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Crystal Structure and Absolute Configuration of a Cobalt(III) Complex of a Linear Tetradentate Ligand: $(+)_{470}$-Δ-β-*cis*-Dinitro(5-methyl-1,4,8,11-tetraazaundecane)cobalt(III) Bromide

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The crystal structure and absolute configuration of a Co(III) complex of a linear tetradentate ligand, $(+)_{470}$-Δ-β-*cis*-dinitro-(5-methyl-1,4,8,11-tetraazaundecane)cobalt(III) bromide, $[Co\{NH_2(CH_2)_2NH(CH_2)_2CH(CH_3)NH(CH_2)_2NH_2\}(NO_2)_2]Br$, have been determined by X-ray diffraction methods. The crystals are monoclinic, with $a = 13.383$ (9), $b = 7.724$ (5), $c = 7.554$ (5) Å, $\beta = 110.94$ (2)°, space group $P2_1$, and $Z = 2$. A set of 2570 observed *hkl* reflections was obtained by counter methods. The molecular structure was determined by Patterson methods and refined by least squares to $R_1 = 0.034$ with the adjustment of 270 variables. The absolute configuration was determined with the aid of 200 selected $h\bar{k}l$ reflections. The cation adopts the β-cis geometry, with the substituent methyl group adjacent to the out-of-plane chelate ring. The arrangements at the asymmetric centers are *S* for each nitrogen atom and *R* for the carbon atom. The five-membered rings both have the λ conformation, and the six-membered ring has the chair conformation, with the substituent methyl group in an equatorial position. The coordination around the cobalt atom is slightly distorted from octahedral, with angles between adjacent coordinated atoms varying from 85.0 (2) to 93.7 (2)°. The average Co–N(ligand) distance is 2.000 (2) Å, for three of the ligand atoms, but the in-plane terminal amino group has Co–N = 1.968 (4) Å. The Co–NO_2 distances are 1.936 (2) Å.

Introduction

Recently, several crystal structures of cobalt(III) complexes containing the linear tetradentate ligand triethylenetetramine (trien) have been determined.[2-5] This ligand and other linear tetradentates[6-11] are currently of interest in explaining the origins of optical activity in *trans*-diacidocobalt(III) complexes. The optical properties of these complexes arise from the conformations of the chelate rings since no net chiral nature is associated with these materials. DeHayes, Parris, and Busch have reported on a series of optically active cobalt(III) linear tetradentate complexes containing different ring sizes and have interpreted their CD spectra on the basis of chelate ring conformations.[12] Two of these complexes, (+)-*trans*-$[Co(2,3',2)Cl_2]^+$, where 2,3′,2 is the tetradentate ligand 5-methyl-1,4,8,11-tetraazaundecane, are diastereomeric due to different secondary nitrogen configurations, and it was necessary to ascertain the absolute configuration of the asymmetric carbon atom before their CD spectra could be fully interpreted. Two approaches were undertaken simultaneously to elucidate the configuration. The first involved a synthesis of the tetradentate ligand from (*S*)-1,3-butanediamine[13] and the second a single-crystal analysis of a complex containing the optically active ligand.

Attempts to grow a single crystal of the *trans*-$[Co(2,3',2)Cl_2]^+$ complex suitable for X-ray diffraction were not successful. However, a suitable crystal of the *cis*-dinitro complex $(+)_{470}$-[β-*cis*-$(2,3',2)(NO_2)_2$]Br was obtained and this report deals with the single-crystal analysis and determination of the absolute configuration of this complex. The dinitro complex can be converted stereospecifically to enantiomers of the *trans*-dichloro species discussed earlier through a series of chemical processes using concentrated hydrochloric acid.[14]

Assigning geometry to cobalt(III) complexes containing the 2,3′,2 ligand and two coordinated nitro groups by methods other than X-ray analysis is tenuous. Although the trans species (Figure 1) can in principle be distinguished from the cis isomers using infrared[14] and ultraviolet[15] spectroscopy, distinguishing the α- and β-cis isomers is particularly difficult. Furthermore, identification with regard to positional isomerism due to the methyl group for the two β-cis isomers (Figure 1) is nearly impossible using other methods and is best left for a single-crystal analysis.

Experimental Section

A sample of $(+)_{470}$-β-*cis*-$[Co(2,3',2)(NO_2)_2]Br$ was generously supplied by Dr. E. H. Hung, who has described it synthesis elsewhere.[14] Recrystallization of this material from hot water produced orange square plates with sharply defined edges, as well as fibrous crystals. The latter were unsuitable for X-ray analysis. Both crystalline forms gave identical absorption and CD spectra. Photographs of the *h*0*l*, *h*1*l*, 0*kl*, and *hk*0 nets obtained by the Weissenberg and precession methods from a large platelike crystal indicated monoclinic symmetry, with the only condition 0*k*0, *k* = 2*n*. This condition is consistent with either of the space groups $P2_1$ ($C_2{}^2$) or $P2_1/m$ ($C_{2h}{}^2$). Since the complex is optically active, the space group is defined unambiguously as $P2_1$.

The unit cell dimensions were obtained by a least-squares method using 18 independent reflections aligned on a Picker four-circle diffractometer with a very narrow slit.[16] The temperature was 25° and the radiation used was Mo Kα (λ (Kα_1) 0.70926 Å). The dimensions were found to be $a = 13.383$ (9), $b = 7.724$ (5), $c = 7.554$ (5) Å, and $\beta = 110.94$ (2)°. The measured density of 1.83 (1) g/cm^3, obtained by flotation techniques in carbon tetrachloride–1,2-dibromoethane mixtures, agrees closely with the calculated density of 1.823 g/cm^3 for two formula units per unit cell.

Several attempts to grow crystals with dimensions compatible with the linear absorption coefficient of $\mu = 40.1$ cm^{-1} were unsuccessful. The crystal finally used was cut from a larger plate and had approximate dimensions of 0.3 × 0.3 × 0.3 mm. It was mounted on a glass

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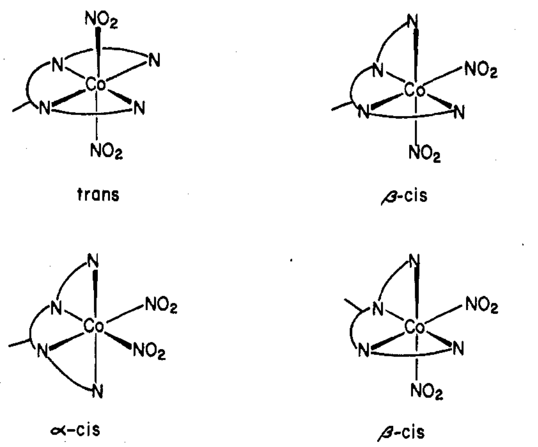

Figure 1. Possible geometric isomers for $[Co(2,3',2)(NO_2)_2]^+$.

fiber normal to one of the cut faces, assigned as the $21\bar{3}$ face. Data were collected by the θ-2θ scan method, with Mo Kα radiation, on a Picker four-circle diffractometer controlled by an EMR 6130 computer. The beam incident on the crystal was the 200 reflection from an oriented graphite monochromator crystal, 16 cm from the data crystal. The takeoff angle was 1.4°, resulting in a peak intensity of 70% of the maximum value as a function of takeoff angle. All independent data for the $+h,+k,\pm l$ quadrant to $(\sin\theta)/\lambda = 0.78$ ($2\theta = 67°$) were recorded, with a 2θ scan rate of 2.0°/min. For the 764 reflections with $2\theta \leqslant 40°$, a symmetrical 2θ scan of 2.0° was employed, with a 10-sec background count at the edge of each scan. For the data where $40° < 2\theta \leqslant 55°$ the scan width was increased to 2.40°, with 20-sec backgrounds. The final shell was collected with a 2.80° scan width and 20-sec backgrounds. Reflections whose observed maximum count rate exceeded 9000 cps were remeasured with an attenuated beam. The diffracted beams were passed through a limiting aperture 6.5 × 6.5 mm set 21 cm from the data crystal, and their intensities were recorded by a scintillation counter. The pulse height analyzer was set to accept about 98% of the energy centered on the Mo Kα peak. The intensities of 18 standard reflections having a wide range of intensities and spatial distributions were monitored every 400 reflections. These standards showed only a 1-2% random variation in intensity, for which no correction was made.

A set of 200 reflections was later recorded in the $+h,-k,\pm l$ quadrant, using the same scan width and background times as for the final shell of the first quadrant. These reflections are not equivalent to the corresponding reflections in the first quadrant owing to the anomalous scattering from the bromine and cobalt atoms. They were measured in order to assist in establishing the abolute configuration of the complex, and they were selected by the use of the condition

$$\frac{|F^+|_c - |F^-|_c}{\sigma(F_o)} \geqslant 2.2$$

where $\sigma(F_o)$ is the estimated standard deviation of an observed structure factor, defined below, and $|F^+|_c$ and $|F^-|_c$ represent structure factors calculated for the Δ and Λ structures, respectively, at an intermediate stage in the refinement ($R_1 = 0.08$).

The intensity data were corrected for background and were assigned standard deviations, using formulas described previously.[17] A factor $(pI)^2$, with $p = 0.05$, was added to the estimated variances, to allow for systematic effects.[16] Lorentz-polarization and absorption corrections were applied, and the intensities were reduced to a set of structure factors, F. The geometric corrections took the form

$$(Lp)^{-1} = (\sin 2\theta)/(\cos^2 2\theta_m + \cos^2 2\theta)$$

where θ_m is the angle at the monochromator crystal. This expression does not include the constant factor $(1 + \cos^2 2\theta_m)$. For the absorption correction, the bounding planes were assigned indices 100, $\bar{1}00$, 110, $\bar{1}10$, 001, $\bar{2}01$, $2\bar{3}0$, and $21\bar{3}$, the last two corresponding to the two cut faces of the crystal. The absorption corrections were found to vary from 2.06 to 2.69 on F^2. The method used was that described by Busing and Levy.[18] The description of the morphology of this irregular crystal required careful comparison of computer plots with views of the crystal in the microscope.

Of 3285 reflections measured, a total of 2569 reflections from both quadrants had $F^2 > 2\sigma(F^2)$ and were counted as observed.[19]

Solution and Refinement of the Structure

A sharpened Patterson function calculated using the 764 low-angle reflections revealed the positions of the cobalt and bromine atoms. In space group $P2_1$, the origin in the y direction is not fixed by symmetry, and the y coordinate of the bromine atom was arbitrarily fixed at 0.5. A weighted minimum function based on the coordinates of the cobalt and bromine atoms revealed the positions of all the rest of the atoms with the exception of the methyl carbon atom, which could be bonded either to C(5) or to C(7). After preliminary refinement of the partial structure by least squares, a difference Fourier synthesis was calculated. The methyl group was represented by a peak of height 2.7 e/Å^3 near C(7). At this point, the high-angle data and the 200 $h\bar{k}l$ reflections were introduced.

The model was now refined by block-diagonal least-squares methods, where the quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, with $w = 1/\sigma^2|F_o|$. Individual 9 × 9 matrices were constructed for the heavy atoms, which were refined anisotropically, and 4 × 4 matrices were constructed for the light atoms. Scattering factors for neutral Co, O, N, and C atoms were those tabulated by Hanson, *et al.*,[20] for the Br$^-$ ion, those by Cromer and Waber,[21] and for the H atoms those by Stewart, *et al.*[22] Anomalous scattering by the bromine and cobalt atoms was allowed for[23] using $\Delta f'$ and $\Delta f''$ values of Cromer.[24] Refinement converged with values of $R_1 = \Sigma|\Delta|/\Sigma|F_o|$ and $R_2 = [\Sigma w\Delta^2/\Sigma w|F_o|^2]^{1/2}$ of 0.053 and 0.066 where $\Delta = |F_o| - |F_c|$. On allowing the lighter atoms to vibrate anisotropically, R_1 and R_2 dropped to values of 0.044 and 0.054, representing a significant, although not overwhelming, improvement in the model.

The idealized locations of the hydrogen atoms in the methylene groups and in the terminal amino groups were calculated assuming C-H = 1.0 Å, N-H = 0.95 Å, and H-X-H = 109.5°.[25] Hydrogen atoms on the secondary amine nitrogen atoms and on the asymmetric carbon atom were located in a similar fashion.[26] A difference Fourier synthesis calculated at this stage revealed peaks above background at or close to each of these calculated positions and allowed a choice of the orientation of the methyl group. On including fixed contributions from all 22 hydrogen atoms with an isotropic thermal parameter $B = 3.0$ Å^2, further refinement of the nonhydrogen parameters converged with $R_1 = 0.0353$ and $R_2 = 0.0395$. When the parameters associated with the hydrogen atoms were also allowed to vary, convergence was reached after several cycles with final values of R_1 and R_2 of 0.0340 and 0.0375. The last two cycles of refinement involved the complete matrix.[27] The final parameters are listed in Tables I and II. The maximum discrepancy between the parameters obtained after convergence with the block diagonal method and these final parameters was 0.1σ. The structure factors calculated after the last cycle are given in Table III.[28] The average value of $w|\Delta|^2$ was 1.0, and the local average varied by no more than 1% in different ranges of $|F|$, while the variation with θ was from 1.1 at low angles to 0.95 at high angles.

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(28) Table III, a listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1734.

Table I. Positional and Thermal Parameters for All Atoms except Hydrogen

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{23}	β_{31}
Br	0.82105 (4)[b]	0.5	−0.23267 (6)	62.4 (3)	130.3 (8)	150.6 (9)	3.4 (5)	35.8 (8)	43.4 (4)
Co	0.79586 (3)	0.09455 (8)	0.16508 (6)	23.7 (2)	65.1 (6)	76.0 (7)	−2.8 (4)	9.3 (7)	14.6 (3)
N(1)	0.8546 (3)	0.2605 (5)	0.3727 (5)	46 (2)	87 (5)	103 (6)	−14 (3)	−15 (5)	22 (3)
C(2)	0.8301 (4)	0.4380 (6)	0.2978 (7)	64 (3)	70 (6)	139 (8)	−14 (4)	−19 (6)	34 (4)
C(3)	0.7156 (4)	0.4355 (6)	0.1660 (7)	61 (3)	79 (6)	148 (9)	20 (4)	4 (6)	39 (4)
N(4)	0.7017 (3)	0.2909 (5)	0.0293 (5)	38 (2)	88 (5)	99 (5)	10 (3)	13 (4)	28 (3)
C(5)	0.5869 (3)	0.2546 (7)	−0.0758 (6)	27 (2)	154 (9)	144 (8)	22 (4)	27 (7)	22 (3)
C(6)	0.5700 (3)	0.1201 (8)	−0.2281 (6)	26 (2)	182 (10)	112 (7)	7 (4)	31 (8)	2 (3)
C(7)	0.6155 (3)	−0.0572 (6)	−0.1637 (5)	29 (2)	138 (7)	86 (6)	−20 (3)	−6 (6)	12 (3)
Me(7)	0.5816 (4)	−0.1853 (9)	−0.3258 (7)	54 (3)	185 (11)	138 (9)	−43 (5)	−34 (8)	26 (4)
N(8)	0.7362 (3)	−0.0513 (4)	−0.0657 (4)	31 (2)	79 (5)	94 (5)	−8 (2)	0 (4)	19 (3)
C(9)	0.7908 (3)	−0.0064 (7)	−0.2020 (6)	40 (2)	108 (7)	124 (7)	−11 (4)	−4 (7)	42 (3)
C(10)	0.9067 (3)	0.0304 (7)	−0.0890 (6)	34 (2)	123 (7)	136 (7)	4 (3)	−5 (6)	40 (3)
N(11)	0.9094 (3)	0.1548 (5)	0.0617 (5)	30 (2)	84 (5)	121 (6)	−3 (3)	26 (5)	22 (3)
Nit(1)	0.8887 (2)	−0.0863 (5)	0.3111 (5)	29 (2)	89 (5)	126 (6)	−2 (3)	26 (5)	19 (3)
O(11)	0.9129 (3)	−0.2110 (5)	0.2345 (5)	75 (3)	93 (5)	208 (7)	27 (3)	31 (5)	48 (4)
O(12)	0.9240 (3)	−0.0754 (6)	0.4859 (5)	63 (2)	202 (8)	121 (6)	33 (4)	37 (6)	0 (3)
Nit(2)	0.6942 (2)	0.0104 (6)	0.2725 (4)	31 (2)	122 (6)	84 (5)	−5 (3)	18 (6)	21 (2)
O(21)	0.6716 (3)	−0.1427 (5)	0.2624 (4)	56 (2)	136 (6)	159 (7)	−33 (3)	10 (5)	47 (3)
O(22)	0.6550 (3)	0.1111 (6)	0.3576 (5)	64 (2)	173 (7)	180 (6)	12 (4)	9 (7)	73 (3)

[a] The β_{ij} have been multiplied by 10^4. The expression for the anisotopic temperature factor is $T = \exp[-2\pi(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2kl\beta_{23} + 2lh\beta_{31})]$. [b] The estimated standard deviations are given in terms of the last digit quoted.

Table II. Atomic Parameters for the Hydrogen Atoms

Atom	x	y	z	B,[a] Å^2
H(1)	0.931 (4)	0.261 (7)	0.438 (7)	2.1
H(2)	0.819 (4)	0.233 (8)	0.453 (7)	2.7
H(3)	0.873 (4)	0.482 (7)	0.220 (6)	1.7
H(4)	0.840 (4)	0.519 (11)	0.400 (9)	4.2
H(5)	0.695 (4)	0.529 (8)	0.102 (7)	2.1
H(6)	0.661 (4)	0.418 (7)	0.231 (7)	1.9
H(7)	0.728 (4)	0.322 (7)	−0.053 (6)	1.7
H(8)	0.554 (4)	0.360 (8)	−0.132 (7)	2.4
H(9)	0.553 (3)	0.225 (7)	0.019 (6)	1.9
H(10)	0.596 (4)	0.167 (8)	−0.304 (8)	3.4
H(11)	0.493 (4)	0.112 (7)	−0.290 (6)	2.1
H(12)	0.582 (3)	−0.097 (6)	−0.075 (6)	0.9
H(13)	0.504 (6)	−0.208 (10)	−0.366 (9)	4.6
H(14)	0.600 (5)	−0.301 (11)	−0.312 (9)	4.9
H(15)	0.597 (5)	−0.143 (10)	−0.439 (9)	4.5
H(16)	0.755 (4)	−0.159 (9)	−0.027 (8)	3.3
H(17)	0.756 (4)	0.094 (9)	−0.274 (7)	2.7
H(18)	0.777 (4)	−0.102 (7)	−0.271 (6)	1.4
H(19)	0.935 (3)	0.092 (8)	−0.178 (6)	1.9
H(20)	0.941 (5)	−0.079 (11)	−0.039 (9)	4.7
H(21)	0.973 (4)	0.151 (7)	0.137 (7)	1.9
H(22)	0.901 (3)	0.254 (7)	0.022 (6)	1.1

[a] The average standard deviation of the isotropic temperature factors was 1.0 Å^2.

The weighting scheme appears to be satisfactory. A final difference Fourier synthesis had as its most prominent features several peaks of heights 0.4–1.0 e/Å^3 in the neighborhood of the bromine and cobalt atoms.

The final structure has the Δ configuration.[29] When the final coordinates in Table I were inverted so as to give the Λ structure, convergence was reached with $R_1 = 0.0526$ and $R_2 = 0.0700$, values which are significantly higher than the corresponding values of 0.0341 and 0.0375 for the Δ structure. Of the 200 hkl-$h\bar{k}l$ pairs, 187 had observed ratios $|F_o(hkl)|/|F_o(h\bar{k}l)|$ which indicated the Δ structure. In none of the remaining 13 cases was the observed difference between $|F_o(hkl)|$ and $|F_o(h\bar{k}l)|$ significant at the 95% confidence level. Table IV lists data on those planes for which $|F_c(hkl)| - |F_c(h\bar{k}l)|$ exceeded 3 times the estimated standard deviation of this quantity.

Description and Discussion of the Structure

This analysis establishes the β-cis geometry for the present compound, $(+)_{470}$-[Co(2,3′,2)(NO$_2$)$_2$]Br, with the methyl substituent of the six-membered ring bonded to the carbon atom adjacent to the out-of-plane chelate ring. The absolute configuration of the cation is Δ, and the arrangements of groups around the asymmetric atoms N(4), C(7), and N(8) are *S*, *R*, and *R*, respectively, using the notation of Cohn, Ingoll, and Prelog.[30] The five-membered rings both have the λ conformation,[29] and the six-membered ring has the chair conformation. The thermal motions of the atoms are indicated in the stereoscopic pair in Figure 2, and a projection of the structure down the *a* axis is given in Figure 3. Intramolecular bond distances and angles and their standard deviations are reported in Table V. To date, only one crystal structure has been reported for a metal complex of a linear tetradentate ligand containing six-membered chelate rings, the ligand in that case being 1,5,8,12-tetraazaduodecane (3,2,3) bound in the trans geometry.[11]

Table IV. Selected Pairs of Reflections Demonstrating the Absolute Configuration of $(+)_{470}$-*β-cis*-[Co(2,3′,2)(NO$_2$)$_2$]Br

$h\ k\ l$	$\lvert F_o(hkl)\rvert$, e	$\lvert F_o(h\bar{k}l)\rvert$, e	$\lvert F_c(hkl)\rvert$, e Δ	 Λ
$\bar{9}$ 1 1	30.9	26.4	31.5	27.6
3 1 1	49.4	44.5	51.4	45.9
9 1 1	19.0	21.4	19.1	21.7
11 1 1	9.1	11.1	8.7	11.3
7 2 1	27.6	25.3	28.1	24.7
$\overline{11}$ 3 1	21.0	18.2	21.0	18.5
0 5 1	21.3	17.1	21.6	18.2
$\bar{7}$ 1 2	28.6	32.6	28.8	33.3
0 1 2	9.5	5.3	9.5	6.9
1 1 2	6.2	11.4	5.9	10.2
$\bar{5}$ 1 3	53.4	45.9	52.1	45.2
1 1 3	17.9	20.4	17.7	20.0
3 1 3	16.4	19.5	16.5	18.8
5 1 3	8.6	7.0	8.4	6.1
6 1 3	15.5	19.4	15.4	18.6
1 2 3	22.2	19.1	22.9	19.7
$\overline{11}$ 2 4	29.3	25.9	30.1	26.9
$\bar{5}$ 1 5	17.9	22.7	17.5	21.3
3 1 5	11.5	15.0	11.0	14.3
$\bar{7}$ 2 5	21.6	18.7	21.3	18.7
0 1 6	12.7	8.2	12.2	9.7

In spite of the asymmetry imposed by the β-cis geometry, the geometries of the five-membered chelate rings in the present compound are remarkably similar. The Co-N(1) bond length is 1.968 (4) Å after correction for thermal motion assuming the nitrogen to ride on the cobalt atom. This distance is significantly shorter than the values of 2.008 (4), 1.991 (4), and 2.001 (3) Å for the chelate bonds Co-N(4),

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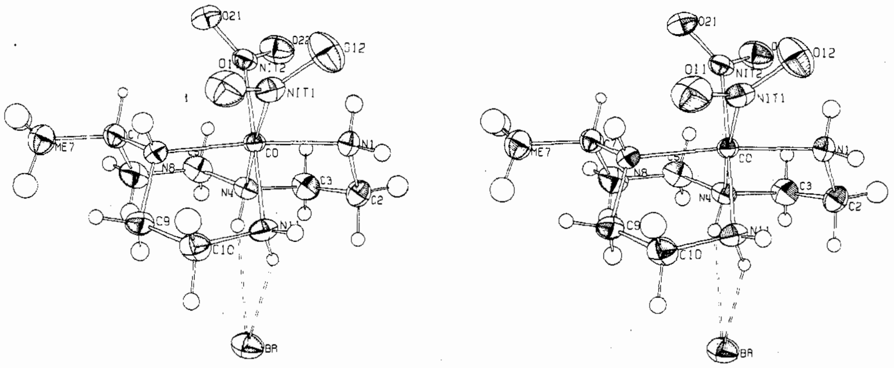

Figure 2. Stereoscopic pair showing atom numbering and thermal motion in $[Co(2,3',2)(NO_2)_2]Br$. The anisotropic atoms are plotted as 50% probability ellipsoids of thermal motion, while the hydrogen atoms are plotted as 20% probability bonding spheres. H(1) and H(2) are bonded to N(1), and H(21) and H(22) are bonded to N(11). The numbering system used in the crystallographic analysis is different from that used in the systematic name of the tetradentate ligand.

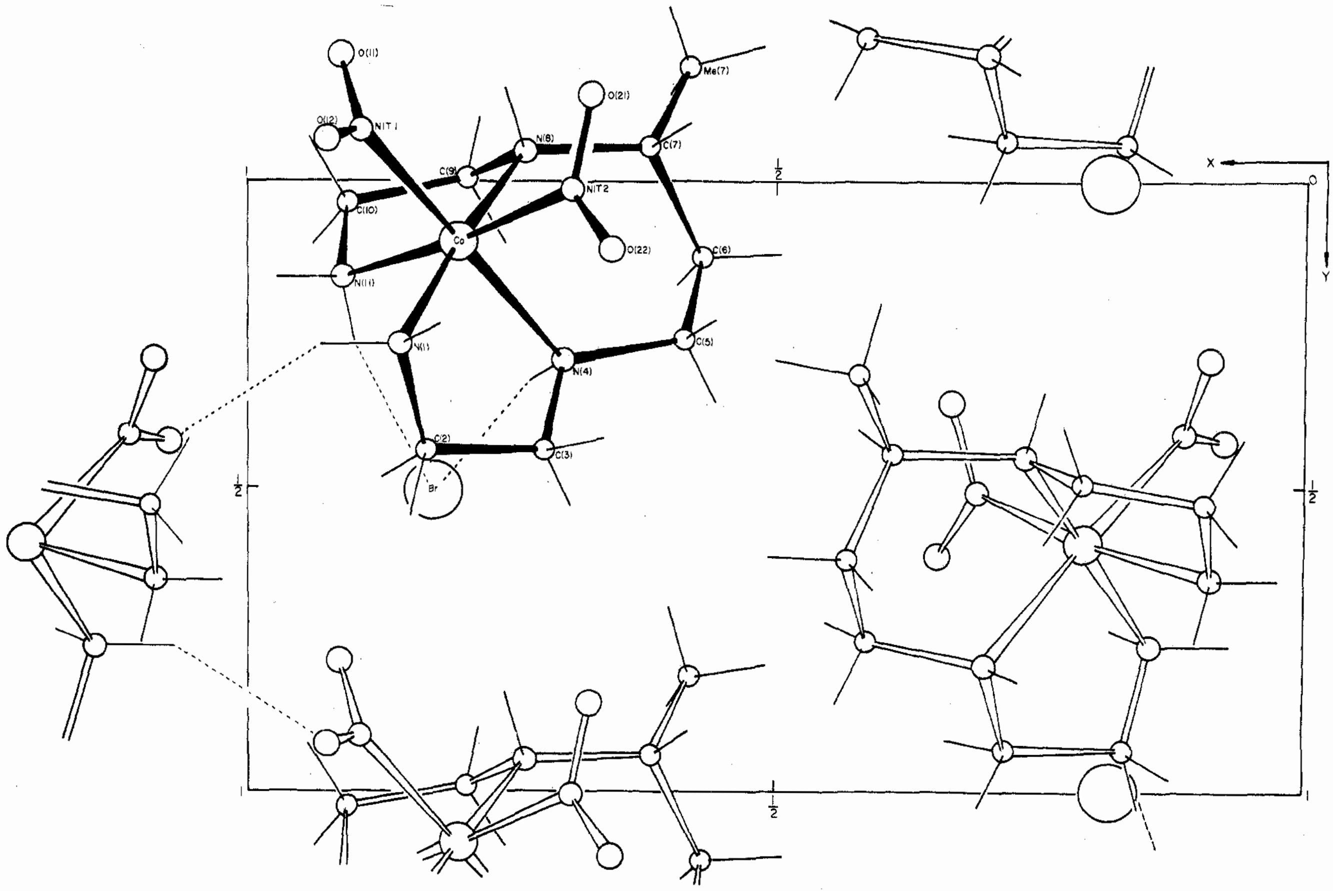

Figure 3. Projection of the crystal structure of $[Co(2,3',2)(NO_2)_2]Br$ down the *c* axis.

Co-N(8), and Co-N(11), respectively. These last three bond lengths have an average value of 2.000 (2) Å. The Co-N(1) distance is the same as an unweighted average Co-N distance of 1.969 (2) Å, found in a number of recent determinations of the tris(ethylenediamine)cobalt(III) cation,[31-36] and is in the range of Co-N distances of 1.90-1.97 Å reported for a number of cis structures containing the 2,2,2 ligand trien: *β-cis*-$[Co(trien)(Cl)(H_2O)]^{2+}$, *α-cis*-$[Co(trien)(NH_3)(Cl)]^{2+}$, L-*β-cis*-(*SSS*)-[Co(trien)(*S*-Pro)]$^{2+}$, and D-*β-cis*-(*SSS*)-[Co(trien)(*S*-Pro)]$^{2+}$ [2-5] (*S*-Pro = (*S*)-prolinato). The ring angles at the cobalt atom for the five-membered rings, N(1)-Co-N(4) and N(8)-Co-N(11), are identical at 85.0 (2)°. These angles appear normal for Co(III) five-membered chelate rings, comparing well with a value of 85.1 (2)° averaged over six recent determinations of structures containing the $[Co(en)_3]^{3+}$ cation.[31-36] In the series of trien compounds mentioned earlier, the ring angles at the cobalt atom range from 84.5 (4) to 87.3 (3)°, this last for the heavily strained central ring in the α-cis trien structure. In the trans 3,2,3 complex, the corresponding angle is 85.6°.[11] Apparently, this particular parameter of the five-membered chelate ring is relatively insensitive to the presence of fused rings.

The angle at cobalt for the six-membered ring, N(4)-Co-

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Table V. Bond Distances and Bond angles

Atoms	Distance, Å Uncor	Distance, Å Cor for thermal motion[a]	Atoms	Angle, deg	Atoms	Angle, deg
Co-N(1)	1.960 (4)	1.968	N(1)-Co-N(4)	85.0 (2)	Co-N(1)-C(2)	109.3 (3)
Co-N(4)	2.004 (4)	2.008	N(1)-Co-N(8)	173.4 (2)	Co-N(11)-C(10)	109.7 (2)
Co-N(8)	1.988 (3)	1.991	N(1)-Co-N(11)	91.0 (2)	Co-N(4)-C(3)	108.3 (3)
Co-N(11)	1.997 (3)	2.001	N(1)-Co-Nit(1)	91.4 (2)	Co-N(8)-C(9)	109.2 (3)
Co-Nit(1)	1.932 (4)	1.938	N(1)-Co-Nit(2)	91.4 (2)	Co-N(4)-C(5)	118.2 (3)
Co-Nit(2)	1.929 (3)	1.934	N(4)-Co-N(8)	89.9 (2)	Co-N(8)-C(7)	117.9 (2)
Nit(1)-O(11)	1.225 (5)	1.248	N(4)-Co-N(11)	92.9 (2)	N(1)-C(2)-C(3)	106.1 (4)
Nit(1)-O(12)	1.236 (5)	1.264	N(4)-Co-Nit(1)	176.3 (2)	N(4)-C(3)-C(2)	108.4 (4)
Nit(2)-O(21)	1.216 (6)	1.233	N(4)-Co-Nit(2)	93.5 (2)	N(8)-C(9)-C(10)	108.0 (3)
Nit(2)-O(22)	1.239 (5)	1.261	N(8)-Co-N(11)	85.0 (2)	N(11)-C(10)-C(9)	107.2 (3)
N(1)-C(2)	1.475 (6)		N(8)-Co-Nit(1)	93.7 (2)	N(6)-C(5)-C(6)	112.5 (3)
C(2)-C(3)	1.499 (7)		N(8)-Co-Nit(2)	93.2 (1)	N(8)-C(7)-C(6)	111.5 (3)
C(3)-N(4)	1.488 (6)		N(11)-Co-Nit(1)	88.2 (1)	N(8)-C(7)-Me(7)	111.9 (4)
N(4)-C(5)	1.482 (6)		N(11)-Co-Nit(2)	173.3 (2)	C(6)-C(7)-Me(7)	111.3 (4)
C(5)-C(6)	1.506 (7)		Nit(1)-Co-Nit(2)	85.5 (2)	C(5)-C(6)-C(7)	116.5 (3)
C(6)-C(7)	1.508 (7)		Co-Nit(1)-O(11)	121.6 (3)	Co-N(1)-H(1)	118 (3)
C(7)-Me(7)	1.513 (7)		Co-Nit(1)-O(12)	118.9 (3)	Co-N(1)-H(2)	103 (3)
C(7)-N(8)	1.518 (5)		Co-Nit(2)-O(21)	119.9 (3)	Co-N(11)-H(21)	117 (3)
N(8)-C(9)	1.500 (5)		Co-Nit(2)-O(22)	120.0 (3)	Co-N(11)-H(22)	109 (3)
C(9)-C(10)	1.507 (6)		O(11)-Nit(1)-O(12)	119.6 (4)	C(2)-N(1)-H(1)	104 (3)
C(10)-N(11)	1.480 (6)		O(21)-Nit(2)-O(22)	120.0 (3)	C(2)-N(1)-H(2)	112 (4)
N-H	0.82-0.96		Av X-N-H (N secondary)	106 (1)	C(10)-N(11)-H(21)	104 (3)
Av N-H	0.88 (2)		Av C-C-H (methyl)	115 (4)	C(10)-N(11)-H(22)	112 (3)
C-H	0.85-1.02		Av H-C-H (methyl)	103 (4)		
Av C-H	0.96 (2)		Av H-C-H (methylene)	109 (2)		
			Av H-N-H	108 (4)		

[a] Correction for riding motion assumes that the second atom rides on the first.

Table VI

Selected Least-Squares Planes[a]

Plane	Atoms forming plane	Eq of plane:[b] $aX + bY + cZ = d$ a	b	c	d
1	Co, N(1), N(4), N(8), Nit(1)	0.8908	0.2961	−0.3447	8.929
2	Co, N(1), N(8), N(11), Nit(2)	−0.4568	0.7292	−0.5096	−4.731
3	Co, N(4), N(11) Nit(1), Nit(2)	0.1385	0.6119	0.7787	2.778

Displacements from Planes

Plane	Displacement, Å Co	N(1)	N(4)	N(8)	N(11)	Nit(1)	Nit(2)
1	−0.024	0.052	−0.40	0.048		−0.037	
2	0.009	0.009		0.097	−0.102		−0.098
3	−0.010		0.048		−0.044	0.054	−0.047

[a] These unweighted least-squares planes were calculated with a program by Palenik [G. J. Palenik, Chemistry Dept., University of Florida, private communication]. [b] The coordinates X, Y, and Z are expressed in angstroms relative to a cartesian set of axes parallel to a, b, and c^*.

Table VII. Selected Torsional Angles (deg)

Co-N(1)-C(2)-C(3)	−43.9 (4)
N(1)-C(2)-C(3)-N(4)	51.8 (5)
C(2)-C(3)-N(4)-Co	−35.4 (4)
C(3)-N(4)-Co-N(1)	8.8 (3)
N(4)-Co-N(1)-C(2)	19.8 (3)
Co-N(8)-C(9)-C(10)	−37.2 (4)
N(8)-C(9)-C(10)-N(11)	50.5 (5)
C(9)-C(10)-N(11)-Co	−39.4 (4)
C(10)-N(11)-Co-N(8)	15.3 (3)
N(11)-Co-N(8)-C(9)	12.4 (3)
Co-N(4)-C(5)-C(6)	59.2 (4)
N(4)-C(5)-C(6)-C(7)	−61.5 (5)
C(5)-C(6)-C(7)-N(8)	61.3 (5)
C(6)-C(7)-N(8)-Co	−59.7 (4)
C(7)-N(8)-Co-N(4)	48.0 (3)
N(8)-Co-N(4)-C(5)	−48.0 (3)

N(8), is 89.9 (2)°, not different from the idealized value of 90° for octahedral coordination. This angle is significantly larger than the angle in the central ring in the cis trien structure, but it is smaller than the N-Co-N angles of the six-membered rings in other cobalt complexes. In the 3,2,3 complex the angles are 92.5 (3) and 92.6 (3)°,[11] while in the complexes *trans*-$[Co(tn)_2(Cl)_2]Cl \cdot HCl \cdot 2H_2O$[37] and $[Co(tn)_3]Br_3 \cdot H_2O$,[38] where tn represents the simple bidentate ligand trimethylenediamine, the angles are 95.4 and 94.5°, respectively. Clearly the magnitude of the N-Co-N angle of the six-membered rings depends on the degree to which the N atoms are constrained. In the tn complexes, where the N atoms are both primary, the angle at the cobalt atom is 95°; in the 3,2,3 complex, where one N atom is primary and the other secondary, the angle is 92.5°; and in the present 2,3′,2 complex, where the N atoms are both secondary, the angle is reduced to 90°.

With the exception of C(7)-N(8), the average C-N distance is 1.485 (3) Å. The bond distance C(7)-N(8) is 1.518 (5) Å which is significantly longer than the other C-N bonds, perhaps due to strain caused either by the neighboring methyl group or the adjacent out-of-plane chelate ring. The $C\text{-}NH_2$ bond lengths appear to be very slightly shorter than the C-NH bonds, but the difference is barely significant. The average C-C distance is 1.507 (2) Å.

The bond angles at nitrogen within the six-membered ring average 118.1 (2)°, very much larger than the angles at nitrogen atoms within the five-membered rings, which average 109.1 (2)°. There is no significant difference between angles at the primary and secondary nitrogen atoms in the latter case. The N-C-C angles in the six-membered chelate ring average 112.0 (3)°, very similar to the angles of

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(37) K. Matsumoto, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Jap.*, 43, 1903 (1970).

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Table VIII

(a) Interionic Distances[a]

Atom 1	Atom 2	Symmetry of atom 2	Dist, Å
H(1)	O(12)	$2-x, {}^1/_2+y, 1-z$	2.21
H(3)	O(11)	$x, 1+y, z$	2.42
H(9)	H(12)	$1-x, {}^1/_2+y, \bar{z}$	2.43
H(20)	H(22)	$2-x, y-{}^1/_2, \bar{z}$	2.44
H(7)	Br	x, y, z	2.55
H(22)	Br	x, y, z	2.64
C(2)	O(11)	$x, 1+y, z$	3.03
N(1)	O(21)	$2-x, {}^1/_2+y, 1-z$	3.04
C(2)	O(12)	$2-x, {}^1/_2+y, 1-z$	3.11
C(9)	O(22)	$x, y, z-1$	3.30
C(5)	O(21)	$1-x, {}^1/_2+y, \bar{z}$	3.33
Br	N(4)	x, y, z	3.37
Br	N(11)	x, y, z	3.40
C(10)	O(12)	$x, y, z-1$	3.40
C(3)	O(21)	$x, 1+y, z$	3.43
N(1)	O(11)	$2-x, {}^1/_2+y, 1-z$	3.45
Me(7)	O(22)	$1-x, y-{}^1/_2, z$	3.47
C(9)	O(12)	$x, y, z-1$	3.47

(b) Intraionic Distances[b]

Atom 1	Atom 2	Dist, Å	Atom 1	Atom 2	Dist, Å
H(10)	H(17)	2.15	H(3)	H(22)	2.42
H(7)	H(22)	2.24	H(12)	O(21)	2.42
H(12)	O(22)	2.26	H(20)	O(11)	2.45
H(15)	H(18)	2.31			

[a] All distances up to 3.5 Å are listed for the nonhydrogen atoms. Distances involving hydrogen are given up to 2.5 Å, except for the H· · ·Br contacts. [b] Distances up to 2.5 Å are given for nonbonding contacts excluding second and third neighbor contacts.

111.5° in cyclohexane.[39] In the five-membered rings, the N-C-C angles are smaller, averaging 107.5 (5)°, the angles involving the primary nitrogen atoms being smaller than those involving the secondary nitrogen atoms. The angles involving the amine hydrogen atoms appear quite regular, although not necessarily tetrahedral, and this is true also for the angles involving the other hydrogen atoms.

The bond angles around the cobalt atom between adjacent coordinated atoms range from 85.0 (2)° for N(8)-Co-N(11) to 93.7 (2)° for N(4)-Co-Nit(1), while the angles between trans-related atoms deviate from 180° as far as a value of 173.3 (2)° for N(11)-Co-Nit(2). Thus the symmetry of the coordination sphere is significantly lower than octahedral. The two nitro groups (Nit) are pushed together by the folded ligand, the angle Nit(1)-Co-Nit(2) being reduced to 85.5 (2)°.

Least-squares planes through the cobalt atom and three different groups of nitrogen atoms are presented in Table VI. Due to the steric requirements of the ligand, none of the equatorial groups of atoms in the cobalt octahedron are particularly planar. The nitro groups do not lie in any of the equatorial planes, the group containing Nit(1), O(11), and O(12) lying at an angle of 21.3° with the best plane through Co, N(1), N(4), N(8), and Nit(1), while the other nitro group lies at a larger angle of 38.4° with the best plane through Co, N(1), N(8), N(11), and Nit(2). The planes through the nitro groups make an angle of 71° with each other.

The geometry of the coordinated nitro groups in the present compound is closely similar to that found in related complexes. The distances Co-Nit(1) and Co-Nit(2) are identical within experimental error, averaging 1.936 (2) Å after correction for thermal motion, while the mean corrected N-O distance is 1.252 (7) Å. These compare with corresponding distances of 1.954 (7) and 1.257 (7) Å in the related trans 3,2,3 complex.[11] Values ranging from 1.90 to 1.97 Å are reported for the Co-N distance in a variety of nitro complexes of Co(III).[40]

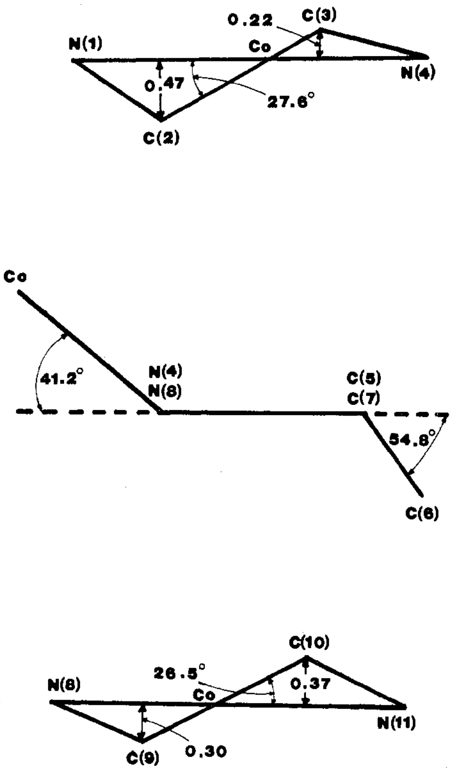

Figure 4. The conformations of the chelate rings.

The conformations of the three chelate rings in this structure are represented diagrammatically in Figure 4, and relevant torsional angles are given in Table VII. The two five-membered rings each have the λ conformation,[29] and the carbon atoms in each case are displaced on opposite sides of the appropriate N-Co-N plane. Interestingly, it is the out-of-plane ring (Co, N(8), C(9), C(10), N(11)) which is the more symmetric. This is in contrast to the β-cis trien complexes, where the central rings are the more symmetric.[2-5] The amelioration of this distortion in the present complex is presumably due to the strain-relieving effects of the central six-membered ring relative to the five-membered ring in a trien complex. The conformations of five-membered chelate rings have also been represented in terms of torsional angles α and β,[41] where α is the angle between the CoN_2 and the CoC_2 planes, and β is the dihedral angle down the C-C bond. These parameters show the conformations of the two terminal chelate rings to be very similar in the present compound, the values of α and β being 27.6 and 51.8° and 26.5 and 50.0° for the in-plane and out-of-plane chelate rings, respectively. These values are closely similar to average values α = 27.0 (4)° and β = 50.4 (7)°, which we have calculated from parameters given in recent determinations of the $[Co(en)_3]^{3+}$ cation,[31-36] and are also consistent with the corresponding angles for equivalent rings in the β-cis trien complexes.

The central six-membered ring of the Co(2,3′,2) complex has a chair conformation, the atoms N(4), C(5), C(7), and N(8) being strictly coplanar. The tilt angles represented in

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Figure 4[42] and the torsional angles in Table VII indicate puckering of the carbon portion of the chelate ring relative to cyclohexane, where the tilt angle is 49.6°, and the torsional angles are 54.6°. This puckering is in response to the long Co-N bond and the small ring angle at cobalt of 90°. The terminal angle C(5)-C(6)-C(7) is 116.5°, considerably larger than in cyclohexane.

The molecular packing is illustrated in Figure 3 and some nonbonding distances are given in Table VIII. There are two N-H· · ·Br hydrogen bonds, of lengths 3.37 and 3.40 Å, linking the bromide ion to the same cation. The resulting ion pair is linked by an N-H· · ·O hydrogen bond to a screw-related ion pair, the distance N(1)· · ·O(21) being 3.04 Å and the angle at the hydrogen atom being 145°. The distance between C(2) and O(11) of the molecule related by a translation along *b* is quite short at 3.03 Å, but there is no evidence for C-H· · ·O hydrogen bonding, the distances H(3)· · ·O(11) and H(4)· · ·O(11) being 2.42 and 2.78 Å, respectively. The shortest contact within the cation is between H(10) and H(17), at 2.15 Å.

Registry No. Δ-*β*-*cis*-Dinitro(5-methyl-1,4,8,11-tetraazaundecane)cobalt(III) bromide, 39561-37-0.

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Crystal and Molecular Structure of a Stable π-Oxopropenylmanganese Tricarbonyl Complex

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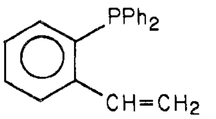
The crystal and molecular structure of a stable π-oxopropenyl complex 2-(1′,2′-dimethyloxopropenyl)phenyldiphenylphosphinomanganese tricarbonyl, $[\pi\text{-}\{O\cdots C(CH_3)\cdots C(CH_3)\}C_6H_4P(C_6H_5)_2Mn(CO)_3]$, has been determined from three-dimensional X-ray data collected by counter methods. Crystals are triclinic, space group $P\bar{1}$ (C_i^1, No. 2), with $a = 9.303$ (5), $b = 11.689$ (6), $c = 10.654$ (6) Å, $\alpha = 81.90$ (2), $\beta = 96.64$ (2), $\gamma = 83.71$ (2)°, $Z = 2$. The measured and calculated densities are 1.38 (1) and 1.38 g cm^{-3}, respectively. The structure was solved by conventional heavy-atom techniques and was refined by block-diagonal least-squares methods to weighted and unweighted *R* factors of 0.053 and 0.038, respectively, for the 2953 independent reflections with $I/\Delta(I) \geq 3.0$. The coordination at the manganese atom is essentially a distorted octahedron, with three carbonyl ligands occupying mutually cis sites. The remaining sites are occupied by the phosphorus atom and the delocalized pseudo-π-allylic oxopropenyl substituent of the 2-(1′,2′-dimethyloxopropenyl)phenyldiphenylphosphine ligand. The π-oxopropenyl group is asymmetrically coordinated to the manganese atom, the Mn–C distances being 2.219 (3) and 2.126 (3) Å. The Mn–O distance is 2.058 (2) Å. Within the π-oxopropenyl moiety, the C–C and C–O distances [1.427 (5) and 1.295 (4) Å, respectively] are intermediate between their respective single- and double-bond distances, confirming the formulation as a delocalized π-bonded system.

Introduction

Methylmanganese pentacarbonyl, $[CH_3Mn(CO)_5]$, reacts with a variety of ligands to give acyl derivatives of general formula $[(CH_3CO)Mn(CO)_4(\text{ligand})]$.[1-10] These acyl complexes are thought to result from migration of the methyl group from the manganese atom to a coordinated carbonyl ligand.

The reaction of $[CH_3Mn(CO)_5]$ with the potentially bidentate ligand 2-vinylphenyldiphenylphosphine [*o*-CH_2=$CHC_6H_4P(C_6H_5)_2$, 1 (sp)] gives two yellow isomeric, air-stable crystalline complexes, 2 and 3, of empirical formula $C_{25}H_{20}MnO_4P$.[11] Crystal structure analyses together with



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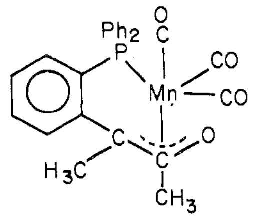

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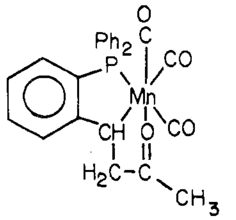

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