

Studies on Lanthanide Mixed Complexes

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A few heptacoordinated mixed ligand complexes of the type $[\text{Ln}(\text{L})(\text{L}')_3\text{Cl}_2]\text{Cl} \cdot n\text{H}_2\text{O}$ where $\text{Ln} = \text{Y(III)}, \text{La(III)}, \text{Pr(III)}, \text{Nd(III)}, \text{Sm(III)}, \text{Gd(III)}$ and Dy(III) , $\text{L} = \text{diacetylmonoxime}$, $\text{L}' = \text{thiourea}$, N-phenylthiourea and $\text{N,N'-diphenylthiourea}$ and $n = 3$ or 4 have been prepared and characterised by elemental analysis, electronic spectra, IR, thermo-analytical and conductivity measurements.

INTRODUCTION

Several lanthanide complexes with systems containing both nitrogen and oxygen donors have been reported¹⁻⁵. Recently interest has increased in the preparation and characterisation of solid lanthanide mixed complexes⁶⁻⁸ where the second ligand is basically a neutral one. An attempt was made to study the nature of bonding with sulphur donor ligands⁹. This communication details the preparation and characterisation of several lanthanide mixed complexes where diacetylmonoxime is used as primary ligand and thiourea (TU), N-phenylthiourea (PTU) and N,N'-diphenylthiourea (DPTU) are used as secondary ligands.

EXPERIMENTAL

Spectrographically pure rare-earth oxides used in this investigation were obtained from B.A.R.C., Trombay, Bombay. Solvents used were purified by the standard methods. Diacetylmonoxime m.p. 78-79°C (E. Merck) and thiourea, m.p. 179-80°C (E. Merck) employed in this investigation were recrystallised before use. N-phenylthiourea, m.p. 153-54°C and N,N'-diphenylthiourea m.p. 152-53°C were synthesised in the laboratory by adopting the methods of Davis *et al*¹⁰ and Vogel¹¹ respectively.

The simple lanthanide-diacetylmonoximates were prepared by employing the method reported by Rao *et al*^{2,3}. The mixed complexes using thiourea and substituted thioureas as secondary ligands were synthesised by adopting the following procedure. A weighed amount of the simple

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lanthanide diacetylmonoximate was dissolved in ethanol and mixed with a calculated amount of the second ligand (metal-ligand ratio *ca.* 1 : 3.5) in ethanol. The pH of the solution was recorded and has been found to be 5.8. The resulting solution was concentrated on a steam-bath when the solid separated. The compounds were washed with either acetone or ether as the case may be to remove the excess ligand. They were further purified from ethanol and vacuum dried over fused calcium chloride for 48 hrs. The analytical data of the several lanthanide mixed complexes along with molar conductance values are given in Table 1.

The UV spectra (in methanol) and the visible spectra (in DMSO) were recorded on a Beckmann D.B. model spectrophotometer having a strip chart recording arrangement and the I.R. spectra on Parkin Elmer-227 spectrophotometer as KBr pellets. The thermal analysis of some mixed complexes was carried out using MOM Budapest derivatograph at a heating rate of 10°/minute in an air flow at atmospheric pressure. All conductance measurements were carried out in methanol and dimethylformamide on Systronics Direct Reading Conductivity Meter Type-303. Carbon and hydrogen determination was carried out at the R.S.I.C., C.D.R.I., Lucknow.

RESULTS AND DISCUSSION

In the UV region one could observe only the changes in the ligand characteristic bands. The primary ligand, diacetylmonoxime, has a band around 210–15 nm ($\log \epsilon$ 4.14). The secondary ligands, thiourea, phenylthiourea and diphenylthiourea, exhibit two bands around 205–215 nm ($\log \epsilon$ 4.02–4.44) and 240–270 nm ($\log \epsilon$ 4.02–4.32). In all the mixed complexes the characteristic band of primary ligand i.e. around 210–215 nm has merged with the band of the secondary ligand in that region and appeared as a single band. The other band of the secondary ligand, i.e., around 240–270 nm is located with a slight shift in all the complexes. However, there is an intensification of absorption. The $\log \epsilon$ values in all the complexes are in the range of 4.44–6.02 nm.

In the visible region one is interested to find out the phenomenon of red shift which was explained¹² as an expansion of lanthanide orbital due to covalent bonding and contraction in highly electrostatic bonding. Jorgensen¹³ explained this as nephelauxetic effect and he tried to give a quantitative picture of the same. Angelov¹⁴ tried to compare the shifted lanthanide transitions in the complexes with those of Ln³⁺ aquo-ion. Sinha¹⁵ tried to explain the covalency of M–L bonding in Nd³⁺ complexes and calculated the percentage covalency (δ).

In this investigation, in Pr, Nd and Sm complexes it was observed that the maximum red shift, of a particular band is obtained in the case of Nd³⁺ ion. From an examination of covalency parameter it was postulated that the value decreases in the order of Nd > Pr > Sm. The covalency

TABLE I
ANALYTICAL AND MOLAR CONDUCTANCE DATA OF MIXED LANTHANIDE COMPLEXES

| Complex | % Carbon found (calcd.) | % Hydrogen found (calcd.) | % Metal found (calcd.) | % Chloride found (calcd.) | % Nitrogen found (calcd.) | % Sulphur found (calcd.) | λ_m ohm ⁻¹ mole ⁻¹ cm ² | |
|--|-------------------------|---------------------------|------------------------|---------------------------|---------------------------|--------------------------|--|-------|
| | | | | | | | Methanol | DMF |
| Y(DAMO) (TU) ₃ Cl ₃ ·4H ₂ O | | | 14.63 (14.90) | 17.59 (17.85) | 16.28 (16.43) | 15.90 (16.09) | | |
| La(DAMO) (TU) ₃ Cl ₃ ·4H ₂ O | 12.70 (12.99) | 4.00 (4.17) | 21.22 (21.48) | 16.23 (16.47) | 15.00 (15.16) | 14.69 (14.85) | 99.58 | 90.85 |
| Pr(DAMO) (TU) ₃ Cl ₃ ·4H ₂ O | | | 21.41 (21.73) | 16.18 (16.42) | 14.93 (15.11) | 14.63 (14.80) | | |
| Nd(DAMO) (TU) ₃ Cl ₃ ·4H ₂ O | 12.68 (12.88) | 4.00 (4.14) | 21.98 (22.13) | 16.00 (16.34) | 14.85 (15.03) | 14.52 (14.73) | 102.20 | 96.95 |
| Sm(DAMO) (TU) ₃ Cl ₃ ·4H ₂ O | | | 22.62 (22.86) | 15.94 (16.18) | 14.69 (14.89) | 14.44 (14.59) | | |
| Gd(DAMO) (TU) ₃ Cl ₃ ·4H ₂ O | 12.23 (12.63) | 3.90 (4.06) | 23.37 (23.65) | 15.90 (16.02) | 14.52 (14.74) | 14.28 (14.44) | 98.56 | 94.98 |
| Dy(DAMO) (TU) ₃ Cl ₃ ·4H ₂ O | | | 23.96 (24.18) | 15.70 (15.89) | 14.38 (14.62) | 14.20 (14.32) | | |
| Y(DAMO) (PTU) ₃ Cl ₃ ·4H ₂ O | | | 10.85 (11.02) | 12.70 (13.20) | 11.61 (12.15) | 11.42 (11.90) | | |
| La(DAMO) (PTU) ₃ Cl ₃ ·4H ₂ O | 34.90 (35.02) | 3.50 (3.62) | 15.69 (16.22) | 11.92 (12.43) | 11.02 (11.44) | 11.00 (11.21) | 104.18 | 87.62 |
| Pr(DAMO) (PTU) ₃ Cl ₃ ·3H ₂ O | | | 16.00 (16.41) | 11.85 (12.40) | 10.90 (11.41) | 10.82 (11.18) | | |

| | | | | | | | | |
|--|------------------|----------------|------------------|------------------|------------------|------------------|--------|--------|
| Nd(DAMO) (PTU) ₂ ·Cl ₃ ·3H ₂ O | 34.50 (34.81) | 3.40 (3.59) | 16.32 (16.73) | 11.70 (12.35) | 10.82 (11.37) | 10.71 (11.14) | 105.96 | 103.62 |
| Sm(DAMO) (PTU) ₂ ·Cl ₃ ·3H ₂ O | | | 16.88 (17.33) | 11.63 (12.27) | 10.76 (11.29) | 10.65 (11.06) | | |
| Gd(DAMO) (PTU) ₂ ·Cl ₃ ·3H ₂ O | 33.90 (34.30) | 3.35 (3.54) | 17.70 (17.97) | 11.51 (12.17) | 10.66 (11.20) | 10.50 (10.97) | 115.10 | 104.24 |
| Dy(DAMO) (PTI) ₂ ·Cl ₃ ·3H ₂ O | | | 18.05 (18.46) | 11.40 (12.10) | 10.57 (11.13) | 10.43 (10.90) | | |
| Y(DAMO) (DPTU) ₂ ·Cl ₃ ·3H ₂ O | | | 8.20 (8.59) | 10.10 (10.29) | 9.30 (9.47) | 9.00 (9.28) | | |
| La(DAMO) (DPTU) ₂ ·Cl ₃ ·3H ₂ O | 47.10 (47.58) | 4.20 (4.52) | 12.49 (12.80) | 9.58 (9.82) | 8.90 (9.03) | 8.66 (8.85) | 108.36 | 94.24 |
| Pr(DAMO) (DPTU) ₂ ·Cl ₃ ·3H ₂ O | | | 12.67 (12.97) | 9.49 (9.80) | 8.88 (9.02) | 8.61 (8.83) | | |
| Nd(DAMO) (DPTU) ₂ ·Cl ₃ ·3H ₂ O | 46.95 (47.35) | 4.35 (4.49) | 12.95 (13.23) | 9.35 (9.77) | 8.69 (8.99) | 8.59 (8.81) | 115.90 | 101.19 |
| Sm(DAMO) (DPTU) ₂ ·Cl ₃ ·3H ₂ O | | | 13.37 (13.72) | 9.31 (9.71) | 8.63 (8.94) | 8.51 (8.76) | | |
| Gd(DAMO) (DPTU) ₂ ·Cl ₃ ·3H ₂ O | | | 14.00 (14.28) | 9.27 (9.65) | 8.52 (8.88) | 8.47 (8.70) | | |
| Dy(DAMO) (DPTU) ₂ ·Cl ₃ ·3H ₂ O | 46.20 (46.55) | 4.32 (4.42) | 14.34 (14.66) | 9.21 (9.61) | 8.48 (8.54) | 8.36 (8.66) | 116.24 | 105.73 |

DAMO = Diacetylmonoxime, TU = Thiourea, PTU = N-phenylthiourea, DMF = Dimethylformamide, DPTU = N,N'-diphenylthiourea.

parameter ($b^{1/2}$) is 0.08 in those complexes where there is a red shift of 8 nm and 0.041–0.058, where there is a red shift of 2–4 nm. The 'δ' values, calculated according to the formula of Sinha, are positive indicating slight covalent character. These values are comparable with those complexes where there is oxygen coordination. Since all the secondary ligands contain sulphur it was postulated that these ligands equally compete with oxygen and nitrogen for complexation (Table 2).

The analysis of IR-spectra of the primary ligand (DAMO) shows a band around 3410 cm^{-1} and 3350 cm^{-1} assignable to N–OH stretch of oxime⁵. These bands have been lowered in all the complex indicating that there is an N–M bond contributed for primary ligand. However, the secondary ligands do have bands in the region $3140\text{--}3180\text{ cm}^{-1}$. These bands have not been shifted in the different complexes indicating the non-involvement of the nitrogen of the secondary ligands. In view of this even though the primary ligand bands have been lowered, they could not be isolated distinctly because of the reason that they have merged with the secondary ligand bands in this region. The primary ligand DAMO has a band around 1655 cm^{-1} which is due to the $\nu(\text{C}=\text{O})$ stretch. This band is not located in any of the mixed complexes, where TU, PTU and DPTU are used as secondary ligands. From this observation it can be concluded that carbonyl oxygen is involved in bond formation. From this observation and lowering of the N–OH stretch of the primary ligand it can be concluded that DAMO has acted as a bidentate ligand with bonding from carbonyl oxygen and from nitrogen of the oxime group.

The secondary ligands (TU, PTU, DPTU) exhibit bands in the region $1595\text{--}1600\text{ cm}^{-1}$ which are due to $-\text{NH}_2$ bending vibrations. These bands have either been shifted to a higher frequency or remained stationary in the several lanthanide complexes indicating the non-involvement of nitrogen in bond formation. Similarly the N–C–N stretch of the secondary ligands between $1465\text{--}1510\text{ cm}^{-1}$ has either been shifted to a higher frequency or remained stationary in the lanthanide mixed complexes indicating the absence of N–M bond from the secondary ligands.

Olliff¹⁶ observed that if there is a co-ordination through sulphur, there could be an increase in double bond character of C–N bond and N–C–N stretch should be shifted to a higher frequency. In all the present mixed complexes the bands due to N–C–N stretch have either shifted to a higher frequency or remained stationary in position. These observations are in conformity with the observations of Olliff¹⁶ and gives an indirect proof of the sulphur bonding.

The secondary ligands exhibit a band between $1410\text{--}1445\text{ cm}^{-1}$ which is due to $\nu(\text{C-S})$, NH_2 rocking and N–C–N bending. However, these bands have predominant $\nu(\text{C-S})$ stretch. As a general feature the bands in this region have been lowered in all the lanthanide complexes. Since

TABLE 2
VISIBLE ABSORPTION AND COVALENCY PARAMETER OF Pr, Nd AND Sm COMPLEXES

| Wavelength nm | log ϵ | Complex (DMSO) | Wavelength | | log ϵ | $b^{1/2}$ | $\delta\%$ |
|--------------------------------------|----------------|---|------------|------------------|----------------|-----------|------------|
| | | | nm | cm^{-1} | | | |
| <i>Praseodymium chloride (water)</i> | | | | | | | |
| 444 | 22497 | Pr(DAMO) (TU) ₃ Cl ₃ ·4H ₂ O | 446 | 22421 | 2.48 | 0.04123 | 0.3009 |
| 482 | 20738 | Pr(DAMO) (PTU) ₃ Cl ₃ ·3H ₂ O | 485 | 20618 | 2.40 | 0.0585 | 0.5833 |
| | | Pr(DAMO) (DPTU) ₃ Cl ₃ ·3H ₂ O | 446 | 22421 | 2.11 | 0.04123 | 0.3009 |
| | | | 446 | 22421 | 2.12 | 0.04123 | 0.3009 |
| <i>Neodymium chloride (water)</i> | | | | | | | |
| 521 | 19164 | Nd(DAMO) (TU) ₃ Cl ₃ ·4H ₂ O | 524 | 19083 | 1.35 | 0.04636 | 0.3918 |
| 574 | 17406 | Nd(DAMO) (PTU) ₃ Cl ₃ ·3H ₂ O | 582 | 17182 | 1.26 | 0.08031 | 1.1750 |
| | | | 524 | 19083 | 1.57 | 0.04636 | 0.3918 |
| | | | 582 | 17182 | 1.46 | 0.08031 | 1.1750 |
| | | Nd(DAMO) (DPTU) ₃ Cl ₃ ·3H ₂ O | 524 | 19083 | 1.56 | 0.04636 | 0.3918 |
| | | | 582 | 17182 | 1.49 | 0.08310 | 1.1750 |
| <i>Samarium chloride</i> | | | | | | | |
| 402 | 24875 | Sm(DAMO) (TU) ₃ Cl ₃ ·4H ₂ O | 404 | 24752 | 1.95 | 0.05 | 0.5025 |
| | | Sm(DAMO) (PTU) ₃ Cl ₃ ·3H ₂ O | 404 | 24752 | 2.00 | 0.05 | 0.5025 |
| | | Sm(DAMO) (DPTU) ₃ Cl ₃ ·3H ₂ O | 406 | 24630 | 2.55 | 0.07 | 0.9900 |

there is a predominance of ν (C-S) str, one can say as a first approximation that sulphur of the secondary ligand is involved in bonding. Further, the bands around 1340 and 1310 cm^{-1} in DPTU which are due to C-S str. and partly C-N str.¹⁷ have been lowered in most of the lanthanide complexes giving an indication of sulphur bonding in this complex.

The bands around 1055–1080 cm^{-1} in all the secondary ligands which are due to N-C-N and ν (C-S) str. have been lowered, split into two inflections. Further a change in intensity is also observed. One could conclude from the above changes that sulphur of the secondary ligands is bonded to the several lanthanide ions. The above results are in conformity with the observation made by Nabar¹⁸ in a study of bis-(1-phenyl-2-thiourea) copper (I) chloride complex and Gosavi *et al*^{19, 20} in a study of dialkyl thiourea complexes with Cu(I), Pd(II), Cd(II) and Ln(III).

The N-O str. of oxime of primary ligand around 975 cm^{-1} is located in all the complexes indicating that the bonding is through nitrogen of the oxime group. The bands around 715–807 cm^{-1} in the secondary ligands which are due to combination of N-C-N and C=S str. have been considerably lowered in all the complexes indicating the involvement of sulphur in bonding. From a study of I.R. spectra (Table 3) one could as a first approximation postulate (i) The primary ligand has acted as a bidentate ligand and the bonding is through nitrogen of the oxime group and the oxygen of the C=O group. (ii) The secondary ligands, i.e., TU, PTU and DPTU have acted as a monodentate ligand and the bonding is through sulphur.

From the TG-studies it was observed that the water molecules are lost below 150°C indicating that they are present as lattice water. Further the analysis indicated the initial loss of primary ligand and subsequent loss of secondary ligands leading to the formation of sesquioxide.

The conductivity measurements of a few representative samples is recorded in the solvents methanol and dimethylformamide. The molar conductance values in these solvents are in the range 99–116 $\text{ohm}^{-1} \text{mole}^{-1} \text{cm}^2$ and 90–105 $\text{ohm}^{-1} \text{mole}^{-1} \text{cm}^2$ respectively (Table 1). The molar conductance values in both the solvents obtained in the lanthanide complexes are well within the range for a 1 : 1 electrolyte system^{21, 22}

From the above observations as a first approximation a coordination No. seven is postulated for the lanthanide ion in the mixed complexes. The following tentative structure is proposed for the complexes.



where Ln = Y, La, Pr, Nd, Sm, Gd and Dy; L = DAMO; L' = TU, PTU, DPTU; n = 3, 4.

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TABLE 3
IR ABSORPTION BANDS (cm⁻¹) OF LANTHANIDE DIACETYLMONOXIME MIXED COMPLEXES

| DAMO | L | Y(III) complex | La(III) complex | Pr(III) complex | Nd(III) complex | Sm(III) complex | Gd(III) complex | Dy(III) complex | Assignments |
|---------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|------------------------------|-------------------------------|-------------------------------|--|
| | | <i>Thiourea</i> | | | | | | | |
| 3410 sh | | | | | | | | | O-H of oxime |
| 3350 sm | 3350 b 3260 l 3140 bm | 3320 bl 3220 l — | 3320 bm 3230 bm 3130 bm | 3320 bm 3220 bm 3120 bm | 3360 bm — 3140 bm | 3500 bm — 3100 bm | 3360 bs 3260 bs 3160 bs | 3360 bs 3260 bs 3160 bs | N-H stretch |
| 1655 ss | 1600 ss | 1595 ss | 1595 ss | 1580 sm | 1585 sm | 1620 bl 1585 sl | 1588 ss | 1635 ss 1515 ss | C=O + C=N stretch NH ₂ deformation |
| | 1465 ss | — | — | — | 1460 sm 1430 bm | 1460 bl | 1465}bs 1455} 1430 sl | 1480 sl 1450 bm | N-C-N bending |
| | 1480 ss | 1395 l | 1400 sm | 1400 l | 1395 bm | 1400 bm | 1390 bm | — | C=S stretch |
| | 1080 ss | 1075 sl | 1070 sm | 1075 sm | 1085 sl | 1080 bm | 1090 sm | 1135 sm | NH ₂ rocking |
| 975 sm | — | 965 l | 975 l | 960 l | — | — | 980 l | — | N-O str. of oxime |
| | 730 ss | 720 ss | 725 sm | 715 ss | 725 sm | 725 sm | 725 sm | 670 l | C=S + N-C-N str. |
| | | <i>Phenylthiourea</i> | | | | | | | |
| | 3380 ss 3240 bm 3140 bs | 3380 sm 3240 bm 3140 bm | 3380 ss 3250 sl 3140 sm | 3380 sm 3240 bm 3140 bm | 3380 sm 3240 bm 3140 sm | 3380 ss 3240 l 3140 bs | 3380 ss 3240 ss 3140 ss | 3380 sm 3280 sl 3140 bm | NH ₂ stretch |
| | 1598 ss | 1598 s | 1600 ss | 1600 ss | 1600 ss | 1600 ss | 1598 ss | 1600 ss | NH ₂ bending vibr. |
| | 1582 sh 1580 sm | — 1575 sm | 1580}ss 1574} | 1575 sm | 1578 sh | 1575 ss | 1582 sh 1575 ss | 1575 sm | Aromatic ring vibration |

TABLE 3 (cont.)

| DAMO | phenyl-thiourea | Y(III) complex | La(III) complex | Pr(III) complex | Nd(III) complex | Sm(III) complex | Gd(III) complex | Dy(III) complex | Assignments |
|-------------------------|----------------------------|----------------------------|----------------------------|----------------------------|---------------------------|-------------------------------|------------------------------|-----------------------------|---|
| | 1510 ss | 1500 sh | 1500 sm | 1500 bm | 1520 sm 1505 bm | 1500 bm | 1520 l 1500 sm | 1500 sm | N-C-N str. |
| | 1475 sm | 1480 l | 1480 l | 1480 l | 1470 l | 1470 sh | 1480 l 1470 sh | 1470 l | N-C-N str. |
| | 1435 ss | — | — | — | — | — | — | — | NH ₂ rocking+N-C-N bending+ν(C-S) str. |
| | 1068 sh 1055 ss | 1065 sh 1050 sm | 1060 sh 1055 sm | 1060 sh 1055 sm | 1065 l 1050 sm | 1062 sh 1050 sm 1015 sl | 1060 sh 1050 sm 1015 l | 1065 l 1050 sm 1015 l | N-C-N bending+(C-S) str. |
| | — | 955 sl | 955 bm | 910 sl | 910 sl | 955 sl | 960 bl | 960 bl | N-O str. of oxime |
| | 807 ss 745 ss 715 sm | 805 ss 745 sm 715 sl | 805 ss 745 sl 715 sl | 805 sm 745 sm 715 sl | 805 sm 745 sm 715 l | 805 ss 745 ss 715 l | 805 sl 745 ss 715 l | 805 sm 745 sm 715 sl | ν(C-S) str. |
| <i>Diphenylthiourea</i> | | | | | | | | | |
| | 3180 ss | 3190 ss | 3190 ss | 3200 ss | 3190 ss | 3200 ss | 3220 ss | 3190 bs | N-H str. |
| | 3000 } 2980 } Dsm | 3000 bs | 3000 bm | 3000 } 2980 } D | 3000 | 3030 } 3000 } D | 3050 } 3020 } Dsl | 3020 } 3000 } D | C-H aromatic str. |
| | 1595 ss | 1590 ss | 1590 ss | 1590 sm | 1590 sm | 1590 sm | 1598 sm | 1590 sm | N-H bending+aromatic ring vibr. |
| | 1585 sm | 1580 sm | 1585 sh | 1580 sh | 1580 sh | 1580 sl | 1588 sl | 1580 sh | |
| | 1540 ss | 1535 ss | 1538 ss | 1540 ss | 1535 ss | 1540 ss | 1545 ss | 1535 ss | N-H deformation+C-N asy. vibr. |
| | 1490 ss | 1485 ss | 1488 sm | 1485 sm | 1485 sm | 1485 sm | 1480 sm | 1485 sm | (B ₁)N-C-N str. |

| | | | | | | | | |
|---------|----------|---------|----------|---------|---------|---------|---------|--|
| 1445 ss | 1440 ss | 1440 ss | 1440 ss | 1440 ss | 1440 ss | 1450 ss | 1440 ss | (A) N-H rocking + N-C-N bending + ν (C-S) str. |
| 1340 ss | 1330 ss | 1332 ss | 1335 sm | 1335 sm | 1335 ss | 1340 ss | 1330 ss | Mainly from C-S str. and part. of C-N str. |
| 1310 sm | 1300 sm | 1302 sm | 1305 sl | 1305 sl | 1305 sl | 1310 sl | 1300 sm | |
| 1065 sm | 1060 sm | 1060 sm | 1065 sm | 1065 sl | 1065 sl | 1070 sl | 1060 sl | N-C-N bending + ν (C-S) str. |
| 1000 sm | 1000 sm | 995 sl | 1000 sm | 995 sl | 995 sl | 1005 sl | 1000 sl | Sym. C-N + N-H rocking vibration |
| | 975 } bl | 970 sl | 975 } DI | 965 I | 965 I | 935 sm | 925 sm | N-O str. of oxime |
| | 965 } | | 970 } | | | | | |
| 765 sh | 760 sh | 760 sh | 762 sh | 760 sh | 760 sh | 765 sh | 760 sh | 50% or more (C-S) str. + (C-N) str. |
| 760 ss | 750 ss | 750 ss | 755 sm | 760 sm | 760 sm | 750 sm | 750 ss | |
| 695 ss | 690 ss | 690 ss | 695 ss | 690 ss | 690 ss | 695 ss | 690 ss | |

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