Mono and Trinuclear Complexes of α-Oximinoacetoacetylpyridine-4-phenylthiosemicarbazone

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Complexes of several transition metal ions with α-oximinoacetoacetyl pyridine-4-phenylthiosemicarbazone (H_3OAPT) have been prepared. Attempts were made to elucidate their geometries by elemental analysis, molar conductance, magnetic measurements and by some spectroscopic (IR, ESR and electronic) techniques. All the investigated metal ions form mononuclear complexes except for Cu^{II}, which forms mononuclear and trinuclear complexes with its chloride and acetate salts, respectively. The IR spectra show that the ligand behaves as a mono or binegative tridentate. Moreover, it acts as a trinegative hexadentate in the trinuclear Cu^{II} complex. The protonation constants ($\log K_1^H=9.9$ and $\log K_2^H=6.0$), as well as the stability constants of the metal complexes, are determined by the pH-titration of H_3OAPT and its metal(II) complexes against 0.01 M NaOH. Cu^{II} complexes possess square-planar stereochemistry while Co^{II} and Ni^{II} have an octahedral one. The crystal field parameters of Co^{II} and Ni^{II} complexes are evaluated.

Key words complexe; synthesis; stability constant; thiosemicarbazone

Coordination compounds containing ONS donors are of considerable importance due to their possibility for dimetallation leading to the formation of compounds having a toxophoric nature.[1] Moreover, they have antibacterial,[2] antifungal[3] and antitumour activities. Thiosemicarbazones have been paid considerable attention due to their activity against smallpox,[4] virus diseases[5] and tuberculosis.[6] Great attention is also due to their carcinostatic properties against a spectrum of transplaced neoplasm[7] which possess some degree of cytotoxic activity.[8] α-Oximinohydrazones have antiparasitic, fungicidal and bactericidal properties.[9] Metal complexes of α-oximinoaceto-*o*/*p*-anisidide thiosemicarbazones were prepared and characterized.[10] The coordination sites were found to be through the nitrogens of oximino and azomethine groups, as well as the thiol sulfur atoms which form a bridge between the metal ions. Complexes of α-oximineacetoacetyl pyridine were prepared and characterized.[11] No work has been done on α-oximinoacetoacetylpyridine-4-phenyl thiosemicarbazone which contains eight active coordination sites capable of forming stable complexes with more than one metal atom.

Experimental

All chemicals are of analytical high grade purity materials. The oxime derivative was synthesized according to a well known method.[12] The thiosemicarbazone oxime derivative is prepared by mixing equimolar amounts of oxime derivative and 4-phenylthiosemicarbazide in absolute EtOH. The mixture was stirred under reflux for 3 h on a water bath. The product thus formed on cooling was filtered off, recrystallized from EtOH and dried in a desiccator over anhydrous $CaCl_2$.

Preparation of Metal Complexes Solid complexes were prepared by mixing equimolar amounts of the metal salts and the ligand in absolute EtOH (in case of the chloride salts) and in EtOH–H_2O in the acetate salts. However, in the preparation of uranyl acetate complex, absolute EtOH was used. The mixture was heated under reflux on a water bath for 0.5—4 h. The same procedure was used with $PdCl_2$ but 0.5 g CH_3COONa was added. In each case, the reaction product was filtered immediately, washed several times with hot EtOH, dried and kept in a desiccator over anhydrous $CaCl_2$.

All measurements were carried out as previously reported.[13] The ESR spectrum of the trinuclear Cu(II) complex was measured using a JEOL JES RE_2XG spectrometer (100 KHz magnetic field modulation) at Tanta University. Thermogravimetry (TG) and differential thermal analyses (DTA) measurements were made in a N_2 atmosphere between 20 and 1000 °C using a Shimadzu Thermogravimetric Analyzer at Mansoura University. The pH-meter readings were measured to 0.01 units with an Orion Research Model 601A/digital ionalyzer before, then checked after each titration with buffer solutions produced by Fisher (New Jersey, U.S.A.). Solutions of metal ions (0.01 M) in twice distilled water and H_3OAPT (0.01 M) in dioxane were prepared and diluted to the necessary volume. A carbonate-free sodium hydroxide solution was prepared and standardized. Potassium chloride was used to maintain constant ionic strength ($\mu=0.1$). The prepared solutions were titrated potentiometrically by successive additions of 0.01 ml standardized 0.01 M NaOH in 50% (v/v) dioxane–water solvent.

Results and Discussion

Analytical results, together with some physical properties of H_3OAPT and its metal(II) complexes, are listed in Table 1. The complexes are stable in air and insoluble in most common organic solvents, but are easily soluble in DMF. The molar conductivities in dimethylformamide (DMF) at 25 °C are in the 5—29 $ohm^{-1}\,cm^2\,mol^{-1}$ range, indicating a nonelectrolytic nature. All complexes have melting points >300 °C except [Cu(H_2OAPT)Cl] which has a MP of 208 °C. The complexes formed are accompanied by the replacement of one, two or three hydrogen atoms.

The uncomplexed molecule (H_3OAPT) is white crystalline with a melting point of 140 °C. Chart 1 is supported by: i) the amide (I—IV) bands which appear at 1674, 1518, 1281 and 737 cm^{-1}; ii) the thioamide (I—IV) bands at 1528, 1299, 950 and 777 cm^{-1}; iii) the ν(C=N) bands of pyridine ring, oxime and thiosemicarbazone moieties at 1577, 1592 and 1618 cm^{-1}, respectively; iv) the stretching and bending vibrations of OH oxime at 3375 and 1386 cm^{-1}; v) the bands observed at 3252 and 3151 cm^{-1} being assigned to ν(N^4H) and ν(N^2H), respectively and vi) the ν(NO) of the oxime group at 992 cm^{-1} combined with the ν(N–N) of the hydrazine moiety.

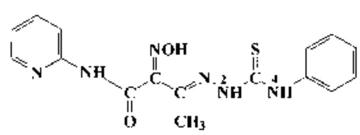

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Table 1. Analytical and Physical Data of H_3OAPT and Its Metal(II) Complexes

Compound	Color	mp (°C)	% Found (Calcd) C	H	Cl	M	μ_{eff} (B.M.)	Λ_m [a]
H_3OAPT	White	140	54.4 (53.9)	4.4 (4.5)	—	—	—	—
$[Ni(HOAPT)(H_2O)_3]$	Brown	>300	41.5 (41.1)	4.0 (4.3)	—	13.1 (12.5)	3.28	10
$[Co(H_2OAPT)_2]\cdot 2H_2O$	Gray	>300	47.0 (47.7)	3.3 (4.3)	—	7.2 (7.3)	5.17	6
$[Fe(H_2OAPT)Cl_2]\cdot 3H_2O$	Yellow	>300	35.3 (36.0)	3.8 (4.0)	13.5 (13.3)	11.1(10.8)	3.63	29
$[Zn(HOAPT)(H_2O)]$	White	>300	43.2 (43.9)	3.5 (3.7)	—	14.6 (14.9)	0.00	13
$[Pd(H_2OAPT)_2]$	Pale Yellow	>300	47.3 (47.1)	3.9 (3.7)	—	13.3 (12.9)	0.00	10
$[UO_2(HOAPT)(H_2O)]\cdot 2H_2O$	Yellow	>300	27.9 (28.3)	2.3 (3.0)	—	36.0 (35.1)	0.00	8
$[Cu(H_2OAPT)Cl]$	Olive Green	208	41.9 (42.3)	3.2 (3.3)	7.4(7.8)	14.4 (14.0)	1.9	23
$[Cu_3(OAPT)(AcO)_2(OH)(H_2O)]\cdot 2H_2O$	Green	>300	34.2 (33.5)	3.6 (3.5)	—	27.3 (26.6)	1.5	—

a) In $ohm^{-1}\,cm^2\,mol^{-1}$.

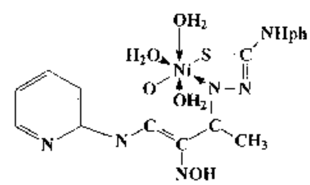
Table 2. IR Spectra of H_3OAPT and Its Metal Complexes

Compound	ν(OH)	$\nu(N^4H)$	$\nu(N^2H)$	ν(NH)	ν(C=O)	$\nu(C=N)_{py}$	$\nu(C=N)_{ox}$	$\nu(C=N)_{thio}$	ν(NO)	ν(C=S)	ν(M–O)	ν(M–S)	ν(M–N)
H_3OAPT	3375	3252	3151	3330	1674	1577	1592	1618	992	777	—	—	—
$[Co(H_2OAPT)_2]\cdot 2H_2O$	3410	3250	—	3325	1670	1575	1590	1602	1160	—		410	445
$[Fe(H_2OAPT)Cl_2]\cdot 3H_2O$	3415	3250	—	3330	1670	1575	1590	1600	1165	—		410	450
$[Cu(H_2OAPT)Cl]$	3408	3250	—	3330	1670	1575	1580	1600	1161	—	—	410	460
$[Pd(H_2OAPT)_2]$	3405	3240	—	3330	1670	1575	1592	1602	1152	—	—	410	450
$[Ni(HOAPT)(H_2O)_3]$	3370	3250	—	—	—	1580	1595	1600	990	—	385	410	450
$[Zn(HOAPT)(H_2O)]$	3375	3245	—	—	—	1577	1590	1600	990	—	380	405	455
$[UO_2(HOAPT)H_2)]\cdot 2H_2O$	3375	3248	—	—	—	1575	1590	1600	990	—	380	400	440
$[Cu_3(OAPT)(OH)(OAc)_2$-$(H_2O)]\cdot 2H_2O$	—	3252	—	—	—	1560	1580	1595	1010	—	340	405	441

Characterization of Ni(II), Zn(II) and U(VI)O_2 Complexes The ligand in its reaction with the acetate salts of Co(II), Ni(II), Zn(II) and U(VI)O_2 forms complexes insoluble in most common organic solvents. The complexes have melting points above 300 °C. The mode of chelation is suggested based on the following facts: i) the disappearance of ν(C=O) and ν(NH) vibrations with the appearance of new bands at 1610, 1240 and *ca.* 380 cm^{-1} in each complex assigned to ν(C=N), ν(C–O) and ν(M–O) vibrations, respectively, confirming the enolization of an amide group as well as chelation through its oxygen atom, ii) the disappearance of thioamide IV and $\nu(N^2H)$ bands in the spectra of complexes with the simultaneous appearance of new bands at *ca.* 700 and 400 cm^{-1} due to ν(C–S)[14] and ν(M–S)[15] support the sulphur chelation, iii) the shift to a lower wave number of the band due to $\nu(C=N)_{thio}$, observed at 1618 cm^{-1} in the ligand spectrum and iv) bands due to $\nu(C=N)_{Py}$, $\nu(C=N)_{oxime}$, ν(NO) and ν(OH) vibrations, while they more or less exist at the same position as in the spectrum of the ligand, confirm the non participation of these groups in bonding. Chart 2 is a representative example of the isolated complexes.

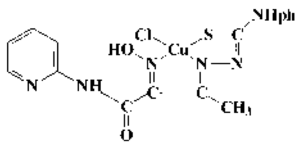
The bands observed at 3400, 1630, 900 and 630 cm^{-1} are assigned to ν(OH), $\delta(OH_2)$, $\rho_T(H_2O)$ and $\rho_W(H_2O)$ vibrations, respectively, of the coordinated water.

The electronic spectrum of the Ni(II) complex shows two bands at 14084 and 25000 cm^{-1}, which are assigned to the $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ and $^3A_{2g}\rightarrow{}^3T_{2g}(P)$ transitions, respectively.[16] The position of these bands together with the calculated 10 Dq (8480 cm^{-1}), β (0.87) and B (905 cm^{-1}) values suggest an octahedral configuration. The measured magnetic moment value (3.28 BM) lies within the range reported for octahedral Ni(II) complexes.



(2)

Characterization of Cu(II), Co(II), Pd(II) and Fe(III) Complexes H_3OAPT chelates with the chloride salts of Cu(II), Co(II), Pd(II) and Fe(III) as a mononegative tridentate molecule coordinated through the thiol sulphur (C–S) and the azomethine nitrogens of oxime and thiosemicarbazone moieties based on the following evidence: i) the disappearance of bands due to thioamide II and IV as well as $\nu(N^2H)$ with the simultaneous appearance of a new band at *ca.* 700 cm^{-1} due to ν(C–S) vibration[14]; the absence of any bands due to ν(SH) vibration confirms the liberation of thiol hydrogen during the complex formation, (ii) the appearance of *ca.* 410 cm^{-1} band, due to ν(M–S) vibration,[15] suggests sulphur coordination, iii) the ν(OH) band is observed at *ca.* 3410 cm^{-1} while that of NO is shifted to a higher wave number (1150—1165 cm^{-1}); the shift indicates coordination through the nitrogen not the oxygen of the oxime group, iv) the shift of ν(C=N) of the C=NOH group to a lower wave number confirms the nitrogen chelation, v) the lower shift of the bands at 1618 cm^{-1} due to ν(C=N) of the thioseicarbazone moiety proved its nitrogen coordination (this phenomenon is supported by the appearance of a new band in the 500—400 cm^{-1} region, due to ν(M–N) vibration) and finally (vi) the ν(M–Cl) vibration[17] is observed at 285 cm^{-1} in the spectrum of $[Cu(H_2OAPT)Cl]$ indicating the existence of



(3)

a chloride ion inside the coordination sphere.

The magnetic moment value (1.9 B.M), as well as its electronic spectral band, confirm a square-planar geometry around the Cu(II) ion (Chart 3), indicates the absence of any spin coupling between unpaired electrons belonging to different copper atoms and excludes a polymeric structure. The broad band centered at 12820 cm^{-1} is assigned to a combination of the $^2B_{1g}\rightarrow{}^2E_g$ and $^2B_{1g}\rightarrow{}^2A_{1g}$ transitions in a square-planar configuration[18].

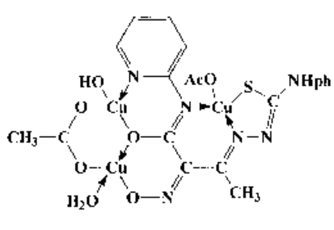
The electronic spectrum of the Co(II) complex shows two broad bands, in Nujol mull, at 14120 and 19120 cm^{-1} assigned to the $^4T_{1g}\rightarrow{}^4A_{2g}$ (ν_2) and $^4T_{1g}\rightarrow{}^4T_{1g}(P)$ (ν_3) transitions, respectively. The ν_1 transition ($^4T_{1g}\rightarrow{}^4T_{2g}$) was not recorded due to limitations in our instrument and was calculated theoretically. The calculated values of β (0.83), B (800 cm^{-1}) and 10 Dq (6360 cm^{-1}) are in good agreement with those previously reported for an octahedral structure.[19] Also, its magnetic moment value (5.17 B.M.) corresponds to the presence of three unpaired electrons and lies within the values reported for octahedral complexes.

The lower magnetic moment value (3.63 B.M.) measured for the Fe(III) complex may be attributed to an antiferromagnetic exchange due to either direct metal–metal interaction or super exchange through an S-bridge.

The Pd(II) complex is found to be diamagnetic suggesting a square planar 4-coordinate structure. Its electronic spectrum shows a characteristic band at 19570 cm^{-1} corresponding to the $^1A_{1g}\rightarrow{}^1B_{1g}$ transition in a planar configuration.

Characterization of [Cu_3(OAPT)(OH)$(AcO)_2(H_2O)$]·$2H_2O$ A trinuclear complex is isolated when the ligand reacts with $Cu_2(AcO)_4\cdot 2H_2O$. The complex is insoluble in H_2O and all common organic solvents. It has a melting point >300 °C and is green in color. The presence of eight active coordination sites in the ligand may help in the formation of a trinuclear molecule. The ability of the ligand to form five and six membered rings with the three metal ions gives high stability to the formed complex with high yield. Its IR spectrum suggests the hexadentate behavior of the ligand towards the three copper atoms as shown in Chart 4.

This mode of chelation is suggested on the basis of: i) the disappearance of bands due to ν(OH), ν(NH), ν(C=O), $\nu(N^2H)$ and thioamide IV to confirm the deprotonation of OH, enolization of CONH and enethiolization of CSNH groups, ii) the appearance of new bands due to ν(C–O) and



(4)

ν(C–S) at 1123 and 625 cm^{-1} is further support for the enolization and thioenolization processes, iii) the appearance of bands at 441, 405 and 340 cm^{-1} assigned to ν(M–N), ν(M–S) and ν(M–O) vibrations, respectively, confirms the participation of nitrogen, sulphur and oxygen in chelation, iv) the shifts to lower wave numbers of the bands due to $\nu(C{=}N)_{py}$ and $\nu(C{=}N)_{thio}$ observed at 1577 and 1618 cm^{-1} in the spectrum of the uncomplexed molecule support the coordination *via* their nitrogens, v) the shift to higher wave numbers for the bands due to ν(NO) and ν(N–N) vibrations confirms the participation of oxime oxygen and one of the hydrazinic nitrogens in chelation, and vi) the appearance of a broad band at 3400 cm^{-1} is due to a combination between ν(OH) vibrations of the coordination water and that chelated with the Cu(II) ion, and finally the acetate groups act as monodentate[13] and bridged or bidentate ligands, as confirmed from the difference between the ν_s and ν_{as} bands observed at 1386 (or 1447) and 1606 cm^{-1}, respectively. Comparing the IR spectra of H_3OAPT and its Cu(II) complex, one can conclude that the spectrum of the complex is completely different from that of the ligand, confirming that most of the ligand groups are affected during the complex formation.

The magnetic moment value calculated for each copper atom in [Cu_3(OAPT)(OH)$(AcO)_2(H_2O)$]·$2H_2O$, 1.6 BM, corresponds to the presence of one unpaired electron. Its electronic spectrum shows a charge transfer band at 28000 cm^{-1} and one asymmetric band at 12820 cm^{-1} due to the d–d transition in a square-planar Cu(II) complex[20].

The ESR spectrum in the solid state and at room temperature shows an isotropic signal at $g_o=2.077$ which corresponds to the values reported for Cu(II) complexes in a square-planar geometry.[21]

Attempts to measure the ESR spectrum in solution and to grow a single crystal for the trinuclear complex for further structural studies did not succeed due to its insolubility in most common organic solvents.

The TG thermogram (20—800 °C) of the complex is characterized by a series of degradation stages. The first stage at 100—150 °C, with 4.6% weight loss, is assigned to the removal of two crystalline water molecules. As the temperature is raised, the DTA curve exhibits an endothermic peak at 220 °C, followed by an exothermic one at 280 °C, accompanied by 10.2% weight loss in the TG curve; this loss corresponds to the removal of the coordinated water molecule and the monodentate acetate group. In the temperature range of 290—350 °C, the TG curve displays 8.5% weight loss which is correlated with the elimination of bidentate acetate groups. The relatively high temperature difference for the elimination of one acetate compared to the other is mainly due to their different manners of chelation. The endothermic peak at 336 °C and the weight loss of 11.0% corresponds to the liberation of the pyridyl group. Next, over the temperature range 410—800 °C, the DTA displays a series of thermal effects due to the full decomposition of the complex and loss of the organic portion, leaving behind CuO and Cu_2O (minor). The remaining residue comprises 32.0% of the initial mass of the complex.

$$[Cu_3(OAPT)(OH)(AcO)_2(H_2O)]\cdot 2H_2O \xrightarrow[-2H_2O]{100\text{—}150\,^{\circ}C}$$

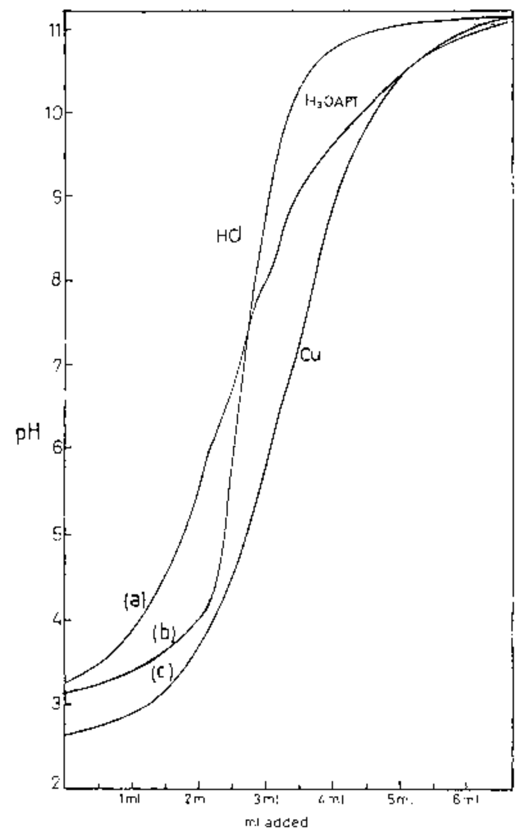


Fig. 1. Potentiometric Titration Curves

a) 2.5 ml HCl, 0.1 M+2.5 ml KCl 1 M. b) a+2.5 ml 5×10^{-3} M of ligand. c) b+2.5 ml of 5×10^{-4} M of metal. The volume of mixtures a—c) is completed to 25 ml with a water-dioxane mixture in order to keep a 50% dioxane ratio, and it is titrated with 0.01 M NaOH solution at 25 °C.

$$[Cu_3(OAPT)(OH)(AcO)_2(H_2O)] \xrightarrow[-2H_2O,\ -AcO]{150\text{—}290\ ^\circ C}$$

$$[Cu_3(OAPT)(OH)(AcO)] \xrightarrow[-AcO]{290\text{—}350\ ^\circ C}$$

$$[Cu_3(OAPT)(OH)] \xrightarrow[-Py]{350\text{—}410\ ^\circ C} [Cu_3(OAPT\text{-}Py)(OH)]$$

$$\xrightarrow{410\text{—}800\ ^\circ C} CuO + Cu_2O \text{ (minor)}$$

pH-Metric Studies The pH-metric titrations of 5×10^{-3} M H_3OAPT with 0.01 M NaOH in the presence of 0.1 M HCl and in a 50% water–dioxane mixture at $\mu=0.1$ and at 25 ± 0.1 °C were carried out using the procedure developed by Clavin and Bjerrum.[22] Representative curves are shown in Fig. 1. It is clear that the metal-ligand titration curve is shifted from those of acid and ligand mixtures, indicating the formation of complexes. The consumption of excess NaOH may be related to deprotonation of the ligand during complexation. The $n_{\bar{A}}$, $\bar{n}$ and p^{L} were calculated at different pH values using the Irving–Rossotti equations.[23] Plotting $n_{\bar{A}}$ against pH gives the proton-ligand formation curve. The $\log K_1$ and $\log K_2^{H}$ values were determined to be at 9.9 and 6.0, respectively. The metal-ligand stability constants were obtained from the interpolation at half $\bar{n}$ values in the curves drawn between $\bar{n}$ and p^{L}. The calculated ($\log K_1$) values are 10.5, 10.5, 9.75, 9.70 and 7.23 for Cu(II), UO_2(II), Ni(II), Co(II) and Zn(II), respectively. The variations in stability may be due to differences in the effective electric field strength (F^*) of the metal ion, $F^*=z^*/r^2$, where z^* and r are the effective change and radius of the investigated cations, respectively. The values of $\log K_1$ for the metal complexes are plotted against ionic potential (z^2/r). A linear relationship with a correlation coefficient of $r\geq0.78$ suggests that the metal complexes are electrostatic in nature.[24]

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