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(Acetonitrile)-*trans*-dichloro-*mer*-tris[(dimethyl)phenylphosphine]osmium(III); the Kinetically Controlled Electrogenerated Isomer

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Abstract

The electrosynthesized compound, *trans-mer*-$[OsCl_2(C_2H_3N)(C_8H_{11}P)_3]$, contains a nearly linear MeC≡N—Os linkage [Os(1)—N(1)—C(1) 179(1)°] and the phenyl substituents on neighbouring phosphines are specifically oriented about the nitrile ligand.

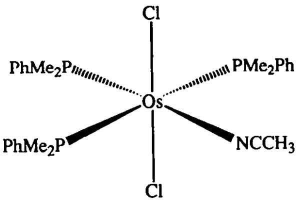
Comment

trans-mer-$[Os^{II}Cl_2(PMe_2Ph)_3(MeCN)]$, (I), is formally an MeCN-substituted analogue of the more familiar complex *trans*-$[Os^{II}Cl_2(PMe_2Ph)_4]$, but is actually isolated in a redox-induced halide displacement reaction:

$$\underset{}{mer\text{-}[Os^{III}Cl_3(PR_3)_3]} \xrightarrow{+1e^-} Cl^- + \underset{\text{very reactive}}{\{Os^{II}Cl_2(PR_3)_3\}} \xrightarrow{+\text{MeCN}} \underset{\text{(I)}}{[OsCl_2(PR_3)_3(MeCN)]}$$

Such electrosynthetic procedures have been elevated to the status of 'rational pathways to osmium(II) complexes' (Coombe, Heath, Stephenson, Whitelock & Yellowlees, 1985).

All potential isomers of (I) (*trans-mer*, *cis-mer* and *cis-fac*) possess inequivalent phosphine ligands in the ratio 1:2, as required by the ^{31}P NMR data, and this is the first X-ray confirmation of the *trans-mer* assignment for the kinetically controlled product. On standing in solution, (I) relaxes to the presumed *cis-mer* isomer.



(I)

The pertinent bond lengths and angles in (I) are unexceptional, and compare well with, for example, *trans*-$[OsCl_2(dppe)_2]$ (Levason, Champness & Webster, 1993), with Os—Cl = 2.434 Å, and Os—P(mean) = 2.36 Å. A greater *trans*-influence of PMe_2Ph compared with MeCN on Os—P bond lengths is also evident [the difference between Os—P(1,3) and Os—P(2) being approximately 0.05 Å].

The *trans*-MeCN—Os—P moiety is essentially linear and comparable to the MeCN—Ru—NCMe fragment recently described for *trans*-$[RuCl_4(MeCN)_2]^-$ (Gheller, Heath & Hockless, 1995).

The phenyl substituents on neighbouring phosphines seem specifically oriented about the nitrile ligand. Viewed down the P(1)–P(3) axis, these rings are eclipsed (and accidentally perpendicular to this axis) and are seen to partially enclose the MeCN group, with both phosphines tilted slightly in this direction.

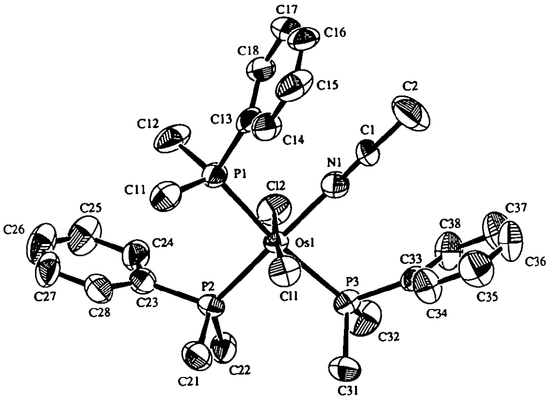


Fig. 1. View of (I) showing the labelling of all non-H atoms. Displacement ellipsoids are shown at the 50% probability level.

Experimental

X-ray quality crystals of (I) were obtained exactly as described by Coombe, Heath, Stephenson, Whitelock & Yellowlees (1985), and their identity as the initial kinetic product confirmed by $^{31}P\{^1H\}$ NMR. For the crystals redissolved in CD_2Cl_2: P_A = −47.3 (*t*), P_B = −35.5 p.p.m. (*d*) ($^2J_{P-P}$ = 21 Hz).

Crystal data

$[OsCl_2(C_2H_3N)(C_8H_{11}P)_3]$
M_r = 716.60

Mo $K\alpha$ radiation
λ = 0.7107 Å

Triclinic
$P\overline{1}$
$a = 9.132$ (2) Å
$b = 12.248$ (2) Å
$c = 13.622$ (3) Å
$\alpha = 95.72$ (2)°
$\beta = 105.60$ (2)°
$\gamma = 89.91$ (2)°
$V = 1459.7$ (5) Å^3
$Z = 2$
$D_x = 1.630$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 16.1$–19.9°
$\mu = 4.728$ mm^{-1}
$T = 295$ K
Prism
0.18 × 0.08 × 0.08 mm
Yellow

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: azimuthal ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.746$, $T_{\max} = 1.000$
5504 measured reflections
5150 independent reflections

4256 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.032$
$\theta_{\max} = 25.05°$
$h = 0 \rightarrow 10$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 15$
3 standard reflections monitored every 150 reflections intensity decay: 2.55%

Refinement

Refinement on F
$R = 0.044$
$wR = 0.061$
$S = 2.59$
4256 reflections
299 parameters
H-atom parameters not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.019F_o^2)^2]$
$(\Delta/\sigma)_{\max} = 0.007$

$\Delta\rho_{\max} = 2.26$ e Å^{-3}
$\Delta\rho_{\min} = -1.87$ e Å^{-3}
Extinction correction: Zachariasen (1967) type 2 Gaussian isotropic
Extinction coefficient: 2.9 (5) × 10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
Os(1)	0.03302 (5)	0.24307 (4)	0.27837 (3)	0.0334 (1)
Cl(1)	0.1198 (4)	0.2253 (3)	0.1227 (2)	0.052 (1)
Cl(2)	−0.0714 (4)	0.2659 (3)	0.4254 (2)	0.061 (1)
P(1)	0.1926 (4)	0.4014 (2)	0.3333 (2)	0.044 (1)
P(2)	0.2100 (3)	0.1251 (2)	0.3599 (2)	0.0396 (1)
P(3)	−0.1431 (4)	0.1000 (3)	0.1992 (2)	0.043 (1)
N(1)	−0.132 (1)	0.3469 (8)	0.2092 (8)	0.052 (4)
C(1)	−0.222 (2)	0.405 (1)	0.171 (1)	0.067 (5)
C(2)	−0.337 (2)	0.478 (1)	0.117 (2)	0.129 (9)
C(11)	0.380 (1)	0.394 (1)	0.310 (1)	0.071 (5)
C(12)	0.237 (2)	0.462 (1)	0.466 (1)	0.078 (6)
C(13)	0.115 (1)	0.5164 (9)	0.2626 (9)	0.047 (4)
C(14)	0.126 (2)	0.522 (1)	0.1629 (9)	0.055 (5)
C(15)	0.064 (2)	0.608 (1)	0.106 (1)	0.075 (6)
C(16)	−0.008 (2)	0.687 (1)	0.150 (1)	0.065 (5)
C(17)	−0.019 (2)	0.689 (1)	0.247 (1)	0.073 (5)
C(18)	0.036 (1)	0.6022 (10)	0.3021 (10)	0.055 (4)
C(21)	0.321 (1)	0.052 (1)	0.285 (1)	0.060 (5)
C(22)	0.137 (1)	0.013 (1)	0.4147 (9)	0.053 (4)
C(23)	0.357 (1)	0.1825 (9)	0.4753 (9)	0.047 (4)
C(24)	0.313 (1)	0.213 (1)	0.562 (1)	0.060 (5)
C(25)	0.421 (2)	0.257 (1)	0.653 (1)	0.076 (6)
C(26)	0.571 (2)	0.266 (1)	0.651 (1)	0.081 (6)
C(27)	0.614 (2)	0.235 (1)	0.567 (1)	0.073 (6)
C(28)	0.508 (1)	0.193 (1)	0.477 (1)	0.055 (5)
C(31)	−0.075 (1)	−0.017 (1)	0.133 (1)	0.060 (5)
C(32)	−0.250 (2)	0.034 (1)	0.274 (1)	0.070 (6)
C(33)	−0.299 (1)	0.1412 (9)	0.0933 (9)	0.043 (4)
C(34)	−0.276 (1)	0.147 (1)	−0.0012 (9)	0.056 (5)
C(35)	−0.392 (2)	0.178 (1)	−0.081 (1)	0.077 (6)
C(36)	−0.526 (2)	0.209 (1)	−0.065 (1)	0.071 (6)
C(37)	−0.551 (2)	0.208 (1)	0.026 (1)	0.076 (6)
C(38)	−0.436 (1)	0.173 (1)	0.109 (1)	0.063 (5)

Table 2. *Selected geometric parameters* (Å, °)

Os(1)—Cl(1)	2.447 (3)	Os(1)—P(3)	2.350 (3)
Os(1)—Cl(2)	2.432 (3)	Os(1)—N(1)	2.06 (1)
Os(1)—P(1)	2.362 (3)	N(1)—C(1)	1.14 (1)
Os(1)—P(2)	2.298 (3)	C(1)—C(2)	1.46 (2)
Cl(1)—Os(1)—Cl(2)	175.6 (1)	P(1)—Os(1)—P(2)	95.1 (1)
Cl(1)—Os(1)—P(1)	87.5 (1)	P(1)—Os(1)—P(3)	170.5 (1)
Cl(1)—Os(1)—P(2)	93.7 (1)	P(1)—Os(1)—N(1)	86.2 (3)
Cl(1)—Os(1)—P(3)	86.9 (1)	P(2)—Os(1)—P(3)	92.9 (1)
Cl(1)—Os(1)—N(1)	88.6 (3)	P(2)—Os(1)—N(1)	177.4 (3)
Cl(2)—Os(1)—P(1)	93.5 (1)	P(3)—Os(1)—N(1)	86.0 (3)
Cl(2)—Os(1)—P(2)	90.5 (1)	Os(1)—N(1)—C(1)	179 (1)
Cl(2)—Os(1)—P(3)	91.4 (1)	N(1)—C(1)—C(2)	176 (1)
Cl(2)—Os(1)—N(1)	87.2 (3)		

Anomalous-dispersion effects were included in F_c; the values for f' and f'' were those of Creagh & McAuley (1992). The θ scan width used was $(0.80 + 0.3\tan\theta)°$ at a speed of 8.0° min^{-1} (in ω). The weak reflections were rescanned a maximum of four times and the counts accumulated to ensure good counting statistics. Stationary background counts were made on each side of the reflection with a 2:1 ratio of peak to background counting time. H atoms were fixed at idealized positions with $U_{\rm iso} = 1.2U_{\rm eq}$(C). The structure was solved using Patterson methods and expanded using Fourier techniques (Beurskens *et al.*, 1992).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *DIRDIF PATTY* (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: TA1024). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Dinuclear Copper(II) Complex Bridged by a *trans*-Oxamidate Ligand

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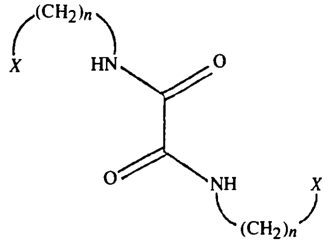
Abstract

The title complex, μ-*N*,*N*′-bis(2-aminoethyl)oxamidato-*N*,*O*′:*N*′,*O*-bis[(thiocyanato-*N*)copper(II)], $[Cu_2(NCS)_2(C_6H_{12}N_4O_2)]$, forms a centrosymmetric binuclear molecule with oxen^{2-} [*N*,*N*′-bis(2-aminoethyl)oxamide dianion] acting as a bis-chelating terdentate ligand. The structure consists of molecular Cu^{II}–Cu^{II} units in which the Cu^{2+} ions are bridged by an oxamidato group in a *trans* conformation, and are located in an approximately square-planar environment.

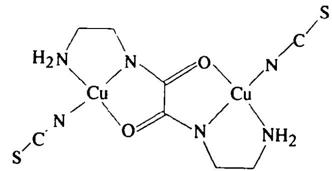
Comment

The *N*,*N*′-disubstituted oxamides, such as H$_2$oxen, constitute one of the most thoroughly investigated families of bridging ligands (Ojima & Nonoyama, 1988).



H_2oxen ($X = NH_2$, $n = 2$)

The versatility of these ligands is based on (i) the bidentate character of their mononuclear complexes, which can be used as chelating units towards a second metal ion to form polymetallic species (Journaux, Sletten & Kahn, 1985, 1986), (ii) the wide variety of substituted derivatives which can be obtained, yielding different numbers of chelate rings with different donor atoms (Ojima & Nonoyama, 1988), and (iii) their facile *cis*–*trans* conformational change affording symmetric and asymmetric bridges (Lloret *et al.*, 1992). Most of the copper(II) complexes have symmetrical *cis* oxamidato bridges; there are very few reports of crystal structures of copper(II) complexes with oxamidato bridges exhibiting the *trans* conformation (Bencini, Di Vaira, Fabretti, Gatteschi & Zanchini, 1984). The present paper describes the crystal structure of a dinuclear copper(II) complex of *N*,*N*′-bis(2-aminoethyl)oxamide, (I), with the *trans* conformation.



(I)

This complex forms a centrosymmetric binuclear molecule with oxen^{2-} acting as a bis-chelating terdentate ligand. The Cu^{II} ions are bridged by a *trans*-oxamidato group with an inversion centre at the midpoint of the C(1)—C(1*a*) bond, as illustrated in Fig. 1, which also shows the atom-labelling scheme. The packing of the crystal is depicted in Fig. 2.

Each Cu^{II} atom is in an approximately square-planar environment with three atoms [O, N(1) and N(2)] from the oxen^{2-} ligand and one atom [N(3)] from a thiocyanate. The largest deviation from the least-square plane through N(1), N(2), N(3) and O is 0.1405 Å at the O-atom site, and the Cu atom lies only 0.0543 Å out of this plane. The Cu—N(1) bond distance [1.928 (2) Å], which is shorter than Cu—O and Cu—N(2) [2.035 (1) and 2.038 (2) Å, respectively], is in agreement with those found in other oxamidato-bridged copper(II) complexes (Lloret *et al.*, 1992; Okawa, Matsumoto, Koikama, Takede & Kida, 1990). The significant shortening of the Cu—N(1) bond length agrees with the strong basicity of the deprotonated amide N atom.

The deprotonated oxen^{2-} ligand adopts the *trans* conformation forming a five-membered chelate ring with each metal ion. The three atoms Cu, C(2) and C(1*a*) around N(1) lie in a plane with bond angles about N(1) of 116.4 (1), 116.6 (1) and 126.5 (2)° for Cu—N(1)—C(2), Cu—N(1)—C(1*a*) and C(2)—N(1)—C(1*a*), respectively. These data, together with the bond lengths and planarity of the oxamidato bridge, reveal that N(1) and its symmetry-related atom N(1*a*) are sp^2 hybridized and that the π electrons of C(1)—O and C(1*a*)—O(*a*) are delocalized to form a conjugated

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