Intramolecular Co-ordination by a Hydroxy-group to Methylmercury(II). Synthesis and Characterization of Complexes [HgMe(L)]NO_3 containing Polydentate Ligands (L), and the Crystal Structure of the Tris(*N*-methylimidazol-2-yl)methanol Complex *

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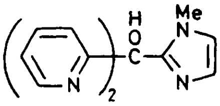
Methylmercury(II) nitrate forms cationic complexes [HgMe(L)]NO_3 [L = bis(*N*-methylimidazol-2-yl)-methanol, bis(*N*-methylimidazol-2-yl)(pyridin-2-yl)methanol, or tris(*N*-methylimidazol-2-yl)methanol (tmm)]. The crystal structure of [HgMe(tmm)]NO_3 has been determined by single-crystal *X*-ray diffraction at 295 K and refined by least-squares methods to R = 0.041 for 2 453 'observed' reflections. The $[HgMe(tmm)]^+$ cations have *one* *N*-methylimidazol-2-yl group co-ordinated to mercury, with Hg–N 2.125(7) Å and C–Hg–N angle 176.1(5)°, together with an additional weak intramolecular Hg · · · OH interaction [2.680(6) Å]. Comparison of the ^1H n.m.r. spectra of the complexes with those of related complexes does not permit assignment of the co-ordination mode of the ligands, although multidentate co-ordination is indicated. Crystal data: monoclinic, space group $P2_1/n$, with a = 14.421(4), b = 11.819(2), c = 10.985(3) Å, β = 107.41(2)°, and Z = 4.

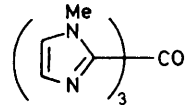
Structural studies of several complexes of methylmercury(II) with neutral bidentate ligands indicate that the co-ordination geometries are dominated by an almost linear C–Hg–N group, 164(1)—178.5(7)°, with one Hg–N bond, 2.16(1)—2.24(3) Å, significantly shorter than the more weakly bound nitrogen(s), 2.43(3)—2.96(2) Å.[1-4] A similar situation occurs for the tridentates 4,4′,4″-triethyl-2,2′:6′,2″-terpyridyl [2,3] and *N*-methylimidazol-2-ylbis(pyridin-2-yl)methanol (mbpm),[5] for which the dominant C–Hg–N moieties form angles of 171(1) and 170(0)°, respectively.

However, the complex with tris(pyridin-2-yl)methanol (tpm) has a more regular, although still distorted, geometry with C–Hg–N angles 150(1), 132(1), and 119(1)° and Hg–N distances 2.28(1), 2.45(1), and 2.53(1) Å, respectively, in marked contrast to the other complexes.[5] In particular, bond distances to the more weakly bound nitrogen atoms are significantly shorter than for the closely related bidentate ligand bis(pyridin-2-yl)methane (bpme), which has a T-shaped geometry and a weakly bound ring with Hg–N 2.75(2) Å.[2,3]

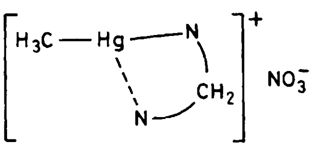
This unexpected result suggests that the $Hg^{II}Me$ group may be more flexible in the co-ordination geometry it will adopt than indicated by the earlier structural work, particular for co-ordination number four for mercury. To develop further this theme we have synthesized complexes of polydentate ligands containing *N*-methylimidazolyl donor groups, [HgMe(L)]NO_3 [L = bis(*N*-methylimidazol-2-yl)-, bis(*N*-methylimidazol-2-yl)(pyridin-2-yl)-, and tris(*N*-methylimidazol-2-yl)-methanol; bmm, bmpm, and tmm]. The complex with tmm is the *N*-methylimidazole analogue of tpm and its structure has been determined crystallographically. The ligand tmm is also of interest as a model ligand for the co-ordination environment in carbonic anhydrase.[6]



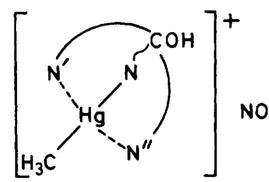
mbpm



tmm



bpme complex



tpm complex
C–Hg–N 150(1)°

Experimental

The ligands [7] and methylmercury(II) nitrate [8] were prepared as reported, and protonation constants (in 50% dioxane–water) for the ligands were measured as described.[3] Microanalyses were by the Australian Microanalytical Service, and ^1H n.m.r. spectra were recorded in CD_3OD with a JEOL JNM-4H-100 spectrometer. Chemical shifts were measured relative to 1,4-dioxane internal standard (3.64 p.p.m. from $SiMe_4$). Infrared spectra as Nujol mulls between KBr plates were obtained with a Perkin-Elmer 577 spectrophotometer.

Preparation of Complexes.—[HgMe(bmm)]NO_3. A solution of HgMe(NO_3) (0.518 g, 1.86 mmol) and bmm (0.358 g, 1.86 mmol) in acetone (50 cm^3)–ethanol (30 cm^3) was allowed to evaporate, forming crystals when almost dry. The crystals were stirred with acetone for 1 h and collected (0.624 g, 71%).

[HgMe(tmm)]NO_3. On addition of HgMe(NO_3) (0.201 g, 0.723 mmol) in acetone (20 cm^3) to a solution of tmm (0.197 g, 0.723 mmol) in acetone (20 cm^3) a microcrystalline precipitate of the product formed and was collected (0.310 g, 78%).

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* Methyl[tris(*N*-methylimidazol-2-yl)methanol-*N′O*]mercury nitrate.

Supplementary data available (No. SUP 23623, 13 pp.): thermal parameters, H-atom co-ordinates, ligand planes, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Analytical and spectroscopic data

	Analysis (%)[a]				^{1}H N.m.r.[c]		
	C	H	Hg	ν(Hg–C)[b]	δ(MeHg)	$\lvert ^2J(^1H-^{199}Hg)\rvert$	Ligand protons[d]
[HgMe(bmm)]NO_3	25.4 (25.6)	3.4 (3.2)	42.7 (42.7)	550w	−2.70	222.6	0.07, **6**, *s*, NMe; 3.50, **2**, *d*, H^4 or H^5; 3.70, **2**, *d*, H^5 or H^4; $J(H^4H^5)$ *ca.* 1.4
[HgMe(bmpm)]NO_3	32.7 (32.9)	3.5 (3.3)	36.9 (36.7)	568m	−2.83	225.3	−0.08, **6**, *s*, NMe; 3.48, **2**, *d*, H^4 or H^5; 3.67, **2**, *d*, H^5 or H^4; $J(H^4H^5)$ *ca.* 1; 3.8, **1**, *s*, H^5; 4.32, **2**, *m*, $H^{3'}$,$H^{4'}$; 4.84, **1**, *d*, $H^{6'}$; $J(H^{5'}H^{6'})$ = 4.5
[HgMe(tmm)]NO_3	30.6 (30.6)	3.7 (3.5)	36.4 (36.5)	562m	−2.76	224.5	−0.02, **9**, *s*, NMe; 3.41, **3**, *s*, H^4 or H^5; 3.67, **3**, *s*, H^5 or H^4

[a] Calculated values are given in parentheses. [b] In cm^{-1}, for Nujol mulls. [c] In CD_3OD, p.p.m. from internal 1,4-dioxane reference; coupling constants in Hz. [d] Given as chemical shift, **relative intensity**, *multiplicity*, assignment.

Table 2. Non-hydrogen atom co-ordinates

Atom	*x*	*y*	*z*
Hg	0.446 61(3)	0.599 57(3)	0.670 64(3)
C_{Me}	0.496 6(9)	0.629 4(12)	0.863 6(11)
Ligand, ring a			
N(1)	0.302 5(5)	0.483 8(6)	0.295 0(6)
C(11)	0.241 6(8)	0.403 5(8)	0.202 5(8)
C(2)	0.327 3(6)	0.477 7(7)	0.424 1(8)
N(3)	0.387 1(5)	0.562 5(6)	0.473 3(7)
C(4)	0.398 1(7)	0.626 6(7)	0.372 3(9)
C(5)	0.343 3(7)	0.579 0(8)	0.262 0(9)
Ligand, ring b			
N(1)	0.334 1(5)	0.183 1(6)	0.554 0(7)
C(11)	0.277 9(8)	0.161 9(8)	0.642 6(10)
C(2)	0.339 1(6)	0.278 6(7)	0.489 6(8)
N(3)	0.398 6(5)	0.266 3(6)	0.417 4(8)
C(4)	0.430 9(7)	0.157 3(8)	0.439 2(11)
C(5)	0.394 8(7)	0.106 0(8)	0.523 7(10)
Ligand, ring c			
N(1)	0.119 9(5)	0.472 2(6)	0.420 7(7)
C(11)	0.143 3(9)	0.594 4(8)	0.446 9(12)
C(2)	0.180 5(6)	0.380 1(7)	0.445 0(8)
N(3)	0.132 5(5)	0.285 4(6)	0.409 3(7)
C(4)	0.035 6(7)	0.318 4(9)	0.360 1(9)
C(5)	0.029 8(7)	0.430 2(9)	0.369 2(10)
Ligand, central atoms			
C	0.290 1(6)	0.390 1(7)	0.497 1(8)
O *	0.318 4(4)	0.429 0(5)	0.626 1(8)
Anion			
N	0.200 4(7)	0.352 2(7)	0.840 2(9)
O(1)	0.170 5(6)	0.392 5(7)	0.729 9(8)
O(2)	0.144 9(8)	0.321 0(9)	0.898 4(9)
O(3)	0.288 1(7)	0.351 1(11)	0.888 2(10)

* From difference-map considerations, the associated hydrogen atom is postulated to lie at 0.290, 0. 402, 0.680, O–H being 0.87 Å and H–O–C 120°. It is hydrogen bonded to nitrate O(11,13) at 1.96, 2.38 Å, and may be responsible for the diminished angle [115.8(11)°] between these atoms.

[HgMe(bmpm)]NO_3. This was prepared similarly in 58% yield.

Analytical and spectroscopic data for the complexes are presented in Table 1.

Crystallography.—Crystals of [HgMe(tmm)]NO_3 were obtained by slow evaporation, at ambient temperature, of an aqueous solution of the complex.

Crystal data. $C_{14}H_{19}HgN_7O_4$, M = 549.9, Monoclinic, space group $P2_1/n$ (variant of C^5_{2h}, no. 14), a = 14.421(4), b = 11.819(2), c = 10.985(3) Å, β = 107.41(2)°, U = 1 785.1(7) Å^3, D_m = 2.03(1), Z = 4, D_c = 2.05 g cm^{-3}, $F(000)$ = 588, monochromatic Mo-K_α radiation, λ = 0.710 69 Å, μ = 87 cm^{-1}. Specimen: 0.36 × 0.26 × 0.20 mm. T = 295 K.

Structure determination. A unique data set was measured with the limit $2\theta_{max.}$ = 50° using a Syntex $P2_1$ four-circle diffractometer in conventional 2θ—θ scan mode, yielding 3 156 independent reflections, 2 453 with $I > 2\sigma(I)$ being considered 'observed' and used in the least-squares refinement (six blocks) after absorption correction and solution of the structure by the heavy-atom method. Anisotropic thermal parameters were refined for the non-hydrogen atoms; hydrogen atoms (x, y, z, U) were constrained at estimated values. At convergence, R and R' were 0.041 and 0.047. Reflection weights were $[\sigma^2(F_o) + 0.0005\,(F_o)^2]^{-1}$. Neutral-atom scattering factors were used, all except H being corrected for anomalous dispersion ($f'f''$).[9–11] Computation used the *X*-RAY 76 program system[12] implemented by S. R. Hall on a Perkin-Elmer 3240 computer.

Ligand-atom labelling is as shown in Figure 2(*a*), hydrogen-atom labelling following that of the parent atom, suffixed A, B, C in the case of the methyl hydrogens.

Results

The complexes [HgMe(L)]NO_3, which were obtained from solutions of methylmercury(II) nitrate and ligand, have appropriate microanalyses (C, H, and Hg), and their ^{1}H n.m.r. spectra show resonances due to the 'HgMe' group and ligand with appropriate integration and with ligand resonances altered from those of the unco-ordinated ligand (Table 1). Similarly, i.r. spectra indicate the presence of both HgMe and ligand with absorption altered from that of the free ligand.

Structure of [HgMe(tmm)]NO_3 *in the Solid State.*—Aspects of the molecular geometry of the complex are given in Tables 2—4, and views of the structure in Figures 1 and 2.

The structure determination confirms the stoicheiometry to

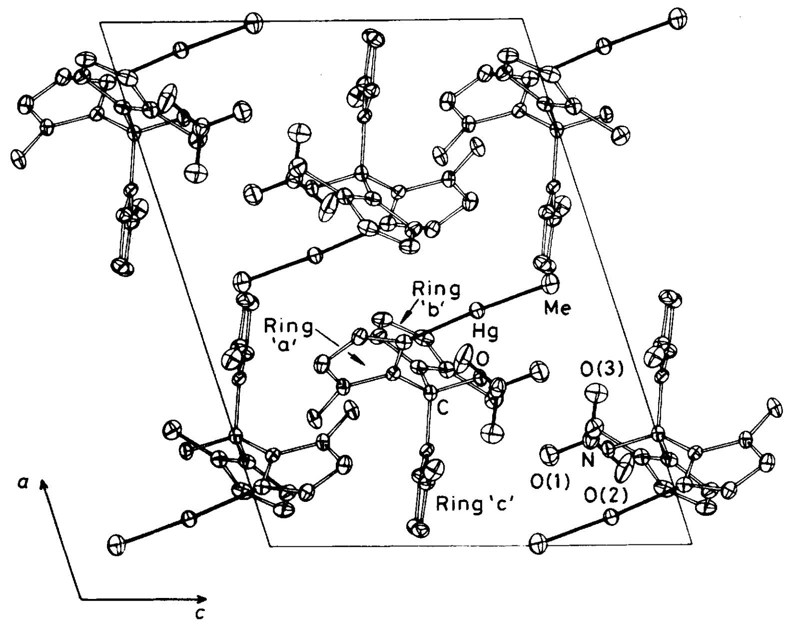

Figure 1. Projection of the unit-cell contents down *b*, showing 20% thermal ellipsoids for the non-hydrogen atoms

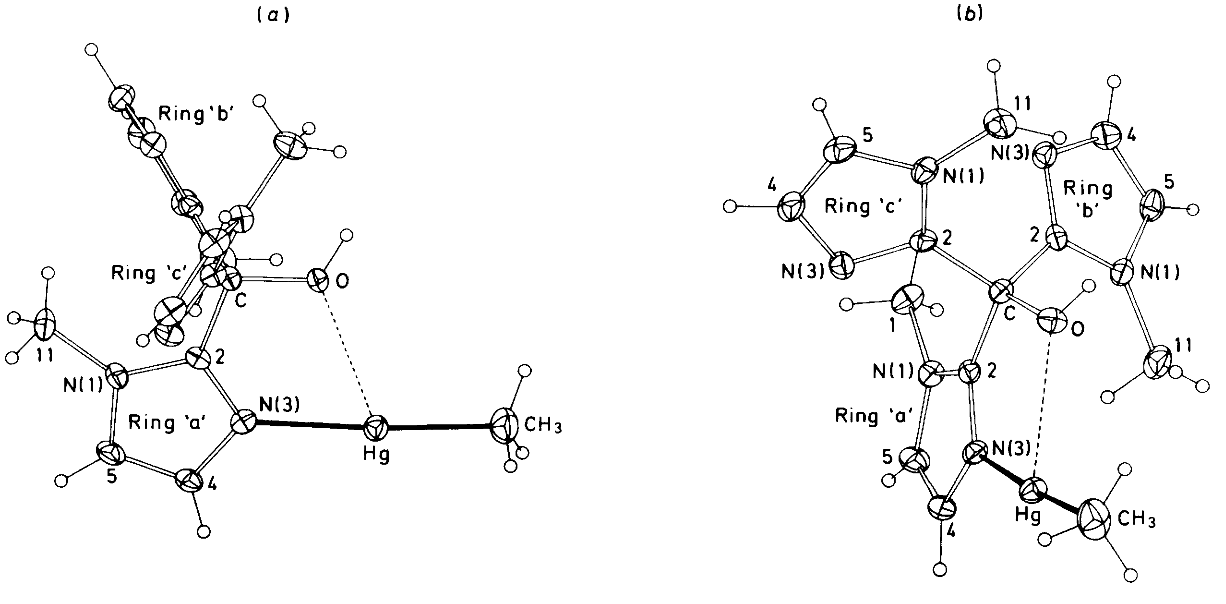

Figure 2. Two views of the molecule, (*a*) being normal to the ' co-ordination plane ' of the mercury atom. Hydrogen atoms have arbitrary radii of 0.1 Å

be as assigned above, the structure essentially being a mononuclear species containing a linearly co-ordinated mercury atom, the co-ordinating species being the methyl group and the unmethylated nitrogen atom of one of the rings of the potentially tridentate ligand (Figure 2). The angle subtended at the mercury atom deviates from 180°, being 176.1(5)°; the disposition is such that a close contact by the ligand oxygen atom at 2.680(6) Å is contained by the obtuse angle, rather than the reflex angle, suggesting that contacts to neighbouring species in the lattice may be responsible for the non-linear perturbation. None is observed at distances less than 3 Å. The single cation and the accompanying anion make up the asymmetric unit of the structure. The Hg–N bond length, 2.125(7) Å, compares well with that for the related complex [HgMe(mbpm)]NO_3 which has Hg–N(imidazole) 2.13(1) Å.[5] The imidazole rings are planar [maximum deviation from mean planes, 0.07 Å for C(11) in ring a], and the mercury atom is also only 0.07 Å from the mean plane of ring a.

Structures of the Complexes in Methanol.—As $Hg^{II}Me$ complexes with polydentate nitrogen-donor ligands have only one strong Hg–N bond, with the remaining Hg $\cdots$ N or Hg $\cdots$ O interaction(s) much weaker, the structure in solution may involve a lower co-ordination number for mercury than that observed in the solid state. However, the co-ordination behaviour of the ligand in solution can often be inferred from the value of $^2J(^1H-^{199}Hg)$ and δ(MeHg) for the complex, and log K_H for the ligand, where log K_H is the protonation constant of the ligand, *i.e.* a measure of the donor ability of the ligand. Thus, for bpme (log K_H 3.94) the complex has

Table 3. Ligand non-hydrogen geometry; distances in Å, angles in degrees

	Ring *n*		
	a	b	c
C–O	1.43(1)		
C–C(*n*2)	1.50(1)	1.51(1)	1.52(1)
C(*n*2)–N(*n*1)	1.36(1)	1.35(1)	1.37(1)
C(*n*2)–N(*n*3)	1.33(1)	1.34(1)	1.31(1)
N(*n*1)–C(*n*5)	1.39(1)	1.37(1)	1.35(1)
N(*n*1)–C(11)	1.47(1)	1.46(2)	1.49(1)
C(*n*5)–C(*n*4)	1.34(1)	1.34(2)	1.33(1)
C(*n*4)–N(*n*3)	1.39(1)	1.37(1)	1.39(1)
O–C–C(*n*2)	105.5(6)	109.6(6)	110.8(8)
C(*n*2)–C–C(*n* + 1,2)	109.0(8)	111.3(7)	110.5(6)
C–C(*n*2)–N(*n*1)	124.8(7)	127.2(9)	122.9(7)
C–C(*n*2)–N(*n*3)	126.5(7)	121.3(8)	125.2(7)
N(*n*1)–C(*n*2)–N(*n*3)	108.7(8)	111.4(7)	111.7(7)
C(*n*2)–N(*n*1)–C(*n*11)	127.1(8)	128.4(8)	129.6(9)
C(*n*2)–N(*n*1)–C(*n*5)	108.5(7)	107.0(8)	105.6(7)
C(*n*5)–N(*n*1)–C(*n*11)	124.4(7)	124.7(8)	124.8(8)
N(*n*1)–C(*n*5)–C(*n*4)	106.1(9)	106.0(8)	108.8(8)
C(*n*5)–C(*n*4)–N(*n*3)	109.1(8)	111.5(10)	109.1(8)
C(*n*4)–N(*n*3)–C(*n*2)	107.5(7)	104.1(8)	104.8(7)

Table 4. Mercury and anion geometries; distances in Å, angles in degrees

Hg–C_{Me}	2.05(1)	N–O(1)	1.25(1)
Hg–O	2.680(6)	N–O(2)	1.22(2)
Hg–N(a3)	2.125(7)	N–O(3)	1.22(1)
C_{Me}–Hg–O	109.1(4)	Hg–O–C	113.5(5)
C_{Me}–Hg–N(a3)	176.1(5)	Hg–N(a3)–C(a2)	125.9(6)
O–Hg–N(a3)	67.2(2)	Hg–N(a3)–C(a4)	126.4(5)
O(1)–N–O(2)	122.2(10)		
O(1)–N–O(3)	115.8(11)		
O(2)–N–O(3)	122.0(10)		

$^2J(^1H-^{199}Hg)$ 235.4 Hz, *ca.* 5.5 Hz higher than expected for unidentate pyridine donors[3] for which $^2J(^1H-^{199}Hg) = -2.96\log K_H + 241.6$ Hz (correlation coefficient −0.99, determined for 15 pyridines).[13] For the four complexes of potential bidentate ligands examined crystallographically, all the ligands show bidentate behaviour in the solid state,[1–4] and they have higher $^2J(^1H-^{199}Hg)$ values than their unidentate analogues.[2,3,13,14]

For the complex of bmm (log K_H 6.17) the coupling constant is 222.6 Hz, *ca.* 3.5 Hz higher than expected for unidentate N-substituted imidazoles, for which $^2J(^1H-^{199}Hg) = -2.50\log K_H + 234.6$ Hz (correlation coefficient −0.98).[3]

For the potential tridentates bmpm and tmm (log K_H 5.44 and 5.25, respectively) the $Hg^{II}Me$ complexes also have $J(^1H-^{199}Hg)$ values *ca.* 3—4.3 Hz above that expected for unidentate N-substituted imidazoles. For bmpm the dominant Hg–N bond is assumed to involve an imidazole donor, rather than pyridine, since the complex with mbpm has the imidazole ring most strongly bound to $Hg^{II}Me$,[5] and the ambidentate ligand *N*-(pyridin-2-yl)imidazole binds to $Hg^{II}Me$ *via* the imidazole ring rather than the pyridine ring.[3] The complexes of both bmpm and tmm have $Hg^{II}Me$ proton chemical shifts of −2.83 and −2.76 p.p.m. respectively, slightly upfield from the range observed for unidentate N-substituted imidazoles, −2.61 to −2.67 p.p.m., and for bmm (−2.70 p.p.m.). The extra upfield shift is consistent with the presence of an unco-cordinated aryl group providing anisotropic shielding from the orientation of the group, *e.g.* as observed for *N*-methyl-2-phenylimidazole (−2.80 p.p.m.)[3] and 2-benzylpyridine (−2.85 p.p.m.).[14] However, the extra upfield shift does not indicate whether one or two imidazole rings are unco-ordinated, and thus the ^1H n.m.r. spectra do not fully elucidate the co-ordination behaviour of the ligands, although they are consistent with multidentate co-ordination.

Discussion

The crystal structure shows the first reported example of co-ordination by a hydroxy-group to methylmercury(II). The interaction is weak as the dominant C–Hg–N moiety is almost linear, and the Hg ··· O interaction [2.680(6) Å] is considerably longer than the Hg–N bond [2.125(7) Å], although significantly shorter than the sum of covalent radii for mercury (*ca.* 1.73 Å)[15] and oxygen (1.4 Å).[16] Very similar, although slightly longer, interactions occur in recently reported complexes of bis(pyridin-2-yl)methanediol (bpmd), which has a similar skeleton to that of tmm with two hydroxy-groups on the apical carbon atom.[17] The complexes $[AuCl_2(bpmd)]Cl$ and $[PdCl_2(bpmd)]$ have square-planar geometry for gold and palladium with weak axial Au ··· OH [2.77(1) Å] and Pd ··· OH [2.824(6) Å] interactions.[17]

The structure is in marked contrast to that for the tpm complex, which has three Hg–N bonds 2.28(1)—2.53(1) Å. However, introduction of one imidazole group, in mbpm, results in a strong Hg–N(imidazole) bond with much weaker Hg–N(pyridine) interactions, 2.66(1) and 2.71(1) Å. Thus, the more basic imidazole donor group gives lower Lewis acidity for the mercury atom in the ' HgMe(imidazole) ' group. With low Lewis acidity for mercury in this environment the carbinol group of tmm may be better situated structurally and, as a weak donor group, more suitable for interaction with mercury, than the two unco-ordinated imidazole groups.

Acknowledgements

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References

1 A. J. Canty and B. M. Gatehouse, *J. Chem. Soc., Dalton Trans.*, 1976, 2018.

2 A. J. Canty, G. Hayhurst, N. Chaichit, and B. M. Gatehouse, *J. Chem. Soc., Chem. Commun.*, 1980, 316.

3 A. J. Canty, N. Chaichit, B. M. Gatehouse, E. E. George, and G. Hayhurst, *Inorg. Chem.*, 1981, **20**, 2414.

4 A. J. Canty, C. V. Lee, N. Chaichit, and B. M. Gatehouse, *Acta Crystallogr., Sect. B*, 1982, **38**, 743.

5 A. J. Canty, N. Chaichit, B. M. Gatehouse, and E. E. George, *Inorg. Chem.*, 1981, **20**, 4293.

6 C. C. Tang, D. Davalian, P. Huang, and R. Breslow, *J. Am. Chem. Soc.*, 1978, **100**, 3918; R. S. Brown and J. Huguet, *Can. J. Chem.*, 1980, **58**, 889.

7 A. J. Canty, E. E. George, and C. V. Lee, *Aust. J. Chem.*, 1983, **36**, 415.

8 A. J. Canty and R. S. Tobias, *Inorg. Chem.*, 1979, **18**, 413.

9 D. T. Cromer and J. B. Mann, *Acta Crystallogr.*, 1968, **24**, 321.

10 D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

11 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

12 'The *X*-RAY System, Version of March 1976,' Technical Report TR-446, ed. J. M. Stewart, Computer Science Centre, University of Maryland.

13 A. J. Canty and C. V. Lee, *Organometallics*, 1982, **1**, 1063.

14 A. J. Canty and A. Marker, *Inorg. Chem.*, 1976, **15**, 425.

15 A. J. Canty and G. B. Deacon, *Inorg. Chim. Acta*, 1980, **45**, L225.

16 L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 260.

17 G. Annibale, L. Canovese, L. Cattalini, G. Natile, M. Biagini-Cingi, A.-M. Manotti-Lanfredi, and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 1981, 2280.

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