

mixed-valence compound  $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\text{ClO}_4)_4$  (Kida, 1965). In this case, the Cl atom is expected to be loosely bonded to the Pt atom; the Pt—Cl bond as well as the thermal parameter of the Cl atom, however, is quite normal, and shows no such indication. The compound  $[\text{Pt}(\text{en})_2]\text{Cl}_2$  which takes the *meso* form for the ring conformation is colourless (Sato, Haruki & Kurita, 1990). In the compound  $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\text{ClO}_4)_4$ , the conformation is not *meso* but  $\delta\delta$  [Matsumoto, Yamashita, Ueda & Kida (1978); the absolute configuration has not been determined]. The structure of the present compound differs greatly from that of the undoped crystal. Further investigations are necessary to clarify the changes that arise in the structure.

#### References

BAERISWYL, D. & BISHOP, A. R. (1987). *Phys. Ser.* **T19**, 239–245.

COPPENS, P., GURU ROW, T. N., LEUNG, P., STEVENS, E. D., BECKER, P. J. & YANG, Y. W. (1979). *Acta Cryst.* **A35**, 63–72.  
 DONOHUE, R. J., EKBERG, S. A., TAIT, C. D. & SWANSON, B. I. (1989). *Solid State Commun.* **71**, 49–52.  
 HARUKI, M. & KURITA, S. (1989). *Phys. Rev. B*, **37**, 5706–5712.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham, Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)  
 JOHNSON, C. K. (1971). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.  
 KIDA, S. (1965). *Bull. Chem. Soc. Jpn*, **38**, 1804.  
 KURITA, S. & HARUKI, M. (1989). *Synth. Met.* **29**, F129–F136.  
 KURITA, S., HARUKI, M. & MIYAGAWA, M. (1988). *J. Phys. Soc. Jpn*, **57**, 1789–1796.  
 KURODA, N., SAKAI, M., NISHINA, Y., TANAKA, M. & KURITA, S. (1987). *Phys. Rev. Lett.* **58**, 2122–2125.  
 MATSUMOTO, N., YAMASHITA, M., UEDA, I. & KIDA, S. (1978). *Mem. Fac. Sci. Kyushu Univ. Ser. C*, **11**, 209–216.  
 ONODERA, Y. (1987). *J. Phys. Soc. Jpn*, **56**, 250–254.  
 SAKURAI, T. (1987). Editor. *Universal Crystallographic Computation Program System*. The Crystallographic Society of Japan, Tokyo, Japan.  
 SATO, S., HARUKI, M. & KURITA, S. (1990). *Acta Cryst.* **C46**, 1107–1108.

*Acta Cryst.* (1990). **C46**, 1815–1818

## Two Dimolybdenum Tetracarboxylato Compounds from Heteroaromatic Acids, 2-Thiophenecarboxylate and Nicotinic Acid

BY F. ALBERT COTTON,\* LARRY R. FALVELLO, AUSTIN H. REID JR AND WIESLAW J. ROTH

*Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, TX 77843, USA*

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**Abstract.** Bis(tetrahydrofuran)tetra- $\mu$ -2-thiophenecarboxylato-(*O,O'*)-dimolybdenum(II) (1),  $[\text{Mo}_2(\text{C}_5\text{H}_3\text{O}_2\text{S})_4(\text{C}_4\text{H}_8\text{O})_2]$ ,  $M_r = 816.44$ , monoclinic,  $P2_1/n$ ,  $a = 10.274$  (1),  $b = 9.990$  (1),  $c = 15.904$  (3) Å,  $\beta = 90.60$  (2)°,  $V = 1632$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.66$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 5.87$  cm<sup>-1</sup>,  $F(000) = 404$ ,  $T = 293$  K,  $R = 0.0336$  for 1310 observed reflections. The centrosymmetric molecule has Mo—Mo = 2.102 (1), mean Mo—O(carbox) = 2.107 (3), and Mo—O(THF) = 2.593 (5) Å. Dichlorotetra- $\mu$ -nicotinato-(*O,O'*)-dimolybdate(II) dichloride hexahydrate (2),  $[\text{Mo}_2(\text{Cl})_2(\text{C}_6\text{H}_4\text{NO}_2)_4]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ ,  $M_r = 934.23$ , monoclinic,  $P2_1/c$ ,  $a = 10.154$  (1),  $b = 17.681$  (4),  $c = 9.825$  (2) Å,  $\beta = 91.42$  (2)°,  $V = 1763$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.759$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 5.55$  cm<sup>-1</sup>,  $F(000) = 454$ ,  $T = 293$  K,  $R = 0.0245$  for 2604 observed reflections. The centrosymmetric molecule has Mo—Mo = 2.122 (1), mean Mo—O(carbox) =

2.113 (4) and Mo—Cl = 2.835 (1) Å. All pyridyl N atoms are protonated and there is an extensive series of hydrogen bonds.

**Introduction.** Many  $\text{Mo}_2(\text{O}_2\text{CR})_4$  compounds have been structurally characterized, but nearly all have contained non-aromatic *R* groups; the only exceptions are  $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$  and its diglyme adduct (Cotton & Walton, 1982). Questions concerning the chemistry and spectroscopy of  $\text{Mo}_2(\text{O}_2\text{CR})_4$  compounds generated interest in the structures and other properties of those with heteroaromatic *R* groups. The structures of two such compounds have been determined and are reported here.

**Experimental.** To prepare (1),  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  (0.10 g) was added to a solution of 2-thiophenecarboxylic acid (0.149 g) in 25 ml of THF under argon with stirring. The slurry, initially yellow, became bright orange over 5 min. The orange solid was collected by filtration, washed with THF and

\* Author to whom correspondence should be addressed.

Table 1. *Crystallographic data for*  
[Mo<sub>2</sub>(C<sub>5</sub>H<sub>3</sub>O<sub>2</sub>S)<sub>4</sub>(C<sub>4</sub>H<sub>8</sub>O)<sub>2</sub>], (1), and  
[Mo<sub>2</sub>(Cl)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)<sub>4</sub>]Cl<sub>2</sub>·6H<sub>2</sub>O, (2)

|  | (1)  | (2)   |
|--|--|---|
| Systematic absences  | 0k0, $k \neq 2n$ ;<br>$h0l$ , $h + l \neq 2n$                  | 0k0, $k \neq 2n$ ;<br>$h0l$ , $l \neq 2n$                         |
| Crystal size (mm)  | 0.15 × 0.25 × 0.25   | 0.35 × 0.30 × 0.20  |
| Orientation reflections,<br>number, range (2θ°)            | 25, 25–50  | 25, 16–45   |
| Scan method  | $\omega$ -2θ   | $\omega$ -2θ  |
| Data col. range (2θ°)                                      | 2–55   | 2–50  |
| Range of $hkl$   | $-6 \leq h \leq 6$<br>$0 \leq k \leq 10$<br>$0 \leq l \leq 17$ | $-12 \leq h \leq 12$<br>$-20 \leq k \leq 0$<br>$0 \leq l \leq 11$ |
| No. of unique data, total<br>with $F_o^2 > 3\sigma(F_o^2)$ | 1472<br>1310   | 2778<br>2604  |
| No. of parameters refined                                  | 201  | 257   |
| Refinement on  | $F$  | $F$   |
| $R$  | 0.0336   | 0.0245  |
| $wR^*$   | 0.0481   | 0.0340  |
| Quality-of-fit indicator:                                  | 1.253  | 1.077   |
| $g$  | 0.001  | 0.0025  |
| Largest shift/e.s.d., final cycle                          | 0.06   | 0.02  |
| Largest peak (e Å <sup>-3</sup> )                          | 0.36, -0.31  | 0.37, -0.54   |

$$*w = 1/[\sigma^2(F_o) + g(F_o)^2].$$

Table 2. *Positional parameters and equivalent isotropic displacement parameters (Å<sup>2</sup>) and their e.s.d.'s for* [Mo<sub>2</sub>(C<sub>5</sub>H<sub>3</sub>O<sub>2</sub>S)<sub>4</sub>(C<sub>4</sub>H<sub>8</sub>O)<sub>2</sub>], (1)

$$B_{eq} = (1/3) \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j.$$

|         | x            | y           | z           | B <sub>eq</sub> (Å <sup>2</sup> ) |
|---------|--------------|-------------|-------------|-----------------------------------|
| Mo(1)   | -0.00930 (6) | 0.04865 (5) | 0.05822 (3) | 2.79 (2)                          |
| O(17)   | -0.0603 (6)  | 0.1282 (6)  | 0.2096 (3)  | 6.0 (2)                           |
| O(1)    | -0.0684 (5)  | 0.2294 (4)  | 0.0002 (2)  | 3.2 (1)                           |
| O(2)    | 0.0522 (5)   | -0.1240 (4) | 0.1228 (3)  | 3.5 (1)                           |
| O(3)    | 0.1835 (5)   | 0.1203 (4)  | 0.0558 (3)  | 3.2 (1)                           |
| O(4)    | -0.2028 (5)  | -0.0187 (4) | 0.0678 (3)  | 3.3 (1)                           |
| C,S(1)* | -0.1450 (4)  | 0.3502 (3)  | -0.2233 (2) | 5.3 (1)                           |
| C(1)    | -0.0756 (7)  | 0.2284 (6)  | -0.0798 (4) | 3.2 (2)                           |
| C(2)    | -0.1105 (7)  | 0.3511 (6)  | -0.1251 (4) | 3.1 (2)                           |
| S,C(3)† | -0.1247 (4)  | 0.4971 (3)  | -0.0788 (2) | 5.4 (1)                           |
| C(4)    | -0.167 (1)   | 0.5762 (8)  | -0.1633 (6) | 6.1 (3)                           |
| C(5)    | -0.1751 (9)  | 0.5018 (8)  | -0.2325 (5) | 5.4 (3)                           |
| S,C(2)‡ | 0.4434 (3)   | 0.2546 (3)  | 0.0541 (1)  | 5.53 (8)                          |
| C(6)    | 0.2508 (9)   | 0.0932 (6)  | -0.0094 (4) | 3.5 (2)                           |
| C(7)    | 0.3812 (8)   | 0.1450 (7)  | -0.0175 (4) | 3.1 (2)                           |
| C,S(8)§ | 0.4664 (7)   | 0.1128 (7)  | -0.0844 (5) | 5.0 (2)                           |
| C(9)    | 0.589 (1)    | 0.1873 (9)  | -0.0690 (5) | 5.3 (3)                           |
| C(10)   | 0.5858 (9)   | 0.2660 (9)  | 0.0025 (5)  | 5.9 (3)                           |
| C(17)   | -0.063 (1)   | 0.041 (1)   | 0.2811 (7)  | 9.8 (4)                           |
| C(27)   | -0.183 (2)   | 0.068 (1)   | 0.327 (1)   | 12.3 (6)                          |
| C(37)   | -0.261 (1)   | 0.160 (2)   | 0.279 (1)   | 12.4 (6)                          |
| C(47)   | -0.164 (1)   | 0.224 (1)   | 0.2166 (7)  | 9.3 (4)                           |

\*Scatterer at C,S(1) modeled as 0.583 (8)C + 0.417 (8)S.

†Scatterer at S,C(3) modeled as 0.583 (8)S + 0.417 (8)C.

‡S,C(2) modeled as 0.898 (8)S + 0.102 (8)C.

§C,S(8) modeled as 0.898 (8)C + 0.102 (8)S.

vacuum dried to yield 0.19 g (> 95%) of product. X-ray-quality crystals of (1) were grown by slow diffusion of a layer of hexane into a THF solution. The nicotinate (2) was prepared by dissolving (pyH)<sub>3</sub>Mo<sub>2</sub>Cl<sub>8</sub>H (0.15 g) (pyH = C<sub>5</sub>H<sub>6</sub>N) in 25 ml of oxygen-free conc. HCl, followed by addition of nicotinic acid (0.20 g). Upon heating, the color changed from black to green to brown and finally to dark red. The solution was reduced in volume to ca

3 ml, warmed on a water bath and then slowly cooled. The yield of red-green dichroic crystals was ca 0.10 g.

Crystal parameters and information relating to data collection and structure refinement are summarized in Table 1. An Enraf-Nonius CAD-4 instrument employing graphite-monochromated Mo  $K\alpha$  radiation was employed in both cases. Structures solved by direct methods. The program *SHELX76* (Sheldrick, 1976) and the package *SDP* (B. A. Frenz & Associates, Inc., 1981) were used for all calculations. Scattering factors were from Cromer (1974), Cromer & Mann (1968), and Cromer & Waber (1974). No absorption corrections were made.\*

**Discussion.** Although the crystal of compound (1) was not a strong scatterer, sufficient data were obtained in order to conduct a full, convergent refinement with a data-to-parameter ratio of ca 6.5. Positional parameters are listed in Table 2.

In the crystal of compound (1), the two independent thiophenyl rings are disordered. The disorder is twofold in each case, and superimposes the  $\beta$  and  $\beta'$  S- and C-atom sites. The populations of S and C scattering factors were refined for each of these sites, with the usual constraints – that the total population of each site be 1.0, and that each thiophenyl ring have the correct overall stoichiometry – that is, C<sub>4</sub>H<sub>3</sub>S. Each site was refined with its own set of anisotropic displacement parameters, in order that the observed scattering density be modeled as accur-

\* Lists of structure factors and anisotropic displacement parameters, for (1) and (2), and H-atom parameters and hydrogen-bond interactions in (2) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52943 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

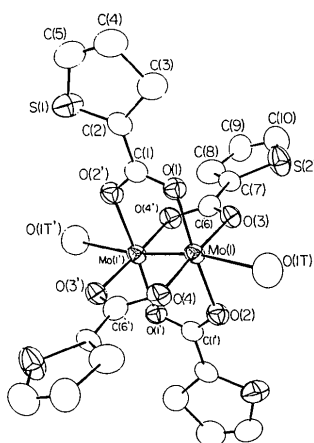


Fig. 1. The [Mo<sub>2</sub>(C<sub>5</sub>H<sub>3</sub>O<sub>2</sub>S)<sub>4</sub>(C<sub>4</sub>H<sub>8</sub>O)<sub>2</sub>] molecule (with the tetrahydrofuran moieties omitted). Atoms are represented by their displacement ellipsoids at the 50% probability level.

Table 3. Bond distances (Å) and selected bond angles (°) in  $[\text{Mo}_2(\text{C}_5\text{H}_3\text{O}_2\text{S})_4(\text{C}_4\text{H}_8\text{O})_2]$ , (1)

|                    |            |                  |            |
|--------------------|------------|------------------|------------|
| Mo(1)—Mo(1')       | 2.102 (1)  | C(1)—C(2)        | 1.465 (9)  |
| Mo(1)—O(17)        | 2.593 (5)  | C(2)—S,C(3)      | 1.640 (7)  |
| Mo(1)—O(1)         | 2.114 (4)  | S,C(3)—C(4)      | 1.613 (10) |
| Mo(1)—O(2)         | 2.101 (4)  | C(4)—C(5)        | 1.331 (12) |
| Mo(1)—O(3)         | 2.107 (5)  | S,C(2)—C(7)      | 1.699 (7)  |
| Mo(1)—O(4)         | 2.105 (5)  | S,C(2)—C(10)     | 1.689 (9)  |
| O(17)—C(17)        | 1.434 (12) | C(6)—C(7)        | 1.443 (12) |
| O(17)—C(47)        | 1.439 (15) | C(7)—C,S(8)      | 1.423 (10) |
| O(1)—C(1)          | 1.273 (7)  | C,S(8)—C(9)      | 1.479 (12) |
| O(2)—C(1')         | 1.271 (7)  | C(9)—C(10)       | 1.382 (12) |
| O(3)—C(6)          | 1.282 (9)  | C(17)—C(27)      | 1.47 (3)   |
| O(4)—C(6')         | 1.285 (8)  | C(27)—C(37)      | 1.44 (3)   |
| C,S(1)—C(2)        | 1.598 (7)  | C(37)—C(47)      | 1.55 (2)   |
| C,S(1)—C(5)        | 1.553 (9)  |                  |            |
| Mo(1')—Mo(1)—O(17) | 168.7 (1)  | O(17)—Mo(1)—O(4) | 80.3 (2)   |
| Mo(1')—Mo(1)—O(1)  | 92.2 (1)   | O(1)—Mo(1)—O(2)  | 176.4 (2)  |
| Mo(1')—Mo(1)—O(2)  | 91.2 (1)   | O(1)—Mo(1)—O(3)  | 88.2 (2)   |
| Mo(1')—Mo(1)—O(3)  | 92.7 (1)   | O(1)—Mo(1)—O(4)  | 92.1 (2)   |
| Mo(1')—Mo(1)—O(4)  | 90.6 (1)   | O(2)—Mo(1)—O(3)  | 90.5 (2)   |
| O(17)—Mo(1)—O(1)   | 94.8 (2)   | O(2)—Mo(1)—O(4)  | 89.0 (2)   |
| O(17)—Mo(1)—O(2)   | 82.0 (2)   | O(3)—Mo(1)—O(4)  | 176.7 (2)  |
| O(17)—Mo(1)—O(3)   | 96.4 (2)   |                  |            |

ately as possible. Fig. 1 shows the structure of one molecule, with the atomic sites labeled according to one of the disordered congeners. The S(1), C(3), S(2) and C(8) sites have mixed populations. S(1) was refined to a sulfur population of 0.417 (8), S(2) to 0.898 (8); C(3) and C(8) are complementary to S(1) and S(2), respectively. As Table 3 shows, the bond distances involving the disordered sites are, as expected, between the ideal values for  $\text{S}\cdots\text{C}$  and  $\text{C}\cdots\text{C}$  values in this ligand. The entity of chemical interest, the inner part of the molecule, is clearly defined, and has geometry fully in accord with expectation. The Mo—Mo bond distance, 2.102 (1) Å, is within the range of distances found previously for quadruply bonded dimolybdenum tetracarboxylates (Cotton & Walton, 1982). Thus, the presence of a heteroaromatic bridging ligand in this compound does not effect an unusual geometry for the quadruply bonded chromophore. There is a slight torsional displacement between the thiophenyl and carboxylato moieties of each bridging ligand. Remembering that the  $\beta$  C- and S-atom sites have mixed populations, we note the following representative torsion angles: O(1)—C(1)—C(2)—C(3), 7.5 (1.0)°, O(1)—C(1)—C(2)—S(1), -169.2 (6)°, O(3)—C(6)—C(7)—S(2), -5.9 (9)° and O(3)—C(6)—C(7)—C(8), 175.3 (6)°. The molecules of (1) are packed in such a way that there is weak contact between the thiophene moieties of two adjacent molecules (related by a  $\mathbf{b}$  translation). The distance between the two ring centroids is *ca* 3.9 Å.

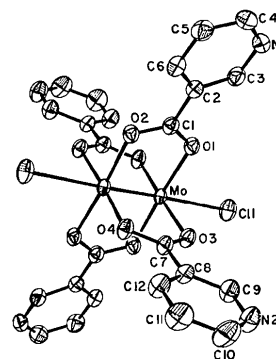
Compound (2) has a remarkably rigid and well defined crystal structure. The positional parameters are listed in Table 4 and the principal bond lengths and angles are given in Table 5. The structure of the  $[\text{Mo}_2(\text{O}_2\text{CC}_5\text{N})_4\text{Cl}_2]^{2+}$  unit is shown in Fig. 2. There

Table 4. Positional parameters and equivalent isotropic displacement parameters and their *e.s.d.*'s for  $[\text{Mo}_2(\text{Cl})_2(\text{C}_6\text{H}_4\text{NO}_2)_4]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ , (2)
$$B_{\text{eq}} = (1/3) \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

|       | <i>x</i>     | <i>y</i>    | <i>z</i>     | $B_{\text{eq}}$ (Å <sup>2</sup> ) |
|-------|--------------|-------------|--------------|-----------------------------------|
| Mo    | -0.04867 (2) | 0.00688 (1) | -0.09599 (2) | 1.792 (4)                         |
| Cl(1) | -0.18192 (9) | 0.03515 (5) | -0.34786 (8) | 3.29 (2)                          |
| Cl(2) | 0.3586 (1)   | 0.32354 (8) | 0.3686 (1)   | 5.81 (3)                          |
| O(1)  | 0.0932 (2)   | 0.1095 (1)  | 0.1070 (2)   | 2.24 (4)                          |
| O(2)  | -0.0079 (2)  | 0.1238 (1)  | -0.0961 (2)  | 2.27 (4)                          |
| O(3)  | 0.1261 (2)   | -0.0184 (1) | -0.2015 (2)  | 2.25 (4)                          |
| O(4)  | 0.2277 (2)   | -0.0326 (1) | 0.0016 (2)   | 2.35 (4)                          |
| O(5)  | 0.4754 (3)   | -0.0869 (2) | -0.6633 (3)  | 4.96 (6)                          |
| O(6)  | 0.2133 (3)   | 0.7790 (2)  | 0.3013 (3)   | 5.33 (7)                          |
| O(7)  | 0.3426 (3)   | 0.7585 (2)  | 0.0507 (3)   | 6.92 (9)                          |
| N(1)  | 0.1615 (3)   | 0.3366 (1)  | 0.1367 (3)   | 3.06 (6)                          |
| N(2)  | 0.4617 (3)   | -0.0911 (2) | -0.3925 (3)  | 3.56 (6)                          |
| C(1)  | 0.0512 (3)   | 0.1504 (2)  | 0.0085 (3)   | 2.22 (5)                          |
| C(2)  | 0.0704 (3)   | 0.2331 (2)  | 0.0186 (3)   | 2.15 (6)                          |
| C(3)  | 0.1464 (3)   | 0.2619 (2)  | 0.1227 (3)   | 2.61 (6)                          |
| C(4)  | 0.1037 (4)   | 0.3857 (2)  | 0.0514 (3)   | 3.41 (7)                          |
| C(5)  | 0.0296 (4)   | 0.3599 (2)  | -0.0564 (3)  | 3.07 (7)                          |
| C(6)  | 0.0106 (3)   | 0.2833 (2)  | -0.0727 (3)  | 2.56 (6)                          |
| C(7)  | 0.2269 (3)   | -0.0353 (2) | -0.1279 (3)  | 2.32 (6)                          |
| C(8)  | 0.3482 (3)   | -0.0609 (2) | -0.1946 (3)  | 2.35 (6)                          |
| C(9)  | 0.3513 (3)   | -0.0683 (2) | -0.3335 (3)  | 2.84 (6)                          |
| C(10) | 0.5723 (4)   | -0.1057 (2) | -0.3212 (4)  | 4.11 (8)                          |
| C(11) | 0.5738 (4)   | -0.0996 (2) | -0.1830 (4)  | 4.16 (8)                          |
| C(12) | 0.4622 (3)   | -0.0778 (2) | -0.1189 (3)  | 3.22 (7)                          |

Table 5. Principal bond distances (Å) and angles (°) in  $[\text{Mo}(\text{Cl})_2(\text{C}_6\text{H}_4\text{NO}_2)_4]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ , (2)

|               |            |                |           |
|---------------|------------|----------------|-----------|
| Mo—Mo'        | 2.122 (1)  | O(1)—C(1)      | 1.273 (3) |
| Mo—Cl         | 2.835 (1)  | O(2)—C(1)      | 1.268 (3) |
| Mo—O(1)       | 2.109 (2)  | O(3)—C(7)      | 1.274 (3) |
| Mo—O(2')      | 2.108 (2)  | O(4)—C(7)      | 1.273 (3) |
| Mo—O(3)       | 2.125 (2)  | C(1)—C(2)      | 1.478 (4) |
| Mo—O(4')      | 2.110 (2)  | C(7)—C(8)      | 1.480 (4) |
| Mo—Mo'—Cl     | 176.29 (2) | Mo—O(3')—C(7)  | 116.2 (2) |
| Mo—Mo'—O(1)   | 91.62 (5)  | Mo—O(4')—C(7)  | 117.6 (2) |
| Mo—Mo'—O(2')  | 91.47 (5)  | O(1)—C(1)—O(2) | 123.3 (3) |
| Mo—Mo'—O(3)   | 91.90 (5)  | O(1)—C(1)—C(2) | 118.0 (3) |
| Mo—Mo'—O(4')  | 91.21 (5)  | O(2)—C(1)—C(2) | 118.8 (3) |
| O(1)—Mo—O(2') | 176.87 (7) | O(3)—C(7)—O(4) | 122.9 (3) |
| O(3)—Mo—O(4)  | 178.88 (7) | O(3)—C(7)—C(8) | 119.1 (3) |
| Mo—O(1)—C(1)  | 116.6 (2)  | O(4)—C(7)—C(8) | 118.0 (3) |
| Mo'—O(2)—C(1) | 116.9 (2)  |                |           |

Fig. 2. The  $[\text{Mo}_2(\text{Cl})_2(\text{C}_6\text{H}_4\text{NO}_2)_4]^{2+}$  unit, showing the atom-labeling scheme. Each atom is represented by its displacement ellipsoid scaled to the 50% probability level.

are two of these per unit cell, each residing on an inversion center. Each ring N atom is protonated, as is clear not only from the stoichiometry but from actual observation of these H atoms in a difference map. The pyridinium rings are essentially coplanar with the attached carboxyl groups. The axial chloride ligands are only loosely bound at a distance of 2.835 (1) Å. This is quite typical for axial Mo—Cl bonds in Mo<sub>2</sub>(O<sub>2</sub>CR)<sub>4</sub>Cl<sub>2</sub> species, where five previously observed values are in the range 2.829 (2) to 2.907 (1) Å, with a mean of 2.869 Å (Bino & Cotton, 1980). The Mo—Mo distance of 2.122 (1) Å is comparable to other such bond lengths in similar compounds.

All H atoms were found and refined, and their positions are listed in the deposited material.

In the pyridinium rings the ten N—H and C—H distances range from 0.84 (3) to 0.99 (3) Å with an average value of 0.91 Å and an average e.s.d. of 0.04 Å. The six O—H distances in the water molecules ranged from 0.93 (3) to 1.11 (3) Å with an average value of 1.00 Å and an average e.s.d. of 0.03 Å.

There is an extensive set of hydrogen bonds throughout the crystal. The water molecules H(15)—O(6)—H(16) and H(17)—O(7)—H(18) are linked into an infinite chain ...H(15)—O(6)···H(18)—O(7)···, with alternating O to O distances of 2.83 and 2.84 Å. The free chloride ion,

Cl(2), interacts with N(1), O(5) and O(7) at distances of 3.01, 3.10 and 3.32 Å, respectively. The corresponding angles about the H atoms [Cl(2)···H(1)—N(1), 146 (3), Cl(2)···H(13)—O(5), 173.1 (2) and Cl(2)···H(17)—O(7), 156.2 (2)°] along with the contact distances, indicate that these are hydrogen-bond interactions. The hydrogen bonds mediate the packing in this structure, in which there are no van der Waals contacts between pyridinyl moieties of adjacent molecules.

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#### References

- B. A. FRENZ & ASSOCIATES, INC. (1981). *SDP-Plus Structure Determination Package*. College Station, Texas, USA.  
 BINO, A. & COTTON, F. A. (1980). *J. Am. Chem. Soc.* **102**, 3014–3017.  
 COTTON, F. A. & WALTON, R. A. (1982). *Multiple Bonds Between Metal Atoms*, pp. 85–91. New York: John Wiley.  
 CROMER, D. T. (1974). *International Tables for X-ray Crystallography*. Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)  
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.  
 CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*. Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)  
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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## Structures of Tetraethylammonium Tetrachloroferrate(III) and the Mixed Halide Iron(III) Complex, [NEt<sub>4</sub>][FeBrCl<sub>3</sub>]

BY DAVID J. EVANS, ADRIAN HILLS, DAVID L. HUGHES AND G. JEFFERY LEIGH

*AFRC Institute of Plant Science Research, Nitrogen Fixation Laboratory, University of Sussex, Brighton BN1 9RQ, England*

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**Abstract.** Tetraethylammonium tetrachloroferrate(III), [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>][FeCl<sub>4</sub>], *M<sub>r</sub>* = 327.91, hexagonal, *P*6<sub>3</sub>*mc*, *a* = 8.212 (1), *c* = 13.201 (1) Å, *V* = 770.9 Å<sup>3</sup>, *Z* = 2, *F*(000) = 338, *D<sub>x</sub>* = 1.413 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 16.5 cm<sup>-1</sup>, *T* = 293 K, *R* = 0.055 for all 293 reflections. Tetraethylammonium bromotrichloroferrate(III), [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>][FeBrCl<sub>3</sub>], *M<sub>r</sub>* = 372.36, hexagonal, *P*6<sub>3</sub>*mc*, *a* = 8.230 (1), *c* = 13.242 (1) Å, *V* = 776.7 Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.592 g cm<sup>-3</sup>, *F*(000) = 374, λ(Mo *K*α) = 0.71069 Å, μ = 40.1 cm<sup>-1</sup>, *T* = 293 K, *R* = 0.055 for all 295

reflections. The crystals are isostructural; in both cases, the cations are disordered about a 3*m* symmetry site. The [FeCl<sub>4</sub>]<sup>-</sup> ion is well resolved with 3*m* (and almost perfect tetrahedral) symmetry and mean Fe—Cl 2.185 (1) Å. The [FeBrCl<sub>3</sub>]<sup>-</sup> ion is disordered with Br replacing Cl in either of its two sites.

**Introduction.** The title compound [NEt<sub>4</sub>][FeBrCl<sub>3</sub>] was initially obtained as a by-product of reactions to prepare novel Fe<sub>4</sub>S<sub>4</sub> metal clusters by 'spontaneous self-assembly' reactions. Below a direct procedure is