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Coordination Compounds of 1-nitroso-2-naphthol and 2-nitroso-1-naphthol

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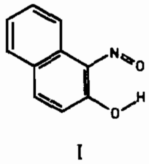
The complexes $Mn(L_1)_2$, $Mn(L_2)_2$, $Fe(L_1)_3$, $Fe(L_2)_3$, $Co(L_1)_3$, $Co(L_2)_3$, $Ni(L_1)_2 . 2H_2O$, $Ni(L_2)_2$, $Cu(L_1)_2$, $Cu(L_2)_2$, $Zn(L_1)_2$, $Zn(L_2)_2$, $Cd(L_1)_2$, $Cd(L_2)_2$, $Hg(L_1)_2$, and $Hg(L_2)_2$, (L_1 = 1-nitroso-2-naphthol, L_2 = 2-nitroso-1-naphthol), have been prepared. The i.r. spectra show that these compounds have a quinone oximic structure in the solid state. The u.v. spectra show that $Mn(L_1)_2$, $Fe(L_1)_3$, $Co(L_1)_3$, $Ni(L_1)_2 . 2H_2O$, and $Cu(L_1)_2$ in ethanol solution have the quinone oximic and the naphtholic structures in equilibrium, whereas $Zn(L_1)_2$, $Cd(L_1)_2$, and $Hg(L_1)_2$ have only the quinone oximic structure; all the complexes of 2-nitroso-1-naphthol in ethanol solution have the naphtholic structure.

A contribution to the controversial assignment of the CO, CN, and NO vibration modes for the two ligands is also offered.

Introduction

One of us[1] has previously studied some coordination compounds of N,N-dimethylanilin-4-nitroso and found that this ligand behaves as monodentate and coordinates through the oxygen atom. Later Popp and Ragsdale[2] came to the same conclusion. As a continuation of our studies on nitroso-derivative ligands, we have now investigated 1-nitroso-2-naphthol, its isomer 2-nitroso-1-naphthol, and their coordination compounds with Mn^{II}, Fe^{III}, Co^{III}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}, and Hg^{II}. The existence of these compounds in solution is mentioned by many authors;[3-7] the preparation of $Mn(L_1)_2$, $Fe(L_1)_3$, $Co(L_1)_3$, and $Cu(L_1)_2$ has been described previously.[8,10]

The two ligands can exist, according to experimental conditions, in naphtholic (I, III) and quinone oximic (II, IV) tautomeric forms. Various authors have investigated i.r. and u.v spectra but they have often reached conflicting conclusions.[9,11-15] Hadzi[11] states that 1-nitroso-2-naphthol and its isomer 2-nitroso-1-naphthol in the solid state are in the quinone oximic forms II and IV. At variance, Birca and coworkers[12,16] state that these ligands are in naphtholic forms I and III and they admit to the contemporary existence of a dimeric and a monomeric form for 1-nitroso-2-naphthol. Sterk and Ziegler[14] assume the naphtholic form I as well as the oximic form II.



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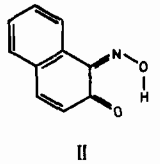

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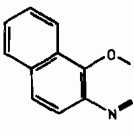

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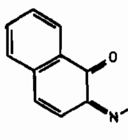
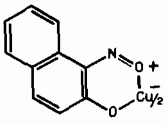


IV

Chatterjee[15] assumes the structures V and VI in 50% resonance for bis(1-nitroso-2-naphthol)Cu in ethanol solution; for the same complex in the solid state, Charalambous and co-workers[9] propose a resonance between structures VII and VIII.



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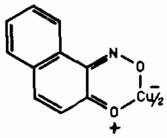

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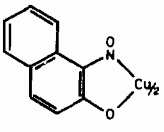

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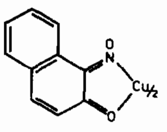

VIII

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(1) G. Condorelli, S. Gurrieri, and S. Musumeci, *Boll. Acc. Gioenia*, *8*, 791 (1966).

(2) C. J. Popp and R.O. Ragsdale, *Inorg. Chem.*, *7*, 1845 (1968).

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(8) R.A. Coleman and J.L. Rodgers, *U.S. 2*, 971, 921 (1961); *cf. C.A.*, *55*, P 10098g.

(9) J. Charalambous, M.J. Frazer, and F.B. Taylor, *J. Chem. Soc.*, 2787 (1969).

(10) I. Bellucci and A. Chiucini, *Gazz. Chim. Ital.*, *49*, II 187 (1919).

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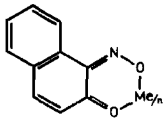
(12) D. Birca-Galateanu, L. Arcan., and C. Lupu, *Revue de Physique*, *5*, 147 (1960).

(13) A. Burawoy, M. Cais, J.T. Chamberlain, F. Liversedge, and A.R. Thompson, *J. Chem. Soc.*, 3727 (1955).

(14) H. Sterk and E. Ziegler, *Monatsch. Chem.*, *97*, 1131 (1966).

We have now found that in the solid state all the coordination compounds we have studied have the structures IX or XI. In ethanol solution $Mn(L_1)_2$, $Fe(L_1)_3$, $Co(L_1)_3$, $Ni(L_1)_2 . 2H_2O$, and $Cu(L_1)_2$ have the structures IX and X in equilibrium; $Zn(L_1)_2$, $Cd(L_1)_2$, and $Hg(L_1)_2$ have only structure IX, whereas all the complexes of 2-nitroso-1-naphthol have structure XII.



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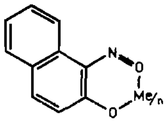

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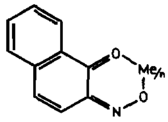

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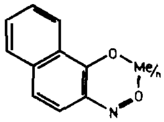

XII

By comparing the i.r. spectra of 1-nitroso-2-naphthol and 2-nitroso-1-naphthol with those of their coordination compounds and those of their parent naphthols, we shall offer a contribute to the controversial assignment of CO, CN, and NO vibration modes for the two ligands.

Experimental Section

Materials The salts were of reagent grade purity (C. Erba R.P.) and were used without further purification. 1-nitroso-2-naphthol, 2-nitroso-1-naphthol, 1-naphthol, and 2-naphthol (C. Erba R.P.) were purified by conventional methods.

Preparation of Complexes. Bis(1-nitroso-2-naphthol) manganese (dark brown) and bis(1-nitroso-2-naphthol) nickel dihydrate (yellow) were obtained by treating a 0.1 *M* solution of the corresponding metal chlorides with an excess of a 50% hydroalcoholic solution containing 2% of 1-nitroso-2-naphthol. *Anal.*: Calcd for $Mn(C_{10}H_6NO_2)_2$: Mn, 13.76; C, 60.16; N, 7.02; Found: Mn, 13.69; C, 59.55; N, 6.92. Calcd for $Ni(C_{10}H_6NO_2)_2 . 2H_2O$: Ni, 13.37; C, 54.71; N, 6.38; H_2O, 8.21; Found: Ni, 13.32; C, 53.67; N, 6.31; H_2O, 8.40 (by thermogravimetric analysis).

Tris(1-nitroso-2-naphthol)cobalt (red), tris(1-nitroso-2-naphthol)iron (black), and bis(1-nitroso-2-naphthol)-copper (dark brown), were obtained by treating aqueous 0.1 *M* solutions of the corresponding metal chlorides with a slight excess of a 10% 1-nitroso-2-naphthol solution in 50% acetic acid in the presence of 2 ml of HCl.[10] *Anal.*: Calcd for $Co(C_{10}H_6NO_2)_3$: Co, 10.24; C, 62.62; N, 7.30; Found: Co, 10.27; C, 61.63; N, 7.22. Calcd for $Fe(C_{10}H_6NO_2)_3$: Fe, 9.76; C, 62.95; N, 7.34; Found: Fe, 9.82; C, 62.55; N, 7.37. Calcd for $Cu(C_{10}H_6NO_2)_2$: Cu, 15.59; C, 58.89; N, 6.87; Found: Cu, 15.54; C, 58.30; N, 6.90.

Bis(1-nitroso-2-naphthol)zinc (brown), bis(1-nitroso-2-naphthol)cadmium (brown), and bis(1-nitroso-2-naphthol)mercury (orange) were obtained by treating aqueous solutions of zinc acetate, cadmium nitrate, and mercuric chloride respectively with 1-nitroso-2-naphthol in glacial acetic acid. *Anal.*: Calcd for $Zn(C_{10}H_6NO_2)_2$: Zn, 15.96; C, 58.63; N, 6.84; Found: Zn, 16.00; C, 58.28; N, 6.80. Calcd for $Cd(C_{10}H_6NO_2)_2$: Cd, 24.61; C, 52.59; N, 6.13; Found: Cd, 24.50; C, 52.62; N, 6.02. Calcd for $Hg(C_{10}H_6NO_2)_2$: Hg, 36.81; C, 44.08; N, 5.14; Found: Hg, 36.85; C, 43.88; N, 5.08.

Bis(2-nitroso-1-naphthol)manganese (black), and bis(2-nitroso-1-naphthol)nickel (red) were prepared similarly to the analogous complexes of 1-nitroso-2-naphthol, except for the medium (the former in sodium acetate solution and the latter in very dilute ammonia solution). *Anal.*: Calcd for $Mn(C_{10}H_6NO_2)_2$: Mn, 13.76; C, 60.16; N, 7.02; Found: Mn, 13.67; C, 59.41; N, 7.01. Calcd for $Ni(C_{10}H_6NO_2)_2$: Ni, 14.56; C, 59.60; N, 6.95; Found: Ni, 14.59; C, 59.15; N, 7.00.

Tris(2-nitroso-1-naphthol)cobalt (black), tris(2-nitroso-1-naphthol)iron (black), and bis(2-nitroso-1-naphthol)copper (black) were prepared similarly to the analogous complexes of 1-nitroso-2-naphthol. *Anal.*: Calcd for $Co(C_{10}H_6NO_2)_3$: Co, 10.24; C, 62.62; N, 7.30; Found: Co, 10.21; C, 62.03; N, 7.26. Calcd for $Fe(C_{10}H_6NO_2)_3$: Fe, 9.76; C, 62.95; N, 7.34; Found: Fe, 9.79; C, 62.46; N, 7.29. Calcd for $Cu(C_{10}H_6NO_2)_2$: Cu, 15.59; C, 58.89; N, 6.87; Found: Cu, 15.62; C, 58.48; N, 6.79.

Bis(2-nitroso-1-naphthol)zinc (orange), bis(2-nitroso-1-naphthol)cadmium (red), and bis(2-nitroso-1-naphthol)mercury (violet) were obtained by treating aqueous solutions of zinc acetate, cadmium nitrate, and mercury chloride with a slight excess of a boiling aqueous solution of 2-nitroso-1-naphthol. *Anal.*: Calcd for $Zn(C_{10}H_6NO_2)_2$: Zn, 15.96; C, 58.63; N, 6.84; Found: Zn, 15.98; C, 58.22; N, 6.79. Calcd for $Cd(C_{10}H_6NO_2)_2$: Cd, 24.61; C, 52.59; N, 6.13; Found: Cd, 24.49; C, 52.12; N, 6.08. Calcd for $Hg(C_{10}H_6NO_2)_2$: Hg, 36.81; C, 44.08; N, 5.14; Found: Hg, 36.70; C, 43.96; N, 5.12.

The compounds were analyzed by conventional methods; they are micro-crystalline, slightly soluble in water, chloroform, acetone, ethanol, ether, and decompose before melting.

Spectral Measurements

Ultraviolet spectra. These were obtained using a Optica mod. CF4NU spectrophotometer (280-500 mμ). The spectra of 1-nitroso-2-naphthol and 2-nitroso-1-naphthol were recorded in ethanol, 0.1 N $HClO_4$ ethanol and in 0.1 N KOH ethanol solutions. The spectra of complexes were recorded in ethanol. The solutions used for the absorption measurements were 10^{-4}-10^{-5} *M*. The results are reported in Table I.

Infrared spectra. These were obtained as KBr pellets using a Perkin-Elmer mod. 257 spectrophotometer (4000-625 cm^{-1}). The results are reported in Table II and in Figure 1 (for 2-naphthol, 1-nitroso-2-naphthol, and its coordination compounds) and in Fi-

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(16) D. Birca-Galateanu, *Revue de Physique*, 177 (1959).
(15) K.K. Chatterjee, *Anal. Chim. Acta*, 20, 423 (1959).

Table I. Characteristic u.v. absorption bands of 1-nitroso-2-naphthol (L$_1$), 2-nitroso-1-naphthol (L$_2$), and of their complexes in ethanol solution.

Complex	mμ	Complex	mμ
L$_1$	370	L$_2$	390
L$_1$ [a]	370	L$_2$ [a]	400
L$_1$ [b]	425	L$_2$ [b]	440
MnL$_1$)$_2$	410	Mn(L$_2$)$_2$	450
FeL$_1$)$_3$	405	Fe(L$_2$)$_3$	450
Co(L$_1$)$_3$	410	Co(L$_2$)$_3$	440
Ni(L$_1$)$_2$. 2H$_2$O	390	Ni(L$_2$)$_2$	460
Cu(L$_1$)$_2$	405	Cu(L$_2$)$_2$	430
Zn(L$_1$)$_2$	370	Zn(L$_2$)$_2$	450
Cd(L$_1$)$_2$	370	Cd(L$_2$)$_2$	450
Hg(L$_1$)$_2$	370	Hg(L$_2$)$_2$	460

[a] in 0.1 N HClO$_4$ ethanol solution; [b] in 0.1 N KOH ethanol solution.

Table II. Characteristic infrared absorption bands (KBr pellets) of 1-nitroso-2-naphthol (L$_1$) and of its complexes (cm^{-1}) [a].

Complex	ν(O–H)	ν(C=N)	ν(C=O)	ν(N–O)	δ(O–H)
L$_1$	—	1656 (m)	1612 (s))	1078 (vs)	990 (s)
2-naphthol	3280	—	—	—	975 (s)
Mn(L$_1$)$_2$ [b]	—	1485 (m)	1315 (s)	1190 (m)	—
Fe(L$_1$)$_3$	—	1475 (m)	1320 (s)	1190 (m)	—
Co(L$_1$)$_3$	—	1475 (m)	1320 (s)	1180 (m)	—
Ni(L$_1$)$_2$. 2H$_2$O	3420	1476 (m)	1314 (s)	1195 (m)	968 (m)
Cu(L$_1$)$_2$ [b]	—	1475 (m)	1315 (s)	1195 (m)	—
Zn(L$_1$)$_2$	—	1485 (m)	1318 (s)	1195 (m)	—
Cd(L$_1$)$_2$	—	1485 (m)	1312 (s)	1190 (m)	—
Hg(L$_1$)$_2$	—	1478 (m)	?	1185 (m)	—

[a] The values reported for the complexes are the most probable. [b] The band at 1612 cm^{-1} is still present.

gure 2 (for 1-naphthol, 2-nitroso-1-naphthol, and its coordination compounds).

Results and Discussion

Ultraviolet Spectra. 1-nitroso-2-naphthol in ethanol and in HClO$_4$ 0.1 N ethanol solution absorbs at 370 mμ whereas in KOH 0.1 N ethanol solution it absorbs at 425 mμ.[15] For its complexes with Mn, Fe, Co, Ni, and Cu in ethanol solution the absorption band is shifted to 390-410 mμ, suggesting a resonance between the quinone oximic structure IX and the naphtholic structure X.[15] The complexes of 1-nitroso-2-naphthol with Zn, Cd, and Hg compounds in ethanol solution absorb at 370 mμ and their spectra are very similar to those of the free ligand in HClO$_4$ 0.1 N ethanol solution; this suggests the quinone oximic structure IX for these compounds.

2-nitroso-1-naphthol in ethanol and in HClO$_4$ 0.1 N ethanol solution absorbs at 390 and 400 mμ respectively, whereas in KOH 0.1 N ethanol solution it absorbs at 440 mμ. In agreement with Chatterjee's[15] findings for the other isomer, the quinone oximic form predominates for this ligand in ethanol solution. Its coordination compounds in ethanol have a similar spectrum to that of the free ligand in KOH 0.1 N ethanol solution and the characteristic absorption band occurs at 430-460 mμ, indicating the predominance of structure XII.

Infrared Spectra. The spectrum of *1-nitroso-2-naphthol* in the range 4000-2000 cm^{-1} does not show absorption bands; the OH stretching vibration does not appear due to intramolecular hydrogen bonding.[17] In the range 1700-1500 cm^{-1}, where the C=O, C=N, and N=O stretching vibrations occur, the spectrum displays four absorption bands at 1656 (m), 1625 (vs), 1612 (s), and 1595 (s) cm^{-1}. Sterk and Ziegler[14] assign the bands at 1656 and 1625 cm^{-1} to the C=O and C=N stretching vibrations respectively, while Hadzi[11] attributes only the latter to the C=O vibration. None of these authors has assigned the band at 1612 cm^{-1}; this is rather strong, so that it cannot be an overtone or combination band. The band at 1595 cm^{-1} is attributed by Sterk and Ziegler to the aromatic ring vibration and by Birca and co-workers to the N=O stretching vibration. Two other bands are found, at 1570 (s) and 1520 (vs) cm^{-1}, which are both attributed by Hadzi to the C=N stretching vibration, whereas Sterk and Ziegler attribute only the latter to the N=O stretching vibration.

Although these assignments are controversial, we have compared the spectrum of 1-nitroso-2-naphthol with that of 2-naphthol. Bands at 1625 (vs), 1595 (s), 1560 (s), and 1510 (vs) cm^{-1} are found in the latter. It does not seem reasonable to assign the bands found in the spectrum of 2-naphthol to the C=N or N=O stretching vibration. One of these stretching modes could be associated to the band at 1656 cm^{-1}. The N=O group usually absorbs in the range 1420-1310 cm^{-1}; higher values (1653 and 1538 cm^{-1}) reported in other works are considered unlikely.[18] Colthup and co-workers[19] report that the

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(17) P.M. Boll, *Acta Chem. Scand.*, *12*, 1777 (1958).

(18) L.J. Bellamy, « The Infra-red Spectra of Complex Molecules », Methuen et Co., 1954.

(19) N.B. Colthup, L.H. Daly, and S.E. Wiberley, « Introduction to Infrared and Raman Spectroscopy », Academic Press., 1964.

stretching vibration involving this group in aromatic compounds absorbs in the range 1513-1488 cm^{-1}. Therefore we believe that the band at 1656 cm^{-1} is to be attributed to the C=N oximic stretching vibration rather to the N=O naphtholic streching. Furher, this absorption is usually a weak one[19] and the band at 1656 cm^{-1} is missing in the spectra of complexes. On the other hand, this band could not be due to the C=O stretching, which normally gives a strong band.[19] We rather think that the C=O stretching vibration can be associated with the band at 1612 cm^{-1}, which is missing in the spectra of 2-naphthol and in its metal compounds. The oximic N–O stretching and the out-of-plane deformation fall in the range 1300-900 cm^{-1}, where many bands can be observed. Two bands, at 1078 (vs) and 990 (s) cm^{-1}, are of particular interest. The former is assigned by Birca[12] to the C–N and by Hadzi[11] to the N–O stretching vibration; we believe that it is to be associated to the N–O stretching because it is missing in the spectra of 2-naphthol and of the complexes. The latter band, at 990 cm^{-1}, is attributed by Birca[12] to the out-of-plane O–H deformation; we think that this assignment is correct because the band is present also in the spectrum of 2-naphthol and is missing in the spectra of the complexes.

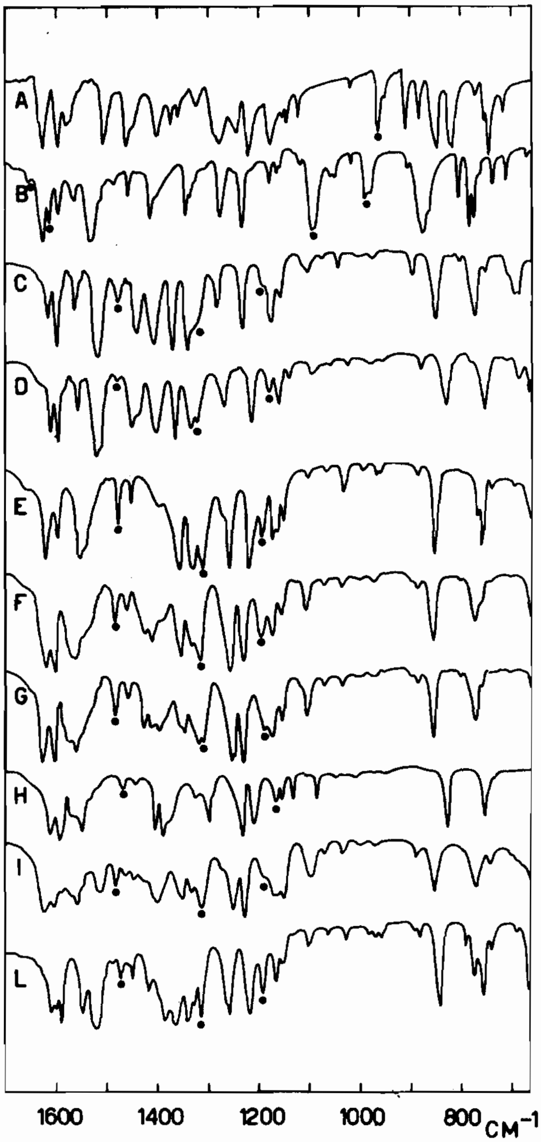

Figure 1. I.R. spectra (KBr pellets) of: 2-naphthol (A), 1-nitroso-2-naphthol (B) and of complexes of 1-nitroso-2-naphthol with Fe (C), Co (D), Ni (E), Zn (F), Cd (G), Hg (H), Mn (I), and Cu (L).

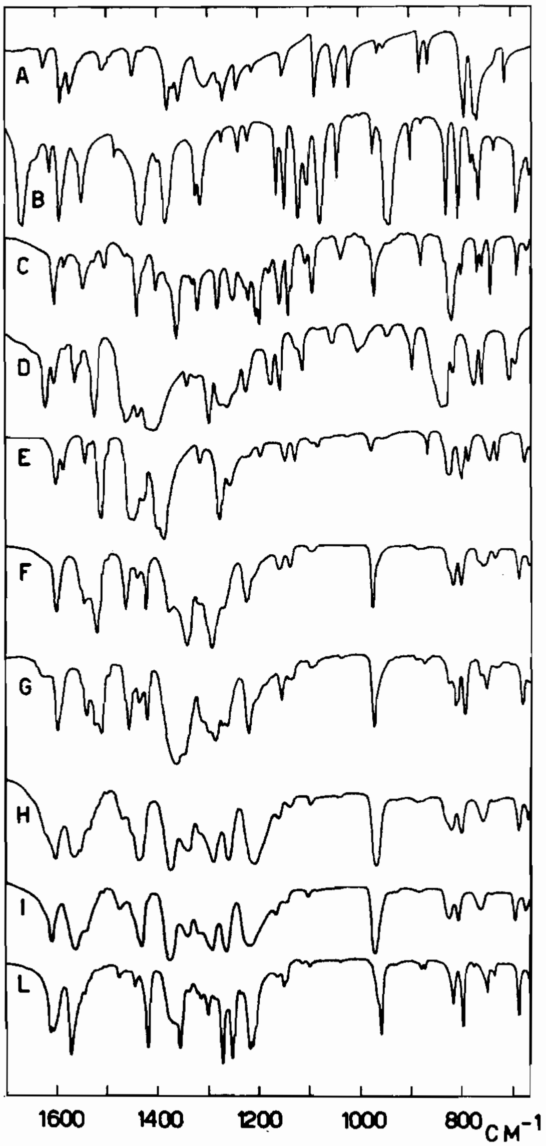

Figure 2. I.R. spectra (KBr pellets) of: 1-naphthol (A), 2-nitroso-1-naphthol (B) and of complexes of 2-nitroso-1-naphthol with Mn (C), Fe (D), Co (E), Ni (F), Cu (G), Zn (H), Cd (I), and Hg (L).

Spectra of *1-nitroso-2-naphthol complexes.* We believe that during formation of the solid complexes the structure II of the ligand is converted into structure IX. This brings about a lengthening of the C=O and C=N bonds and a shortening of the N–O bond. In fact, on comparing the spectrum of the free ligand with those of the complexes it appears that the bands corresponding to the C=N and C=O stretching vibrations are shifted upon coordination towards lower wavenumbers whereas the N–O stretching vibration is shifted towards higher wavenumbers. For some complexes the localization of these bands is not so evident because of the complexity of the spectra; it seems that the C=N band is shifted to 1475-1485 cm^{-1} and is superimposed to a very weak band of the ligand; the C=O band is shifted to 1312-1320 cm^{-1} and the N–O band is shifted to 1180-1195 cm^{-1}. It is not clear why the band at 1612 cm^{-1}, which is assigned to the C=O stretching vibration of the ligand is retained in the spectra of Mn and Cu complexes although a new band appears at 1315 cm^{-1}. Moreover, according to structure IX, the band associated with the out-of-plane O–H deformation is not found in the spectra of complexes except, obviously, for $Ni(L_1)_2 . 2H_2O$. The characteristic absorption bands of these complexes are reported in Table II.

The spectrum of *2-nitroso-1-naphthol* has a broad absorption band at 3280 cm^{-1} due to the O–H stretching vibration; this low value is caused by intramolecular association.[17] In the range 1700-1500 cm^{-1} five bands, at 1668 (vs), 1645 (w), 1612 (m), 1595 (vs), and 1550 (s) cm^{-1} occur. Hadzi[11] assigns the band at 1668 cm^{-1} to the C=O stretching vibration of the oximic form and the band at 1550 cm^{-1} to the C=N stretching vibration; Birca-Galateanu[16] assigns the band at 1595 cm^{-1} to the N=O stretching vibration. Therefore even for this ligand a comparison between its spectrum and that of the parent naphthol is useful. In the spectrum of the latter bands are found at 1628 (m), 1595 (vs), and 1575 (s) cm^{-1}. In agreement with Hadzi, we attribute the band at 1668 cm^{-1} to the C=O stretching vibration; in fact, since there is no chelation for this ligand, the C=O group has a greater double bond character and therefore it absorbs at normal values. As for 1-nitroso-2-naphthol, we feel that it is not correct to attribute the bands at 1595 and 1550 cm^{-1} to the N=O and C=N stretchings, since these bands are present also in spectrum of 2-naphthol (the latter one is shifted to 1575 cm^{-1}, but is similar in appearance and intensity). We believe that the C=N stretching vibration can be associated with the band at 1645 cm^{-1} because it is missing in the spectra of 1-naphthol and of complexes of 2-nitroso-1-naphthol and because its shape is similar to the band of 1-nitroso-2-napthol at 1656 cm^{-1}. The band at 1612 cm^{-1}, which is shifted to 1628 cm^{-1} in spectrum of 1-nahpthol, should be due to the aromatic ring. In the range 1300-900 cm^{-1}, two bands among others are found, at 1070 (vs) and at 930 (vs) cm^{-1}; the former is assigned by Hadzi[11] to the N–O stretching vibration and the latter by Birca[16] to the out-of-plane O–H deformation. We believe that the band at 1070 cm^{-1}, which is shifted to 1090 cm^{-1} in the spectrum of 1-naphthol and is missing in the spectra of complexes, is due to the out-of-plane O–H deformation of the oximic group; besides, we believe that the band at 930 cm^{-1} could be associated to the vibration of the oximic N–O group, since this band is missing in the spectrum of 1-naphthol and is shifted towards higher wavenumbers upon coordination.

The spectra of *2-nitroso-1-napthol complexes.* For these compounds also we can develop similar arguments as those made for the complexes of the other isomer as far as the vibrations of the CO, CN, NO, and OH groups, although almost all the absorption bands are shifted upon coordination. It is evident that the C=N and C=O stretching vibrations are shifted towards lower wavenumbers whereas the N–O stretching vibration is shifted towards higher wavenumbers. In fact, the C=O and C=N stretching vibrations for the free ligand fall at 1668 and 1645 cm^{-1} respectively and are not found at such wavenumbers in the spectra of all the complexes. Since no new band appears at higher wavenumbers, these bands should be shifted towards lower values, but the spectra in the region 1500-1200 cm^{-1} show so many bands that it is not possible to establish with certainty where such bands fall. In the range 1200-1000 cm^{-1}, there is observed either a disappearance or a marked attenuation of the numerous and strong bands of 2-nitroso-1-naphthol. Since the spectra of the complexes in the range 1000-625 cm^{-1} are again very similar to those of the ligand, it seems reasonable to assume that the disappearing bands are shifted towards wavenumbers over 1200 cm^{-1}. The N–O stretching vibration which falls at 930 cm^{-1} in the ligand, is not found at this value in the spectra of complexes; since at lower wavenumbers the spectra of all complexes are similar to those of the free ligand, even this band should be shifted over 1200 cm^{-1}, but in this region it is difficult to identify it with certainty, as mentioned before. The stretching and the out-of-plane O–H deformation vibrations cannot be located in the spectra of any of the complexes investigated, in agreement with structure XI.