

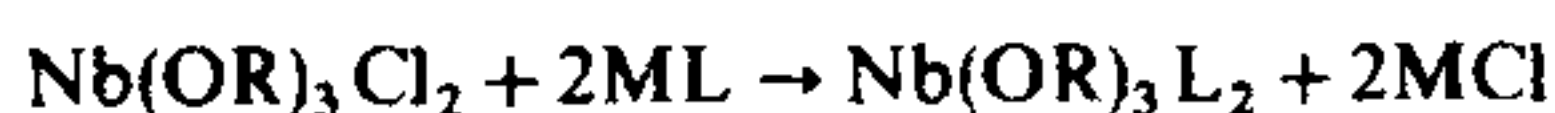
NITRO, NITRITO AND NITRATO DERIVATIVES OF DICHLORO NIOBIUM(V) TRIALKOXIDES AND TRIPHENOXIDES

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THE nitrito ion NO_2^- can coordinate a metal atom in distinct ways, giving rise to 'ligand isomers', by the formation of metal nitrogen bond, giving nitro-complexes; by formation of a metal-oxygen bond, giving nitrito complexes. Cyclopentadienyl nitro complexes have been reported in the case of Mo(VI)¹, W(VI)², Ce(IV)³, Cr(VI)⁴, Ti(III)⁵, Ti(IV)⁶, Nb(IV)⁷. However, there is no reference in literature about the nitro, nitrito and nitrate derivatives of dichloroniobium(V) trialkoxide and triphenoxide. The present communication reports the synthesis, some characteristic properties and infrared spectral studies of these derivatives.

The general procedure followed for the preparation of these complexes involved the reaction of dichloroniobium(V) trialkoxide^{8, 8a} or dichloroniobium(V) triphenoxide⁹ with NaNO_2 , AgNO_2 or AgNO_3 in tetrahydrofuran. The general equations, representing the above reaction can be written as



where $(\text{OR})_3 = (\text{OCH}_3)_3, (\text{OC}_2\text{H}_5)_3, (i\text{-OC}_3\text{H}_7)_3, (\eta\text{-OC}_4\text{H}_9)_3, (\text{OC}_6\text{H}_5)_3, (\text{OC}_6\text{H}_4\text{O}), (\text{OC}_6\text{H}_4\text{OH}), (\text{O}_2\text{C}_6\text{H}_3\text{OH}), (\text{OC}_6\text{H}_3(\text{OH})_2)$, $\text{L} = \text{NO}_2^-, \text{ONO}^-$ or ONO_2^- , $\text{M} = \text{Na}$ or Ag .

All the compounds prepared are very sensitive to moisture. Hence special precautions were taken to exclude moisture. All glass apparatus fitted with standard interchangeable joints were used. All the solvents used were dried by standard methods¹⁰. Carbon and hydrogen were determined by micro-analytical methods and niobium was determined gravimetrically. Infrared spectra of the compounds were recorded in KBr pellets on a Nicolet-5-MX spectrophotometer.

Preparation of nitro, nitrito and nitrate derivatives of Nb(OR)₃Cl₂: To 0.001 mol of dichloroniobium(V) trialkoxide/phenoxide in 100 ml of dry tetrahydrofuran was added 0.002 mol of NaNO_2 , AgNO_2 or AgNO_3 . The reaction mixture was stirred and refluxed for 8–9 hr at $\sim 70^\circ\text{C}$. The resulting product was filtered through a G-4 sintered glass disc and the

residue was washed with additional solvent. The filtrate was evaporated to dryness under reduced pressure. It was washed several times with petroleum ether ($40\text{--}60^\circ\text{C}$) and dried to give the solid product.

Analytical data of niobium, alkoxy, carbon and hydrogen reveal the general composition of compounds as $\text{Nb(OR)}_3\text{L}_2$. The alkoxy derivatives are yellowish brown in colour while phenoxy derivatives are reddish brown. They are stable only in dry and inert atmosphere and are soluble in common organic solvents. They decompose on heating beyond 110°C .

The infrared spectra of the above compounds taken in KBr pellets indicate the presence of alkoxy, phenoxy, nitro, nitrito and nitrate groups. The C–O stretching band for the alkoxy group should appear^{11–13} in the spectra in the region $1000\text{--}1200\text{ cm}^{-1}$. The presence of C–O stretching vibration frequency has been located by the presence of a band at 1060 cm^{-1} indicating methoxy, 1100 cm^{-1} for ethoxy, 1130 cm^{-1} for propoxy and 1150 cm^{-1} for butoxy groups.

The presence of monohydric phenolate compounds is indicated¹⁴ by the presence of bands at $1500, 1570, 750, 685,$ and 1240 cm^{-1} . Also the infrared spectra of these compounds do not show any band in the range $3600\text{--}3500\text{ cm}^{-1}$ indicating thereby the absence of free hydroxyl group^{15, 16} unlike catecholate and pyrogallolate complexes where the band is present. The catecholate complexes are indicated by the appearance of bands at $\sim 1575, 1445, 1180, 1070$ and 740 due to C–H stretching and C–H out of plane deformation^{14–17}. The 1,2,3-trisubstituted phenyl ring in pyrogallolate complexes is indicated by the bands¹⁷ at $\sim 1580, 1500, 1150, 1100, 1060, 980$ and 770 cm^{-1} .

The presence of the nitro, nitrito and nitrate groups is indicated by asymmetric and symmetric N–O stretching vibrations. The bands assigned to M–NO₂ (nitro) and M–O–N–O (nitrito) asymmetric and symmetric stretching vibrations (table 1) are in accordance with literature^{18–20}. The asymmetric stretching vibration for both the ligand isomers appear at the same position, $\sim 1460\text{ cm}^{-1}$. But the symmetric stretching vibration appears at different positions for both compounds. For nitro compounds it occurs in the range of $1340\text{--}1370\text{ cm}^{-1}$ but for nitrito compounds it occurs in the range of $1040\text{--}1060\text{ cm}^{-1}$. The nitrito derivatives, are not so stable and on standing change to nitro derivatives as is indicated by the IR spectrum of an aged sample of a nitrito complex. The presence of the nitrate group is indicated by asymmetric and symmetric stretching vibrations in the region^{17, 21, 22} $1530\text{--}1480$ and $1280\text{--}1240\text{ cm}^{-1}$. A medium intensity

Table 1 Some I.R. bands (cm^{-1}) of the compounds

Compounds	(N-O) Sym. str.	(N-O) Asym. str.	NO ₂ deform- ation
Nb(OCH ₃) ₃ (NO ₂) ₂	1340 (s)	1440 (s)	830 (m)
Nb(OCH ₃) ₃ (ONO) ₂	1040 (s)	1450 (s)	825 (m)
Nb(OCH ₃) ₃ (ONO ₂) ₂	1260 (s)	1480 (s)	795 (m)
Nb(OC ₂ H ₅) ₃ (NO ₂) ₂	1360 (s)	1480 (s)	825 (m)
Nb(OC ₂ H ₅) ₃ (ONO) ₂	1060 (s)	1455 (s)	820 (m)
Nb(OC ₂ H ₅) ₃ (ONO ₂) ₂	1240 (s)	1530 (s)	805 (m)
Nb(OC ₃ H ₇) ₃ (NO ₂) ₂	1370 (s)	1440 (s)	830 (m)
Nb(OC ₃ H ₇) ₃ (ONO) ₂	1040 (s)	1460 (s)	730 (m)
Nb(OC ₃ H ₇) ₃ (ONO ₂) ₂	1270 (s)	1530 (s)	805 (m)
Nb(OC ₄ H ₉) ₃ (NO ₂) ₂	1360 (s)	1450 (s)	825 (m)
Nb(OC ₄ H ₉) ₃ (ONO) ₂	1050 (s)	1460 (s)	820 (m)
Nb(OC ₄ H ₉) ₃ (ONO ₂) ₂	1280 (s)	1490 (s)	795 (m)
Nb(OC ₆ H ₅) ₃ (NO ₂) ₂	1340 (s)	1440 (s)	830 (m)
Nb(OC ₆ H ₅) ₃ (ONO) ₂	1040 (s)	1460 (s)	825 (m)
Nb(OC ₆ H ₅) ₃ (ONO ₂) ₂	1260 (s)	1520 (s)	785 (m)
Nb(OC ₆ H ₄ O)(OC ₆ H ₄ OH)(NO ₂) ₂	1370 (s)	1460 (s)	830 (m)
Nb(OC ₆ H ₄ O)(OC ₆ H ₄ OH)(ONO) ₂	1050 (s)	1440 (s)	825 (m)
Nb(OC ₆ H ₄ O)(OC ₆ H ₄ OH)(ONO ₂) ₂	1270 (s)	1490 (s)	805 (m)
Nb(O ₃ C ₆ H ₄)(O ₃ C ₆ H ₅)(NO ₂) ₂	1350 (s)	1450 (s)	820 (m)
Nb(O ₃ C ₆ H ₄)(O ₃ C ₆ H ₅)(ONO) ₂	1240 (s)	1470 (s)	830 (m)
Nb(O ₃ C ₆ H ₄)(O ₃ C ₆ H ₅)(ONO ₂) ₂	1265 (s)	1540 (s)	805 (m)

band at $\sim 781\text{--}830\text{ cm}^{-1}$ appears in the spectra can be assigned as deformation vibration in all the compounds due to O-N-O bending²³.

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SYNTHESIS AND STUDIES OF SOME FIRST-ROW TRANSITION METAL COMPLEXES WITH SCHIFF BASE DERIVED FROM 2-HYDROXY-1-NAPHTHALDEHYDE AND *m*-ANISIDINE

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RECENT studies have thrown light on the synthesis of first-row transition metal complexes¹⁻³ of some new Schiff bases. However, no work seems to have been done on the metal complexes of Schiff bases derived from 2-hydroxy-1-naphthaldehyde and anisidines. This work is aimed at studying some metal complexes of Schiff bases from the point of their structural characteristics and deals with the isolation of Cu(II), Ni(II), Co(II), Zn(II), Mn(II) and Cr(III) complexes with the bidentate Schiff base derived from 2-hydroxy-1-naphthaldehyde and *m*-anisidine.

Preparation of the Schiff base: It was synthesised⁴ by mixing equimolar amounts of 2-hydroxy-1-naphthaldehyde (3.44 g *i.e.*, 0.02 mol) and freshly distilled *m*-anisidine (2.2 ml *i.e.*, 0.02 mol) in absolute ethanol and refluxing the mixture on water bath in the presence of piperidine (2-3 drops) as the condensing agent for 2 hr. On ice-cooling shining orange-coloured Schiff base was crystallized out. It was filtered, washed, dried and recrystallized from ethanol solution. The Schiff base was analyzed and characterized by its elemental analysis (table 1) and IR spectral studies. On the basis of these studies, the structure as shown in figure 1 is proposed.

Preparation of the metal complexes: Ethanolic solution of the Schiff base and the metallic chlorides were mixed in 1:2 molar ratio and the mixture refluxed on water

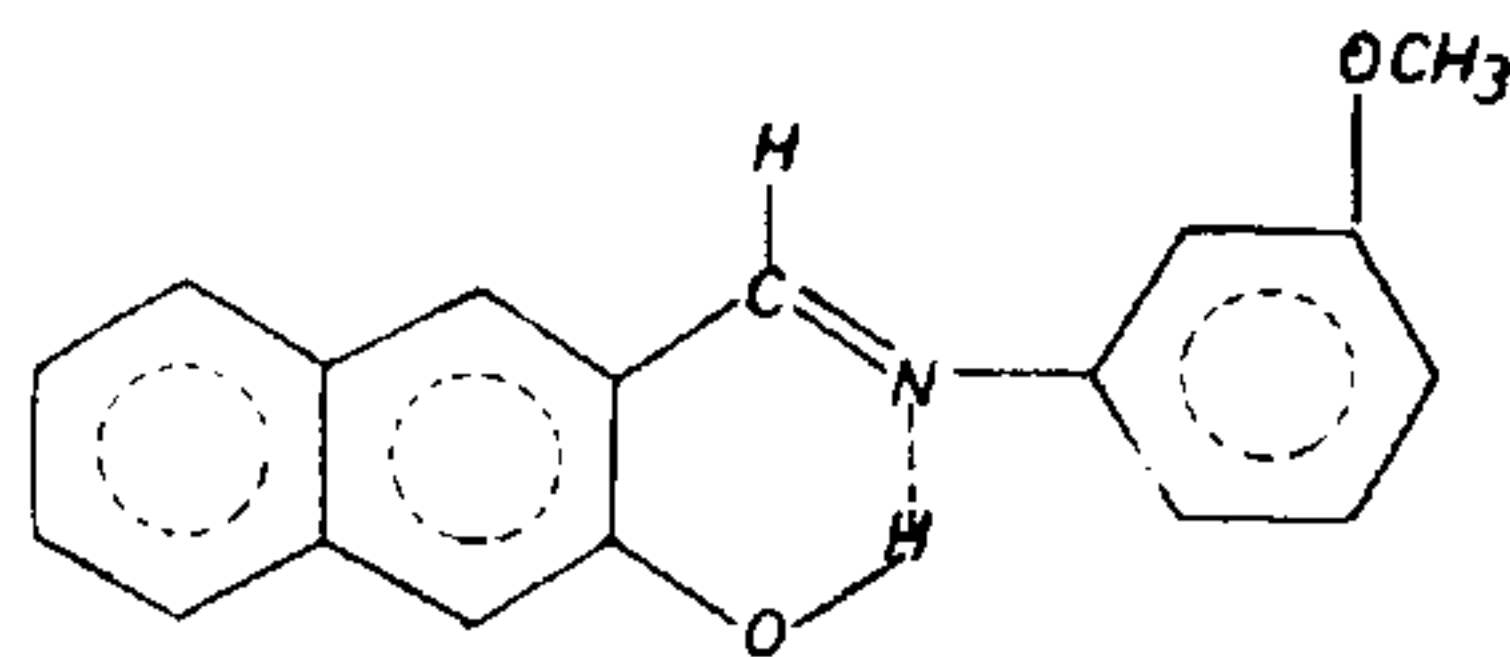


Figure 1.

bath for 2-3 hr. The reaction mixture was concentrated and then cooled. On adjusting the pH of the medium between 4 and 5 in the case Cu(II) derivative and about 8 in the other cases, solid derivatives were separated out by adding dilute ammonia solution. These were filtered, washed and finally air-dried.

The prepared metal derivatives were analyzed for metal, C, H, N and chlorine. C and H were analyzed by Leibigs method and nitrogen by Dumas's method.

Chlorine was estimated as AgCl gravimetrically⁵. For the assay of chlorine, the weighed amount of metal derivative was fused with Na₂CO₃ and the melt, cooled and extracted with boiling distilled water, and filtered. The extract was acidified with concentrated HNO₃ and chlorine precipitated as AgCl. The magnetic susceptibilities were measured on a Gouy magnetic susceptibility balance by employing Gouy's method at room temperature. Diamagnetic corrections were made with Pascal's Constants⁶.

The analytical and magnetic moment data of the complexes are given in table 1. The experimental values of the analyses for C, H and chlorine in the metal derivatives, agreed with the calculated values within the limits of experimental error.

Infrared spectra: The site of coordination of the Schiff base was inferred from IR studies. The Schiff base acts as a bidentate ligand, with the hydroxyl oxygen and the imino nitrogen atom as the principal bonding sites. The assignments of the IR bands of ligand and complexes, are based on earlier studies^{7,8}. The ligand shows a band at 2800 cm⁻¹ which is assigned to ν_{OH} involved in intramolecular H-bonding⁹ with basic azomethine nitrogen. This band is absent in the complexes indicating the breaking of H-bonding leading to deprotonation during coordination to the metal ion resulting in the formation of the O-M bond¹⁰. Further, the spectrum of the Schiff base shows a strong sharp band at 1610 cm⁻¹ assigned to ν(C=N), which in the complexes was shifted towards the lower