attraction between the silicon and hydrogen atoms, or due to any inherent differences in properties of the manganese or tungsten complexes with regard to the rhenium analogues, but results from steric crowding which forces the hydride ligands close to the silicon atoms. Thus, we believe that in $Re_2(CO)_8H_2Si(C_6H_5)_2$, $Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$, and $Re_2(CO)_7H_2(Si(C_2H_5)_2)_2$ *the hydride ligands are bonded terminally to the rhenium atoms with no attractive interactions with the silicon atoms.*

Acknowledgment. We thank the National Research Council of Canada and the University of Alberta for financial support of this research. We are indebted to Dr. J. K. Hoyano and Professor W. A. G. Graham for supplying the crystals and for many helpful discussions. M.C. thanks the National Research Council of Canada for a graduate scholarship.

Registry No. $Re_2(CO)_7H_2(Si(C_2H_5)_2)_2$, 63301-80-4.

Supplementary Material Available: Table I, listing the observed and calculated structure amplitudes (9 pages). Ordering information is given on any current masthead page.

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Contribution from the The Guelph-Waterloo Centre for Graduate Work in Chemistry,
University of Guelph, Guelph, Ontario, Canada, N1G 2W1

Structural Studies of Steric Effects in Phosphine Complexes. Synthesis and Crystal and Molecular Structure of the Dinitrato(tricyclohexylphosphine)mercury(II) Dimer

ELMER C. ALYEA,* SHELTON A. DIAS, GEORGE FERGUSON,* and RODERIC J. RESTIVO

Received January 24, 1977 AIC700650

The synthesis and crystal and molecular structure of the dinitrato(tricyclohexylphosphine)mercury(II) dimer is reported. The compound $[Hg(PCy_3)(NO_3)_2]_2$ belongs to the monoclinic space group $P2_1/c$ (C^5_{2h}, No. 14) with $a = 11.143$ (2) Å, $b = 17.956$ (2) Å, $c = 11.756(1)$ Å, and $\beta = 105.98$ (1)° and with two centrosymmetric dimers in the unit cell. The structure was refined anisotropically to final discrepancy indices of $R_F = 0.032$ and $R_{wF} = 0.037$ for 2105 independent reflections measured by diffractometer. In the dimeric molecule the unique mercury atom is coordinated to phosphorus (Hg–P 2.359 (2) Å), to a bidentate nitrato group (Hg–O 2.150 (10), 2.728 (12) Å), and to a monodentate nitrato group (Hg–O 2.504 (9) Å) which forms a bridge to the other centrosymmetrically related mercury atom (Hg–O 2.477 (8) Å). The mercury coordination is distorted square pyramidal with a bridging oxygen atom O(11′) in the apical position and the mercury atom is 0.26 Å above the basal plane. The torsion angles Hg–P–C–H (95°, 65°, 172°) for the three cyclohexyl rings define their orientation with respect to the Hg–P bond. Cone angle calculations are made for PCy_3 ($\theta = 181$ (1)°) and a "ligand profile" is given for PCy_3 in $[Hg(PCy_3)(NO_3)_2]_2$.

Structural studies of tertiary phosphine derivatives of various metals are in progress in our laboratories in an attempt to relate steric and electronic properties of the ligands to molecular stereochemistry. The steric influence of bulky tricyclohexyl and tri-*tert*-butyl groups was evident in the crystal structures found for $Cu(PCy_3)_2ClO_4$[1] and $[t\text{-}Bu_3PH][(t\text{-}Bu_3P)NiBr_3]$.[2] Whereas less sterically hindered phosphines such as Et_3P and Ph_3P give 1:1 complexes with mercuric halides that are formulated as halogen-bridged dimers on the basis of infrared studies,[3] bulkier phosphines might be expected to restrict the mercury from adopting a tetrahedral geometry. Thus, from a vibrational study $Hg(PCy_3)(SCN)_2$ was recently suggested[4] to have a trigonal configuration around mercury similar to that found[5] for $Hg(AsPh_3)(SCN)_2$; an x-ray analysis of $Hg(PCy_3)(SCN)_2$ has shown, however, that it is a polymer with trigonal-pyramidal coordination at mercury.[6] In an investigation of complexes of the type $Hg(PR_3)X_2$, where R is cyclohexyl, *o*-tolyl, or *tert*-butyl, we have synthesized a complex with empirical formula $Hg(PCy_3)(NO_3)_2$, for which vibrational spectra suggest that two types of coordinated nitrato groups are present. In this paper we report the x-ray structural determination of this new complex and compare the x-ray data with those recently reported[7] for the analogous triphenylphosphine derivative.

Experimental Section

The $Hg(PCy_3)(NO_3)_2$ complex was prepared by refluxing a mixture of PCy_3 and $Hg(NO_3)_2 \cdot H_2O$ in a 1:1 molar ratio for 2 h in ethanol. After filtration and cooling, the colorless crystals were washed with ether and dried in vacuo over P_4O_{10}. The product, which could be recrystallized from dichloromethane and methanol, had a melting point of 200–202 °C dec. A solution (8.6×10^{-4} M) in dry nitromethane had molar conductance 22 Ω^{-1} cm^{-2}. The ^1H NMR spectrum in dimethyl-d_6 sulfoxide showed a broad unresolved multiplet between δ 0.93 and 2.20. Nitrate infrared spectral bands (in cm^{-1})(halocarbon and Nujol mulls) are 1496 (vs), 1308 (s), 1263 (vs), 1038 (m), 998 (vs), 818 (m), 750 (m), and 722 (m); nitrate Raman spectral bands (in cm^{-1}) (solid in capillary) are 1497 (w, b), 1467 (vs), 1442 (m, sh), 1309 (w), 1288 (vw), 1035 (vs), 994 (m), 825 (w), 747 (w), and 719 (m).

The vibrational spectra of $Hg(PCy_3)(NO_3)_2$ clearly show the absence of ionic nitrate in the solid state and thus we attribute the slight conductance in nitromethane to partial dissociation in solution. The presence of coordinated nitrate groups is indicated by the large number of bands assignable to the nitrate group in the IR and Raman spectra, whereas ionic nitrate only exhibits three absorptions in each region.[8] Specifically, the characteristic bands near 1400 and 700 cm^{-1} are split and the normally infrared-inactive symmetric stretch ($\sim$1030 cm^{-1}) becomes active. The splitting of these bands, particularly the latter into two components separated by 40 cm^{-1}, implies the presence of two kinds of nitrato groups. A monomeric structure containing a monodentate and a bidentate nitrate would be consistent with the observed vibrational spectra but the insolubility of $Hg(PCy_3)(NO_3)_2$ in all solvents tried militates against this possibility and also prevents a Raman depolarization study and a molecular weight determination. A dimeric or polymeric structure as proved for $Hg(PPh_3)(NO_3)_2$,[7] involving both monodentate (or bidentate) and bridging nitrato groups, would appear to be the most reasonable formulation. As such a structural assignment can only be inconclusive, determination of the structure of $Hg(PCy_3)(NO_3)_2$ by a single-crystal x-ray analysis was undertaken.

Crystallographic Measurements. Transparent needle-shaped crystals of what were later shown to be $C_{36}H_{66}Hg_2H_4O_{12}P_2$, mol wt 1210, were examined by Weissenberg and precession photography, and they showed systematic absences uniquely determining the space group $P2_1/c$ (C^5_{2h}, No. 14). Unit cell dimensions a = 11.143 (2) Å, b = 17.956 (2) Å, c = 11.756 (1) Å, and β = 105.98 (1)° were obtained by least-squares refinement of the setting angles of 12 general reflections accurately centered in a 3.5 mm diameter circular receiving aperture on a Hilger and Watts Y290 four-circle computer-controlled diffractometer (λ(Mo Kα) 0.71069 Å, T = 22 °C) equipped with a graphite monochromator. The calculated density, 1.78 g cm^{-3} for two dimers in the unit cell, agrees with the measured value (1.78) found by flotation in aqueous zinc bromide solutions. $F(000)$ = 1192.

Diffraction data were collected from a well-formed transparent needle crystal with dimensions 0.30 × 0.06 × 0.05 mm mounted on an eucentric goniometer head with the a^* axis approximately parallel to the Φ axis. The six bounding faces of the crystal were identified and their distances from an arbitrary crystal center measured using a calibrated graticule in a binocular microscope. The θ–2θ scan technique and Mo Kα radiation were used to record the intensities of a unique quadrant of data within the limits $2 < 2\theta < 46°$. A symmetric scan range of 0.6° in 2θ, centered on the calculated peak position (λ(Mo Kα) 0.71069 Å), was composed of 60 steps of 1-s duration. Stationary-crystal, stationary-counter background counts (b_1, b_2) were measured for 15 s at the beginning and end of the scan range. Reflections for which the intensity of the diffracted beam exceeded 10000 counts/s were automatically remeasured with aluminum foil attenuators inserted in order to be within the linear response range of the scintillation counter, which was located with its receiving aperture 200 mm from the crystal. The intensities of two standard reflections, monitored at 100 reflection intervals, decreased by 6.4% during data collection; the transparent crystal turned slightly dark under exposure to the x-ray beam, indicating that a small amount of surface decomposition probably took place.

Data were corrected for Lorentz and polarization factors[9] [$1/Lp = \sin 2\theta_s(\cos^2 2\theta_m + 1)/(\cos^2 2\theta_m + \cos^2 2\theta_s)$ where $2\theta_s$ and $2\theta_m$ are the angles at the sample crystal and monochromator, respectively] and, subsequently, for absorption[10](μ(Mo Kα) = 70.7 cm^{-1}) using Gaussian integration. Maximum and minimum values of transmission coefficients are 0.745 and 0.604, respectively. Standard deviations were assigned to intensity values according to $\sigma(I) = (S + B)^{1/2}$ where S is the scan count and B equals $4(b_1 + b_2)$. Of the 3150 measured reflections, 2105 with $I > 3\sigma(I)$ were used in the final refinement of the structure parameters.

Structure Solution and Refinement. An estimate of the overall scale factor was obtained using Wilson's method, and fractional coordinates for the unique mercury atom were readily obtained from a sharpened three-dimensional Patterson map. A Fourier synthesis based on these mercury phases revealed all 27 nonhydrogen atoms. Full-matrix least-squares refinement using anisotropic temperature factors for Hg and P and isotropic parameters for the other nonhydrogen atoms, then yielded a value for $R_F = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.056. The scattering functions of Cromer and Mann[11] were used for all nonhydrogen atoms treated as neutral species and the curve for the mercury atom was corrected for the real and the imaginary part of the anomalous dispersion.[12] A difference Fourier synthesis calculated at this stage showed maxima in expected positions for all the hydrogen atoms; these were then allowed for (in chemically predicted positions with C–H = 0.95 Å,[13] with isotropic U values of 0.063 $Å^2$ and scattering factors from ref 14) but not refined in subsequent calculations. Four further cycles of refinement with anisotropic thermal parameters for all nonhydrogen atoms converged with R_F = 0.032 and $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, the function minimized, = 0.037. The satisfactory weighting scheme which was employed is $w^{1/2} = 1/[\sigma^2(F) + pF^2]^{1/2}$ with $p = 5 \times 10^{-4}$, a factor introduced to avoid overweighting strong reflections.[15] The error in an observation of unit weight is 1.07 and a final difference Fourier showed no significant features. The largest shift/error ratio was 0.28 for the x coordinate of C(25). A listing of observed and calculated structure factors is available.[16]

Final positional and thermal parameters for the nonhydrogen atoms, along with their standard deviations as estimated from the inverse matrix, are listed in Table I. The calculated positions of the hydrogen atoms are in Table II. Interatomic distances and angles are in Table III.

Discussion

The x-ray analysis of $[Hg(PCy_3)(NO_3)_2]_2$ shows that the crystal structure consists of discrete dimeric molecules separated by van der Waals contacts (Figure 1). A view of the complete coordination sphere about one unique mercury atom of the dimer, along with the molecular labeling scheme, is seen in Figure 2.

The coordination about the unique mercury atom is best described as a distorted square pyramid with O(11′) at the apex; the Hg atom is then 0.26 Å above the basal plane defined by the four atoms P, O(21), O(22), and O(11). Considerable distortion from idealized geometry occurs due to the disparity of the ligands and the presence of an asymmetrically bound nitrato group; interatomic distances and angles for $Hg(PCy_3)(NO_3)_2$ are given in Table III. Five-coordination is known for mercury, though four-coordinate tetrahedral and lower geometries are more common.[17] The coordination about mercury in $Hg(PPh_3)(NO_3)_2$ has been described as very distorted tetrahedral by considering the terminal nitrato group to be unidentate; the alternative with a bidentate nitrato group and square-pyramidal description was considered and rejected.[7] The "uncoordinated" Hg–O bond length in that complex (2.686 (11) Å) is, however, shorter than the sum of the van der Waals radii of mercury (1.5 Å) and oxygen (1.4 Å) and the difference in bond length between this and the stronger (2.190 (8) Å) Hg–O interaction, 0.50 Å, is well within the normal range assigned[8] to asymmetrical bidentate behavior of the nitrato group. Similarly, the difference between the Hg–O(21) and Hg–O(22) distances of 0.578 (17) Å in the case of $Hg(PCy_3)(NO_3)_2$ is compatible with the square-pyramidal description of the mercury geometry. The possibility

Table I. Final Positional[a] and Thermal[b] Parameters for $[(C_6H_{11})_3PHg(NO_3)_2]_2$

Atom	x	y	z	Atom	x	y	z
Hg	0.32104 (4)	0.03371 (2)	0.01782 (4)	C(15)	−0.0329 (10)	0.2113 (8)	−0.0354 (10)
P	0.3016 (2)	0.1156 (1)	0.1686 (2)	C(16)	0.0927 (9)	0.1717 (6)	−0.0093 (9)
O(11)	0.5004 (7)	0.0539 (4)	−0.0684 (7)	C(21)	0.3035 (9)	0.0596 (5)	0.2990 (8)
O(12)	0.3946 (9)	0.1339 (5)	−0.1891 (7)	C(22)	0.2075 (10)	−0.0038 (6)	0.2688 (10)
O(13)	0.5561 (13)	0.0817 (7)	−0.2175 (12)	C(23)	0.2165 (12)	−0.0516 (6)	0.3778 (12)
O(21)	0.2569 (8)	−0.0312 (6)	−0.1410 (9)	C(24)	0.2042 (13)	−0.0057 (8)	0.4793 (12)
O(22)	0.1010 (11)	−0.0381 (7)	−0.0796 (12)	C(25)	0.2960 (14)	0.0561 (7)	0.5103 (10)
O(23)	0.0923 (8)	−0.0861 (5)	−0.2491 (8)	C(26)	0.2869 (10)	0.1065 (6)	0.4022 (9)
N(1)	0.4814 (9)	0.0912 (5)	−0.1603 (8)	C(31)	0.4333 (8)	0.1796 (5)	0.2021 (8)
N(2)	0.1491 (9)	−0.0495 (5)	−0.1625 (9)	C(32)	0.4417 (9)	0.2171 (5)	0.0862 (9)
C(11)	0.1538 (7)	0.1679 (5)	0.1244 (8)	C(33)	0.5539 (10)	0.2697 (5)	0.1068 (10)
C(12)	0.1624 (9)	0.2453 (5)	0.1791 (9)	C(34)	0.6747 (10)	0.2301 (6)	0.1707 (12)
C(13)	0.0389 (10)	0.2838 (6)	0.1509 (10)	C(35)	0.6637 (9)	0.1946 (6)	0.2828 (10)
C(14)	−0.0197 (11)	0.2887 (7)	0.0196 (11)	C(36)	0.5567 (8)	0.1404 (5)	0.2617 (9)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg	5.25 (2)	5.10 (2)	6.11 (2)	−0.12 (2)	1.96 (2)	−1.57 (2)
P	2.91 (12)	3.83 (12)	4.83 (14)	−0.12 (10)	0.90 (11)	−0.45 (10)
O(11)	8.5 (5)	9.5 (6)	8.9 (5)	4.0 (4)	5.4 (5)	5.1 (4)
O(12)	13.0 (8)	11.0 (7)	8.4 (6)	7.0 (6)	3.4 (6)	1.8 (5)
O(13)	25.6 (15)	17.3 (11)	21.1 (13)	12.8 (11)	19.4 (12)	11.5 (10)
O(21)	6.7 (5)	15.4 (8)	12.9 (8)	−1.7 (6)	3.5 (5)	−7.8 (7)
O(22)	12.6 (9)	19.4 (12)	17.2 (11)	−5.8 (8)	6.6 (8)	−8.6 (9)
O(23)	7.9 (6)	12.9 (7)	10.8 (7)	−0.8 (6)	0.8 (5)	−5.7 (6)
N(1)	10.4 (7)	8.0 (6)	6.8 (6)	3.3 (6)	4.5 (6)	1.6 (5)
N(2)	6.8 (6)	9.3 (7)	10.3 (7)	0.8 (5)	3.0 (6)	−5.5 (6)
C(11)	2.5 (5)	5.3 (5)	5.3 (6)	0.8 (4)	0.3 (4)	0.3 (4)
C(12)	5.1 (6)	4.9 (6)	6.4 (6)	2.0 (5)	0.9 (5)	0.0 (5)
C(13)	6.5 (7)	7.8 (7)	8.4 (8)	3.2 (6)	1.7 (6)	0.0 (6)
C(14)	7.4 (8)	9.6 (9)	9.2 (9)	5.2 (7)	1.3 (7)	0.7 (7)
C(15)	5.4 (7)	13.9 (11)	5.8 (7)	3.4 (8)	−0.7 (6)	−0.2 (7)
C(16)	5.6 (6)	7.6 (7)	6.6 (7)	1.7 (6)	1.3 (6)	−0.4 (6)
C(21)	5.0 (6)	4.4 (5)	5.3 (6)	0.1 (4)	1.8 (5)	0.2 (4)
C(22)	6.9 (7)	5.6 (6)	8.4 (8)	−0.6 (5)	3.8 (6)	0.8 (5)
C(23)	9.9 (9)	6.4 (8)	11.3 (10)	−0.7 (7)	5.5 (8)	1.2 (7)
C(24)	11.3 (11)	9.7 (9)	10.4 (10)	1.5 (8)	5.9 (9)	5.0 (8)
C(25)	12.7 (11)	8.9 (8)	6.1 (7)	2.3 (8)	3.8 (8)	0.9 (6)
C(26)	7.9 (7)	5.7 (6)	5.5 (6)	0.8 (6)	2.1 (6)	0.2 (5)
C(31)	3.4 (5)	4.3 (5)	4.7 (5)	−0.1 (4)	0.7 (4)	−0.5 (4)
C(32)	4.7 (6)	5.3 (6)	7.0 (7)	−0.8 (5)	1.4 (5)	0.4 (5)
C(33)	5.9 (7)	5.5 (6)	7.5 (7)	0.1 (5)	2.1 (6)	0.9 (5)
C(34)	4.3 (6)	7.6 (8)	13.0 (11)	−1.2 (6)	3.3 (7)	−0.2 (7)
C(35)	3.9 (6)	8.6 (8)	8.1 (8)	−1.2 (6)	0.6 (5)	0.4 (6)
C(36)	3.6 (5)	5.4 (6)	6.9 (6)	−0.7 (5)	0.8 (5)	0.4 (5)

[a] The estimated standard deviations of the last digit are in parentheses. [b] The thermal parameters U_{ij} (Å × 10^2) are terms in the expression $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

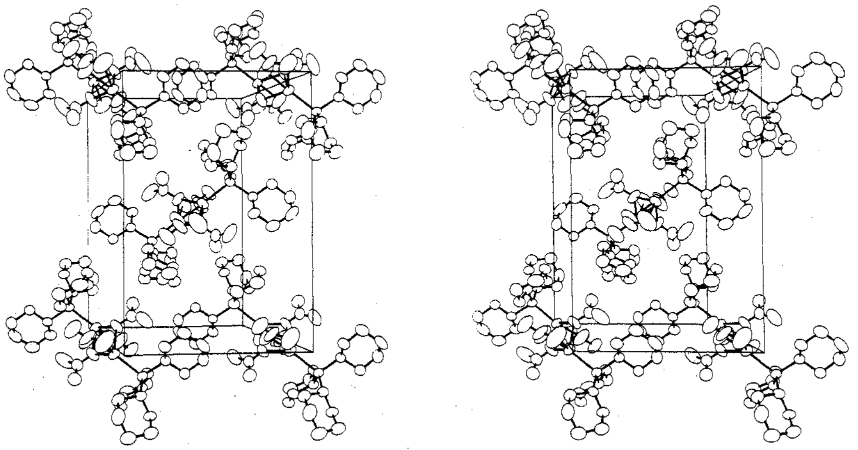

Figure 1. Stereoview of the molecular packing diagram for $[Hg(PCy_3)(NO_3)_2]_2$.

of higher coordination numbers for mercury by virtue of interaction with the outer oxygen atoms of the bridging nitrato group can be ruled out because the oxygen atoms are too distant (Hg···O(12) = 3.305 (10) Å, Hg···O(13′) = 3.148 (13) Å, see Figure 2). Similarly, a trigonal-planar geometry (with weak axial interactions) as recently reported for $Hg(AsPh_3)(SCN)_2$[5] is not a feasible representation for the present complex.

The structure of $[Hg(PCy_3)(NO_3)_2]_2$ differs from that reported for $Hg(PPh_3)(NO_3)_2$ primarily in the mode of bonding of the bridging nitrato groups. Bridging nitrato groups usually adopt either the anti–anti or syn–anti conformation

Table II. Positional Parameters for the Hydrogen Atoms of $[(C_6H_{11})_3PHg(NO_3)_2]_2$

Atom	*x*	*y*	*z*
H(11)	0.099	0.137	0.158
H(121)	0.196	0.242	0.264
H(122)	0.220	0.275	0.150
H(131)	−0.020	0.254	0.180
H(132)	0.044	0.331	0.187
H(141)	−0.092	0.318	−0.002
H(142)	0.043	0.318	−0.015
H(151)	−0.086	0.181	0.000
H(152)	−0.073	0.209	−0.120
H(161)	0.085	0.122	−0.042
H(162)	0.147	0.199	−0.044
H(21)	0.384	0.037	0.318
H(221)	0.125	0.017	0.243
H(222)	0.221	−0.034	0.205
H(231)	0.159	−0.092	0.366
H(232)	0.301	−0.076	0.405
H(241)	0.122	0.018	0.455
H(242)	0.208	−0.034	0.548
H(251)	0.282	0.085	0.576
H(252)	0.378	0.035	0.539
H(261)	0.210	0.132	0.381
H(262)	0.353	0.144	0.422
H(31)	0.420	0.218	0.255
H(321)	0.449	0.179	0.030
H(322)	0.365	0.244	0.050
H(331)	0.560	0.291	0.034
H(332)	0.542	0.310	0.156
H(341)	0.690	0.192	0.117
H(342)	0.743	0.264	0.185
H(351)	0.741	0.168	0.318
H(352)	0.654	0.233	0.334
H(361)	0.567	0.100	0.214
H(362)	0.552	0.120	0.337

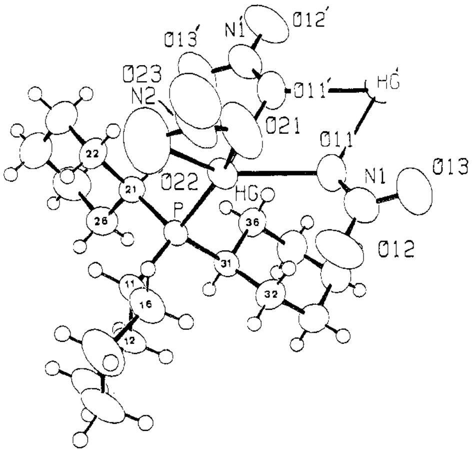

Figure 2. View with 50% probability ellipsoids of $[Hg(PCy_3)(NO_3)_2]_2$ showing molecular geometry and details of the numbering scheme. The cyclohexyl carbon atoms are numbered C(*i*1)···C(*i*6) consecutively around each ring. The atoms marked with a prime are related to the unprimed atoms by the symmetry transformation $1 - x, \bar{y}, \bar{z}$ (symmetry transformation I in Table III).

Table III. Interatomic Distances (Å) and Angles (deg) for $[(C_6H_{11})_3PHg(NO_3)_2]_2$[a]

(a) Intramolecular Distances

Hg-P	2.359 (2)	C(11)-C(12)	1.522 (13)
Hg-O(11)	2.504 (9)	C(12)-C(13)	1.495 (15)
Hg-O(11)^{I}	2.477 (8)	C(13)-C(14)	1.504 (16)
Hg-O(21)	2.150 (10)	C(14)-C(15)	1.523 (18)
Hg-O(22)	2.728 (12)	C(15)-C(16)	1.524 (16)
Hg···O(12)	3.305 (10)	C(11)-C(16)	1.534 (13)
Hg···O(13)^{I}	3.148 (13)		
		C(21)-C(22)	1.536 (14)
P-C(11)	1.842 (8)	C(22)-C(23)	1.523 (18)
P-C(21)	1.829 (10)	C(23)-C(24)	1.487 (21)
P-C(31)	1.820 (9)	C(24)-C(25)	1.484 (19)
		C(25)-C(26)	1.540 (16)
N(1)-O(12)	1.207 (13)	C(21)-C(26)	1.529 (15)
N(1)-O(13)	1.218 (20)		
N(1)-O(11)	1.239 (12)	C(31)-C(32)	1.546 (14)
		C(32)-C(33)	1.532 (14)
N(2)-O(21)	1.204 (13)	C(33)-C(34)	1.525 (14)
N(2)-O(22)	1.252 (19)	C(34)-C(35)	1.498 (19)
N(2)-O(23)	1.230 (13)	C(35)-C(36)	1.506 (14)
		C(31)-C(36)	1.531 (12)

(b) Angles

P-Hg-O(11)	117.6 (2)	O(11)-N(1)-O(12)	120.3 (11)
P-Hg-O(21)	156.0 (2)	O(11)-N(1)-O(13)	115.3 (10)
P-Hg-O(22)	110.6 (3)	O(12)-N(1)-O(13)	123.4 (11)
P-Hg-O(11)^{I}	116.7 (2)	O(21)-N(2)-O(22)	114.1 (10)
O(11)-Hg-O(21)	80.7 (3)	O(21)-N(2)-O(23)	125.1 (12)
O(11)-Hg-O(22)	128.6 (4)	O(22)-N(2)-O(23)	120.0 (11)
O(11)-Hg-O(11)^{I}	60.7 (3)		
O(21)-Hg-O(22)	48.2 (4)	C(11)-C(12)-C(13)	112.4 (8)
O(21)-Hg-O(11)^{I}	85.3 (3)	C(12)-C(13)-C(14)	111.5 (11)
O(22)-Hg-O(11)^{I}	111.7 (3)	C(13)-C(14)-C(15)	110.3 (10)
Hg-O(11)-Hg	119.3 (3)	C(14)-C(15)-C(16)	111.3 (9)
Hg-O(11)-N(1)	117.8 (7)	C(15)-C(16)-C(11)	110.5 (9)
Hg'-O(11)-N(1)	119.1 (7)	C(16)-C(11)-C(12)	110.6 (7)
Hg-O(21)-N(2)	113.8 (8)	C(21)-C(22)-C(23)	110.0 (8)
Hg-O(22)-N(2)	82.7 (9)	C(22)-C(23)-C(24)	111.3 (10)
Hg-P-C(11)	111.5 (3)	C(23)-C(24)-C(25)	113.7 (13)
Hg-P-C(21)	107.8 (3)	C(24)-C(25)-C(26)	110.6 (9)
Hg-P-C(31)	108.7 (3)	C(25)-C(26)-C(21)	109.6 (8)
C(11)-P-C(21)	108.7 (4)	C(26)-C(21)-C(22)	111.3 (9)
C(11)-P-C(31)	110.1 (4)		
C(21)-P-C(31)	110.1 (4)	C(31)-C(32)-C(33)	112.0 (7)
		C(32)-C(33)-C(34)	111.3 (8)
P-C(11)-C(12)	113.5 (5)	C(33)-C(34)-C(35)	110.9 (10)
P-C(11)-C(16)	114.9 (7)	C(34)-C(35)-C(36)	112.5 (8)
P-C(21)-C(22)	111.5 (6)	C(35)-C(36)-C(31)	110.4 (8)
P-C(21)-C(26)	112.7 (6)	C(36)-C(31)-C(32)	109.8 (8)
P-C(31)-C(32)	109.0 (5)		
P-C(31)-C(36)	112.2 (6)		

(c) Intermolecular Contacts ⩽3.5 Å for Nonhydrogen Atoms and ⩽2.50 Å for Hydrogen Atoms

C(12)···O(12)^{II}	3.40 (1)	H(351)···H(141)^{III}	2.41
C(33)···O(13)^{II}	3.37 (2)	H(262)···H(322)^{IV}	2.50

[a] The superscripts on the second atom refer to the following transformations: I, $1 - x, -y, -z$; II, $x, {}^1/_2 - y, {}^1/_2 + z$; III, $1 + x, {}^1/_2 - y, {}^1/_2 + z$; IV, $x, {}^1/_2 - y, {}^1/_2 + z$.

with two of the oxygen atoms participating in the bridging arrangement.[8] In $Hg(PPh_3)(NO_3)_2$ the mercury atoms are separated by 5.526 Å and are connected to the bridging nitrato group in a syn–anti arrangement, resulting in infinite $-Hg-NO_3-Hg-$ chains. However, the present $[Hg(PCy_3)(NO_3)_2]_2$ complex shows the more unusual situation of the bridge being formed by a single oxygen atom, as was found in $[Cu(py)_2(NO_3)_2]_2py$.[18] The bridging atom O(11) is essentially equidistant from each mercury atom (bond length difference of 0.027 (12) Å) whereas, as mentioned above, the other two oxygen atoms of this bridging nitrato group are not within bonding distances of either mercury atom; the separation of the mercury atoms (4.297 (2) Å) precludes any Hg–Hg bonding. In spite of the difference in the bonding mode of the bridging nitrato groups, the coordination geometry of the mercury atom in the present complex is virtually identical with that found in $Hg(PPh_3)(NO_3)_2$.[7] The greater steric hindrance of PCy_3 relative to PPh_3 must account for the formation of a dimeric molecule rather than a polymeric structure. The specific steric requirements of PCy_3 as determined from the present x-ray data are described below.

The nitrato groups have N–O bond lengths between 1.204 (13) and 1.252 (19) Å and O–N–O angles ranging between 115.3 (10) and 125.1 (12)°. Although the noncoordinated N–O bond lengths should be shorter than the coordinated N–O bond lengths, as expected for covalently bonded nitrato groups,[8] the variation in N–O distances is only 1–2 σ. Accordingly, no meaningful information is available with respect to the

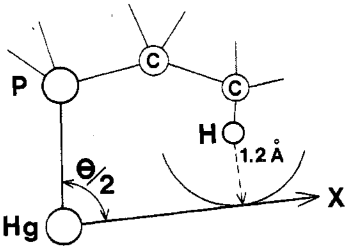

Figure 3. The maximum semicone angle, $\theta/2$, for a cyclohexyl ring of the $HgPCy_3$ moiety in $[HgPCy_3(NO_3)_2]_2$. The point of contact of the cone-generating vector Hg→X from the mercury with the van der Waals sphere of the hydrogen atom is coplanar with the mercury, phosphorus, and hydrogen atoms.

monodentate or bidentate behavior of the terminal nitrato group. We have already observed[19] that there is no definitive correlation between M–O distances and the relevant (adjacent) N–O distances. The bond angles involving the terminal nitrato group are, however, compatible with bidentate behavior; as previously observed,[8,19,20] the O(21)–N(2)–O(22) angle (114.1 (10)°) is contracted on bidentate coordination. The degree of asymmetry in the coordination of the bidentate nitrato group is reflected in the Hg–O(21)–N(2) and Hg–O(22)–N(2) angles, 113.8 (8) and 82.9 (7)°, respectively.

The coordination about phosphorus is essentially tetrahedral, with Hg–P–C angles averaging 110.6 (3)° and the C–P–C angles, 109.6 (4)°. The Hg–P bond length of 2.359 (2) Å is identical with that found in $Hg(PPh_3)(NO_3)_2$ and significantly shorter than that reported for tetrahedral $Hg(PPh_3)_2(SCN)_2$ (2.488 (3) Å).[21] The mean P–C bond length (1.830 (6) Å), the average C–C bond length (1.52 (2) Å), and the average C–C–C angle (111.1 (2)°) in the cyclohexyl rings are in agreement with reported values.[1,22,23] All the cyclohexyl rings adopt chair conformations and their orientations with respect to the Hg–P bond can be described quantitatively by the appropriate Hg–P–C(*i*1)–H torsion angles; these are 95, 65, and 172° for C(11), C(21), and C(31), respectively. This arrangement effectively minimizes C···C inter-ring and intermolecular contacts (Table III); such meshing of the cyclohexyl rings in a cog-like fashion appears to be a common feature of $M\text{–}PCy_3$ complexes.[6]

As a result of studies which showed that the bulkiness of phosphorus ligands influenced their binding energies and exchange equilibria in solutions of $[NiL_4]$ (L = phosphorus ligands) more than their electronic character, Tolman[24] introduced the concept of a ligand cone angle θ to describe this steric effect. For symmetric ligands the steric parameter θ is the apex angle of a cylindrical cone centered 2.28 Å (2.85 cm using CPK molecular models) from the center of the P atom, which just touches the van der Waals radii of the outermost atoms of the model. Recent experimental and theoretical considerations have led various workers[24c,25,26] to postulate that the estimated cone angle for PCy_3 (179 ± 10° by the Tolman CPK model) should be revised downwards slightly to a value nearer 170°.

The x-ray coordinates (Table I) were used in conjunction with an assumed van der Waals radius of hydrogen of 1.2 Å and C–H distance of 1.08 Å to calculate the maximum values of $\theta/2$ in Figure 3 for each cyclohexyl ring; the three values are 90.9, 90.5, and 89.9° with a mean $\theta/2 = 90.4\ (6)°$; thus the effective cone angle θ for PCy_3 is 181 (1)°. For $Cu(PCy_3)_2ClO_4$ a similar treatment using the published coordinates[1] yields $\theta/2$ values of 82.6, 85.8, and 92.9° for the three independent cyclohexyl rings with a mean value 87 (3)° leading to a cone angle θ of 174 (6)° for the same PCy_3 ligand. The calculated "maximum" cone angles for PCy_3 are in remarkable agreement with the values estimated using CPK models,[24] keeping in mind that in that case a C–H distance of 1.10 Å and a van der Waals radius for hydrogen of 1.00 Å is assumed.

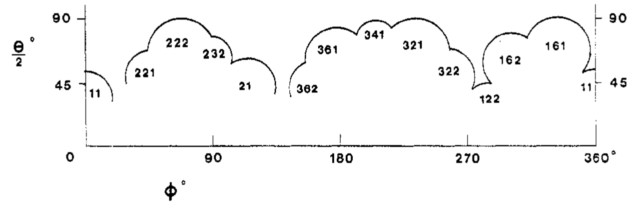

Figure 4. Ligand profile for PCy_3 in $[HgPCy_3(NO_3)_2]_2$. The ordinate is the maximum semicone angle $\theta/2$. The abscissa is the angle ϕ through which the vector Hg→X has been rotated about the Hg–P bond; the origin was arbitrarily chosen at H(11). The numbers under the curves denote the hydrogen atoms (cf. Table II), whose van der Waals spheres define the ligand profile.

While it is generally accepted that the cone angle concept provides some measure of the bulkiness of a ligand, it does not bring out the fact the ligands are not *solid* cones. A description which emphasizes the cog-like nature of the ligand is obtained by plotting the maximum angle $\theta/2$ which the vector Hg→X (Figure 3) makes as it is rotated about the Hg–P bond, just touching the van der Waals spheres of the atoms of the ligand. This "ligand profile" for PCy_3 in $[Hg(PCy_3)(NO_3)_2]_2$ is illustrated in Figure 4; the maximum for each cyclohexyl ring yields the semicone angle quoted above but the profile also shows clearly the gaps between the cyclohexyl rings.

Further x-ray studies are in progress to provide more quantitative data on steric effects in other bulky phosphine complexes.[6]

Acknowledgment. We are grateful to the National Research Council of Canada for operating grants (to G.F. and E.C.A.).

Registry No. $[Hg(PCy_3)(NO_3)_2]_2$, 63181-12-4.

Supplementary Material Available: Listing of structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
University of Virginia, Charlottesville, Virginia 22901

Synthesis and Relation between Magnetic and Structural Properties of a Series of Monomeric and Dimeric Nickel(II) Complexes. Crystal and Molecular Structures of Bis(2,2′-biquinolyl)di-μ-chloro-dinickel(II), (2,2′-Biquinolyl)dibromonickel(II), Bis(2,9-dimethyl-1,10-phenanthroline)di-μ-chloro-dinickel(II), Bis(2,9-dimethyl-1,10-phenanthroline)di-μ-bromo-dinickel(II), and (2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline)diiodonickel(II)

RAY J. BUTCHER and EKK SINN*

Received January 24, 1977 AIC70062N

A series of nickel(II) complexes has been synthesized with halogen and substituted phenanthroline or bipyridyl ligands. The relation between the magnetic and structural properties of the complexes has been investigated, and the crystal and molecular structures of five of them have been determined by single-crystal x-ray diffraction, using counter methods. It appears that the chloro complexes form only dimeric antiferromagnetic molecules containing five-coordinated nickel(II) atoms and that the bromo complexes can form either dimeric antiferromagnetic or pseudotetrahedral, monomeric normal paramagnetic molecules, while the iodo complexes appear to form four-coordinated paramagnetic monomers. Steric factors can weaken the bridging bonds between the halves of the dimeric molecules or prevent the dimerization which results from a drive to attain five-coordination about the nickel(II) atom. The ligand environment about the nickel atom is distorted tetrahedral in the monomeric complexes and may be regarded as either distorted square pyramidal or distorted trigonal bipyramidal in the dimers. Crystal data for bis(2,2′-biquinolyl)di-μ-chloro-dinickel(II), $[\mathrm{Ni(biq)Cl_2}]_2$: $\mathrm{Ni_2Cl_4N_4C_{36}H_{24}}$, space group $P\bar{1}$, $Z = 1$, $a = 9.521$ (4) Å, $b = 9.570$ (3) Å, $c = 11.226$ (3) Å, $\alpha = 95.23$ (3)°, $\beta = 117.43$ (4)°, $\gamma = 112.73$ (3)°, $V = 791$ Å^3, $R = 2.6\%$, 1977 reflections. Crystal data for (2,2′-biquinolyl)dibromonickel(II), $\mathrm{Ni(biq)Br_2}$: $\mathrm{NiBr_2N_2C_{18}H_{12}}$, space group $P2_1/c$, $Z = 4$, $a = 7.929$ (3) Å, $b = 12.432$ (6) Å, $c = 17.158$ (6) Å, $\beta = 102.90$ (3)°, $V = 1649$ Å^3, $R = 3.1\%$, 1621 reflections. Crystal data for (2,9-dimethyl-1,10-phenanthroline)di-μ-chloro-dinickel(II), $[\mathrm{Ni(dmp)Cl_2}]_2$: $\mathrm{Ni_2Cl_4N_4C_{28}H_{24}}$, space group $P\bar{1}$, $Z = 1$, $a = 9.090$ (1) Å, $b = 9.287$ (2) Å, $c = 10.327$ (2) Å, $\alpha = 100.28$ (2)°, $\beta = 113.19$ (1)°, $\gamma = 111.24$ (2)°, $V = 692$ Å^3, $R = 3.6\%$, 2083 reflections. Crystal data for (2,9-dimethyl-1,10-phenanthroline)-di-μ-bromo-dinickel(II), $[\mathrm{Ni(dmp)Br_2}]_2$: $\mathrm{Ni_2Br_4N_4C_{28}H_{24}}$, space group $P\bar{1}$, $Z = 1$, $a = 7.891$ (2) Å, $b = 10.259$ (3) Å, $c = 10.319$ (4) Å, $\alpha = 100.48$ (3)°, $\beta = 116.49$ (2)°, $\gamma = 99.56$ (1)°, $V = 706$ Å^3, $R = 4.2\%$, 2244 reflections. Crystal data for (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)diiodonickel(II), $\mathrm{Ni(bc)I_2}$: $\mathrm{NiI_2N_2C_{26}H_{20}}$, space group $P2_1/c$, $Z = 4$, $a = 12.873$ (6) Å, $b = 23.248$ (7) Å, $c = 8.310$ (5) Å, $\beta = 101.56$ (4)°, $V = 2436$ Å^3, $R = 3.8\%$, 2270 reflections.

Introduction

Ring-substituted ligands of the phenanthroline and bipyridyl type have been shown to form monomeric and dimeric complexes with nickel(II) and manganese(II) halides,[1-4] though only one such nickel complex has so far been reported.[5] When the halide, X, is Cl, chlorine-bridged dimers $[\mathrm{MLX_2}]_2$, containing five-coordinated nickel or manganese,[2] are formed. The manganese(II) complexes can be hydrated to form five-coordinated species of the type $[\mathrm{MnLX_2(H_2O)}]$ which contain no metal–halogen bridging but do tend to form polymeric hydrogen-bridged chains.[3,4] When the halide is Br the (anhydrous) manganese(II) complexes studied to date are discrete monomers. We show here that the nickel(II) complexes are halide-bridged dimers with X = Cl, while both bridged and unbridged species form when X = Br depending on the experimental conditions. Only monomeric complexes appear to form with X = I. The dimeric manganese complexes display intramolecular ferromagnetic interactions,[2,4] but we find that halogen bridging in the nickel complexes leads to antiferromagnetic interactions for X = Cl or Br, despite a similarity between the geometries of the dimeric nickel and manganese complexes. The only nickel complex of this type previously studied by x-ray diffraction was reported to have equal Ni–Cl bridging bonds,[5] but we find all the dimeric complexes to be bridged by two unequal Ni–X bonds.

Experimental Section

Syntheses. (a) $[\mathrm{Ni(Biq)Cl_2}]_2$ and $\mathrm{Ni(biq)Br_2}$. A 1-mmol amount of ligand was dissolved in warm benzene and a solution containing 1.1 mmol of the appropriate nickel halide dissolved in 1:1 methanol triethoxymethane was added. The precipitate which formed immediately was filtered off and recrystallized from nitrobenzene (with a small amount of TEOF added). The crystals used in the x-ray study were grown by slow evaporation of the nitrobenzene solution.

(b) $[\mathrm{Ni(dmp)Cl_2}]_2$, $[\mathrm{Ni(dmp)Br_2}]_2$, and $\mathrm{Ni(bc)I_2}$. A 1-mmol amount of ligand was dissolved in a minimum of chloroform with 10 mL of TEOF added and this solution was treated with 1.1 mmol of the appropriate nickel halide dissolved in methanol/triethoxymethane solution. The complexes were obtained in crystalline form by evaporation of this solution and recrystallization by slow evaporation in air from chloroform with some triethoxymethane added to remove water.

Crystal densities were measured by flotation in aqueous potassium iodide containing a small amount of detergent as wetting agent.

Crystal data for bis(2,2′-biquinolyl)di-μ-chloro-dinickel(II), $[\mathrm{Ni(biq)Cl_2}]_2$: $\mathrm{Ni_2Cl_4N_4C_{36}H_{24}}$, yellow-green crystal, mol wt 772,