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The Preparation and Crystal Structure of 1,10-Phenanthrolinemercury(I) Nitrate, $Hg_2(phen)(NO_3)_2$[1]

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Abstract: The preparation of a new compound of mercury(I), 1,10-phenanthrolinemercury(I) nitrate, is reported, and the determination of its structure by three-dimensional, single-crystal X-ray analysis is described. The crystal is triclinic, space group $P\bar{1}$, with four mercury atoms per unit cell of parameters: $a = 6.83$ A, $b = 10.55$ A, $c = 10.58$ A, $\alpha = 98.6°$, $\beta = 93.6°$, and $\gamma = 97.6°$. The compound contains discrete $Hg_2(phen)^{2+}$ complex ions in which the phenanthroline, functioning as a bidentate ligand, is coordinated, through both of its nitrogen atoms, to one of the mercury atoms.

With few exceptions (notably the aniline complex $C_6H_5NH_2Hg_2^{2+}$ which has been quantitatively characterized in aqueous solution[2]), complexes of mercury(I) with nitrogen ligands generally appear to be unstable. This apparent instability has been attributed[2–4] to the tendency of such ligands to induce dismutation of the mercurous ion, due to the relatively greater stability of the corresponding mercury(II) complexes.

The possible existence of a 1,10-phenanthroline (subsequently abbreviated as phen) complex of mercury(I) is suggested by the preparation by Anderegg[5] of a salt having the composition $Hg_2(phen)_2(NO_3)_2$. This salt was reported[5] to be sparingly soluble in water, the solubility being governed by the solubility product relation $[Hg_2^{2+}][phen]^2[NO_3^-]^2 = K = 10^{-24.70}$ at 20°. While no evidence was reported concerning the existence of mercury(I)–phenanthroline complexes in solution, it should be noted that the solubility behavior described above is not inconsistent with the presence of mercury(I) in solution in the form of complex ions, *i.e.*, $Hg_2(phen)_2^{2+}$ and/or $Hg_2(phen)^{2+}$, under the conditions of the measurements (phenanthroline in appreciable excess over mercury(I)).

We have confirmed the preparation of $Hg_2(phen)_2(NO_3)_2$, and of the corresponding perchlorate salt, as well as of the corresponding salts of bis(2,2′-dipyridyl)mercury(I). In qualitative experiments we have also observed that the solubility of $Hg_2(phen)_2(NO_3)_2$ in water is markedly increased by the addition of $Hg_2(NO_3)_2$, presumably due to the shifting of the equilibrium

$$Hg_2(phen)_2^{2+} + Hg_2^{2+} \rightleftharpoons 2Hg_2(phen)^{2+} \quad (1)$$

in the direction of the more soluble $Hg_2(phen)^{2+}$ complex. Furthermore, from such solutions containing Hg_2^{2+} in large excess, we were able to obtain crystals of a new compound, $Hg_2(phen)(NO_3)_2$, whose structure determination by X-ray crystallographic analysis is described in this paper.

Attempts to obtain crystals of $Hg_2(phen)_2(NO_3)_2$, suitable for X-ray analysis, have thus far proved unsuccessful.

Experimental Section

Preparation of $Hg_2(phen)(NO_3)_2$. To a saturated aqueous solution of $Hg_2(NO_3)_2$ containing 0.1 *M* HNO_3, maintained at 70°, was slowly added, with stirring, a solution of 0.1 *M* 1,10-phenanthrolinium nitrate until the first formation of a permanent precipitate was detected. Sufficient $Hg_2(NO_3)_2$ was added to just redissolve the precipitate, and the resulting solution was cooled slowly to room temperature. On standing for several days at room temperature, small colorless, nearly prismatic, crystals of $Hg_2(phen)(NO_3)_2$, averaging about 0.2 × 0.2 × 5 mm in size, separated out.

Structure Determination. Examination of the crystals with a precession camera revealed that they were triclinic. A least-squares analysis of the data obtained using a single crystal on a General Electric XRD-5 diffractometer yielded the following cell constants and estimated errors: $a = 6.83 \pm 0.02$ A, $b = 10.55 \pm 0.03$ A, $c = 10.58 \pm 0.03$ A, $\alpha = 98.6 \pm 0.1°$, $\beta = 93.6 \pm 0.1°$, $\gamma = 97.6 \pm 0.1°$. The calculated volume per unit cell is 744 ± 4 A^3. The measured value of the density was 3.04 ± 0.06 g cm^{-3}. Assuming two molecules of $Hg_2(phen)(NO_3)_2$ per unit cell, the calculated density is 3.15 ± 0.02 g cm^{-3}.

Intensity data were collected with a General Electric XRD-5 diffractometer using molybdenum radiation, a zirconium filter, and pulse height analysis. The reflections in the sphere $\sin \theta < 0.34$ were examined with the stationary crystal–stationary counter technique (SCSC)[6] using 10-sec counts of peaks and backgrounds,

(1) This research was supported by grants from the National Science Foundation and the Advanced Research Projects Agency.

(2) T. H. Wirth and N. Davidson, *J. Am. Chem. Soc.*, **86**, 4314 (1964).

(3) R. A. Potts and A. L. Allred, *Inorg. Chem.*, **5**, 1066 (1966).

(4) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1966, pp 613–614.

(5) G. Anderegg, *Helv. Chim. Acta*, **42**, 344 (1959).

(6) T. C. Furnas, Jr., "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957. The time required for measurements using the SCSC method was only about half that needed for the θ, 2θ method. The peak heights were subsequently corrected to yield integrated intensities using the *experimentally* determined relation between the two.

which were measured by offsetting 1.33° in 2θ. Of the reflection intensity data collected, 1250 were found to be nonzero and were used in the subsequent refinement. During the data collection two monitor peaks were used to check alignment. The crystal changed from colorless to pale yellow during the course of the measurements; however, the monitor peaks decreased in intensity by only 3% so that no correction for the apparent decomposition was deemed necessary. The absorption of X-rays by this material is severe (μ = 203.5 cm^{-1}), and absorption corrections were therefore applied as described below.

The raw intensity data were corrected for backgrounds and LP factors and a Patterson function was calculated.[7] The map could be interpreted on the basis of the space group P$\bar{1}$ with two mercury atoms in the asymmetric unit. The two atoms were separated by 2.5 A, in good agreement with the distance expected for a mercurous ion.[8] A Wilson plot, as well as the eventual successful refinement of the structure, confirmed the correctness of the choice of space group P$\bar{1}$. Using the positions found for the mercury atoms a structure factor calculation gave a conventional discrepancy index,[9] R = 34.2%.

A Fourier synthesis, using the signs calculated above applied to the observed data, gave reasonable positions for all nonhydrogen atoms. A structure factor calculation on this model yielded R = 31.9%; refinement of all positional parameters reduced this to R = 26.5%.

An empirical absorption correction was applied to make the data approximate those from a cylindrical specimen, using a table of $\sqrt{I_{max}/I_\phi}$, where I_{max} was the maximum intensity measured for the 4,0,0 reflection at χ = 90.0°, ϕ = 30.0°, and I_ϕ was the intensity of this reflection measured at 10° intervals from 0 to 350° in ϕ. The data were then further corrected using Bond's[10] table for cylindrical specimens as applied to the XRD-5 geometry.

Refinement of all positional parameters led to R = 22.3%. The data were sorted in order of increasing sin θ/λ and the function $psr = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ summed for each of 30 groups of 40 reflections. There was a large dependence on sin θ/λ from psr (sin θ/λ = 0.04) = +24% to psr (sin θ/λ = 0.45) = −34%, with all points falling close to a smooth curve.

The empirical absorption correction was replaced by a correction obtained by numerical integration using ORABS.[11] The crystal of six faces was approximated by the six equations of the form $ax + by + cz + d = 0$ with coefficients listed in Table I.

Table I. Coefficients[a] of the Crystal Face Equations

Coef	Eq 1	Eq 2	Eq 3	Eq 4	Eq 5	Eq 6
a	−16.9	16.9	−9.43	9.43	0.0	−1.38
b	16.9	−16.9	−9.43	9.43	0.0	0.53
c	2.22	−2.0	2.0	−2.0	40.0	−2.0
d	−1.0	−1.0	−1.0	−1.0	−1.0	−1.0

[a] Units are mm^{-1}.

These data gave an R value of 22.4%. All further calculations were carried out on this data set. Both sets of corrected data gave an almost identical dependence of psr on sin θ/λ. Indeed, on cursory examination, the second correction, which might be more appealing due to its *a priori* nature, does not seem to differ much from the empirical one.

The version of the least-squares program used allows for the application of real and imaginary corrections for anomalous dispersion, of the form $f = f_o + \Delta f' + i\Delta f''$, as well as refinement of some atoms with isotropic thermal parameters and others with anisotropic values. The scattering[12] of the mercury atoms was corrected by $\Delta f' = -2.7$ and $\Delta f'' = 10.3$.

Refinement with anisotropic mercury atoms led to an R value of 15.4%; however, the psr dependence on sin θ/λ was still as great as before. The crystal was remounted and 25 reflections in the range sin θ/λ <0.48 were (i) measured by the θ, 2θ scan technique[6] to give I, the integrated intensity, and (ii) remeasured by the SCSC technique to give P, the peak height. The ratio $\sqrt{I/P}$ showed a marked increase with increasing sin θ/λ, indicating that only part of the intensity was being measured at high sin θ/λ by the SCSC technique. A least-squares straight line

$$\sqrt{I/P} = 0.3923 \sin \theta/\lambda + 0.7651 \qquad (2)$$

was used to apply a correction to the data for this effect. This correction reduced the range of variation of psr to about 15% of the original range.

The data were weighted for final refinement using two least-squares lines (eq 3 and 4) obtained by plotting Δ_{av}^2 ($= W^{-1}$) *vs*

$$W^{-1} = -14.52 \sin \theta/\lambda + 6.58 \qquad (\sin \theta/\lambda \leqslant 0.354) \quad (3)$$

$$W^{-1} = 5.66 \sin \theta/\lambda - 0.56 \qquad (\sin \theta/\lambda > 0.354) \quad (4)$$

sin θ/λ. Four cycles of refinement of all parameters gave a final R = 10.15% and wR[13] = 10.02%. For the 1111 reflections greater than three times the minimum value observed, the final discrepancy index was R' = 9.6%, wR' = 9.9%.[14] A difference Fourier showed no peaks greater than two electrons. The largest peak (1.9 e) was located near N_1 and the second largest (1.8 e) on the position O_{32}. Most of the other peaks exceeding one electron were less than 2 A from one of the mercury atoms.

All positional changes were less than six-tenths of an estimated standard deviation on the last cycle. Four of the light atom temperature parameters shifted slightly more than an estimated standard deviation and one other (that of O_{23}) changed by three standard deviations. This indicates the limited physical significance that can be attached to these parameters in a structure where the scattering is dominated to such a large extent by the mercury atoms. The dominance of the mercury atom scattering and the importance of correcting for both real and imaginary parts of the anomalous dispersion is evidenced by the fact that for 10% of the reflections, the calculated imaginary part of the scattering was greater than one-fourth of the calculated real scattering for all atoms in the crystal.

The final atomic parameters are listed in Table II and the anisotropic temperature parameters in Table III. The bond lengths and angles determined are listed in Tables IV and V. Calculations relating to the planes of the phenanthroline molecule and nitrate ions are summarized in Table VI.

All of the contacts found between nonbonded atoms appear to be at least as great as those predicted using van der Waals radii. The shortest contacts between two adjacent phenanthroline rings are C_5–C_{11}, 3.35; C_5–C_{12}, 3.34; C_{13}–C_{11}, 3.46; C_9–C_4, 3.53; C_7–C_3, 3.53; C_8–C_3, 3.56; C_8–C_4, 3.56 A. The shortest contacts between nitrate oxygen atoms and a phenanthroline ring are O_{32}–C_3, 2.95; O_{22}–C_2, 3.09; O_{21}–C_7, 3.13; O_{21}–C_2, 3.26; O_{22}–N_1, 3.24 A.

Discussion

The existence of a stable 1,10-phenanthroline complex of mercury(I), which has been confirmed in this study, is consistent with an earlier suggestion by Wirth and Davidson[2] that complexing with mercury(I) should be favored for amines of low basicity.

(7) The Patterson and Fourier syntheses were calculated using ERFR-2, Fourier summation program of W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, Esso Research, CBRL-22M-52, June 1962. Structure-factor calculations and least-squares refinements were performed with local versions of ORFLS Oak Ridge FORTRAN least squares; W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory, ORNL-TM-305, Aug 1962.

(8) The Hg-Hg separation in $Hg_2(H_2O)_2(NO_3)_2$ is 2.54 ± 0.01 A.

(9) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

(10) W. L. Bond in "International Tables for X-ray Crystallography," Vol. II, Kynoch Press, Birmingham, England, 1959, pp 295–298.

(11) ORABS, a FORTRAN program for calculating crystal absorption corrections: D. J. Wehe, W. R. Busing, and H. A. Levy, ORNL-TM-229, April 1962.

(12) The scattering curves used were those for zerovalent mercury, oxygen, nitrogen, and carbon as listed in ref 10, Vol. III, Table 3.3.1 A, pp 202–207.

(13) $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$.

(14) Observed and calculated structure factors have been deposited as Document No. 9698 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20025. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make check or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Table II. Final Atomic Parameters[a]

Atom	x	y	z	B
Hg_1	0.5307 (4)	0.1902 (2)	0.2553 (3)	...[b]
Hg_2	0.2376 (4)	0.0365 (3)	0.1419 (3)	...[b]
N_2	0.884 (7)	0.014 (4)	0.315 (4)	5 (2)
O_{21}	1.014 (5)	−0.036 (4)	0.333 (4)	6 (1)
O_{22}	0.701 (6)	−0.014 (4)	0.361 (4)	6 (2)
O_{23}	0.869 (4)	0.105 (3)	0.247 (3)	5 (1)
N_3	−0.078 (11)	0.225 (7)	0.003 (6)	7 (4)
O_{31}	−0.006 (5)	0.123 (4)	−0.045 (3)	5 (2)
O_{32}	−0.246 (8)	0.220 (5)	0.027 (5)	11 (3)
O_{33}	0.029 (7)	0.317 (5)	0.064 (4)	7 (2)
N_1	0.654 (6)	0.280 (4)	0.481 (4)	3 (1)
N_{10}	0.644 (5)	0.403 (4)	0.243 (4)	2 (1)
C_2	0.658 (8)	0.211 (5)	0.577 (5)	5 (2)
C_3	0.729 (8)	0.282 (6)	0.711 (6)	6 (2)
C_4	0.777 (7)	0.413 (5)	0.714 (5)	4 (2)
C_5	0.843 (7)	0.624 (4)	0.616 (4)	3 (1)
C_6	0.826 (8)	0.684 (5)	0.516 (6)	5 (2)
C_7	0.775 (11)	0.685 (7)	0.263 (8)	8 (4)
C_8	0.693 (9)	0.603 (6)	0.156 (6)	6 (3)
C_9	0.642 (7)	0.471 (5)	0.157 (5)	4 (2)
C_{11}	0.717 (8)	0.483 (6)	0.374 (5)	4 (2)
C_{12}	0.712 (7)	0.413 (5)	0.487 (6)	2 (1)
C_{13}	0.780 (7)	0.484 (5)	0.613 (5)	3 (2)
C_{14}	0.773 (10)	0.629 (6)	0.380 (7)	7 (3)

[a] Coordinates are in fractions of a cell edge; the figures in parentheses are the uncertainties in the last digit of the preceding numbers. [b] These atoms were given anisotropic temperature factors as explained in the text.

Table III. Anisotropic Thermal Vibration Parameters[a]

Atom	Root-mean-square displacement	Direction cosines L	M	N
Hg_1	0.147	0.897	0.044	0.440
	0.220	−0.400	−0.343	0.850
	0.313	−0.188	0.940	0.290
Hg_2	0.155	0.932	0.024	0.363
	0.234	−0.305	−0.493	0.815
	0.307	−0.198	0.870	0.452

[a] The root-mean-square displacements in angstroms are referenced to an orthogonal coordinate system where x is the vector $Hg_2–Hg_1 = \mathbf{U}$, $y = (\mathbf{U} \times \mathbf{V}) \times \mathbf{U}$, where $\mathbf{V}$ is the vector $C_2–C_9$, and z completes the right-handed system.

Table IV. Selected Interatomic Distances[a]

$Hg_1–Hg_2$	2.516 (7)	$N_1–C_2$	1.34 (6)
		$N_1–C_{12}$	1.40 (5)
$Hg_1–N_1$	2.48 (4)	$N_{10}–C_{11}$	1.53 (6)
$Hg_1–N_{10}$	2.30 (4)	$N_{10}–C_9$	1.24 (6)
		Av N–C	1.38 (5)
$Hg_1–O_{22}$	2.91 (4)		
$Hg_1–O_{23}$	2.59 (3)	$C_2–C_3$	1.52 (7)
$Hg_{1x}–O_{32}$	3.47 (5)	$C_3–C_4$	1.36 (7)
$Hg_2–O_{21x}$	2.75 (4)	$C_4–C_{13}$	1.40 (6)
$Hg_2–O_{23x}$	2.95 (3)	$C_{13}–C_5$	1.47 (6)
$Hg_2–O_{31'}$	2.22 (4)	$C_{13}–C_{12}$	1.44 (6)
$Hg_2–O_{31}$	2.84 (4)	$C_{12}–C_{11}$	1.50 (6)
$Hg_2–O_{32'}$	2.81 (5)	$C_5–C_6$	1.31 (6)
$Hg_2–O_{23x'}$	4.15 (5)	$C_6–C_{14}$	1.48 (8)
$Hg_2–O_{21x'}$	5.21 (6)	$C_{14}–C_{11}$	1.53 (7)
		$C_{14}–C_7$	1.44 (8)
$N_2–O_{21}$	1.11 (5)	$C_7–C_8$	1.36 (8)
$N_2–O_{22}$	1.38 (5)	$C_8–C_9$	1.39 (7)
$N_2–O_{23}$	1.29 (5)	Av C–C	1.43 (2)
$N_3–O_{31}$	1.29 (7)		
$N_3–O_{32}$	1.16 (7)		
$N_3–O_{33}$	1.21 (7)		
Av N–O	1.24 (4)		

[a] All distances are in angstroms. An atom designated with the subscript x refers to the corresponding unsubscripted atom translated to $(x - 1)$. Primed atoms are generated from corresponding unprimed ones by inversion through the origin.

Table V. Selected Bond Angles[a]

	Angles about Hg_1		
$Hg_2–Hg_1–O_{22}$	93.0 (8)	$Hg_2–Hg_1–O_{23}$	115.6 (7)
$Hg_2–Hg_1–O_{32}$[b]	93.3 (9)	$Hg_2–Hg_1–N_1$	136.7 (9)
$Hg_2–Hg_1–N_{10}$	131.7 (9)	$N_1–Hg_1–N_{10}$	78 (1)
$N_1–Hg_1–O_{22}$	73 (1)	$N_1–Hg_1–O_{23}$	84 (1)
$N_1–Hg_1–O_{32}$	130 (1)	$N_{10}–Hg_1–O_{32}$	68 (1)
$N_{10}–Hg_1–O_{23}$	98 (1)	$N_{10}–Hg_1–O_{22}$	134 (1)
$O_{32}–Hg_1–O_{23}$	66 (1)	$O_{32}–Hg_1–O_{22}$	106 (1)
$O_{22}–Hg_1–O_{23}$	45 (1)		
	Angles about Hg_2		
$Hg_1–Hg_2–O_{31'}$	171 (1)	$Hg_1–Hg_2–O_{31}$	119 (1)
$Hg_1–Hg_2–O_{32'}$	126 (1)	$Hg_1–Hg_2–O_{21x}$	105 (1)
$Hg_1–Hg_2–O_{23x}$	110 (1)	$O_{31}–Hg_2–O_{31'}$	69 (2)
$O_{31}–Hg_2–O_{32'}$	101 (1)	$O_{31}–Hg_2–O_{21x}$	110 (1)
$O_{31}–Hg_2–O_{23x}$	69 (1)	$O_{31'}–Hg_2–O_{32'}$	46 (2)
$O_{31'}–Hg_2–O_{21x}$	75 (1)	$O_{31'}–Hg_2–O_{23x}$	76 (1)
$O_{32'}–Hg_2–O_{21x}$	93 (1)	$O_{32'}–Hg_2–O_{23x}$	119 (1)
$O_{21x}–Hg_2–O_{23x}$	45 (1)		
	Nitrate Angles		
$O_{21}–N_2–O_{22}$	125 (5)	$O_{21}–N_2–O_{23}$	129 (5)
$O_{22}–N_2–O_{23}$	106 (4)	$O_{31}–N_3–O_{32}$	113 (8)
$O_{31}–N_3–O_{33}$	121 (8)	$O_{32}–N_3–O_{33}$	126 (8)
	Phenanthroline Angles		
$C_{12}–N_1–C_2$	128 (5)	$N_1–C_2–C_3$	118 (5)
$C_2–C_3–C_4$	113 (5)	$C_3–C_4–C_{13}$	129 (5)
$C_4–C_{13}–C_{12}$	116 (5)	$C_{13}–C_{12}–N_1$	116 (5)
$C_{12}–C_{13}–C_5$	114 (5)	$C_{13}–C_5–C_6$	125 (5)
$C_5–C_6–C_{14}$	129 (6)	$C_6–C_{14}–C_{11}$	107 (6)
$C_{14}–C_{11}–C_{12}$	125 (5)	$C_{11}–C_{12}–C_{13}$	119 (5)
$C_{11}–C_{14}–C_7$	120 (6)	$C_{14}–C_7–C_8$	115 (7)
$C_7–C_8–C_9$	121 (7)	$C_8–C_9–N_{10}$	133 (6)
$C_9–N_{10}–C_{11}$	112 (4)	$N_{10}–C_{11}–C_{14}$	117 (5)

[a] All angles are in degrees; the central atom in the list is at the vertex. [b] Atom O_{32} in the list of angles about Hg_1 corresponds to atom O_{32} in Table II translated to $(x + 1)$. All other atoms are as in Table IV and in Figure 1.

Table VI. Least-Squares Best Planes and Distances[a]

Group	Direction cosines and distance of best plane		Distance of atom from plane			
Phenanthroline	L	−0.954	N_1	0.02 (3)	C_{14}	0.01 (6)
	M	0.264	N_{10}	−0.01 (3)	C_7	−0.07 (7)
	N	0.142	C_2	−0.01 (4)	C_8	0.03 (6)
	Dist	−2.71	C_3	−0.03 (5)	C_9	0.02 (5)
			C_4	0.02 (5)	C_{11}	−0.03 (5)
			C_{13}	0.01 (4)	C_{12}	0.02 (4)
			C_5	−0.03 (4)	Hg_1	0.172 (2)
			C_6	0.06 (5)		
Nitrate (2)	L	0.228	N_2	0.01 (4)		
	M	0.535	O_{21}	0.00 (3)		
	N	0.814	O_{22}	0.00 (3)		
	Dist	3.35	O_{23}	0.00 (3)		
			Hg_1	0.183 (2)		
Nitrate (3)	L	−0.264	N_3	0.03 (6)		
	M	−0.495	O_{31}	−0.01 (4)		
	N	0.828	O_{32}	−0.01 (4)		
	Dist	−1.07	O_{33}	−0.01 (4)		
			Hg_2	0.207 (2)		

[a] All distances are in angstroms. The figure in parentheses is the uncertainty in the position of the atom in the direction perpendicular to the plane. The planes were determined using only the light atoms.

The essential structural features of $Hg_2(phen)(NO_3)_2$ are summarized in Tables IV–V and depicted in Figure 1. The compound contains discrete $Hg_2(phen)^{2+}$ ions, separated by layers of nitrate ions which lie approximately in the plane $x = 0$. The coordination environ-

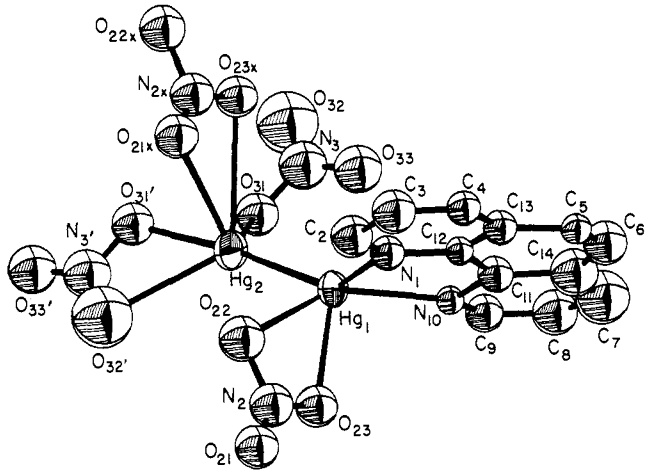

Figure 1. A parallel projection of the $Hg_2(phen)^{2+}$ ion and the four nearest nitrate ions onto the *xy* plane. The orthogonal coordinate system (**U** is the vector N_1–C_{12}, **V** is the vector C_{12}–C_4, x = **U**, y = (**U** × **V**) × **U**, z completes the right-handed system) has been rotated 70° clockwise looking down positive x and 10° clockwise looking down positive y.

ments of the two Hg atoms are dissimilar. One of the mercury atoms (Hg_1) has essentially five nearest neighbor atoms, namely, the other mercury atom (Hg_2) at a distance of 2.516 A, two nitrogen atoms (at 2.30 and 2.48 A) belonging to the same phenanthroline molecule, and two oxygen atoms (at distances of 2.59 and 2.91 A) belonging to the same nitrate ion. The nearest neighbors of the other mercury atom (Hg_2) comprise, in addition to the first mercury atom, one oxygen atom ($O_{31'}$) at a distance of 2.22 A and four other oxygen atoms at somewhat greater distances (2.75, 2.95, 2.84, and 2.81 A). The coordination of the closest oxygen atom corresponds to a nearly linear arrangement of atoms $O_{31'}$–Hg_2–Hg_1 ($\angle$ = 171°) reminiscent of the structure of the $[H_2O\text{–}Hg\text{–}Hg\text{–}OH_2]^{2+}$ units[15] in $Hg_2(H_2O)_2(NO_3)_2$ for which, r_{Hg-O} = 2.15 A; r_{Hg-Hg} = 2.54 A; $\angle_{O-Hg-Hg}$ = 160°. All other atoms in $Hg_2(phen)(NO_3)_2$ are located at distances considerably greater than 3 A from the mercury atoms.

No significance is attached to the small distortions from the expected regular planar configurations of the nitrate ions and phenanthroline molecules. These distortions, as well as the fact that the mercury atom coordinated to phenanthroline lies outside (by 0.17 A) the plane of the phenanthroline ligand, may well be due to packing effects. One such effect, that may be of importance, is the stacking of the phenanthroline molecules in parallel pairs separated by approximately 3.5 A, which is close to the expected van der Waals separation.

The geometry of coordination about the mercury atoms in $Hg_2(phen)(NO_3)_2$ is irregular and, apart from the approximately linear $O_{31'}$–Hg_2–Hg_1 arrangement referred to earlier, neither the coordination numbers nor geometry bear any obvious relation to those reported for other compounds of mercury(I). In $Hg_2(H_2O)_2(NO_3)_2$ each mercury atom has four nearest neighbors consisting of the other mercury atom and three oxygen atoms, one (at 2.15 A) belonging to a water molecule and the other two (at 2.40 and 2.42 A) belonging to the same nitrate ion.[15] The solid mercurous halides, on the other hand, consist of essentially discrete linear X–Hg–Hg–X molecules.[16,17] A number of compounds of mercury(I) containing neutral ligands (L = $(C_6H_5)_3PO$ or C_5H_5NO) have recently been reported[3] having the compositions $HgL_4(ClO_4)_2$ and $Hg_2L_5SiF_6$, but the structures of these compounds, and the coordination numbers of the mercury atoms in them, have not yet been determined.

The Hg–Hg bond length of 2.516 A in $Hg_2(phen)(NO_3)_2$ lies in the range of Hg–Hg bond lengths found for other compounds of mercury(I), *i.e.*, $Hg_2(H_2O)_2(NO_3)_2$, 2.54 A; Hg_2F_2, 2.43 A; Hg_2Cl_2, 2.58 A; Hg_2Br_2, 2.58 A; and Hg_2I_2, 2.69 A.[15–17] These data appear to reflect a, not unexpected, trend of increasing Hg–Hg bond length with increasing covalency and/or polarizability of the ligands. The rather short Hg–Hg bond in $Hg_2(phen)(NO_3)_2$ (intermediate between that in Hg_2F_2 and $Hg_2(H_2O)_2(NO_3)_2$) is somewhat surprising in the light of this trend, although the interpretation of this result is complicated by the fact that only one of the Hg atoms is coordinated to phenanthroline. It would be of interest to determine the Hg–Hg bond lengths in $Hg_2(phen)_2(NO_3)_2$ as well as in mercury(I) complexes of various substituted phenanthrolines containing σ- and π-electron-donating and -withdrawing substituents. Further studies, directed at this objective, are in progress.

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