Complexes of 2-Aminophenol (H_2amp) and its Derivatives and the Crystal Structure of *cis*-[MoO_2(Hamp)$_2$]†

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The new complexes *cis*-[MoO_2(Hamp)$_2$] and [Os(amp)$_3$] (H_2amp = 2-aminophenol) have been isolated as well as *cis*-[MoO_2(HL)$_2$] (H_2L = 2-amino-4-chlorophenol or 2-amino-4-methylphenol) and [OsL_3] (H_2L = 2-amino-4-methylphenol or 2-amino-4-*tert*-butylphenol). The crystal structure of *cis*-[MoO_2(Hamp)$_2$] has been determined. The crystals are orthorhombic, space group *Pbna*, a = 5.767(2), b = 9.833(3), c = 23.437(6) Å, Z = 4, R = 0.028 from 697 observed reflections. The ligand binds *via* a deprotonated oxygen and NH_2. Raman, IR, and ^{13}C NMR spectra of the complexes have been recorded.

There has been considerable interest in non-innocent ligands such as catechol and 1,2-diaminobenzene;[1,2] 2-aminophenol (H_2amp) also forms complexes in which there is ambiguity as to the distribution of electrons between the ligand and metal.[3] There are few known transition-metal complexes[4] or crystal structures[5,6] of such species. Here we report the synthesis of a range of molybdenum and osmium complexes of 2-aminophenol and its derivatives and the crystal structure of *cis*-[MoO_2(Hamp)$_2$], in which H_2amp donates with the phenolic proton removed, *i.e.* as $C_6H_4(NH_2)O^-$.

Results and Discussion

Synthesis.—The molybdenum oxo complexes were made by treating the aminophenols with ammonium molybdate or *cis*-[MoO_2(acac)$_2$] (acac = acetylacetonate) while the osmium complexes were made from potassium osmate, K_2[*trans*-$OsO_2(OH)_2$]. Attempts to obtain crystals of the complexes were successful in the case of *cis*-[MoO_2(Hamp)$_2$] only.

Crystal Structure of cis-[MoO_2(Hamp)$_2$].—Table 1 gives the fractional atomic coordinates and Table 2 selected bond lengths and angles. Fig. 1 shows a perspective view of the complex with the atom numbering.

The 2-aminophenol co-ordinates as the monoanion $C_6H_4(NH_2)O^-$, chelating *via* the nitrogen atom of the amino group and the deprotonated oxygen atom. This is similar to the bonding reported for [$Mo_2(OMe)_2(NNPh)_4\{C_6H_4(NH_2)O\}_2$][5] but contrasts with the arrangement in *cis*-[$Pt(PPh_3)_2\{C_6H_4(NH)O\}$] in which 2-aminophenol chelates as an amidophenolate.[6] The molybdenum atom is octahedrally co-ordinated with each of the nitrogen atoms of the Hamp ligands *trans* to the two *cis* oxo ligands. This *trans* geometry is consistent with the *trans* effect of the oxo ligands as observed in analogous species.[7] The complex has crystallographic C_2 symmetry and the co-ordination geometry is appreciably distorted with the angles at molybdenum in the ranges 75–107 and 155–162°. The plane containing the molybdenum and the two oxo atoms is rotated by *ca.* 17° about the C_2 axis with respect to the molybdenum–nitrogen–nitrogen plane. The molybdenum–oxo bond lengths are characteristically short at 1.696(4) Å and the *trans* molybdenum–oxygen (phenolic) distances at 1.961(3) Å are comparable with those found in bis(8-hydroxyquinolinato)dioxomolybdenum *cis*-[$MoO_2(C_9H_6NO)_2$][8] and other molybdenum(VI) catecholato complexes.[7] The molybdenum–nitrogen

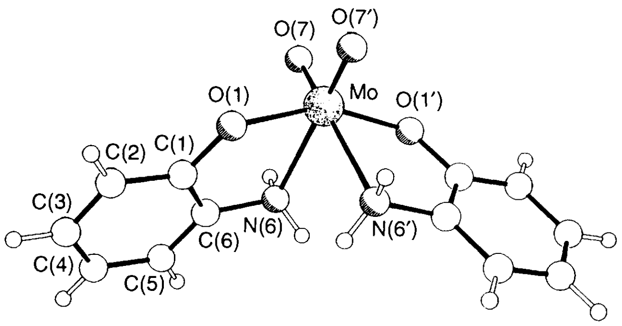

Fig. 1 Molecular structure of *cis*-[MoO_2(Hamp)$_2$]

Table 1 Aomic coordinates (× 10^4) for *cis*-[MoO_2(Hamp)$_2$]

Atom	*x*	*y*	*z*
Mo	1219(1)	2500	0
O(1)	478(6)	1389(3)	670(1)
C(1)	−1079(8)	1793(6)	1078(2)
C(2)	−1366(9)	1058(6)	1575(2)
C(3)	−2966(11)	1508(7)	1971(2)
C(4)	−4236(11)	2670(6)	1875(3)
C(5)	−3947(9)	3400(6)	1381(2)
C(6)	−2360(9)	2952(5)	979(2)
N(6)	−1883(7)	3617(5)	441(2)
O(7)	2972(6)	3738(4)	260(2)

Table 2 Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses

Mo–O(1)	1.961(3)	C(1)–C(6)	1.378(7)
Mo–O(7)	1.696(4)	C(1)–C(2)	1.380(7)
Mo–N(6)	2.340(4)	C(2)–C(3)	1.382(8)
C(1)–O(1)	1.371(6)	C(3)–C(4)	1.376(9)
C(6)–N(6)	1.447(6)	C(4)–C(5)	1.371(8)
		C(5)–C(6)	1.385(8)
O(1)–Mo–N(6)	75.0(1)	O(7)–Mo–O(7′)	106.8(2)
N(6)–Mo–O(1′)	85.8(1)	O(1)–Mo–O(7)	104.0(2)
N(6)–Mo–O(7)	87.7(2)	O(1)–Mo–O(1′)	154.8(2)
O(1)–Mo–O(7′)	91.0(2)	N(6)–Mo–N(6′)	80.3(2)
O(7)–Mo–N(6′)	162.1(2)	Mo–O(1)–C(1)	122.7(3)
Mo–N(6)–C(6)	108.6(3)		

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 3 Analytical and spectroscopic data for the complexes

	Analysis (%)[a]			Vibrational spectroscopic data[b] (cm^{-1})		
Complex	C	H	N	ν(NH)	ν(CN/CO)	ν(MoO_2)
[MoO_2(Hamp)$_2$]	41.4	3.3	8.1	3247s, 3190s	1278s, 1265vs	918s, 901s
	(41.9)	(3.5)	(8.1)	*3241(1)*	*1280(4), 1268(5)*	*916(10)*
[MoO_2(Hamcp)$_2$]	34.7	2.6	6.8	3240s, 3177m	1276vs, 1255s	918vs, 892vs
	(34.9)	(2.4)	(6.8)		*1281(6), 1253(1)*	*919(10)*
[MoO_2(Hammp)$_2$]	44.7	3.7	7.5	3235vs, 3194m	1283vs, 1228vs	920vs, 901vs
	(45.2)	(4.3)	(7.5)	*3236(1)*	*1289(7), 1221(1)*	*919(10)*
[Os(amp)$_3$]	41.5	2.7	7.9	3164m	1280m, 1253m	
	(42.3)	(3.0)	(8.2)			
[Os(ammp)$_3$]	44.7	3.8	7.0	3192vs	1274s, 1220s	
	(45.6)	(3.8)	(7.6)			
[Os(ambp)$_3$]	51.9	5.5	5.8		1283s, 1224s	
	(51.6)	(5.9)	(6.0)			

[a] Calculated values in parentheses. [b] All data measured on solids. Raman data are italicised with relative intensities in parentheses.

Table 4 Carbon-13 NMR data for 2-aminophenol derivatives and their complexes[a]

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Substituents
H_2amp[b]	144.8	137.0	115.5	120.4	117.6	115.3	
[MoO_2(Hamp)$_2$]	161.5	129(sh)	129.3	121.0	128.2	115.5	
H_2ammp	142.5	136.9	116.0	128.6	117.6	115.0	21.2 (methyl)
[MoO_2(Hammp)$_2$]	160.0	130(sh)	129.4	130.4	129.4	115.6	20.3 (methyl)
[Os(ammp)$_3$]	171.6	154.1	119.9	131.8	126.9	116.1	20.6 (methyl)
H_2amcp[b]	143.6	138.7	114.4	124.0	116.0	116.5	
[MoO_2(Hamcp)$_2$]	160.1	129.1	130.1	123.8	129(sh)	119.0	

[a] All ligands run as solutions in $(CD_3)_2SO$, all complexes as solids. [b] Assignments based on the work of Llinares *et al.*[13]

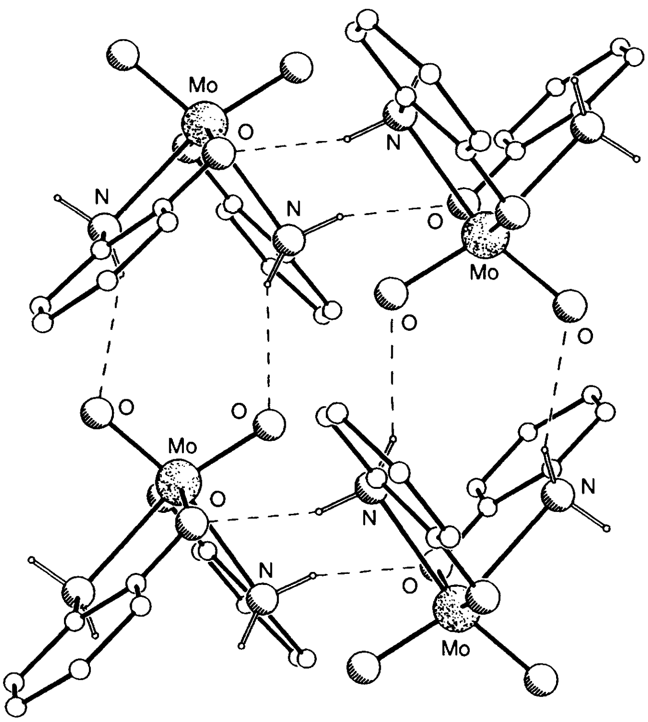


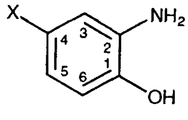
Fig. 2 Part of the two-dimensional network of hydrogen bonding which extends in the crystallographic *a* and *b* directions

distances [2.340(4) Å] are long but similar to those observed for other molybdenum(VI) amine compounds, *e.g.* (diethylenetriamine)trioxomolybdenum, [MoO_3(dien)].[9] The C–O and C–N distances [1.371(6) and 1.447(6) Å respectively] are similar to those found in catechol and 1,2-diaminobenzene complexes.[2,7] Compared with the platinum amidophenolate complex,[6] the C–N distance is longer by 0.04 Å reflecting its single-bond character. The 2-aminophenol ligand is folded slightly (by *ca.* 7°) out of the co-ordination plane of the molybdenum atom. The molybdenum atom lies 0.21 Å out of the ligand plane.

There is a network of hydrogen bonds which extends in two directions in the crystal involving both amino protons and all four co-ordinated oxygen atoms (Fig. 2). The NH ··· O (oxo) hydrogen bonds (3.00 Å) are significantly longer than the NH ··· O (phenolic) hydrogen bonds (2.89 Å). We believe that this extensive hydrogen-bonding network may account for the insolubility of the complex in a wide range of solvents.

Vibrational Spectra.—In Table 3 we give selected bands for the Raman and IR spectra of the ligands and their complexes. The symmetric and asymmetric stretch $\nu_{sym}(MoO_2)$ and $\nu_{asym}(MoO_2)$ of *cis*-[MoO_2(Hamp)] are easily identified as intense bands in the IR at 918 and 901 cm^{-1} respectively and also in the Raman at 916 cm^{-1}; these values are close to those observed for other complexes containing the *cis*-MoO_2 moiety.[10] The low solubility of the complexes (see above) prevents measurements of the spectra of solutions, although surface-enhanced Raman spectroscopy (SERS) of *cis*-[MoO_2(Hamp)$_2$] in methanol (10^{-6} mol dm^{-3} in a silver colloid made by citrate reduction[11]) is identical with that observed for 2-aminophenol[12] itself suggesting that the complex is at least partially dissociated in solution to give 2-aminophenol.

^{13}C *NMR Spectra.*—The ^{13}C NMR data are given in Table 4. We have measured the ^{13}C NMR spectrum of 2-amino-4-methylphenol in $(CD_3)_2SO$. The assignments are similar to those for 2-aminophenol and 2-amino-4-chlorophenol[13] (see diagram for atom-numbering scheme). The low solubility of the complexes prevents measurement of the ^{13}C NMR spectra in solution. The solid-state spectra however have been measured for all the molybdenum complexes and the osmium complex of 2-amino-4-methylphenol. For the osmium complex, the resonances for C(1) and C(2) shift by *ca.* 30 and 20 ppm downfield respectively compared with the free aminophenol. Similar



X = H, Me, or Cl

downfield shifts of 20 ppm attributed to the spreading of electron density to the metal atom were also noted for catecholato complexes.[14] For all three molybdenum complexes however a consistent feature is that the resonance of C(1) shifts downfield by about 15–20 ppm from the value of the free aminophenol while the resonance of C(2) shifts upfield by about 8–10 ppm.

For aromatic compounds, substituents OH and NH_2 make large downfield contributions to the chemical shift of the carbon atom to which they are attached, and slightly smaller upfield contributions to the chemical shift of the *ortho*-carbon; the magnitudes of these contributions are thought to be related to conjugation between the lone pairs on O or N and the ring electrons.[15] In the molybdenum complexes the lone pair of the nitrogen is used in co-ordination and hence the NH_2 group can be considered as contributing little to the chemical shifts. By this simple model the chemical shift of C(1) should move downfield and C(2) upfield on co-ordination. The fact that both these shifts are observed further downfield than would be predicted indicates that deshielding by the metal is still a major factor.

For diamagnetic $[Os(ammp)_3]$ (H_2ammp = 2-amino-4-methylphenol) the resonances of C(1) and C(2) both shift substantially downfield, as do the corresponding resonances for the catecholato complex $[Os(cat)_3]$.[16] We believe that this suggests that the osmium complexes contain the ligands deprotonated at both amino and phenolic sites, *i.e.* as $C_6H_4(NH)O^{2-}$.

Experimental

Preparations.—The aminophenols were obtained from Aldrich and used without further purification. The complex *cis*-$[MoO_2(acac)_2]$ was made by the method of Chakravorti and Bandyopadhyay[17] and K_2[*trans*-$OsO_2(OH)_2$] by that of Malin.[18]

$[MoO_2(Hamp)_2]$. Ammonium molybdate $[NH_4]_6[Mo_7O_{24}]\cdot 4H_2O$ (0.45 g, 0.0023 mol) was dissolved in degassed water–methanol–acetone (5 : 4 : 1, 100 cm^3) at 50 °C followed by 2-aminophenol (0.5 g, 0.0046 mol). The orange solution was left to cool on the bench over 24 h. The small yellow platy needles formed were filtered off, washed with water and dried in air. Alternatively, the complex can be made, albeit in a less crystalline form, by adding *cis*-$[MoO_2(acac)_2]$ dissolved in 50% methanol–water to a similar solution of the free aminophenol (2 : 1) and heating the resultant solution until yellow solids are formed. Yield *ca.* 40%.

$[MoO_2(HL)_2]$ [H_2L = *2-amino-4-chlorophenol* (H_2amcp) *or 2-amino-4-methylphenol* (H_2ammp)]. The complex *cis*-$[MoO_2(acac)_2]$ (0.326 g, 0.001 mol) was dissolved in methanol–water (2 : 1, 30 cm^3), followed by 2-amino-4-chlorophenol (0.28 g, 0.002 mmol) or 2-amino-4-methylphenol (0.24 g, 0.002 mol) dissolved in the same solvent (15 cm^3). The brown solution was heated to boiling, whereupon small orange-yellow plates formed. These were washed with water and acetone and dried in air. Yield *ca.* 40%.

$[Os(amp)_3]$. Potassium osmate, K_2[*trans*-$OsO_2(OH)_4$] (0.05 g, 0.13 mmol), was dissolved in water (2 cm^3) and added to a degassed solution of 2-aminophenol (0.028 g, 0.26 mmol) dissolved in ethanol (2 cm^3). The fine blue-black precipitate was centrifuged, washed with water and methanol and dried in air.

$[OsL_3]$ [H_2L = H_2ammp *or 2-amino-4-*tert*-butylphenol* (H_2ambp)]. These complexes were prepared in a similar fashion to $[Os(amp)_3]$. Yields *ca.* 25%.

Crystallography.—*Crystal data for cis*-$[MoO_2(Hamp)_2]$. $C_{12}H_{12}MoN_2O_4$, $M = 344.18$, orthorhombic, space group *Pbna* (no. 60), $a = 5.767(2)$, $b = 9.833(3)$, $c = 23.437(6)$ Å, $U = 1329.0(6)$ Å^3, $Z = 4$, $D_c = 1.720$ g cm^{-3}, Cu-Kα radiation, $\lambda = 1.541\ 78$ Å, μ(Cu-Kα) = 82 cm^{-1}, $F(000) = 688$.

Data were measured on a Siemens P3/PC diffractometer with Cu-Kα radiation (graphite monochromator) using ω scans. A crystal of dimensions 0.046 × 0.086 × 0.200 mm was used. 915 Independent reflections were measured ($2\theta \leqslant 116.0°$), of which 697 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors and for absorption (numerical correction for a face-indexed crystal; minimum and maximum transmisstion factors 0.506 and 0.723).

Structure analysis and refinement. The structure was solved by the heavy-atom method and the non-hydrogen atoms refined anisotropically. All hydrogen positions were revealed in a ΔF map and those of the amino groups were refined isotropically subject to an N–H distance constraint. The positions of the remaining hydrogen atoms were idealised (C–H 0.96 Å), assigned isotropic thermal parameters $U(H) = 1.2\ U_{eq}(C)$ and allowed to ride on their parent carbons. Refinement was by full-matrix least squares to $R = 0.028$, $R' = 0.031$ [$w^{-1} = \sigma^2(F) + 0.0005F^2$]; the maximum and minimum electron densities in the final ΔF map were 0.34 and -0.52 e Å^{-3}. Computations were carried out on an IBM 386 personal computer using the SHELXTL PC program system.[19]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Characterisation.—Infrared spectra were measured as KBr discs on a Perkin Elmer 1720 Fourier-transform spectrometer, Raman spectra with a Perkin Elmer 1700X Fourier-transform spectrometer with a Spectron Laser Systems Nd/YAG laser (excitation at 1064 nm). Proton decoupled ^{13}C NMR spectra of the aminophenols in $(CD_3)_2SO$ were run on a JEOL JNM-EX270 270 MHz Fourier transform spectrometer, ^{13}C solid-state magic-angle spinning spectra with Nuclear Quadrupole Total Suppression of Side-bands (NQTOSS) on a Bruker MSL-300 instrument at University College, London.

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