

Structural Studies of Precursor and Partially Oxidized Conducting Complexes. X. A Neutron Diffraction Study of Potassium Sodium Tetracyanoplatinate(II) Trihydrate, $\text{KNa}[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}^*$

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The crystal and molecular structures of potassium sodium tetracyanoplatinate(II) trihydrate, $\text{KNa}[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$, have been determined by a single-crystal neutron diffraction study. The compound, KNaTCP , crystallizes with four formula units in the monoclinic space group Cc (C_2^2) with cell dimensions $a = 12.965$ (8), $b = 13.765$ (8), $c = 6.522$ (4) Å, and $\beta = 115.09$ (3)°. 1896 reflections were averaged to yield 1595 independent reflections [1455 with $F_o^2 > \sigma(F_o^2)$]. The structure was determined by direct methods and refined by full-matrix least-squares techniques to a final $R(F_o^2)$ value of 0.076 (all data). The structure consists of chains of $\text{Pt}(\text{CN})_4^{2-}$ groups wherein the Pt–Pt distance is 3.263 (2) Å and the Pt–Pt–Pt angle is 176.4 (1)°. Alternate $\text{Pt}(\text{CN})_4^{2-}$ groups are staggered giving C–Pt–Pt–C torsional angles of 34.5 (8), 34.5 (8), 34.5 (16), and 34.4 (15)°. The hydrogen-bonding scheme and the coordination spheres about Na^+ and K^+ are described. Comparisons are made with the structures of related partially oxidized tetracyanoplatinate (POTCP) complexes.

Introduction

Partially oxidized tetracyanoplatinate (POTCP) complexes are of current interest because of their novel conduction properties. The chains of Pt atoms are a common feature of compounds such as $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot \text{Br}_{0.3} \cdot 3\text{H}_2\text{O}$, $\text{KCP}(\text{Br})$ (Williams, Petersen, Gerdes & Peterson, 1974; Williams, Ross, Iwata, Petersen, Peterson, Lin & Keefer, 1975; Williams, Iwata, Ross, Petersen & Peterson, 1975; Williams, 1977; Deiseroth & Schulz, 1974, 1975; Heger, Renker, Deiseroth, Schulz & Scheiber, 1975; Peters & Eagen, 1975, 1976); $\text{K}_{1.75}[\text{Pt}(\text{CN})_4] \cdot 1.5\text{H}_2\text{O}$, $\text{K}(\text{def})\text{TCP}$ (Keefer, Washecheck, Enright & Williams, 1976; Reis, Peterson, Washecheck & Miller, 1976*a,b*; Williams, Keefer, Washecheck & Enright, 1976). Electrical conductivity is much higher parallel to these Pt chains, as compared to the perpendicular directions, and hence these complexes are described as one-dimensional conductors. Another common feature of these compounds is a nearly square-planar configuration of cyanide groups surrounding Pt. Water molecules play an important role in these compounds and form hydrogen-bonding interactions with the N atoms of the cyanide groups. Lastly, the K^+ ions are surrounded by both O and N atoms.

While Pt^{II} compounds do not show the unusual electrical conductivity, the above features of nearly square-planar $\text{Pt}(\text{CN})_4^{2-}$ groups, Pt–Pt chains, and hydrogen bonding are observed in Pt^{II} compounds as well as in partially oxidized compounds. This work describes the findings of a single-crystal neutron diffraction study of $\text{KNa}[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$, hereinafter KNaTCP .

Experimental

Crystal preparation

$\text{KNa}[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ was prepared by reacting equimolar amounts of potassium and sodium sulfate with barium tetracyanoplatinate in aqueous solution. Large, yellow crystals were grown by slow evaporation, at room temperature, of a saturated aqueous solution.

Unit cell and space group

The preliminary cell constants were available from earlier X-ray studies by Moreau-Colin (1968) and Monfort (1942). The unit-cell parameters determined here by a least-squares analysis of the centered angles 2θ , χ , and φ (30 reflections) were: $a = 12.965$ (8), $b = 13.765$ (8), $c = 6.522$ (4) Å, $\beta = 115.09$ (3)° and $V_c = 1054.1$ Å³, with $\lambda = 1.142$ Å based on $a_o(\text{NaCl}) = 5.6397$ Å and $a_o(\text{Si}) = 5.430$ Å at $20 \pm 2^\circ\text{C}$.

There had been some discrepancy in the literature regarding the correct space group. Monfort (1942) reported the space group as $C2/m$ while Moreau-Colin (1968) corrected this to either $C2/c$ or Cc and the latter

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chose to work with Ic , an alternative setting of Cc . The observed neutron diffraction conditions for absences were $h + k$ odd for hkl data and l odd for $h0l$ data. This result confirms the finding of Moreau-Colin (1968) and therefore the space group is $C2/c$ or Cc . The choice of Cc was made to conform to the standard setting for this space group. The crystal density of $2.55(2) \text{ g cm}^{-3}$, measured by flotation, agrees with a calculated value of 2.59 g cm^{-3} for four formula units in the unit cell.

Data collection

A well formed crystal weighing 42.2 mg was sealed in a lead-glass capillary for protection during data collection. The approximate crystal dimensions were $1.3 \times 2.4 \times 5.9 \text{ mm}$ with the crystal mounted about c . Three-dimensional data were collected on an Electronics and Alloys four-circle diffractometer located at the CP-5 reactor at Argonne National Laboratory. This fully automated instrument operates remotely under the control of the ANL Chemistry Division Sigma V computer.

Data were automatically collected with a $\theta-2\theta$ step-scan technique with 0.1° step intervals over scan ranges of 36–58 steps. The background was established at each extremity of the scan, with the crystal and counter in a stationary position. 1896 reflections were collected to a minimum d spacing of 0.691 \AA . The equivalent reflections were averaged to yield 1595 unique data of which 1455 were greater than one e.s.d. The agreement index $[R(F_o^2) = \Sigma(F_{\text{avg}}^2 - F_o^2)/\Sigma F_o^2]$ between averaged reflections was 0.029. Two standard reflections were remeasured after every 50 measurements and a 6% maximum fluctuation was observed during the course of data collection.

Structure factors were derived by applying Lorentz and absorption corrections ($\mu = 3.17 \text{ cm}^{-1}$) and the magnitude of the latter correction ranged from 1.47 to 2.04. Standard errors were assigned to the data with the standard counting statistics formula with $(0.06I)^2$ added to the variances to adjust for systematic error. The data were placed on an approximately absolute scale by comparison with a standard NaCl crystal.

Structure solution and refinement

Intensity statistics (see Table 1) clearly indicate the structure to be noncentrosymmetric in agreement with the chosen space group Cc . Calculations using

Table 1. *Intensity statistics for* $\text{KNa}[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$

	Experimental	Theoretical	
		Centrosymmetric	Noncentrosymmetric
$\langle E^2 \rangle$	0.9998	1.0000	1.0000
$ \langle E^2 - 1 \rangle $	0.7716	0.9680	0.7360
$ \langle E \rangle $	0.8732	0.7980	0.8860

the program *MULTAN* (Declercq, Germain, Main & Woolfson, 1973) yielded the positions of the nine atoms in the $\text{Pt}(\text{CN})_4^{2-}$ group and the remaining atoms, K, Na, O, H, were readily located from difference maps. In the refinement the function minimized was $\Sigma w(F_o^2 - F_c^2)^2$, where F_o and F_c are the observed and calculated structure amplitudes, and the weights are defined as $w = 1/\sigma^2(F_o^2)$. The agreement indices are defined as $R_F = \Sigma |F_o| - |F_c| / \Sigma F_o$, $R_{F^2} = \Sigma (F_o^2 - F_c^2) / \Sigma F_o^2$ and $\sigma_1 = [\Sigma w(F_o - F_c)^2 / (N_o - N_r)]^{1/2}$ where N_o is the number of independent observations and N_r is the number of parameters varied.

The final refinement included anisotropic temperature factors for all atoms and anisotropic extinction (Coppens & Hamilton, 1970) of type 2 (185 total parameters). The final values of R_{F^2} were 0.076 based on all data and 0.074 based on data greater than 1σ . The corresponding values of R_F were 0.058 and 0.048. For all data, the final value of σ_1 was 1.02. The final positional parameters are listed in Table 2.* The neutron scattering amplitudes used were as follows: $b_{\text{Pt}} = 0.95$, $b_{\text{C}} = 0.663$, $b_{\text{N}} = 0.94$, $b_{\text{O}} = 0.575$, $b_{\text{H}} = -0.372$, $b_{\text{Na}} = 0.351$, and $b_{\text{K}} = 0.37 \times 10^{-12} \text{ cm}$ (*International Tables for X-ray Crystallography*, 1974).

The previous X-ray diffraction study (Moreau-Colin, 1968) was based on two zones of data and the Na^+ and the K^+ ions overlapped in both cases. Hence no definitive distinction between Na^+ and K^+ could be made based on the diffraction data. However, the identity of Na^+ and K^+ can be inferred by considering

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32649 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Atomic crystal coordinates* ($\times 10^4$)

	x	y	z
Pt	0	-37 (1)	0
C(1)	479 (3)	-1426 (2)	408 (6)
C(2)	1616 (3)	403 (2)	1389 (5)
C(3)	-524 (3)	1334 (2)	-356 (6)
C(4)	-1611 (3)	-465 (2)	-1488 (6)
N(1)	724 (3)	-2240 (1)	649 (5)
N(2)	2553 (2)	666 (2)	2145 (5)
N(3)	-857 (3)	2121 (2)	-533 (5)
N(4)	-2548 (2)	-717 (2)	-2381 (5)
O(1)	4971 (3)	658 (2)	3295 (7)
O(2)	3682 (4)	1451 (3)	-2770 (7)
O(3)	1461 (4)	3328 (4)	2320 (9)
K	2771 (5)	2402 (4)	-169 (10)
Na	473 (4)	4065 (4)	-4879 (9)
H(1)	5390 (6)	1092 (5)	4522 (13)
H(2)	4184 (6)	709 (5)	3061 (12)
H(3)	3180 (6)	976 (6)	-3760 (17)
H(4)	3803 (7)	1903 (6)	-3747 (14)
H(5)	1269 (10)	2742 (7)	2875 (24)
H(6)	2143 (9)	3533 (12)	3403 (20)

their coordination contact distances. In Moreau-Colin's (1968) study, the Na^+ had a closest contact of 2.39 Å while that for K^+ was 2.91 Å. In this work we observe an atom 2.40 Å from that assigned as Na^+ and 2.77 Å from that assigned as K^+ . The ordered K^+ and Na^+ placement was confirmed from the neutron diffraction data by allowing the neutron scattering lengths to be variables in later least-squares refinements. The neutron scattering lengths refined to 0.358 (7) for Na^+ and $0.380 (10) \times 10^{-12}$ cm for K^+ . These values are within 1σ of the generally accepted values and support our assignment of Na^+ and K^+ .

Structure description

The structure consists of discrete chains of $\text{Pt}(\text{CN})_4^{2-}$ groups, H_2O molecules, Na^+ , and K^+ as illustrated in Fig. 1. The $\text{Pt}(\text{CN})_4^{2-}$ groups are stacked in a pancake-like array parallel to the c axis. Therefore, the Pt atoms can be described as forming chains just as in KCP(Br) and K(def)TCP although the C—Pt—Pt—C torsional angles are different. However, the Pt—Pt' distance in this compound is 3.263 (2) Å compared with 2.890 (1) Å in KCP(Br), and 2.963 (1) Å in K(def)TCP, and this results in KNaTCP not having the unusual conductivity features of the partially oxidized compounds. The Pt—Pt'—Pt'' chain is nearly linear with an angle of 176.4° (1). Symmetry requires the Pt—Pt'—Pt'' angle to be exactly 180° in KCP(Br) while a Pt—Pt'—Pt'' angle of 173.25 (3)° was determined from the neutron diffraction study of K(def)TCP. The environment about the $\text{Pt}(\text{CN})_4^{2-}$ group is asymmetric and is shown in Fig. 2.

Bond lengths and angles are given in Table 3. All atoms are in general positions of space group Cc and

hence no symmetry is imposed on any part of the molecule. The $\text{Pt}(\text{CN})_4^{2-}$ groups are nearly square planar as can be seen in Table 3(F). The dihedral angle between adjacent planes in the chain is 2.3°.

The Pt—C distances are 1.982 (3), 1.986 (3), 1.992 (3) and 1.993 (3) Å which compare with an average of 1.984 (3) Å in $\text{Na}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ (Johnson, Koch & Williams, 1977), and 1.989 (2) Å in $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ (Washecheck, Peterson, Reis & Williams, 1976). For the partially oxidized compounds, KCP(Br) and K(def)TCP, the average Pt—C distances are 2.001 (1) and 1.999 (4) Å respectively. It appears that the partially oxidized compounds have longer Pt—C distances by about 2σ with respect to the unoxidized compounds.

The average C—N distance in KNaTCP is 1.156 (3) Å which is in excellent agreement with the values

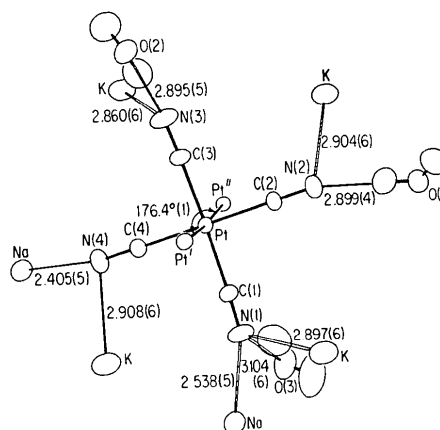


Fig. 2. Diagram of the asymmetric environment about Pt.

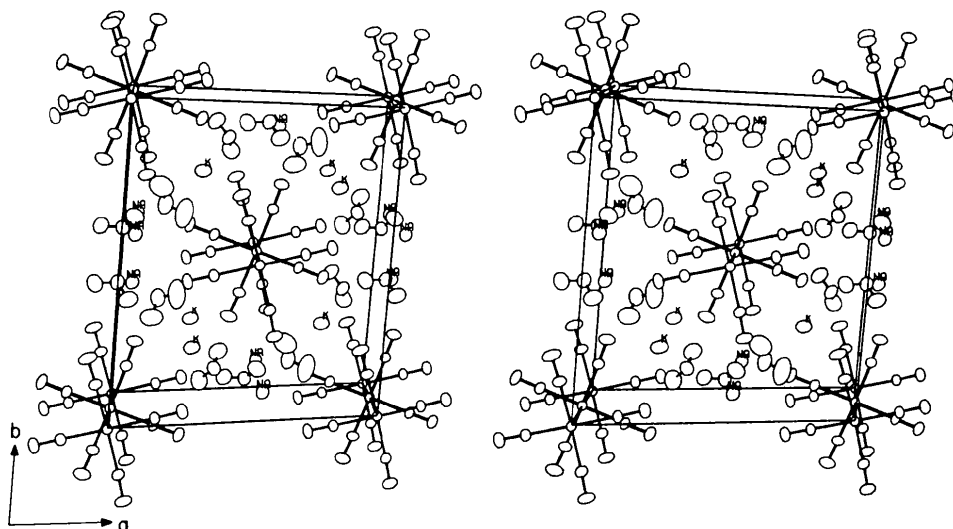


Fig. 1. Stereoscopic drawing of the unit cell of $\text{KNa}[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ with thermal ellipsoids drawn on a 50% probability scale.

Table 3. *Interatomic distances (Å) and bond angles (°) for KNa[Pt(CN)₄].3H₂O*

Superscripts refer to symmetry positions listed below. If no superscript appears *x,y,z* is implied.

(i) $x, -y, \frac{1}{2} + z$	(vi) $\frac{1}{2} + x, \frac{1}{2} + y, 1 + z$
(ii) $x, -y, z - \frac{1}{2}$	(vii) $\frac{1}{2} + x, \frac{1}{2} + y, z$
(iii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$	(viii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$
(iv) $x, y, z - 1$	(ix) $x - \frac{1}{2}, \frac{1}{2} + y, z - 1$
(v) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$	

(A) Distances around Pt atoms

Pt—C(1)	1.993 (3)	Pt—C(4)	1.982 (3)
Pt—C(2)	1.992 (3)	Pt—Pt ⁱ	3.263 (2)
Pt—C(3)	1.986 (3)	Pt—Pt ⁱⁱ	3.263 (2)

(B) C—N distances in cyanide groups

C(1)—N(1)	1.156 (3)	C(3)—N(3)	1.153 (3)
C(2)—N(2)	1.158 (3)	C(4)—N(4)	1.156 (3)

(C) Water molecule distances

O(1)—H(1)	0.961 (8)	0.989 (9)*
O(1)—H(2)	0.969 (7)	0.985 (7)*
O(2)—H(3)	0.955 (8)	1.013 (9)*
O(2)—H(4)	0.950 (9)	0.975 (10)*
O(3)—H(5)	0.959 (12)	1.019 (13)*
O(3)—H(6)	0.911 (12)	0.991 (14)*

(D) H atom interactions

H(1)—O(3 ⁱⁱⁱ)	1.936 (9)	O(1)—H(1)—O(3)	165.3 (7)
H(1)—N(3 ⁱⁱⁱ)	2.936 (8)	O(1)—H(1)—N(3)	113.4 (5)
H(2)—N(2)	1.940 (6)	O(1)—H(2)—N(2)	170.0 (6)
H(3)—N(2 ^{iv})	2.477 (10)	O(2)—H(3)—N(2)	131.6 (9)
H(3)—N(2 ⁱⁱ)	2.554 (10)	O(2)—H(3)—N(2)	130.0 (9)
H(4)—N(3 ^v)	1.948 (8)	O(2)—H(4)—N(3)	175.4 (8)
H(5)—N(1 ⁱ)	2.310 (12)	O(3)—H(5)—N(1)	139.7 (11)
H(5)—N(3)	2.841 (14)	O(3)—H(5)—N(3)	106.2 (10)
H(6)—N(3 ⁱⁱⁱ)	2.548 (12)	O(3)—H(6)—N(3)	130.1 (12)
H(6)—N(4 ^{vi})	2.803 (13)	O(3)—H(6)—N(4)	124.2 (10)

(E) K⁺ and Na⁺ interactions

K—O(2)	2.773 (7)	Na—O(2 ^{viii})	2.396 (6)
K—N(3 ⁱⁱⁱ)	2.860 (6)	Na—N(4 ^{vii})	2.405 (5)
K—N(1 ⁱⁱ)	2.897 (6)	Na—O(1 ^{ix})	2.448 (6)
K—N(2)	2.904 (6)	Na—O(1 ^{viii})	2.449 (7)
K—N(4 ^{vii})	2.908 (6)	Na—N(1 ⁱⁱ)	2.538 (5)
K—O(3)	3.080 (8)	Na—O(3 ^{iv})	2.826 (8)

(F) Angles of Pt chain and bonded atoms

Pt ⁱ —Pt—Pt ⁱⁱ	176.4 (1)	C(1)—Pt—C(4)	89.1 (1)
Pt—C(1)—N(1)	177.7 (3)	C(2)—Pt—C(3)	90.3 (1)
Pt—C(2)—N(2)	178.4 (2)	C(3)—Pt—C(4)	89.3 (1)
Pt—C(3)—N(3)	177.5 (3)	H(1)—O(1)—H(2)	105.7 (7)
Pt—C(4)—N(4)	179.1 (3)	H(3)—O(2)—H(4)	104.8 (9)
C(1)—Pt—C(2)	91.3 (1)	H(5)—O(3)—H(6)	106.7 (14)

* Corrected for thermal motion, H assumed to ride on O.

of 1.158 (2), 1.158 (6), 1.159 (3), and 1.158 (3) Å in KCP(Br), K(def)TCP, KTCP, and NaTCP respectively.

With respect to torsional angles formed by C—Pt—Pt—C, the unoxidized compounds show considerable variation. In NaTCP the average torsion angle is 0°. In KTCP there is a slight staggering of the CN⁻ groups with an average torsion angle of 16.2° while a greater degree of staggering is found in KNaTCP [34.5 (8), 34.5 (8), 34.5 (16), and

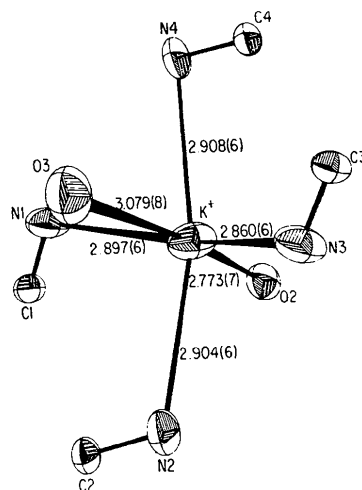


Fig. 3. K⁺ coordination sphere and interaction distances.

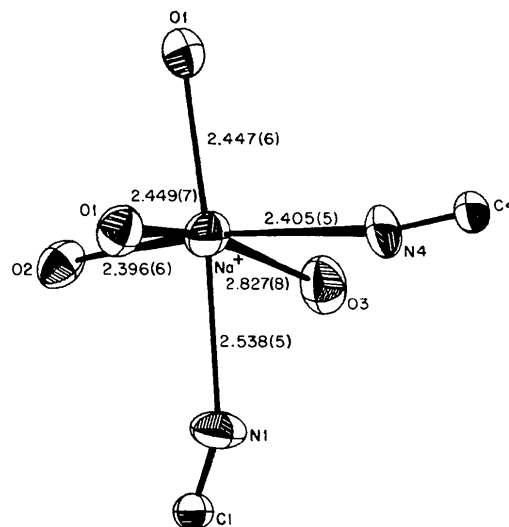


Fig. 4. Na⁺ coordination sphere and interaction distances.

35.4 (15)°]. The common characteristic of partially oxidized Pt compounds observed to date is a *non-eclipsed* configuration of adjacent platinumocyanide groups.

The coordination sphere surrounding K⁺ is given in Fig. 3. There is a sixfold coordination arrangement resulting in a distorted octahedron. The number of coordinating groups is greater in KCP(Br) and KTCP where the former has eightfold antiprism geometry and the latter has a sevenfold distorted capped trigonal prism.

The coordination sphere surrounding Na⁺ is sixfold resulting in a nearly regular octahedron as shown in Fig. 4. The same result was observed in NaTCP where

the five crystallographically distinct Na⁺ atoms all have sixfold regular octahedral geometries.

The strongest hydrogen bonding found in this compound involves water molecule H(1)–O(1)–H(2). H(1) forms a hydrogen bond to O(3) with an O–O distance of 2.876 Å, while H(2) forms a hydrogen bond to N(2) with an O–N distance of 2.899 Å. The other two water molecules do not participate in strong hydrogen bonding, the only exception being H(4), which is bonded to N(3) (O–N distance = 2.985 Å). The atoms H(3), H(5), and H(6) all participate in weaker hydrogen bonding of the bifurcated type as shown in Table 3(D).

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The Crystal and Molecular Structure of Bis(difluoroborondimethylglyoximate)nickel(II)

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The structure of the title compound has been refined to R 0.093 for 964 photographic reflexions. The monoclinic unit cell, space group $C2/c$, has $a = 20.815$ (40), $b = 7.860$ (18), $c = 19.545$ (40) Å, $\beta = 110.8$ (1)°, $Z = 8$. The complex consists of molecular dimers showing a weak Ni–Ni interaction of length 3.207 (6) Å; the space group imposes 2 (C_2) symmetry on these units. The dimethylglyoxime residues and the Ni atom in each formula unit are coplanar and the BF₂ groups are displaced out of the plane and away from the other formula moiety. The environment about each Ni is distorted square-planar with average Ni–N = 1.87 (1) Å and N–Ni–N = 83.5 (8) and 96.5 (8)°. Each planar formula unit is rotated some 92° relative to the other in the dimer around the Ni–Ni direction.

Introduction

Much of the current interest in transition-metal chelates of substituted glyoximes is centred on their use as chemical models for biological processes such as vitamin B₁₂ (Brown, 1973; Pratt & Craig, 1973; Schrauzer, 1976) and oxygen transport (McLendon &

Martell, 1976) functions, their activity in biological test systems (Carlsson, Charlson & Watton, 1974; Takamiya, 1960) and their semiconducting properties in the solid state (Thomas & Underhill, 1969, 1972; Underhill, Watkins & Pethig, 1973). These chelates appear to be quite stable, both thermodynamically and chemically, although those of Co demonstrate an