

## CNDO/2 calculations for $\alpha$ -oximinoacetoacetanilide thiosemicarbazone and synthesis and characterization of some metal chelates derived from it

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**Abstract.** Solid complexes of  $\alpha$ -oximinoacetoacetanilide thiosemicarbazone (OAATS) with Ni(II), Co(II), Zn(II), Mn(II), Cd(II), Hg(II) and UO<sub>2</sub>(II) have been prepared and characterized on the basis of their elemental analyses, conductivity, differential scanning calorimetry, thermogravimetric analysis, infrared and electronic spectral measurements, in conjunction with magnetic susceptibility measurements. Molecular orbital calculations employing the CNDO/2 method have been made for a number of conformations of the ligand molecule to ascertain the most stable one.

**Keywords.** Solid complexes;  $\alpha$ -oximinoacetoacetanilide thiosemicarbazone; CNDO/2 molecular orbital method.

### 1. Introduction

The coordination chemistry of thiosemicarbazones assumed new importance because of the antibacterial and antitumour activities of some thiosemicarbazones and few of their metal complexes (Orlova *et al* 1968). Thiosemicarbazone which comprises a well-known group of nitrogen and sulphur donors has been extensively used for complex formation (Campbell 1975; Patel *et al* 1981). The present communication reports investigations on  $\alpha$ -oximinoacetoacetanilide thiosemicarbazone (OAATS) and its complexes with Ni(II), Co(II), Zn(II), Mn(II), Hg(II), Cd(II) and UO<sub>2</sub>(II) ions. Structures of the complexes have been established using analytical, thermal and magnetic measurements, IR and electronic spectral data. The CNDO/2 molecular orbital method has been employed to determine the most probable conformation of the ligand molecule.

### 2. Experimental

#### 2.1 *Materials and ligand preparation*

All the chemicals used were of AR grade. The ligand (OAATS) was synthesized by the known method (Patel 1963).

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## 2.2 Synthesis of metal complexes

The ligand OAATS (0.01 mol) was dissolved in about 100 ml of ethanol. To this 50 ml of an aqueous solution of Ni(II) acetate monohydrate (0.005 mol) were added, when a chocolate coloured product separated out. The mixture was digested on a water-bath for an hour. The product was suction-filtered, washed with hot distilled water, ethanol and dried under vacuum. The yield was quantitative. Metal complexes of the other metal ions were prepared in a similar manner. All the complexes are insoluble in common organic solvents.

## 2.3 Measurements

The IR spectra (KBr disks) were recorded on a Perkin-Elmer-983 spectrophotometer. The diffuse reflectance spectra of the finely powered chelates were scanned on a Beckman DK-2A spectrophotometer using MgO as reference material. Magnetic studies of the complexes were carried out at room temperature by the Gouy method using mercurytetrathiocyanatocobalt(II) as the calibrant. Metal estimations were carried out by standard methods (Vogel 1962). Nitrogen was estimated by Kjeldahl's method. Sulphur was estimated by the fusion method (Weinig and Schoder 1939). TG and DSC thermograms were scanned on a Du-Point Thermal Analyzer and a Du Point Analyzer-9990, respectively. The electrical conductivity was measured over a wide range of temperature in air using a Hewlett-Packard 4329-A high resistance meter. Molecular orbital calculations were done on an HCL-Busybee-386 computer.

## 3. Results and discussion

The magnetic, analytical and electrical conductivity data of the complexes are presented in table 1. Elemental analyses of the complexes indicate 1:1 stoichiometry.

### 3.1 Magnetic and reflectance spectral studies

The Ni(II) complex is diamagnetic in nature indicating that it has square-planar structure. The reflectance spectrum of Ni(II) exhibits two bands at  $20,200\text{ cm}^{-1}$  and  $14,295\text{ cm}^{-1}$  which may be assigned to  ${}^1A_{1g} \rightarrow {}^1A_{2g}$  and  ${}^1A_{1g} \rightarrow {}^1B_{1g}$  transitions, respectively, suggesting square-planar structure (Singh *et al* 1984). The Co(II) complex shows a magnetic moment of 4.2 BM which indicates the presence of three unpaired electrons. The reflectance spectrum of Co(II) exhibits three bands at 9045, 16,405 and  $24,695\text{ cm}^{-1}$  which may be assigned to  ${}^4A_2 \rightarrow {}^4T_1(F)$ ,  ${}^4A_2 \rightarrow {}^4T_1(P)$  and charge transfer transitions respectively for tetrahedral geometry (Figgis and Nyholm 1959). The magnetic moment 5.41 BM for the Mn(II) complex is lower than the spin only value (5.92 BM) which may be due to partial aerial oxidation of Mn(II) to Mn(III) during synthesis. The reflectance spectrum of the Mn(II) complex exhibits three bands at 16,260, 20,000 and  $24,980\text{ cm}^{-1}$ , which may be assigned to  ${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4G)$ ,  ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$  and  ${}^6A_{1g} \rightarrow {}^4E_g \cdot {}^4A_{1g}({}^4G)$  transitions, respectively, in octahedral symmetry. Zn(II),  $\text{UO}_2(\text{II})$ , Cd(II) and Hg(II) complexes are found to be diamagnetic. The reflectance spectrum of the dioxouranium (VI) chelate exhibits two absorption bands at 20,830

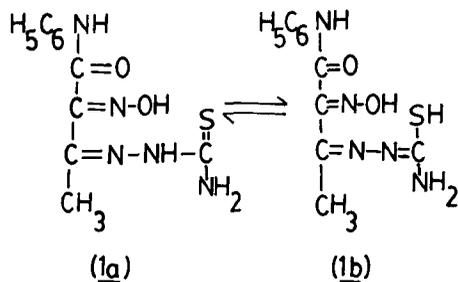
Table 1. Magnetic, analytical and electrical data of the chelates.

Chelate	Colour	Elemental analysis – found (calcd) (%)			$\mu_{\text{eff}}$ (BM)	Conductivity ( $\times 10^{-13}$ ) at room temperature (ohm $^{-1}$ cm $^{-1}$ )	Activation energy (eV)
		M	N	S			
OAATS	White	—	24.82 (25.08)	11.28 (11.46)	—	25.2	0.109
Ni(OAATS)	Chocolate	17.41 (17.48)	20.62 (20.85)	9.41 (9.53)	diamagnetic	6.32	0.0593
Co(OAATS)	Brown	17.19 (17.54)	20.33 (20.83)	9.39 (9.52)	4.2	5.27	0.057
Mn(OAATS)·2H <sub>2</sub> O	Brown	14.90 (15.09)	19.11 (19.23)	8.63 (8.79)	5.41	84.5	0.1689
Zn(OAATS)	Yellow	18.88 (19.09)	20.29 (20.44)	9.21 (9.34)	diamagnetic	0.395	0.0649
Hg(OAATS)	Light yellow	42.00 (42.00)	14.54 (14.68)	6.44 (6.70)	diamagnetic	0.852	0.0683
Cd(OAATS)	Dull yellow	28.54 (28.86)	17.68 (17.97)	8.07 (8.21)	diamagnetic	26.2	0.054
UO <sub>2</sub> (OAATS)·2H <sub>2</sub> O	Brick red	46.14 (46.31)	11.83 (12.00)	5.31 (5.48)	diamagnetic	0.473	0.085

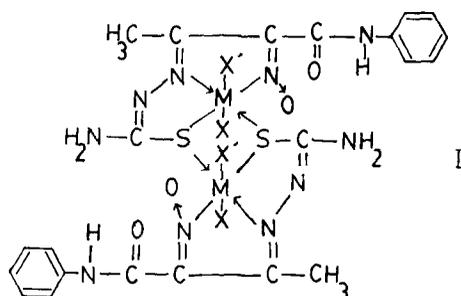
and 22,730 cm $^{-1}$  which may be assigned to the  ${}^1\Sigma_g^+ - {}^3\Pi_u$  and charge transfer transitions, respectively, for octahedral stereochemistry (Kariya and Bhawe 1987).

### 3.2 Infrared spectral studies

Complete assignment of all the absorptions of the ligand is not attempted here, only a prominent few, essential for the determination of the bonding sites in the ligand, are assigned. The absence of absorption due to  $\nu$  S–H stretching at  $\sim 2570$  cm $^{-1}$  in the ligand indicates that the ligand remains in thioketo form (1a) at least in the solid state (Bellamy 1968). However, in solution, the existence of thioketo (1a) and thioenol (1b), tautomerism may be expected. The C=O stretching frequency appears at 1660 cm $^{-1}$  as a very strong absorption (Nakanishi 1964). It shows a blue shift of about 10 cm $^{-1}$  in the complexes. This blue shift may be traced to the breaking of the hydrogen bond between C=O and N–OH moieties. This replacement of a hydrogen bond is further supported by



the disappearance of the ligand peak in the range  $2700\text{--}2800\text{ cm}^{-1}$  after complex formation. The characteristic absorption due to the N–O stretching of the NOH moiety in the ligand occurs at  $960\text{ cm}^{-1}$  (Smith and Robertson 1968). This disappears in the complexes where a new band around  $1340\text{ cm}^{-1}$  appears which may be assigned to N→O stretching (Chakravorty and Kalia 1968). This suggests the presence of M–N→O bonding. In comparison with related molecules the  $855\text{ cm}^{-1}$  absorption in the free ligand may be attributed to  $\nu\text{ C=S}$  (Ray and Sathyanarayana 1975). On complexation this bond completely disappears and a new band around  $660\text{ cm}^{-1}$  appears. This may be assigned to  $\nu\text{ C-S}$ . This compares well with the single-bonded C–S stretching more usually assigned around  $700\text{ cm}^{-1}$  (Bellamy 1968; Syamal and Bari Niazi 1985). This observation indicates the presence of M–S–C bonding in the metal complexes. The use of the absorption due to C=N stretching frequency in identifying the bonding site is somewhat difficult here because of the complex nature of absorption bands in the region  $1550\text{--}1630\text{ cm}^{-1}$ . However, the strong peak of the free ligand at  $1600\text{ cm}^{-1}$  registers substantial decrease in the intensity after complex formation. This band may be assigned to a complex vibration involving  $\nu\text{ C=N}$ ,  $\delta\text{ NH}_2$  and the benzene ring (Nakanishi 1964; Ray and Sathyanarayana 1975). The bonding of the metal ions with the C=N moiety causes a decrease in the intensity of the ligand band. The  $1540\text{ cm}^{-1}$  ligand band is probably due to a coupled vibration of  $\delta\text{ NH}$  (of the HNC=O moiety) and  $\nu\text{ C=N}$  shifts to  $1520\text{ cm}^{-1}$  after complexation (Uno *et al* 1970). The  $\nu\text{ N-N}$  stretching in the ligand is assigned to  $1060\text{ cm}^{-1}$ . This band shifts to  $1040\text{ cm}^{-1}$  in the complexes (Geetharani and Sathyanarayana 1977). The band at  $3350\text{--}3370\text{ cm}^{-1}$  region in the Mn(II) and UO<sub>2</sub>(II) complexes shows the presence of coordinated water molecules (Matho 1981). As already stated the elemental analyses indicate a 1:1 metal to ligand ratio in all these complexes. However, to account for the transitions in the visible region, it is necessary to propose binuclear complexation which satisfactorily explains the electronic and vibrational transitions. On the basis of this evidence, it is shown that the ligand forms binuclear metal (II) complexes bridged by the deprotonated thiolic sulphur (Sankhala *et al* 1983). The probable structure is shown in figure 1.



**Figure 1.** The probable structure of the metal (II)-ligand complex (I). X and X' = H<sub>2</sub>O, when M = Mn(II) or UO<sub>2</sub>(II), otherwise there are no atoms or groups in these positions.

### 3.3 Molecular orbital studies of the ligand

Infrared study suggests that the ligand molecule in the solid state probably exists in thioketo form of the oxime (Ia) while the complex formation is through the thioenol moiety (1b) of  $N \rightarrow O$  (i.e.  $\text{>C=N} \begin{smallmatrix} \text{O} \\ \text{H} \end{smallmatrix}$ ) form. This necessitates determining the stabilities of the different conformations of the ligand molecule. Hence the CNDO/2 method was employed to calculate the energy of many possible conformations of the ligand (Pople and Segal 1966). The CNDO/2 method was used because this has been found to be effective for similar studies (Klopman and Ray 1982). The CNDO/2 method as developed by Pople and Segal (1966) has been used as such without any change of the semi-empirical parameters. The elements of Fock-operation are constructed in the usual way and solved. The iteration is continued until self-consistency is obtained in the total energy.

The geometrical parameters needed were taken from comparable molecules (Ray and Sathyanarayana 1975). Since no optimization was done, it was necessary to keep the length of similar bonds and the magnitude of comparable angles constant in all the conformations, so that the change of electronic environment due to the rotation about the specific bond mainly influences the orbital energies. The total energy of the different conformations obtained by rotating the molecule about various single bonds lie in the range  $-5375.6$  to  $-5376.3$  eV. The energy difference among different conformations is not much. However, the most stable conformation is as shown in figure 2, having total energy =  $-5376.3$  eV. It is interesting to note that in this conformation, the benzene and H (of  $\text{NH}\phi$ ) are also in the plane of the molecule. The total energy of the  $N \rightarrow O$  form (figure 3) of the most stable conformation (figure 2) was also obtained from CNDO/2 calculation and found to be  $-5374.9$  eV. Consequently, the  $\text{>C=NOH}$  is preferred to the  $\text{>C=N} \begin{smallmatrix} \text{O} \\ \text{H} \end{smallmatrix}$  form. Also, the energies of the S-H forms (i.e. deprotonation of NH) of both the oxime and the nitrone determined by CNDO/2 calculation to be around  $-5375.10$  and  $-5375.6$  eV, respectively, indicate that figure 2 probably represents the most stable conformation of the ligand molecule. The preference for the thioenol form of the nitrone ( $N \rightarrow O$ ) in complex formation may be traced to the stability achieved by the formation of a five-membered chelate ring on complexation which overcomes the instability acquired due to the transition to the thioenol form of the N-O from the thioketo of the oxime (figure 2).

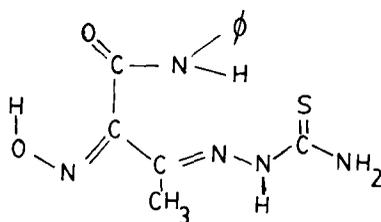


Figure 2. The most stable conformation of the ligand.

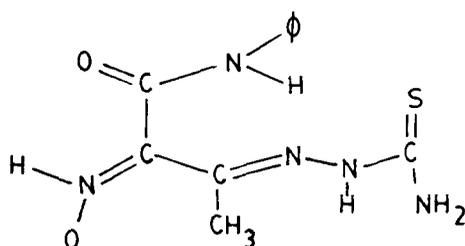


Figure 3. The N→O form of the ligand molecule.

Table 2. TG and DSC data of ligand and chelates.

Compound	TG					DSC			
	$T_s$ (°C)	$T_E$ (°C)	Weight loss (%)	Activation energy ( $E_a$ ) (Kcal/mol)	Order of reaction ( $n$ )	$T_s$ (°C)	$T_E$ (°C)	Peak tempera- ture (°C)	$\Delta H$ (J/g)
OAATS	190	325	73.0	6.4	1	219	260	241	22.18
Ni-OAATS	315	380	45.0	4.05	1	290	345	330	24.43
Co-OAATS	250	280	48.3	3.42	1	260	340	327	36.03
Zn-OAATS	300	350	40.7	5.36	1	280	317	291	58.67
						325	375	356	16.72
Mn(OAATS)·2H <sub>2</sub> O	225	285	45.0	4.37	1	200	240	208	14.19
Cd-OAATS	250	350	49.0	3.89	1	290	355	314	53.7
Hg-OAATS	250	300	60.0	3.78	1	200	270	248	25.8
UO <sub>2</sub> (OAATS)·2H <sub>2</sub> O	310	410	65.0	5.31	1	290	350	333	12.81

$T_s$  = starting temperature;  $T_E$  = ending temperature.

### 3.4 Electrical conductivity measurements

Electrical conductivities of the ligand and its metal chelates were studied over a wide range of temperature. The electrical conductivity ( $\sigma$ ) varies exponentially with the absolute temperature according to the relationship  $\sigma = \sigma_0 \exp(-E_a/kT)$  where  $\sigma$  is the conductivity at  $T$  K,  $\sigma_0$  is a constant,  $E_a$  is the activation energy and  $k$  is the Boltzman constant. The activation energy decreases in the order, Mn > OAATS > Cd > Hg > UO<sub>2</sub> > Zn > Ni > Co, which is in partial agreement with reported results (D'Sa *et al* 1979).

### 3.5 Thermal study

Examination of the results of TG and DSC (table 2) reveals that metal chelates follow a single-step decomposition. From TG data, it is observed that the rates of decomposition of metal chelates are higher than that of the ligand. The Broido method was applied to the TG data to determine the energy of activation and the order of the reaction (Broido 1969). The two water molecules in the Mn(II) and UO<sub>2</sub>(II) complexes were lost around 150°C, indicating that these molecules are coordinated to the

respective metal ion (Nakolaev *et al* 1969). The trend in thermal stability of the metal chelates on the basis of  $E_a$  values in decreasing order is as follows: OAATS >  $Zn^{+2}$  >  $UO_2^{+2}$  >  $Mn^{+2}$  >  $Ni^{+2}$  >  $Cd^{+2}$  >  $Hg^{+2}$  >  $Co^{+2}$ . From DSC it is observed that a single-step decomposition of ligand and its metal complexes is indicated by the presence of a single exothermic peak in all the traces. However, in the Zn(II) chelate, complex exothermic peaks are present. This may be justified by the fact that Zn-chelate is thermally most stable with high  $E_a$  involved in its decomposition process. The metal chelates under study do not undergo any observable physical or chemical changes before their thermal decomposition. The loss of two water molecules is indicated by the presence of a weak endothermic peak in Mn(II) and  $UO_2$ (II) traces.

## References

- Bellamy L J 1968 *Advances in infrared group frequencies* (London: Methuen)
- Broido A B 1969 *J. Polym. Sci.* **7** 1761
- Campbell M J M 1975 *Coord. Chem. Rev.* **15** 279
- Chakravorty A and Kalia K C 1968 *Inorg. Chem.* **7** 2016
- D'Sa J T, Rao V J, Patel K C and Patel R D 1979 *Angew. Makromol. Chem.* **79** 133
- Figgis B N and Nyholm R S 1959 *J. Chem. Soc.* 338
- Geetharani K and Sathyanarayana D N 1977 *Aust. J. Chem.* **30** 1617
- Kariya K P and Bhawe N S 1987 *Indian J. Chem.* **26** 788
- Klopman G and Ray A 1982 *Cancer Biochem. Biophys.* **6** 31
- Matho C B 1981 *J. Indian Chem. Soc.* **51** 935
- Nakanishi K 1964 *IR absorption spectroscopy* (Tokyo: Nankodo)
- Nakolaev M A, Logvinenko V A and Myachina L I 1969 *Thermal analysis* (New York: Academic Press) vol. 2, 779
- Orlova N N, Aksenova V R, Sclidovkin D N, Bogdanova N S and Perkhin G N 1968 *Russ. Pharmacol. Toxicol.* **348**
- Patel M, Patel M M, Ray A and Patel M R 1981 *J. Inorg. Nucl. Chem.* **43** 509
- Patel M R 1963 *Studies on the arylamides of acetoacetic acid*, Ph D thesis, Sardar Patel University, Vallabh Vidyanagar
- Pople J A and Segal G A 1966 *J. Chem. Phys.* **44** 3289
- Ray A and Sathyanarayana D N 1975 *Spectrochim. Acta* **A31** 899
- Sankhala B S, Mathur S and Meghsingh 1983 *Synth. React. Inorg. Met.-Org. Chem.* **13** 45
- Singh B, Yadav B P and Agarwal R C 1984 *Indian J. Chem.* **A23** 441
- Smith P A S and Robertson J E 1968 *J. Am. Chem. Soc.* **84** 1197
- Syamal A and Bari Niazi 1985 *Synth. React. Inorg. Met.-Org. Chem.* **15** 505
- Uno T, Machida K and Saito Y 1970 *Spectrochim. Acta* **A26** 2089
- Vogel A I 1962 *Text book of quantitative analysis* (London: Longmans Green)
- Weinig A J and Schoder W P 1939 *Technical methods of ore analysis* (New York: John Wiley and Sons) pp. 233