

Table 4. Comparison of Mn—O bond distances (Å) in Mn(bppd)₂(H₄furan)₂ with those of related complexes

| Complex | r(Mn—O) |
|---|--|
| Mn(bppd) ₂ (H ₄ furan) ₂ | to bppd: 2.088 (1), 2.136 (1) to (H ₄ furan): 2.285 (2) |
| Mn(C ₅ H ₇ O ₂) ₂ ·2H ₂ O ^(a) | to C ₅ H ₇ O ₂ : 2.129 (7), 2.150 (8) to H ₂ O: 2.267 (8) |
| Mn(CHO) ₂ ·2H ₂ O ^(b) | to CHO: 2.172 (12) to H ₂ O: 2.216 (13), 2.168 (15) |
| Mn ₂ (C ₃ H ₈ N) ₂ (C ₅ H ₇ O ₂) ₂ ^(c) Mn ²⁺ (POCl ₂) ₂ (MeCO ₂ Et) ₂ ^(d) | to C ₅ H ₇ O ₂ : 2.14 (2) to POCl ₂ : 2.12, 2.14 to EtO ₂ CMe: 2.17, 2.24 |
| Mn(C ₅ O ₅)(H ₂ O) ₃ ^{(e), (f)} | to C ₅ O ₅ : 2.172 (8), 2.253 (8) to H ₂ O: 2.210 (8), 2.226 (9) |
| (Pyridoxylidenevaline)- manganese(II) ^(g) | 2.08 (1), 2.17 (1) |

(a) Onuma & Shibata (1970); Montgomery & Lingafelter (1968).
(b) Osaki, Nakai & Watanabe (1964). (c) Koda, Ooi & Kuroya (1972). (d) Danielson & Rasmussen (1963). (e) C₅O₅ = croconate.
(f) Glick & Dahl (1965). (g) Willstader, Hamor & Hoard (1963).

gane(II) (Montgomery & Lingafelter, 1968; Onuma & Shibata, 1970), diaquabis(formato)manganese(II) (Osaki, Nakai & Watanabe, 1964), and dimeric allylaminebis(2,4-pentanedionato)manganese(II) (Koda, Ooi & Kuroya, 1972) as well as the complex [Mn²⁺(POCl₂)₂(EtO₂CMe)₂] (Danielson & Rasmussen, 1963) all possess six-coordination of this type.

The Mn—O bond distances to the β-ketoenolate O atoms [2.088 (1) and 2.136 (1) Å] are in good agreement with those in similar complexes (Table 4). The coordinate Mn—O(H₄furan) bond distance is not unexpectedly longer [2.285 (2) Å], and is marginally longer than the coordinate bond distances between Mn and the O atoms of water and ethyl acetate (Table 4).

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Bis(1-tert-butyl-2,3-dimethylisourea)dichloropalladium(II)

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Abstract. [Pd(C₇H₁₆N₂O)₂Cl₂], C₁₄H₃₂Cl₂N₄O₂Pd, monoclinic, C2/c, *a* = 12.947 (9), *b* = 17.362 (13), *c* = 10.194 (6) Å, β = 112.16 (2)°, *V* = 2122.0 Å³, *Z* = 4,

The (bppd) group chelates the Mn almost symmetrically, although the difference in the two Mn—O bond distances (0.048 Å) is substantially greater than the estimated standard deviations. The two endocyclic C—O [C(11)—O(2) and C(13)—O(1)] and C—C [C(11)—C(12) and C(12)—C(13)] bond distances are nearly equal, within experimental error, and have values which are intermediate between those for single and double bonds, indicating complete π-electron delocalization over the β-ketoenolate system.

Because of the crystallographic centrosymmetry of the molecule, the coordinated H₄furan molecules, which occupy mutually *trans* positions, are exactly coplanar, as are the two equivalent β-ketoenolate-manganese heterocycles. The two phenyl rings are twisted with respect to the β-ketoenolate-manganese rings by 25.63 and 15.88°.

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*D*_c = 1.46, *D*_m = 1.45 Mg m⁻³, Mo Kα₁ radiation, λ = 0.70926 Å, μ(Mo Kα) = 1.12 mm⁻¹, final *R* = 0.054 for 1510 observed reflections, *T* = 293 (1) K. The Pd atom has a *trans* square-planar environment, being coordinated to the Cl atoms (along a crystallographic twofold axis) and to the imine N atoms of the isourea ligands. Significant bond lengths are Pd—Cl =

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2.305 (3) and 2.309 (3) Å, Pd–N = 2.017 (5) Å, C(OMe)–N(Me) = 1.311 (8) Å and C(OMe)–N(Bu^t) = 1.327 (8) Å.

Introduction. Crystals of the title compound were brownish-orange and generally in the shape of rectangular needles. Weissenberg photographs of the *hk0* and *hkl* reciprocal-lattice layers were taken as well as precession photographs of the layers *h0l*, *h1l*, *hk2h* and *h,k,2h + 2*. Monoclinic symmetry was indicated with systematic absences *hkl*, *h + k = 2n + 1* and *h0l*, *l = 2n + 1*. The space group could be either *Cc* or *C2/c*; the structure analysis is consistent with *C2/c*.

A crystal 0.40 × 0.15 × 0.22 mm was used for intensity collection. Cell dimensions were obtained by least squares from the 2θ values for 12 strong reflections ($2\theta > 25^\circ$) centered on the Mo $K\alpha_1$ peak ($\lambda = 0.70926$ Å). During intensity collection a θ – 2θ scan base width of 1.20° was used.

1867 unique reflections were recorded, of which 1510 were classed as observed, *i.e.* $I > 2.35\sigma(I)$, $\sigma(I) = [(T) + (t_s/t_b)^2(B_1 + B_2) + (KI)^2]^{1/2}$ where T = total count, t_s = scan time, t_b = total background count time, B_1 and B_2 are the background counts, $K = 0.03$, and I is the net count.

Intensities were corrected for Lorentz and polarization effects. After solution of a Patterson

function for the Pd, Cl and coordinated N atoms, $R = 0.245$ was obtained ($R = \sum |F_o| - |F_c| / \sum |F_o|$). Further difference maps and least-squares refinement gave the positions for all but three methyl H atoms. These remaining H-atom positions were calculated. H-atom coordinates were not refined.

For the final stages weights determined from counter statistics ($1/\sigma_p^2$) were used. The last cycle of full-matrix least-squares refinement gave $R = 0.054$ ($R_w = 0.068$) with all non-hydrogen atoms allowed anisotropic thermal parameters.

Scattering factors for the non-hydrogen atoms were from Cromer & Waber (1965) and for H from Stewart, Davidson & Simpson (1965). Anomalous-dispersion corrections were made with values given in *International Tables for X-ray Crystallography* (1962a). The computer programs used were those described by Einstein & Jones (1972).

Table 1 contains atomic coordinates, Table 2 bond distances and angles.* Fig. 1 illustrates the molecule and gives the atom labelling.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34296 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$; $\times 10^3$ for H, $\times 10^5$ for Pd) with *e.s.d.*'s

| | x | y | z |
|-------|----------|-----------|------------|
| Pd | 50000 | 35279 (4) | 25000 |
| Cl(1) | 5000 | 4855 (1) | 2500 |
| Cl(2) | 5000 | 2198 (1) | 2500 |
| O(1) | 7551 (4) | 3778 (3) | 2389 (5) |
| N(1) | 5695 (4) | 3534 (3) | 1031 (6) |
| N(2) | 6933 (4) | 4015 (4) | 77 (6) |
| C(1) | 4846 (6) | 3485 (4) | -400 (8) |
| C(2) | 6691 (5) | 3768 (4) | 1158 (7) |
| C(3) | 7590 (6) | 3273 (5) | 3526 (9) |
| C(4) | 8054 (5) | 4075 (4) | -5 (8) |
| C(5) | 7842 (7) | 4141 (6) | -1565 (10) |
| C(6) | 8641 (8) | 4783 (6) | 750 (11) |
| C(7) | 8732 (7) | 3352 (5) | 563 (10) |
| H(1) | 635 | 413 | -92 |
| H(11) | 432 | 310 | -28 |
| H(12) | 451 | 397 | -66 |
| H(13) | 514 | 319 | -81 |
| H(31) | 841 | 322 | 428 |
| H(32) | 724 | 351 | 402 |
| H(33) | 738 | 286 | 320 |
| H(51) | 745 | 364 | -198 |
| H(52) | 760 | 460 | -180 |
| H(53) | 851 | 419 | -175 |
| H(61) | 908 | 460 | 167 |
| H(62) | 811 | 516 | 80 |
| H(63) | 910 | 503 | 33 |
| H(71) | 902 | 340 | 153 |
| H(72) | 930 | 328 | 19 |
| H(73) | 824 | 289 | 29 |

Table 2. Bond distances (Å) and angles ($^\circ$)

| | | | |
|----------------|-----------|----------------|-----------|
| Pd–Cl(1) | 2.305 (3) | N(1)–C(2) | 1.311 (8) |
| Pd–Cl(2) | 2.309 (3) | N(2)–C(2) | 1.326 (8) |
| Pd–N(1) | 2.017 (5) | N(2)–C(4) | 1.487 (8) |
| O(1)–C(2) | 1.327 (8) | C(4)–C(5) | 1.51 (1) |
| O(1)–C(3) | 1.440 (9) | C(4)–C(6) | 1.50 (1) |
| N(1)–C(1) | 1.461 (9) | C(4)–C(7) | 1.52 (1) |
| Cl(1)–Pd–Cl(2) | 180.0 | N(2)–C(2)–O(1) | 113.8 (6) |
| Cl(1)–Pd–N(1) | 89.7 (2) | N(1)–C(2)–N(2) | 123.4 (6) |
| Cl(2)–Pd–N(1) | 90.3 (2) | N(2)–C(4)–C(5) | 105.6 (6) |
| C(2)–O(1)–C(3) | 121.0 (5) | N(2)–C(4)–C(6) | 110.2 (6) |
| Pd–N(1)–C(1) | 111.3 (4) | N(2)–C(4)–C(7) | 110.9 (6) |
| Pd–N(1)–C(2) | 128.7 (5) | C(5)–C(4)–C(6) | 109.5 (7) |
| C(1)–N(1)–C(2) | 117.3 (6) | C(5)–C(4)–C(7) | 108.2 (7) |
| C(2)–N(2)–C(4) | 127.6 (6) | C(6)–C(4)–C(7) | 112.1 (8) |
| N(1)–C(2)–O(1) | 122.7 (6) | | |

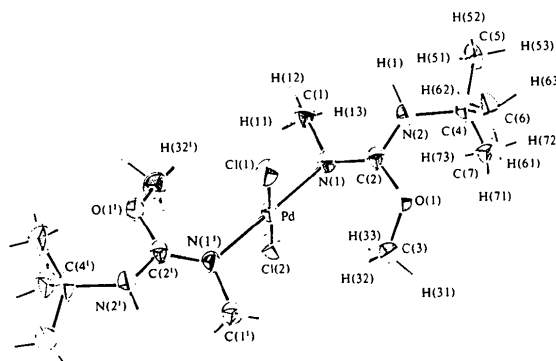


Fig. 1. The molecular structure of $\text{PdCl}_2[\text{MeN}_2:(\text{OMe})\text{C.HNBu}^t]$.

Discussion. Alcohols are unreactive towards carbodiimides [RN:C:NR' (R, R' = alkyl or aryl)] at room temperature, but recent work (Bycroft & Cotton, 1973) has shown that the 1,2-addition of methanol to a carbodiimide to give the appropriate isourea is promoted by Pd^{II}, e.g. by Na₂PdCl₄. NMR studies suggest that two possible isomers are obtained in methanol solution, depending on the direction of addition of methanol to the carbodiimide; these are (for R = Me, R' = Bu^t) either the 2,3-dimethyl [MeN:(OMe)C.HNBu^t], or the 1,2-dimethyl isomer [MeNH.C(OMe):NBu^t]. Single crystals of a complex of stoichiometry (isourea)₂PdCl₂ were isolated from solution, and this study was undertaken to identify the isourea ligands, and to investigate the method of bonding of the isourea ligands to the transition metal.

The molecule has a crystallographic twofold axis which passes through the Pd and both Cl atoms. Bonds from the Pd to the Cl atoms, and from the Pd to the imine N atoms of the isourea ligands describe the square-planar geometry of the complex. The Pd atom and the methoxy group are *cis*, which results in the Pd-H(32) distance, 2.7 Å, being quite short. Weak Pd-H interactions of this type have been proposed in other cases (Cotton & Wilkinson, 1972) and would complete an irregular octahedral environment about Pd in this complex. Indeed the environment of the Pd is entirely similar to that of the Pd atom in the parent carbodiimide complex, PdCl₂(Bu^tN:C:NBu^t)₂ (Anderson & Einstein, 1978).

Both isourea ligands coordinate to the Pd as the 2,3-dimethyl isomer. Since the ligands formally contain C=N, the possibility of coordination either through the imine N lone pair or through the π system exists; in fact, bonding is through the lone pair as in the parent carbodiimide complex and in two other cases (Khare, Little, Veal & Doedens, 1975; Gasparrini, Misiti & Cernia, 1976). Theoretically coordination through the NH nitrogen is also possible, but Bycroft & Cotton (1973) have suggested that this is unlikely for steric reasons (Stephenson, 1963). C(2)-N(1), 1.311 (8) Å, is not significantly shorter than C(2)-N(2), 1.326 (8) Å. These bond lengths approximate to the 1.32 Å for a partial C-N double bond (*International Tables for X-ray Crystallography*, 1962b). Thus there is evidence that the lone pair on the NBu^t nitrogen participates in a π system delocalized over N(1), C(2), O(1) and N(2). Table 3 indicates that these atoms are coplanar.

Table 3. Atomic deviations (Å) from the least-squares plane through N(1), C(2), O(1) and N(2)

| Interception equation | | | |
|--|-------------|------|-------------|
| $-4.1575X + 16.1977Y + 2.7717Z = 3.6424$ | | | |
| N(1) | 0.000 (10)* | Pd | 0.686 (2) |
| C(2) | 0.000 (14) | C(1) | -0.123 (16) |
| O(1) | 0.000 (10) | C(3) | -0.392 (17) |
| N(2) | 0.000 (12) | H(1) | 0.152 |

* Errors quoted refer to twice the radius of the error sphere.

The crystal structure contains no short or otherwise unusual intermolecular contacts.

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