# MOLECULAR STRUCTURE OF THE CHELATE COMPLEX (3,5-DIMETHYLBENZYL)DIPHENYLPHOSPHITODICARBONYL-CHROMIUM

A.N. NESMEYANOV, Yu.T. STRUCHKOV, V.G. ANDRIANOV, V.V. KRIVYKH
and M.I. RYBINSKAYA*

*Institute of Organo-Element Compounds, Academy of Sciences, Vavilova 28, Moscow
117813 (U.S.S.R.)*

(Received June 20th, 1978)

## Summary

The chelate phosphitoalkylarenedicarbonylchromium complex has been studied by single-crystal X-ray diffraction. The presence of the short bridge (—$CH_2O$—) leads to noticeable distortions of the molecular geometry which may be the reason why complexes of this type containing one more chelate cycle of the same size could not be isolated. The Cr—P bond in the complex 2.201 Å, : the shortest Cr—P bond reported thus far.
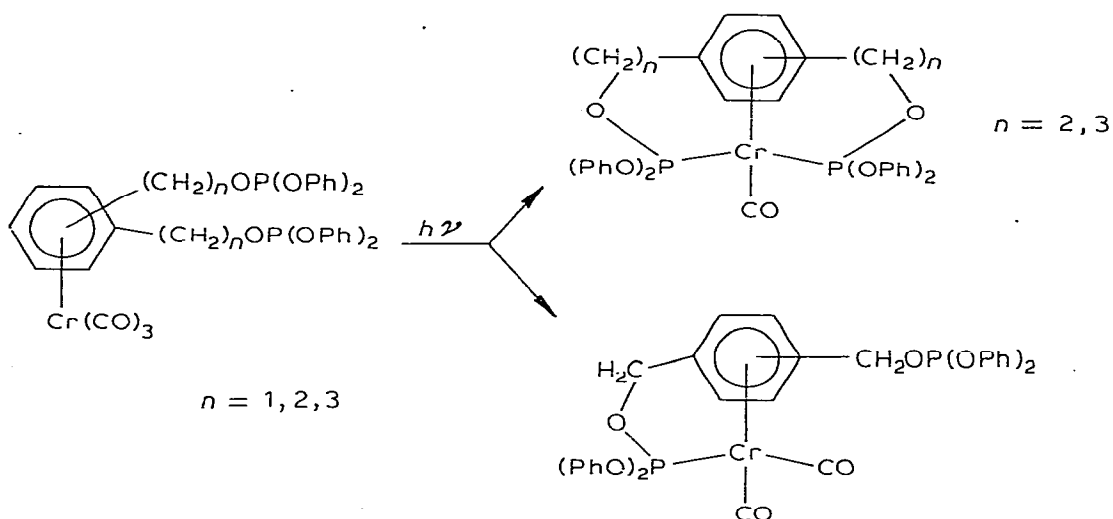
## Introduction

In recent years, the new type of compounds, organometallic chelates with a π-bonded cyclic ligand as one of the coordinated groups, has attracted much interest [1—5]. Most work in this direction has been done on arenecarbonyl-chromium complexes of types I and II where X is a bridging group and Y a coordinated group ($CH_2$=CH—, —P(OR)$_2$)



(I)                    (II)
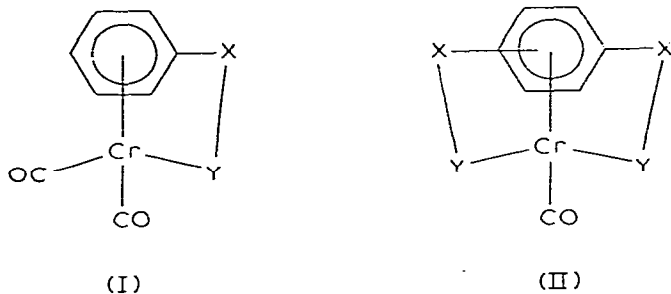
With Y = $CH_2$=CH—, chelate cycles may only be formed if X is a di- or tri-atomic bridge (X = —$OCH_2$—, —$CH_2CH_2$—, —$CH_2OCH_2$—, —$CH_2CH_2CH_2$—) as

has almost simultaneously been shown by us [1] and by Trahanovsky and Hall [3]. We have also found that the chelate cycle bridge length depends on the nature of the coordinating group, Y. Thus with Y = P(OR)$_2$, chelate cycles may include two-, three-, and even four-atomic bridges.

Two-bridge chelates II pose some difficulties compared with one-bridge species I. Thus with Y = P(OPh)$_2$, two-bridge chelates are only formed with three- and four-atomic bridges. One-cycle chelates involving two-atomic bridges are known, but coordination of the second group does not occur in that case. Prolonged UV irradiation only leads to gradual decomposition of the one-bridge chelate. It should also be noted that the results are practically indepen-

dent of the position of the second bridge (*ortho-*, *meta-*, or *para-*) for *n* equal to 1, 2, and 3.

In order to determine the geometry of the complexes of this type containing short bridges and to find out why the second chelate cycle can not be made, we have undertaken an X-ray study of compound III containing a two-atomic bridge.

(III)
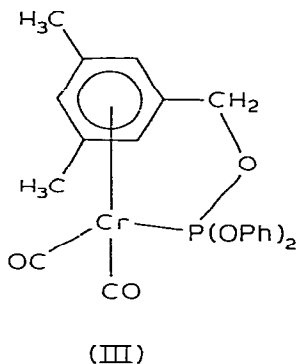
## Experimental

Compound III was prepared according to the procedure described in ref. 5. The crystals were grown from ethanol. The compound forms rhombic crystals, $a$ 33.413(12), $b$ 7.747(2), $c$ 16.444(11) Å, $V$ 4257(1) Å$^3$, $M$ 460.4, $d_{exptl.}$ 1.44, $d_{calcd.}$ 1.445 g/cm$^3$ for $Z = 8$, Sp.gr. *Pbca*. Intensities of 918 reflections with $I \geqslant 2\,\sigma(I)$ were measured with an automatic Syntex P2$_1$ diffractometer (Mo-radiation, graphite monochromator, $\nu/2\nu$ scan, $2\nu \geqslant 40°$); no absorption corrections were made. The structure was solved by the standard heavy-atom method and refined to $R = 0.082$ using the full matrix anisotropic for Cr and and isotropic for other atoms approximation. The computations were made with the XTL programs.

## Structure data and discussion

The atomic coordinates and their temperature factors are listed in Table 1, the bond lengths in Table 2, and the bond angles in Table 3. In Fig. 1, the molecular configuration of III together with bond lengths is depicted. As in other ($\eta^6$-arene)Cr(CO)$_3$ complexes, Cr has an octahedral environment. The (O)C— Cr—C(O) angle is narrowed to 85.9(8)° and the P—Cr—C(O) ones are widened
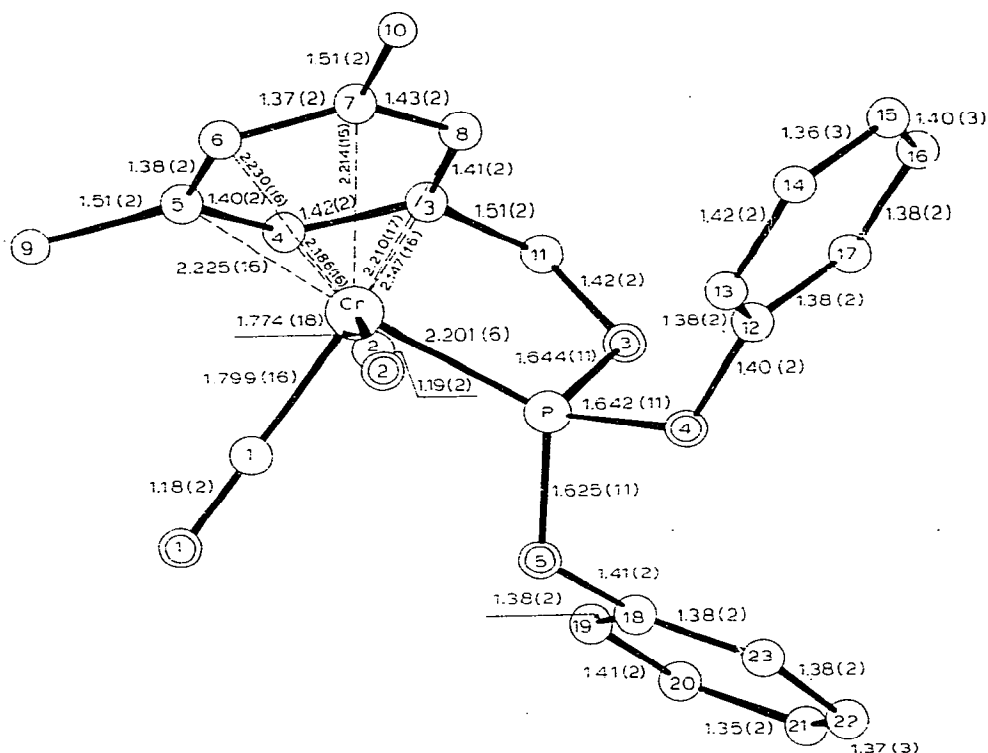


Fig. 1. Molecular geometry of [3,5-(CH$_3$)$_2$C$_6$H$_3$CH$_2$OP(OPh)$_2$] · Cr(CO)$_2$.

TABLE 1

ATOMIC COORDINATES ($\times 10^5$ FOR Cr AND P AND $\times 10^4$ FOR OTHER ATOMS) AND THEIR TEMPERATURE FACTORS IN $A^2$

| Atom | $x$ | $y$ | $z$ | $B$ |
|------|-----|-----|-----|-----|
| Cr | 6594(8) | 19233(34) | 13886(15) | $a$ |
| P | 12167(14) | 6016(66) | 10406(27) | $a$ |
| O(1) | 170(3) | −1283(15) | 1322(7) | 55(3) |
| O(2) | 744(4) | 1131(13) | 3141(7) | 58(3) |
| O(3) | 1432(3) | 1549(13) | 260(6) | 33(3) |
| O(4) | 1614(3) | 389(13) | 1618(6) | 31(3) |
| O(5) | 1205(3) | −1404(13) | 751(6) | 37(3) |
| C(1) | 367(5) | −21(20) | 1320(11) | 36(4) |
| C(2) | 713(6) | 1410(22) | 2335(11) | 55(5) |
| C(3) | 859(5) | 3417(22) | 366(10) | 32(4) |
| C(4) | 451(5) | 2997(23) | 234(9) | 35(4) |
| C(5) | 157(5) | 3362(22) | 815(9) | 31(4) |
| C(6) | 265(5) | 4230(20) | 1511(10) | 32(4) |
| C(7) | 652(6) | 4723(19) | 1658(9) | 38(4) |
| C(8) | 954(5) | 4385(21) | 1066(10) | 34(4) |
| C(9) | −267(5) | 2789(21) | 640(9) | 37(4) |
| C(10) | 768(5) | 5191(23) | 2422(12) | 64(5) |
| C(11) | 1191(5) | 2748(21) | −172(9) | 39(4) |
| C(12) | 1796(4) | 1860(23) | 1950(9) | 26(4) |
| C(13) | 1719(4) | 2277(21) | 2750(10) | 36(4) |
| C(14) | 1912(5) | 3702(23) | 3120(11) | 54(5) |
| C(15) | 2174(5) | 4638(23) | 2661(11) | 51(5) |
| C(16) | 2257(5) | 4196(25) | 1855(11) | 55(5) |
| C(17) | 2067(4) | 2804(21) | 1498(9) | 40(4) |
| C(18) | 1480(5) | −2132(22) | 202(10) | 33(4) |
| C(19) | 1353(5) | −2270(21) | −593(10) | 37(4) |
| C(20) | 1616(5) | −3026(22) | −1158(10) | 50(5) |
| C(21) | 1978(5) | −3592(23) | −913(11) | 50(5) |
| C(22) | 2096(5) | −3486(24) | −117(12) | 55(5) |
| C(23) | 1850(5) | −2709(23) | 446(10) | 47(5) |

| Atom | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|------|----------|----------|----------|----------|----------|----------|
| Cr | 36(1) | 28(1) | 21(1) | 0(2) | 3(2) | 2(2) |
| P | 36(3) | 25(2) | 26(3) | −4(3) | 1(2) | 2(2) |

$a$ Anisotropic temperature factors in the form $T = \exp[-1/4 \cdot 10^{-1}(B_{11}h^2a*^2 + \dots B_{23}klb*c*)]$.

TABLE 2

BOND LENGTHS $d$ (Å)

| Bond | $d$ | Bond | $d$ | Bond | $d$ |
|------|-----|------|-----|------|-----|
| Cr—P | 2.201(6) | C(2)—O(2) | 1.19(2) | C(12)—C(13) | 1.38(2) |
| Cr—C(1) | 1.799(16) | O(3)—C(11) | 1.42(2) | C(13)—C(14) | 1.42(2) |
| Cr—C(2) | 1.774(18) | O(4)—C(12) | 1.40(2) | C(14)—C(15) | 1.36(3) |
| Cr—C(3) | 2.147(16) | O(5)—C(18) | 1.41(2) | C(15)—C(16) | 1.40(3) |
| Cr—C(4) | 2.186(16) | C(11)—C(3) | 1.51(2) | C(16)—C(17) | 1.38(2) |
| Cr—C(5) | 2.225(16) | C(3)—C(4) | 1.42(2) | C(17)—C(12) | 1.38(2) |
| Cr—C(6) | 2.230(16) | C(4)—C(5) | 1.40(2) | C(18)—C(19) | 1.38(2) |
| Cr—C(7) | 2.214(15) | C(5)—C(6) | 1.38(2) | C(19)—C(20) | 1.41(2) |
| Cr—C(8) | 2.210(17) | C(6)—C(7) | 1.37(2) | C(20)—C(21) | 1.35(2) |
| P—O(3) | 1.644(11) | C(7)—C(8) | 1.43(2) | C(21)—C(22) | 1.37(3) |
| P—O(4) | 1.642(11) | C(8)—C(3) | 1.41(2) | C(22)—C(23) | 1.38(2) |
| P—O(5) | 1.625(11) | C(9)—C(5) | 1.51(2) | C(23)—C(18) | 1.38(2) |
| C(1)—O(1) | 1.18(2) | C(10)—C(7) | 1.51(2) | | |

TABLE 3

BOND ANGLES ω (DEGREES)

| Angle | ω | Angle | ω | Angle | ω |
|---|---|---|---|---|---|
| P—Cr—C(1) | 93.1(6) | O(3)—C(11)—C(3) | 110.4(1.3) | O(4)—C(12)—C(17) | 120.3(1.4) |
| P—Cr—C(2) | 93.6(6) | C(11)—C(3)—C(4) | 122.4(1.4) | C(12)—C(13)—C(14) | 120.4(1.5) |
| C(1)—Cr—C(2) | 85.9(8) | C(11)—C(3)—C(8) | 119.8(1.4) | C(13)—C(14)—C(15) | 118.0(1.6) |
| Cr—P—O(3) | 111.5(4) | C(3)—C(4)—C(5) | 121.7(1.5) | C(14)—C(15)—C(16) | 121.5(1.7) |
| Cr—P—O(4) | 125.5(4) | C(4)—C(5)—C(6) | 118.8(1.5) | C(15)—C(16)—C(17) | 120.2(1.6) |
| Cr—P—O(5) | 120.0(4) | C(5)—C(6)—C(7) | 122.0(1.5) | C(16)—C(17)—C(12) | 120.0(1.5) |
| O(3)—P—O(4) | 98.2(5) | C(6)—C(7)—C(8) | 119.8(1.5) | C(17)—C(12)—C(13) | 120.8(1.5) |
| O(3)—P—O(5) | 102.1(6) | C(7)—C(8)—C(3) | 119.7(1.5) | O(5)—C(18)—C(19) | 116.0(1.4) |
| O(4)—P—O(5) | 95.4(6) | C(8)—C(3)—C(4) | 117.6(1.5) | O(5)—C(18)—C(23) | 122.1(1.4) |
| Cr—C(1)—O(1) | 176.1(1.5) | C(9)—C(5)—C(4) | 118.0(1.4) | C(18)—C(19)—C(20) | 117.8(1.5) |
| Cr—C(2)—O(2) | 117.4(1.5) | C(9)—C(5)—C(6) | 123.2(1.4) | C(19)—C(20)—C(21) | 119.9(1.6) |
| P—O(3)—C(11) | 115.7(9) | C(10)—C(7)—C(8) | 118.4(1.5) | C(20)—C(21)—C(22) | 121.6(1.7) |
| P—O(4)—C(12) | 119.6(9) | O(4)—C(12)—C(13) | 118.7(1.4) | C(21)—C(22)—C(23) | 119.9(1.7) |
| P—O(5)—C(18) | 123.7(1.0) | C(10)—C(7)—C(6) | 121.8(1.5) | C(22)—C(23)—C(18) | 118.8(1.6) |
| | | | | C(23)—C(18)—C(19) | 121.9(1.5) |

to 93.4(6)° from the ideal value of 90° because of the presence of bulky phosphite ligands. In [2,5-Me$_2$C$_6$H$_3$CH$_2$OCH$_2$CH=CH$_2$]Cr(CO)$_2$ (IV) having a similar structure [2], the (O)C—Cr—C(O) angle is also narrowed to 84.6°. Other distortions of the coordination octahedron due to the contracting action of the bridge are the inequality of the Q—CrC(O) (126.7 and 129.6°) and Q—Cr—P (117.9°) angles (Q is the centre of gravity of the benzene ring).

The relative orientations of the arene ligand and CrP(CO)$_2$ grouping in III correspond to the conformation intermediate between staggered and eclipsed forms (Fig. 2). This may be explained by the rigidity of the chelate cycle containing a short bridge between the benzene nucleus and the metal atom. In complex IV, the relative orientations of the arene and three other ligands correspond to the staggered conformation because the chelate cycle comprises a longer bridge which makes it more flexible and mobile than the chelate cycle in III. For the same reason, the torsion angle about the —CH$_2$—O— bond is only 23.2° in III, whereas in IV, it amounts to 66.1°.

The average Cr—C(arene) distance in III equal to 2.202(16) Å is near to those observed in similar arenechromium tricarbonyl complexes though individual Cr—C bonds have somewhat different lengths, the Cr—C(3) bond being the shortest one (2.147(16) Å) because of the contracting action of the bridge.

Unlike in IV where the benzene ring shows a slight departure from planarity towards a boat-wise conformation with carbon atoms bearing methyl substituents bent away from the metal atom (by 0.030 and 0.040 Å) and the methyl substituents displaced still further (by 0.075 and 0.193 Å), the arene ligand in III is planar (the maximal deviation from the plane is equal to 0.03(2) Å) and the methyl groups lie in the ring plane to within ±0.01(2) Å. The C(11) atom of the bridge group is, however, displaced from that plane by 0.27(2) Å in the direction of the Cr atom (a smaller displacement, as little as 0.030 Å, occurs in IV).

The C—C bond lengths in the benzene ring have the usual mean of 1.40(2) Å. The C—C distances between the ring and exocyclic carbon atoms are practically
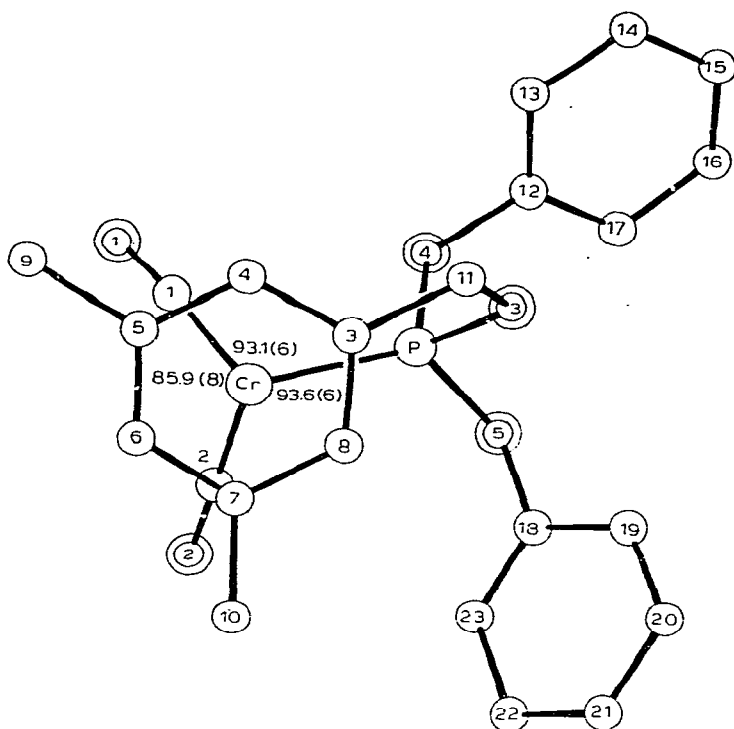
Fig. 2. Projection of the molecule onto the benzene ring plane.

identical (1.51(2) Å) and coincide with the standard C($sp^2$)—C($sp^3$) ordinary bond length [6].

The unusual Cr—P bond length, 2.201(6) Å, is noteworthy. This is not only greatly shortened from the sum of the single-bonded covalent radii (Cr, 1.46 Å [7], P, 1.10 Å [6]) but is also the shortest Cr—P bond ever observed. Thus, the phosphite complexes Cr(CO)$_5$P(OPh)$_3$ (V) [8] and trans-Cr(CO)$_4$[P(OPh)$_3$]$_2$ (VI) [9] contain Cr—P bonds of 2.309 and 2.525 Å, respectively. Two reasons explain the observed shortening of the Cr—P bond in III: significant $d_\pi$(Cr) → $d_\pi$(P) interactions favoured by the presence of electronegative substituents at P (oxygen atoms), and the chelate effect known to cause shortening of bonds to metal atoms.

The P atom has a distorted tetrahedral bond configuration with the valence angles Cr—P—O and O—P—O (119.0(4) and 98.6(6)° on average, respectively) being significantly different from the ideal value of 109.5°. Similar deviations from the ideal tetrahedral bond configuration occur in all transition metal complexes with phosphite ligands, e.g. in V and VI where the Cr—P—O angles are equal to 117.8 and 117.1° and the O—P—O angles to 100.0 and 100.8°, respectively. The mean P—O (1.637(11) Å) and O—C (1.41(2) Å) distances have the usual values and are similar to those observed in V and VI (P—O, 1.603 (III), 1.604 (IV); O—C, 1.399 (III), 1.403 Å (IV)). The phenyl rings are planar with the mean C—C bond length of 1.38(2) Å, the O atoms are coplanar to the rings they are bonded to.

The metal carbonyl groups are linear (the Cr—C—O valence angles are equal to 176.1(1.5) and 177.4(1.5)°), the Cr—C mean bond lengths (1.79(2) Å) and C—O distances (1.18(2) Å) differ only insignificantly from the ones typical for chromium carbonyl complexes.

The X-ray structure analysis results show that the formation of chelate cycles in complexes of type III leads to significant distortions of the molecular geometries. The main manifestations of the chelate cycle formation are the reduction of the Q—Cr—P angle and displacement of the bridge atom C(11) from the arene plane in the direction of the chromium atom. A noticeable though slight displacement of the arene ligand is also observed as may be seen from the difference in the Cr—C(arene) bond lengths.

The data obtained thus show that the formation on one more chelate cycle with X = —$CH_2O$— is hampered to a considerable extent by the presence of the first one and for that reason does not occur under the conditions used for the formation of the one-cycle chelate. We can not however rule out the possibility that the molecular geometry distortions may prove insufficient to bar the formation of the two-cycle chelate under some other, more suitable conditions.

## References

1  A.N. Nesmesyanov, M.I. Rybinskaya, V.V. Krivykh and V.S. Kaganovich, J. Organometal. Chem. 93(1975)C8.
2  Yu.T. Struchkov, V.G. Andrianov, A.N. Nesmeyanov, V.V. Krivykh, V.S. Kaganovich and M.I. Rybinskaya, J. Organometal. Chem., 117(1976) C81.
3  W.S. Trahanovsky and R. Hall, J. Organometal. Chem., 96(1975)71.
4  P. Eilbracht and P. Dahler, J. Organometal. Chem., 127 (1977) C48.
5  A.N. Nesmeyanov, V.V. Krivykh, P.V. Petrovskii and M.I. Rybinskaya, Dokl. Akad. Nauk SSSR, 231 (1976) 110.
6  L. Pauling, The Nature of Chemical Bond, Cornell University Press, Ithacha, N.Y., 3rd ed., 1960.
7  V.G. Andrianov, B.P. Biryukov and Yu.T. Struchkov, Zh. Strukt. Khim., 10 (1969) 1129.
8  H.J. Plastas, J.M. Stewart and S.O. Grim, J. Amer. Chem. Soc., 91(1969)4326.
9  H.S. Presten, J.M. Stewart and H.J. Plastas, Inorg. Chem., 11 (1972) 161.