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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

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To cite this Article Aggarwal, R. C. and Singh, Bachcha(1978) 'SYNTHESIS AND STRUCTURAL STUDIES OF OXALYLDIACETONE HYDRAZONE COMPLEXES OF Mn(II), Fe(II), Co(II), Ni(II), Cu(II) AND Zn(II)', *Journal of Coordination Chemistry*, 7: 4, 245 – 248

To link to this Article: DOI: 10.1080/00958977808079918

URL: <http://dx.doi.org/10.1080/00958977808079918>

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SYNTHESIS AND STRUCTURAL STUDIES OF OXALYLDIACETONE HYDRAZONE COMPLEXES OF Mn(II), Fe(II), Co(II), Ni(II), Cu(II) AND Zn(II)

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(Received January 6, 1977; in final form April 12, 1977)

INTRODUCTION

In continuation of our earlier work¹ on VO(IV) complexes of diacetone hydrazones, we report here the results of our studies on Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of ODAH. While oxovanadium(IV) yielded only adducts with all diacetone hydrazones, ODAH has been found to form adducts as well as deprotonated complexes with a number of other first row transition metal ions in the present study.

EXPERIMENTAL

All the chemicals used in this study were of BDH or equivalent quality. ODAH was prepared as described earlier.¹

The adducts $[(MCl_2(ODAH)) \cdot 2H_2O]$ were prepared by mixing together ethanolic solutions of metal chloride and ODAH in about 1:1 molar ratio while deprotonated complexes $[M(ODAH-2H)(H_2O)_2]$ were prepared by mixing the aqueous solutions of the metal chloride and ODAH in the same molar ratio and raising the pH by sodium acetate-acetic acid or NH_4Cl-NH_4OH buffer solution. The complexes thus precipitated were filtered, washed and dried in vacuo.

The complexes were analysed gravimetrically for metal using standard literature procedures,² while nitrogen, hydrazine, chloride and water content were determined as described earlier.³ The analytical data are given in Table I. Electronic and infrared spectra of the complexes were recorded on a Cary-14 spectrophotometer and Perkin-Elmer spectrophotometer, model 621 respectively in nujol.

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RESULTS AND DISCUSSION

All the adducts lose the water molecules completely in 100–110° temperature range while the deprotonated complexes do so in the temperature range 130–150° yielding anhydrous complexes in both the cases. The anhydrous adducts start decomposing with splitting of HCl (~160°) but only in the case of Co(II), Ni(II) and Zn(II), complexes of a definite stoichiometry $[MCl(ODAH-H)]$ were obtained in 180–200° temperature range. The compositions of these complexes were further confirmed by hydrazine and/or chloride analysis.

The loss of water molecules at lower temperature in adducts and at relatively high temperature in deprotonated complexes, the presence of a band characteristic of coordinated water in 780–825 cm^{-1} range in the hydrated deprotonated complexes and its absence in the hydrated adducts show clearly that the water molecules are in lattice^{4a} in adducts and coordinated^{4b} in the deprotonated complexes.

All the complexes are insoluble in water and common organic solvents. The Mn(II) and Fe(II) adducts are fairly soluble in DMSO in cold while all the other complexes including the anhydrous ones are only slightly soluble in hot DMSO. The non-melting nature and insolubility of the complexes in common organic solvents suggest polymetallic structures.

The very low values (0.172, 0.132 $ohm^{-1} cm^2 / mole$) of molar conductance of Mn(II) and Fe(II) adducts in DMSO show that they are nonelectrolytes.⁵ Because of the low solubility, molar conductance of the other complexes could not be determined.

The room temperature magnetic moments⁶ (Table I) indicate spin free octahedral geometry for all Fe(II), Co(II) and Ni(II) complexes and spin free

TABLE I
Analytical, magnetic moment and electronic spectral data of ODAH complexes

Complex	Colour	Metal %	Chloride/nitrogen %	Hydrazine %	Loss of water %	μ_{eff} B.M.	Electronic bands (nm)	10Dq (cm^{-1})
[MnCl ₂ (ODAH)]·2H ₂ O	White	14.95 (15.26)	19.25 (19.28)	17.85 (17.78)	9.72 (9.77)	5.98	—	—
[FeCl ₂ (ODAH)]·2H ₂ O	Yellow	15.58 (15.47)	19.55 (19.68)	17.35 (17.74)	10.20 (9.98)	5.55	975	10260
[CoCl ₂ (ODAH)]·2H ₂ O	Pink	16.10 (16.19)	19.48 (19.51)	17.42 (17.59)	9.92 (9.89)	5.22	1200, 650, 487	7047
[NiCl ₂ (ODAH)]·2H ₂ O	Light blue	16.05 (16.14)	19.31 (19.53)	17.10 (17.60)	9.73 (9.90)	3.12	1030, 625, 380	9709
[CuCl ₂ (ODAH)]·2H ₂ O	Green	17.03 (17.25)	19.35 (19.27)	17.48 (17.37)	9.63 (9.77)	2.05	700	14290
[ZnCl ₂ (ODAH)]·2H ₂ O	White	17.30 (17.66)	19.10 (19.18)	17.00 (17.29)	9.81 (9.72)	Diamagnetic	—	—
[Mn(ODAH-2H)(H ₂ O) ₂]	Light yellow	19.32 (19.14)	19.45 (19.52)	22.05 (22.30)	12.34 (12.54)	6.01	—	—
[Co(ODAH-2H)(H ₂ O) ₂]	Pink	19.85 (20.26)	19.00 (19.25)	22.00 (22.01)	12.14 (12.38)	5.19	1200, 500	8765
[Ni(ODAH-2H)(H ₂ O) ₂]	Blue	20.05 (20.19)	19.10 (19.27)	22.24 (22.02)	12.48 (12.39)	3.18	1012, 625	9880
[Cu(ODAH-2H)(H ₂ O) ₂]	Green	21.18 (21.51)	18.78 (18.95)	21.52 (21.66)	12.30 (12.18)	1.91	687	14560
[Zn(ODAH-2H)(H ₂ O) ₂]	White	21.58 (21.91)	18.90 (18.84)	20.92 (21.53)	12.51 (12.11)	Diamagnetic	—	—
[CoCl ₂ (ODAH)]	Pink	—	21.30 (21.65)	19.25 (19.51)	—	5.40	1200, 625, 500	7667
[NiCl ₂ (ODAH)]	Blue	—	21.46 (21.66)	19.15 (19.52)	—	3.30	1000, 625	10000
[CoCl(ODAH-H)]	Light pink	—	24.25 (24.36)	21.80 (21.95)	—	5.04	1150, 500	9850
[NiCl(ODAH-H)]	Light blue	—	24.10 (24.38)	21.55 (21.97)	—	3.32	1025, 637	9755
[ZnCl(ODAH-H)]	White	—	23.64 (23.83)	21.50 (21.48)	—	Diamagnetic	—	—
[Co(ODAH-2H)]	Pink	—	—	25.04 (25.12)	—	5.07	1175, 575, 500	8880
[Ni(ODAH-2H)]	Blue	—	—	24.90 (25.10)	—	3.38	1000, 625, 387	10000

Calculated values are given in parenthesis.

tetrahedral or octahedral geometry for Mn(II) complexes. The μ_{eff} values of Cu(II) complexes correspond to one unpaired electron from which it is not possible to say anything about the stereochemistry.

The octahedral geometry⁸⁻¹⁰ of Fe(II), Co(II) and Ni(II) complexes is further confirmed by the number and position of the electronic spectral bands. The bands observed in the spectra of Cu(II) adduct and deprotonated complex are considerably blue shifted compared to the first band maxima of the corresponding Ni(II) complexes owing to Jahn-Teller distortion of 2E_g state. The ratio ν_{Cu}/ν_{Ni} (cm^{-1}) comes out 1.472 for adduct and 1.473 for deprotonated complex indicating considerable distortion¹¹ in the octahedral geometry of the above complexes. The various ligand field parameters such as $10Dq$, B , β , β^o and LFSE have been calculated¹² and found to lie in range 7047–14560 cm^{-1} , 727–880 cm^{-1} , 0.747–0.858, 14.17–25.26% and 11.69–34.34 Kcals/mole respectively. The $10Dq$ values of ODAH complexes indicate that the above ligand occupies a place between water and ammonia in the spectrochemical series.

The bonding sites in the ODAH complexes have been established by a careful comparison of i.r. spectra of the complexes with solution spectrum of the ligand. The spectra of the complexes and the parent ligand are very broad in the NH stretching frequency region and hence no meaningful conclusions could be drawn regarding the involvement of secondary amide nitrogens of the ligand in bonding.

The bands appearing in the solution spectrum of the ligand at 1690, 1640, 1530, 1275 and 875 cm^{-1} are assigned¹ to amide I, $\nu(\text{C}=\text{N})$, amide II, amide III and $\nu(\text{N}-\text{N})$ respectively. In the spectra of the adducts amide I and amide II bands undergo a negative shift of 65–20 and 30–5 cm^{-1} respectively and amide III a positive shift of 35–55 cm^{-1} indicating coordination of both the carbonyl oxygens of the ligand in above complexes. The disappearance of these bands and appearance of new bands, characteristic¹³ of $\nu(\text{NCO}^-)$ in 1540–1566 and 1295–1315 cm^{-1} regions in the spectra of the hydrated and anhydrous deprotonated complexes, absence of original anion in these complexes and their 1:1 metal ligand stoichiometry show the destruction of both the keto groups presumably via enolization and bonding through the two resulting-enolic oxygens. The presence of only one band due to coordinated $>\text{C}=\text{N}$ groups in the range 1610–1625 cm^{-1} shows the involvement in bonding of both the azomethine nitrogens of the ligand in adducts, and hydrated and anhydrous deprotonated complexes. The occurrence of $\nu(\text{N}-\text{N})$

in 910–935 cm^{-1} region (characteristic of monodentate linking of $>\text{N}-\text{N}<$ moiety) in adducts and hydrated deprotonated complexes and at ~ 965 cm^{-1} in $\text{N}-\text{N}$ bridging¹⁴ region in anhydrous deprotonated complexes shows that only two azomethine nitrogens are involved in bonding in the former complexes and all the four nitrogens of the ligand in the latter complexes.

In $[\text{MCl}(\text{ODAH}-\text{H})]$ complexes both the carbonyl oxygens are involved in bonding, one in the keto-form and the other in the enol form as is evident from a negative shift in amide I (~ 30 cm^{-1}) and occurrence of new bands due to $\nu(\text{NCO}^-)$ in 1560–1570 and 1305–1310 cm^{-1} regions. The i.r. spectra of the above complexes also show features, characteristics of coordination through both the azomethine and amide nitrogen atoms as discussed earlier.

The i.r. spectra thus indicate that ODAH behaves as a tetradentate ligand in all the complexes except anhydrous deprotonated complexes where it functions as a hexadentate ligand.

Based on chemical compositions and physico-chemical studies polymeric structures having octahedrally coordinated metal centres may be tentatively proposed for the ODAH complexes.

ACKNOWLEDGEMENTS

Authors are thankful to the Head of the Department of Chemistry, B.H.U., for providing laboratory facilities and one of us (B. Singh) is thankful to C.S.I.R., New Delhi for awarding a Junior Research Fellowship.

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