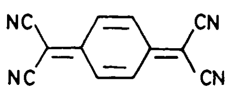
X-Ray Crystal Structure and Properties of (1,4-Pyrazinio)bis(dicyanomethylide) (DiazaTCNQ)

Gen-etsu Matsubayashi, Yoshito Sakamoto, and Toshio Tanaka *
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565, Japan
Kazumi Nakatsu
Department of Chemistry, Faculty of Science, Kwansei Gakuin University, Uegahara, Nishinomiya, Hyogo 662, Japan

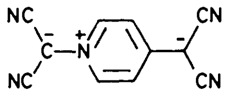
The title compound has been synthesized by the reaction of pyrazine with tetracyanoethylene oxide in refluxing toluene. Single-crystal *X*-ray structure analysis has been performed on tetragonal crystals of space group $P4_2/mnm$ with $Z = 2$. The cell constants are $a = 8.781(2)$, $c = 5.916\,8(7)$ Å, and $V = 456.2(2)$ Å^3. Block-diagonal least-squares refinement, based on 341 independent reflections with $|F_0| > 3\sigma(F)$, yields R 0.047. The centres of the strictly planar diazaTCNQ (DATCNQ) molecules are located on (0,0,1/2) and on (1/2,1/2,0), the molecular planes being parallel to the *c* plane and perpendicular to one another. DATCNQ exhibits a band at 635 nm due to an intermolecular interaction in the powder reflectance spectrum and behaves as a semiconductor with an electrical resistivity of 2.6×10^{10} Ω cm as a compacted pellet at 25 °C. DATCNQ reacts with bromine in hexane to give DATCNQ·Br$_x$ ($x = 0.05$ and 0.11), which exhibits resistivities of 2.2×10^8 and 3.2×10^6 Ω cm at 25 °C.

7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ) (**1**) is known as a good electron acceptor, and low-dimensional organic and inorganic TCNQ$^{\cdot-}$ radical anion salts have been extensively investigated.[1] (4-Dicyanomethyl-1-pyridinio)dicyanomethanide anion (AzaTCNQ$^-$) (**2**) is isostructural with TCNQ[2,3] and we have recently reported geometries and electrical properties of AzaTCNQ$^-$ anion salts with several tetrakis(isocyanide)-rhodium(I) cations[3] and with *N*-alkylpyridinium and related cations.[4] Although neutral (1,4-pyrazinio)bis(dicyanomethylide) (DiazaTCNQ; DATCNQ) (**3**) is also expected to be isostructural with TCNQ and its electrical properties are of much interest, it has not yet been characterized.

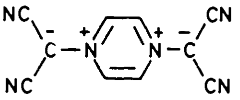
This paper reports the first synthesis of DATCNQ and its *X*-ray crystal structure together with spectroscopic and electrical properties.



(**1**)



(**2**)



(**3**)

Experimental

Preparation of (1,4-Pyrazinio)bis(dicyanomethylide) (DATCNQ) (**3**).—A toluene (60 cm^3) solution containing pyrazine (0.61 g, 7.6 mmol) and tetracyanoethylene oxide[5] (2.71 g, 18.9 mmol) was refluxed for 6 h under nitrogen. The resulting precipitate was collected by filtration and recrystallized from acetonitrile to afford metal-lustered violet crystals (0.72 g, 45%), m.p. 250 °C (decomp.) (Found: C, 57.5; H, 2.1; N, 40.4. Calc. for $C_{10}H_4N_6$: C, 57.7; H, 1.9; N, 40.4%); δ([$^2H_6$]DMSO) 8.19 (s); *m/e* 208 (M^+); $\nu_{max.}$ 3 058(w), 2 195(s), 2 166(s), 1 517(m), 1 480(s), 1 315(sh), 1 300(s), 1 249(w), 1 044(m), 1 013(s), 1 003(s), and 848(m) cm^{-1}; Raman $\nu_{max.}$ 2 204(w), 2 168(w), 1 650(m), 1 485(w), 1 464(w), 1 355(s), 1 341(s), 1 241(w), 997(w), and 747(s) cm^{-1}.

X-*Ray Crystal Structure Determination*.—Preliminary oscillation and Weissenberg photographs indicated a tetragonal system, and the space group $P4_2/mnm$ was later proved to be correct on the basis of the successful analysis. Accurate cell parameters were determined by the least-squares treatment of the angular co-ordinates of 38 reflections with 2θ values from 15 to 42°, which were measured on a Rigaku four-circle diffractometer.

Crystal Data.—$C_{10}H_4N_6$, $M = 208.18$. Tetragonal, space group $P4_2/mnm$, $a = 8.781(2)$, $c = 5.916\,8(7)$ Å, $V = 456.2(2)$ Å^3, $Z = 2$, $D_c = 1.516(1)$ g cm^{-3}, $F(000) = 212.0$, μ(Mo-K_α) = 1.1 cm^{-1}.

Intensities were collected in the range $4° < 2\theta < 60°$ for a crystal with approximate dimensions $0.34 \times 0.34 \times 0.10$ mm, using graphite-monochromatized Mo-K_α ($\lambda = 0.710\,69$ Å) radiation. Of 394 unique reflections measured 341 had significant counts $|F_0| > 3\sigma(F)$. Lorentz and polarization factors were applied, but no absorption correction was made.

The structure was solved by the MULTAN direct method,[6] which enabled the positions of all the non-hydrogen atoms to be readily located. By assuming the space group $P4_2/mnm$, the block-diagonal, least-squares refinement with anisotropic thermal parameters for these atoms led to a residual index $R = \Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.050$. The hydrogen atom was found in a difference-Fourier map. The final refinement with anisotropic thermal parameters for carbon and nitrogen and with an isotropic thermal one for hydrogen converged at $R = 0.047$ and $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2} = 0.061$, using the weighting scheme, $1/w = \sigma^2(F_0) + 0.001F_0^2$. The final difference-Fourier map had no positive maxima > 1 e Å^{-3}. Atomic scattering factors used in the refinement were taken from ref. 7. The final atomic co-ordinates with standard deviations are

Table 1. Atomic co-ordinates ($\times 10^4$) for DATCNQ with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
N(1)	1 127(2)	1 127(2)	5 000
N(2)	1 768(2)	5 104(2)	5 000
C(1)	2 247(2)	2 247(2)	5 000
C(2)	1 889(2)	3 800(2)	5 000
C(3)	−392(2)	1 489(2)	5 000
H(3)	−630(30)	2 570(30)	5 000

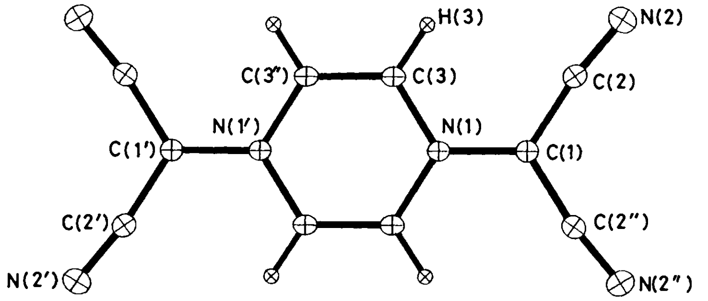


Figure 1. The molecular structure of DATCNQ, together with the atom-labelling scheme. Thermal ellipsoids for carbon and nitrogen atoms are drawn at the 30% probability level and hydrogen atoms are illustrated by spheres with an arbitrary radius

listed in Table 1. Lists of thermal parameters are in Supplementary Publication No. SUP 56239 (3 pp.).*

Crystallographic calculations were performed on an ACOS 900S computer at the Crystallographic Research Centre, Institute for Protein Research, Osaka University. Figures 1 and 2 were drawn by the local version of ORTEP-II program.[8]

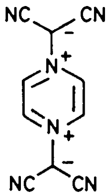
Physical Measurements.—Electronic absorption, powder reflectance, and e.s.r. spectra were obtained as described previously.[4] I.r. spectra were measured on a Hitachi 215 spectrophotometer. Raman spectra were measured on a Nippon Bunko R-500 spectrophotometer for a KBr pellet set on a rotating holder to suppress decomposition in the laser beam (an NEC GLG-3200 argon ion laser, λ 514.5 nm). ^{1}H N.m.r. spectra were recorded on a JNM PS-100 spectrometer in [$^2H_6$]dimethyl sulphoxide with tetramethylsilane as internal standard. Mass spectra were measured with a Hitachi RMU-6E spectrometer. Cyclic voltammetric measurements were performed in acetonitrile using tetrabutylammonium perchlorate as a supporting electrolyte, as described elsewhere.[9] Electrical resistivities were measured for compacted samples by the conventional two-probe method.[10]

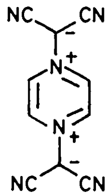
The Reaction of DATCNQ with Bromine.—Finely powdered DATCNQ (0.060 g, 0.29 mmol) was suspended in a diethyl ether (50 cm^3) solution of bromine (0.22 g, 1.5 mmol) and the mixture was stirred for 1 day at room temperature under nitrogen. The suspension remained and the resulting solid, DATCNQ·$Br_{0.05}$, was collected by filtration and dried *in vacuo* (Found: C, 56.9; H, 2.0; N, 39.6. Calc. for $C_{10}H_4N_6Br_{0.05}$: C, 56.6; H, 1.9; N, 39.2%). A similar reaction of DATCNQ (0.06 g, 0.29 mmol) with bromine (0.46 g, 2.9 mmol) in diethyl ether (50 cm^3) for 3 d gave DATCNQ·$Br_{0.11}$ (Found: C, 55.4; H, 2.05; N, 38.7. Calc. for $C_{10}H_4N_6Br_{0.11}$: C, 55.7; H, 1.9; N, 38.0%).

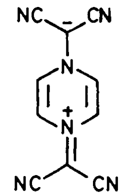
Table 2. Selected distances (Å) and angles (°) for DATCNQ with estimated standard deviations in parentheses

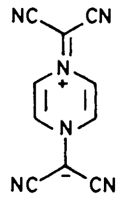
N(1)–C(1)	1.391(3)	N(1)–C(3)	1.371(2)
N(2)–C(2)	1.149(3)	C(1)–C(2)	1.400(3)
C(3)–C(3'')	1.363(2)		
N(2) ··· C(12)*	3.385(2)	N(2) ··· C(13)*	3.359(2)
C(2) ··· C(13)*	3.359(2)		
C(1)–N(1)–C(3)	121.6(2)	N(1)–C(1)–C(2)	122.0(2)
N(2)–C(2)–C(1)	172.3(2)	N(1)–C(3)–C(3'')	121.6(2)

* C(12) and C(13) are related to C(2) and C(3) by the symmetry operation derived from the space group *P*4$_2$/*mnm*.


(A)


(B)


(C)


(D)

Results and Discussion

X-Ray Crystal Structure of DATCNQ.—Figure 1 shows the molecular structure of DATCNQ with the atom-labelling scheme. All the atoms are on a plane and the molecule lies on a symmetry centre; N(1'), N(2'), C(1'), and C(2') are related to N(1), N(2), C(1), and C(2), respectively. C(2''), N(2''), and C(3'') are minor images of C(2), N(2), and C(3). Bond distances and angles as well as relevant intermolecular atom–atom contacts are listed in Table 2.

The N(1)–C(1) bond [1.391(3) Å] is appreciably short compared with N–C(alkyl) bonds of *N*-methylpyridinium iodide [1.46(2) Å][11] and of *N*-propylpyridinium-TCNQ salt [1.486(4) Å][12] and the N–C single bond adjacent to the N=C double bond of butyltrichloro(*N'*-phenylpyridine-2-carbaldimine)tin(IV) [1.441(5) Å].[13] In addition, the C(3)–C(3'') bond [1.363(2) Å] is significantly shorter than that of pyrazine (1.378 Å) and the N(1)–C(3) distance [1.371(2) Å] is longer than that of pyrazine (1.334 Å).[14] These results suggest that DATCNQ in the ground state may have contributions from the canonical structures (**C**) and (**D**) as well as (**A**) and (**B**). The N–C ylide distance (1.42 Å) observed previously for (1-pyrazinio)dicyanomethylide[15] has not been significantly different from the length expected for a single C(sp^2)–N(sp^2) bond, the C–C–N unit making a dihedral angle of 3° with respect to the pyridinium ring. On the other hand, DATCNQ has the strictly planar molecular plane and the appreciably short N(1)–C(1) ylide bond. Such a stabilization of the $\overset{+}{N}$–$\overset{-}{C}$ ylide bond is consistent with the intramolecular charge transfer (c.t.) absorption band observed at considerably longer wavelength as described in the following paragraph. Furthermore, strictly planar DATCNQ is geometrically rather close to TCNQ whose C–C bonds [1.346(3) and 1.374(3) Å][16] are compared with the C(3)–C(3'') and N(1)–C(1) bonds of DATCNQ, respectively.

Perspective views of the packing of the DATCNQ molecules in the unit cell along *c* and *a* axes are illustrated in Figure 2. The centre of the molecule is located at (0,0,1/2) and (1/2,1/2,0), the two molecules being perpendicular to one another with both the molecular planes strictly parallel to the *c* plane. The interplanar distance between two molecules centered on (0,0,1/2) and (1/2,1/2,0) is 2.958(1) Å. The closest intermolecular atom–atom distance [C(2)–C(13), 3.359(1) Å] is somewhat shorter than the

---

* See Instructions for Authors in *J. Chem. Soc., Perkin Trans. 2*, 1985, Issue 1.

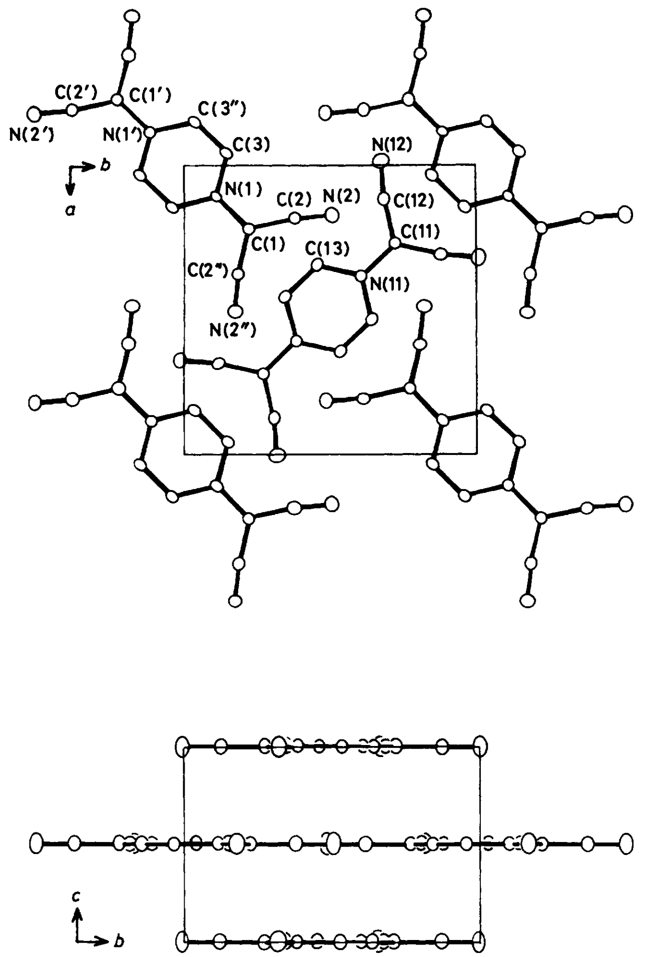


Figure 2. Perspective views of a unit cell of DATCNQ along the *c* and *a* axes

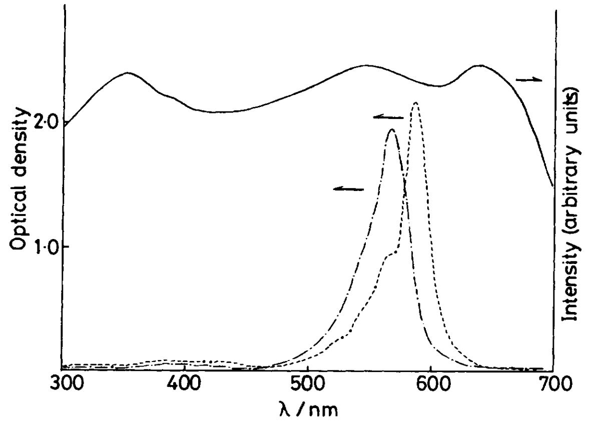


Figure 3. Electronic absorption spectra of DATCNQ (2.0 × 10^{-5} mol dm^{-3}) in dichloromethane (- - - - -) and in acetonitrile (— · —) and the powder reflectance spectrum (——)

carbon–carbon van der Waals distance of 3.5 Å.[17] This closeness may be caused by the Coulomb interaction through the polarized moieties of the DATCNQ molecules consisting of the rather positively polarized pyrazinium ring and the negatively polarized dicyano group.

Table 3. Electronic absorption maxima ($\lambda_{max.}$) of DATCNQ in various solvents with molar absorption coefficients (log ε) in brackets

Solvent (Dielectric constant)	$\lambda_{max.}$/nm	log(ε/mol^{-1} cm^{-1} dm^3)
Benzene (2.27)	593	4.90
Tetrahydrofuran (7.39)	577	4.94
Dichloromethane (8.9)	586	5.04
Buthanol (17.7)	572	4.92
Ethanol (24.3)	567	4.82
Methanol (32.6)	566	5.00
Acetonitrile (37.5)	568	5.00
Dimethyl sulphoxide (48.9)	564	4.92

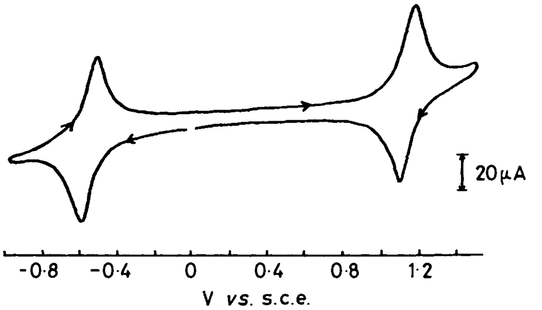


Figure 4. Cyclic voltammogram of DATCNQ (4.0 × 10^{-4} mol dm^{-3}) in acetonitrile (0.1 mol dm^{-3} [$NBu^n{}_4$]ClO_4); scan rate, 0.5 V s^{-1}

Electronic Spectra.—Figure 3 shows the electronic absorption spectra of DATCNQ in dichloromethane and in acetonitrile together with the powder reflectance spectrum. In dichloromethane an intense band is observed at 586 nm, whose absorption maximum is shifted to a short wavelength on increasing the polarity of a solvent, as seen in Table 3 (see also Figure 3). Thus, the band may be assigned to the intramolecular c.t. transition due to the $\overset{+}{N}$–$\overset{-}{C}$ ylide bond. This assignment is compatible with that for the 455 nm band observed in K^+ [AzaTCNQ]$^-$ in acetonitrile.[4] It should be noted that the spectrum in dichloromethane exhibits an asymmetric band shape with vibrational fine structures in the high-frequency region. This asymmetry suggests that there may be a resemblance in the geometry between the excited state and the ground state in DATCNQ.[18] The spacing of the vibrational fine structures has been determined as 760 ± 30 cm^{-1}, which corresponds to the strong Raman band at 748 cm^{-1} observed in KBr disks. The Raman band can be assigned to the C–H out-of-plane vibration of a b_{2g} species, referring to the vibrational studies on pyrazine and related compounds.[19–21]

The reflectance spectrum shows two broad bands at 350 and 635 nm in addition to the intramolecular c.t. band at 545 nm (Figure 3). Thus, the former two bands may be assignable to the intermolecular c.t. transition between the DATCNQ molecules. This is compatible with an appreciable intermolecular interaction in the solid state, as revealed by the *X*-ray crystallographic analysis.

Electrical Properties.—The cyclic voltammogram of DATCNQ measured in acetonitrile is depicted in Figure 4, which shows two reversible redox couples at +1.15 (DATCNQ^0–DATCNQ$^{\cdot+}$) and −0.54 V (*versus* s.c.e.) (DATCNQ^0–DATCNQ$^{\cdot-}$). This is in contrast with the redox wave at +0.17 V of TCNQ (TCNQ^0–TCNQ$^{\cdot-}$)[22] which is isostructural with DATCNQ. Since DATCNQ contains two more electrons in the molecule than TCNQ, the former compound is less easily reduced than the latter. On the other hand, the oxidation potential is appreciably lowered in

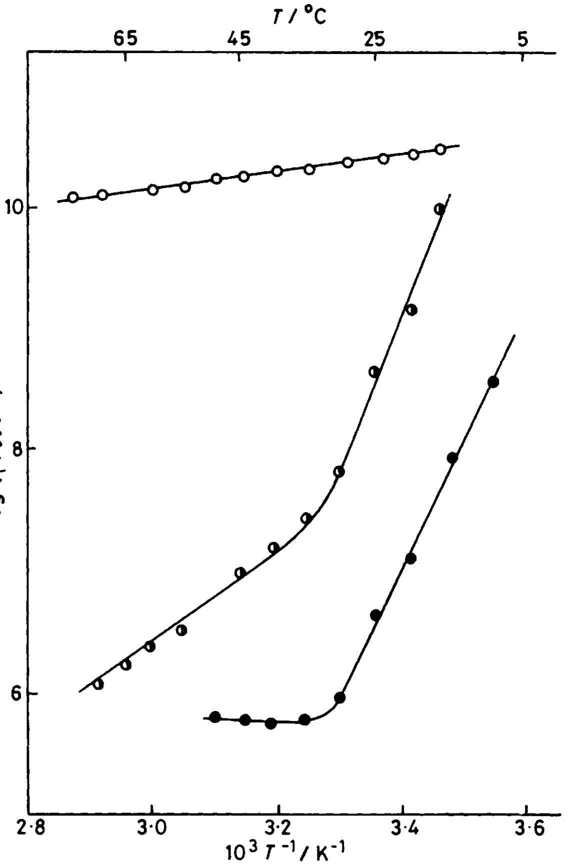


Figure 5. Temperature dependence of the specific resistivities (ρ) of DATCNQ (○), DATCNQ·$Br_{0.05}$ (◑), and DATCNQ·$Br_{0.11}$ (●)

DATCNQ, while the oxidation potential of TCNQ was reported to be estimated at *ca.* 10 eV.[23]

DATCNQ behaves as a typical semiconductor in the temperature range measured, 15—70 °C (Figure 5). The specific resistivity (ρ) at 25 °C measured for a compacted pellet was 2.5×10^{10} Ω cm and the activation energy (E_a) for the electrical conduction was 0.15 eV, where ρ was calculated from the equation $\rho = \rho_0 \exp(E_a/kT)$, where ρ_0, k, and T are a constant value, the Boltzmann's constant, and the temperature, respectively. These results are consistent with the crystal structure consisting of closely located DATCNQ molecules to one another and the occurrence of the intermolecular c.t. band in the powder reflectance spectrum. On doping bromine into DATCNQ, the resistivity is significantly lowered: DATCNQ·$Br_{0.05}$, 2.2×10^8 and DATCNQ·$Br_{0.11}$, 3.2×10^6 Ω cm at 25 °C for compacted pellets. Plots of log ρ *versus* $1/T$ for two bromine-doped DATCNQ gave linear relationships with the reproducibility only below 30 °C, while there were deviations from the straight lines above this temperature, as shown in Figure 5. The two bromine-doped DATCNQ compounds exhibited essentially the same i.r. spectra as that of DATCNQ, suggesting that the dopant has little influence on the DATCNQ skeleton. In the electronic reflectance spectra, however, the intermolecular c.t. band at 635 nm was shifted to 20 nm longer wavelength. Furthermore, DATCNQ·$Br_{0.11}$ exhibited an e.s.r. signal at *g* 2.004 at room temperature, although no detectable signal occurred in DATCNQ·$Br_{0.05}$. Based on the signal intensity in comparison with that of diphenylpicrylhydrazyl, spin concentrations have been estimated as $3.5 \times 10^{-3}\%$. Thus, only a small portion of DATCNQ may be oxidized by bromine to form radical cations, which may contribute to the increasing conductivity of bromine-doped DATCNQ.

References

1 A. F. Garito and A. J. Haeger, *Acc. Chem. Res.*, 1974, **7**, 232; J. B. Torrance, *ibid.*, 1979, **12**, 79.
2 F. Wudl, 'Chemistry and Physics of One-dimensional Metals,' ed. H. J. Keller, NATO Adv. Study Inst., Plenum Press, New York, 1977, p. 249.
3 G. Matsubayashi, H. Tanaka, T. Tanaka, and K. Nakatsu, *Inorg. Chim. Acta*, 1982, **63**, 217.
4 H. Tanaka, G. Matsubayashi, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 2198.
5 W. J. Linn, O. W. Webster, and R. E. Benson, *J. Am. Chem. Soc.*, 1965, **87**, 3651.
6 P. Main, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, and M. M. Woolfson, 'A System of Computer Programms for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data, MULTAN 78,' University of York, York, 1978.
7 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, vol. 4, 1974.
8 C. K. Johnson, 'ORTEP-II: A FORTRAN Thermal-Ellipsoid Program for Crystal Structure Illustrations, ORNL-5183,' Oak Ridge National Laboratory, Oak Ridge, 1976.
9 G. Nagao, K. Tanaka, and T. Tanaka, *Inorg. Chim. Acta*, 1980, **42**, 43.
10 S. Araki, H. Ishida, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 407.
11 R. A. Lalancette, W. Furey, J. N. Costanzo, P. R. Hemmes, and F. Jordan, *Acta Crystallogr.*, 1978, **B34**, 2950.
12 M. Konno and Y. Saito, *Acta Crystallogr.*, 1981, **B37**, 2034.
13 G. Matsubayashi, T. Tanaka, S. Nishigaki, and K. Nakatsu, *J. Chem. Soc., Dalton Trans.*, 1979, 501.
14 P. J. Wheatley, *Acta Crystallogr.*, 1957, **10**, 182.
15 C. Bugg and R. L. Sass, *Acta Crystallogr.*, 1965, **18**, 591.
16 R. E. Long, R. A. Sparks, and K. N. Trueblood, *Acta Crystallogr.*, 1965, **18**, 932.
17 L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, 3rd. edn., 1960.
18 C. N. Banwell, 'Fundamentals of Molecular Spectroscopy,' McGraw-Hill, New York, 1972, p. 210.
19 R. C. Lord, A. L. Marston, and F. A. Miller, *Spectrochim. Acta*, 1957, **9**, 113.
20 G. Sbrana, V. Schettino, and R. Righini, *J. Chem. Phys.*, 1973, **59**, 2441.
21 M. Ito and I. Suzuka, *Chem. Phys. Lett.*, 1975, **31**, 467.
22 R. C. Wheland and J. L. Gillson, *J. Am. Chem. Soc.*, 1976, **98**, 3916.
23 B. V. Kotov and V. K. Potapov, *Khim. Vys. Energ.*, 1972, **6**, 375 (*Chem. Abstr.*, 1972, **77**, 118 552z).

Received 10*th July* 1984; *Paper* 4/1195