Organometallic Chemistry

Dinitramide and its salts
8.* Synthesis, spectra, and the structure of mercury(II) dinitramidate

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Mercury(II) dinitramidate $Hg(N_3O_4)_2$ (MDNA) has been synthesized. Its electronic and vibrational spectra show that in the crystalline state and in solutions in nonpolar solvents, MDNA is a covalent compound, the mercury atom being bound to the oxygen atoms. In polar solvents, MDNA dissociates to give mercury(II) cation and dinitramide anion $N_3O_4^-$.

Key words: mercury(II) dinitramidate; electronic spectra, vibrational spectra.

The mercury(II) salt of trinitromethane occupies a special place among trinitromethane derivatives regarding both its structure and chemical properties. For example, in the crystalline state and in weakly polar solvents, $Hg[C(NO_2)_3]_2$ is a covalent compound with a mercury—carbon bond.[1]

Our study of mercury(II) dinitramidate $Hg(N_3O_4)_2$ (MDNA) was based on some of its properties that distinguish it from other metal salts of dinitramide.[2] In the present work we synthesized MDNA and studied its structure by UV and IR spectroscopy.

Experimental

To prepare MDNA, freshly precipitated HgO (1.7 g) was added to an ethereal solution of dinitramide (DNA) obtained from KN_3O_4 (2.17 g, 15 mmol) (see Ref. 2), the mixture was stirred for 1.5 h at 20 °C and filtered, and the filtrate was concentrated *in vacuo* using a rotary evaporator, the temperature being maintained below +5 °C. The residue was washed with dry CH_2Cl_2 and evacuated for 1 h at 0—5 °C (~1 Torr) to give MDNA. Yield 2.76 g (89.3 %), temperature of decomposition 93—103 °C (depends on the rate of heating). The melting point was determined in a glass capillary using a metallic block. Found (%): N, 20.33. HgN_6O_8. Calculated (%): N, 20.26.

The resulting MDNA samples contained 1.5 to 2.8 % H_2O. The anhydrous salt was obtained by recrystallization from anhydrous benzene. MDNA can also be recrystallized from anhydrous $MeNO_2$ by heating to 50 °C and subsequent cooling to 0 °C. We used nonrecrystallized samples, because recrystallization leads to a substantial loss of the product. MDNA is readily soluble in water, alcohols, ether, ethyl acetate, and tetrahydrofuran and is insoluble in chloroform and dichloromethane.

Electronic spectra of MDNA in the crystalline state (films resulting from evaporation of an ethereal solution) and in various solvents were recorded on a Unicam Sp-800A spectrophotometer. IR spectra of solutions in KRS or Ge cells, and of thin crystalline films of MDNA prepared by evaporation of an ethereal solution on a germanium plate or Teflon film in an

* For Communication 7, see Ref. 3

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 447—450, February, 1996.

1066-5285/96/4502-0430 $15.00

Table 1. Vibrational spectra of MDNA

IR spectra				Raman spectra								
Crystalline film on Teflon or Ge	Ethereal solution	Aceto-nitrile solution	Solution in H_2O or D_2O	Crystalline film on Teflon or Ge	Solution in H_2O			Ethereal solution			Acetonitrile solution		
					ν	*I*	ρ	ν	*I*	ρ	ν	*I*	ρ
				1638 w				1620	15	dp			
1610 s	1605 vs			1606 br							1590	8	0.73
1590		1585 vs			1578	9							
	1545 m		1544 s	1538 br				1538	4				
1530 s													
	1516 m	1516 vs			1506	9					1518	4	0.58
1305 m	1310 m	1315	1340 br	1310 s				1310	61	0.2	1314	61	0.26
1285 m								1274	sh	dp			
1220 vs	1225 vs	1225 vs			1214	13		1214	8	dp	1220	9	dp
1285 m								1274	sh	dp			
1220 vs	1225 vs	1225 vs			1214	13		1214	8	dp	1220	9	dp
		1190 s	1200 vs										
1285 m								1274	sh	dp			
1220 vs	1225 vs	1225 vs			1214	13		1214	8	dp	1220	9	dp
		1190 s	1200 vs										
1055 vs			1030 m	1041 br									
1015	1015	1015						1010	9				
995 s	972 s	988 s		968 br									
863				855 s									
830 s	830 m	835 s			831	100	0.32	831	100	0.25	831	100	0.22
765 s	765 s	765 s									754	7	0.53
740 s	740 s	740 s		724 br									
				466 s	466	40	0.40						
				450				450	61	0.34	454	25	0.35
				320 s	318	64	0.16	316	56	0.16	310	42	0.18
				179 m									
				110 m									

argon atmosphere, were recorded on a UR-20 spectrophotometer. Raman spectra were measured on a DFS-12 spectrophotometer using an He—Ne laser for excitation.

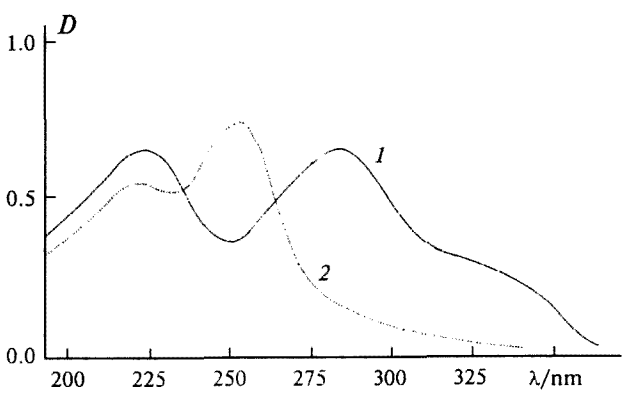
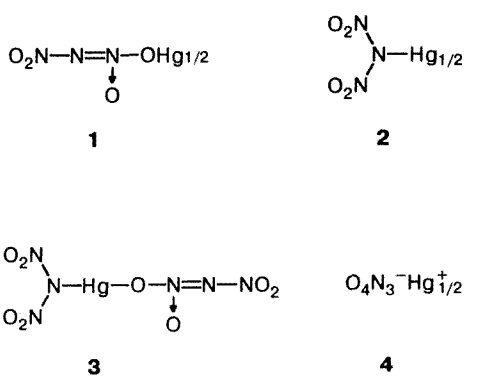


Fig. 1. UV spectra of $Hg(N_3O_4)_2$: aqueous solution (*1*); crystalline film or a solution in anhydrous ether (*2*).

Results and Discussion

MDNA can be represented by several distinctly different structures, namely, covalent structures with Hg—O bonds (**1**) and Hg—N bonds (**2**), their combination (**3**), and an ionic structure (**4**).



Each of these structures should apparently possess its own spectroscopic characteristics.

We found that the UV, IR, and Raman spectra of dilute aqueous solutions of MDNA almost do not differ from the corresponding spectra of the alkali metal salts of DNA, therefore, under these conditions, mercury dinitramidate has an ionic structure (**4**). Conversely, the spectra of the crystalline films of MDNA or its solutions in nonpolar solvents (Fig. 1, Table. 1) differ dramatically from the spectra of other dinitramide salts including DNA in the NH form.[3,4]

In fact, UV spectra of a crystalline film of MDNA, and also of its solution in anhydrous ether exhibit absorption maxima at 250 and 217 nm, which differ from the absorption maxima of the $N_3O_4^-$ anion (285 and 223 nm) or the NH form of DNA (210 nm). Thus, in the crystalline state and in nonpolar solvents, MDNA is a covalent compound; and the fact that the UV absorption band is close to that of the DNA aci-form (λ = 250 nm) makes it possible to prefer structure **1**. This choice was also confirmed by comparing the IR and Raman spectra of MDNA (see Table 1) with the spectra of DNA salts, alkyldinitramines, and O-alkyl ethers of aci-dinitramide[5,6] (Table 2).

For example, the central region of the IR spectrum of $Hg(N_3O_4)_2$ contains strong bands at 1610, 1530, 1220, and 1060 cm^{-1}, and the spectrum of KN_3O_4 exhibits bands at 1535, 1435, 1202, 1180, and 1032 cm^{-1} (the data were obtained for crystalline samples). For comparison, note that the absorption frequencies of nitro groups in mercury polynitro derivatives $Hg[C(NO_2)_2X]$ (X = H, NO_2) in which the mercury atom is bound to the carbon atom by a covalent bond,[1] differ only slightly (by no more than 10—20 cm^{-1}) from the frequencies of the nitro groups in alkyl derivatives of di- and trinitromethane. In view of the known analogy between the structures and the spectra of C- and N-nitro compounds, one might expect that structure **2** would exhibit spectra, similar to those of *N*-alkyl-*N*,*N*'-dinitramines; however, this is not the case for DNA.

Thus, in our opinion in the crystalline state and in nonpolar solvents, MDNA has the structure represented by formula **1**. In dilute aqueous solutions, MDNA dissociates into ions; however, in saturated aqueous solutions, MDNA is not wholly dissociated, according to spectroscopic data.

Table 2. IR spectra (ν/cm^{-1}) of *N*,*N*-dinitro-*N*-ethylamine and propyl and isopropyl ethers of aci-dinitramide

$EtN(NO_2)_2$	$PrON{=}N(\downarrow O)NO_2$	$Me_2CHON{=}N(\downarrow O)NO_2$
1640 vs	—	—
1605 vs	1615 s	1620 (9)
	1555 s	1555 (8)
1450 m	1455 w	1450—1470 (4)
1420 m		
	1370 vs	1380 (10)
1330 m		
	1295 m	1295 (7)
1250 vs		
	1220 s	1220 (8)
	1180 w	1180 (5)
1162 vw	1150 w	1145 (5)
1080 m	1099 m	
	992 s	995 (6)
860 s	875 m	880 (4)
830 s	830 s	830 (6)
	765 s	770 (6)
600	—	—

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Received June 27, 1995