342. *Some Oxyanion Complexes of Mercury*(II)

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The preparation and infrared spectra of a number of oxyanion complexes of mercury(II) are reported, and the structures of these complexes discussed. The bonding of sulphite to mercury(II) through sulphur is demonstrated, and a new mode of bonding of ligand nitrite is suggested.

PREVIOUS work in this laboratory has been concerned with the identification of the mercury(II) species extracted by methyldioctylamine (in chloroform) from aqueous nitrate,[1] sulphate, selenate, and oxalate[2] media. The present Paper reports the preparation of some related crystalline solids, and discusses the structural information obtained from the infrared spectra of these substances.

Tetranitratomercurate(II).—The species extracted from aqueous nitric acid solutions of mercury(II) by methyldioctylamine in chloroform has been identified as $[Hg(NO_3)_4]^{2-}$. Attempts to prepare salts containing this anion by crystallisation of aqueous solutions of mercuric and (say) potassium nitrate were unsuccessful, as were attempted preparations of the pyridinium salt (see below), but the salt $(Me_4N)_2[Hg(NO_3)_4]$ was obtained by crystallising a mixture of the two nitrates in ethanol.

The infrared (i.r.) spectrum of tetramethylammonium nitrate (Nujol mull) shows bands at 723w, 840m, 1050w, and 1330s cm.$^{-1}$ due to nitrate; there may also be a band at ∼1420 cm.$^{-1}$, partially obscured by the C–H and C–N vibrations of the cation. This is in good agreement with the absorptions reported by Addison and Walker[3] for the ionic nitrates of magnesium, calcium, strontium, and barium, and suggests that interaction between the nitrate ion and the cation lowers the D_{3h} symmetry of NO_3^-. The spectrum of mercuric nitrate hydrate shows a strong sharp band at 3550 cm.$^{-1}$, and weaker bands at 3350 and 3200 cm.$^{-1}$, due to water, as is the band at 1630 cm.$^{-1}$; a broad absorption at ∼650 cm.$^{-1}$, and a band at 820 cm.$^{-1}$, may also arise from water.[4] The remaining infrared absorptions are at 845m, 1040m, 1100w, ∼1300s, ∼1420s, 1650sh, and 1780w, which indicate that in this compound nitrate is covalently bonded to mercury(II).

The i.r. spectrum of $(Me_4N)_2[Hg(NO_3)_4]$ shows a large number of bands; those not due to the cation are 710m, 720m, 738m, 800m, 810m, 845w, 1010s, 1035s, 1260s, and 1300s. There may also be vibrations in the 1400—1500 cm.$^{-1}$ region obscured by those of the cation. The probable reasons for this multiplicity is that the overall symmetry of the anion is lower than T_d, either because of lattice interactions, or because the orientation of the four nitrate groups is such as to remove some of the T_d symmetry elements. The

[1] Choi and Tuck, *Inorg. Chem.*, 1963, **2**, 780.
[2] Bullock and Tuck, unpublished work.
[3] Addison and Walker, *J.*, 1963, 1220.
[4] Cf. Nakamoto, " Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, 1963, p. 156.

strong doublet at 1010 and 1035 cm.$^{-1}$ confirms the presence of ligand nitrate, and this together with the difference in the physical properties from those of the two starting materials (see Experimental section) is evidence for the existence of the $[Hg(NO_3)_4]^{2-}$ anion.

*Bis(pyridine)mercury*(II) *Nitrate.*—As noted above, attempts to prepare the pyridinium salt of $[Hg(NO_3)_4]^{2-}$ failed to give the desired product; analytical results suggested that an adduct of pyridine and mercuric nitrate was being obtained. That such a compound exists was shown by preparing $Hg(py)_2(NO_3)_2$ by reaction of yellow mercuric oxide with (effectively) pyridinium nitrate in ethanol. The i.r. spectrum of the crystalline product showed strong or medium bands at 660, 690, 720, 760, 825, 890, 1020, 1030, 1040, 1070, 1160, 1205, 1280, 1305, 1440(sh), 1460, 1490, 1575, and 1605 cm.$^{-1}$. Interpretation of the spectrum is complicated by the presence of ligand pyridine [5] (clearly not pyridinium ion [5]), but the absence of any absorption in the 1300—1400 cm.$^{-1}$ region shows that ionic nitrate is absent,[3] while bands at 825, 1030, 1280, and 1460 cm.$^{-1}$ would agree with the presence of ligand nitrate. The compound is therefore formulated as

$$\text{PY} \diagdown \quad \diagup \text{NO}_3$$
$$\text{Hg}$$
$$\text{PY} \diagup \quad \diagdown \text{NO}_3$$
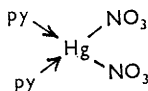
Potassium Tetranitritomercurate(II) *Nitrate.*—The composition of the salt which crystallises from aqueous solutions of potassium nitrite and mercuric nitrate has long been in dispute,[6] but Hall and Holland [7] have recently shown that it is in fact $K_3[Hg(NO_2)_4]NO_3$.

The differentiation between nitrito (−ONO) and nitro(−NO$_2$) ligand by i.r. spectroscopy has been discussed by Penland, Lane, and Quagliano.[8] The present compound, in addition to bands at 730m, 830s, and 1377s cm.$^{-1}$ assigned to the ionic nitrate group in the lattice, has a sharp triplet at 840, 845, and 852 cm.$^{-1}$, a broad strong band centred at approx. 1200 cm.$^{-1}$, and a medium intensity doublet at 1394 and 1377 cm.$^{-1}$. On this evidence one can eliminate nitrito-ligand from the structure, and assign these bands as ν_2, ν_3, and ν_1 of a C_{2v} nitro-group, with the splitting of ν_2 and ν_1, and the unresolved ν_3, ascribed to a lowering of the total molecular symmetry as in the tetranitrato-complex. In addition, there is a sharp weak band at 1770 cm.$^{-1}$, which may be associated with the ionic nitrate group (cf. potassium nitrate [9]).

Hall and Holland have however shown by X-ray methods that in the $[Hg(NO_2)_4]^{2-}$ anion, mercury has eight oxygens as its nearest neighbours, and in fact the NO_2^- group is co-ordinating through oxygen; this arrangement also leads to C_{2v} symmetry in the ligand. This may be the first example of 8-co-ordinate mercury(II). In terms of the bonding involved, however, an alternative explanation is possible. Mercury(II) is tetrahedrally co-ordinated in many of its complexes, using its own sp^3 (or sd^3) hybrid orbitals, so that in the $[Hg(NO_2)_4]^{2-}$ anion, bonding could involve overlap of such an orbital with a non-bonding sp^2 hybrid [10] of each oxygen as in (I).

$$sp^3 \text{ or } sd^3 \text{ of Hg} \qquad sp^2 \text{ of O} \qquad (\text{I})$$
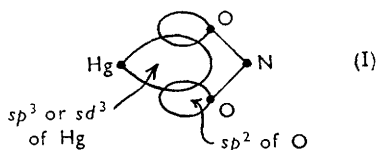
[5] Greenwood and Wade, *J.,* 1960, 1130; Gill, Nuttall, Scaife, and Sharp, *J. Inorg. Nuclear Chem.,* 1961, **18**, 79; Mitchell, *ibid.,* 1961, **21**, 382.

[6] See, *e.g.,* Sidgwick, " The Chemical Elements and their Compounds," Oxford University Press, 1950, Vol. 1, p. 329.

[7] Hall and Holland, *Proc. Chem. Soc.,* 1963, 204.

[8] Penland, Lane, and Quagliano, *J. Amer. Chem. Soc.,* 1956, **78**, 887.

[9] Ref. 4, p. 92.

[10] See Cotton and Wilkinson, " Advanced Inorganic Chemistry," Interscience, New York, 1962, p. 83.

This three-centre bonding would give three molecular orbitals (bonding, non-bonding, and anti-bonding) with only the lower two filled. A consequence of this scheme is that the N–Hg–N angles should be tetrahedral; the angles actually found [11] are 112, 106(2), 103(2), and 127°. Furthermore, there should be free rotation of the ONO group, and in agreement with this, the arrangement of the eight oxygen atoms is that expected if electrostatic repulsions are minimised.[11] A lack of precise data on the bond angle and distances in the free nitrite ion [12] prevents a more quantitative discussion of the other implications of this type of bonding at present. Similar arguments can also be advanced to explain the bonding in certain complexes containing formally bidentate nitrate.

Mercury(II)–*Sulphite Complexes.*—There is strong evidence of the complexing of mercury(II) by sulphite ion in aqueous solution.[13] Salts of the general formula $M_2Hg(SO_3)_2$ were first prepared by Barth,[14] who regarded these as salts of $H_2[Hg(SO_3)_2]$ containing S-bonded SO_3^{2-}, apparently by analogy with the aminetrisulphonate anion $[N(SO_3)_3]^{3-}$. We have prepared the anhydrous ammonium salt,[15] whose infrared spectrum shows bands at 665s, 720w, 1020s, and 1120s cm.$^{-1}$, compared with 496, 633, 961, and 1010 cm.$^{-1}$ in sulphite ion.[16] The C_{3v} symmetry does not change on complexing, but all the vibrations move to higher frequency; an increase in the force constant on complexing was noted by Woodward and Hall [17] for the isoelectronic ligand phosphorus trifluoride. The spectrum of the ligand vibrations is therefore consistent with Barth's formulation of the $[Hg(SO_3)_2]^{2-}$ anion as a disulphonatomercurate(II).

A related compound also reported by Barth,[14] and by Spacu and Dragulescu,[15] is $[Hg(SO_3)Cl]$. The i.r. spectrum shows six bands in the region studied by us, suggesting a lowering of the symmetry of the SO_3 group to C_s. The relationship between C_{3v} and C_s symmetries, as exemplified by SeO_3^{2-} and $OSeO_2^{2-}$ [actually $OSe(OH)_2$], is [16]
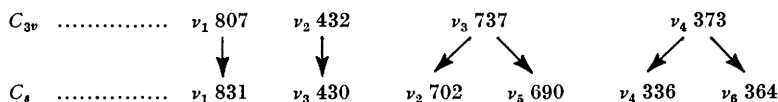
The corresponding values for SO_3^{2-} in $[Hg(SO_3)_2]^{2-}$ (C_{3v}) and $[Hg(SO_3)Cl]^-$ (C_s ?), assigned by analogy with SeO_3^{2-}, are
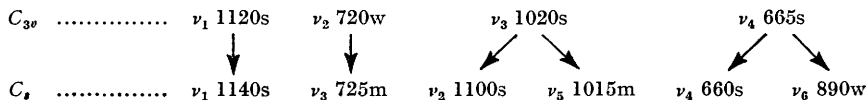
The lowering of the symmetry is related to the chemical properties of $(NH_4)[Hg(SO_3)Cl]$ which spontaneously decomposes [14] at room temperature

$$2(NH_4)[Hg(SO_3)Cl] \longrightarrow (NH_4)_2[Hg(SO_3)_2] + HgCl_2$$
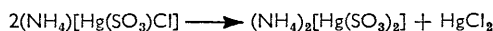
We find a corresponding series of changes in the i.r. spectrum; during about 48 hours the 6-band (C_s) spectrum of the $[Hg(SO_3)Cl]^-$ anion is gradually replaced completely by the 4-band (C_{3v}) spectrum of $[Hg(SO_3)_2]^{2-}$. In general, then, our results confirm Barth's observations, and suggest that in the crystal of $NH_4[Hg(SO_3)Cl]$ the anions lie sufficiently close to interact physically (as shown by the lowering of the symmetry of the SO_3^{2-} group) and chemically.

Mercury(II) *Sulphate.*—Solvent-extraction experiments gave evidence for the existence of $[Hg(SO_4)_2]^{2-}$ species in aqueous solution,[2] but no complexes corresponding to this are

[11] Hall, private communication.
[12] Ref. 10, p. 261.
[13] Ref. 6, p. 321.
[14] Barth, *Z. phys. Chem.*, 1892, **9**, 193.
[15] Spacu and Dragulescu, *Z. anorg. Chem.*, 1935, **224**, 273.
[16] Ref. 4, p. 87.
[17] Woodward and Hall, *Spectrochim. Acta*, 1960, **16**, 654.

known. A double salt $K_2SO_4,3HgSO_4,2H_2O$ can however be crystallised from solution. The i.r. spectrum of the sulphate group in this compound has a strong doublet at 600 and 633 cm.$^{-1}$, and bands, superimposed on a strong broad band, at 955, 1008, 1085, and 1178 cm.$^{-1}$, plus absorptions due to water at 1625 and 3400 cm.$^{-1}$. The sulphate is clearly not present as ionic SO_4^{2-}, but it is said to be impossible to distinguish between monodentate (C_{3v}) and bidentate or bridging (C_{2v}) ligand.[18] It is possible to construct structural formulæ, in agreement with the spectral evidence, in which the anion contains mercury(II) bridged by sulphate and water, and further work is planned on this question.

It is worth noting that mercuric sulphate itself has bands at 587s, 667s, 985s, 1045s, 1115s, and 1152, with the last four again superimposed on a broad band, so that in this compound too there is apparently a bonding interaction between mercury(II) and sulphate. We conclude that complexing of this cation with oxyanions is more common than was at one time supposed.[19]

<div align="center">EXPERIMENTAL</div>

Spectra.—Infrared spectra were run as mulls in Nujol or Halocarbon oils, on Unicam S.P. 100 or S.P. 200 spectrophotometers, over the range 4000—650 cm.$^{-1}$.

Tetramethylammonium tetranitratomercurate(II).—Tetramethylammonium nitrate was prepared by adding the stoicheiometric amount of silver nitrate to aqueous tetramethylammonium bromide, and crystallisation. It had m. p. 152—153° (lit.,[20] 152—153°).

Mercuric nitrate hydrate (BDH Laboratory reagent) was dried (P_2O_5); *ca.* 1·5 g. (~5 mmoles) of this material was dissolved in ethanol (20 ml.), to which a few drops of concentrated nitric acid was added to prevent hydrolysis. An equal volume of ethanol containing 10 mmoles of tetramethylammonium nitrate was then added, and the mixture left to evaporate over concentrated sulphuric acid in a partial vacuum. Despite the presence of acid, the crystals which formed within 24 hr. apparently contained hydrolysis products, and were rejected; the second crop was of white needles, m. p. 97—98°, stable in air and non-hygroscopic [unlike $Hg(NO_3)_2H_2O$] [Found: C (wet oxidation), 16·1; Hg (mercuric sulphide precipitation [21]), 33·5; NO_3^- (nitron precipitation), 42·1. $C_8H_{24}N_2Hg(NO_3)_4$ requires C, 16·1; Hg, 33·5; NO_3^-, 41·6%].

Bis(pyridine)mercury(II) *Nitrate.*—Dry pyridine (20 ml.) was dissolved in ethanol (10 ml.) and 10M-nitric acid (20 ml.) added; yellow mercuric oxide (4 g.) was then added, and the mixture refluxed gently for 20 min. When the mixture was cooled, white crystals separated; these were filtered off, washed with ethanol, and dried (P_2O_5 and H_2SO_4). The yield (5·1 g.) was ~56% of theory (Found: C, 24·8; H, 2·15; N, 10·2; Hg, 41·1. $C_{10}H_{10}N_4HgO_6$ requires C, 24·9; H, 2·1; N, 11·6; Hg, 41·6%). The compound exploded on being heated, and dissolved slowly in water, releasing pyridine (detected by smell), and rapidly in dilute hydrochloric acid.

Potassium Tetranitritomercurate(II) *Nitrate.*—The preparative method was essentially that used by Hall and Holland,[7] and our analyses confirm their formulation [Found K (flame photometry): 20·5; Hg, 35·8; NO_2^- (ceric sulphate titration [22]), 32·2; total N, 12·5. $K_3[Hg(NO_2)_4]NO_3$ requires K, 20·0; Hg, 35·9; NO_2^-, 33·0; N, 12·5%].

Ammonium Disulphanatomercurate(II).—This compound was prepared by the method described by Spacu and Dragulescu [15] [Found: Hg, 50·3; SO_3^{2-} (iodine titration [23]), 39·7. $(NH_4)_2[Hg(SO_3)_2]$ requires Hg, 50·6; SO_3^{2-}, 40·3%].

Ammonium Chlorosulphanatomercurate(II).—The preparative method again was that of ref. 15 {Found: Hg, 60·1; SO_3^{2-}, 23·0; Cl (silver nitrate titration), 10·5. $(NH_4)[Hg(SO_3)Cl]$ requires Hg, 60·0; SO_3^{2-}, 23·5; Cl, 10·6%}.

Potassium Mercuric Sulphate.—On the addition of aqueous potassium sulphate to a 1M-solution of mercuric sulphate (B.D.H. Laboratory reagent), a precipitate was formed; this was redissolved in excess of potassium sulphate. The solution was warmed, then allowed to

[18] Barraclough and Tobe, *J.*, 1961, 1993; compare Nakamoto, Fujita, Tanaka, and Kobayashi, *J. Amer. Chem. Soc.*, 1957, **79**, 4904.
[19] Ref. 6, p. 330.
[20] Bielstein, " Handbuch," Band IV, 1922, p. 47.
[21] Vogel, " Textbook of Quantitative Inorganic Analysis," Longmans, London, 3rd edn., 1961, p. 486.
[22] Ref. 21, p. 322.
[23] Ref. 21, p. 370.

cool; crystals separated,[24] and were removed and dried (P_2O_5) [Found: K, 7·2; Hg, 54·1; SO_4^{2-} ($BaSO_4$ precipitation), 35·8. $K_2SO_4,3HgSO_4,2H_2O$ requires K, 7·1; Hg, 54·7; SO_4^{2-}, 35·8%].

[24] See Mellor, " Comprehensive Treatise on Inorganic Chemistry," Longmans, London, 1923, Vol. IV, p. 976.