*Inorganica Chimica Acta*, 63 (1982) 17–22

# Unusual Infinite-Chain Anion $[Cu_2I_3^-]_\infty$ in the Structure of its Thiopyrilium Salt

A. S. BATSANOV, Yu. T. STRUCHKOV*
*Nesmeyanov Institute of Organoelement Compounds, Vavilov Street 28, Moscow, U.S.S.R.*

L. YU. UKHIN and N. A. DOLGOPOLOVA
*Physical and Organic Chemistry Research Institute, Rostov University, Rostov-on-Don, U.S.S.R.*

Received March 29, 1982

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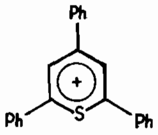
*The crystal structure of* $[C_{23}H_{17}S]^+[Cu_2I_3]^-$ *(*$C_{23}H_{17}S$ *= 2,4,6-triphenylthiopyrilium) has been determined at −120 °C and refined by least-squares to R = 0.033 using 2861 intensities collected by the counter method. Black crystals obtained are hexagonal, a = 13.856(5), c = 20.778(4) Å, space group* $P6_1$*, Z = 6. The structure contains infinite anions* $[Cu_2I_3^-]_\infty$*, the chains of* $I_4$ *tetrahedra being centered by Cu atoms and joined via their faces and edges. The shortest Cu···Cu distances were 2.479 and 2.634 Å. The discrete* $[C_{23}H_{17}S]^+$ *cations are disordered. Similar complexes with other heterocyclic cations have been prepared.*

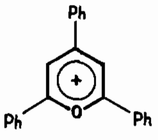
## Introduction

When studying the behaviour of organic cations in the presence of transition metal compounds, we obtained anionic Cu(I) complexes of empirical formula $A^+[Cu_2I_3]^-$, where

$A^+$ =



(1)



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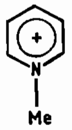

(3)

Crystals I and II of the salts with cations (1) and (2) unexpectedly turned out to be extraordinarily deeply coloured, in sharp contrast both with III, *i.e.* the cation (3) salt, and with previously described complex halides of the IB group metals with a similar stoichiometry, which are weakly coloured or colourless compounds [1, 2]. At the same time the solutions of I and II in organic solvents are as weakly coloured as III.

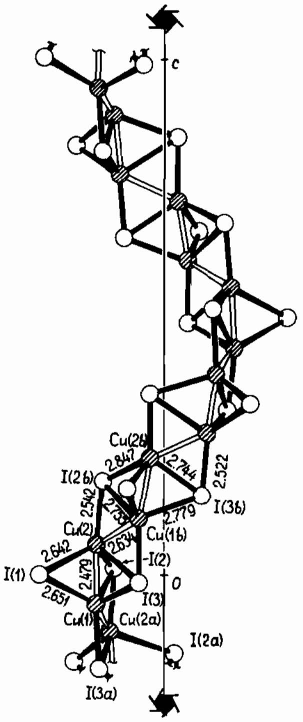

Fig. 1. Anionic chain of 1 with bond lengths (e.s.d.s 0.002 Å). Projection on the (0 1 0) plane.

Such transitions from an intensive colour in the solid state to almost colourless solutions is characteristic of some metal complexes, in crystals of which molecules form infinite stacks with short metal–metal distances. Typical examples of such compounds are bis-carbonylacetylacetonates of monovalent rhodium and iridium, (acac)$Rh(CO)_2$ and (acac)-$Ir(CO)_2$ [3].

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*Author to whom correspondence should be addressed.

0020-1693/82/0000-0000/$02.75

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TABLE I. Bond Angles (degrees) in the Anion.

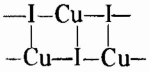
| Angle | | Angle | |
|---|---|---|---|
| I(1)Cu(1)I(2) | 102.70(5) | I(1)Cu(2)I(3) | 103.22(5) |
| I(1)Cu(1)I(3) | 102.04(5) | I(1)Cu(2)I(2) | 100.50(5) |
| I(1)Cu(1)I(3a) | 121.08(6) | I(1)Cu(2)I(2b) | 124.63(6) |
| I(2)Cu(1)I(3) | 99.57(5) | I(2)Cu(2)I(3) | 98.18(5) |
| I(2)Cu(1)I(3a) | 119.75(6) | I(3)Cu(2)I(2b) | 119.46(6) |
| I(3)Cu(1)I(3a) | 108.33(5) | I(2)Cu(2)I(2b) | 106.04(5) |
| Cu(2)Cu(1)I(1) | 61.90(5) | Cu(1)Cu(2)I(1) | 62.26(5) |
| Cu(2)Cu(1)I(2) | 65.66(5) | Cu(1)Cu(2)I(3) | 64.06(5) |
| Cu(2)Cu(1)I(3) | 62.61(5) | Cu(1)Cu(2)I(2) | 61.84(5) |
| Cu(2)Cu(1)I(3a) | 170.76(7) | Cu(1)Cu(2)I(2b) | 167.81(8) |
| Cu(2)Cu(1)Cu(2a) | 121.87(7) | Cu(1)Cu(2)Cu(1b) | 119.89(7) |
| Cu(2a)Cu(1)I(1) | 127.90(6) | Cu(1b)Cu(2)I(1) | 132.85(7) |
| Cu(2a)Cu(1)I(2) | 56.23(5) | Cu(1b)Cu(2)I(3) | 55.90(4) |
| Cu(2a)Cu(1)I(3) | 126.56(6) | Cu(1b)Cu(2)I(2) | 122.48(6) |
| Cu(2a)Cu(1)I(3a) | 64.26(5) | Cu(1b)Cu(2)I(2b) | 64.29(5) |
| Cu(1)I(1)Cu(2) | 55.85(5) | Cu(1)I(3)Cu(2) | 53.33(4) |
| Cu(1)I(2)Cu(2) | 52.49(4) | Cu(2)I(3)Cu(1b) | 59.84(5) |
| Cu(1)I(2)Cu(2a) | 59.47(5) | Cu(1)I(3)Cu(1b) | 113.12(5) |
| Cu(2)I(2)Cu(2a) | 111.95(5) | | |

X-ray structure analysis has shown that crystals I are built of the infinite chain anions $[Cu_2I_3^-]_\infty$ and the discrete cations of 2,4,6-triphenylthiopyrilium (1).

The structure of the anionic chain is shown in Fig. 1; bond angles are given in Table I. Both crystallographically-independent copper atoms have a distorted tetrahedral coordination by four iodine atoms. All iodine atoms are bridging, the I(1) atom connecting two copper atoms Cu(1) and Cu(2), while each of the I(2) and I(3) atoms is bonded to three copper atoms, *viz.* Cu(1), Cu(2), Cu(2a)* and Cu(1), Cu(2), Cu(1b), respectively.

The anion structure can be described as an infinite chain of iodine tetrahedra, containing copper atoms in their centers. Each tetrahedron has a common face with one of its neighbours and a common edge with another neighbour, *e.g.* the tetrahedron centered by Cu(2) shares its face I(1)I(2)I(3) with the one centered by Cu(1), and shares its edge I(3)–I(2b) with the one centered by Cu(1b). This chain is coiled in a helix around the $6_1$ axis (*i.e.* the lattice axis *c*) with 12 tetrahedra or 6 formula units per translation.

A motive of tetrahedra linked in chains is specific for complex halides of the IB group metals, *viz.* $CsAg_2I_3$, $CsCu_2Cl_3$ [1], $(Me_4N)Ag_2I_3$ [2], however, the mode of polyhedra joining found in crystal I has not been described earlier. In the structures of complexes $(C_5H_5N)CuI$ [4] and $(2\text{-}MeC_5H_4N)Cu_2I_2$ [5] the ribbons



exist with the nitrogen-containing heterocycles as terminal ligands at copper atoms, completing their tetrahedral coordination.

It is worth noting that the anion corresponds approximately to the $P6_122$ space group symmetry (the I(1) atom is on the 2 axis, while I(2) and I(3), Cu(1) and Cu(2) are linked pairwise by this axis), however the cation arrangement does not agree with this symmetry at all.

The Cu(2)···Cu(2a) distances of 2.634 Å and, especially, Cu(1)···Cu(2) of. 2479 Å are rather short. In fact, Cu–Cu distances usual for the Cu(I) cluster complexes with iodine bridges are 2.546–2.73 Å [6], while in metallic copper this distance is 2.551 Å [7], and the minimum distance observed until now (in tetrameric 4-methyl-2-cupriobenzyldimethylamine) is 2.377–2.389 Å [8]. In the $(C_5H_5N)CuI$ and $(2\text{-}MeC_5H_4N)Cu_2I_2$ structures the shortest Cu···Cu distances are considerably longer: 2.875 and 2.824 Å, respectively.

The Cu–I distances for the bridging I(1) are essentially equal (2.642 and 2.651 Å) and close to the limits usual for the $\mu_2$-bridges (2.510–2.648 Å) [6]. Each of the I(2) and I(3) atoms form one short and two long Cu–I bonds. However, both the

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*The labels a and b denote atoms generated from the basic atom by rotation around the $6_1$ axis with a shift by $-c/6$ and $+c/6$, respectively.

individual values of these bond lengths (and their difference) are unexceptional for Cu(I) iodide complexes [6, 9, 10]. More unusual is the fact that in this case each $\mu_3$-bridging iodine atom is almost coplanar (within 0.02–0.03 Å) with three copper atoms bonded to it, while Cu–I bonds are usually directed along the edges of a trigonal pyramid with an iodine atom at its vertex. At the same time the Cu–I–Cu angles in the structure I (52.49–59.84°) are within the limits usual for iodine bridges: 52.6–69.6° [4, 6, 9, 10].

The copper atoms Cu(1) and Cu(2) situated at the shortest distance from one another are bridged by three iodine atoms, while the copper atoms Cu(2) and Cu(1b) more distant from each other (Fig. 1) are bridged by only two iodine atoms. This situation is in a formal agreement with the viewpoint of Churchill *et al.* [9], explaining short Cu···Cu distances only by the tendency of Cu(I) atoms to acquire a regular tetrahedral coordination and of iodine atoms to form acute Cu–I–Cu angles.

In general, short distances between metal centers in complex compounds are usually assumed to be indicative of metal–metal bonds or of a shrinking effect of bridging ligands. According to MO calculations [11], copper(I) atoms in clusters can form weak metal–metal bonds, but these bonds have only a secondary influence on the complex geometry, which is determined by steric requirements of the central atom and bridging ligands. However, in the present case it is evident that the cations play a decisive role in forming the unusual joining of the tetrahedral fragments and, consequently, in the realization of the shortest Cu···Cu distance. A significant effect of the cation nature on the mode of packing of moieties which unite into a polymeric anion in crystal is a well-known fact. This effect manifests itself, in particular, in the ion–radical tetracyanoquinodimethane salts, wherein anions forming stacks are not linked either by bridging ligands or by direct bonds, so that the dependence of mutual arrangement of anions in a stack and of the distances between them on the cation size and geometry becomes apparent [8].

In our opinion, the degree of delocalization of the positive charge in the cation is at least as important: of the three cations similar in size and geometry but differing in delocalization degree, *viz.* (1), (2) and 2,4,6-triphenylpyridinium, only (1) and (2) with a more uniform charge distribution in their heterocycles form the intensive coloured salts with Cu(I) halides.

The triphenylthiopyrilium cation in the structure I (Fig. 2, bond angles in Table II) is situated almost parallel to the (001) plane and disordered over three orientations, so that the S atom occupies positions 1, 3 and 5 with unequal occupancy factors. Due to this disorder, the accuracy of the heterocycle geometrical parameters is rather small. The average C–C and C–S bond lengths are 1.43(3) and 1.68(3) Å; the latter value is very close to that found in thiophene (1.717 Å) by electron diffraction [13]. The

TABLE II. Bond Angles (degrees) in the Cation.

| Angle | |
|---|---|
| C(2)C(1)C(6) | 125(2) |
| C(2)S(1)C(6) | 99.8(6) |
| C(1)C(2)C(3) | 114(1) |
| C(1)C(2)S(3) | 128(1) |
| S(1)C(2)C(3) | 125.7(9) |
| C(1)C(2)C(21) | 122(1) |
| S(1)C(2)C(21) | 110.6(8) |
| C(3)C(2)C(21) | 124(1) |
| S(3)C(2)C(21) | 109.9(8) |
| C(22)C(21)C(26) | 119.3(9) |
| C(22)C(21)C(2) | 119.4(9) |
| C(26)C(21)C(2) | 121.3(9) |
| C(21)C(22)C(23) | 120.5(9) |
| C(22)C(23)C(24) | 121(1) |
| C(23)C(24)C(25) | 119(1) |
| C(24)C(25)C(26) | 119(1) |
| C(25)C(26)C(21) | 121.3(9) |
| C(2)C(3)C(4) | 127(1) |
| C(2)S(3)C(4) | 98.2(7) |
| C(3)C(4)C(5) | 112(1) |
| C(3)C(4)S(5) | 126(1) |
| S(3)C(4)C(5) | 127(1) |
| C(3)C(4)C(41) | 123(1) |
| S(3)C(4)C(41) | 107.6(8) |
| C(5)C(4)C(41) | 125(1) |
| S(5)C(4)C(41) | 110.9(9) |
| C(42)C(41)C(46) | 117.8(9) |
| C(42)C(41)C(4) | 119.1(9) |
| C(46)C(41)C(4) | 123.1(9) |
| C(41)C(42)C(43) | 120(1) |
| C(42)C(43)C(44) | 121(1) |
| C(43)C(44)C(45) | 119(1) |
| C(44)C(45)C(46) | 123(1) |
| C(45)C(46)C(41) | 120(1) |
| C(4)C(5)C(6) | 131(2) |
| C(4)S(5)C(6) | 101.2(8) |
| C(5)C(6)C(1) | 111(1) |
| C(5)C(6)S(1) | 124(1) |
| S(5)C(6)C(1) | 126(1) |
| C(5)C(6)C(61) | 125(1) |
| S(5)C(6)C(61) | 110.0(8) |
| C(1)C(6)C(61) | 124(1) |
| S(1)C(6)C(61) | 110.8(8) |
| C(62)C(61)C(66) | 119.0(9) |
| C(62)C(61)C(6) | 119.5(9) |
| C(66)C(61)C(6) | 121.5(9) |
| C(61)C(62)C(63) | 120(1) |
| C(62)C(63)C(64) | 121(1) |
| C(63)C(64)C(65) | 119(1) |
| C(64)C(65)C(66) | 120(1) |
| C(65)C(66)C(61) | 120.6(9) |

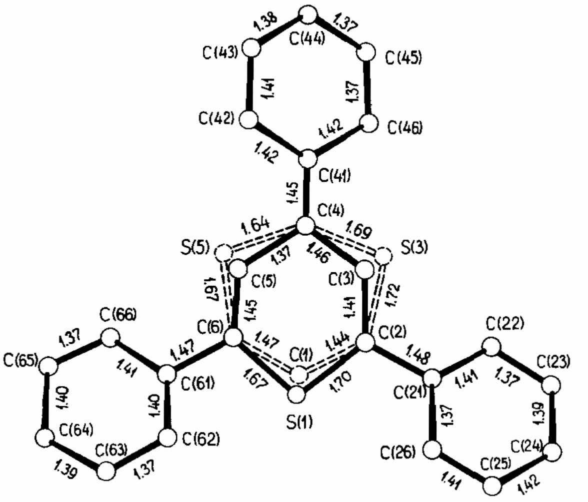

Fig. 2. Structure of the cation (1) with bond lengths (e.s.d.s 0.01–0.02 Å). Projection on the (0 0 1) plane.

heterocycle is approximately planar. The planes of the phenyl substituents in the 2, 4 and 6 positions form the dihedral angles of 16.6, 15.8, 15.9° with the mean plane of the heterocycle. In the three 2,4,6-triphenylpyrilium salts studied the corresponding angles are of the same order of magnitude, though they vary strongly under the influence of crystal packing: 2.3–18.0° in 1,1,3,3-tetracyanopropenide [14], 11.5–29.5° in tetrachloroferrate [15], and 12.3–29.3° in pentaiodide [16]. The average lengths of exocyclic C–C bonds in these salts (1.463(8), 1.45(3) and 1.463(15) Å respectively) are almost the same as in III (1.47(1) Å).

Cations are situated at usual Van der Waals distances from one another. Specific cation–anion interactions are not observed either. The shortest S(1)···I(1)* distance of 3.88 Å is close to the sum of the Van der Waals radii of I (2.15 Å [17]) and S (1.84 Å [18]). In the crystalline state the compound I is diamagnetic.

## Experimental

The synthesis of starting thiopyrilium and pyrilium perchlorates is described in [19].

*$[C_{23}H_{17}S]^+[Cu_2I_3]^-$ (I)*

0.3 g of 2,4,6-triphenylthiopyrilium perchlorate and 0.8 g of CuI in 70 ml of acetonitrile were boiled for 3 minutes, the hot solution was filtered and cooled. The black precipitate was filtered off and dried. 0.36 g, m.p. 286–289 °C (from $CH_3CN$). Found, %: C 33.38, H 2.61, S 3.84, I 45.29, Cu 15.96. Calculated, %: C 33.13, H 2.04, S 3.84, I 45.73, Cu 15.24.

*$[C_{23}H_{17}O]^+[Cu_2I_3]^-$ (II)*

0.2 g of 2,4,6-triphenylpyrilium perchlorate and 0.28 g of CuI in 10 ml of acetonitrile were boiled for 3 minutes and cooled. The black precipitate formed was filtered off and recrystallized from 70 ml of acetonitrile. 0.36 g, m.p. 318–322 °C. Found, %: C 33.73, H 2.34, I 45.78, Cu 14.47. Calculated, %: C 33.78, H 2.08, I 46.63, Cu 15.54.

*$[C_6H_8N]^+[Cu_2I_3]^-$ (III)*

0.2 g of N-methylpyridinium iodide and 0.5 g of CuI were boiled in 25 ml acetonitrile until dissolution of the precipitate, the hot solution was then filtered and cooled. The precipitate formed was filtered off, washed with ether and hexane, and dried in air. Light–yellow needles, 0.36 g, m.p. 166–170 °C. Found, %: C 12.19, H 1.75, N 2.28, I 63.27, Cu 21.38. Calculated, %: C 11.94, H 1.33, N 2.32, I 63.18, Cu 21.23.

An X-ray experiment was carried out with an automatic 4-circle Syntex $P2_1$ diffractometer using $MoK_\alpha$ radiation (graphite monochromator) at −120 °C, the structure determination was performed with an Eclipse S/200 computer by modified EXTL programs**.

Crystals of I are hexagonal, $C_{23}H_{17}Cu_2I_3S$, $a$ = 13.856(5), $c$ = 20.778(4) Å, $V$ = 3454 Å$^3$, $M$ = 833.23, $d_{meas}$ = 2.29 g/cm$^3$, $d_{calc}$ = 2.40 g/cm$^3$, $Z$ = 6, space group $P6_1$.

Intensities of 2950 reflections were measured by the $\theta/2\theta$ scan technique ($\theta \leqslant 25°$), 2872 of them with $I \geqslant 2\sigma$ were used in structure determination and refinement. The structure was solved by a direct method using the MULTAN program (Cu and I atoms located) and refined in isotropic approximation to R = 0.15. All non-hydrogen atoms were located in the subsequent electron density synthesis, however peak heights in the 1, 3 and 5 positions of the heterocycle showed the S atom disordered over these three positions with unequal occupancies. An attempt to distinguish C and S atoms in the positions 1, 3 and 5 directly in a difference Fourier synthesis was unsuccessful. Thus C(n) and S(n) atoms (n = 1, 3, 5) were placed in geometrically calculated positions, and their positional parameters and occupancies G

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*Generated from the basic atom by the transformation 1 − x, 1 − y, ½ + z.

**Modification of the programs was carried out by A. I. Yanovskii and R. G. Gerr in the X-ray crystal analysis Laboratory of the Nesmeyanov Institute of Organoelement Compounds of the USSR Academy of Sciences.

TABLE III. Atomic Coordinates ($\times 10^5$ for Cu and I, $\times 10^4$ for S and C).

| Atom | x | y | z |
|---|---|---|---|
| Cu(1) | 18941(10) | −1777(11) | −5644(7) |
| Cu(2) | 21160(11) | 1640(11) | 6116(7) |
| I(1) | 36697(4) | −516(5) | 0* |
| I(2) | 1622(4) | −17636(5) | 1616(4) |
| I(3) | 19349(5) | 17271(5) | −1072(4) |
| C(2) | 4114(8) | 9866(8) | 3397(4) |
| C(4) | 2144(8) | 8147(7) | 3423(5) |
| C(6) | 3840(7) | 7881(7) | 3398(5) |
| C(21) | 4855(7) | 11091(7) | 3363(4) |
| C(22) | 4399(7) | 11770(8) | 3210(5) |
| C(23) | 5062(8) | 12908(8) | 3191(5) |
| C(24) | 6204(8) | 13412(9) | 3300(5) |
| C(25) | 6675(8) | 12736(9) | 3444(5) |
| C(26) | 5969(7) | 11576(8) | 3489(5) |
| C(41) | 947(8) | 7692(7) | 3433(5) |
| C(42) | 244(8) | 6546(8) | 3579(6) |
| C(43) | −922(9) | 6091(9) | 3588(6) |
| C(44) | −1387(8) | 6738(8) | 3428(5) |
| C(45) | −698(9) | 7850(9) | 3310(6) |
| C(46) | 437(9) | 8336(8) | 3299(5) |
| C(61) | 4293(8) | 7120(7) | 3420(4) |
| C(62) | 5417(8) | 7540(8) | 3580(6) |
| C(63) | 5849(8) | 6839(9) | 3592(6) |
| C(64) | 5180(8) | 5704(9) | 3478(5) |
| C(65) | 4054(9) | 5280(8) | 3326(5) |
| C(66) | 3617(8) | 5973(8) | 3302(5) |

Disordered Atoms

| Atom | x | y | z | $B_{iso}$, Å | G |
|---|---|---|---|---|---|
| S(1) | 4867(6) | 9205(5) | 3338(3) | 2.2(1) | 0.45 |
| S(3) | 2750(7) | 9548(7) | 3463(4) | 1.9(2) | 0.30 |
| S(5) | 2450(9) | 7150(11) | 3383(5) | 2.3(2) | 0.25 |
| C(1) | 4538(17) | 9106(15) | 3374(9) | 1.8(4) | 0.55 |
| C(3) | 2941(12) | 9341(12) | 3425(7) | 2.2(3) | 0.70 |
| C(5) | 2667(14) | 7534(15) | 3410(8) | 3.0(3) | 0.75 |

*Fixed to define the origin.

TABLE IV. Calculated Coordinates for Hydrogen Atoms* ($\times 10^3$).

| Atom | x | y | z | Atom | x | y | z |
|---|---|---|---|---|---|---|---|
| H(22) | 358 | 1142 | 312 | H(45) | −104 | 832 | 323 |
| H(23) | 474 | 1340 | 307 | H(46) | 92 | 915 | 320 |
| H(24) | 671 | 1426 | 328 | H(62) | 590 | 835 | 368 |
| H(25) | 749 | 1309 | 353 | H(63) | 666 | 716 | 370 |
| H(26) | 632 | 1111 | 362 | H(64) | 551 | 519 | 349 |
| H(42) | 58 | 607 | 368 | H(65) | 356 | 445 | 323 |
| H(43) | −142 | 528 | 370 | H(66) | 281 | 567 | 321 |
| H(44) | −222 | 639 | 340 | | | | |

*Having the same numbers as the carbon atoms to which they are bonded.

refined (with fixed $B_{iso}$ = 2.3 Å$^2$, equal to the mean current value for the ordered atoms of the cycle). The resulting G values, *viz.* C(1) 0.67(9), C(3) 0.90(7), C(5) 0.91(7), S(1) 0.43(3), S(3) 0.28(2), S(5) 0.20(2), were then normalized to satisfy the equations G[C(1)] + G[C(3)] + G[C(5)] = 2, G[S(1)] + G[S(3)] + G[S(5)] = 1 and G[C(n)] + G[S(n)] = 1. The normalized G values (see Table III) were fixed and all atoms were then refined in the usual way (Cu and I with anisotropic thermal factors, others with isotropic ones) to R = 0.043. Hydrogen atoms were included in geometrically calculated positions and their parameters were not refined. At the final stage the weighting scheme $w^{-1} = \sigma_F^2 + (0.01|F_o|)^2$ was introduced, and 11 inaccurately measured reflections were discarded. The refinement was then continued with all ordered atoms in anisotropic approximation, and for disordered atoms in isotropic one to R = 0.033 and $R_w$ = 0.040. The final atomic positional parameters are listed in Table III*.

## References

1 C. Brink, N. F. Binnedijk and J. van de Linde, *Acta Cryst.*, *7,* 176 (1954).
2 H.-J. Meyer, *Acta Cryst.*, *16,* 788 (1963).
3 T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev.*, *1,* 99 (1972).
4 E. Eitel, D. Oelkrug, W. Hiller and J. Strähle, *Z. Naturforsch.*, *35b,* 1247 (1980).
5 J. Strähle, W. Hiller, E. Eitel and D. Oelkrug, *Z. Kristallogr.*, *153,* 277 (1980).
6 G. Nardin, L. Randaccio and E. Zangrando, *J. Chem. Soc. Dalton,* 2566 (1975).
7 A. F. Wells, 'Structural Inorganic Chemistry', Clarendon Press, Oxford (1973), p. 1021.
8 J. M. Guss, R. Mason, I. Sotofte, G. van Koten and J. G. Noltes, *Chem. Commun.*, 446 (1972).
9 M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, *13,* 1899 (1974).
10 V. Schramm, *Inorg. Chem.*, *17,* 714 (1978).
11 P. K. Mehrotra and R. Hoffman, *Inorg. Chem.*, *17,* 2187 (1978).
12 E. B. Yagubskii and M. L. Hidekel, *Uspekhi Khimii, 41,* 2132 (1972).
13 W. R. Harshbarger and S. H. Bauer, *Acta Cryst.*, *B26,* 1010 (1970).
14 T. Tamamura, T. Yamane, N. Yasuoka and N. Kasai, *Bull. Chem. Soc. Jap.*, *47,* 832 (1974).
15 N. G. Bokii, R. V. Vedrinskii, V. V. Kitaev, N. A. Lopatina and Yu. T. Struchkov, *Koordinatsionnaya Khimiya, 2,* 103 (1976).
16 O. E. Kompan, K. A. Potekhin, N. G. Furmanova and Yu. T. Struchkov, *Zh. Strukt. Khim.*, *21,* 194 (1980).
17 L. Pauling, 'The Nature of the Chemical Bond', Cornell University Press, Ithaca, New York (1960), p. 260.
18 Yu. V. Zefirov and P. M. Zorkii, *Zh. Strukt. Khim.*, *17,* 745 (1976).
19 G. N. Dorofeenko, E. I. Sadekova and E. V. Kuznetsov, 'Preparativnaya khimiya pirilievykh soley', (Preparative Chemistry of Pyrilium Salts), Rostov University Press, Rostov-on-Don, U.S.S.R. (1972) (Russian).

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*A list of structure factors and a table of atomic thermal parameters may be obtained from the authors.