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Nitrogen vs. Oxygen Binding in Metal Complexes of Arylnitroso Ligands. Crystal and Molecular Structure of Dichlorobis(4-nitroso-*N*,*N*-dimethylaniline)cobalt(II)

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Received July 28, 1978

A crystal structure analysis of $CoCl_2(p\text{-}NOC_6H_4N(CH_3)_2)_2$ has shown the nitroso ligand to be bound to cobalt through its nitroso nitrogen atom rather than through oxygen as had originally been proposed. Crystals of this material are monoclinic, space group $I2/a$, with a = 23.518 (3) Å, b = 7.711 (1) Å, c = 20.977 (2) Å, β = 96.211 (8)°, and Z = 8. The structure determination was based upon 2582 nonzero intensity data refined to a final conventional R factor of 0.051. The cobalt atom is bound in a distorted tetrahedral configuration to two chlorine atoms and two nitroso nitrogen atoms. Mean Co–N and Co–Cl distances are 2.024 (4) and 2.237 (1) Å, respectively. The planarity of the amine nitrogen atom and a quinonoid distortion of the phenyl ring are consistent with a significant dipolar character for the nitroso ligand. Published spectroscopic data indicate that known related compounds have a similar mode of ligand binding and that no convincing evidence exists for monodenate O-bonded nitroso ligands.

Introduction

Metal complexes of simple *C*-nitroso ligands are of interest from several viewpoints. The nitroso function is isoelectronic with dioxygen and, like O_2, RN=O ligands have been shown to form adducts with metalloproteins,[1-6] metalloporphyrins,[6] and metallophthalocyanines.[7] An iron(II)–alkylnitroso complex has been proposed as an intermediate in the cytochrome-P450-dependent oxidative metabolism of amphetamines and other amino derivatives.[8] A number of complexes of zerovalent nickel group atoms with substituted nitrosobenzenes have been shown to undergo N–O bond cleavage followed by phenylnitrene and oxygen atom transfer reactions. In one case these reactions have provided a basis for a catalytic cycle.[9] Metal–RNO complexes have also been proposed as reaction intermediates in certain systems.[10,11]

Several modes of binding of RN=O ligands to transition metals have been observed or proposed. The two structurally characterized binding modes are monodentate N bonding[12] and a bridging configuration in which both the N and O atoms are metal bound.[13,14] There is also good evidence for a chelating N,O binding mode,[9,15] though this has not yet been documented by crystallographic data. Monodentate O binding is also possible in principle and has been proposed in a series of metal complexes of *p*-nitroso-*N*,*N*-dimethylaniline (henceforth abbreviated NODMA) and related ligands.[16,17] In an effort to determine whether the O-binding mode is realized in any of these complexes, we have investigated the crystal structure of $CoCl_2(NODMA)_2$; the results of this study are reported here.

Experimental Section

Preparation of the Complex. The procedure described in the literature[16] for preparation of $CoCl_2(NODMA)_2$ yielded a polycrystalline product which we were unable to recrystallize. Hence an alternative procedure was developed which yielded a crystalline material directly from the reaction mixture. In a typical preparation 0.12 g of $CoCl_2{\cdot}6H_2O$ (0.5 mmol) and 0.24 g of NODMA (1.5 mmol), each in 20 mL of warm absolute ethanol, were mixed. The warm solution was stirred for about 5 min and then allowed to stand overnight at room temperature. The dryness of the ethanol proved to be critical, with a noncrystalline precipitate obtained if it was too dry and no solid product forming if it was too wet. A fresh bottle of ethanol with no further drying seemed to give best results; if no solid product formed, crystallization could sometimes be induced by addition of a small amount (~1 mL) of triethyl orthoformate.

Collection and Reduction of the X-ray Data. The above preparative procedure yielded mainly clumps of very small crystals and larger twinned crystals; a few suitable single crystals were also obtained. The crystal used for data collection was a fragment of dimensions 0.32 × 0.24 × 0.17 mm cut from a larger rodlike crystal. Crystal faces were of the {100}, {101}, and {10$\bar{1}$} forms and the cut ends were approximately parallel to the {010} planes. Preliminary precession photographs displayed monoclinic symmetry, with systematic absences (hkl, $h + k + l \neq 2n$, $h0l$, $h \neq 2n$) consistent with space groups Ia and $I2/a$.[18] The density was determined by flotation in aqueous zinc bromide solution. Crystal data are summarized in part A of Table I.

Table I. Crystal Data and Experimental Parameters

A. Crystal Data

formula	$CoCl_2O_2N_4C_{16}H_{20}$	V	3781.7 (8) Å³
formula wt	430.20	Z	8
a	23.518 (3) Å	density(obsd)	1.509 g/cm³
b	7.711 (1) Å	density(calcd)	1.511 g/cm³
c	20.977 (2) Å	space group	$I2/a$
β	96.211 (8)°	μ(Mo Kα)	13.2 cm⁻¹

B. Experimental Parameters

radiation	Mo Kα, $\bar{\lambda}$ 0.710 73 Å, graphite monochromator	scan range	−1.0° from $K\alpha_1$ to +1.0° from $K\alpha_2$
		bkgd counting	stationary counts at each end of scan, each for half of scan time
temp	23 °C		
receiving aperture	circular, 4-mm diam, 20 cm from crystal	2θ(max)	50°
		data collected	3354
scan rate	constant, 2°/min in 2θ	data with $F_o^2 > 3\sigma(F_o^2)$	2582

Two complete sets of intensity data were collected. The solution and preliminary refinement of the structure were based upon 2287 independent nonzero data with $2\theta \leq 50°$, collected by previously described methods[19] on a Picker diffractometer. At an intermediate stage of refinement, it became apparent that this data set contained a few mis-set reflections. Since a new diffractometer was now available, the data were re-collected. The second data set forms the basis for all results reported here; hence only it will be described in detail.

Data were collected on a Syntex $P2_1$ automated diffractometer under the control of a Nova 1200 computer. The crystal was mounted in a glass capillary tube with its b axis approximately parallel to the diffractometer ϕ axis. Initial centering of reflections and generation of possible unit cell vectors were carried out by standard procedures which have been described.[20] Unit cell vectors were chosen to correspond to those previously identified by film methods. Refined cell parameters were based upon the setting angles of 15 reflections with $30° \leq 2\theta \leq 35°$. Profiles of 2θ and ω scans of several representative reflections showed symmetrical peak shapes and normal breadths in ω. Data were collected by the 2θ–θ scan technique in bisecting geometry. The pulse-height analyzer was set to admit approximately 95% of the Mo Kα peak. Other experimental parameters are tabulated in part B of Table I. A coincidence correction was applied to any reflection for which the counting rate exceeded 5000 counts/s. Two reflections (020, 400) had count rates beyond the valid range of this correction (>50 000 counts/s) and were remeasured at a lower filament current. Four standard reflections were

Table II. Atomic Positional and Thermal Parameters for $CoCl_2(p\text{-}NOC_6H_4NMe_2)_2$

(a) Positional and Isotropic Thermal Parameters

atom	*x*	*y*	*z*	$B,^b$ Å^2	atom	*x*	*y*	*z*	$B,^b$ Å^2
Co	0.10728 (3)[a]	0.23703 (8)	0.37949 (3)		C(7)	0.0666 (2)	0.2107 (7)	0.7276 (2)	4.00 (10)
Cl(1)	0.04982 (6)	0.00916 (18)	0.38745 (6)		C(8)	0.1642 (2)	0.3197 (7)	0.7636 (3)	4.19 (10)
Cl(2)	0.05784 (5)	0.48416 (16)	0.36290 (6)		N(2)	0.1225 (2)	0.2670 (5)	0.7101 (2)	3.19 (7)
N(1)	0.16307 (16)	0.30061 (55)	0.45683 (18)		C(11)	0.1499 (2)	0.1903 (6)	0.2476 (2)	2.80 (8)
N(11)	0.15872 (15)	0.16576 (52)	0.31228 (17)		C(12)	0.0972 (2)	0.2628 (6)	0.2211 (2)	3.14 (8)
O(1)	0.20671 (15)	0.37748 (58)	0.44096 (17)		C(13)	0.0851 (2)	0.2844 (6)	0.1571 (2)	3.31 (9)
O(11)	0.20203 (15)	0.08252 (52)	0.33540 (16)		C(14)	0.1253 (2)	0.2383 (6)	0.1143 (2)	3.03 (8)
C(1)	0.1559 (2)	0.2893 (6)	0.5200 (2)	2.99 (8)	C(15)	0.1799 (2)	0.1700 (6)	0.1414 (2)	3.25 (8)
C(2)	0.1044 (2)	0.2183 (6)	0.5368 (2)	3.21 (8)	C(16)	0.1904 (2)	0.1442 (6)	0.2055 (2)	3.26 (9)
C(3)	0.0929 (2)	0.2114 (6)	0.5992 (2)	3.19 (8)	C(17)	0.1561 (3)	0.2240 (7)	0.0058 (3)	4.46 (11)
C(4)	0.1330 (2)	0.2727 (6)	0.6488 (2)	2.84 (8)	C(18)	0.0567 (2)	0.3150 (7)	0.0224 (3)	4.42 (11)
C(5)	0.1868 (2)	0.3390 (6)	0.6318 (2)	3.30 (9)	N(12)	0.1135 (2)	0.2590 (5)	0.0507 (2)	2.38 (7)
C(6)	0.1968 (2)	0.3477 (6)	0.5697 (2)	3.36 (9)					

(b) Anisotropic Thermal Parameters[c]

atom	B_{11}	B_{22}	B_{23}	B_{12}	B_{13}	B_{23}
Co	2.82 (3)	3.60 (3)	2.44 (3)	−0.11 (2)	0.33 (2)	0.06 (2)
Cl(1)	4.49 (6)	4.27 (6)	3.86 (5)	−1.36 (5)	0.29 (4)	−0.15 (5)
Cl(2)	4.27 (6)	3.73 (6)	3.80 (5)	0.44 (5)	0.83 (4)	0.22 (4)
N(1)	2.59 (16)	4.53 (19)	3.00 (16)	−0.24 (15)	0.59 (13)	−0.09 (15)
N(11)	2.38 (15)	3.98 (18)	2.75 (15)	0.44 (14)	0.16 (12)	−0.01 (14)
O(1)	3.88 (17)	7.53 (25)	3.56 (16)	−1.65 (17)	1.16 (13)	−0.59 (16)
O(11)	3.95 (16)	5.75 (20)	3.28 (15)	1.46 (15)	−0.24 (12)	0.03 (14)

[a] In this table and throughout this paper, numbers in parentheses are standard deviations in the least significant figures. [b] Atoms for which no isotropic *B* is given were refined anisotropically. Thermal parameters for these atoms are tabulated in section (b) of this table. [c] The form of the anisotropic thermal ellipsoid is $\exp[-^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

monitored after each 50 data. For each of these standards the experimental standard deviation, based upon the variation of individual measurements from the average intensity, was of a magnitude comparable to that expected on the basis of counting statistics (σ(exptl)/σ(count) = 0.98, 1.06, 1.35, 0.99).

Data processing was carried out by use of the new locally written program SYNOUT. This program rejects redundant and systematically absent reflections, corrects for Lorentz and polarization effects (assuming a 50% mosaic–50% perfect monochromator crystal), analyzes standard reflections, performs some simple checks on peak profiles, and assigns standard deviations. The *p* factor in the expression[19] for the standard deviation of the observed intensities was given a value of 0.05. Sample calculations showed that the maximum range of transmission factors was 0.79–0.85. Hence no correction was made for absorption.

Structure Solution and Refinement. The structure solution presented some complications. Pseudosymmetry in the heavy-atom coordinates yielded a Patterson map[21] whose solution was not straightforward; hence direct methods were attempted. Intensity statistics indicated a centrosymmetric structure and the direct methods program REL yielded four independent sets of phases of high internal consistency. One of these phase sets ultimately led to successful solution of the structure. Isotropic full-matrix least-squares refinement of all nonhydrogen atoms yielded conventional discrepancy factors[22] R_1 = 0.091 and R_2 = 0.118. The final refinement incorporated anisotropic thermal parameters for the Co, Cl, and nitroso N and O atoms. The phenyl hydrogen atoms were included at their calculated positions (on the bisector of the C–C–C angle with C–H = 0.95 Å) but were not refined. A difference Fourier map prior to the final refinement cycles showed no peak greater than 0.7 e/Å^3 in height. No convincing evidence for the methyl hydrogen atoms appeared on this map; hence these atoms were not included in the refinement. At convergence the *R* factors were R_1 = 0.051 and R_2 = 0.073. In the final cycle, no parameter shifted by more than 0.1 of its standard deviation.

In all structure factor calculations, atomic scattering factors (including anomalous terms for Co and Cl) were taken from ref 23. The quantity minimized in least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$. The final standard deviation of an observation of unit weight was 2.21. Calculation of structure factors for the 771 data with $F_o^2 \leq 3\sigma(F_o^2)$ showed 16 reflections with $\Delta(F^2)/\sigma(F^2) > 3$; of these, 6 reflections had $\Delta F/\sigma > 4$ and 2 had $\Delta F/\sigma > 5$.

Final atomic positional and thermal parameters are listed in Table II. Bond distances and angles are tabulated in Tables III and IV, respectively. Data on least-squares planes are given in Table V. Tables of hydrogen atom positional parameters, principal amplitudes of thermal motion, and observed and calculated structure factors are available.[24]

Table III. Bond Distances, Å

Co–Cl(1)	2.234 (1.4)	Co–Cl(2)	2.240 (1.4)
Co–N(1)	2.033 (4)	Co–N(11)	2.016 (4)
N(1)–O(1)	1.261 (5)	N(11)–O(11)	1.272 (5)
N(1)–C(1)	1.356 (6)	N(11)–C(11)	1.363 (6)
C(1)–C(2)	1.408 (6)	C(11)–C(12)	1.419 (6)
C(2)–C(3)	1.365 (6)	C(12)–C(13)	1.352 (6)
C(3)–C(4)	1.410 (6)	C(13)–C(14)	1.416 (6)
C(4)–C(5)	1.444 (6)	C(14)–C(15)	1.446 (6)
C(5)–C(6)	1.349 (6)	C(15)–C(16)	1.355 (6)
C(6)–C(1)	1.415 (6)	C(16)–C(11)	1.413 (6)
C(4)–N(2)	1.336 (6)	C(14)–N(12)	1.343 (6)
N(2)–C(7)	1.468 (6)	N(12)–C(17)	1.474 (7)
N(2)–C(8)	1.466 (6)	N(12)–C(18)	1.466 (7)

Table IV. Bond Angles, Deg

Cl(1)–Co–Cl(2)	111.89 (6)	N(1)–Co–N(11)	104.20 (15)
Cl(1)–Co–N(1)	118.25 (12)	Cl(1)–Co–N(11)	104.18 (12)
Cl(2)–Co–N(1)	101.43 (12)	Cl(2)–Co–N(11)	117.30 (12)
Co–N(1)–O(1)	112.1 (3)	Co–N(11)–O(11)	113.0 (3)
Co–N(1)–C(1)	128.8 (3)	Co–N(11)–C(11)	129.2 (3)
O(1)–N(1)–C(1)	118.6 (4)	O(11)–N(11)–C(11)	117.8 (4)
N(1)–C(1)–C(2)	118.2 (4)	N(11)–C(11)–C(12)	117.7 (4)
N(1)–C(1)–C(6)	123.6 (4)	N(11)–C(11)–C(16)	124.0 (4)
C(1)–C(2)–C(3)	121.5 (4)	C(11)–C(12)–C(13)	121.2 (4)
C(2)–C(3)–C(4)	120.5 (4)	C(12)–C(13)–C(14)	121.0 (4)
C(3)–C(4)–C(5)	118.0 (4)	C(13)–C(14)–C(15)	117.9 (4)
C(3)–C(4)–N(2)	121.4 (4)	C(13)–C(14)–N(12)	121.2 (4)
C(5)–C(4)–N(2)	120.5 (4)	C(15)–C(14)–N(12)	120.9 (4)
C(4)–C(5)–C(6)	120.4 (4)	C(14)–C(15)–C(16)	120.2 (4)
C(5)–C(6)–C(1)	121.3 (4)	C(15)–C(16)–C(11)	121.3 (4)
C(4)–N(2)–C(7)	120.9 (4)	C(14)–N(12)–C(17)	122.1 (4)
C(4)–N(2)–C(8)	123.3 (4)	C(14)–N(12)–C(18)	121.4 (4)
C(7)–N(2)–C(8)	115.8 (4)	C(17)–N(12)–C(18)	116.5 (4)

Description and Discussion of the Structure

A view of the molecular stucture of dichlorobis(4-nitroso-*N*,*N*-dimethylaniline)cobalt(II) is shown in Figure 1. The metal atom is bound, in a slightly distorted tetrahedral

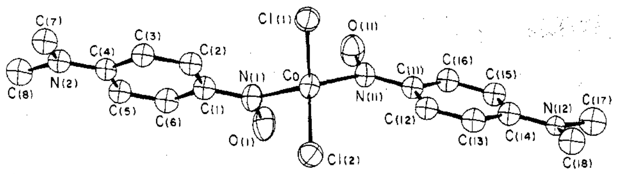


Figure 1. View of the molecular structure of $CoCl_2(NODMA)_2$. Thermal ellipsoids are drawn at the 50% probability level. For clarity, hydrogen atoms have been omitted.

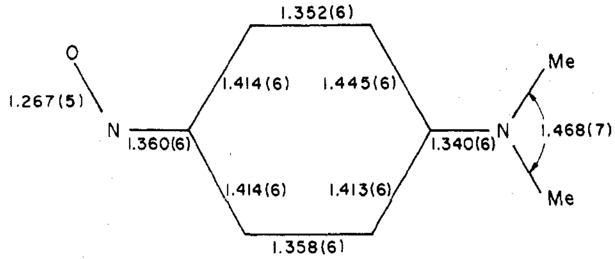
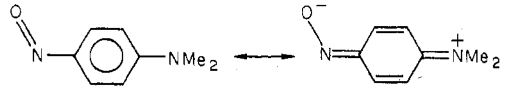


Figure 2. Mean bond distances within the NODMA ligand. Distances shown are averages over the two independent ligands. Figures in parentheses are standard deviations of an individual distance.

configuration, to two chlorine atoms and two monodentate NODMA ligands. The ligands are bound through their nitroso nitrogen atoms in a fashion qualitatively identical with that previously found in the square-planar palladium complex $PdCl_2(C_6H_5NO)_2$.[12] The tetrahedral configuration about the cobalt atom is slightly flattened, with Cl(1)–Co–N(1) and Cl(2)–Co–N(11) angles of 118.25 (12) and 117.30 (12)°, respectively, and Cl(1)–Co–N(11) and Cl(2)–Co–N(1) angles of 104.18 (12) and 101.43 (12)°. The mean Co–Cl and Co–N distances are 2.237 (1) and 2.024 (4) Å, respectively.

The configurations of the two crystallograpically independent NODMA ligands are in excellent agreement with each other; average values of bond distances within the ligand are shown in Figure 2. The distances of the six-membered ring show a definite quinonoid distortion, indicative of contribution to the ligand electronic structure from the dipolar resonance form II. Other distances are consistent with this interpretation, as may be seen by comparison of the nitroso N–C distance of 1.360 (6) Å and the N–O distance of 1.267 (5) Å with the corresponding values of 1.411 (3) and 1.209 (3) Å found in the unsubstituted nitrosobenzene ligands of $PdCl_2(C_6H_5NO)_2$. The structure of the free NODMA ligand is known, but its precision is limited by disorder involving the nitroso group.[25] A better comparison is with the ethyl analogue whose structure at −165 °C has recently been reported[26] and for which disordering appears to affect the precision only of the nitroso N–C and N–O distances. Bond distances in this molecule agree closely with those of the coordinated NODMA ligand, with the maximum difference between corresponding average distances being ~0.02 Å.



As is evident from information tabulated in Table V, the atoms of the ligand six-membered rings are closely coplanar. The NMe_2 and NO groups are, however, twisted by small amounts from the ring planes. The twist angles are 4.4 and 5.4° for the dimethylamino groups, while the nitroso groups are twisted by 5.4 and 7.2°. A comparable small twisting of the NEt_2 group (mean twist angle = 4.1°) is found in $p\text{-}NOC_6H_4NEt_2$. The NO group of that molecule appears to lie in the ring plane, but the disorder makes this conclusion somewhat uncertain. The only substantial difference between the configurations of the coordinated NODMA ligand and its free ethyl analogue involves the C–N–O angle, which is enlarged from its value of 112.6 (6)° in the free molecule to 118.2 (4)° in coordinated NODMA.

Table V. Least-Squares Planes and Dihedral Angles

Planes and Deviations[a]

(1) $-0.4012X + 0.9125Y - 0.0803Z = 0.1535$[b]

C(1)	0.014	C(4)	0.014
C(2)	−0.014	C(5)	−0.014
C(3)	0.000	C(6)	0.000
N(1)[c]	0.074	N(2)[c]	0.026
O(1)[c]	0.215	C(7)[c]	0.144
		C(8)[c]	−0.038

(2) $-0.3807X - 0.9026Y - 0.0869Z = -2.9331$

C(11)	0.006	C(14)	0.012
C(12)	0.010	C(15)	0.004
C(13)	−0.018	C(16)	−0.012
N(11)[c]	0.048	N(12)[c]	0.031
O(11)[c]	0.221	C(17)[c]	−0.060
		C(18)[c]	0.168

(3) $-0.3307X + 0.9406Y - 0.0772Z = 0.3824$

C(4)	0.003	C(7)	0.003
N(2)	−0.009	C(8)	0.003

(4) $-0.2932X - 0.9528Y - 0.0793Z = -2.7295$

C(14)	0.002	C(17)	0.002
N(12)	−0.006	C(18)	0.002

(5) $0.4415X - 0.8973Y - 0.0031Z = -0.9197$

Co	−0.011	O(1)	−0.016
N(1)	0.046	C(1)	−0.018

(6) $-0.4886X - 0.8644Y - 0.1186Z = -3.330$

Co	0.003	O(11)	0.004
N(11)	−0.011	C(11)	0.004

Angles between Normals to Planes, Deg

planes	angle	planes	angle
1–3	4.4	2–4	5.4
1–5	5.4	2–6	7.2

[a] Tabulated values are distances in Å to the plane. [b] Unit weights are employed in the calculations of all planes. The equations of the planes are expressed with respect to coordinates (X, Y, Z) referred to an orthogonal system (A, B, C) oriented with respect to the crystallographic axes such that A is parallel to a, B is parallel to $c^* \times a$, and C is parallel to $A \times B$. [c] These atoms were not used in definition of the plane.

The demonstration of an N-bonded configuration for the NODMA ligand in this complex suggests strongly that N bonding, rather than the proposed O bonding, prevails in the entire series of metal complexes of $p\text{-}NOC_6H_4NR_2$ ligands (NR_2 = NMe_2, NHMe, NH_2).[16,17] All of these complexes have N–O stretching frequencies in the narrow range of 1492–1515 cm^{-1}. These values are only slightly lower than those in the corresponding free nitroso compounds (1512–1539 cm^{-1}), consistent with the small observed changes in ligand geometry upon metal coordination. Other known coordination modes for *C*-nitroso ligands are associated with substantially lower ν(N–O) values; these frequencies are in the vicinity of 1000 cm^{-1} in complexes containing bridging or chelating RNO ligands.[9,15] Similarly reduced frequencies would be expected in complexes derived from the oxime tautomer of the nitroso ligand. Such complexes are known, but their N–O frequencies have not been assigned.[27–31]

In summary, this crystal structure analysis has demonstrated that the nitroso ligand in $CoCl_2(NODMA)_2$ is bound to the metal atom in a monodentate fashion through N rather than through O as had previously been proposed. On the basis of these results, N binding may be inferred in a series of related complexes and it may be concluded that at this time there is no convincing evidence for the existence of metal complexes containing monodentate O-bonded *C*-nitroso ligands.

Acknowledgment. The procedure for obtaining a crystalline sample of this material was developed in large part by Dr. G. P. Khare in this laboratory.

Registry No. $CoCl_2(NODMA)_2$ (N-bonded isomer), 21452-41-5; $CoCl_2(NODMA)_2$ (O-bonded isomer), 21512-32-3.

Supplementary Material Available: Table A, a listing of positional parameters of the phenyl hydrogen atoms, Table B, a tabulation of principal amplitudes of thermal motion, and Table C, a listing of observed and calculated structure amplitudes (20 pages). Ordering information is given on any current masthead page.

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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 8.[1,2] Elucidation of the Geometry and Connectivity of $(\mu\text{-H})Os_3(CO)_9[\overline{\text{CHC(=O)CH=CEtC}}\text{(=CHMe)}]$, a Molecule with a 3-Ethylidene-4-ethyl-1-oxocyclopent-4-en-2-yl Ligand Bridging Three Osmium Atoms

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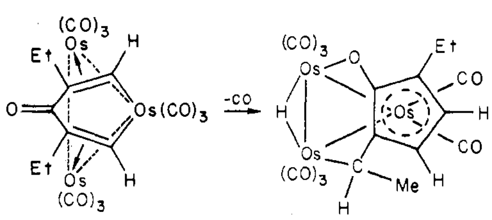
Received April 20, 1978

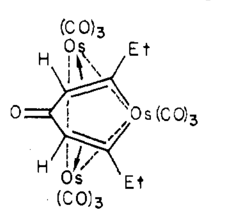
The complex $(\mu\text{-H})Os_3(CO)_9[\overline{\text{CHC(=O)CH=CEtC}}\text{(=CHMe)}]$ crystallizes in the centrosymmetric orthorhombic space group *Pbca* [D_{2h}^{15}; No. 61] with a = 10.984 (2) Å, b = 15.653 (2) Å, c = 25.169 (4) Å, V = 4327 (1) Å^3, Z = 8, and ρ(calcd) = 2.943 g cm^{-3} for mol wt 958.89. Diffraction data [3.5° < 2θ < 45°] were collected with a Syntex $P2_1$ automated diffractometer using graphite-monochromatized Mo Kα radiation. The structure was solved via Patterson, Fourier, and least-squares refinement techniques, the resulting discrepancy indices being R_F = 3.9% and R_{wF} = 3.3% for 2607 independent reflections with $|F_o| > 1.0\sigma(|F_o|)$. The molecule contains a triangular arrangement of osmium atoms, each of which is linked to one axial and two equatorial carbonyl ligands. Metal–metal distances are Os(1)–Os(2) = 2.928 (1) Å, Os(1)–Os(3) = 2.880 (1) Å, and Os(2)–Os(3) = 2.965(1)Å. Geometric considerations allow us to assign the μ_2-hydride ligand to the Os(2)–Os(3) bond. The remainder of the molecule consists of a 3-ethylidene-4-ethyl-1-oxocyclopent-4-en-2-yl ligand which is bonded via η^2 linkages to Os(1) and Os(2) and via an η^1 linkage to Os(3).

Introduction

It has been shown previously[1,3] that pyrolysis of the symmetrical osmiacyclohexadienone complex **1** proceeds cleanly under mild conditions (in refluxing cyclohexane for a short period), yielding a complex of stoichiometry "$Os_3(CO)_9(EtC{\equiv}CH)_2$", which has been identified unambiguously[1] as the hydrido–cyclopentadienyl species **2**. Pyrolysis of the second symmetrical osmiacyclohexadienone complex (**3**) under rather more drastic conditions (in refluxing xylene for $^1/_2$ h) yields a single product (**4**) of stoichiometry "$Os_3(CO)_{10}(EtC{\equiv}CH)_2$". The stereochemistry of this species is unknown; however, ^{1}H NMR studies[4] indicate that it contains a dienone



1 **2**



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