Pakistan J. Sci. Ind. Res., Vol. 27, No. 2, April 1984

STRUCTURAL STUDIES OF 2-ACETO-1-NAPHTHOL-N-SALICYL HYDRAZONE COMPLEXES OF Cu(II), Co(II), Ni(II), Mn(II), Ce(III), AND UO_2^{2+}

M.A. Khattab, G. El-Enany★ and M.E. Soliman

Chemistry Department, Feculty of Science, Mansoura University, Egypt

(Received November 30, 1981)

Complexes of Cu(II), Co(II), Ni(II), Mn(II), Ce(III) and UO_2^{2+} with 2-aceto-l-naphthol-N-salicyl hydrazone (AN.S.H.) have been prepared and characterized on the basis of analytical, spectrophotometric, infrared and magnetic moment data. Isolation of solid complexes and physical measurements revealed the existence of mono- and bis-ligand complexes in the keto-form. Spectrophotometric studies supported the use of this ligand for the micro-determination of metal ions in solution. The apparent formation constants of complexes are also determined. The electronic spectra of the solid complexes in dimethyl formamide indicate that Cu, Ni, Co and Mn complexes have octahedral structure.

INTRODUCTION

Interest in the chemistry of hydrazide has generated, in view of their ability to function as antituberculaus compounds[1], through their ability to form metal chelates [2]. Metal chelates with hydrazide derivatives were the subject of several investigations. The interest in such studies arose mainly from structural problems[3-6]. It was found that chelation through the azomethine group is stabilized by the presence of an auxochrome group in ortho-position.

In continuation of previous studies on metal chelates with hydrazine derivatives[5-8] the complexes formed by the interaction of 2-aceto-l-naphthol-N-salicyl hydrazone (AN.S.H.) with some metal ions in alcoholic solution are investigated by analysis of the solid complexes, UV, visible and IR-spectra as well as conductance studies in view of throwing some light on their stoichiometry, structure and stability.

EXPERIMENTAL

The ligand was prepared by condensation of salicylic hydrazide with 2-aceto-l-naphthol in the usual way used for the preparation of hydrazones[21]. The metal complexes were prepared by mixing a weighed amount of the hydrazone in abs. ethanol with an equivalent amount of the hydrated metal chlorides or nitrates in the same solvent. The reaction mixture was refluxed for about ½-2 hr. The separated solid complexes were filtered, washed with abs. ethanol and dried in a desiccator over silica gel. The complexes were then analysed for their carbon, hydrogen, nitrogen, chloride and metal contents; the results are recorded in Table 4. The complexes isolated are insoluble in water but slightly soluble in organic solvents and dissolve appreciably in dimethyl formamide (DMF). The DMF solutions of complexes are of low conductivity and hence the complexes would be non-ionic in nature.

The electronic absorption spectra were measured with the aid of a Unicam SP 1750 spectrophotometer. The IR spectra of the ligand and its complexes were obtained on a Unicam SP 2000 infrared spectrophotometer as KBr discs. Conductance measurements were made with a PYE conductance bridge. Magnetic susceptibility measurements on the powdered samples were carried out on a Gouy balance.

RESULTS AND DISCUSSION

Isolation of Pure Compounds. The interaction of 2-aceto-l-naphthol-N-salicyl hydrazone (AN.S.H.) with the studied hydrated metal salts gave mono-and bis-ligand complexes. The composition of the isolated pure mono-ligand complexes was $M(AN.S.H.)Cl.nH_2O$ where M = Cu(II) and Ni(II). The colours of aquo complexes change when heated in an electric oven for one hour at 120° but the original colour is regained immediately on exposure to air. Thus it was difficult in most cases to determine the water content for these complexes. The stoichiometry of the isolated pure bis-ligand complexes was $M(AN.S.H.)_2$ where M = Cu, Co, Ni and Mn.

Spectrophotometric Studies. The absorption spectra of

★Present address: Chemistry Department, Faculty of Education, Ain Shams University, Egypt.

the ligand under investigation is characterized mainly by three absorption bands in the region 250-400 nm. The spectra of the ligand is quite different from those of their mixtures with Co^{2+}, Mn^{2+}, Cu^{2+}, Ni^{2+}, Ce^{3+} and UO_2^{2+}. This can be considered as an evidence for complex formation. The first absorption band, can be assigned to intramolecular charge transfer within the whole molecule, acquire an increase in its molar absorptivity and a large red shift of its λ_{max}, on complexation with the metal ions used (Table 1).

Adding to a constant concentration of metal ions in ethanol stepwise small portios of solutions of the ligand in ethanol the absorbance increases steadily up to a constant value. A similar increase in absorbance is obtained by the slow addition of metal ions to a fixed concentration of the ligand in ethanol. The plot of absorbance as a function of the metal ion concentration gave straight lines in the concentration range up to $1.2x10^{-4}$, $5.0x10^{-5}$, $8.0x10^{-5}$. $7.0x10^{-5}$, $1.0x10^{-4}$ and $5.0x10^{-5}$ for Ce^{3+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+} and UO_2^{2+} respectively. Also the high ϵ values ($3.8x10^3$, $3.0x10^3$, $2.3x10^3$, $3.5x10^{-3}$, $5.0x10^3$ and $1.8x10^3$ at λ_{max} for Cu^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, UO_2^{2+} and Ce^{3+} respectively) suggest the possible application of the method for the determination of small amounts of the metal ion.

The stoichimoetry of the complexes formed in solution from reaction of (AN.S.H.) with the metal ions studied was ascertained by applying the conventional spectrophotometric molar ratio and continuous variation method[9,10]. However, in all cases, the blank being a solution of the ligand of the same concentration as in the solution of the complexes. The results revealed the possible formation of 2:1, 1:1 and 1:2 (metal:ligand) complexes in all systems except in Ce(III) system which show only the existence of 2:1 and 1:2 complexes. The conditional stability constants of the complexes, as calculated from the results of molar ratio and continuous variation methods[9,10] are given in Table 2.

The electronic spectra of the solid complexes in DMF indicate that the brown $Ni(C_{19}H_{15}O_3N_2)Cl.4H_2O$ complex shows a strong band at 21276 cm^{-1} due to the transition ${}^1A_{1g} \rightarrow {}^1B_{1g}$ as observed for square planer Ni(II) complexes[11]. But the spectra of $Ni(C_{19}H_{15}O_3N_2)_2$ complex show bands at 26666 and 16181 cm^{-1} due to the transition

$$^3A_{2g} \rightarrow {}^3T_{1g}(P) \text{ and } {}^3A_{2g} \rightarrow {}^3T_{1g}(F)$$

expected for octahedral Ni(II) complexes[12]. The magnetic moment value of $Ni(C_{19}H_{15}O_3N_2)_2$ complex is 3.22 BM. indicating the presence of two unpaired electrons, but $Ni(C_{19}H_{15}O_3N_2)Cl.4H_2O$ complex is diamagnetic. The spectra of $Co(C_{19}H_{15}O_3N_2)_2$ complex shows band at 17699 cm^{-1} due to the transition ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ expected for octahedral Co(II) complexes[13]. The magnetic moment of the complex was found to be 4.23 BM. which is characteristic of high-spinoctahedral Co(II) complex[12]. The spectra of $Cu(C_{19}H_{15}O_3N_2)Cl.2H_2O$ complex has a band at 16129 cm^{-1} coresponding to the transition ${}^2T_{2g} \rightarrow {}^2E_g$. The colour and the position of the above band are inagreement with those generally observed for planar Cu(II) complexes[14]. But $Cu(C_{19}H_{15}O_3N_2)_2$ complex shows a single broad absorption band at 13605 cm^{-1} corresponding to the transition ${}^2E_g \rightarrow {}^2T_{2g}$ which is typical of Cu(II) complexes in octahedral environment[15]. The observed magnetic moment value of Cu(II) complexes are 1.78 and 1.69 BM. For 1:1 and 1:2 complexes respectively denoting a single unpaired electron in Cu(II) complexes.

In case of $Mn(C_{19}H_{15}O_3N_2)_2$, its spectrum exhibits a shoulder at 24691 cm^{-1} which may be assigned to the transition ${}^6A_{1g} \rightarrow {}^4Eg(G)$ in octahedral structure[13]. The observed magnetic moment value 5.83 BM. is consistent with the octahedral sterochemistry for Mn(II).

IR Spectra. The mode of bonding between the ligand and metal ions can be readily revealed by comparing the IR spectra of the solid complexes with those of the organic ligand. The comparison in Table 3 shows that the C=O and C=N bands at 1665 and 1630 cm^{-1} in the spectra of AN.S.H. ligand shift to lower frequencies due to coordination with metal ion. This shows that the carbonyl and azomethine groups are contributing as coordination sites in complex formation. Two bands due to δ -OH groups are observed in the AN.S.H. spectrum at 1315 and 1280 cm^{-1} [16,17]. The latter band would correspond to δ-OH in hydrazide residue, as gathered from the comparison between the spectra of An.S.H. and 2-aceto-l-naphthol-N-Benzoyl hydrazone, and is absent in the spectra of complexes. The disappearance of this band is apparently due to the displacement of a hydrogen ion from the OH group through interaction with the metal ions. The band at 1315 cm^{-1} is still observed in the spectra of all chelates. The presistance of this band indicates that the Oh-group of 2-aceto-l-naphthol part is not involved in chelate formation. The IR spectra of complexes exhibit several bands in the region 650-200 cm^{-1}. A band near 650 cm^{-1} in the complexes is assigned to ν M–O vibration[18]. Two new bands observed in the spectra of the complexes at 415-400 and 350 cm^{-1} are suggested to be due to ν M–N and ν M–Cl vibration[19-20] respectively.

From the results of all previous physicochemisal mea-

Table 1. Characteristic maxima for ligand and metal complexes

	Complexes					
Ligand	Cu^{2+}	Co^{2+}	Ni^{2+}	Mn^{2+}	Ce^{3+}	UO_2^{2+}
363	420 (br)	416	418 396	420	410	400(sh)
305	315	310	320	317	305	305
293	293	293	293	293	293	293
277	277	277	277	277	277	277

Table 2. Apparent stability constant of metal complexes.

(Metal: Ligand)	Mean value of long K					
Stoichiometry	Cu^{2+}	Co^{2+}	Ni^{2+}	Mn^{2+}	UO_2^2	Ce^{3+}
2:1	4.72	4.13	3.12	3.85	–	–
1:1	8.95	6.78	6.32	6.74	4.62	–
1:2	12.43	10.21	10.13	9.83	7.33	5.64

Table 3. Important IR bands for ligand and metal complexes.

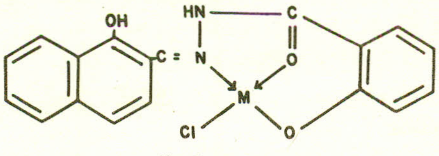
	Frequencies in cm^{-1}						
Compound	ν C=O	ν C=N	δ OH	δ*OH	νM–O	ν M–N	νM -Cl
$(C_{19}H_{16}O_3N_2)$	1665	1630	1315	1280	–	–	–
Cu L $Cl.2H_2O$	1640	1610	1315	–	645	415	350
Ni L $Cl.4H_2O$	1645	1610	1310	–	650	408	355
Cu L_2	1635	1608	1308	–	645	410	–
Ni L_2	1640	1605	1305	–	640	405	–
Co L_2	1640	1610	1310	–	635	400	–
Mn L_2	1640	1610	1315	–	640	405	–

L = $C_{19}H_{15}O_3N_2$; * In hydrazide residue

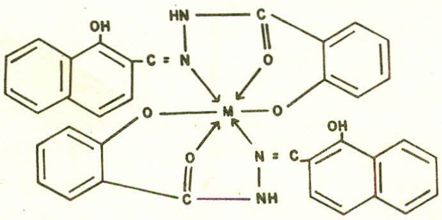
Table 4. Elemental analysis results of complexes.

		Found (Calc.) %				
Complex	M.P.	† C	H	N	Cl	M
Cu $(C_{19}H_{15}O_3N_2)Cl.\ 2H_2O$	296	50.60 (50.22)	3.12 (3.33)	5.87 (6.17)	7.70 (7.80)	14.30 (13.99)
$Ni(C_{19}H_{15}O_3N_2)Cl.4H_2O$	314	47.70 (47.00)	3.21 (3.11)	5.61 (5.77)	7.30 (7.30)	11.50 (12.09)
$Cu(C_{19}H_{15}O_3N_2)_2$	336	65.20 (65.00)	4.30 (4.31)	8.20 (7.98)	– –	8.60 (9.05)
$Ni(C_{19}H_{15}O_3N_2)_2$	3.47	65.40 (65.45)	4.51 (4.34)	8.23 (8.03)	– –	8.55 (8.42)
Co $(C_{19}H_{15}O_3N_2)_2$	>360	65.60 (65.43)	4.11 (4.33)	7.64 (8.03)	– –	8.10 (8.45)
$Mn(C_{19}H_{15}O_3N_2)_2$	>360	65.60 (65.80)	4.23 (4.36)	8.45 (8.08)	– –	8.33 (7.92)

surements the structure of 1:1 and 1:2 complexes may thus be represented as follows:



M= Cu and Ni.



M = Cu, Ni, Co and Mn

REFERENCES

1. H.H. Fox and J.T. Gibas, J. Org. Chem., **21**, 356 (1956).
2. J.C. Craig and D. Edgar, Nature (London), **176**, 34 (1955).
3. G.L. Eichhorn and J.C. Bailar, Am. Chem; Soc., **75**, 2905 (1953).
4. H. El-Khadem, M.F. Iskander and S.E. Zayan, Z. Anorg. Allg. Chem., **109**, 330 (1964).
5. I.M. Issa, F.I. Taha and M.A. Khattab, Eghpt, J.Chem., **14**, 59 (1971); **14**, 553 (1971).

p.213

21. A.I. Vogel, *Text Book of Practical Organic Chemistry*, (Longmans, London, 1962, second edition.

6. R.M. Issa, M.R. Mahmoud and M.A. Khattab, Monatsh, Chem., **107**, 485 (1976).
7. M.A. Khattab and M.I. Khalifa, Pakistan J. Sci. Ind. Res., **20**, 165 (1977); **20**, 172 (1977).
8. M.A. Khattab and F.M. Ebeid, J.Inorg.Nucl., Chem., (1981) in press.
9. J.H. Yoe and A.L. Jones, Indian Eng. Chem. (Anal. Edit.), **16**, 111 (1944).
10. P. Job, Ann. Chim., **6**, 97 (1955); F.G. Sherief and A.M. Awad, Inorg. Nucl. Chem., **24**, 179 (1962).
11. H.B. Gray, *Transition Metal Chemistry*, edited by R.L. Carlin, vol. 1, (Marcel-Dekker, New York 1965)., p.239
12. F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (John Wiley and Sons, London, 1972), p.881
13. T.M. Dunn, *The Visible and Ultraviolet Spectra of Complex Compounds, in Modern Coordination Chemistry*, edited by J. Lewis and R.G. Wilkins (Interscience, New York, 1960), p. 290.
14. L. Sacconi and M. Ciampolini, J. Chem. Soc., 276 (1964).
15. A. Cristini, G. Ponticelli and C. Preti, J. Inorg. Nucl. Chem., **36**, 2475 (1974).
16. C. Tanaka, K. Kurotani and S. Mizushima, Spectro. Chem. Acta, **9**, 264 (1957).
17. L. Holleck, H. Moresen and H.J. Exner, Z. Natuaforch, **96**, 90 (1954).
18. K. Ueno and A. E. Martell, J. Phys. Chem., **59**, 998 (1955); **60**, 1270 (1956).
19. C.W. Schlapder and K. Nakamoto, Inorg. Chim. Acta, **6**, 177 (1972).
20. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds* (John Wiley, New York, 1970),