Metal Chelates of 9-Hydroxy-1-phenalenone

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(Received April 11, 1975)

Metal chelates of 9-hydroxy-1-phenalenone(9-hydroxyperinaphthenone) have been prepared. Metal-ligand compositions were 1 : 2 for Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Mg(II), UO_2(II), and Be(II) chelates and 1 : 3 for Fe(III) and Al(III) chelates. The structure of the Cu(II) chelate was determined to be square-planar by the spectral analogy to copper(II) acetylacetonate. The Ni(II), Co(II), Mn(II), Zn(II), and Mg(II) chelates were octahedral with further coordination of two moles of water. The structure determination dealt at first with the Ni(II) chelate by means of its electronic spectrum and magnetic property; the others were studied using the similarity of their X-ray diffraction diagrams to that of the Ni(II) chelate. The Fe(III) and Al(III) chelates were also octahedral and probably have D_3 symmetry. Infrared spectra were studied for the free ligand and the metal chelates and the assignment of the carbonyl and metal-oxygen stretching vibrations was discussed by comparison with those of metal acetylacetonates.

9-Hydroxy-1-phenalenone (abbreviated as HPNA), which was first synthesized by Laudon,[1] carries a hydroxyl group at a *peri* position to a carbonyl group and can be regarded as a cyclic analogue of an enol form of acetylacetone. Although metal chelates of acetylacetone have been studied extensively, those of HPNA have not been reported so far. The chemical behavior of HPNA is anomalous as a ketone or a phenol because the hydroxyl group is neither acetylated nor methylated and the carbonyl group affords no oxime or Schiff bases. This is assumed to be due to a very strong conjugated hydrogen bonding between the functional groups and it is evidenced by the fact that HPNA exhibits no absorption due to the OH stretching vibration and shows anomalous carbonyl stretching frequency in its infrared spectrum. In this respect the metal chelate formation of this compound as a bidentate ligand will be worth investigating. In this paper, we deal with the synthesis of the metal chelates and their structure determination and will discuss the infrared assignment of the carbonyl and metal-oxygen vibrations in comparison with those of metal acetylacetonates.

Experimental

Infrared absorption spectra were taken by a Koken Model DS-301 with NaCl prism for the 4000—700 cm^{-1} region and by a Hitachi EPI-G2 grating spectrophotometer for the 700—400 cm^{-1}. Electronic reflectance spectra were measured with a Hitachi EPS-3T spectrophotometer. NMR spectra were recorded at 60 MHz in $CDCl_3$ with a Hitachi Model R-24 spectrometer. The chemical shifts are quoted as τ values relative to TMS. X-Ray diffraction diagrams were obtained with a Rigakudenki Geigarflex and magnetic moments were measured by a Faraday method at room temperature.

9-Hydroxy-1-phenalenone(HPNA) was prepared according to the method of Laudon[1] and purified by vacuum sublimation followed by repeated recrystallization from methanol: yellow plates, mp 199—200 °C.

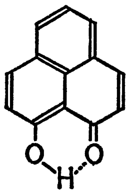
Metal Chelates were prepared by the following general procedure: one mol of HPNA was dissolved in hot ethanol and to this was added 1/2 mol of a divalent metal salt or 1/3 mol of a trivalent metal salt in minimum amount of dilute ethanol. The mixture was heated in a water bath for 30 min and the resulting precipitates were filtered after cooling and washed with ethanol. The crude metal chelates were recrystallized from butanol for those of Ni(II), Co(II), Mn(II), Zn(II), and Mg(II) or from pyridine for those of Cu(II), UO_2(II), Be(II), Al(III), and Fe(III), and dried *in vacuo* at room temperature. When the Ni(II) and Co(II) chelates were recrystallized from pyridine, the dipyridinate complexes were obtained. The metal salts employed in the reactions were acetates, except for beryllium nitrate, potassium alum, and ferric chloride hexahydrate. The sodium salt was prepared by adding excess sodium ethoxide in ethanol to the absolute ethanol solution of HPNA. The elemental analyses of these metal chelates are summarized in Table 1.

Results and Discussion

It has been found that 9-hydroxy-1-phenalenone (HPNA) showed fairly strong chelating tendencies, yielding chelates with a wide variety of metal ions. The elemental analyses revealed that the metal-ligand composition was 1 : 2 for the bivalent metal chelates and that they carried two moles of water, except for the Cu(II) and Be(II) chelates.

Because of their low solubility in ordinary organic solvents, the spectroscopic study of these metal chelates had to be done in the solid state. Figure 1 shows a reflectance spectrum of the Cu(II)-chelate, in which one can observe at least two and probably three d-d transition bands at 18.5×10^3, 15.6×10^3, and 14.5×10^3 cm^{-1}. The spectral pattern is similar to that obtained for bisacetylacetonatocopper(II),[2] whose structure has been established to be square-planar by X-ray crystallography.[3] It is obvious, therefore, that the Cu(II)-chelate has a similar square-planar structure.

The Ni(II) dihydrate complex was paramagnetic (μ_{eff}=3.48 B.M.) and the waters could be replaced by two pyridine molecules by recrystallization from the solvent; the dipyridinate complex was also



HPNA

Scheme 1.

Table 1. Elemental analyses of metal chelates of 9-hydroxy-1-phenalenone

Formula	C%		H%		M%	
	Calcd	Found	Calcd	Found	Calcd	Found
$C_{13}H_7O_2Na$	71.56	71.23	3.23	3.63	10.54	10.31
$C_{26}H_{14}O_4Cu$	68.79	69.17	3.11	3.39	14.00	13.81
$C_{26}H_{14}O_4Ni$	69.53	69.06	3.14	3.09	—	—
$C_{26}H_{14}O_4Ni\ 2H_2O$	64.37	64.13	3.74	3.93	12.10	11.90
$C_{26}H_{14}O_4Ni\ 2C_5H_5N$[a]	71.20	71.09	3.98	3.92	—	—
$C_{26}H_{14}O_4Co\ 2H_2O$	64.34	64.35	3.74	4.01	12.14	12.70
$C_{26}H_{14}O_4Co\ 2C_5H_5N$[b]	71.17	71.15	3.98	4.01	—	—
$C_{26}H_{14}O_4Zn\ 2H_2O$	63.50	63.43	3.69	3.74	13.29	13.62
$C_{26}H_{14}O_4Mn\ 2H_2O$	64.88	64.98	3.73	3.88	11.42	10.14
$C_{26}H_{14}O_4Mg\ 2H_2O$	69.28	69.03	4.03	4.01	5.39	5.93
$C_{26}H_{14}O_6U\ C_5H_5N$[c]	50.35	50.54	2.59	2.88	32.19	33.14
$C_{26}H_{14}O_4Be$	78.19	77.88	3.53	3.36	—	—
$C_{39}H_{21}O_6Al$	76.47	76.32	3.46	3.84	4.41	4.77
$C_{39}H_{21}O_6Fe$	73.03	72.82	3.30	3.57	8.71	8.40

a) Calcd N: 4.61, Found 4.68%. b) Calcd N: 4.61, Found 4.42%. c) Calcd N: 1.89, Found 1.65%.

paramagnetic (μ_{eff}=3.05 B.M.). The reflectance spectrum of the dihydrate complex as well as the dipyridinate complex exhibits d-d transitions around 8×10^3 and 18×10^3 cm^{-1} as seen in Fig. 1. It is due to a partial overlap with a tail-off from the π-π^* transition of the phenalenone ring that the absorption bands are not well defined. They are, however, essentially similar to those for octahedral Ni(II)-complexes such as bisacetylacetonatonickel(II) dihydrate and bissalicylaldehydatonickel(II) dihydrate.[4] Judging from the magnetic and spectral evidence, an octahedral configuration is most probable for the Ni(II) dihydrate and dipyridinate complexes.

The water and pyridine molecules in the Ni(II)-complexes could be eliminated by heating at 150 °C *in vacuo*. The resulting anhydrous Ni(II)-chelate still showed an appreciable magnetic moment (μ_{eff}= 1.5 B.M.). This value is, however, too low to be reliable evidence for adopting a polymeric octahedral structure in which the planar unit is linked by sharing a lone pair of the oxygen atoms. This is probably due to contamination by the paramagnetic dihydrate complex species, because the crystals were fairly hygroscopic and the magnetic moment increased to 2.05 B.M. after standing in air for a while. The chelate which resulted from the dipyridinate complex was identical to the anhydrous one in its electronic spectral pattern, as seen in Fig. 1. The absorption due to the d-d transition, which appears at 15×10^3 cm^{-1} and is absent at lower frequencies, is normally associated with a square-planar configuration.[5]

For the structural determination of other bivalent metal chelates, X-ray powder diffraction diagrams were drawn for the dihydrate complexes of Co(II), Zn(II), Mn(II), and Mg(II), and compared with that of the Ni(II) dihydrate complex. As seen in Fig. 2, all patterns are identical; they are therefore isomorphous and the configurations are all similar to the Ni(II) dihydrate complex. Thus they are octahedral.

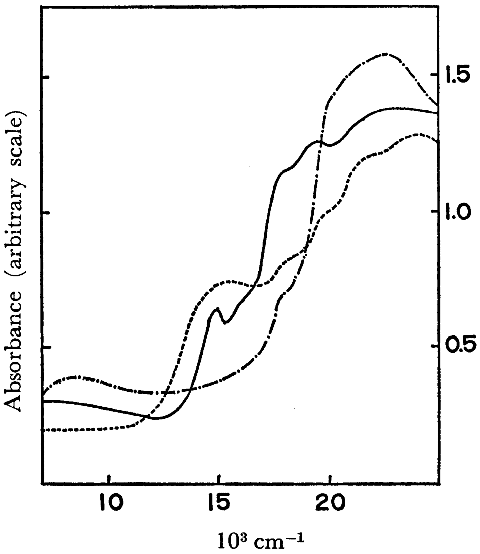


Fig. 1. Reflectance spectra of metal-chelates of HPNA: (----), Cu(II); (——), Ni(II); (—·—), Ni(II)·$2H_2O$.

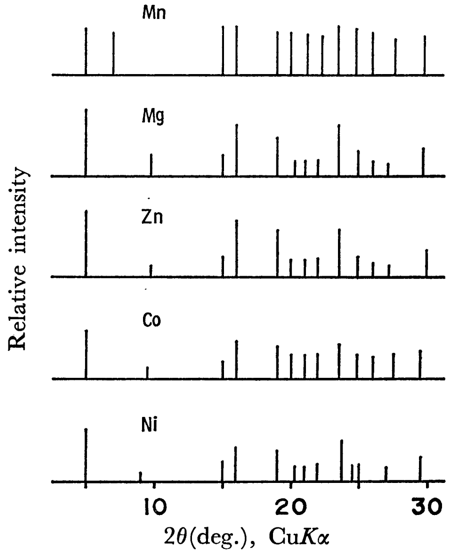


Fig. 2. X-ray powder diffraction diagrams of Mn(II), Mg(II), Zn(II), Co(II), and Ni(II) dihydrate complexes of HPNA.

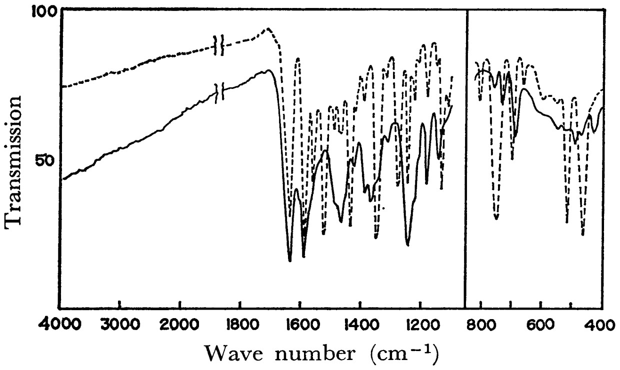


Fig. 3. IR spectra of HPNA (——) and Cu(II)-chelate (----); 4000—1900 cm^{-1} in hexachlorobutadiene, 1900—1100 cm^{-1} in Nujol, and 900—400 cm^{-1} in KBr.

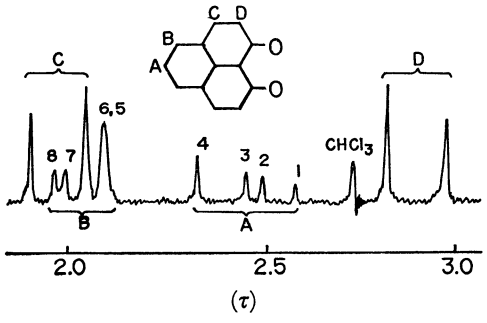


Fig. 4. PMR spectrum of HPNA in $CDCl_3$.

As has been revealed by the elemental analyses, the metal-ligand composition of the Fe(III) and Al(III) chelates was 1 : 3; therefore, they undoubtedly take an octahedral configuration with coordination of three moles of the ligand.

The infrared absorption spectrum of HPNA shown in Fig. 3 exhibits no OH stretching band in the solid state or in benzene or chloroform. This implies the presence of a very strong intramolecular hydrogen bonding with the carbonyl oxygen. The PMR spectrum of the phenalenone ring protons is shown in Fig. 4, in which assignment of the peaks is also illustrated. The spectral pattern can be explained as an $AB_2CC'DD'$ system, providing no spin-spin coupling occurs between B and C protons ($J_{BC}=0$) and $\Delta\nu_{AB}/J_{AB}=2.7$.[6] This leads to two doublets for C(C') and D(D') protons, which appear at τ 2.02 and τ 2.92 respectively with $J_{CD}=10$ Hz. For the AB_2 system there are theoretically eight peaks, as numbered in the spectrum. Peaks 5 and 6 are not resolved in this instance. Consequently the molecule has a C_{2v} symmetry and the two carbon–oxygen bonds are equivalent so far as the PMR spectrum is concerned. The hydroxyl proton resonance appears at very low magnetic field (τ 5.90), which indicates the proton is located in a strong hydrogen bonding evironment.

In the carbonyl region of the IR spectrum the first and the second bands appear at 1637 and 1590 cm^{-1} with similar intensity. In general, the carbonyl frequency of aromatic ketones and quinones is lowered by 20—50 cm^{-1} by intramolecular hydrogen bonding, some examples of which are illustrated in Table 2. Judging from these facts, the PMR evidence, and comparison of the carbonyl vibration with that of phenalenone (1637 cm^{-1}), the band at 1590 cm^{-1} is tentatively assigned to the carbonyl band. The extremely low frequency for a carbonyl stretching vibration is assumed to be due to the high conjugation with the phenalenone ring associated with the intramolecular hydrogen bonding.

Upon metal chelate formation, the spectral patterns became sharp and new bands appeared, along with strengthening of some original bands, as illustrated for the Cu(II)-chelate in Fig. 3. The assignment of the principal absorption bands of the free ligand and the metal chelates are summarized in Table 3.

Nakamoto and Martell assigned the bands in the 1500 cm^{-1} region to the C=O vibration of the metal acetylacetonates from a calculation based on a normal coordinate analysis.[14,15] Providing the degree of the resonance of the metal chelate ring is proportional to the stability of the complex, the more the stability increases, the lower the C=O frequency will become. Although no simple relation existed between the C=O stretching frequency and the stability in a series of metal acetylacetonates, the band which was sensitive to the change in metal ions could be assigned to the C=O absorption. In the present case, the bond order of the carbonyl linkage is intrinsically decreased even in the free ligand by the resonance contribution through the phenalenone ring. In this respect the influence of metal chelate formation against the bond order is assumed to be negligible. Thus the band around 1500 cm^{-1} which was sensitive to the change in metal ions was chosen for the C=O absorption in a series of the metal chelates. The increasing order of the wave number is:

Cu(1525 cm^{-1}) < Ni(1531) < Co(1547) < Zn(1548) < Mg(1550)

TABLE 2. COMPARISON OF HYDROGEN-BONDED AND FREE CARBONYL FREQUENCIES (cm^{-1})

				Δ	Ref.
o-Hydroxyacetophenone	1648	Acetophenone	1691	43	7
1-Hydroxynaphthoquinone	1642	Naphthoquinone	1661	19	8
1-Hydroxy-4-methoxy-8-tetralone	1637	4-Methoxy-8-tetralone	1684	47	9
9-Hydroxy-10-acetylphenanthrene	1611	10-Acetylphenanthrene	1686	75	10
1-Hydroxyanthraquinone	1636	Anthraquinone	1673	37	11
Tropolone	1613	Tropone	1635	32	
	1548		1580	32	12
9-Hydroxy-1-phenalenone	1590	Phenalenone	1637	47	13

TABLE 3. VIBRATIONAL FREQUENCIES AND BAND ASSIGNMENTS OF METAL CHELATES OF 9-HYDROXY-1-PHENALENONE (cm^{-1})

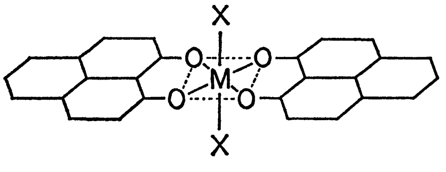
Metal ion	C=O		C$\overset{-}{\cdots}$O	C$\overset{-}{\cdots}$O, C-H				Ring deform., M-O	
H	1637	1590	1590	1468	1372	—	1242	—	—
Na(I)	1634	1597	1558 1543	1443	1357	—	1238	480	442
Be(II)	1631	1585	1515	1437	1357	1285	1246	647	534
Mg(II)[a]	1642	1603	1558 1550	1447 1437	1357	1261	1244	494	460
Mn(II)[a]	1629	1585	1517	1420	1353	1259	1245	489	450
Co(II)[a]	1639	1600 1563	1547	1437 1427	1355	1266	1250	498	454
Ni(II)[a]	1634	1592 1563	1531	1427	1353	1264	1247	504	454
Cu(II)	1634	1587 1565	1524	1433	1351	1271	1248	517	467
Zn(II)[a]	1639	1597	1548	1439 1431	1357	1261	1247	497	450
Al(III)	1631	1590 1567	1527	1447 1435	1357	1276	1245	514	486
Fe(III)	1629	1585 1567	1517	1420	1353	1266	1245	494	462
UO_2(II) (2py)	1629	1587 1565	1517	1415	1350	1260 (905[b], 645[c])	1246	482	455

a) Dihydrate complexes. b) U=O stretching. c) U-Py?

The earlier work of Nakamoto and Martell has revealed that the bands near 400 cm^{-1} were due to a M–O stretching vibration for metal acetylacetonates.[14,15] The decreasing order of the vibration was the same as the stability order: Cu(455 cm^{-1})> Ni(452)>Co(422)≈Zn(422) for the bivalent metal chelates. Nakamoto and coworkers extended the observation of the IR spectra to a lower frequency region and confirmed the M–O stretching mode assignment by using a metal isotope technique.[16] The bands which showed a large isotope shift were 455.0 and 290.5 cm^{-1} for the ^{63}Cu chelate and 421.1 and 228.6 cm^{-1} for the ^{58}Ni chelate, and they were in agreement with the assignment based on a normal coordinate analysis, in which the latter bands were due to a pure M–O stretching vibration.[17] Although we could not use the isotope technique and did not cover the 200 cm^{-1} region, two metal sensitive bands were observed in 400—500 cm^{-1} in each metal chelate. Since the M–O stretching mode is similar to that of metal acetylacetonates, it can be inferred that the strength of the coordinate bond in each transition metal chelate is comparable to that of the corresponding metal acetylacetonate, providing the lower frequency band in Table 3 is taken as the M–O stretching vibration. The markedly different M–O frequency of the Be(II)-chelate will be attributed to the light mass of the beryllium atom and the short Be–O distance.

Conclusion

Judging from the IR and PMR evidence, HPNA is a highly conjugated and symmetrical molecule including the two carbon-oxygen bonds and there exists very strong hydrogen bonding between the two oxygen atoms. The Cu(II) and the anhydrous Ni(II) chelates are monomeric in the solid state and square-planar, while the dihydrate complexes of Mn(II), Ni(II), Co(II), Zn(II), and Mg(II) are octahedral. The two water molecules probably coordinate axially to the chelate plane, as pictured in Fig. 5. The Fe(III) and Al(III) chelates are octahedral and probably have D_3 symmetry like those of acetylacetonates. It is also concluded in the IR band assignment of the metal chelates that the first two bands in the double bond region are due to the skeletal C=C vibration of the phenalenone ring, because similar frequency bands are found in the free ligand and they do not move on metal chelate formation. Consequently, the second band at 1590 cm^{-1} in the free ligand is an overlap with the carbonyl stretching vibration.



M: Cu (X: none); Ni (X: H_2O; Py); Co (X: H_2O; Py)
Zn (X: H_2O); Mn (X: H_2O); Mg (X: H_2O)

Fig. 5. Probable structure of metal-chelates of HPNA.

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