations, and the results are discussed in terms of 5d-orbital participation in bonding.

The linear $\text{Au}(\text{CN})_2^-$ ion is one of the most stable and best structurally characterized two-coordinate complexes known.¹ Solid salts consist of discrete, linear ions, and in solution the complex has virtually no tendency to increase its coordination number beyond two. Indeed, $\text{Au}(\text{CN})_2^-$ may be considered as a prototype of linear, two-coordinate complexes containing π acceptor ligands, and as such, there is considerable interest in its electronic structure and spectra.

Recently, solution electronic absorption and magnetic circular dichroism (MCD) spectra for $\text{Au}(\text{CN})_2^-$ were reported¹ together with some low temperature (40 K) spectra for $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Au}(\text{CN})_2]$, deposited as a thin solid film on quartz. The ion, especially in the solid, exhibits remarkably rich electronic spectra with numerous intense bands observed in the

ultraviolet region between 40 and 54 cm^{-1} . These bands have been assigned^{1–3} to metal to ligand charge transfer (MLCT) transitions from the occupied orbitals which are mainly Au 5d to empty ligand based π^* orbitals. While the MLCT assignment seems firm, the detailed assignment of individual transitions among the numerous spectral features remains a complicated and challenging problem. In an effort to solve this problem, the present paper reports some spectral measurements on solid $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Au}(\text{CN})_2]$ at 1.6 K and some polarized spectra for oriented crystals at room temperature in the energy region below 47 cm^{-1} . The 1.6 K spectra show enhanced resolution over the previous 40 K spectra,¹ while band polarizations allow a more precise description of the symmetries of the low lying excited states. The spectra are