

A low-temperature phase of bis(tetra-butylammonium) octa- μ_3 -chlorido-hexachlorido-octahedro-hexa-tungstate

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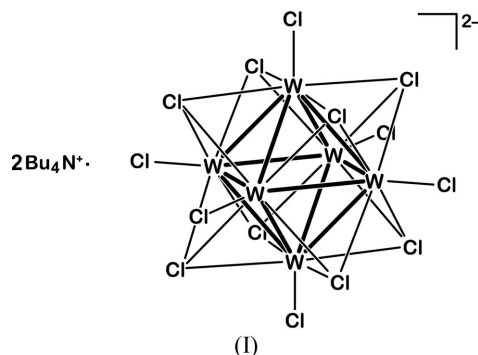
The title compound, $(C_{16}H_{36}N)_2[W_6Cl_{14}]$, undergoes a reversible phase transition at 268 (1) K. The structure at 150 and 200 K has monoclinic ($P2_1/c$) symmetry. Both crystallographically independent tungsten chloride cluster anions sit on crystallographic inversion centers [symmetry codes: $(-x, -y + 1, -z)$ and $(-x + 1, -y + 2, -z)$]. Two previous studies at room temperature describe the structure in the space group $P2_1/n$ with a unit-cell volume approximately half the size of the low-temperature unit cell [Zietlow, Schaefer *et al.* (1986). *Inorg. Chem.* **25**, 2195–2198; Venkataraman *et al.* (1999). *Inorg. Chem.* **38**, 828–830]. The unit cells of the room- and low-temperature polymorphs are closely related. The hydrocarbon chain of one of the tetrabutylammonium cations is disordered at both 150 and 200 K.

Comment

The lower halides of tungsten, including tungsten(II) chloride, have been known for over 100 years (Kepert & Vrieze, 1967; Prokopuk & Shriver, 1999) and numerous methods for their synthesis have been developed (Hogue & McCarley, 1970; Dorman & McCarley, 1974; Kolesnichenko & Messerle, 1998; Ströbele *et al.*, 2009). The structure of the $[(W_6Cl_8)Cl_6]^{2-}$ anion was first determined by Zietlow, Schaefer *et al.* (1986) at room temperature. A subsequent structure determination of the same form was published by Venkataraman *et al.* (1999). The tungsten(II) halide clusters have been intensely studied because of their fascinating photochemical and electrochemical properties (Maverick *et al.*, 1983; Nocera & Gray, 1984; Zietlow *et al.*, 1985; Zietlow, Nocera *et al.*, 1986; Jackson *et al.*, 1990; Mussell & Nocera, 1990; Arratia-Pérez & Hernández-Acevedo, 1997; Gray, 2009).

At low temperature, the two independent $[(W_6Cl_8)Cl_6]^{2-}$ cluster units (Fig. 1) sit on crystallographic inversion centers

and have bond lengths and bond angles comparable to those of previously determined structures (Zietlow, Schaefer *et al.*, 1986; Venkataraman *et al.*, 1999). One hydrocarbon chain of one of the two tetrabutylammonium cations (Fig. 1) is disordered and was modeled with two sites each for three different C atoms. A packing diagram is shown in Fig. 2.



There is a close relationship between the unit cell of the herein reported low-temperature (150 and 200 K) structures and that of the previously determined room-temperature structures. The cell dimensions of the room-temperature unit cell are $a = 18.512 \text{ \AA}$, $b = 11.661 \text{ \AA}$, $c = 12.789 \text{ \AA}$, $\alpha = 90^\circ$, $\beta =$

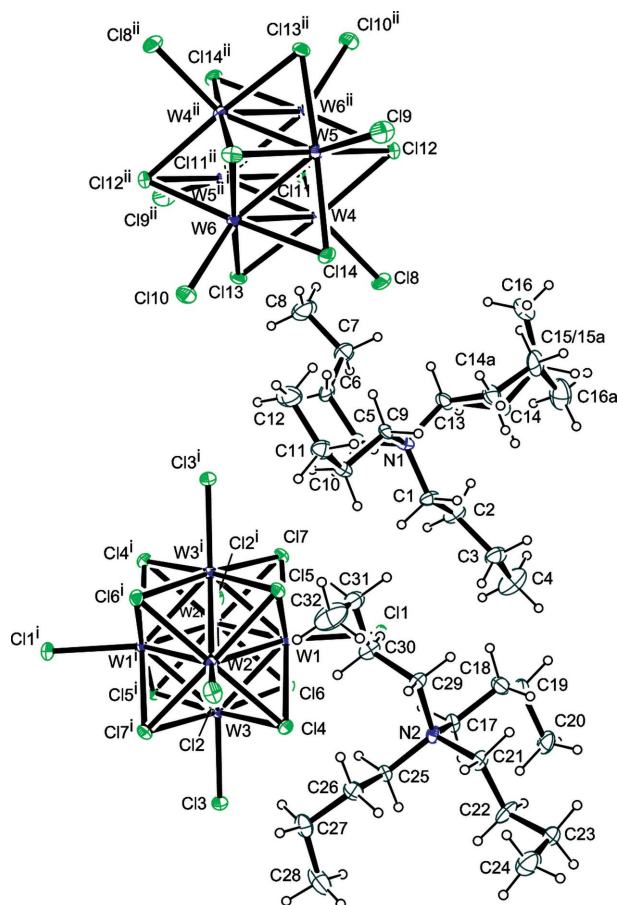


Figure 1
Displacement ellipsoid (50% probability level) drawing of the two individual tungsten cluster anions and the two tetrabutylammonium cations in the asymmetric unit for the 150 K structure, showing the atom-numbering scheme. [Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $-x + 1, -y + 2, -z$.]

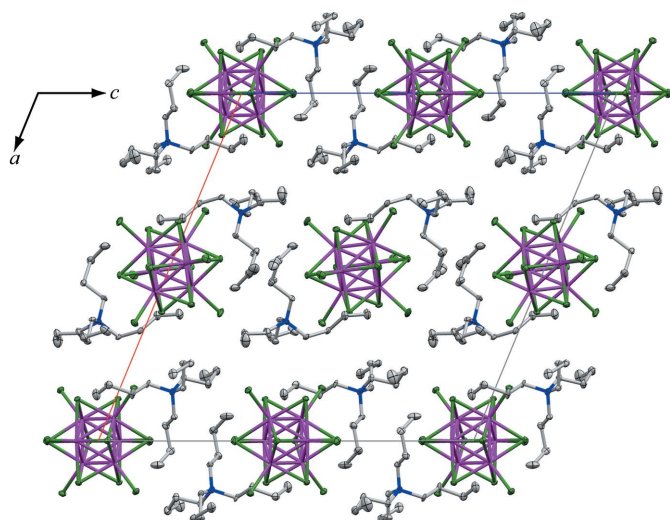


Figure 2
Displacement ellipsoid (50% probability level) drawing of the contents of the unit cell along the *b* axis for the 150 K structure. H atoms and the minor component of the disorder have been omitted for clarity.

90.17° and $\gamma = 90^\circ$ (Zietlow, Schaefer *et al.*, 1986), while at 150 K the unit cell is $a = 22.3152(2)$ Å, $b = 11.7220(1)$ Å, $c = 22.2786(1)$ Å, $\alpha = 90^\circ$, $\beta = 112.451(1)^\circ$ and $\gamma = 90^\circ$. Application of the transformation matrix $\begin{bmatrix} 1/2 & 0 & 1/2 \\ 0 & 1/2 & 0 \\ 1 & 0 & 1/2 \end{bmatrix}$ to the unit cell of the low-temperature form produces the following unit cell, which is approximately identical to the room-temperature cell: $a = 18.534$ Å, $b = 11.722$ Å, $c = 12.395$ Å, $\alpha = 90^\circ$, $\beta = 89.90^\circ$ and $\gamma = 90^\circ$. An overlay of the two unit cells is shown in Fig. 3 (r.m.s. overlay = 0.177 Å for 122 non-H atoms). This transformation is possible because the low-temperature unit cell shows higher metric symmetry, namely the *a* and *c* axes are approximately equal. This allows for a pseudo-orthorhombic C-centered cell to be generated using the transformation matrix $\begin{bmatrix} 1 & 0 & 1/2 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$. The room-temperature cell can be generated from this pseudo-orthorhombic cell by dividing the *a* and *b* axes by two, followed by a rearrangement of the axes.

The relationship between the unit cells was not noticed until after the data collection when the crystal had already been removed from the diffractometer. At a later point, a new crystal of the same sample was mounted on the diffractometer at 150 K and a preliminary unit-cell determination agreed with the cell at 200 K from the data-collection crystal. Then the temperature was raised to 200 K and the unit cell was determined again and it was essentially the same cell. Finally, the temperature was increased to room temperature (293 K) and the unit cell changed to become the room-temperature cell reported in the literature.

A further study was undertaken to determine the phase-transition temperature. A new crystal of the title compound was mounted on a Rigaku SCXmini small-molecule X-ray crystallography system equipped with a Rigaku TEC-50 low-temperature device. The temperature at the sample was verified using a calibrated thermocouple. The previously determined unit cells were confirmed at room temperature and at 223 K. Repeated indexing of the crystal at successively

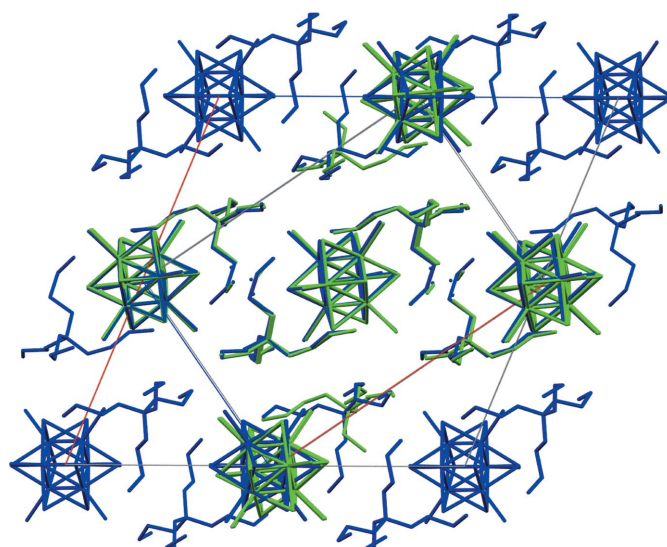


Figure 3
Overlay diagram showing the packing similarity between the current 150 K structure (blue in the electronic version of the paper) and the previously determined room-temperature structure (green), together with both unit cells, as well as the unit cell derived from the low-temperature cell by application of the transformation matrix $\begin{bmatrix} 1/2 & 0 & 1/2 \\ 0 & 1/2 & 0 \\ 1 & 0 & 1/2 \end{bmatrix}$. H atoms and atoms of the minor component of the disorder were not included in the overlay analysis and have been omitted from this figure.

higher temperatures demonstrated that the crystal undergoes a reversible phase transition between 267 and 269 K. This result was reproduced using a different crystal of the same compound.

A search of the Cambridge Structural Database (CSD; Version 5.31; Allen, 2002) revealed that the smaller $P2_1/n$ unit cell observed for the room-temperature structure is common to a range of tetrabutylammonium salts of metal-halide and metal-chalcogenide cluster dianions. Examples include molybdenum halide clusters (Preetz *et al.*, 1992, 1994; Kirakci *et al.*, 2005), molybdenum chalcogenide/halide clusters (Ebihara *et al.*, 1992), tungsten halide clusters (Zietlow, Schaefer *et al.*, 1986; Venkataraman *et al.*, 1999) and rhenium chalcogenide/halide clusters (Gabriel *et al.*, 1993; Uriel *et al.*, 1995, 1996, 2001). Only two examples were found with the same larger $P2_1/c$ unit cell as the low-temperature phase of the title compound: the $[(Os_2Re_4Se_8)Cl_6]^{2-}$ dianion structure determined at 153 K by Tulsy & Long (2001) and the $[(Re_6Se_5Cl_2N-TMS)Cl_6]^{2-}$ (TMS is trimethylsilyl) anion structure determined at room temperature by Uriel *et al.* (1996).

Among these examples, only one structure was found that potentially undergoes a similar phase change. The $[(Re_6Se_6Cl_2)Cl_6]^{2-}$ dianion structure was determined in a tetragonal setting (space group $I4/mmm$; Yaghi *et al.*, 1992) at 198 K, while two other structure determinations of the same compound at room temperature (Uriel *et al.*, 1995, 2001) display the $P2_1/n$ unit cell found for the room-temperature structure of the title compound and many other structures. The analogous $[(Mo_6Br_8)Br_6]^{2-}$ dianion structure, however, has been determined at 100 K and room temperature (Kirakci *et al.*, 2005) and in both cases the $P2_1/n$ unit cell was found.

Experimental

The tungsten(II) chloride cluster was prepared *via* the reduction of tungsten(VI) chloride with bismuth according to published procedures (Kolesnichenko & Messerle, 1998). The hydronium salt was converted to the tetrabutylammonium salt by metathesis with tetrabutylammonium chloride in ethanol solution. The crude product was recrystallized by slow evaporation from an acetone solution. Crystals suitable for X-ray analysis were grown by slow diffusion of diethyl ether into a solution of (I) in dichloromethane.

Compound (I) at 150 K

Crystal data

| | |
|---------------------------------|---|
| $(C_{16}H_{36}N)_2[W_6Cl_{14}]$ | $V = 5387.31 (7) \text{ \AA}^3$ |
| $M_r = 2084.32$ | $Z = 4$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation |
| $a = 22.3152 (2) \text{ \AA}$ | $\mu = 13.48 \text{ mm}^{-1}$ |
| $b = 11.7220 (1) \text{ \AA}$ | $T = 150 \text{ K}$ |
| $c = 22.2786 (1) \text{ \AA}$ | $0.31 \times 0.27 \times 0.23 \text{ mm}$ |
| $\beta = 112.415 (1)^\circ$ | |

Data collection

| | |
|---|--|
| Nonius KappaCCD diffractometer | 137050 measured reflections |
| Absorption correction: multi-scan (SADABS; Bruker, 2008) | 12352 independent reflections |
| $T_{\min} = 0.484$, $T_{\max} = 0.746$ | 9499 reflections with $I > 2\sigma(I)$ |
| | $R_{\text{int}} = 0.086$ |

Refinement

| | |
|---------------------------------|--|
| $R[F^2 > 2\sigma(F^2)] = 0.031$ | 148 restraints |
| $wR(F^2) = 0.054$ | H-atom parameters constrained |
| $S = 1.07$ | $\Delta\rho_{\max} = 1.20 \text{ e \AA}^{-3}$ |
| 12352 reflections | $\Delta\rho_{\min} = -1.69 \text{ e \AA}^{-3}$ |
| 515 parameters | |

Compound (I) at 200 K

Crystal data

| | |
|---------------------------------|---|
| $(C_{16}H_{36}N)_2[W_6Cl_{14}]$ | $V = 5429.13 (8) \text{ \AA}^3$ |
| $M_r = 2084.32$ | $Z = 4$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation |
| $a = 22.3689 (2) \text{ \AA}$ | $\mu = 13.38 \text{ mm}^{-1}$ |
| $b = 11.7596 (1) \text{ \AA}$ | $T = 200 \text{ K}$ |
| $c = 22.3108 (2) \text{ \AA}$ | $0.27 \times 0.19 \times 0.19 \text{ mm}$ |
| $\beta = 112.320 (1)^\circ$ | |

Data collection

| | |
|---|--|
| Nonius KappaCCD diffractometer | 101212 measured reflections |
| Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997) | 12422 independent reflections |
| $T_{\min} = 0.055$, $T_{\max} = 0.079$ | 9227 reflections with $I > 2\sigma(I)$ |
| | $R_{\text{int}} = 0.063$ |

Refinement

| | |
|---------------------------------|--|
| $R[F^2 > 2\sigma(F^2)] = 0.031$ | 148 restraints |
| $wR(F^2) = 0.064$ | H-atom parameters constrained |
| $S = 1.03$ | $\Delta\rho_{\max} = 2.36 \text{ e \AA}^{-3}$ |
| 12422 reflections | $\Delta\rho_{\min} = -2.11 \text{ e \AA}^{-3}$ |
| 515 parameters | |

The asymmetric unit of (I) at both temperatures consists of two tetrabutylammonium cations and two half-octahedra of the $[W_6Cl_{14}]^{2-}$ cluster anion, with each octahedron containing a crystallographic inversion center.

Not surprisingly, the two low-temperature structures, determined at 150 and 200 K, are essentially identical. In both cases, one of the

Table 1

Selected bond lengths (\AA) for (I) at 150 K.

| | | | |
|---------------------|-------------|-----------------------|-------------|
| W1—W2 | 2.6048 (3) | W4—W5 | 2.6092 (3) |
| W1—W2 ⁱ | 2.6212 (3) | W4—W5 ⁱⁱ | 2.6127 (3) |
| W1—W3 | 2.6163 (3) | W4—W6 | 2.6133 (3) |
| W1—W3 ⁱ | 2.6091 (3) | W4—W6 ⁱⁱ | 2.6143 (3) |
| W2—W3 | 2.6120 (3) | W5—W6 | 2.6152 (3) |
| W2—W3 ⁱ | 2.6207 (3) | W5—W6 ⁱⁱ | 2.6071 (3) |
| W1—Cl1 | 2.4181 (13) | W4—Cl8 | 2.4243 (14) |
| W2—Cl2 | 2.4292 (13) | W5—Cl9 | 2.4187 (13) |
| W3—Cl3 | 2.4310 (13) | W6—Cl10 | 2.4328 (13) |
| W1—Cl4 | 2.5037 (12) | W4—Cl11 | 2.4941 (13) |
| W1—Cl5 | 2.5028 (13) | W4—Cl12 | 2.4926 (13) |
| W1—Cl6 | 2.4968 (13) | W4—Cl13 | 2.5034 (12) |
| W1—Cl7 | 2.4934 (12) | W4—Cl14 | 2.4979 (13) |
| W2—Cl4 | 2.5044 (13) | W5—Cl11 ⁱⁱ | 2.4969 (14) |
| W2—Cl5 | 2.4927 (12) | W5—Cl12 | 2.5044 (14) |
| W2—Cl6 ⁱ | 2.4919 (13) | W5—Cl13 ⁱⁱ | 2.4954 (13) |
| W2—Cl7 ⁱ | 2.4987 (12) | W5—Cl14 | 2.4974 (13) |
| W3—Cl4 | 2.4977 (13) | W6—Cl11 ⁱⁱ | 2.4972 (13) |
| W3—Cl5 ⁱ | 2.4856 (12) | W6—Cl12 ⁱⁱ | 2.4978 (13) |
| W3—Cl6 | 2.5090 (13) | W6—Cl13 | 2.5062 (14) |
| W3—Cl7 ⁱ | 2.5055 (13) | W6—Cl14 | 2.4844 (13) |

Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $-x + 1, -y + 2, -z$.

Table 2

Selected bond lengths (\AA) for (I) at 200 K.

| | | | |
|---------------------|-------------|-----------------------|-------------|
| W1—W2 | 2.6056 (3) | W4—W5 | 2.6113 (3) |
| W1—W2 ⁱ | 2.6228 (3) | W4—W5 ⁱⁱ | 2.6157 (3) |
| W1—W3 | 2.6191 (3) | W4—W6 | 2.6169 (3) |
| W1—W3 ⁱ | 2.6101 (3) | W4—W6 ⁱⁱ | 2.6170 (3) |
| W2—W3 | 2.6131 (3) | W5—W6 | 2.6186 (3) |
| W2—W3 ⁱ | 2.6239 (3) | W5—W6 ⁱⁱ | 2.6096 (3) |
| W1—Cl1 | 2.4177 (14) | W4—Cl8 | 2.4187 (16) |
| W2—Cl2 | 2.4289 (14) | W5—Cl9 | 2.4173 (14) |
| W3—Cl3 | 2.4285 (14) | W6—Cl10 | 2.4297 (15) |
| W1—Cl4 | 2.5012 (14) | W4—Cl11 | 2.4928 (14) |
| W1—Cl5 | 2.4961 (14) | W4—Cl12 | 2.4903 (14) |
| W1—Cl6 | 2.4980 (15) | W4—Cl13 | 2.5029 (14) |
| W1—Cl7 | 2.4962 (14) | W4—Cl14 | 2.4965 (14) |
| W2—Cl4 | 2.5067 (14) | W5—Cl11 ⁱⁱ | 2.5003 (16) |
| W2—Cl5 | 2.4905 (14) | W5—Cl12 | 2.5033 (15) |
| W2—Cl6 ⁱ | 2.4864 (14) | W5—Cl13 ⁱⁱ | 2.4932 (14) |
| W2—Cl7 ⁱ | 2.4967 (13) | W5—Cl14 | 2.4967 (14) |
| W3—Cl4 | 2.4965 (13) | W6—Cl11 ⁱⁱ | 2.4964 (15) |
| W3—Cl5 ⁱ | 2.4888 (13) | W6—Cl12 ⁱⁱ | 2.4936 (13) |
| W3—Cl6 | 2.5088 (15) | W6—Cl13 | 2.5046 (14) |
| W3—Cl7 ⁱ | 2.5020 (14) | W6—Cl14 | 2.4836 (13) |

Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $-x + 1, -y + 2, -z$.

hydrocarbon chains was found to be disordered and was modeled with two sites for each of the last three C atoms of the *n*-butyl chain. The occupancies of the two disorder components were refined freely and converged at 0.555 (11) for the 200 K structure and at 0.616 (10) for the 150 K structure; the sum of the site-occupancy factors for each disorder was constrained to unity. The major component of the disordered chain contains atoms C14, C15 and C16, while the minor component consists of atoms C14A, C15A and C16A.

Similarity restraints on 1–2 and 1–3 distances (standard uncertainties = 0.02 and 0.04 \AA , respectively) were used to geometrically relate the two components of the disordered *n*-butyl chain to one another and also to the remaining three butyl chains of the first tetrabutylammonium ion. In addition, similarity restraints on displacement parameters (standard uncertainty = 0.04 \AA^2 , or 0.08 \AA^2 for terminal atoms), as well as rigid-bond restraints for anisotropic displacement parameters (standard uncertainty = 0.01 \AA^2), were applied to all disordered atoms as well as to C13.

The top four peaks in the final difference electron-density map range from 1.09 to 1.20 e Å⁻³ (150 K data) and from 1.62 to 2.35 e Å⁻³ (200 K data). All of these peaks are located within 1.5 Å of a W atom and are presumably Fourier truncation artifacts due to the presence of multiple heavy atoms.

For both compounds, data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997), *Mercury* (Macrae *et al.*, 2008) and *POV-RAY* (Cason, 2004); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MX3029). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Arratia-Pérez, R. & Hernández-Acevedo, L. (1997). *Chem. Phys. Lett.* **277**, 223–226.
- Bruker (2008). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cason, C. J. (2004). *POV-RAY*. Version 3.6. Persistence of Vision Raytracer Pty Ltd, Williamstown, Victoria, Australia.
- Dorman, W. C. & McCarley, R. E. (1974). *Inorg. Chem.* **13**, 491–493.
- Ebihara, M., Isobe, K., Sasaki, Y. & Saito, K. (1992). *Inorg. Chem.* **31**, 1644–1649.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Gabriel, J. C., Boubekeur, K. & Batail, P. (1993). *Inorg. Chem.* **32**, 2894–2900.
- Gray, T. G. (2009). *Chem. Eur. J.* **15**, 2581–2593.
- Hogue, R. D. & McCarley, R. E. (1970). *Inorg. Chem.* **9**, 1354–1360.
- Jackson, J. A., Turró, C., Newsham, M. D. & Nocera, D. G. (1990). *J. Phys. Chem.* **94**, 4500–4507.
- Keper, D. L. & Vrieze, K. (1967). *Halogen Chem.* **3**, 1–54.
- Kirakci, K., Cordier, S., Roisnel, T., Golhen, S. & Perrin, C. (2005). *Z. Kristallogr. New Cryst. Struct.* **220**, 116–118.
- Kolesnichenko, V. & Messerle, L. (1998). *Inorg. Chem.* **37**, 3660–3663.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Maverick, A. W., Najdzionek, J. S., MacKenzie, D., Nocera, D. G. & Gray, H. B. (1983). *J. Am. Chem. Soc.* **105**, 1878–1882.
- Mussell, R. D. & Nocera, D. G. (1990). *Inorg. Chem.* **29**, 3711–3717.
- Nocera, D. G. & Gray, H. B. (1984). *J. Am. Chem. Soc.* **106**, 824–825.
- Nonius (2000). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Preetz, W., Bublitz, D., von Schnering, H. G. & Sassmanhausen, J. (1994). *Z. Anorg. Allg. Chem.* **620**, 234–246.
- Preetz, W., Harder, K., von Schnering, H. G., Kliche, G. & Peters, K. (1992). *J. Alloys Comp.* **183**, 413–429.
- Prokopuk, N. & Shriver, D. F. (1999). *Adv. Inorg. Chem.* **46**, 1–49.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Ströbele, M., Jüstel, T., Bettentrup, H. & Meyer, H.-J. (2009). *Z. Anorg. Allg. Chem.* **635**, 822–827.
- Tulsky, E. G. & Long, J. R. (2001). *Inorg. Chem.* **40**, 6990–7002.
- Uriel, S., Boubekeur, K., Batail, P. & Orduna, J. (1996). *Angew. Chem. Int. Ed. Engl.* **35**, 1544–1547.
- Uriel, S., Boubekeur, K., Batail, P., Orduna, J. & Canadell, E. (1995). *Inorg. Chem.* **34**, 5307–5313.
- Uriel, S., Boubekeur, K., Batail, P., Orduna, J. & Perrin, A. (2001). *New J. Chem.* **25**, 737–740.
- Venkataraman, D., Rayburn, L. L., Hill, L. I., Jin, S., Malik, A.-S., Turneau, K. J. & DiSalvo, F. J. (1999). *Inorg. Chem.* **38**, 828–830.
- Yaghi, O. M., Scott, M. J. & Holm, R. H. (1992). *Inorg. Chem.* **31**, 4778–4784.
- Zietlow, T. C., Hopkins, M. D. & Gray, H. B. (1985). *J. Solid State Chem.* **57**, 112–119.
- Zietlow, T. C., Nocera, D. G. & Gray, H. B. (1986). *Inorg. Chem.* **25**, 1351–1353.
- Zietlow, T. C., Schaefer, W. P., Sadeghi, B., Hua, N. & Gray, H. B. (1986). *Inorg. Chem.* **25**, 2195–2198.