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**Amminebis-(η -cyclopentadienyl)-*N*-(*C*-methyl-*C*-ethylketimino)molybdenum
Bis(hexafluorophosphate)**

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Abstract.

$\{(C_5H_5)_2Mo(NH_3)[HNC(CH_3)(C_2H_5)]\}(PF_6)_2$, $C_{14}H_{23}F_{12}MoN_2P_2$, $M=605.2$, monoclinic, space group $P2_1/c$ (C_{2h}^2 , No. 14); $a=9.647$ (6), $b=18.394$ (10), $c=13.988$ (8) Å, $\beta=121.05$ (5)°, $U=2126.4$ Å³, $D_x=1.88$, $D_c=1.89$ g cm⁻³, $Z=4$. The structure demonstrates the ability of a ketimine to form an unchelated, σ -bonded complex with molybdenum.

Introduction. The dark-red material was provided by Dr F. W. S. Benfield and recrystallized from an acetone-water mixture. A crystal of prismatic habit, approximately $0.4 \times 0.3 \times 0.2$ mm, was mounted about its

longest dimension (100) in a nitrogen-filled Lindemann-glass capillary and set up on a Hilger and Watts PDP8-controlled four-circle diffractometer. Cell dimensions and orientation matrix were obtained by a least-squares fit to the setting angles of 20 reflexions.

The intensities of two equivalents of each independent reflexion with $\sin \theta/\lambda < 0.7$ were measured with an $\omega/2\theta$ scan and the ordinate analysis method (Watson, Shotton, Cox & Muirhead, 1970). Mo $K\alpha$ radiation was used from a graphite monochromator. Reflexions with intensity less than 3σ , where σ is the standard deviation derived from simple counting statistics, or whose apparent centre was more than 0.2° from the

Table 1. *Fractional coordinates ($\times 10^4$) of non-hydrogen atoms with anisotropic temperature-factor components ($\times 10^3$)*

The anisotropic temperature factor has the form:

$$\exp \{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)\}.$$

| | x/a | y/b | z/c | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|-------|------------|------------|------------|----------|----------|----------|-----------|----------|----------|
| Mo | 7933.5 (5) | 1675.8 (2) | 1999.5 (4) | 38 (1) | 31 (1) | 39 (1) | -1 (1) | 22 (1) | 2 (1) |
| N(1) | 6783 (8) | 617 (3) | 1258 (6) | 69 (4) | 42 (3) | 82 (4) | -18 (3) | 42 (3) | -13 (3) |
| N(2) | 71 (6) | 982 (3) | 2589 (5) | 49 (3) | 53 (3) | 57 (3) | 7 (3) | 27 (3) | 14 (2) |
| C(1) | 1623 (9) | 1091 (5) | 3143 (6) | 61 (4) | 84 (5) | 67 (4) | 20 (4) | 34 (3) | 24 (4) |
| C(2) | 2346 (10) | 1821 (6) | 3471 (8) | 59 (4) | 105 (7) | 80 (5) | -6 (5) | 26 (4) | -13 (4) |
| C(3) | 2812 (12) | 484 (6) | 3468 (10) | 81 (6) | 111 (8) | 119 (8) | 41 (6) | 58 (6) | 46 (6) |
| C(4) | 2240 (15) | -230 (7) | 3401 (15) | 92 (7) | 79 (7) | 193 (15) | -11 (7) | 49 (9) | 19 (5) |
| C(11) | 8986 (9) | 2012 (4) | 3813 (6) | 71 (4) | 84 (5) | 53 (3) | -14 (3) | 37 (3) | -4 (4) |
| C(12) | 7683 (10) | 2474 (4) | 3154 (6) | 87 (5) | 56 (4) | 69 (4) | -9 (3) | 52 (4) | 4 (3) |
| C(13) | 6221 (9) | 2058 (4) | 2624 (6) | 67 (4) | 77 (5) | 75 (4) | -2 (4) | 48 (4) | 7 (3) |
| C(14) | 6622 (10) | 1351 (4) | 2976 (7) | 84 (5) | 73 (4) | 83 (5) | -4 (4) | 62 (4) | -9 (4) |
| C(15) | 8323 (10) | 1300 (4) | 3690 (6) | 88 (5) | 74 (4) | 63 (4) | 15 (3) | 51 (4) | 11 (4) |
| C(21) | 6320 (9) | 2085 (4) | 233 (6) | 59 (4) | 73 (4) | 52 (3) | 9 (3) | 20 (3) | 6 (3) |
| C(22) | 6934 (9) | 2704 (4) | 933 (6) | 75 (4) | 51 (3) | 76 (4) | 12 (3) | 46 (4) | 16 (3) |
| C(23) | 8629 (9) | 2737 (4) | 1404 (6) | 72 (4) | 53 (3) | 68 (4) | 8 (3) | 39 (3) | -3 (3) |
| C(24) | 9076 (9) | 2162 (4) | 983 (6) | 65 (4) | 75 (4) | 63 (4) | 19 (3) | 41 (3) | 11 (3) |
| C(25) | 7715 (10) | 1743 (4) | 290 (6) | 88 (5) | 65 (4) | 52 (3) | 5 (3) | 44 (3) | 8 (3) |
| P(1) | 1836 (2) | 3998 (1) | 4957 (2) | 53 (1) | 56 (1) | 71 (1) | 7 (1) | 35 (1) | -4 (1) |
| F(11) | 3258 (9) | 3969 (5) | 4745 (8) | 117 (5) | 215 (9) | 221 (9) | 51 (7) | 123 (6) | 54 (6) |
| F(12) | 1333 (8) | 4743 (4) | 4404 (8) | 121 (5) | 117 (5) | 284 (10) | 112 (6) | 135 (6) | 39 (4) |
| F(13) | 592 (14) | 4083 (5) | 5292 (12) | 279 (12) | 173 (8) | 464 (19) | 120 (10) | 331 (14) | 63 (8) |
| F(14) | 2363 (12) | 3249 (5) | 5521 (11) | 156 (8) | 151 (8) | 315 (13) | 148 (9) | 100 (9) | 40 (6) |
| F(15) | 644 (15) | 3630 (7) | 3937 (9) | 220 (11) | 231 (12) | 182 (10) | -93 (9) | -42 (8) | -39 (10) |
| F(16) | 3143 (15) | 4359 (8) | 6010 (9) | 216 (11) | 333 (16) | 157 (8) | -126 (10) | 67 (8) | -73 (11) |
| P(2) | 3263 (3) | 3989 (1) | 1780 (2) | 73 (1) | 53 (1) | 71 (1) | -8 (1) | 40 (1) | 7 (1) |
| F(21) | 3880 (11) | 4726 (4) | 1597 (9) | 173 (7) | 74 (4) | 272 (11) | 5 (5) | 141 (8) | -5 (4) |
| F(22) | 4529 (11) | 3623 (4) | 1573 (9) | 189 (8) | 108 (5) | 282 (11) | 6 (6) | 186 (8) | 47 (5) |
| F(23) | 2012 (11) | 3961 (8) | 539 (7) | 128 (6) | 399 (17) | 97 (5) | -89 (8) | 32 (5) | -32 (9) |
| F(24) | 1956 (8) | 4401 (4) | 1946 (6) | 118 (5) | 163 (7) | 157 (6) | -19 (5) | 85 (5) | 37 (5) |
| F(25) | 4465 (11) | 4083 (8) | 3005 (7) | 133 (7) | 424 (19) | 91 (5) | 30 (8) | 22 (5) | 39 (9) |
| F(26) | 2765 (17) | 3279 (4) | 2033 (14) | 355 (18) | 97 (6) | 480 (24) | 34 (8) | 339 (20) | -17 (7) |

predicted position were not included in subsequent calculations. Lorentz and polarization corrections, together with an empirical absorption correction (North, Phillips & Mathews, 1968), were applied, leading to a final set of 3305 independent structure amplitudes.

The structure was solved by conventional Patterson and Fourier techniques; hydrogen atoms were located from difference syntheses. Refinement was by least-squares calculations, with a large-block approximation to the normal matrix: a 2×2 block was calculated from the derivatives of the scale and dummy overall temperature factor, three blocks from those of the positional parameters of the cation and two anions respectively, and a further three blocks from those of the corresponding temperature factors. In the final cycles, non-hydrogen atoms were permitted anisotropic temperature factors, whilst hydrogen atoms were refined isotropically; in addition, the carbon-hydrogen and nitrogen-hydrogen bond lengths were constrained (Waser, 1963; Rollett, 1969) to their respective means with a standard deviation of 0.02 Å. The final values of these means were C-H = 1.00, N-H = 0.94 Å.

Each reflexion was assigned a weight $w^{-1} = 1 + \{(|F_o| - 12)/50\}^2$ and the final R was 0.055. All calculations were performed on the Oxford University ICL 1906A computer with the Oxford package of crystallographic programs (Carruthers & Rollett, 1973). Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

Final atomic parameters are given in Tables 1 and 2, and Table 3 shows bond lengths and angles involving

Table 2. Fractional coordinates ($\times 10^4$) and isotropic temperature factors ($\times 10^2$) of the hydrogen atoms

| | x/a | y/b | z/c | U_{iso} | Bonded to |
|-------|----------|----------|----------|-----------|-----------|
| H(1) | 566 (3) | 63 (4) | 84 (5) | 4 (2) | N(1) |
| H(2) | 707 (10) | 50 (4) | 74 (5) | 5 (2) | N(1) |
| H(3) | 693 (14) | 28 (5) | 180 (7) | 10 (4) | N(1) |
| H(4) | -24 (7) | 50 (1) | 243 (5) | 2 (2) | N(2) |
| H(11) | 1016 (3) | 215 (4) | 426 (5) | 4 (2) | C(11) |
| H(12) | 774 (12) | 301 (1) | 307 (7) | 7 (3) | C(12) |
| H(13) | 507 (4) | 222 (5) | 212 (6) | 7 (3) | C(13) |
| H(14) | 584 (7) | 94 (3) | 270 (6) | 4 (2) | C(14) |
| H(15) | 892 (9) | 83 (3) | 401 (7) | 7 (3) | C(15) |
| H(21) | 513 (3) | 198 (4) | -19 (6) | 5 (2) | C(21) |
| H(22) | 622 (11) | 305 (5) | 104 (9) | 9 (4) | C(22) |
| H(23) | 937 (7) | 309 (3) | 198 (4) | 3 (2) | C(23) |
| H(24) | 1023 (4) | 204 (4) | 123 (6) | 5 (2) | C(24) |
| H(25) | 782 (8) | 129 (2) | -6 (5) | 3 (2) | C(25) |
| H(31) | 328 (7) | 177 (4) | 334 (7) | 6 (3) | C(2) |
| H(32) | 288 (22) | 204 (11) | 424 (6) | 23 (9) | C(2) |
| H(33) | 175 (17) | 224 (6) | 296 (11) | 17 (7) | C(2) |
| H(34) | 343 (21) | 41 (10) | 306 (12) | 21 (8) | C(3) |
| H(35) | 339 (18) | 52 (10) | 431 (2) | 20 (8) | C(3) |
| H(36) | 312 (9) | -57 (5) | 391 (7) | 9 (3) | C(4) |
| H(37) | 157 (10) | -27 (5) | 376 (7) | 7 (3) | C(4) |
| H(38) | 181 (16) | -30 (8) | 258 (3) | 14 (6) | C(4) |

non-hydrogen atoms, with estimated standard deviations calculated from the full variance-covariance matrix.*

Discussion. Complexes of chelating ligands containing an imino-nitrogen, such as salicylaldehyde, are well known, but it has been suggested (see, for example, Smith, 1970) that a double-bonded nitrogen is not sufficiently basic to form simple unchelated complexes. However, Benfield & Green (1974) have recently characterized products obtained from the reactions between $[(\eta-C_5H_5)_2Mo(SMe_2)Br](PF_6)$ and ammonia in ketones, $RR'CO$, as $[(\eta-C_5H_5)_2Mo(NH_3)(HNCRR')](PF_6)_2$, postulating a

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30686 (29 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Bond lengths (Å) and angles (°)

| | | | |
|-------------------|-----------|-------------------|-----------|
| Mo—N(1) | 2.216 (6) | Mo—N(2) | 2.192 (5) |
| Mo—C(11) | 2.278 (7) | Mo—C(21) | 2.265 (7) |
| Mo—C(12) | 2.286 (6) | Mo—C(22) | 2.290 (7) |
| Mo—C(13) | 2.340 (6) | Mo—C(23) | 2.353 (7) |
| Mo—C(14) | 2.368 (7) | Mo—C(24) | 2.377 (6) |
| Mo—C(15) | 2.301 (7) | Mo—C(25) | 2.293 (6) |
| N(2)—C(1) | 1.30 (1) | C(1)—C(3) | 1.49 (1) |
| C(1)—C(2) | 1.47 (1) | C(3)—C(4) | 1.41 (2) |
| C(11)—C(12) | 1.40 (1) | C(21)—C(22) | 1.42 (1) |
| C(12)—C(13) | 1.43 (1) | C(22)—C(23) | 1.41 (1) |
| C(13)—C(14) | 1.37 (1) | C(23)—C(24) | 1.38 (1) |
| C(14)—C(15) | 1.42 (1) | C(24)—C(25) | 1.40 (1) |
| C(15)—C(11) | 1.43 (1) | C(25)—C(21) | 1.45 (1) |
| N(1)—Mo—N(2) | 79.1 (2) | N(2)—C(1)—C(3) | 122 (1) |
| Mo—N(2)—C(1) | 135 (1) | C(2)—C(1)—C(3) | 115 (1) |
| N(2)—C(1)—C(2) | 123 (1) | C(1)—C(3)—C(4) | 118 (2) |
| C(11)—C(12)—C(13) | 109 (2) | C(21)—C(22)—C(23) | 109 (1) |
| C(12)—C(13)—C(14) | 108 (2) | C(22)—C(23)—C(24) | 108 (2) |
| C(13)—C(14)—C(15) | 109 (2) | C(23)—C(24)—C(25) | 109 (2) |
| C(14)—C(15)—C(11) | 108 (2) | C(24)—C(25)—C(21) | 108 (2) |
| C(15)—C(11)—C(12) | 107 (2) | C(25)—C(21)—C(22) | 105 (2) |
| P(1)—F(11) | 1.55 (1) | P(2)—F(21) | 1.55 (1) |
| P(1)—F(12) | 1.53 (1) | P(2)—F(22) | 1.55 (1) |
| P(1)—F(13) | 1.50 (1) | P(2)—F(23) | 1.52 (1) |
| P(1)—F(14) | 1.54 (1) | P(2)—F(24) | 1.59 (1) |
| P(1)—F(15) | 1.46 (1) | P(2)—F(25) | 1.50 (1) |
| P(1)—F(16) | 1.51 (1) | P(2)—F(26) | 1.50 (1) |
| F(11)—P(1)—F(12) | 91 (1) | F(12)—P(1)—F(16) | 89 (1) |
| F(11)—P(1)—F(13) | 173 (1) | F(13)—P(1)—F(14) | 92 (1) |
| F(11)—P(1)—F(14) | 89 (1) | F(13)—P(1)—F(15) | 90 (1) |
| F(11)—P(1)—F(15) | 97 (1) | F(13)—P(1)—F(16) | 93 (1) |
| F(11)—P(1)—F(16) | 80 (1) | F(14)—P(1)—F(15) | 88 (1) |
| F(12)—P(1)—F(13) | 88 (1) | F(14)—P(1)—F(16) | 90 (2) |
| F(12)—P(1)—F(14) | 179 (1) | F(15)—P(1)—F(16) | 177 (1) |
| F(12)—P(1)—F(15) | 92 (1) | | |
| F(21)—P(2)—F(22) | 87 (1) | F(22)—P(2)—F(26) | 93 (1) |
| F(21)—P(2)—F(23) | 89 (1) | F(23)—P(2)—F(24) | 88 (1) |
| F(21)—P(2)—F(24) | 90 (1) | F(23)—P(2)—F(25) | 175 (1) |
| F(21)—P(2)—F(25) | 87 (1) | F(23)—P(2)—F(26) | 94 (1) |
| F(21)—P(2)—F(26) | 176 (1) | F(24)—P(2)—F(25) | 89 (1) |
| F(22)—P(2)—F(23) | 91 (1) | F(24)—P(2)—F(26) | 90 (1) |
| F(22)—P(2)—F(24) | 177 (1) | F(25)—P(2)—F(26) | 89 (1) |
| F(22)—P(2)—F(25) | 93 (1) | | |

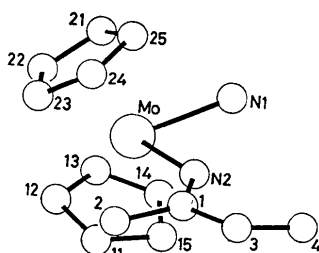


Fig. 1. The cation in projection down *a*. For clarity, carbon atoms are labelled by their serial numbers only and hydrogen atoms have been omitted.

σ -bonded rather than a π -bonded ketimine ligand. King & Douglas (1973) have also reported the existence of $(\text{CH}_3)_2\text{CN}(\text{H})\text{Cr}(\text{CO})_5$. In view of these developments, the crystal structure of Benfield & Green's product from ethyl methyl ketone was determined and is described here.

The observed structure consists of an array of discrete organometallic cations (Fig. 1), in which the presence of a σ -bonded ethyl methyl ketimine ligand is confirmed, and hexafluorophosphate anions. The cations adopt the configuration familiar in many bent bis- η -cyclopentadienyl-metal complexes, with approximate local C_{2v} symmetry at the molybdenum. The molybdenum atom lies 1.98 Å from the best planes of the cyclopentadienyl rings, and the angle between the ring normals is 134°: typical results for $(\eta\text{-C}_5\text{H}_5)_2\text{MoX}_2$ systems (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974). A projection on to the MoN(1)N(2) plane shows that the rings adopt a staggered conformation. The N-Mo-N angle (79.1°) and Mo-N bond lengths (2.216 and 2.192 Å) are in accord with previous results on, for example, amino acid complexes of molybdenum (Prout, Allison, Delbaere & Gore, 1972; Drew & Kay, 1971; Delbaere & Prout, 1971).

The ketimine ligand itself is essentially planar, the only exceptional feature being the short C(3)-C(4) bond. C(4), however, has a large component of ap-

parent thermal motion perpendicular to the ketimine plane and appears elongated in appropriate Fourier syntheses. It therefore seems likely that there is some disordering of C(4) about the plane (the local potential energy field would certainly be nearly symmetrical here) with the result that the mean, refined position is too close to C(3).

As is usually observed with ions having spherical symmetry, the hexafluorophosphate groups have large temperature factors and show considerable apparent distortion.

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