

Complexes of Mercury(II) with *p*-Nitrosodimethylaniline and *p*-Nitrosodiethylaniline

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Complexes of mercury(II) with *p*-nitrosodimethylaniline and *p*-nitrosodiethylaniline have been prepared and characterized by their spectral, magnetic and conductance measurements. Tetrahedral coordination about the mercury(II) ion has been proposed for the halide complexes, while the nitrate complexes assume an octahedral geometry. The electronic spectra indicate a strong ligand absorption with large molar absorptivity in both the solution and solid states. The magnetic data reveal that the molecules are asymmetric, while infrared spectra show that the nitroso moiety is coordinated to the metal.

INTRODUCTION

Complexes of arylnitroso ligands with some transition metals have been investigated.¹⁻⁴ These ligands behave as a monodentate and coordinate through the nitroso nitrogen^{1,4} or nitroso oxygen.^{2,5} A bridging configuration in which both the N and O atoms bind to the metal has also been found in bis-(tricarbonyl-3-chloro-2-methylnitrosobenzene)iron.⁶ Reports available in the literature indicate that *p*-nitroso-dialkylanilines are used as reagents for the spectrophotometric determination of the platinum group metals;⁷⁻⁹ and their complexes act as fungicides.^{10,11}

Recently, we reported the syntheses and physicochemical properties of zinc and cadmium complexes of *p*-nitrosodimethylaniline and *p*-nitrosodiethylaniline.^{5,12} Continuing these studies, we now report on the corresponding complexes of mercury(II) with these ligands.

EXPERIMENTAL

Materials and Methods

Reagents and solvents. *p*-Nitrosodimethylaniline and *p*-nitrosodiethylaniline were prepared by the action of nitrous acid on *N,N*-dimethylaniline and *N,N*-diethylaniline, as described in the literature.¹³ Mercury(II) iodide (red) was prepared by the method outlined by Liptrot.¹⁴ All the other reagents and solvents were com-

mercially available and, except methanol and nitromethane, were used without further purification.

Complexes of *p*-Nitrosodimethylaniline (L)

$\text{HgLCl}_2 \cdot 3.3$ mmole of HgCl_2 in 25 cm³ methanol was mixed with 6.7 mmole of the ligand in 50 cm³ of the same solvent. The mixture was stirred continuously as the solution was heated and evaporated to a small volume. The resulting precipitates were filtered, washed thoroughly with ether to remove the excess ligand and then dried in a vacuum desiccator over P_4O_{10} .

HgL_2Br_2 and HgLL_2^{15} were similarly prepared using the same proportions of the anhydrous metal salt and ligand.

$\text{HgL}_2(\text{NO}_3)_2 \cdot 3.0$ mmole $\text{Hg}(\text{NO}_3)_2 \cdot 0.5$ H₂O was dissolved in 30 cm³ nitric acid mixed with the ligand (6.10 mmole) in 50 cm³, methanol. The solution was stirred and evaporated till crystals appeared. The crystals were filtered, washed several times with ether and dried as before.

Complexes of *p*-Nitrosodiethylaniline (L')

The complexes $\text{HgL}'\text{Cl}_2$, $\text{HgL}'\text{Br}_2$, $\text{HgL}'\text{I}_2$ and $\text{HgL}'_2(\text{NO}_3)_2$ were obtained in a manner similar to the corresponding compounds of *p*-nitrosodimethylaniline described above. The complexes precipitated as powders in most cases.

Elemental analyses for carbon, hydrogen and nitrogen were performed by the Microanalytical Laboratory of the University of Ibadan. The analytical data are presented in Table I.

TABLE I

Analytical data of mercury(II) complexes of *p*-nitrosodimethylaniline (L) and *p*-nitrosodiethylaniline (L')

Compound	Colour	Yield (%)	Calc (%)			Found (%)		
			C	H	N	C	H	N
HgLCl_2	Violet-blue	70	22.79	2.39	6.64	23.23	2.53	6.76
HgL_2Br_2	Dark grey	75	27.58	3.47	8.04	27.14	3.68	7.50
$\text{HgL}_2(\text{NO}_3)_2$	Brown	60	30.75	3.23	13.45	31.02	3.00	13.70
$\text{HgL}'\text{Cl}_2$	Violet-blue	72	26.71	3.14	6.23	27.10	3.30	6.44
$\text{HgL}'\text{Br}_2$	Violet-blue	76	22.30	2.62	5.20	22.90	3.16	5.37
$\text{HgL}'\text{I}_2$	Dark grey	65	18.99	2.23	4.43	18.71	2.69	4.23
$\text{HgL}'_2(\text{NO}_3)_2$	Brown	78	35.27	4.14	12.34	35.56	4.05	12.44

Physical Measurements

The ultraviolet and visible absorption spectra of the complexes in methanol were measured in the 250–700 nm range on a Pye Unicam Sp 8–400 spectrophotometer using 1 cm glass cells. Methanol was purified by the standard method before use.¹⁶ The mull spectra in liquid paraffin were obtained by the method of Kleinberg *et al.*¹⁷ on a Pye Unicam Sp 6–550 Spectrophotometer. The spectral data are given in Table II.

The molar conductance data of the complexes were obtained as described elsewhere,¹² using approximately 1×10^{-4} M solution in each case. All the measurements were carried out at room temperature ($27.0 \pm 1.0^\circ\text{C}$) in purified methanol and nitromethane.¹⁶

The magnetic susceptibilities of the complexes were recorded at room temperature by the Gouy method as reported previously.^{12,13} Each measurement was repeated at least three times until a 1% agreement between successive values was obtained. The experimental magnetic susceptibilities were compared with those calculated from Pascal's constants,¹⁹ in which the molar magnetic susceptibility of the complex was taken as the sum of the diamagnetic susceptibilities of the mercury(II) ion and the ligands. The magnetic data are detailed in Table III.

TABLE II

Electronic spectral data of the complexes of mercury(II) with p-nitrosodimethylaniline and p-nitrosodiethylaniline

Compound	Electronic Spectra		Mull Spectra
	λ_{\max} (nm) (in methanol)		λ_{\max} (nm)
HgLCl ₂	424 (3.8)		430sh, 490, 520sh
HgL ₂ Br ₂	422 (2.6)		405sh, 485, 550sh
HgL ₂ (NO ₃) ₂	344 (5.0), 400sh		400sh, 480, 560sh
HgL'Cl ₂	428 (7.9)		430sh, 480, 530sh
HgL'Br ₂	428 (4.0)		425sh, 500, 550sh
HgL'I ₂	428 (4.1)		400sh, 485, 535sh
HgL' ₂ (NO ₃) ₂	348 (9.0), 400sh		410sh, 470, 570sh

Note: All solutions were 1×10^{-4} M. Figures in parentheses are $\epsilon_{\max} \times 10^4$, mol⁻¹ dm³ cm⁻¹.

TABLE III

Magnetic data of the complexes of mercury(II) with p-nitrosodimethylaniline and p-nitrosodiethylaniline

Compound	Mol. mass (Calc.)	T/K	$-\chi_g \times 10^6$	$-\chi_{\text{Mc}} \times 10^6$	$-\chi_{\text{Mc}} \times 10^6$	$\Delta\chi_{\text{M}} \times 10^6$
HgLCl ₂	421.7	301	0.33	139.2	181.3	42.1
HgL ₂ Br ₂	660.8	300	0.34	224.8	298.2	74.4
HgL ₂ (NO ₃) ₂	625.0	301	0.36	226.9	266.8	39.9
HgL'Cl ₂	449.7	300	0.35	157.4	205.0	47.6
HgL'Br ₂	538.6	301	0.31	167.3	227.4	60.1
HgL'I ₂	632.7	301	0.30	189.8	259.4	69.6

Notes: HgL'₂(NO₃)₂ was very hygroscopic. χ_{Mc} = Experimental magnetic susceptibility; χ_{Mc} = Calculated magnetic susceptibility; $\Delta\chi_{\text{M}} = \chi_{\text{Mc}} - \chi_{\text{Mc}}$.

The infrared spectra of the complexes between 4,000–300 cm⁻¹ were recorded as KBr pellets on a Perkin-Elmer Grating Infrared Spectrophotometer Model IR-457. The instrument was calibrated with polystyrene film. The relevant spectral data are listed in Table IV.

TABLE IV

Important infrared spectral bands (cm⁻¹) of ligands L and L' and their mercury(II) complexes

Compound	$\nu\text{C}=\text{C}$	$\nu\text{N}=\text{O}$	νNO_3^-	N—O bend	Hg-L
L	1611 s	1527 w		823 m	
L'	1610 s	1523 w		824 m	
HgLCl ₂	1606 s	1541 m		831 m	
HgL ₂ Br ₂	1611 s	?		831 s	400 w
HgL ₂ (NO ₃) ₂	1621 s	1521 s	1411 s	840 vs	421 vw
	1590 s		1391 vs		401 vw
HgL'Cl ₂	1611 s	1511 br		841 vs	400 m
HgL'Br ₂	1600 vs	1531 m		831 s	431 w
HgL'I ₂	1601 vs	1521 br		831 s	401 w
HgL' ₂ (NO ₃) ₂	1621 s	1551 br	1421 s	831 s	401 w
	1601 m	1511 w	1390 vs		

vs = very strong; s = strong; m = medium; w = weak; vw = very weak; br = broad.

RESULTS AND DISCUSSION

The complexes isolated in this study were quite stable though in some cases hygroscopic. They were moderately soluble in polar solvents like water, methanol, ethanol etc. but less soluble in non-polar solvents. Their colours varied from dark grey and violet-blue to brown (Table I). In most cases the metal to ligand ratio was 1 : 1, showing the low-coordination associated with these ligands.^{1-4,12}

Electronic Spectra

The halide complexes had one strong absorption band between 422—428 nm in methanol. This band was identified as a $\pi-\pi^*$ transition of the ligand.^{12,20} The nitrate complexes exhibited this absorption band at a higher energy (lower wavelength, 344—348 nm) compared to the ligands, and had a shoulder around 400 nm. A similar splitting and displacement of this band, though to a lower energy, on complex formation has been observed in the Pd(II) complexes.²⁰ The mull spectra of the complexes resemble the solution spectra in having one prominent absorption band centered around 470—500 nm. The shoulders appearing on either side of this band were masked in the solution spectra, especially the halide complexes. The similarity of the mull and solution spectra indicates that we are observing the same species in both phases. The shift of this band to a longer wavelength in the solid state is due to molecular association.

Conductance Data

The molar conductances of the complexes were obtained on a 10^{-4} M solution due to their low solubility in the solvents. For a more valid comparison with literature, 10^{-3} M solutions ought to be used.²¹ However, the conductance data in both solvents were quite similar, unlike the corresponding cadmium complexes,¹² and indicate that the complexes are non-electrolytes.

Magnetic Data

The magnetic susceptibilities of the complexes (Table III) show that they are diamagnetic, as it could be expected. As with the corresponding cadmium complexes,¹² the measured molar susceptibilities differed considerably from the values calculated from the additivity rule, using Pascal's constants.¹⁹ As explained earlier,¹² this is due to the presence of polarization paramagnetism associated with diamagnetic molecules and the formation of the strongly polarized donor-acceptor bond in the complexes. The difference, $\Delta\chi_M$, between the measured and calculated molar magnetic susceptibilities is believed to be a measure of the degree of asymmetry of the complexes and parallels the change in their dipole moments.^{22,23}

Infrared Spectra

The important infrared vibrational frequencies listed in Table IV were assigned by comparison with related compounds.^{2,3,20} The C=C stretching vibration was quite strong in all the complexes in the region of 1600 cm^{-1} . The nitrate complexes had two bands in this region (Table IV), probably

indicating C=C bonds in different environments. However, it has been observed that bidentate nitrate ions have bands above 1600 cm^{-1} . Thus, one of the bands in this region in $\text{HgL}_2(\text{NO}_3)_2$ and $\text{HgL}'_2(\text{NO}_3)_2$ may be due to the bidentate nitrate groups.²⁴ The $\nu\text{N}=\text{O}$ around 1500 cm^{-1} was weak in some of the complexes due to the strong C=C absorption. The involvement of the $-\text{N}=\text{O}$ group in coordination was marked by a shift of the frequency of this mode from the free ligand values. Both O and N bonding is possible in these compounds.^{2,4,12}

The N—O bending vibration around $820\text{--}840\text{ cm}^{-1}$ in all the complexes shifted to a higher frequency with respect to the ligand in accord with previous studies.^{12,20} The metal-ligand vibrations are taken as weak bands in the region of 400 cm^{-1} . The nitrate complexes $\text{HgL}_2(\text{NO}_3)_2$ and $\text{HgL}'_2(\text{NO}_3)_2$ had two bands at 1411, 1390 and 1421, 1390 cm^{-1} , respectively, attributed to asymmetric NO_3^- stretching vibrations. The splitting of this mode is the evidence for coordination of the nitrate group, as shown by the molar conductance data of these compounds. However, Popp and Ragsdale have attributed the presence of two nitrate bands in this region to the coordinated and uncoordinated nitrate groups.² The mode of coordination of the nitrate ion is difficult to infer from IR spectral studies. It is, however, known that most nitrate complexes are bidentate or bridging.²⁴

Conclusion

CONCLUSION

As with the cadmium and other metal complexes of these and related ligands, the mercury(II) complexes are low-coordinate with respect to the ligands. The magnetic, conductance and spectral data show that the complexes formed by the two ligands are structurally similar. The low values of the conductances, along with the low metal — ligand stoichiometries, indicate that the halide and nitrate ions participate in coordination, thereby making HgCl_2 , HgL_2 ,¹⁵ $\text{HgL}'\text{Cl}_2$, $\text{HgL}'\text{Br}_2$ and $\text{HgL}'\text{I}_2$ three-coordinate. These complexes are most likely to have dimeric tetrahedral structures with halide bridges similar to other three-coordinate mercury(II) complexes.^{25,26} HgL_2Br_2 , like the corresponding aniline and substituted aniline complexes,²⁵ has a tetrahedral environment about the mercury(II) ion. Bidentate coordination of the nitrate groups in $\text{HgL}_2(\text{NO}_3)_2$ and $\text{HgL}'_2(\text{NO}_3)_2$ is presumed to make the mercury(II) ion six-coordinate and octahedral with the ligand molecules occupying the axial positions. However, in the absence of X-ray structural data, the above deductions are only tentative.

It is worth noting that these compounds are generally toxic and produce itching. One of us, V.UN., developed a rash all over her body while working with these compounds and those of Al(III), Sb(III) and Ag(I) and was treated for chemical poisoning.

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SAŽETAK

Kompleksi žive(II) s *p*-nitrozodimetilanilinom i *p*-nitrozodietilanilinom

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Opisan je postupak priprave kompleksnih spojeva žive(II) s *p*-nitrozodimetilanilinom i *p*-nitrozodietilanilinom kao ligandima. Spojevi su karakterizirani spektralnim i magnetskim podacima, te mjerenjem električne vodljivosti u otopini. Tetraedarska koordinacija žive(II) se očekuje za halogenidne komplekse, a oktaedarska za nitratne. Elektronski spektri ukazuju na jake apsorpcije koordiniranih liganada kako u otopini tako u čvrstom stanju.