

Table 3. Bond distances (Å), bond angles (°) and deviations (Å) of atoms from the least-squares-fit plane in the coordination sphere

| | [Ni(bchtn)(H ₂ O) ₂]Cl ₂ (M = Ni) | [Cu(bchtn)(ClO ₄) ₂] [*] (M = Cu) |
|----------------------------------|--|---|
| M—O(1) | 2.056 (2) | 1.966 (7) |
| M—N(2) | 2.085 (2) | 1.998 (10) |
| M—O(long axis) | 2.159 (2) | 2.641 (11) |
| M—O(short axis) | 2.100 (3) | 2.448 (11) |
| O—M—O | 178.8 (1) | 163.5 (3) |
| Bite angles around the metal ion | | |
| O(1)—M—N(2) | 90.8 (1) | 93.1 (3) |
| N(2)—M—N(2') | 97.1 (1) | 93.1 (4) |
| N(2')—M—O(1') | 90.8 (1) | 93.4 (3) |
| O(1)—M—O(1') | 81.2 (1) | 81.2 (3) |

* N(2') = N(3) and O(1') = O(2) in the Cu complex (Lee *et al.*, 1984).

The Ni^{II} ion, the two O atoms of the water molecules and the OH group are all on a mirror plane, $y = 0.25$. All other atoms in the complex are mirror-related. Fig. 1(a) indicates that C(2) and C(2') are 0.350 (4) Å above the equatorial plane and the whole molecule has a boat shape as shown in Fig. 1(b); C(5) on the middle chelate ring is 0.118 (3) Å below this plane. The chelate ring, Ni—N(2)—C(4)—C(5)—C(4')—N(2'), is in a stable chair form.

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Studies of Tetramethylammonium Tetrabromometallates. II. Structure of Tetramethylammonium Tetrabromozincate, [N(CH₃)₄]₂[ZnBr₄], in its Low-Temperature Phase

BY PATRICK TROUÉLAN, JACQUES LEFEBVRE AND PATRICK DEROLLEZ

Laboratoire de Dynamique des Cristaux Moléculaires (ERA 465), Université des Sciences et Techniques de Lille I, 59655 Villeneuve d'Ascq CEDEX, France

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Abstract. $M_r = 533.0$, monoclinic, $P2_1/a$, $a = 12.534(2)$, $b = 9.142(3)$, $c = 15.772(4)$ Å, $\gamma = 89.69(2)^\circ$, $V = 1807(2)$ Å³, $Z = 4$, $D_x = 1.898$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 108$ cm⁻¹, $F(000) = 1024$, $T = 193$ K, final $R = 0.101$ for 2408 observed reflections. No superlattice reflection appears in the low-temperature phase. Domains were exhibited in the crystal and a program has been written to solve this structure. Compared with the high-temperature phase, a large decrease of the temperature factors is observed. Bond lengths and angles of the [ZnBr₄]²⁻ tetrahedron are almost identical with those of the high-temperature phase.

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Table 4. Bond distances (Å) and bond angles (°)

| (a) Covalent bond lengths | | | |
|--|-------------|-----------------|------------|
| C(1)—O(1) | 1.243 (3) | C(3)—N(2) | 1.476 (4) |
| C(1)—N(1)(amide) | 1.324 (5) | C(4)—N(2) | 1.480 (4) |
| C(1)—C(2) | 1.509 (5) | C(4)—C(5) | 1.522 (4) |
| C(2)—C(3) | 1.519 (5) | C(5)—O(10) | 1.434 (5) |
| (b) Bond angles around the chelate rings | | | |
| Ni—O(1)—C(1) | 129.2 (3) | C(3)—N(2)—Ni | 111.9 (2) |
| O(1)—C(1)—C(2) | 122.0 (3) | N(2)—C(4)—C(5) | 111.6 (3) |
| C(1)—C(2)—C(3) | 113.9 (2) | C(4)—C(5)—C(4') | 113.0 (3) |
| C(2)—C(3)—N(2) | 111.9 (2) | O(10)—C(5)—Ni | 85.3 (3) |
| (c) Parameters for the hydrogen bonds | | | |
| O—H...Cl | O...Cl | H...Cl | ∠O—H...Cl |
| OW(1)—H(10)...Cl(1) | 3.171 (2) Å | 2.390 (1) Å | 139.8 (2)° |
| OW(2)—H(11')...Cl(1') | 3.166 (2) | 2.270 (1) | 159.4 (2) |

Symmetry code: (') $x, -y, z$.

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Introduction. It is well known that many crystals of the A_2XY_4 family have a sequence of successive phase transitions [$A = \text{K, Rb, NH}_4, \text{N}(\text{CH}_3)_4$; $X = \text{Zn, Cu, Co}$; $Y = \text{Cl, Br}$]. Most of the members of this family present an incommensurate phase transition. As regards the structural aspects, they have an orthorhombic high-temperature phase with space group $Pnma$ and generally very large temperature factors (Wiesner, Srivastava, Kennard, Di Vaira & Lingafelter, 1967; Clay, Murray-Rust & Murray-Rust, 1975; Kamenar & Nagl, 1976; Kallel, Bats & Daoud, 1981). For the structures of the other phases, few studies have been made. To our knowledge, only the $(\text{NH}_4)_2[\text{ZnCl}_4]$

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compound has been structurally investigated in its four phases (Matsunaga, 1982).

In a previous paper (Trouélan, Lefebvre & Derollez, 1984), the structures of tetramethylammonium tetrabromocuprate and -zincate $\{[N(CH_3)_4]_2[MBr_4]; M = Cu \text{ and } Zn \text{ respectively}\}$ in their high-temperature phase ($T = 293 \text{ K}$) have been reported. The former compound has four phases, one of which is incommensurate and will be studied in a later paper, whereas the latter has only two phases with a transition at $T = 286 \text{ K}$ (Gesi, 1982). In our study of $[N(CH_3)_4]_2[MBr_4]$ compounds, the second step is the structure determination of the low-temperature phase ($T = 193 \text{ K}$) of $[N(CH_3)_4]_2[ZnBr_4]$ (hereafter abbreviated as TMAT BrZn). A comparison of this structure with that of the high-temperature phase is made in order to understand the mechanism induced by the phase transition.

Experimental. Single crystals of TMAT BrZn grown by the slow-evaporation method from an aqueous solution containing stoichiometric proportions of $[N(CH_3)_4]Br$ and $ZnBr_2$. D_m not determined. Crystal $0.30 \times 0.30 \times 0.25 \text{ mm}$. Diffraction intensity measurements collected using a Philips PW 1100 automatic diffractometer with monochromated $Mo K\alpha$ radiation. Crystal temperature controlled at 193 K by a stream of cold nitrogen gas and temperature fluctuations kept within $\pm 0.5 \text{ K}$. 25 reflections used for measuring lattice parameters. θ - 2θ scan method with $3 < \theta < 28^\circ$ ($0.07 < \sin \theta / \lambda < 0.62 \text{ \AA}^{-1}$), scan width 1.2° , scan speed $0.024^\circ \text{ s}^{-1}$. Background counted for half total scan on each side of $K\alpha$ position. Three standard reflections monitored every hour (022, 0 $\bar{2}2$ and 401), no significant change in intensities. 4763 hkl and $\bar{h}kl$ reflections measured corresponding to 2408 non-equivalent reflections with $I > 3\sigma(I)$ in range $-16 \leq h \leq 16$, $0 \leq k \leq 12$, $0 \leq l \leq 20$. Data corrected for Lorentz and polarization effects. Because of the complicated shape of the single crystal it was difficult to correct for absorption effects.

Low-temperature phase characterization

TMAT BrZn undergoes a second-order phase transition at 286 K (Gesi, 1982). The evolution of the three lattice parameters is reported in Fig. 1.* The b parameter has no change in its slope and thermal expansion is similar in the two phases. The a and more particularly the c parameters exhibit an evolution typical of a crystal with an order-disorder phase transition (see, for example, $NaNO_3$, Terauchi & Yamada, 1972): in the low-temperature phase, near the transition, the parameter increases strongly and the transition is characterized by a change of slope. The transition temperature agrees with Gesi's result.

* Table 1, which gives the exact values reported in Fig. 1, has been deposited (see deposition footnote).

To look for possible superlattice reflections, rotation zero- and first-layer-line Weissenberg diagrams were obtained around b at 193 K . No additional peak appears: the primitive cell of the low-temperature phase is the same as the high-temperature one.

Intensity measurements of hkl , $\bar{h}kl$ and $hk\bar{l}$ reflections exhibit the following intensity relations: $I(hkl) = I(h\bar{k}l) \neq I(\bar{h}kl) = I(h\bar{k}l)$, characteristic of a monoclinic lattice with the twofold axis along c . Systematic absences of $hk0$ reflections for $h = 2n + 1$ and $00l$ for $l = 2n + 1$ allow us to conclude that $P2_1/a$ is the correct space group. This space group is one of the two possible space groups deduced by Perret *et al.* (1983) from NQR measurements and symmetry arguments.

In the lattice parameter *versus* temperature measurements, the deviation $\Delta\gamma$ of the monoclinic angle from 90° is found to be very small and almost constant between 227 and 286 K : $\Delta\gamma = 0.30^\circ$ ($\cos \gamma = \pm 0.0052$). Later, in order to make the comparison with the high-temperature phase, the monoclinic axis is chosen along c and the monoclinic angle γ is taken lower than 90° .

Structure determination

Starting from the atomic positions of the high-temperature phase, cycles of refinement were made using *SHELX76* (Sheldrick, 1976) for space group $P2_1/a$ with four molecules per unit cell. Subsequent

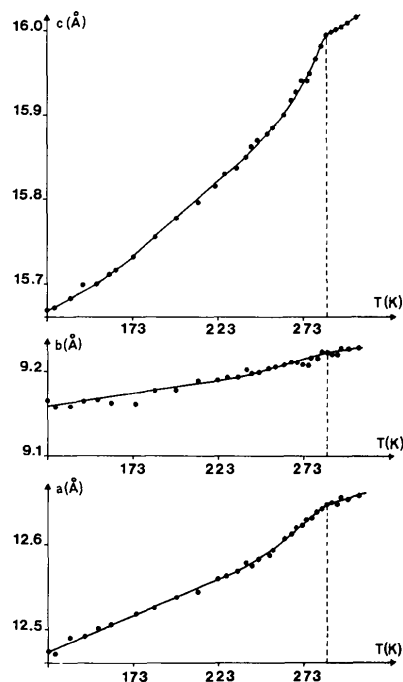


Fig. 1. Lattice-parameter evolution with temperature of TMAT BrZn.

least-squares refinements with anisotropic temperature factors for all atoms only reduced the reliability index R to the final value of 0.214. A series of Fourier difference syntheses exhibited peaks of the order of $4 \text{ e } \text{Å}^{-3}$ approximately symmetrically located on heavy-atom sites with respect to the mirror plane of space group $Pnma$ of the high-temperature phase. A variance analysis showed that the better values are obtained for the $0kl$ and $h0l$ reflections: $v(0kl) = 9.17$; $v(h0l) = 9.51$ whereas $v(hkl) = 16.86$ {with unit weights, $v = [\sum (F_o - |F_c|)^2 / N]^{1/2}$ where the summation runs over the N reflections of the group}.

The poor value of the reliability index obtained with a conventional refinement program and the two remarks made above suggest the existence of domains when the single crystal is cooled from its high-temperature phase to its low-temperature one. In the high-temperature phase, the central atoms of the ZnBr_4 and NC_4 tetrahedra lie in the mirror plane of space group $Pnma$. With the loss of this mirror plane, two possibilities arise for these central atoms when crossing the transition:

(i) the four common symmetry operations of $Pnma$ and $P2_1/a$ are kept: (x, y, z) , $(\bar{x}, \bar{y}, \bar{z})$, $(\frac{1}{2} + x, y, \frac{1}{2} - z)$ and $(\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z)$;

(ii) the four non-common symmetry operations of these two space groups are kept: $(x, \frac{1}{2} - y, z)$, $(\bar{x}, \frac{1}{2} + y, \bar{z})$, $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z)$ and $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z)$.

In this second case, it is possible to find the four symmetry operations of space group $P2_1/a$ from the following relations for the coordinates (see Fig. 2):

$$\begin{aligned} x' &= -x \\ y' &= y - \frac{1}{2} \\ z' &= -z. \end{aligned}$$

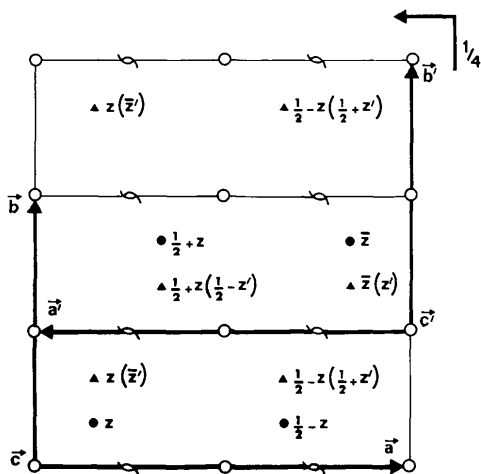


Fig. 2. The unit cell of the two domains of the low-temperature phase of TMAT BrZn. Equivalent positions for the first domain (unprimed system) are given by full circles, and for the second domain (primed system) by full triangles.

If the small $\Delta\gamma$ value of the monoclinic angle is neglected, the existence of domains requires the simultaneous measurement of hkl reflections for the first domain and $\bar{h}\bar{k}\bar{l}$ for the second. More exactly, if x represents the volume ratio of the first domain in relation to the total volume, the measured intensity can be expressed as:

$$I = xF^2(hkl) + (1 - x)F^2(\bar{h}\bar{k}\bar{l}).$$

The existence of two domains in the low-temperature phase allows explanations of the non-convergence of the fit when using *SHELX76*, of the electron density of the difference Fourier map and of the better values of the variance for $0kl$ and $h0l$ reflections. It should be noted that a value of 50% for x involves equal intensities for hkl and $\bar{h}\bar{k}\bar{l}$ reflections. In such a case the monoclinic structure resolution becomes impossible. A program has been written by the authors in order to introduce this new calculated structure factor.

Starting from the atomic parameters of the *SHELX76* refinement, several cycles using 2408 independent reflections with anisotropic thermal parameters first for heavy atoms and then for all non-hydrogen atoms brought R to the final value of 0.101 [$wR = 0.124$, $w = (\sigma^2 + 0.0002F_o^2)^{-1/2}$]; $\sum w(\Delta F)^2$ minimized; H atoms not located. Shifts in atomic parameters in final cycle $< 0.1\sigma$. Eight reflections with a high intensity and a low-angle reflection were removed because of the possibility of extinction effects. A_i , b_i and c coefficients for analytical approximation to the scattering factors for Zn, Br, N and C^{val} from *International Tables for X-ray Crystallography* (1974); anomalous-dispersion effects for heavy atoms taken into account (Cromer & Liberman, 1970).

Discussion. The final atomic coordinates are reported in Table 2,* bond lengths and angles in Table 3. An *ORTEPII* (Johnson, 1976) drawing of the structure of TMAT BrZn at 193 K is shown in Fig. 3.

The ratio x between the volume of the main domain and the whole crystal is found to be 0.719 (4). This value allows a good refinement of the monoclinic structure.

By comparison with the structure of the high-temperature phase (Trouélan *et al.*, 1984), there is a large decrease of the thermal parameters in the low-temperature phase. The equivalent isotropic thermal parameters U_{eq} are divided by factors of 2 and 3 for central and peripheral atoms of the tetrahedra respectively. In the harmonic approximation and for an ordered crystal, thermal parameters are proportional to

* Lists of structure factors and anisotropic thermal parameters and Table 1 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42020 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the temperature (Cruickshank, 1956). In this study, the temperature ratio is about $\frac{1}{2}$; the origin of the large values for the thermal parameters of the high-temperature phase is probably orientational disorder.

Table 2. Positional parameters and equivalent Debye-Waller factors ($\text{\AA}^2 \times 10^3$) of TMAT BrZn at $T = 193$ K with e.s.d.'s in parentheses

| | x | y | z | $U_{\text{eq}} = \frac{1}{3} \text{trace (U)}$ |
|-------|------------|------------|------------|--|
| Zn | 0.2507 (2) | 0.2300 (3) | 0.4067 (2) | 25 (2) |
| Br(1) | 0.0614 (2) | 0.2730 (3) | 0.4047 (2) | 34 (2) |
| Br(2) | 0.2932 (2) | 0.0115 (4) | 0.3274 (2) | 43 (2) |
| Br(3) | 0.3172 (2) | 0.2007 (4) | 0.5482 (2) | 50 (2) |
| Br(4) | 0.3346 (2) | 0.4376 (4) | 0.3423 (2) | 52 (2) |
| N(1) | 0.153 (2) | 0.261 (3) | 0.102 (2) | 37 (13) |
| C(11) | 0.268 (2) | 0.213 (4) | 0.098 (3) | 61 (21) |
| C(12) | 0.087 (3) | 0.162 (6) | 0.154 (3) | 89 (34) |
| C(13) | 0.110 (4) | 0.253 (8) | 0.012 (2) | 100 (35) |
| C(14) | 0.145 (4) | 0.420 (6) | 0.135 (5) | 123 (45) |
| N(2) | -0.010 (2) | 0.246 (3) | 0.668 (2) | 33 (14) |
| C(21) | -0.047 (3) | 0.240 (5) | 0.760 (2) | 60 (22) |
| C(22) | 0.014 (2) | 0.104 (3) | 0.636 (3) | 43 (19) |
| C(23) | -0.101 (3) | 0.315 (4) | 0.616 (3) | 59 (23) |
| C(24) | 0.082 (3) | 0.350 (5) | 0.659 (2) | 72 (27) |

Table 3. Bond lengths (\AA) and angles ($^\circ$) of TMAT BrZn at $T = 193$ K with e.s.d.'s in parentheses

| | | | |
|------------------|-----------|------------------|------------|
| Zn-Br(1) | 2.404 (6) | Zn-Br(3) | 2.399 (9) |
| Zn-Br(2) | 2.414 (9) | Zn-Br(4) | 2.400 (11) |
| N(1)-C(11) | 1.51 (7) | N(2)-C(21) | 1.53 (7) |
| N(1)-C(12) | 1.48 (12) | N(2)-C(22) | 1.42 (8) |
| N(1)-C(13) | 1.52 (9) | N(2)-C(23) | 1.54 (10) |
| N(1)-C(14) | 1.55 (12) | N(2)-C(24) | 1.51 (10) |
| Br(1)-Zn-Br(2) | 110.0 (5) | Br(2)-Zn-Br(3) | 108.4 (5) |
| Br(1)-Zn-Br(3) | 111.9 (4) | Br(2)-Zn-Br(4) | 109.9 (5) |
| Br(1)-Zn-Br(4) | 107.5 (4) | Br(3)-Zn-Br(4) | 109.2 (5) |
| C(11)-N(1)-C(12) | 112 (8) | C(21)-N(2)-C(22) | 112 (6) |
| C(11)-N(1)-C(13) | 107 (7) | C(21)-N(2)-C(23) | 107 (7) |
| C(11)-N(1)-C(14) | 111 (7) | C(21)-N(2)-C(24) | 110 (7) |
| C(12)-N(1)-C(13) | 107 (9) | C(22)-N(2)-C(23) | 110 (7) |
| C(12)-N(1)-C(14) | 111 (9) | C(22)-N(2)-C(24) | 112 (7) |
| C(13)-N(1)-C(14) | 110 (9) | C(23)-N(2)-C(24) | 105 (8) |

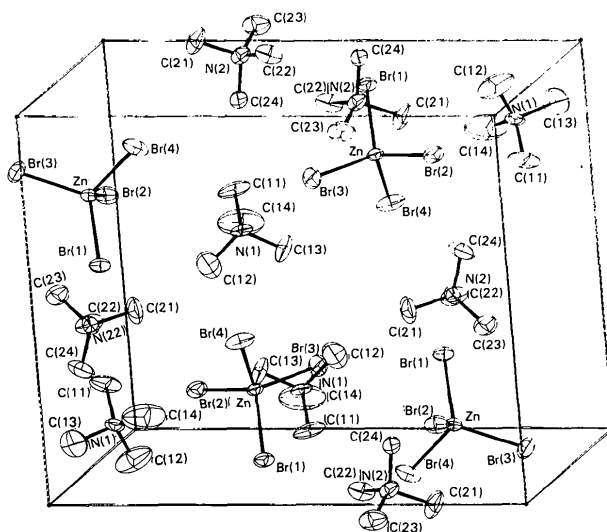


Fig. 3. ORTEP drawing of the unit-cell contents of TMAT BrZn at $T = 193$ K.

Table 4. Rigid-body vibration parameters for the heavy tetrahedron $[\text{ZnBr}_4]^{2-}$ at $T = 193$ K relative to orthogonal axes

| | | | |
|---------------------------------|---------|----------|---------|
| $T(\text{\AA}^2 \times 10^4)$ | 147 (8) | 6 (11) | 20 (10) |
| | | 337 (10) | 14 (9) |
| | | | 264 (9) |
| $L(\text{rad}^2 \times 10^4)$ | 89 (3) | -16 (6) | -10 (5) |
| | | 47 (5) | 2 (4) |
| | | | 18 (4) |
| $S(\text{\AA rad} \times 10^4)$ | 1 (5) | 0 (5) | 20 (5) |
| | -2 (4) | -5 (8) | -12 (4) |
| | -6 (5) | 10 (4) | 5 (13) |
| R.m.s. ($U^p - U^c$) | 8 | | |
| ($\text{\AA}^2 \times 10^4$) | | | |
| E.s.d. U_{ij}^p | 13 | | |
| ($\text{\AA}^2 \times 10^4$) | | | |

A rigid-body analysis (Schomaker & Trueblood, 1968) has been carried out from the calculated final U_{ij} values. Results are given for the heavy tetrahedron in Table 4. As for the U_{ij} , translational and librational vibrations decrease quite satisfactorily in comparison with those of the high-temperature phase. The librational tensor L always exhibits a significant anisotropy: L_{11} is about two and four times higher than L_{22} and L_{33} respectively.

The mean value for Zn-Br is 2.403 \AA , nearer the uncorrected high-temperature-phase value (2.394 \AA) than the corrected one (2.447 \AA) (Trouélan *et al.*, 1984). This point also confirms the existence of disorder in the high-temperature phase: the correction for thermal motion has been overestimated because of large values of the librational tensor. The $[\text{ZnBr}_4]^{2-}$ tetrahedron is slightly distorted in a flattened form with angles ranging from 107.6 to 111.9 $^\circ$. For $[\text{N}(\text{CH}_3)_4]^+$ tetrahedra, C-N-C angles range from 106 to 112 $^\circ$ with a large error bar of 8 $^\circ$ which does not allow any conclusion.

The structural result provoked by this second-order transition is the destruction of the mirror plane m_y required by the space group $Pnma$ of the high-temperature phase. Therefore, there is no longer any atom fixed by symmetry for a given molecule. If t and θ represent the global translation and rotation of tetrahedra when crossing the transition, it can be noted that only the t_y , θ^x and θ^z components have significant values. These characteristics agree with a typical T_3^+ mode (Perret *et al.*, 1983). T_y , θ^x and θ^z values for the heavy tetrahedron are -0.182 \AA , 3.4 and -7.5 $^\circ$ respectively.

The orientational disorder in the high-temperature phase of TMAT BrZn has been shown unambiguously. A redetermination of the structure taking this into account has been performed. The heavy tetrahedron has two equivalent positions symmetrically located with respect to the mirror plane of the space group $Pnma$ with a site-occupation factor of 0.5. Two attempts were made using *SHELX76* and *ORION* (Andre, Fourme & Renaud, 1971) but no satisfactory result has been obtained.

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Structures of Two 6,6-Diarylfulvene Complexes of Rhodium: (1,5-Cyclooctadiene)-(6,6-diphenylfulvene)rhodium(I) Perchlorate, $[\text{Rh}(\text{C}_8\text{H}_{12})(\text{C}_{18}\text{H}_{14})]\text{ClO}_4$, (I), and [6,6-Bis(4-chlorophenyl)fulvene]bis(triphenyl phosphite)rhodium(I) Perchlorate, $[\text{Rh}(\text{C}_{18}\text{H}_{12}\text{Cl}_2)(\text{C}_{18}\text{H}_{15}\text{O}_3\text{P})_2]\text{ClO}_4$, (II)

BY ZBIGNIEW DAUTER*

Department of Chemistry, University of York, Heslington, York YO1 5DD, England

LARS K. HANSEN

Chemistry Section, Institute of Mathematical and Physical Sciences, University of Tromsø, Box 790, 9001 Tromsø, Norway

AND ROGER J. MAWBY, E. JANE PROBITTS AND COLIN D. REYNOLDS†

Department of Chemistry, University of York, Heslington, York YO1 5DD, England

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Abstract. Complex (I): $M_r = 540.85$, monoclinic, $P2_1/n$, $a = 14.435$ (5), $b = 10.882$ (3), $c = 15.141$ (4) Å, $\beta = 104.62$ (3)°, $V = 2301.4$ Å³, $Z = 4$, $D_x = 1.561$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu(\text{Cu } K\alpha) = 7.47$ mm⁻¹, $F(000) = 1104$, $T = 290$ (1) K, $R = 0.070$ for 1826 observed reflections. The Rh is coordinated to all five C atoms in the fulvene ring, with Rh–C distances varying between 2.180 (11) and 2.295 (12) Å, and to the four olefinic C atoms in the

1,5-cyclooctadiene, with Rh–C distances in the range 2.145 (14)–2.183 (14) Å. Complex (II): $M_r = 1122.19$, triclinic, $P\bar{1}$, $a = 11.537$ (2), $b = 12.276$ (2), $c = 20.135$ (2) Å, $\alpha = 75.83$ (1), $\beta = 76.72$ (1), $\gamma = 65.44$ (1)°, $V = 2488.15$ Å³, $Z = 2$, $D_x = 1.498$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 0.620$ mm⁻¹, $F(000) = 1144$, $T = 290$ (1) K, $R = 0.031$ for 9098 observed reflections. Again the Rh is coordinated to all five fulvene-ring C atoms, with Rh–C distances between 2.224 (2) and 2.412 (2) Å. The Rh–P distances are 2.226 (1) and 2.203 (1) Å. In each complex the exocyclic C atom in the fulvene ligand is bent away from the metal [by 4.4 and 8.8° in (I) and (II) respectively].

* Permanent address: Department of Biochemistry, Technical University of Gdansk, Gdansk, Poland.

† Present address: Biophysics Laboratory, Department of Physics, Liverpool Polytechnic, Byrom Street, Liverpool L3 3AF, England.